

Synthesis and Electrochemical Properties of HT-LiCo_{0.8}Ni_{0.2}O₂ Prepared by Molten Salt Synthesis Method using 0.59LiNO₃-0.41LiOH System

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Abstract—LiCo_{0.8}Ni_{0.2}O₂ powders were prepared by molten salt synthesis method using a 0.59LiNO₃-0.41LiOH melt. The physico-chemical properties of the LiCo_{0.8}Ni_{0.2}O₂ powders were investigated by powder X-ray diffraction method, field emission scanning electron microscopy, cyclic voltammetry, and charge-discharge cycling. Uniform size nanocrystalline powder (~40 nm) could be obtained at temperature ranges of 280-480 °C. These nanocrystalline powders showed poor electrochemical properties because of presence of the low temperature phase. Pure single-phase HT-LiCo_{0.8}Ni_{0.2}O₂ powder could be obtained at 580 °C. Charge-discharge measurements indicated that this exhibited a good capacity and cyclability without further heat treatment at higher temperatures.

Key words: Molten Salt Synthesis, LiCo_{0.8}Ni_{0.2}O₂, Lithium Battery

INTRODUCTION

In an effort to improve energy density of Li-ion cells, LiNiO₂ has been studied extensively as a cathode material by many investigators because its specific capacity is higher than that of LiCoO₂, which is presently used in most commercially available Li-ion cells [Ohzuku et al., 1997; Li et al., 1997]. However, LiNiO₂ shows a disadvantage such as cycling-induced microcracks due to the structural transformations of the hexagonal phases above 4.2 V; this causes a rapid capacity fading on cycling. When x is smaller than 0.3 in Li_xNiO₂, the lattice parameter c rapidly decreases from 14.4 Å to 13.5 Å, while the lattice parameter a remains almost constant. This corresponds to 9% change in the c direction that causes a fracture in the LiNiO₂ particles [Wang et al., 1999]. Another problem is that the LiNiO₂ phase shows a lower onset temperature of the exothermic peak at around 30-40 °C. At or above a critical temperature, LiNiO₂ is significantly unstable compared to LiCoO₂, and liberates oxygen gas as a result of decomposition. The oxygen gas evolved at the charged state significantly affects the safety of the Li-ion cell. Also it is difficult to synthesize in consistent quality. Because of these difficulties, a Li-ion cell fabricated with LiNiO₂ as the cathode material is not yet commercially available.

Recently, lithium cobalt nickel oxides LiCo_{1-x}Ni_xO₂ have been identified as one of the most attractive materials to solve these problems by stabilizing the structure of LiNiO₂. Extensive studies have shown that LiCo_{1-x}Ni_xO₂ with 0 < x < 1 performs better on electrochemical cycling than the end members of the system LiCoO₂ (x=0) and LiNiO₂ (x=1). The synthesis of LiCo_{1-x}Ni_xO₂ is carried out by the solid-state reaction method involving mechanical mixing of lith-

ium, cobalt, and nickel salts followed by firing for over 24 h above 800 °C with intermittent grindings. This process inevitably leads to the abnormal grain growth and poor control of stoichiometry of the product. Wang et al. [1998] reported that the LiNiO₂ compound decomposed to Li_{1-x}Ni_{1+x}O₂, Li₂O, and O₂ at above 860 °C. The decomposition product Li_{1-x}Ni_{1+x}O₂ has a disordered cation distribution with nickel ions partially occupying the lithium sites in the layered structure. These nickel ions impede the diffusion of lithium ions. Thus, the electrochemical properties of such disordered LiNiO₂ are very poor. Gummow et al. [1993] also reported that LT-LiCo_{1-x}Ni_xO₂ could be synthesized in air at 400 °C for five days with poor electrochemical properties. In this regard, it is worthwhile to synthesize HT-LiCo_{1-x}Ni_xO₂ having good electrochemical properties at lower temperatures.

The Molten salt synthesis (MSS) method has been reported to be one of the most effective and simplest methods in the preparation of multi-component oxides with desirable characteristics such as good chemical homogeneity, very fine size, and narrow size distribution. Since the formations of desired compounds in molten salt are much faster than those in solid state reaction, the various powders, e.g., lead magnesium niobate, ceria, and lithium manganate could be prepared at significantly lower temperatures [Kim et al., 2001]. Nonetheless, the MSS method has seldom been applied to the synthesis of lithium transition metal oxide including LiCoO₂ and LiCo_{1-x}Ni_xO₂. In the previous studies, we demonstrated the possibility of the low temperature synthesis of HT-LiCoO₂ powders by MSS method using 0.6LiCl-0.4Li₂CO₃ and 0.58LiOH-0.42LiCl melts [Han et al., 2001]. These led us to conclude that HT-LiCoO₂ could be prepared at much lower temperatures if a suitable molten salt with low melting point is provided.

This paper reports on the synthesis, characterization, and the electrochemical performance of LiCo_{1-x}Ni_xO₂ powders prepared in the eutectic mixture of 0.59LiNO₃-0.41LiOH (183 °C). As far as we know, this mixture has the lowest melting point among various lithium salts: for example, 0.87LiNO₃-0.13LiCl (244 °C), LiNO₃ (253

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°C), and LiOH (477 °C). We show that the polycrystalline HT-Li_{Co_{0.8}Ni_{0.2}O₂} powders prepared at 580 °C, have good electrochemical performances without a further heat treatment at higher temperatures.

EXPERIMENTAL

The molten salt reaction was carried out in aluminar crucibles. First, mixed Ni-Co hydroxides were obtained by adding aqueous solution of Co(NO₃)₂ and Ni(NO₃)₂ in the desired molar ratios to a stirred aqueous solution of LiOH. The full description is reported elsewhere [Jang et al., 1999]. Appropriate amounts of LiNO₃ and LiOH·H₂O were first mixed with a mortar and pestle and heated at temperatures from 280 to 580 °C in air to a mixture melt. The heating rate was fixed to 200 °C/h for all the temperature settings. Then the Ni-Co hydroxide was poured into the melts. The hydroxide to flux weight ratio was set to 1 : 10. After the heating, the obtained powders were cooled to ambient temperature and residual fluxes were removed from the products by washing with distilled water. Finally, the products were oven-dried at 120 °C.

The thermal behavior was studied by thermogravimetry and differential thermal analysis in air at a heating rate of 5 °C/min, using simultaneous TGA/DTA equipment (Dupont SDT 2960). To investigate the structure of the sample, the obtained powders were analyzed by powder X-ray diffraction (XRD) method using MAC science MXP3A-HF diffractometer employing Cu-K α radiation. The scan data were collected in the 15-100° 2 θ range at room temperature. The step size was 0.026° with the counting time of 3 sec. The crystal structure was refined by the Rietveld method using the Fullprof program [Carvajal, 1997]. The peak shape was described by pseudo-voigt function. The background level was defined by a polynomial function. For each diffraction pattern, the scale factor, the counter zero point, the peak asymmetry, and unit-cell dimension were refined in addition to the atomic parameter. Morphology and microstructure of the samples were examined by field emission scanning electron microscopy (FE-SEM, Hitachi S-4300). The samples were sputtered by ion sputter (Hitachi E-1030) of which the accelerating voltage and emission current were 20 kV and 8,000 nA, respectively.

The electrochemical characteristics were studied by using a two-electrode cell. The working electrode—consisting of 16 mg of LiCo_{0.8}-Ni_{0.2}O₂ (80 wt% by mass), 3 mg of acetylene black (15 wt%) and 1 mg of PTFE (5 wt%)—was pressed and then vacuum dried at 120 °C for 24 h. The lithium metal and polypropylene film were used as counter electrode and separator, respectively. The electrolyte used was a 1 M LiPF₆ in 1 : 1 ethylene carbonate/dimethyl carbonate solution. The charge-discharge test was conducted by using a constant current of 70 mA/g at the voltage ranges of 4.3-2.8 V with the Arbin charge/discharge cycler (BT 2042). The cyclic voltammetry (CV) was performed at a scan rate of v =100 μ V/s with a Zahner AC impedance analyzer (IM6).

RESULTS AND DISCUSSION

A reaction process was determined by the TGA/DTA of the starting mixture, composed of Co_{0.8}Ni_{0.2}(OH)₂ and 10×(0.59LiNO₃-0.41LiOH), as shown in Fig. 1. The DTA/TGA analysis indicated three endothermic peaks corresponding to the dehydration of some water

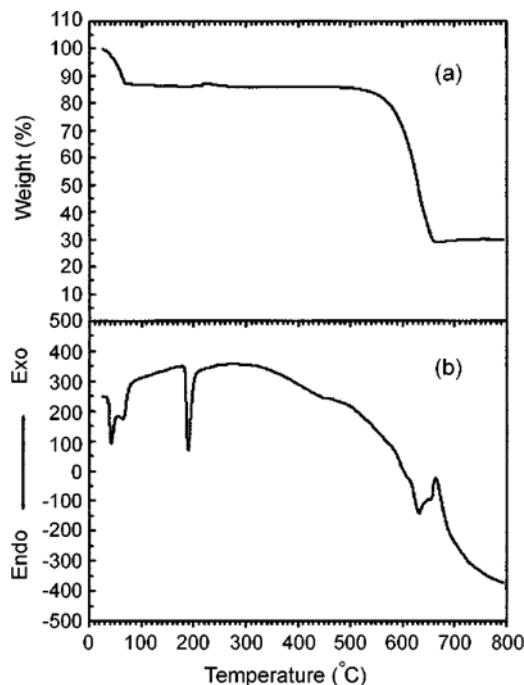


Fig. 1. TGA (a) and DTA (b) curves of starting mixture composed of Co_{0.8}Ni_{0.2}(OH)₂ and 10×(0.59LiNO₃-0.41LiOH) with a heating rate of 5 °C/min in air.

at 55 °C, the melting point of 0.59LiNO₃-0.41LiOH at 190 °C and evaporation of lithium salt at 650 °C, respectively. Abrupt weight loss due to the evaporation of lithium salts began at 580 °C.

The various co-precipitated hydroxide compounds, Co_{1-x}Ni_x(OH)₂ (0≤x≤0.5) were reacted in the 0.59LiNO₃-0.41LiOH system at 280 °C for 48 h. The powder XRD patterns of the samples are presented in Fig. 2. Above x=0.3, the unwanted NiO phase was observed besides LiCo_{1-x}Ni_xO₂. The NiO is one of the most stable phases in the nickel oxide compounds, and reaction with lithium salt to lithium

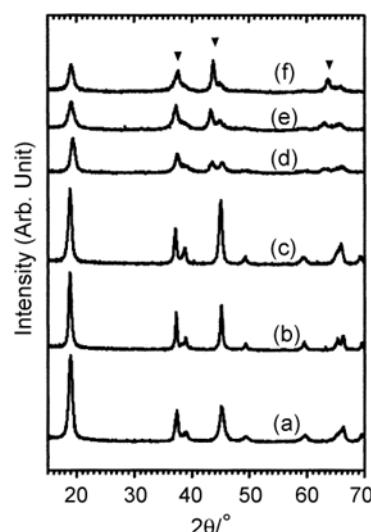


Fig. 2. XRD patterns of the LiCo_{1-x}Ni_xO₂ powders prepared at 280 °C for 48 h with various levels of nickel substitution. (a) x=0, (b) x=0.1, (c) x=0.2, (d) x=0.3, (e) x=0.4, and (f) x=0.5. ▼: NiO

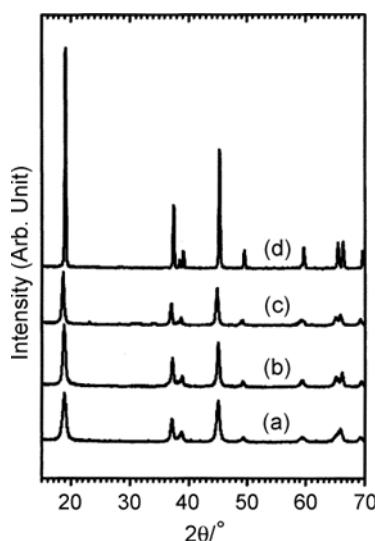


Fig. 3. XRD patterns of the LiCo_{0.8}Ni_{0.2}O₂ powders prepared at (a) 280 °C, (b) 380 °C, (c) 480 °C, and (d) 580 °C for 48 h.

nickel oxide compound is very slow. Therefore, the LiCo_{0.8}Ni_{0.2}O₂ is the compound with maximum nickel composition that could be obtained by MSS method using 0.59LiNO₃-0.41LiOH.

The Rietveld analysis of the XRD pattern of LiCo_{0.8}Ni_{0.2}O₂ prepared at 280 °C showed that it consisted of the mixed phase of HT-LiCo_{0.8}Ni_{0.2}O₂ and LT-LiCo_{0.8}Ni_{0.2}O₂. To obtain a pure HT-LiCo_{0.8}Ni_{0.2}O₂, the reaction temperature was elevated. Fig. 3 shows the XRD patterns of the LiCo_{0.8}Ni_{0.2}O₂ powders prepared at different temperatures for 48 h. The weight percentages of each phase and the unit cell parameters are given in Table 1. Gummow et al. [1993] reported that LT-LiCo_{0.8}Ni_{0.2}O₂ can be indexed either to a trigonal unit cell (*R*-3*m*) with *a*=2.833, and *c*=13.881 Å, or to a face-centered cubic unit cell (*Fd*3*m*) with *a*=8.013 Å. We conducted the refinement of LT-LiCo_{0.8}Ni_{0.2}O₂ using a face-centered cubic unit cell (*Fd*3*m*). The unit cell parameter (8.013 Å) of the sample prepared at 380 °C is in good agreement with that obtained by Gummow et al. With increasing reaction temperature, the LT-LiCo_{0.8}Ni_{0.2}O₂ disappeared while HT-LiCo_{0.8}Ni_{0.2}O₂ increased and at 580 °C, single phase HT-LiCo_{0.8}Ni_{0.2}O₂ could be obtained. The measured, calculated, and difference XRD profiles for the sample prepared at 580 °C are shown in Fig. 4. The good agreement between the measured pattern and the fitted pattern for HT-LiCo_{0.8}Ni_{0.2}O₂ is indicative of a reliable refinement. The refined cell parameters of *a* and *c* are 2.824 and 14.078 Å, respectively.

Scanning electron microphotographs of the LiCo_{0.8}Ni_{0.2}O₂ pow-

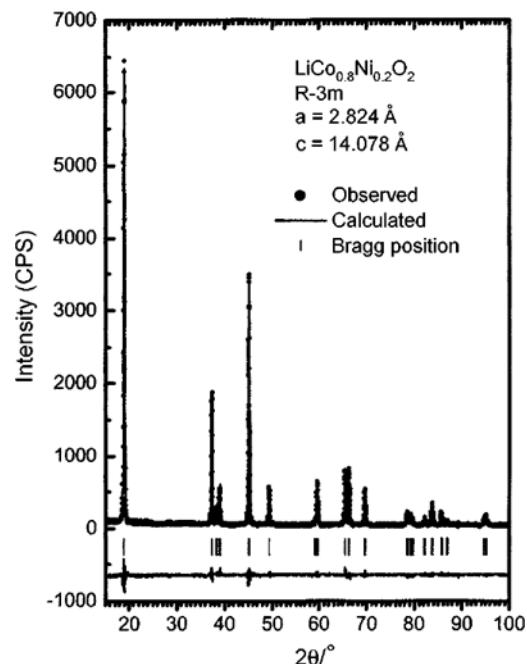


Fig. 4. Observed, calculated, and difference powder XRD profile for the LiCo_{0.8}Ni_{0.2}O₂ powder prepared at 580 °C.

ders obtained at different synthesis temperatures are given in Fig. 5. Up to 480 °C, the powder morphologies of LiCo_{0.8}Ni_{0.2}O₂ are composed of hexagonal individual particles of about 40 nm with uniform size, irrespective of synthesis temperatures. The particle size of the sample prepared at 580 °C is about three times larger than that of the samples prepared at lower temperatures. According to the DTA/TGA result, lithium salts began to evaporate at 580 °C. Thus it seems that the evaporation of lithium salt affects the particle size, and uniformly sized nanocrystalline powders could be obtained below 500 °C. Charge-discharge curves at a constant current density of 1.5 mA/cm² for LiCo_{0.8}Ni_{0.2}O₂ powders prepared at various temperatures are presented in Fig. 6. Cells composed of the powders prepared at below 480 °C show two charge-discharge plateaus at around 3.9 and 3.6 V due to the mixed phase of HT-LiCo_{0.8}Ni_{0.2}O₂ and LT-LiCo_{0.8}Ni_{0.2}O₂ respectively, as confirmed by the XRD result. A cell composed of the powder prepared at 580 °C shows only one plateau at 3.9 V. The lithium intercalation-deintercalation properties of the LiCo_{0.8}Ni_{0.2}O₂ powders were also studied by cyclic voltammetry. The cyclic voltammograms of the LiCo_{0.8}Ni_{0.2}O₂ powders prepared at 280 °C and 580 °C are given in Fig. 7(a) and (b), respectively. For the sample prepared at 280 °C, one could observe

Table 1. Phase composition and unit cell parameters with various synthetic temperatures

Synthetic temperature (°C)	Percentage of phase (wt%)		Unit cell parameter				
	HT-LiCo _{0.8} Ni _{0.2} O ₂	LT-LiCo _{0.8} Ni _{0.2} O ₂	LT-LiCo _{0.8} Ni _{0.2} O ₂	HT-LiCo _{0.8} Ni _{0.2} O ₂	a (Å)	a (Å)	c (Å)
280	89	11	8.009(4)	2.823(4)	2.823(4)	2.823(4)	14.069(4)
380	91	9	8.013(5)	2.832(2)	2.832(2)	2.832(2)	14.081(9)
480	95	5	8.139(6)	2.825(5)	2.825(5)	2.825(5)	14.099(4)
580	100	-	-	2.824(2)	2.824(2)	2.824(2)	14.078(5)

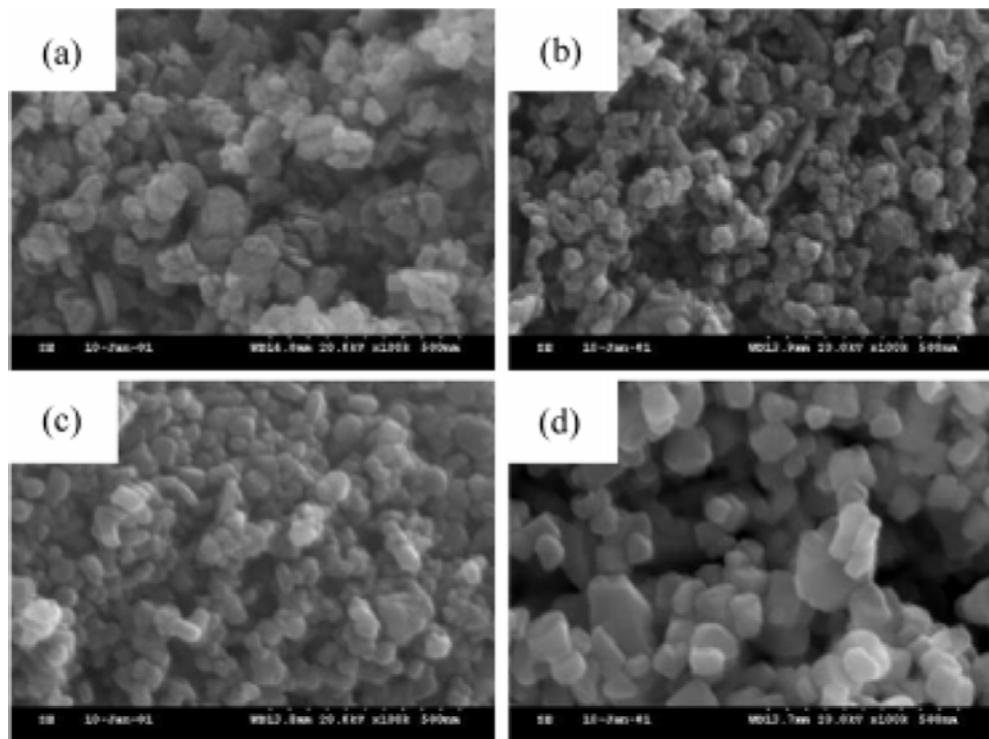


Fig. 5. SEM of the powders prepared at (a) 280 °C, (b) 380 °C, (c) 480 °C, and (d) 580 °C.

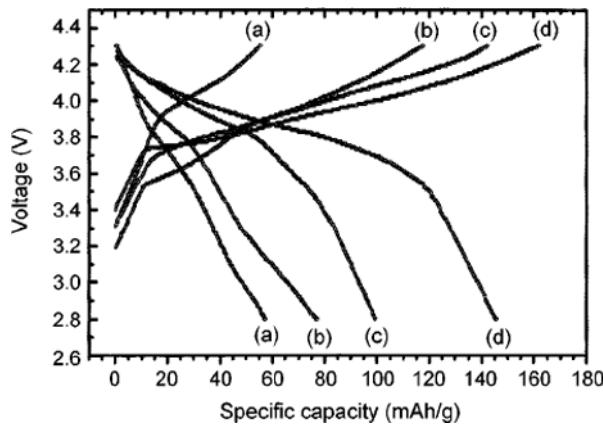


Fig. 6. Voltage profiles of first charge-discharge cycle of the $\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{O}_2$ powders prepared at (a) 280 °C, (b) 380 °C, (c) 480 °C, and (d) 580 °C.

two peaks at 4.05 and 3.75 V in the anodic scan. These peaks shifted to 3.95 and 3.65 V at the second cycle. These oxidation peaks correspond to the extractions of Li^+ ions from the $\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{O}_2$ host. During the cathodic scan, the main reduction peak was found at 3.8 V, and minor peak at 3.5 V. According to Garcia et al. [1997], LT-LiCoO₂ obtained at 400 °C is characterized by broad anodic and cathodic peaks at 3.75 and 3.45 V respectively and HT-LiCoO₂ obtained at 800 °C is characterized by anodic and cathodic peaks at 3.97 and 3.93, respectively. Thus the two anodic and cathodic peaks at near 3.9 and 3.5 V are considered to come from HT-LiCo_{0.8}Ni_{0.2}O₂, and LT-LiCo_{0.8}Ni_{0.2}O₂ respectively. These results indicate that LiCo_{0.8}Ni_{0.2}O₂ shows similar electrochemical properties with LiCoO₂. For the sample prepared at 580 °C, well-defined anodic

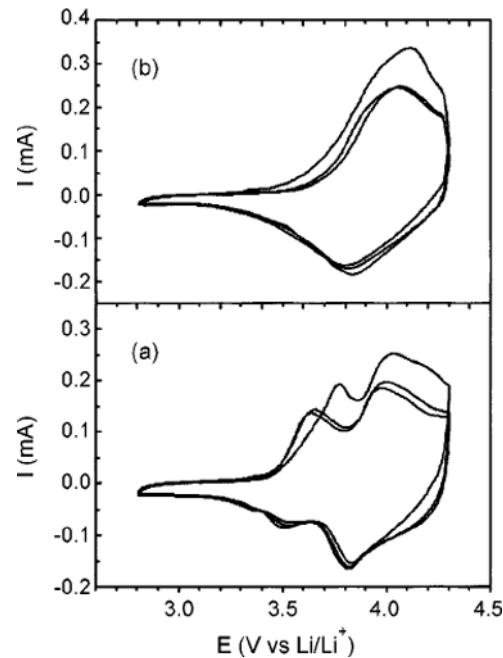


Fig. 7. Cyclic voltammogram of the $\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{O}_2$ powders prepared at (a) 280 °C, and (b) 580 °C at a scan rate of 100 $\mu\text{V/s}$.

and cathodic peaks are observed at 4.0 and 3.8 V, respectively, in agreement with previous reports on HT-LiCoO₂.

The evolution of the specific capacity of the $\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{O}_2$ powders prepared at various temperatures as a function of cycle number is illustrated in Fig. 8. For comparison, the specific capacity of the LiCoO₂ powder prepared at 900 °C in 0.6LiCl-0.4Li₂CO₃ melt

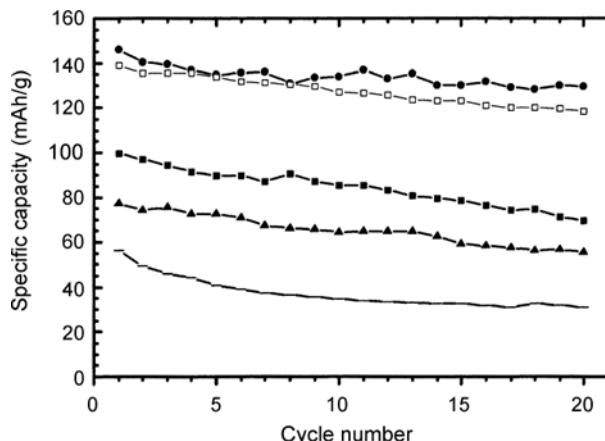


Fig. 8. Evolution of discharge capacities with number of cycles of LiCo_{0.8}Ni_{0.2}O₂ powders prepared at various temperatures, and LiCoO₂ powder prepared at 900 °C.
 -▽- 580 °C, -△- 480 °C, -○- 380 °C, -◇- 280 °C, -□- LiCoO₂ 900 °C.

was included. The first discharge capacity increases from 56 to 146 mAh/g, as the reaction temperature increases from 280 to 580 °C. It is worthy to note that HT-LiCo_{0.8}Ni_{0.2}O₂ with good cyclability can be prepared at 580 °C. For the powders prepared at below 480 °C, the discharge capacities rapidly fade out due to the presence of the LT-LiCo_{0.8}Ni_{0.2}O₂. Actually, one of the most significant problems in the powders prepared at low temperatures is that the powders should be annealed at higher temperatures to impart an enhanced electrochemical property. However, the LiCo_{0.8}Ni_{0.2}O₂ powder prepared at 580 °C in 0.59LiNO₃-0.41LiOH melt shows higher discharge capacity (146 mAh/g at the first cycle) and better cyclability (130 mAh/g at the twentieth cycle) than that of the LiCoO₂ prepared at 900 °C (140 mAh/g at the first cycle and 118 mAh/g at the twentieth cycle).

CONCLUSION

The LiCo_{0.8}Ni_{0.2}O₂ is the compound with maximum nickel composition that can be obtained by MSS using 0.59LiNO₃-0.41LiOH. A single phase, impurity free, HT-LiCo_{0.8}Ni_{0.2}O₂ powder was prepared at 580 °C. The morphologies of the LiCo_{0.8}Ni_{0.2}O₂ powder ob-

tained at 580 °C exhibited a clear hexagonal shape together with a considerable fineness and homogeneous size distribution (about 100 nm). The charge-discharge test of this powder showed good electrochemical properties without further heat treatment. The discharge capacity and cyclability of the LiCo_{0.8}Ni_{0.2}O₂ powder obtained at 580 °C were better than those of the LiCoO₂ powder obtained at 900 °C.

REFERENCES

- Garcia, B., Farcy, J. and Pereira-Ramos, J. P., "Electrochemical Properties of Low Temperature Crystallized LiCoO₂," *J. Electrochem. Soc.*, **144**, 1179 (1997).
- Gummow, R. J. and Thackeray, M. M., "Characterization of LT-Li_{1-x}Co_{1-y}Ni_yO₂ Electrodes for Rechargeable Lithium Cells," *J. Electrochem. Soc.*, **140**, 3365 (1993).
- Han, C.-H., Hong, Y.-S., Park, C.M. and Kim, K., "Synthesis and Electrochemical Properties of Lithium Cobalt Oxides Prepared by Molten-Salt Synthesis Using the Eutectic Mixture of LiCl-Li₂CO₃," *J. Power Sources*, **92**, 95 (2001).
- Jang, Y.-I., Huang, B., Wang, H., Sadoway, D. R., Geder, G., Chiang, Y.-M., Liu, H. and Tamura, H., "LiAl_{1-x}Co_{1-y}O₂ (R-3m) Intercalation Cathode for Rechargeable Lithium Batteries," *J. Electrochem. Soc.*, **146**, 862 (1999).
- Kim, S.-J., Hong, Y.-S., Park, H.-B., Park, S.-Y. and Kim, K., "(1-x) PMN-xPFN Powders by Molten Salt Synthesis," *J. Mater. Sci. Lett.*, **15**, 1443 (1996).
- Li, W. and Currie, J., "Morphology Effects on the Electrochemical Performance of LiNi_{1-x}Co_xO₂," *J. Electrochem. Soc.*, **144**, 2773 (1997).
- Ohzuku, T., Yangawa, T., Kouguchi, M. and Ueda, A., "Innovation Insertion Material of LiAl_{1/4}Ni_{3/4}O₂ (R-3m) for Lithium Ion (Shuttlecock) Batteries," *J. Power Sources*, **68**, 131 (1997).
- Rodriguez-Carvajal, J., Program FULLPROF, version 3.2, January 1997, LLB.
- Wang, G. X., Zhong, S., Bradhurst, D. H., Dou, S. X. and Liu, H. K., "Fabrication of LiMn₂O₄ thin Films by Sol-Gel Method for Cathode Materials of Microbattery," *J. Power Sources*, **76**, 141 (1998).
- Wang, H., Jang, Y., Huang, B., Sadoway, D. R. and Chiang, Y., "TEM Study of Electrochemical Cycling-Induced Damage and Disorder in LiCoO₂ Cathodes for Rechargeable Lithium Batteries," *J. Electrochem. Soc.*, **146**, 473 (1999).