

## Synthesis of cathode material $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ by a simplified combustion method

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### Abstract

The optimum conditions for synthesizing  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) by a simplified combustion method, in which the preheating step is omitted, and the electrochemical properties of these materials were investigated. The optimum condition for synthesizing  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  by the simplified combustion method is calcination at  $800^\circ\text{C}$  for 12 h in air in 3.6 mole ratio of urea to nitrate. The  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized under these conditions shows the smallest R-factor  $\{(I_{006} + I_{102})/I_{101}\}$  and the largest  $I_{003}/I_{104}$ , indicating better hexagonal ordering and less cation mixing, respectively. The  $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$  synthesized at  $800^\circ\text{C}$  for 12 h in air in 3.6 mole ratio of urea to nitrate has the largest first discharge capacity  $156.2\text{ mA h g}^{-1}$  at 0.5C and shows relatively good cycling performance. This sample shows better hexagonal ordering and less cation mixing than the other samples. The particle size of the  $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$  is relatively small and its particles are spherical with uniform particle size.

### 1. Introduction

Transition metal oxides such as  $\text{LiMn}_2\text{O}_4$  [1–3],  $\text{LiCoO}_2$  [4–6], and  $\text{LiNiO}_2$  [7–10] have been investigated in order to apply them as cathode materials for lithium secondary batteries.  $\text{LiMn}_2\text{O}_4$  is very cheap and does not cause environmental pollution, but its discharge capacity is small as compared with  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ , and its cycle performance is not good.  $\text{LiCoO}_2$  has large diffusivity and high operating voltage, and can be easily prepared. It has a disadvantage, however, in that it contains an expensive and toxic element, namely, cobalt.  $\text{LiNiO}_2$  is a very promising cathode material since it has a large discharge capacity [11] and is relatively good in terms of economics and environmental pollution. On the other hand, its preparation is very difficult compared with that for  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$ . In order to overcome the drawbacks of  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$ , solid solutions  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  have been studied.

The solid-state reaction method has disadvantages; difficulty in the homogeneous formation of phase, formation of particles with size and shape which are not uniform and difficulty in the formation of the compound with the stoichiometric composition.

The combustion method can solve these problems. A simplified combustion method, in which a preheating

step is omitted, is developed in this work. The optimum conditions for synthesis of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) by the simplified combustion method are investigated. In addition the electrochemical properties of these materials are also examined.

### 2. Experimental

Starting materials were  $\text{LiNiO}_3$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_2\text{CONH}_2$  (urea) with purities 98%. The starting materials in the planned compositions were mixed homogeneously with the help of a magnetic stirrer. The color of the mixed samples were light reddish green. These mixed samples were calcined at  $750\text{--}900^\circ\text{C}$  for 3–24 h in air in different mole ratios of urea to nitrate (0.6–4.8). The phase identification of the prepared samples was carried out by X-ray diffraction (XRD, Rigaku III/A type) analysis using  $\text{CuK}_\alpha$  radiation. The morphologies of the samples were observed using a scanning electron microscope (SEM). To measure the electrochemical properties, the electrochemical cells consisted of the prepared sample as a positive electrode, Li metal as a negative electrode, and an electrolyte of 1 M  $\text{LiPF}_6$  in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). A piece of Whatman porous glass was used as a separator. The cells were

assembled in an argon-filled dry box. To fabricate the positive electrode, active material, acetylene black and polyvinylidene fluoride (PVDF) binder with N-methyl-2-pyrrolidone (NMP) were mixed in a weight ratio of 85:10:5 on Al foil. By introducing the Li metal, the Whatman glass-fiber, the positive electrode and the electrolyte, the cell was assembled. All the electrochemical tests were performed at room temperature with a battery charge–discharge cycle tester at 0.1 and 0.5C in a potential range from 3.0 to 4.4 V. Figure 1 summarizes the experimental procedure.

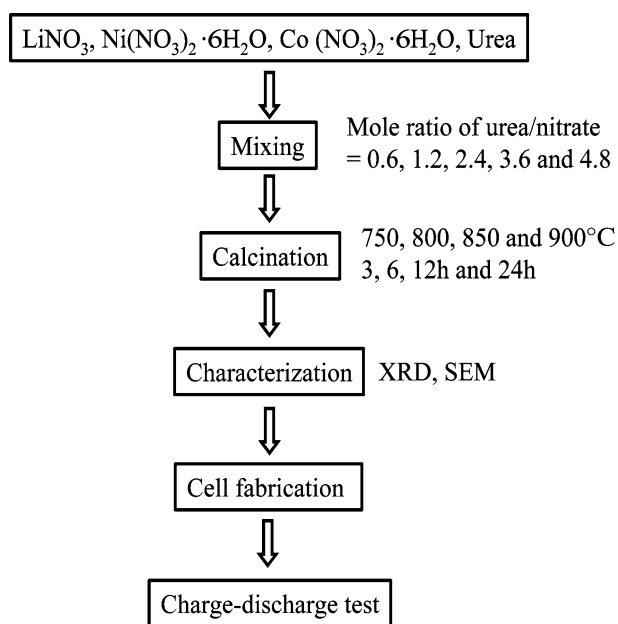


Fig. 1. Experimental procedure for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  electrodes prepared by the combustion method.

### 3. Results and discussion

Figure 2 shows XRD patterns for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized by the combustion method at  $750^\circ\text{C}$  for 12 h in air in different mole ratios of urea to nitrate (0.6–4.8). In the case of 0.6 mole ratio of urea/nitrate, some phase with  $R\bar{3}m$  structure was formed, but it was not in the powder state. In the case of 2.4 mole ratio of urea/nitrate, small amounts of  $\text{Li}_2\text{CO}_3$  and  $\text{NiO}$  in addition to the phase with the  $R\bar{3}m$  structure were obtained. In the case of 3.6 and 4.8 mole ratios of urea/nitrate, the sample shows good XRD patterns for the  $R\bar{3}m$  structure.

Figure 3 gives SEM photographs of the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized at  $750^\circ\text{C}$  for 12 h in the different mole ratios of urea to nitrate (0.6–4.8). In the case of 0.6 mole ratio of urea/nitrate, spherical particles with diameters of 1–2  $\mu\text{m}$  are in clusters. For 2.4 mole ratio of urea/nitrate, the sample contains relatively large particles and small particles. In the case of 3.6 and 4.8 mole ratios of urea to nitrate, the sample exhibits homogeneous and fine spherical particles. The particles for 4.8 mole ratio of urea/nitrate are smaller than those for 3.6 mole ratio.

Figure 4 gives XRD patterns for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized for various times at  $750^\circ\text{C}$  in 3.6 mole ratio of urea to nitrate. In the case of the calcinations for 3 h, the sample contains  $\text{Li}_2\text{CO}_3$  in addition to the phase with  $R\bar{3}m$  structure. The samples calcined for more than 6 h do not show any impurity and exhibit similar XRD patterns.

Figure 5 shows SEM photographs of the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized for various times at  $750^\circ\text{C}$  in 3.6 mole ratio of urea to nitrate. The sample calcined for 3 h has the smallest particle size. The sample calcined

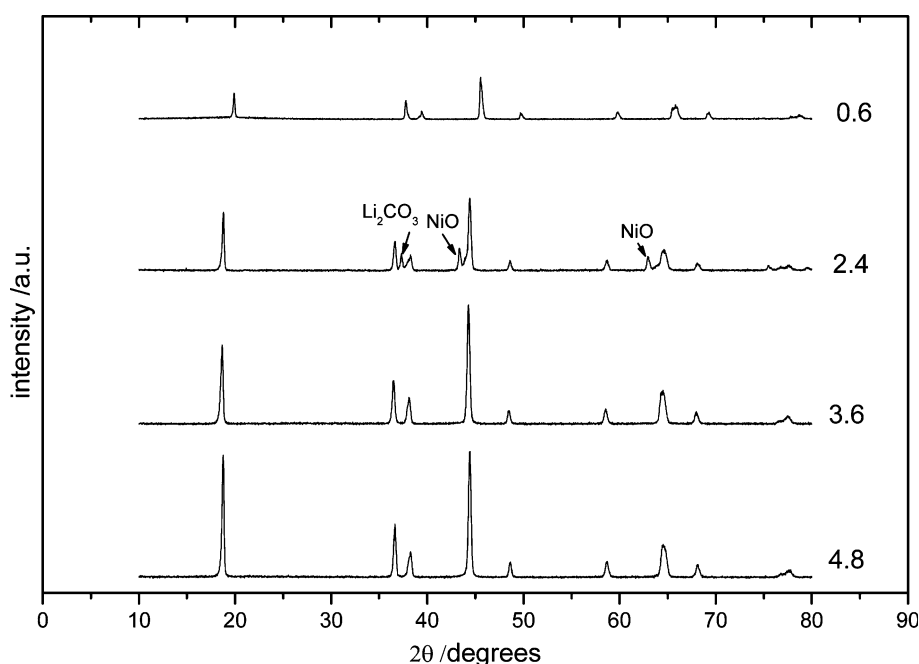


Fig. 2. XRD patterns for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized by the combustion Method at  $750^\circ\text{C}$  for 12 h in the different mole ratios of urea to nitrate.

for 24 h exhibits the largest particles, showing that the grains grow larger as the time of calcination becomes longer. We selected 12 h as the time of synthesis.

Figure 6 gives XRD patterns for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized at various temperatures for 12 h in 3.6 mole ratio of urea to nitrate. All the samples show the XRD patterns for the  $R\bar{3}m$  structure.

Figure 7 shows the variations of the ratios of intensities of XRD peaks for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  with the

synthesis temperature for 12 h in 3.6 mole ratio of urea to nitrate. It is known that the smaller value of the ratio  $(I_{006} + I_{102})/I_{101}$ , called the R-factor, is related to higher hexagonal ordering and the large value of the ratio  $I_{003}/I_{104}$  is related to the smaller cation mixing [12, 13]. The R-factor decreases as the synthesizing temperature increases from 750 to 800 °C, and then increases again as the synthesis temperature increases from 800 to 850 °C through 900 °C. The value of  $I_{003}/I_{104}$  is the

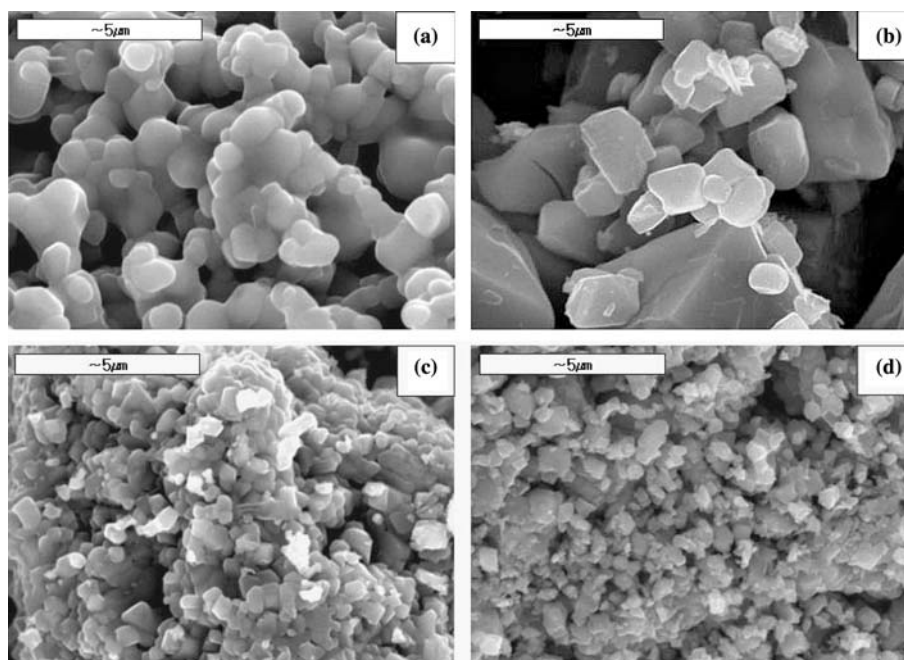


Fig. 3. SEM photographs of the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized by the combustion method at 750 °C for 12 h in the different mole ratios of urea to nitrate; (a) 0.6, (b) 2.4, (c) 3.6 and (d) 4.8.

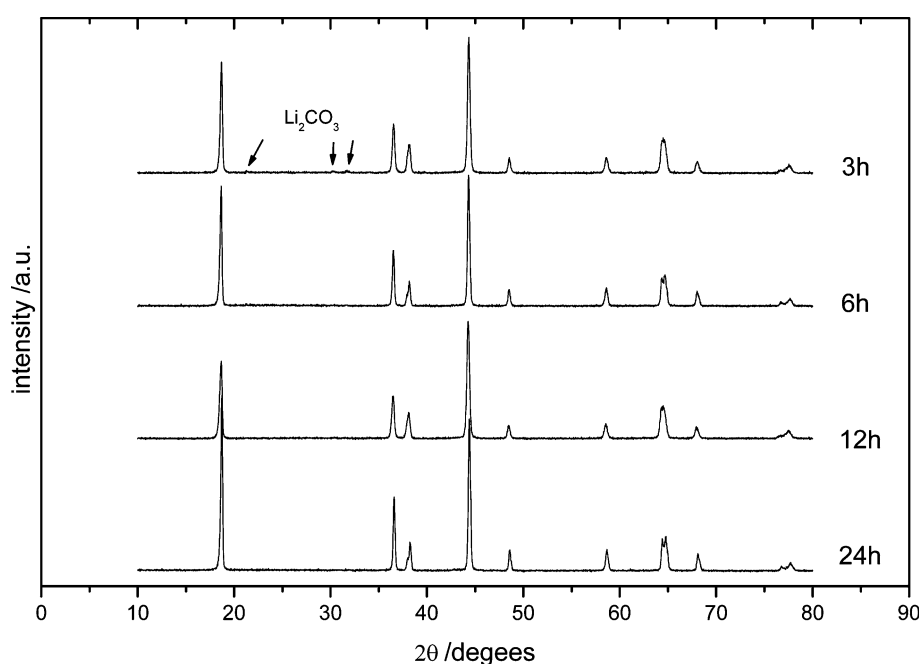


Fig. 4. XRD patterns for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized by the combustion method for various times at 750 °C in 3.6 mole ratio of urea to nitrate.

smallest at 750 °C, increases as the synthesis temperature increases from 750 to 800 °C, and then decreases as the synthesis temperature increases from 800 to 850 °C. It increases again at 900 °C. Since the R-factor is the smallest and the value of  $I_{003}/I_{104}$  is the largest in the sample synthesized at 800 °C, 800 °C is considered to be the optimum temperature for synthesizing the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ . The direction of the c-axis is distorted in the  $R\bar{3}m$  structure. This is reflected by the splitting of the 006 and 102 peaks, and 108 and 110 peaks in the XRD

patterns. The sample synthesized at 800 °C shows clear splitting of these peaks (Figure 6).

Figure 8 shows the SEM photographs for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized at various temperatures for 12 h in the 3.6 mole ratio of urea to nitrate. The particle size increases as the synthesis temperature increases. The particle size of the sample synthesized at 750 °C is the smallest. The particles synthesized at 800 °C are spherical and have diameters of about 1–2.5  $\mu\text{m}$ . The particles synthesized at 850 and 900 °C are relatively large and in clusters.

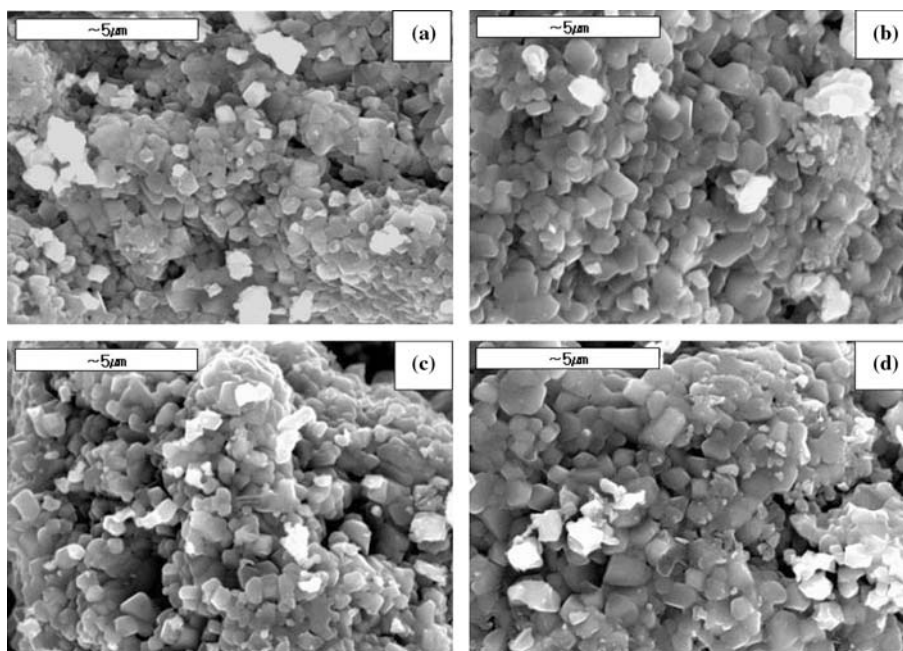


Fig. 5. SEM photographs of the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized by the combustion method for various times at 750 °C in 3.6 mole ratio of urea to nitrate; (a) 3 h, (b) 6 h, (c) 12 h and (d) 24 h.

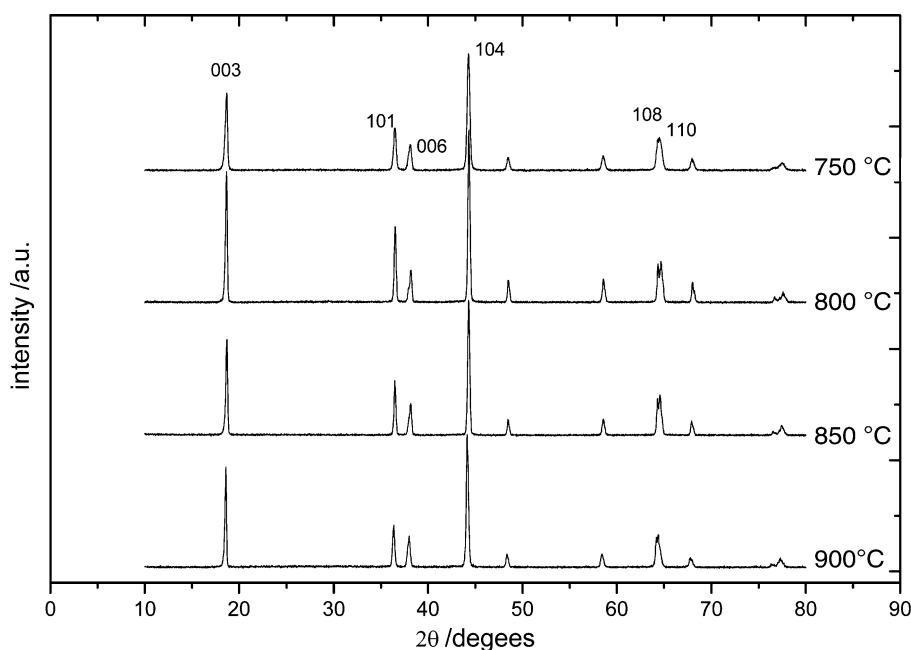


Fig. 6. XRD patterns for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized by the combustion method at various temperatures for 12 h in 3.6 mole ratio of urea to nitrate.

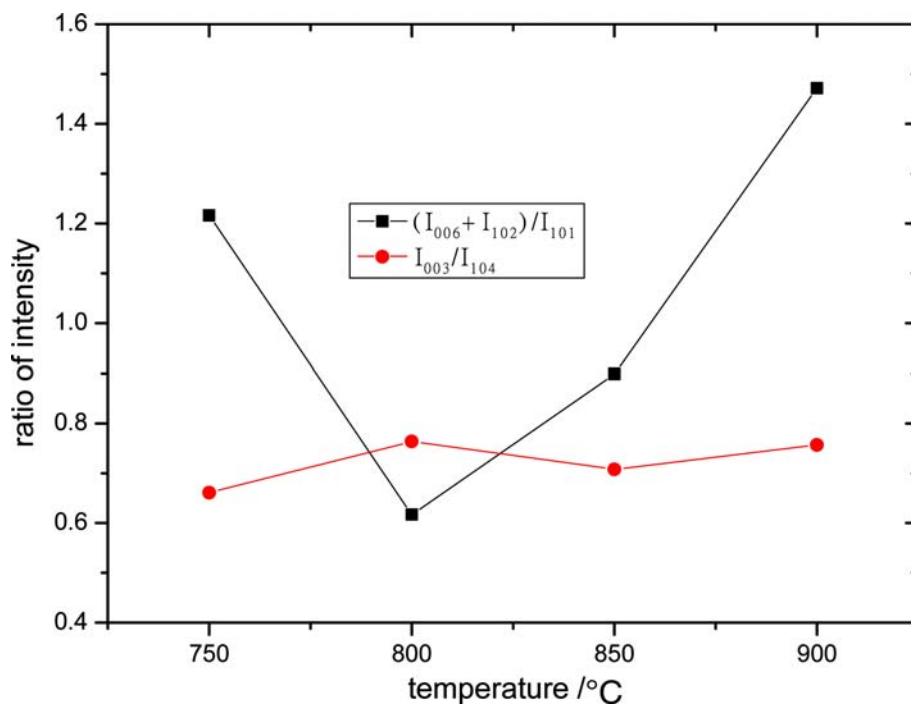


Fig. 7. Variations of the ratios of intensities of XRD peaks for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized by the combustion method with the synthesizing temperature for 12 h in 3.6 mole ratio of urea to nitrate.

From these results, the optimum condition for synthesizing  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  by the combustion method, is calcination at 800 °C for 12 h in air in 3.6 mole ratio of urea to nitrate.

Figure 9 gives the XRD patterns for  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) synthesized by the combustion method at 800 °C for 12 h in air in 3.6 mole ratio of urea/nitrate. All the samples revealed the formation of

the phase with  $R\bar{3}m$  structure. The intensities of the peaks decrease as the value of  $y$  increases.

Figure 10 shows the variations of the ratios of intensities of XRD peaks  $I_{003}/I_{104}$  and  $(I_{006} + I_{102})/I_{101}$  as a function of  $y$  for the  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) synthesized at 800 °C for 12 h in 3.6 mole ratio of urea/nitrate. As the value of  $y$  increases,  $I_{003}/I_{104}$  increases and  $(I_{006} + I_{102})/I_{101}$  decreases. The

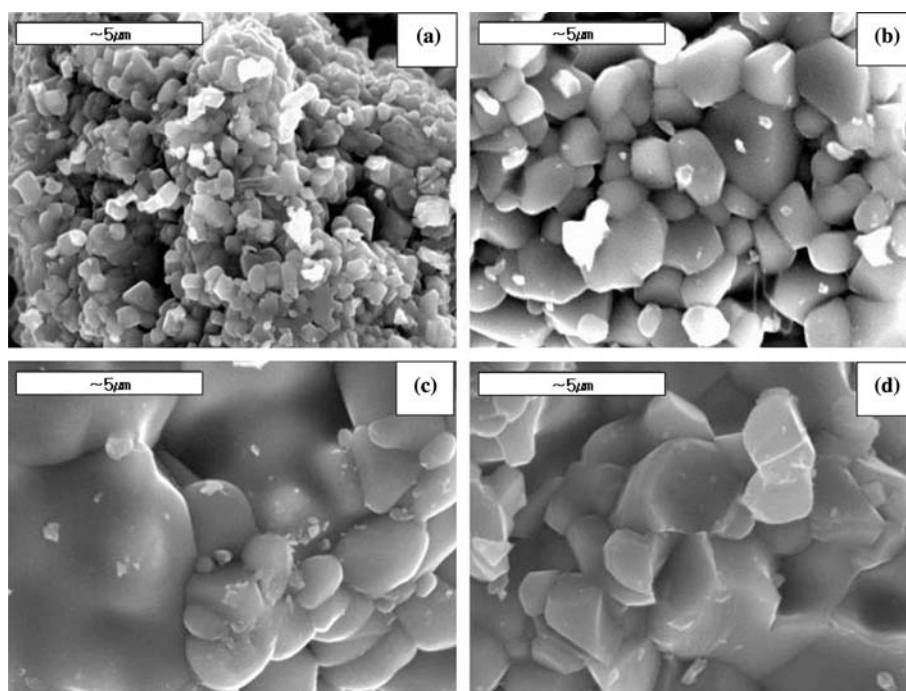


Fig. 8. SEM photographs for the  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized by the combustion method at various temperatures for 12 h in 3.6 mole ratio of urea to nitrate; (a) 750 °C, (b) 800 °C, (c) 850 °C and (d) 900 °C.

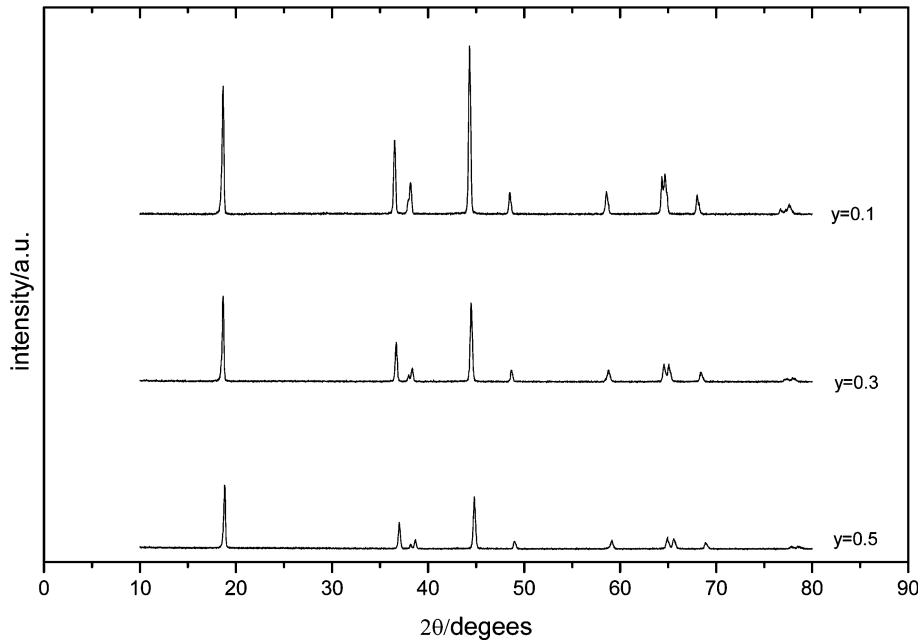


Fig. 9. XRD patterns for the  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) synthesized by the combustion method at  $800^\circ\text{C}$  for 12 h.

increase in  $I_{003}/I_{104}$  and the decrease in  $(I_{006} + I_{102})/I_{101}$  with increase in  $y$  suggest an decrease in the cation mixing and an increase in the hexagonal ordering. The easier synthesis of the phase with the  $R\bar{3}m$  structure as the value of  $y$  increases is considered to lead to a decrease in cation mixing and an increase in hexagonal ordering.

Figure 11 gives the SEM photographs of the  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) synthesized at  $800^\circ\text{C}$  for 12 h in 3.6 mole ratio of urea/nitrate. The particle size

decreases as the value of  $y$  increases. The particles with  $y=0.3$  are spherical with uniform particle size.

Figure 12 shows the variations of discharge capacities at 0.5C and 0.1C with the number of cycles for the  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) synthesized by the combustion method at  $800^\circ\text{C}$  for 12 h in air in 3.6 mole ratio of urea to nitrate. The first discharge capacities at 0.5C are  $84.5$  ( $y=0.1$ ),  $156.2$  ( $y=0.3$ ) and  $134.5$  ( $y=0.5$ )  $\text{mAh g}^{-1}$ . The sample with  $y=0.3$  has the largest first discharge capacity and relatively good cycling

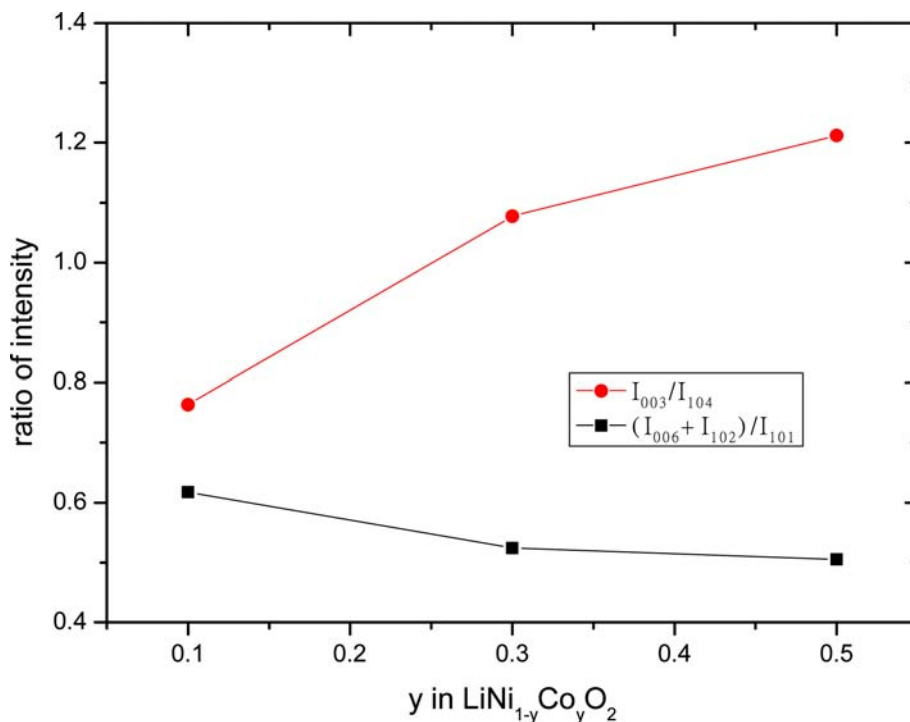


Fig. 10. Ratios of intensities of XRD peaks for the  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) synthesized by the combustion method at  $800^\circ\text{C}$  for 12 h.

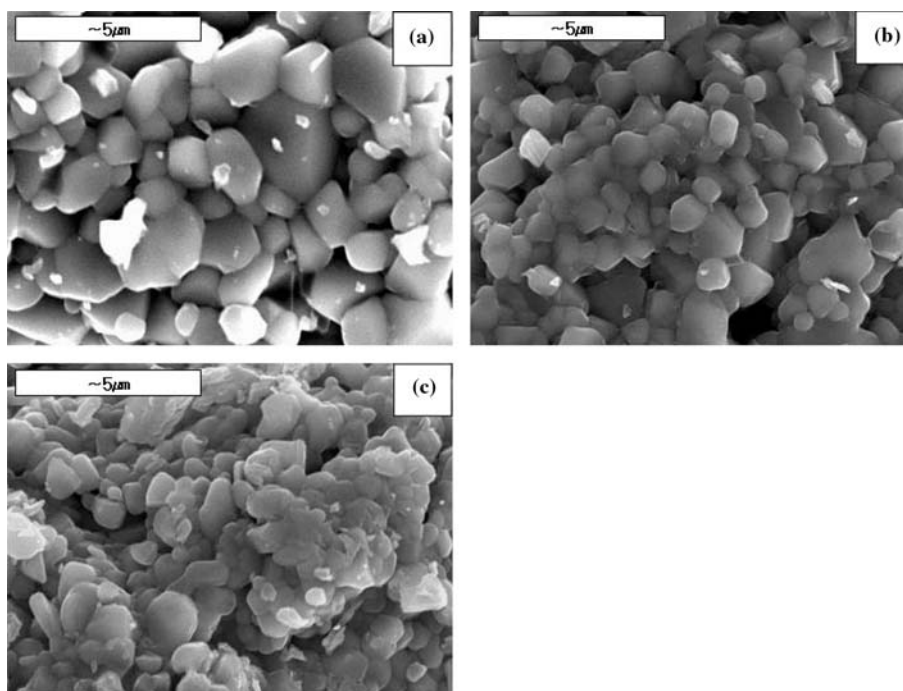


Fig. 11. SEM photographs of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) synthesized by the combustion method at  $800\text{ }^\circ\text{C}$  for 12 h; (a)  $y=0.1$ , (b)  $y=0.3$  and (c)  $y=0.5$ .

performance. The sample with  $y=0.3$  shows the first discharge capacity at  $0.1\text{C}$  of  $181\text{ mA h g}^{-1}$ , but its cycling performance is worse than that at  $0.5\text{C}$ .

#### 4. Conclusions

The optimum condition for synthesizing  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  by the combustion method is calcination at  $800\text{ }^\circ\text{C}$  for

12 h in air in 3.6 mole ratio of urea to nitrate. The  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized under these conditions shows the smallest R-factor  $\{(I_{006} + I_{102})/I_{101}\}$  and the largest  $I_{003}/I_{104}$ , indicating better hexagonal ordering and less cation mixing, respectively.

The  $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$  synthesized at  $800\text{ }^\circ\text{C}$  for 12 h in air in 3.6 mole ratio of urea to nitrate has the largest first discharge capacity  $156.2\text{ mA h g}^{-1}$  at  $0.5\text{C}$  and shows relatively good cycling performance. This sample shows

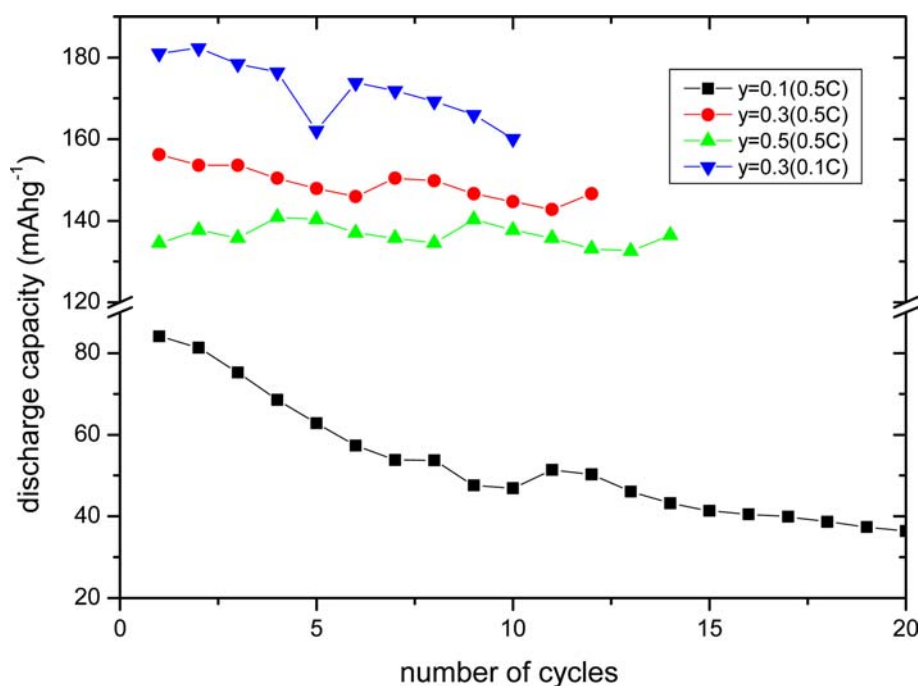


Fig. 12. Variations of discharge capacities with the number of cycles for the  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.5$ ) synthesized by the combustion method.

better hexagonal ordering and less cation mixing than the other samples. The particle size of the  $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$  is relatively small and its particles are spherical with uniform particle size.

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