

# Synthesis and Electrochemical Characterization of Gradient Composite $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ Used as Cathode Materials in Lithium-ion Battery

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Gradient composites,  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ , are synthesized from coated spherical  $\text{Ni}(\text{OH})_2$  precursor. These composites could be applied as new cathode materials in lithium-ion batteries because they have low cobalt content ( $y \leq 0.2$ ) and exhibit excellent properties during high-rate charge/discharge cycles. The initial discharge capacity of coated composite of  $\text{LiNi}_{0.95}\text{Co}_{0.05}\text{O}_2$  is 186 mAh/g, and the decreasing rate of the capacity is 3.2% in 50 cycles at 1 C rate. It has been verified by TEM and EDX experiments that a core-shell structure of the composite particles develops because of the cobalt enrichment near the surfaces, and the formation of the cobalt enrichment layer is sensitive to sintering temperature. High cobalt surface concentration may reduce the undesired reactions and stabilize the structure of the particles.

**Keywords**    lithium-ion battery, cathode material, gradient material, lithium nickel oxide, cobalt concentration

## Introduction

The  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  oxides have been extensively studied in literature because of their potential application as cathode materials in lithium-ion batteries. Typically, partial substitution of cobalt for nickel is believed to improve not only 2D structural characters of  $\text{NiO}_2$  slabs, but also the cycling properties during the charge/discharge process by facilitating the lithium intercalation.<sup>1-6</sup>

Many methods, such as solid state reaction, co-precipitation method,<sup>7,8</sup> sol-gel<sup>9,10</sup> etc., have been conducted to distribute cobalt uniformly in the  $\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  slabs. Although the solid solution,  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ , can be easily synthesized in acceptable qualities with these methods, the performance is not satisfied in terms of the cycling properties and thermal stability. During the charging process,  $\text{NiO}_2$  reacts with the organic electrolyte and induces the dissolution of Ni ions into solution, which deteriorate the cycling performance. On the other hand, it was speculated that the exothermic decomposition of electrolyte is triggered by dissociation of the metal-oxygen bond, which is accompanied by the evolution of oxygen.<sup>11,12</sup> These reactions near the surfaces of the particles have negative effects on the performance of the cathode material. In the present work, we try to reduce these reactions by modifying the characteristics of the surface. A series of gradient composite materials with low cobalt content,  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  ( $0 < y < 0.2$ ), were synthesized at lower sintering temperatures. Experimental results indicate that the gradient composite

cathode materials exhibit excellent cycle-life performance. The enrichment of the cobalt on the surfaces decreases the cobalt content in the composite particles and causes the improvement of cycling performance. Higher Co concentration on the surfaces may reduce the undesired reactions, and stabilize the structure of the particles.

## Experimental

Composite cathode materials were prepared by coating the spherical  $\text{Ni}(\text{OH})_2$  particles with a layer of  $\text{Co}(\text{OH})_2$  precursor. Spherical  $\text{Ni}(\text{OH})_2$  particles, which was used as cathode material with high density in Ni/MH batteries, were suspended in distilled water containing ammonia at 55 °C. Then, an appropriate amount of  $\text{CoSO}_4$  and  $\text{NaOH}$  solution was added into the suspension respectively. With adequate stirring, a layer of  $\text{Co}(\text{OH})_2$  precipitated on the surface of spherical  $\text{Ni}(\text{OH})_2$  particles. The coated precursors with different Ni/Co ratio were uniformly mixed with lithium salts in the ratio of  $(\text{Li}/(\text{Co},\text{Ni})=1.05)$ , then sintered at various temperatures between 600 and 750 °C to form the composite cathode particles with a cobalt-enriched layer.

The cathode was prepared by mixing the composite cathode materials, acetylene black, PVDF and NMP. Then, the mixed paste was coated on an aluminum foil substrate. The anode was prepared by mixing MCMB and PVDF binder in NMP. Then, the mixed paste was coated on copper foil substrate. Electrolyte was 1 mol/L

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Received December 1, 2003; revised and accepted May 25, 2004.

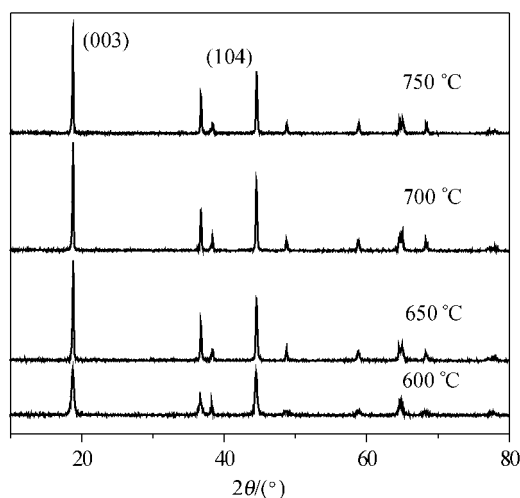
LiPF<sub>6</sub>-EC-DMC (1 : 1 in volume) solution. The electrochemical properties of the composite cathode materials were tested with prismatic battery of 063048. The initial charge/discharge rate was 0.5 C between 2.75 V and 4.1 V, then 1 C between 2.75 and 4.35 V for the following 49 charge/discharge cycles.

Electron microscopies were used to study the distribution of the cobalt and the electrochemical characteristics. These analyses were conducted by using scanning electron microscope (SEM), transmission electron microscope (TEM), and an energy dispersive X-ray (EDX) analyzer attached to TEM. Typically, TEM is applied in thin-film analysis because electrons have limited ability to transmit through materials. In the present study, the surface of the specimen was bombed with argon ion beam in vacuum to obtain a thin film. Atoms near the surface of the specimen were knocked out by the scanning and bombing of ion beam at a certain angle. Then, a thin film of the composite could be obtained which allows electrons to transmit through the specimen. Powder X-ray diffraction (XRD) was used to study structural features of the composites.

## Results and discussion

### XRD characterization of the LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> composites

XRD patterns from the LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> composites sintered at 600, 650, 700 and 750 °C are shown in Figure 1 respectively. The  $\alpha$ -NaFeO<sub>2</sub> structure is formed at each temperature studied. The composites sintered at 650 °C or higher show narrower peaks, which indicate the better crystallization at high temperatures. In addition, the splitting of (018) and (110) peaks as well as (006) and (102) peaks are more evident with the increase of sintering temperature.



**Figure 1** XRD patterns for the composites LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> sintered at 600, 650, 700 and 750 °C, respectively.

Table 1 shows the hexagonal unit cell parameters and the intensity ratios of (003) to (104) for the composites sintered at various temperatures. In these cases,

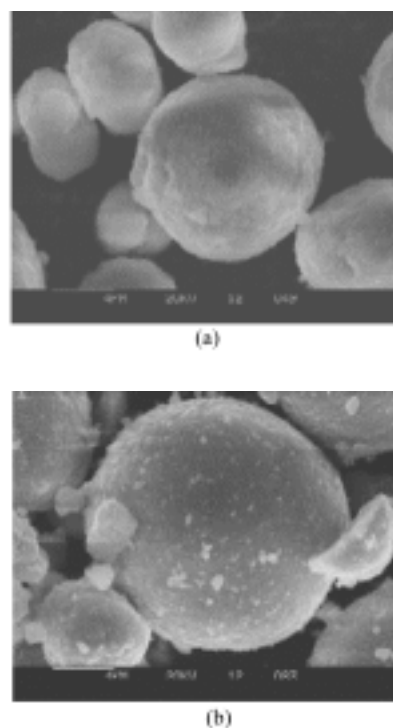
parameters  $a$ ,  $c$  and the volumes for the composites sintered at 600 °C are the smallest because of lower crystallization. The literature 1 shows that ratio of the  $I_{(003)}/I_{(104)}$  is most sensitive to the ordering of lithium and other metal (nickel and/or cobalt) ions in alternating layers of the  $\alpha$ -NaFeO<sub>2</sub> type crystal structure. The composite sintered at 650 °C shows the highest intensity ratio of (003) to (104) and an improved 2D structure. A sintering temperature of 650 °C or higher may be necessary to form the expected pure 2D structure.

**Table 1** Unit cell parameters in  $R\bar{3}m$  and the intensity ratios of (003) to (104)

Sintering temperature/°C	$a/\text{nm}$	$c/\text{nm}$	$c/a$	$V/\text{nm}^3$	$I_{003}/I_{104}$
600	0.2791	1.3817	4.951	9.331	0.980
650	0.2873	1.4199	4.942	10.153	1.403
700	0.2871	1.4183	4.940	10.126	1.282
750	0.2870	1.4171	4.938	10.110	1.136

### Characterization of the particle structure of the LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> composite

Figure 2 shows the SEM photographs of the coated precursor and the composite particles. The appearance of the sintered composite material is similar to that of the spherical coated precursor. The coated precursor and LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> particles show uniform surface texture.



**Figure 2** SEM micrographs of the particle of (a) precursor spherical Ni(OH)<sub>2</sub> coated with Co(OH)<sub>2</sub>, and (b) formed composite LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> sintered at 600 °C.

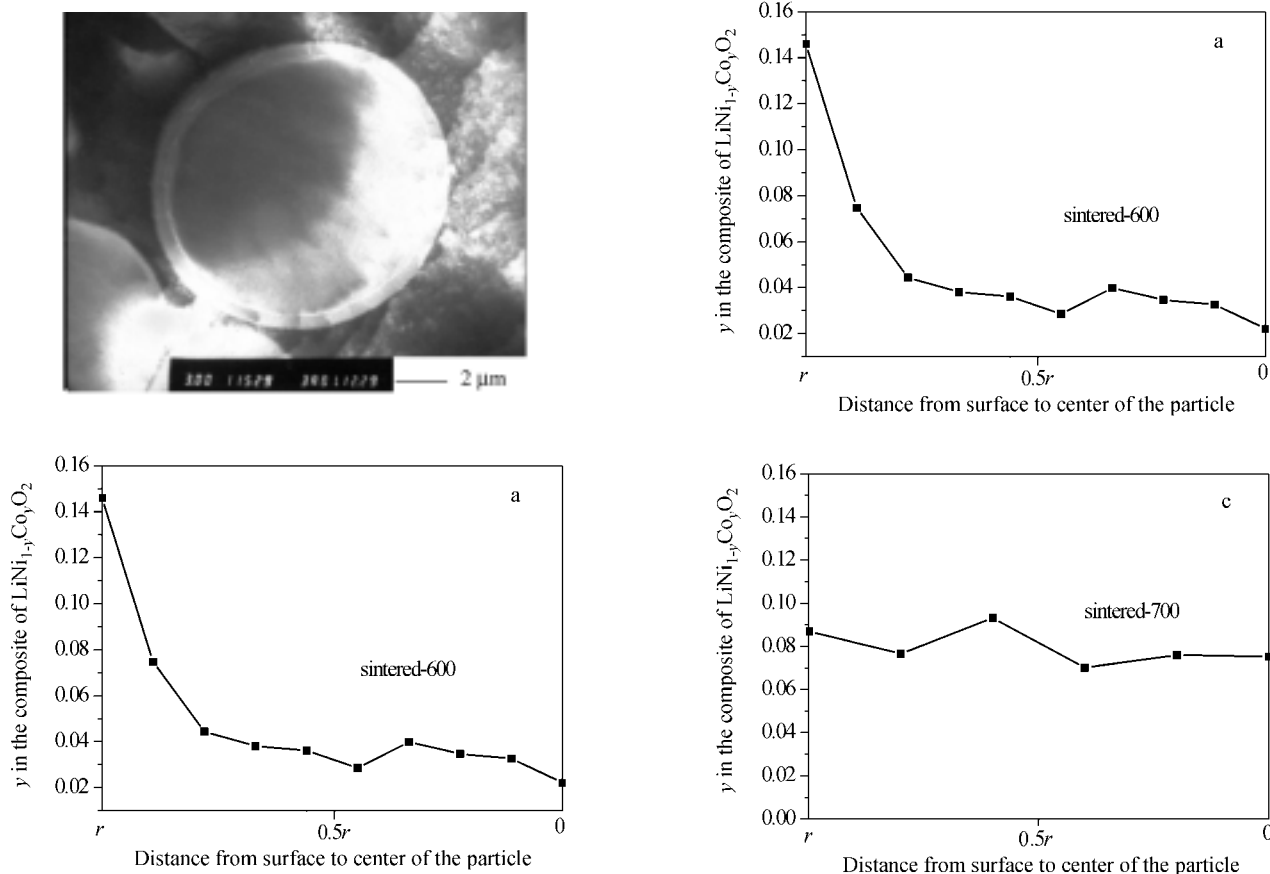
In Figure 3, TEM micrograph shows clearly the

core-shell structure the composite particle, which was covered with a cobalt-rich layer. The concentration of Co through the particle was measured by energy dispersive X-ray (EDX). Testing spots were selected from the surface to the center along the radius of the particle at a fixed step during EDX experiments.

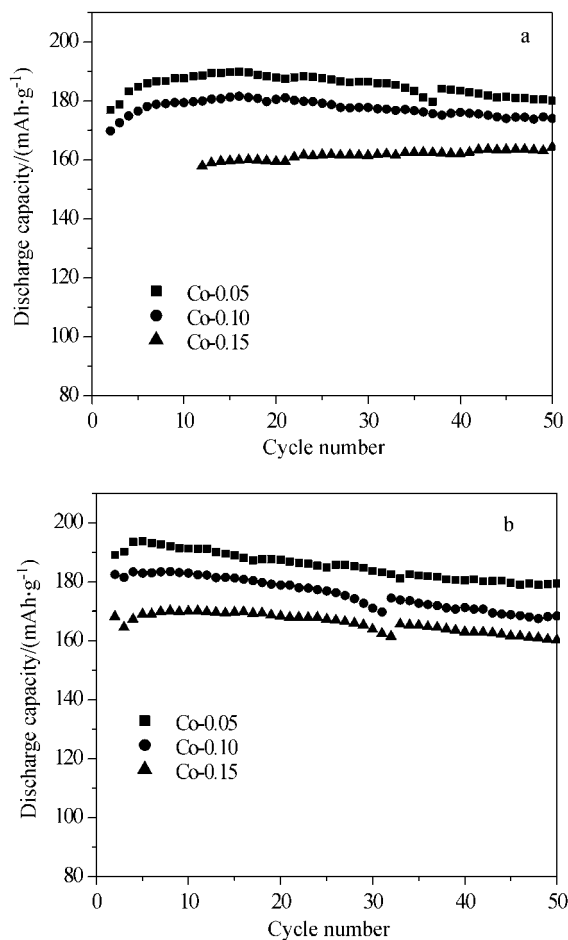
Figures 3a, 3b, and 3c show the distribution of cobalt contents through the composite particles sintered at various temperatures. As shown in Figure 3a where the composite was sintered at 600 °C, cobalt concentration near the surface is much higher than that in matrix, which may be caused by the formation of Co-rich shell around the particle. With increasing sintering temperature, Co content near the surface decreases while the matrix concentration increases, which could be explained by the enhanced diffusivity of Co atoms at high temperatures. Co atoms diffuse to the matrix forming the particles of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  with a more even distribution of Co. In another word, the shell is "dissolved" gradually with increasing sintering temperature. At the sintering temperatures of 700 and 750 °C, Co distribution becomes uniform through the particle. Therefore, the sintering temperature is critical to the formation of the  $\text{LiCoO}_2$  coating layer. According to the variation of the Co concentration through the particle, it is confident to define these materials as gradient composites.

### Electrochemical characterization of the gradient $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ composites

Although the composite particle sintered at 600 °C has a high Co concentration gradient, its special capacity is low, because of the low sintering temperature and bad crystallization shown in the XRD pattern. After sintered at high temperature 750 °C, Co distribution becomes uniform through the particle, and the capacity retainability of these composites decreases to about 90% after 50 cycles. Considering the effect of synthesis temperature and Co content gradient, Figure 4 shows respectively the electrochemical performance of the gradient  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  composites sintered at 650 °C and 700 °C with various cobalt content of  $y=0.05, 0.10$  and  $0.15$ , which exhibit better electrochemical performance. All synthesized gradient composites exhibit excellent cyclic reversibility, particularly at high charge/discharge rate. The composites have very small loss in discharge capacity in comparison with the uniform solid-solution  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  synthesized by the typical solid-state reaction.<sup>2,4</sup> The initial discharge capacity of the gradient composites increases with the increasing sintering temperature, which might be caused by the better crystallization as shown by XRD in Figure 1. From Figures 4a and 4b, composites sintered at 650 and 700 °C exhibiting a slight increase in initial discharge capacity with increasing sintering temperature



**Figure 3** TEM micrograph of the composite particle  $\text{LiNi}_{0.95}\text{Co}_{0.05}\text{O}_2$  sintered at 600 °C and the cobalt concentration through the particle sintered at different temperatures, (a) 600 °C, (b) 650 °C, and (c) 700 °C.



**Figure 4** The cycling performance of the gradient composite cathode materials sintered at (a) 650 °C and (b) 700 °C with different cobalt contents of  $y=0.05$ , 0.10 and 0.15 (total content of Ni plus Co is 1).

is observed. In addition, it is evident that the cycling properties deteriorate with the increasing sintering temperature.

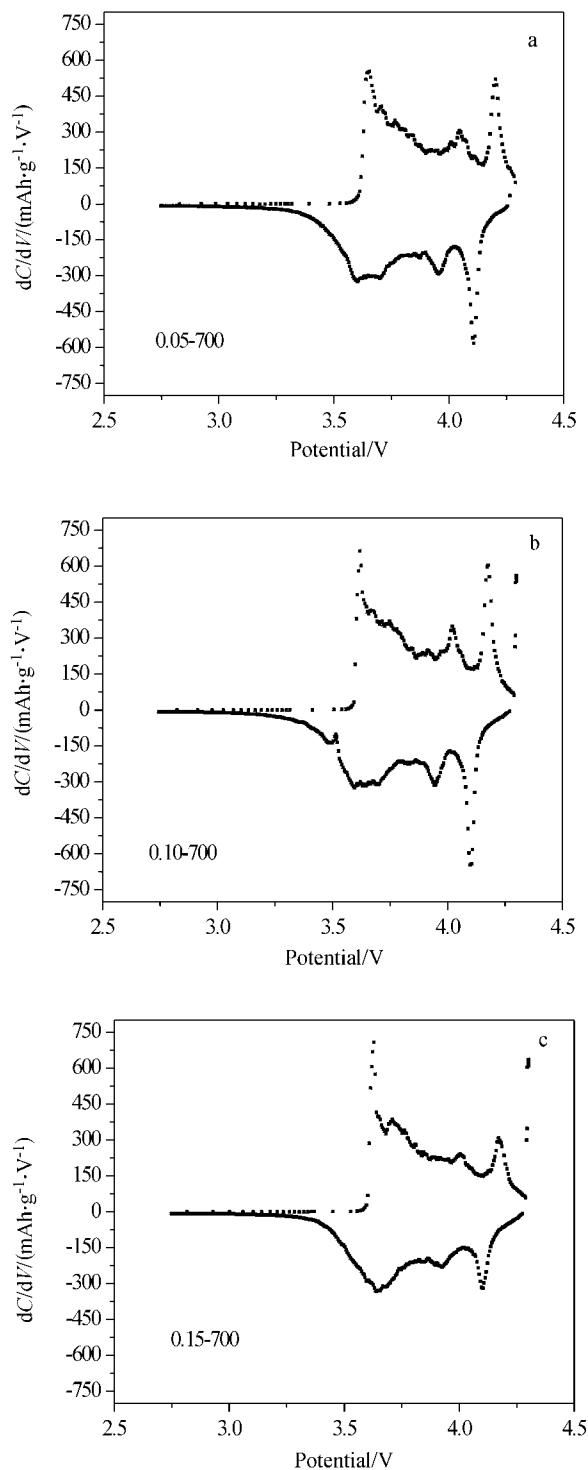
Figure 4 also shows the effects of various cobalt contents on the electrochemical properties of the gradient composite cathode materials. The charge/discharge capacity of the composite materials decreases with an increase of cobalt content. The composite material with cobalt content of  $y=0.05$  shows a high discharge capacity of 190  $\text{mAh}/\text{g}$ , while the composite with higher cobalt content ( $y=0.15$ ) shows a lower discharge capacity of 165  $\text{mAh}/\text{g}$ . The discharge capacity of the composite sintered at 650 °C with cobalt content  $y=0.05$ , which is 186  $\text{mAh}/\text{g}$  (5th cycle) initially at 1 C rate, is reduced to 180.1  $\text{mAh}/\text{g}$  after 45 cycles.

Moreover, the capacity retainability is also improved with the increase of the cobalt content. The composite sintered at 650 °C with  $y=0.15$  exhibits very good cycle reversibility. Even though the initial capacity is as low as 157  $\text{mAh}/\text{g}$ , the cycling reversibility of this composite is much better than that of others at high charge/discharge rate. There is no decrease of the capacity at 1 C in 50 cycles.

Although further studies should be conducted to ver-

ify the structure of the composites and understand the effects on the electrochemical performance, it is reasonable to conclude that the surface enrichment of the cobalt may reduce the undesired reactions, therefore stabilizing the gradient composite particle and improving the cycling properties greatly.

Figure 5 shows the differential capacity curves for



**Figure 5** Differential capacity plots of the gradient composites  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  sintered at 700 °C with different cobalt content (a)  $y=0.05$ , (b)  $y=0.10$ , (c)  $y=0.15$ .

the composites of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  with various cobalt contents. The sharp peaks in the curves indicate that the composites experienced phase transformation during charge/discharge cycle,<sup>13</sup> which could deteriorate the cycling reversibility of the cathode materials. It is different from that of the uniform solid-solution  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  where the sharp peaks in the differential capacity curves disappeared in the uniform Ni-Co system.<sup>14</sup>

Although phase transformation occurs during the electrochemical process, as shown in Figure 4, the cycling properties of the gradient composites  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  with higher cobalt enrichment on the surface are greatly improved. It could be explained by the improved surface-enrichment stability of cobalt and the fine spherical particles. In addition, the composites sintered at lower temperatures have lower densities than those synthesized by solid state reaction at high temperatures. Therefore, the stress induced by the phase transformation during charge/discharge cycles could counteract within the particles.

## Conclusion

A series of gradient  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  composites were synthesized by coating precursors. The results of TEM and EDX experiments verified the gradient distribution of cobalt through the coated particles. The gradient composites provide excellent properties during charge/discharge cycles without a significant deterioration of the initial capacity. The charge/discharge capacity of the composites decreases with the increase of the cobalt content, while the capacity retainability increases. The sintering temperature is critical to the formation of the gradient distribution of cobalt inside the particles.

Although the gradient composites experience phase transformation during charge/discharge cycles, they exhibit excellent cycling performance, which may be caused by the improved stability of the cobalt enrichment near the surface and the fine spherical particles.

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