

Electrochemical characteristics of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ as positive electrode materials for lithium secondary batteries

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Abstract

Physical properties and electrochemical behavior of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($0.1 \leq x \leq 0.9$) were investigated for use as positive electrode material in lithium secondary batteries with long cycle life. $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ are characterized by an $\alpha\text{-NaFeO}_2$ type structure. In a three-electrode test cell, $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ showed a large discharge capacity of 159 Ah kg^{-1} , and good cycle performance, with a discharge capacity deterioration ratio of 0.73% per cycle. In a 2 Wh-class cell, $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ exhibited a discharge capacity of 520 mAh, and good cyclability, with a discharge capacity deterioration ratio of 0.026% per cycle. $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ is a promising positive electrode material, having the largest discharge capacity and the best cycle performance in the series of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ compounds. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium secondary batteries; Longer cycle life; Positive electrode; $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$

1. Introduction

Much attention has been paid to the development of lithium secondary batteries for dispersed energy storage systems, such as home use load leveling systems [1]. Given these batteries are designed to be used as long as 10 years, with a daily charge/discharge cycle, they require a much longer cycle life than batteries used for consumer electrical devices. Such a period requires a cycle life of more than 3500 cycles.

Carbon materials are used as negative electrodes for consumer lithium secondary batteries because they are superior to lithium metal negative electrodes, in terms of cycle performance and safety [2–6]. We have found that a graphite/coke hybrid carbon as the negative electrode material (4:1 in weight ratio) has longer cycle performance than natural graphite, coke or other mixtures of natural graphite and coke [7,8].

Many studies have been conducted on the synthesis and characterization of lithium transition metal oxides as positive electrode materials [9–13]. In these studies, much attention has been given to LiCoO_2 , LiNiO_2 and LiMn_2O_4 .

LiCoO_2 exhibits many attractive characteristics, including high operating voltage, large capacity and long cycle life, but while used commercially, its high cost is problematic. LiNiO_2 was considered a promising positive material, with larger discharge capacity and lower cost than LiCoO_2 . However, irreversible structural change occurs for lithium content lower than 0.5, which modifies electrochemical characteristics and reduces reversible capacity [14].

The use of solid solution between LiCoO_2 and LiNiO_2 results in less structural change, which is more promising for cycle life [15,16]. In this study, $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ were synthesized, and the charge/discharge characteristics and cycle performances of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ were investigated in three-electrode test cells. To investigate cycle performances for longer cycle test, we fabricated 2 Wh-class cylindrical cells and conducted charge/discharge cycle tests.

2. Experimental

2.1. Preparation of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$

$\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0.1\text{--}0.9$) were prepared from a stoichiometric mixture of lithium hydroxide (LiOH), nickel hydroxide (Ni(OH)_2) and cobalt hydroxide (Co(OH)_2) by

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heat-treating at 850°C for 20 h. The crystal structures of these samples were characterized by powder X-ray diffraction (XRD) method using Cu K α radiation.

2.2. Electrochemical behavior of LiNi_{1-x}Co_xO₂

Electrochemical characteristics of LiNi_{1-x}Co_xO₂ were measured in three-electrode experimental cells at room temperature. A mixture of the LiNi_{1-x}Co_xO₂, carbon and binder was used as the working electrode. Reference and counter electrodes were lithium metal. Electrolyte was 1 mol dm⁻³ lithium hexafluorophosphate (LiPF₆) in a mixture of 50% ethylene carbonate (EC) and 50% diethyl carbonate (DEC) in volume. The charge and discharge current densities were 0.25 mA cm⁻² and the potential range was from 2.0 to 4.3 V (versus Li/Li⁺).

2.3. 2 Wh-class cell test

The 2 Wh-class cells (\varnothing 14.2 mm \times 50.0 mm) were fabricated with a positive electrode, a negative electrode, and, as electrolyte, 1 mol dm⁻³ LiPF₆ in a mixture of 50% EC and 50% DEC in volume. In cycle performance testing, the cells were discharged at 515 mA until the voltage reached 2.7 V, after being charged 360 mAh, which is equivalent to 70% the depth of the capacity, at 210 mA. Every 50 cycles in this condition, the full discharge capacity was measured as follows: the cells were charged up to 4.2 V at 72 mA, then discharged at 65 mA until the voltage reached 2.7 V.

3. Results and discussion

3.1. Characterization of LiNi_{1-x}Co_xO₂

The XRD patterns of LiNi_{1-x}Co_xO₂ ($x = 0.1-0.9$) samples appear in Fig. 1. In the composition range ($0.1 \leq x \leq 0.9$), single phases of LiNi_{1-x}Co_xO₂ were obtained, characterized by an α -NaFeO₂ type structure (space group: $R\bar{3}m$) (O3 type structure). The a and c parameters in the hexagonal structure increased continuously, as the content of Ni in LiNi_{1-x}Co_xO₂ increased (Fig. 2). This result corresponds to the results of C. Delmas and coworkers [15,16], and we attribute it to the difference in size of trivalent Ni (0.056 nm) and trivalent Co (0.053 nm) in LiNi_{1-x}Co_xO₂.

3.2. Electrochemical behavior of LiNi_{1-x}Co_xO₂

Electrochemical characteristics of the obtained LiNi_{1-x}Co_xO₂ were measured in three-electrode experimental cells. Fig. 3 shows the initial discharge curves of LiNi_{1-x}Co_xO₂. Every curve was smooth and had the potential plateau at the potential range of 3.5–4.0 V (versus Li/Li⁺), which suggests that less phase transition occurs during the intercalation of Li. As shown in Fig. 4, the initial discharge capacity of the LiNi_{1-x}Co_xO₂ was more than 120 Ah kg⁻¹ and generally

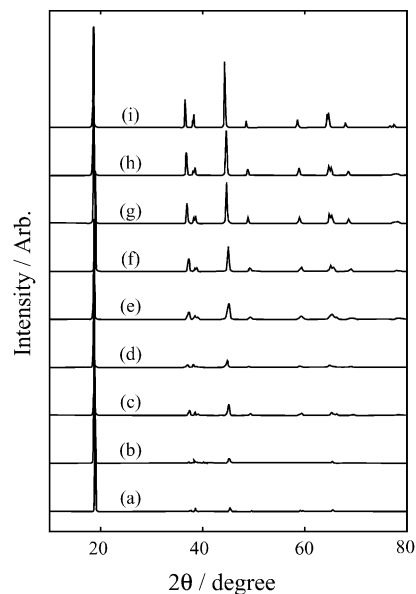


Fig. 1. X-ray powder diffraction patterns of (a) LiNi_{0.1}Co_{0.9}O₂, (b) LiNi_{0.2}Co_{0.8}O₂, (c) LiNi_{0.3}Co_{0.7}O₂, (d) LiNi_{0.4}Co_{0.6}O₂, (e) LiNi_{0.5}Co_{0.5}O₂, (f) LiNi_{0.6}Co_{0.4}O₂, (g) LiNi_{0.7}Co_{0.3}O₂, (h) LiNi_{0.8}Co_{0.2}O₂ and (i) LiNi_{0.9}Co_{0.1}O₂.

increased with the increase of Ni content in the LiNi_{1-x}Co_xO₂. LiNi_{0.5}Co_{0.5}O₂, LiNi_{0.7}Co_{0.3}O₂ and LiNi_{0.8}Co_{0.2}O₂ had large discharge capacities, over 150 Ah kg⁻¹, and LiNi_{0.7}Co_{0.3}O₂ had the largest initial discharge capacity, at 159 Ah kg⁻¹.

The cycle performances of LiNi_{1-x}Co_xO₂ were measured at the same charge/discharge condition as the initial discharge capacity measurement. As shown in Fig. 5, at the 30th cycle, LiNi_{0.7}Co_{0.3}O₂ had the largest discharge capacity, at 125 Ah kg⁻¹, and the smallest discharge capacity deterioration ratio, at 0.73% per cycle. It was said that the unit lattice volume of LiNi_{1-x}Co_xO₂ were almost constant during the charging/discharging [17], and that LiNi_{0.7}Co_{0.3}O₂ had a completely ordered α -NaFeO₂ type structure [16]. The excellent cyclability of LiNi_{0.7}Co_{0.3}O₂ was

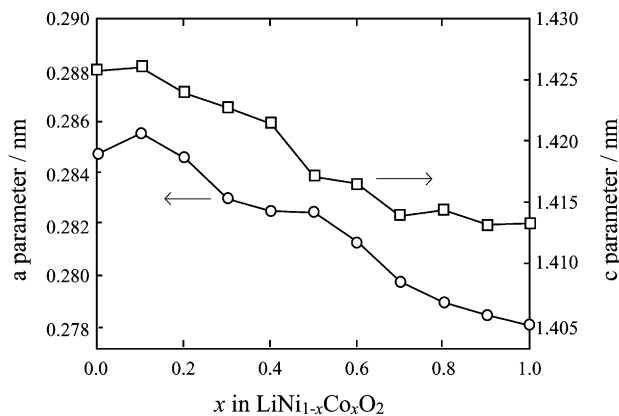


Fig. 2. Variation of the hexagonal cell parameters of LiNi_{1-x}Co_xO₂ ($0.1 \leq x \leq 0.9$).

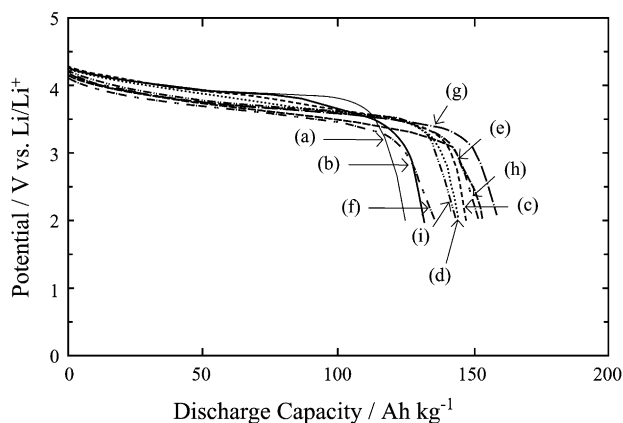


Fig. 3. Initial discharge curves of (a) $\text{LiNi}_{0.1}\text{Co}_{0.9}\text{O}_2$, (b) $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{O}_2$, (c) $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$, (d) $\text{LiNi}_{0.4}\text{Co}_{0.6}\text{O}_2$, (e) $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$, (f) $\text{LiNi}_{0.6}\text{Co}_{0.4}\text{O}_2$, (g) $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$, (h) $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and (i) $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ in a three-electrode test cell at a current density of 0.25 mA cm^{-2} .

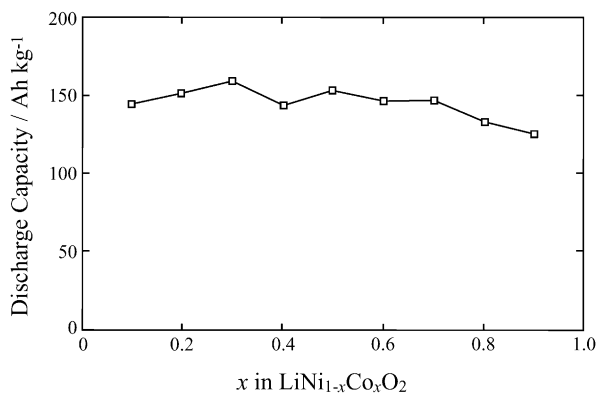


Fig. 4. Variation of the initial discharge capacity of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($0.1 \leq x \leq 0.9$).

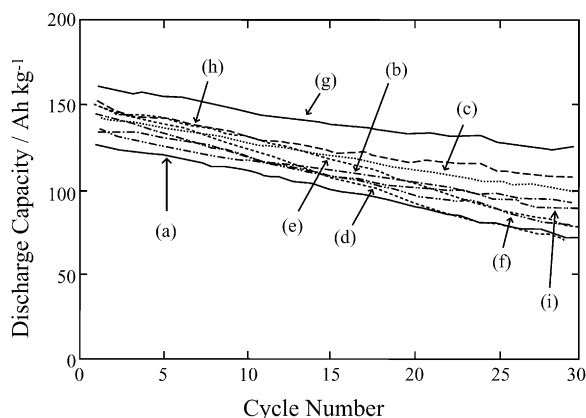


Fig. 5. Cycle performance of (a) $\text{LiNi}_{0.1}\text{Co}_{0.9}\text{O}_2$, (b) $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{O}_2$, (c) $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$, (d) $\text{LiNi}_{0.4}\text{Co}_{0.6}\text{O}_2$, (e) $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$, (f) $\text{LiNi}_{0.6}\text{Co}_{0.4}\text{O}_2$, (g) $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$, (h) $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and (i) $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ in a three-electrode test cell at a charge/discharge current density of 0.25 mA cm^{-2} .

considered to be due to the small lattice volume change and completely ordered structure. Further investigations are needed to explain the superior cyclability of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$.

3.3. Performance of 2 Wh-class cell

To investigate cycle performances of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ for longer cycle test, we fabricated 2 Wh-class cylindrical cells and conducted charge/discharge cycle test. We selected $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ as the positive electrode material, as it had the largest discharge capacity and the smallest discharge capacity deterioration ratio while cycling. For comparison, we chose $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$, which had the second largest energy density, defined as the equation $Q_{\text{dis}}V_{\text{ave}}/w$, where Q_{dis} is the discharge capacity, V_{ave} the average discharge potential, and w the weight of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$. We also used LiCoO_2 and LiNiO_2 as positive electrode materials. As the negative electrode material, we used a graphite/coke hybrid carbon (4:1 in weight ratio), which has longer cycle performance than natural graphite, coke or other mixtures of natural graphite and coke [7,8].

Initial discharge curves of these cells appear in Fig. 6. All cells exhibited discharge capacity exceeding 500 mAh, and the cell using $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ as positive electrode material had the largest discharge capacity, at 558 mAh, and the largest energy density, at 105 Wh kg^{-1} . Furthermore, the cell using LiCoO_2 showed the second largest energy density of the four cells, at 103 Wh kg^{-1} (Table 1). Thus, we selected $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ and LiCoO_2 as the positive electrode material, then carried out the cycle performance test.

Cycle performance of the 2 Wh-class cell using $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ as the positive electrode material appears in Fig. 7. At the 950th cycle, the cell had a capacity of 390 mAh, which is more than the capacity equivalent to 70% the depth of the cell's capacity. The discharge capacity deterioration ratio was 0.026% per cycle. This value was smaller than that

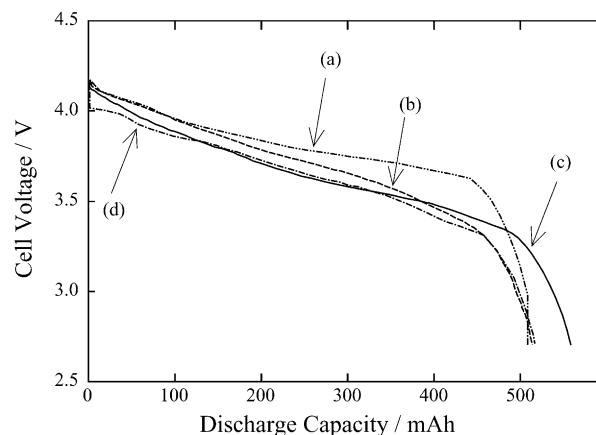


Fig. 6. Discharge curves of 2 Wh-class cells using (a) LiCoO_2 , (b) $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$, (c) $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ and (d) LiNiO_2 as positive electrode material at a discharge current of 65 mA.

Table 1
Discharge capacity and energy density of 2 Wh-class cells

Positive electrode material	LiCoO ₂	LiNi _{0.3} Co _{0.7} O ₂	LiNi _{0.7} Co _{0.3} O ₂	LiNiO ₂
Discharge capacity (mAh)	510	515	558	519
Energy density (Wh kg ⁻¹)	103	101	105	100

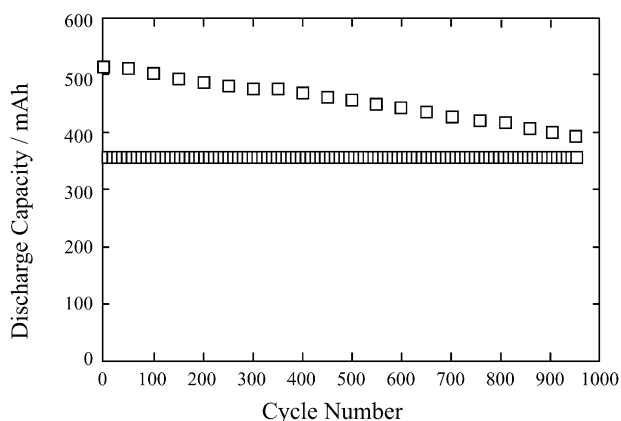


Fig. 7. Cycle performance of 2 Wh-class cell using LiNi_{0.7}Co_{0.3}O₂ as positive electrode material at a charge current of 210 mA and a discharge current of 515 mA.

which was obtained with the three-electrode test cell. This is because the potential range of LiNi_{0.7}Co_{0.3}O₂ on the cycle test in the 2 Wh-class cell was smaller than the potential range in the three-electrode test cell. In contrast, the cell using LiCoO₂ could maintain a capacity of 360 mAh for no longer than 100 cycles, when discharged at 515 mA.

We then conducted the cycle test with a discharge current of 210 mA. The cell using LiCoO₂ could maintain a capacity of 360 mAh for no longer than 400 cycles (Fig. 8). The discharge capacity deterioration ratio was 0.077% per cycle.

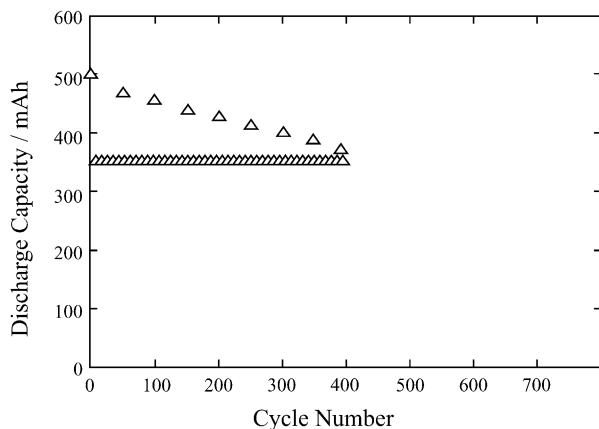


Fig. 8. Cycle performance of 2 Wh-class cell using LiCoO₂ as positive electrode material at a charge current of 210 mA and a discharge current of 210 mA.

4. Conclusion

Single phases of LiNi_{1-x}Co_xO₂ were synthesized from a stoichiometric mixture of Li(OH), Ni(OH)₂ and Co(OH)₂ by heat-treating at 850°C. From the results of XRD, LiNi_{1-x}Co_xO₂ were characterized by an α-NaFeO₂ type structure. In the three-electrode test cells, LiNi_{1-x}Co_xO₂ showed smooth discharge curves, which suggests less structural change with the intercalation of Li. Of the series of LiNi_{1-x}Co_xO₂ compounds, LiNi_{0.7}Co_{0.3}O₂ exhibited the largest discharge capacity, at 159 Ah kg⁻¹, and the highest energy density, exceeding 550 Wh kg⁻¹. Moreover, LiNi_{0.7}Co_{0.3}O₂ showed excellent cycle performance with the smallest discharge capacity deterioration ratio, at 0.73% per cycle. In the 2 Wh-class cell, LiNi_{0.7}Co_{0.3}O₂, used as the positive electrode material, exhibited the largest discharge capacity, at 558 mAh, and excellent cyclability more than 900 cycles, with a discharge capacity deterioration ratio of 0.026% per cycle. Therefore, we conclude LiNi_{0.7}Co_{0.3}O₂ to have the best cycle performance in the series of LiNi_{1-x}Co_xO₂ compounds.

Acknowledgements

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