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Synthesis of $LiNi_{0.9}Co_{0.1}O_2$ from Li_2CO_3, NiO or $NiCO_3$, and $CoCO_3$ or Co_3O_4 and their electrochemical properties

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Abstract

Cathode active materials with a composition of $LiNi_{0.9}Co_{0.1}O_2$ were synthesized by a solid-state reaction method at 850 °C using Li_2CO_3, NiO or $NiCO_3$, and $CoCO_3$ or Co_3O_4, as the sources of Li, Ni, and Co, respectively. Electrochemical properties, structure, and microstructure of the synthesized $LiNi_{0.9}Co_{0.1}O_2$ samples were analyzed. The curves of voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$ for the first charge–discharge and the intercalated and deintercalated Li quantity Δx were studied. The destruction of unstable 3b sites and phase transitions were discussed from the first and second charge–discharge curves of voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$. The $LiNi_{0.9}Co_{0.1}O_2$ sample synthesized from Li_2CO_3, NiO, and Co_3O_4 had the largest first discharge capacity (151 mA h/g), with a discharge capacity deterioration rate of −0.8 mA h/g/cycle (that is, a discharge capacity increasing 0.8 mA h/g per cycle).

Keywords: $LiNi_{0.9}Co_{0.1}O_2$; Solid-state reaction method; Various starting materials; Curve of voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$; Discharge capacity

1. Introduction

One of the most interesting types of rechargeable battery for portable electronics is the lithium secondary battery. It has quite high energy densities, no memory effect, and only a slow charge loss when not in use. Interest is also growing in using the lithium secondary battery for military, electric vehicle, and aerospace applications.

$LiCoO_2$ [1–5], $LiNiO_2$ [6–13], and $LiMn_2O_4$ [14–20] have been studied by many researchers as cathode materials for lithium secondary batteries [21]. $LiMn_2O_4$ contains a relatively inexpensive element, Mn, and is environment-friendly, but its cycling performance is poor. $LiCoO_2$ has a large diffusivity and a high operating voltage, and it can be synthesized relatively easily. However, it has a disadvantage in that it contains an expensive element, Co. $LiNiO_2$ has a large discharge capacity [22], and is relatively excellent economically and environmentally. However, since Li and Ni have similar sizes ($Li^+ = 0.72$ Å and $Ni^{2+} = 0.69$ Å), $LiNiO_2$ is usually obtained in non-stoichiometric compositions, $Li_{1-y}Ni_{1+y}O_2$ [23,24]. The Ni^{2+} ions in the lithium planes obstruct the movement of the Li+ ions during intercalation and deintercalation [5,25].

The shortcomings of $LiCoO_2$ and $LiNiO_2$ were overcome by incorporating $LiCoO_2$ and $LiNiO_2$ phases into $LiNi_{1-y}Co_yO_2$ compositions because the presence of cobalt stabilizes the structure in a strictly two-dimensional fashion, thus favoring good reversibility of the intercalation and deintercalation reactions [26–39]. Rougier et al. [26] reported that the stabilization of the two-dimensional character of the structure by cobalt substitution in $LiNiO_2$ is correlated with an increase in the cell performance, due to the decrease in the amount of extra nickel ions in the inter-slab space which impede the lithium diffusion.

For the synthesis of $LiNiO_2$ and $LiNi_{1-y}Co_yO_2$, several methods have been reported: the solid-state reaction method

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[40,41], the coprecipitation method [42], the sol–gel method [43], the ultrasonic spray pyrolysis method [44], the combustion method [11], and the emulsion method [45]. The solid-state reaction method, which is quite simple, was used in this work.

To synthesize $LiNi_{1-y}Co_yO_2$ by the solid-state reaction method [26–30,32–34,37–39,46] different starting materials have been used by researchers. $LiOH \cdot H_2O$ or Li_2CO_3, NiO or $NiCO_3$, and Co_3O_4 or $CoCO_3$ have been used as starting materials by some researchers [37–39,46].

In this work, $LiNi_{0.9}Co_{0.1}O_2$ cathode materials were synthesized by a solid-state reaction method at 850 °C using Li_2CO_3, NiO or $NiCO_3$, and $CoCO_3$ or Co_3O_4 as the sources of Li, Ni, and Co, respectively. The electrochemical properties of the synthesized samples were then examined. The structure of the synthesized $LiNi_{0.9}Co_{0.1}O_2$ was analyzed, and the microstructures of the samples were observed. The curves of voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$ for the first charge–discharge and the intercalated and deintercalated Li quantity Δx were studied. The destruction of unstable 3b sites and phase transitions were discussed from the first and second charge–discharge curves of voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$.

2. Experimental

Li_2CO_3, NiO or $NiCO_3$, and $CoCO_3$ or Co_3O_4 were used as starting materials in order to synthesize $LiNi_{0.9}Co_{0.1}O_2$ by the solid-state reaction method. All the starting materials (with purities of 99.9%) were purchased from Aldrich Co.

Fig. 1 schematically shows the experimental procedure for the synthesis of $LiNi_{0.9}Co_{0.1}O_2$ from Li_2CO_3, NiO or $NiCO_3$, and $CoCO_3$ or Co_3O_4 as the sources of Li, Ni, and Co, respectively, and the characterization of the synthesized samples. The mixture of the starting materials with the composition of $LiNi_{0.9}Co_{0.1}O_2$ was sufficiently mixed and pelletized. The pellet was then heat-treated in air at 650 °C for 20 h. It was then ground, mixed, pelletized, and calcined at 850 °C for 20 h. Then, this pellet was cooled at a rate of 50 °C/min, and then ground, mixed, and pelletized again. Finally, it was calcined again at 850 °C for 20 h.

The phase identification of the synthesized samples was carried out by X-Ray Diffraction (XRD) analysis using Cu K_α radiation (Mac-Science Co., Ltd.). The scanning rate was 16°/min, and the scanning range of the diffraction angle (2θ) was $10° \le 2\theta \le 70°$. The morphologies of the samples were observed using a scanning electron microscope (SEM).

Electrochemical cells consisted of $LiNi_{0.9}Co_{0.1}O_2$ as a positive electrode, Li foil as a negative electrode, and an electrolyte of 1 M $LiPF_6$ in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Whatman glass–fiber was used as a separator. The cells were assembled in an argon-filled dry box. To fabricate the positive electrode, 89 wt% synthesized oxide, 10 wt% acetylene black, and 1 wt% polytetrafluoroethylene (PTFE) binder were mixed in an agate mortar. By introducing Li metal, Whatman glass–fiber, the positive electrode, and the electrolyte, the cell was assembled. All the electrochemical tests were performed at room temperature with a potentiostatic/galvanostatic system (Mac-Pile system, Bio-Logic Co. Ltd.). The cells were cycled at a current density of 200 μA/cm^2 in a voltage range of 3.2–4.3 V.

3. Results and discussion

The XRD patterns of the $LiNi_{0.9}Co_{0.1}O_2$ and $LiCoO_2$ powders calcined at 850 °C for 40 h using $LiCO_3$, $NiCO_3$ and $CoCO_3$ as starting materials are shown in Fig. 2. The peaks are identified as corresponding to those of the $LiNiO_2$ phase, which has α-$NaFeO_2$ structure with a space

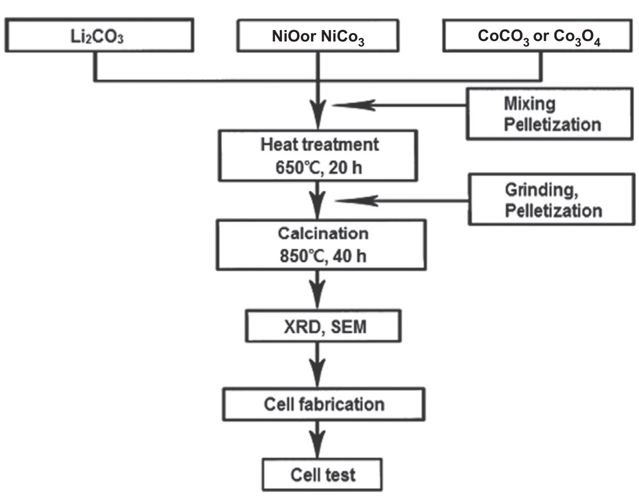

Fig. 1. Experimental procedure for $LiNi_{0.9}Co_{0.1}O_2$ synthesis from Li_2CO_3, NiO or $NiCO_3$, and $CoCO_3$ or Co_3O_4 as the sources of Li, Ni, and Co, respectively, and the characterization of the synthesized $LiNi_{0.9}Co_{0.1}O_2$.

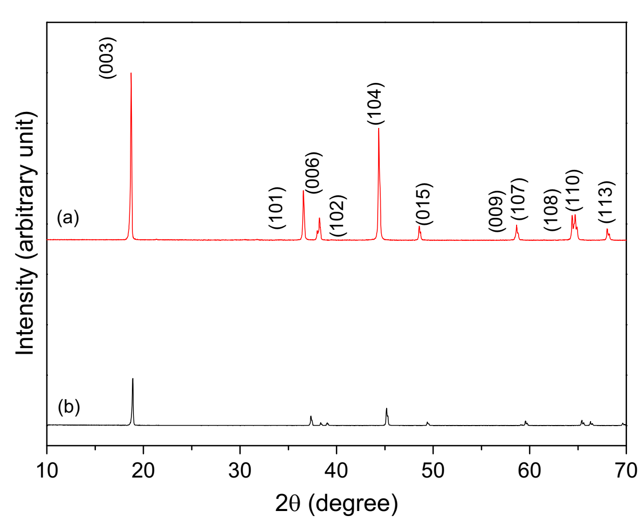

Fig. 2. X-ray (CuKα) diffraction patterns of (a) $LiNi_{0.9}Co_{0.1}O_2$ and (b) $LiCoO_2$ synthesized from Li_2CO_3, $NiCO_3$, and $CoCO_3$.

group of $R\bar{3}m$. The fraction of each phase from the intensity ratios of the 003 and 104 peaks can be calculated since the 003 peak originates from the diffraction of only the R3m α-$NaFeO_2$ structure while the 104 peak originates from the diffractions of both the $R\bar{3}m$ α-$NaFeO_2$ and Fm3m NaCl structures. The value of the intensity ratio of the 003 and 104 peaks, I_{003}/I_{104}, of the completely stoichiometric composition $LiNiO_2$ was reported to be about 1.3 by Morales et al. [24]. Ohzuku et al. [40] reported that the intensity ratio of the 003 and 104 peaks is a key parameter of the degree of displacement of the nickel and lithium ions. As the intensity ratio of the 003 and 104 peaks increases, the degree of displacement of the nickel and lithium ions decreases. They also reported that electroactive $LiNiO_2$ showed a clear split of the (108) and (110) lines, which appear in their XRD patterns at a diffraction angle near $2\theta=65^{\circ}$. The XRD pattern of the $LiNi_{0.9}Co_{0.1}O_2$ powder synthesized using $LiCO_3$, $NiCO_3$, and $CoCO_3$, exhibited in Fig. 2, shows that the intensity ratio of the 003 and 104 peaks is quite high and exhibits a clear split of the (108) and (110) lines.

Fig. 3 shows the SEM micrographs of the $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C from combinations of starting materials: (a) Li_2CO_3, NiO, and $CoCO_3$, (b) Li_2CO_3, NiO, and Co_3O_4, (c) Li_2CO_3, $NiCO_3$, and Co_3O_4, and (d) Li_2CO_3, $NiCO_3$, and $CoCO_3$. Overall, the sample (b) has the largest

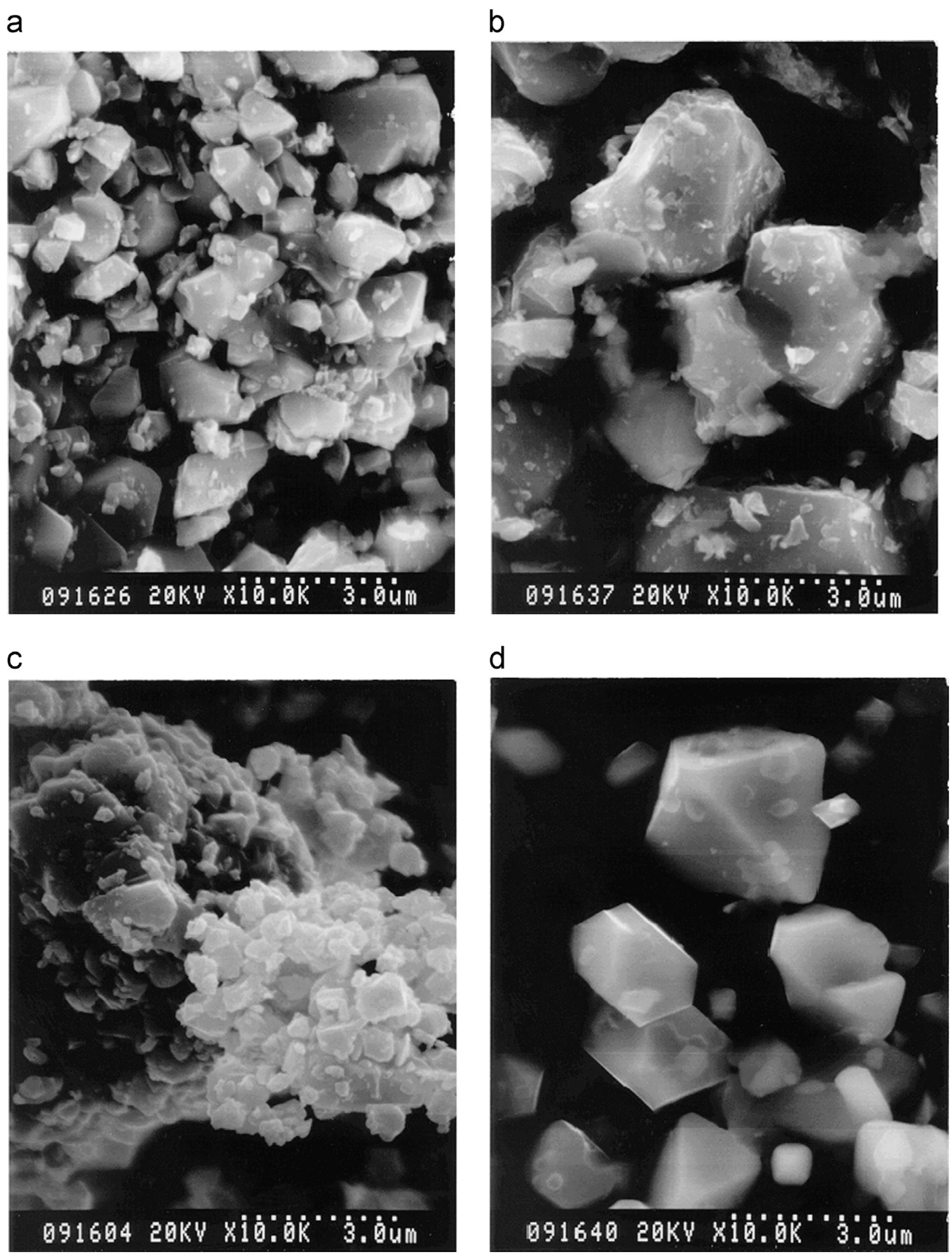

Fig. 3. SEM micrographs of the $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C from combinations of starting materials: (a) Li_2CO_3, NiO, and $CoCO_3$, (b) Li_2CO_3, NiO, and Co_3O_4, (c) Li_2CO_3, $NiCO_3$, and Co_3O_4, and (d) Li_2CO_3, $NiCO_3$, and $CoCO_3$.

particles, followed in order by sample (d), sample (a), and sample (c). The surfaces of the particles of sample (d) are flat, and the particles of sample (d) have sharp edges. The particles of the samples (c) are agglomerated.

The curves of voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$ at a current density of 200 μA/cm^2 for the first charge–discharge of $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C from combinations of starting materials are shown in Fig. 4, for: (a) Li_2CO_3, NiO, and $CoCO_3$, (b) Li_2CO_3, NiO, and Co_3O_4, (c) Li_2CO_3, $NiCO_3$, and Co_3O_4, and (d) Li_2CO_3, $NiCO_3$, and $CoCO_3$.

Polarization is a change in the potentials for the deintercalation and intercalation of lithium atoms. The sample (c) has the smallest polarization, followed in order by sample (a), sample (d), and sample (b). The charge or discharge capacity is proportional to the value of Δx in $Li_xNi_{0.9}Co_{0.1}O_2$. The sample (b) has the largest discharge capacity, followed in order by sample (c), sample (d), and sample (a).

Fig. 5 shows the curves of voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$ for the first and second charge–discharge cycles for $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C from Li_2CO_3, NiO, and Co_3O_4. The value of Δx for the second discharge is very similar to that for the first discharge.

The variations of the discharge capacity with the number of cycles (n) for $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C from (a) Li_2CO_3, NiO, and $CoCO_3$, (b) Li_2CO_3, NiO, and Co_3O_4, (c) Li_2CO_3, $NiCO_3$, and Co_3O_4, and (d) Li_2CO_3, $NiCO_3$, and $CoCO_3$ are shown in Fig. 6. The sample (b) has the largest first discharge capacity (151 mA h/g), followed in order by sample (c) (145 mA h/g), sample (d) (116 mA h/g), and sample (a) (113 mA h/g). The sample (b) has the largest particles with quite flat surfaces (Fig. 3). The sample (d) has the best cycling performance, followed in order by the samples (b), (c), and (a). Kang et al. [39] investigated the structure and electrochemical properties of the $Li_xCo_yNi_{1-y}O_2$ (y=0.1, 0.3, 0.5, 0.7 and 1.0) system synthesized by solid-state reaction with various starting materials to optimize the characteristics and synthetic conditions of the $Li_xCo_yNi_{1-y}O_2$. The first discharge capacities of $Li_xCo_yNi_{1-y}O_2$ were 60–180 mA h/g depending on synthesis conditions.

Fig. 7 shows the variations of the first-discharge capacity and the capacity deterioration rate of the $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C with the following combinations of starting materials: (a) Li_2CO_3, NiO, and $CoCO_3$, (b) Li_2CO_3, NiO, and Co_3O_4, (c) Li_2CO_3, $NiCO_3$, and Co_3O_4, and (d) Li_2CO_3, $NiCO_3$, and $CoCO_3$. The sample (b) has the largest first-discharge capacity, followed in order by sample (c), sample (d), and sample (a). The sample (d) has the smallest capacity deterioration rate (−1.4 mA h/g/cycle), followed in order by sample (b) (−0.8 mA h/g/cycle), sample (c) (3.2 mA h/g/cycle), and sample (a) (4.5 mA h/g/cycle). Negative capacity deterioration rate means that the discharge capacity increases as the number of cycles increases. It is difficult to find any relationship between the magnitude of the first-discharge capacity and that of the capacity deterioration rate.

The curves of the voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$ at a current density of 200 μA/cm^2 for the first charge–discharge of $LiNi_{0.9}Co_{0.1}O_2$ in Fig. 4 show that, compared with the quantity of the deintercalated Li ions by the first charging, that of the intercalated Li ions by the first discharging is quite smaller, which is revealed by the difference in Δx of the first charge and discharge curves for this sample. The lengths of plateaus in the charge and discharge curves are proportional to the charge and discharge capacities. During the first charging, Li ions

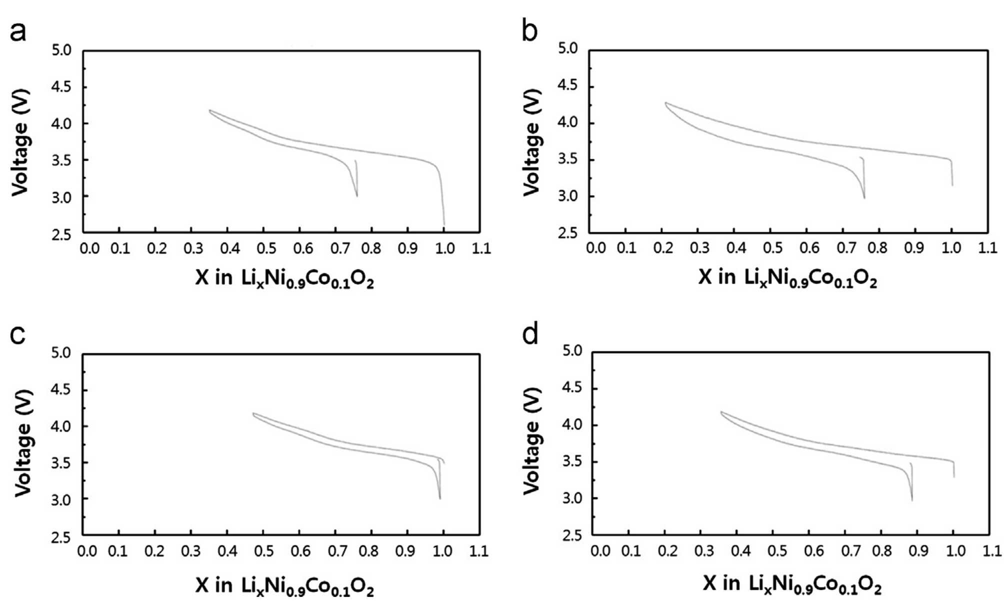

Fig. 4. Curves of voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$ at a current density of 200 μA/cm^2 for the first charge–discharge of $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C from combinations of starting materials: (a) Li_2CO_3, NiO, and $CoCO_3$, (b) Li_2CO_3, NiO, and Co_3O_4, (c) Li_2CO_3, $NiCO_3$, and Co_3O_4, and (d) Li_2CO_3, $NiCO_3$, and $CoCO_3$.

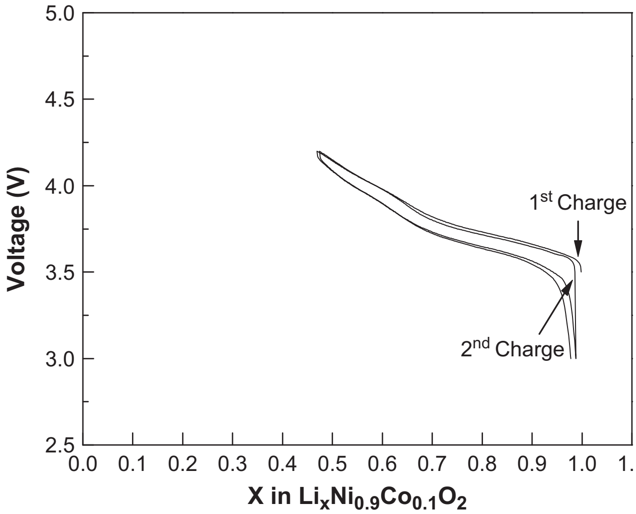

Fig. 5. Curves of voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$ for the first and second charge–discharge cycles for $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C from Li_2CO_3, NiO, and Co_3O_4.

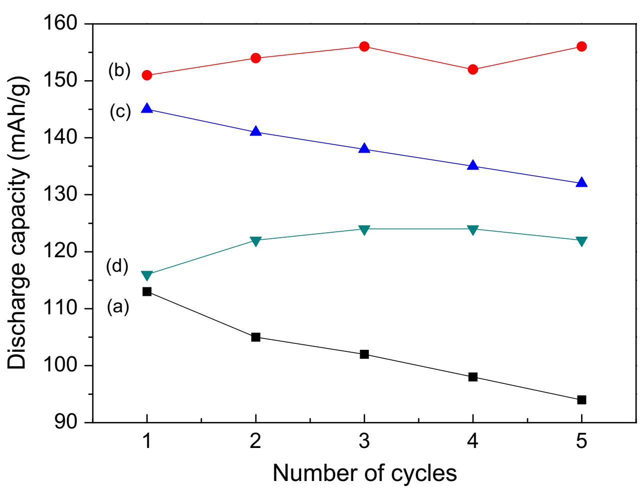

Fig. 6. Variations of the discharge capacity with the number of cycles (n) for $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C from (a) Li_2CO_3, NiO, and $CoCO_3$, (b) Li_2CO_3, NiO, and Co_3O_4, (c) Li_2CO_3, $NiCO_3$, and Co_3O_4, and (d) Li_2CO_3, $NiCO_3$, and $CoCO_3$.

deintercalate not only from stable 3b sites but also from unstable 3b sites. After deintercalation from unstable 3b sites, the unstable 3b sites will be destroyed. This is considered to lead to smaller quantity of the Li ions intercalated by the first discharging than that of the Li ions deintercalated by the first charging.

In the curves of the voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$ for the first and second charge–discharge of $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C from Li_2CO_3, NiO, and Co_3O_4 in Fig. 5, the charge–discharge curves exhibit quite long plateaus, where two phases co-exist [47]. Arai et al. [48] reported that, during charging and discharging, $LiNiO_2$ goes through three phase transitions: from hexagonal structure (H1) to monoclinic structure (M), from monoclinic structure (M) to hexagonal structure (H2), and from hexagonal structure (H2) to hexagonal structure (H3), or vice versa. Ohzuku et al. [40] reported that during charging and discharging, $LiNiO_2$ goes through four phase transitions: from H1 to M, from M to H2, from H2 to hexagonal structures H2+H3, and from H2+H3 to H3, or vice versa. Song et al. [49] reported that $-dx/|dV|$ vs. V curves of $LiNi_{1-y}Ti_yO_2$ (y=0.012 and 0.025) for charging and discharging showed four peaks, revealing four phase transitions from H1 to M, from M to H2, from H2 to H2+H3, and from H2+H3 to H3, or vice versa.

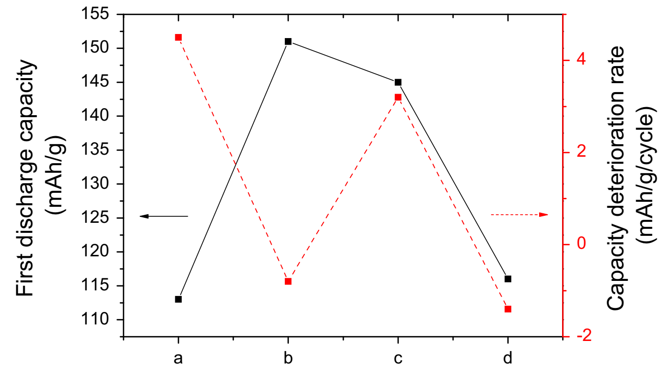

Fig. 7. Variations of the first discharge capacity and the capacity deterioration rate of the $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C with combinations of starting materials: (a) Li_2CO_3, NiO, and $CoCO_3$, (b) Li_2CO_3, NiO, and Co_3O_4, (c) Li_2CO_3, $NiCO_3$, and Co_3O_4, and (d) Li_2CO_3, $NiCO_3$, and $CoCO_3$.

4. Conclusions

$LiNi_{0.9}Co_{0.1}O_2$ cathode materials were synthesized by a solid-state reaction method at 850 °C using Li_2CO_3, NiO or $NiCO_3$, and $CoCO_3$ or Co_3O_4 as the sources of Li, Ni, and Co, respectively. The electrochemical properties of the synthesized samples were then investigated. The $LiNi_{0.9}Co_{0.1}O_2$ sample synthesized from Li_2CO_3, NiO, and Co_3O_4 has the largest first discharge capacity (151 mA h/g) with a discharge capacity deterioration rate of −0.8 mA h/g/cycle. This sample had the largest particles with quite flat surfaces. The curves of the voltage vs. x in $Li_xNi_{0.9}Co_{0.1}O_2$ for the first charge–discharge of $LiNi_{0.9}Co_{0.1}O_2$ showed that after deintercalation from unstable 3b sites, the unstable 3b sites will be destroyed, leading to a smaller quantity of the Li ions intercalated by the first discharging than that of the Li ions deintercalated by the first charging. It was difficult to find any relationship between the magnitude of the first-discharge capacity and that of the capacity deterioration rate.

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