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Dependence of property, crystal structure and electrode characteristics on Li content for $Li_xNi_{0.8}Co_{0.2}O_2$ as a cathode active material for Li secondary battery

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ABSTRACT

We investigated the dependence of the properties, crystal and electronic structures and electrode characteristics of $Li_xNi_{0.8}Co_{0.2}O_2$ as a cathode active material for Li secondary batteries. $Li_xNi_{0.8}Co_{0.2}O_2$ was prepared by a solid-state method and solution method. The crystal structure was determined by neutron and X-ray diffractions using the Rietveld analysis. All the samples were obtained as the α-$NaFeO_2$ type with the space group *R*-3*m*. From the charge–discharge test, the cycle performance was improved with the decreasing Li content ($x \leqq 1.066$) although the discharge capacity decreased. Samples made by the solid-state method showed a better electrode performance than those made by the solution method. We measured the chemical diffusion coefficient of Li ($\widetilde{D_{\mathrm{Li^+}}}$) by the GITT method. The $\widetilde{D_{\mathrm{Li^+}}}$ in the stable cycle region was much improved in the sample prepared by the solid-state method than by the solution method. From the neutron powder diffraction, it was confirmed that Li_2CO_3 was formed by increasing the Li content ($0.994 < x \leqq 1.066$) as a secondary phase. Cation mixing was improved with the decreasing Li content. The bond length of the 3b site–6c site decreased with decreasing Li content. From the electron density images on the (1 1 0) plane for $Li_xNi_{0.8}Co_{0.2}O_2$, the covalent bond of the 3b site–6c site increased with the decreasing Li content. This may be one of the reasons why the cycle performance improved with the decreasing Li content.

1. Introduction

$LiCoO_2$-derived materials are presently the most widely used cathode active material for commercial lithium-ion rechargeable battery electrodes. However, because they contain the rare metal Co, they have associated costs and environmental problems. A search for alternative materials is currently underway [1]. In our laboratory, we have investigated the properties, crystal structure, thermodynamic stability, and battery performances of $Li_xMn_{2-y}M_yO_4$ (M = Li, Mg, Zn, Ni, Co), $Li_xMn_{1-y}M_yO_2$ (M = Al, Cu), and $Li_x(Mn,Co,Ni,M)O_2$ (M = Al, Ti, Fe) [2–6]. The results show that when the lithium composition of $Li_xMn_{1/3}Co_{1/3}Ni_{1/3}O_2$, which has a layered structure, is increased, the discharge capacity increases, and hence the synthesis method influences the battery properties [5,6]. We also clarified that the structural stability, thermodynamic stability, and electrical properties of the material are correlated [5,6]. Recently, Li(Ni, Co)O_2, which has the same layered structure as $Li_xMn_{1/3}Co_{1/3}Ni_{1/3}O_2$, has been gaining attention as a promising alternative to $LiCoO_2$. It can be synthesized relatively easily and has a higher discharge capacity than $LiCoO_2$. Li(Ni, Co)O_2 has been synthesized by a variety of methods and it is known that its solid-state properties and battery performances differ depending on the method of synthesis [7–9]. In general however, in Li–Ni–Co–O type oxides during high-temperature firing, if the Li composition is insufficient, Ni^{2+}, which has nearly the same ionic radius as Li^+, contaminates the empty sites formed due to Li deficiency, and the nonstoichiometric composition $[Li_d{}^{+}Ni_{1-d}{}^{2+}]_{3a}\ [Ni_{1-d}{}^{2+}Ni_{d(2-x)-2(1-x)}{}^{3+}Co_{(1-x)(2-d)}{}^{3+}]_{3b}O_2{}^{2-}$ is generated. The areas in which Ni has contaminated the 3a site are regarded as local NiO disordered array halite layers (space group: *Fm*-3*m*), which obstruct the battery reaction [7].

In this study we synthesized $Li_xNi_{0.8}Co_{0.2}O_2$ with different Li compositions ($0.965 \leq x \leq 1.111$) by two methods, a solid-state method and a solution method, and evaluated the solid-state properties and battery performances. We also made powder neutron diffraction and X-ray diffraction measurements and performed crystal structure analysis based on the Rietveld method and investigated the nuclear and electron density distributions based on the maximum entropy method (MEM). We studied the influence of the synthesis method and Li composition on the solid-state properties, structure, and battery performances. In addition, we performed structural analysis of chemically delithiated specimens and inves-

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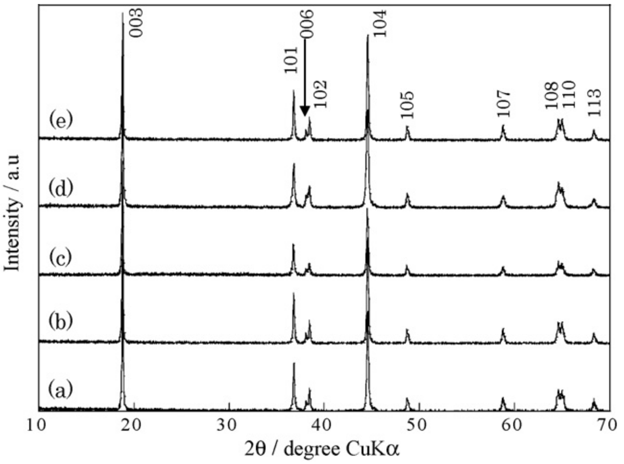

Fig. 1. Powder X-ray diffraction patterns of $Li_xNi_{0.8}Co_{0.2}O_2$ prepared by solid-state method. (a) $x = 0.965$, (b) $x = 0.994$, (c) $x = 1.041$, (d) $x = 1.066$, and (e) $x = 1.111$.

tigated the relationship between the charge and discharge process and the crystal structure.

2. Experimental

For samples synthesized by the solid-state method, $LiOH{\cdot}H_2O$ (99.9%, Wako Pure Chemical Industries, Ltd.), $Ni(OH)_2$(99.9%, Wako Pure Chemical Industries, Ltd.), and CoO(99.9%, Soekawa Chemical Co.) were used as the starting materials. $LiOH{\cdot}H_2O$ was in 5% excess of the nominal composition. The mixture were ground in an agate mortar for 15 h and then pressed into pellets. These pellets were then heated at 600 °C for 15 h in air and then ground into a powder. This powder was again pressed into pellets (40 MPa), then calcined at 800 °C for 15 h in air, then rapidly cooled to room temperature. For the solution method (citrate precursors method), $LiCH_3COO{\cdot}2H_2O$ (99%, Soekawa Chemical Co.), $Ni(CH_3COO)_2{\cdot}4H_2O$ (99%, Soekawa Chemical Co.), and $Co(CH_3COO)_2{\cdot}4H_2O$ (99%, Soekawa Chemical Co.) were dissolved in distilled water and mixed with an aqueous solution of citric acid (as a chelating agent and same weight of $LiCH_3COO{\cdot}2H_2O$). $LiCH_3COO{\cdot}2H_2O$ was in 5% excess of the nominal composition. The solutions were heated at 130 °C for 24 h in air to obtain dry precursors. The precursor was then heated at 600 °C for 15 h in air and then pressed into pellets (40 MPa). Next, it was calcined at 800 °C for 15 h in air, then rapidly cooled to room temperature. To obtain solid-state samples with lower Li contents ($x < 0.965$), a Li^+ extraction was carried out in a batch process by immersing the pellet in a 0.5 mol dm^{-3} $(NH_4)_2S_2O_8$ solution for different times under ambient conditions [10].

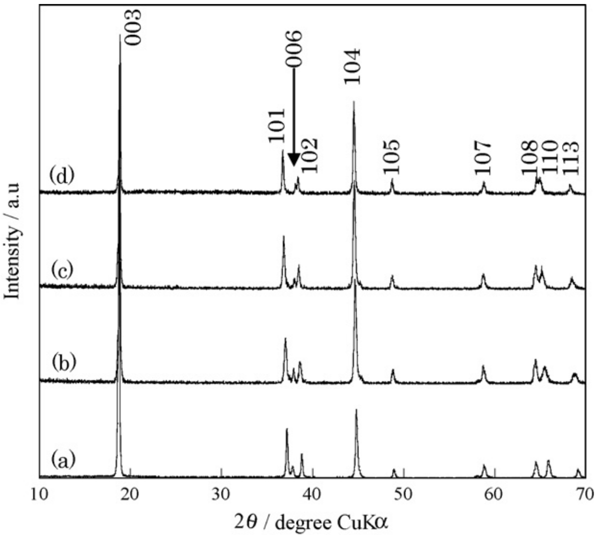

Fig. 2. Powder X-ray diffraction patterns after chemical delithiation for $Li_xNi_{0.8}Co_{0.2}O_2$ prepared by solid-state method. (a) $x = 0.530$, (b) $x = 0.660$, (c) $x = 0.756$, and (d) $x = 0.994$.

Table 1
Lattice constant of $Li_xNi_{0.8}Co_{0.2}O_2$ prepared by various synthetic methods.

Synthetic method	Li content, *x*	*a* (nm)	*c* (nm)
Solid-state method	0.530	0.28344(4)	1.4283(3)
	0.660	0.28507(7)	1.4205(6)
	0.756	0.2861(1)	1.424(9)
	0.965	0.2869(7)	1.419(6)
	0.994	0.2868(2)	1.418(3)
	1.041	0.2868(4)	1.420(4)
	1.066	0.2864(7)	1.415(5)
	1.111	0.2868(5)	1.418(4)
Solution method	0.651	0.28453(7)	1.4305(6)
	0.880	0.28649(6)	1.4213(5)
	0.974	0.2873(1)	1.420(1)
	0.996	0.2871(5)	1.422(2)
	1.082	0.2868(5)	1.419(4)

The obtained samples were characterized by powder XRD (Philips, X'Pert Pro). The composition of the metal components was analyzed by inductive coupled plasma spectrometry (Shimadzu Co., ICPS-750). The crystal structure of the obtained sample was studied by powder neutron diffraction using HERMES [11] of IMR at JRR-3M in JAERI. The data were refined by the Rietveld technique using the Rietan-2000 program [12]. The bond lengths were calculated by the program ORFEE [12] component of Rietan-2000. The bond valence sum [13] was calculated by the VICS program [14]. The nuclear densities analyzed by powder neutron diffraction and the electron densities by powder X-ray diffraction were calculated by the maximum entropy method (MEM) using the PRIMA program [15].

The electrochemical characterization was carried out using HS-cells (Hosen Co.). The cell was composed of the obtained sample as the working electrode, a lithium metal anode as the counter electrode and a polypropylene separator. The cathode was prepared by mixing a 92:4:4 (w/w) ratio of the active materials, acetylene black, and polyvinylidene fluoride binder, respectively, in N-methyl pyrro-

Table 2
Analytical composition of $Li_xNi_{0.8}Co_{0.2}O_2$ prepared by various synthetic methods.

Synthetic method	Li content, *x*	Li	Ni	Co
Solid-state method	0.530	0.530(5)	0.784(5)	0.216(1)
	0.660	0.6600(6)	0.7954(5)	0.2046(3)
	0.756	0.756(1)	0.7930(7)	0.2069(4)
	0.965	0.965(2)	0.805(6)	0.195(3)
	0.994	0.994(2)	0.798(1)	0.202(3)
	1.041	1.041(1)	0.765(2)	0.194(9)
	1.066	1.066(2)	0.740(5)	0.194(4)
	1.111	1.111(8)	0.687(4)	0.202(6)
Solution method	0.438	0.438(2)	0.803(2)	0.197(2)
	0.651	0.651(2)	0.805(2)	0.195(3)
	0.880	0.880(2)	0.806(2)	0.194(5)
	0.974	0.974(5)	0.803(9)	0.197(4)
	0.996	0.996(1)	0.807(2)	0.197(1)
	1.082	1.082(1)	0.734(1)	0.184(2)