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Effects of Zn or Ti substitution for Ni on the electrochemical properties of $LiNiO_2$

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Abstract

$LiNiO_2$ and $LiNi_{1-y}M_yO_2$ (M = Zn and Ti, y = 0.005, 0.01, 0.025, 0.05, and 0.1) were synthesized with a solid-state reaction method by calcination at 750 °C for 30 h under oxygen stream after preheating at 450 °C for 5 h in air. $LiNi_{0.995}Zn_{0.005}O_2$ among the Zn-substituted samples and $LiNi_{0.995}Ti_{0.005}O_2$ among the Ti-substituted samples showed the best electrochemical properties. For similar values of y, $LiNi_{1-y}Ti_yO_2$ had in general better electrochemical properties than $LiNi_{1-y}Zn_yO_2$. Electrochemical properties seem to be closely related to R-factor but less related to I_{003}/I_{104} value. In the FT-IR absorption spectra of $LiNiO_2$ and $LiNi_{1-y}M_yO_2$ (M = Zn and Ti, y = 0.005, 0.01, 0.025, 0.05 and 0.1), Li_2CO_3 was detected even if it is not observed from XRD pattern, with the samples $LiNi_{1-y}Zn_yO_2$ (y = 0.05 and 0.1) showing Li_2ZnO_2 additionally. The smaller cation mixing of the Ti-substituted samples is considered to lead to their better electrochemical properties than the Zn-substituted samples.

Keywords: $LiNiO_2$; Zn or Ti substitution; R-factor; I_{003}/I_{104} value; Cation mixing electrochemical properties

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1. Introduction

Lithium transition metal oxides such as $LiCoO_2$ [1,2], $LiNiO_2$ [3,4], and $LiMn_2O_4$ [5,6] have been investigated as cathode electrode materials for rechargeable lithium batteries. $LiCoO_2$ is studied most intensively for the application to commercial rechargeable batteries because of large diffusivity and high operating voltage. However, it has drawbacks that cobalt is expensive and toxic. $LiMn_2O_4$ has several advantages that Mn is cheaper than other elements and its synthesis is easy, but its cycling performance is not good. $LiNiO_2$ is considered a promising cathode material due to large discharge capacity and low cost. However, due to the size similarity of Li and Ni (Li^+ = 0.72 Å and Ni^{2+} = 0.69 Å), $LiNiO_2$ is practically obtained in the non-stoichiometric composition $Li_{1-y}Ni_{1+y}O_2$ [7,8] and the Ni^{2+} ions in the lithium planes obstruct movement of Li^+ ions during charge and discharge [9,10]. To overcome this disadvantage, Ni in $LiNiO_2$ was substituted partially by Co, Al, Fe, Ti, etc. Gao et al. [11] synthesized $LiNi_{1-y}Ti_{y/2}Mg_{y/2}O_2$ with improved stability. Kim and Amine [12] prepared $LiNi_{1-y}M_yO_2$ (M = Cu, Al, and Ti) by solid state method and showed that $LiNi_{1-y}Ti_yO_2$ had large discharge capacity and good cycling performance.

In this study, $LiNi_{1-y}M_yO_2$ (M = Ni, Zn, and Ti) were synthesized by a solid-state reaction method and the effects of Zn or Ti substitution for Ni on the electrochemical properties of $LiNiO_2$ were investigated.

2. Experimental

$LiNiO_2$ and $LiNi_{1-y}M_yO_2$ (M = Zn and Ti, y = 0.005, 0.01, 0.025, 0.05, and 0.1) were synthesized by a solid-state reaction method. $LiOH{\cdot}H_2O$ (Kojundo Chemical Lab. Co., Ltd, purity 99%), $Ni(OH)_2$ (Kojundo Chemical Lab. Co., Ltd, purity

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99.9%), ZnO (Aldrich Co., purity 99%), and TiO_2 (anatase) (Aldrich Co., purity 99%) were used as starting materials. The starting materials with a composition of $LiNiO_2$ were mixed mechanically by a SPEX mill for 1 h. The mixed material was preheated at 450 °C for 5 h in air, pressed into a pellet and then calcined at various temperatures and times under oxygen stream. The sample calcined at 750 °C for 30 h under oxygen stream showed the best electrochemical properties [13]. $LiNi_{1-y}M_yO_2$ (M = Zn and Ti, $y = 0.005$, 0.01, 0.025, 0.05, and 0.1) were also synthesized under the same conditions. The samples were characterized by X-ray diffraction analysis (Rigaku III/A diffractometer) using Cu Kα radiation. The scanning rate was 6 min^{-1} and the scanning range of diffraction angle (2θ) was $10° \le 2\theta \le 80°$.

The electrochemical cells consisted of $LiNiO_2$ or $LiNi_{1-y}M_yO_2$ as a positive electrode, Li foil as a negative electrode, and electrolyte [Purelyte (Samsung General Chemicals Co., Ltd)] prepared by solving 1 M $LiPF_6$ in an 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The positive electrode consisted of 85 wt% synthesized materials, 10 wt% acetylene black, and 5 wt% polyvinylidene fluoride (PVDF) binder solved in N-methyl-2-pyrrolidinone (NMP). A Whatman glass-filer was used as a separator. The cells were assembled in an argon-filled dry box and the coin-type (2016) cell was employed. All the electrochemical tests were galvanostatically cycled in the voltage range 2.7–4.2 V at 0.1 C-rate.

3. Results and discussion

Fig. 1 shows variations of discharge capacity at 0.1 C-rate with the number of cycles for $LiNi_{1-y}Zn_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05, and 0.1) calcined at 750 °C for 30 h.

Ohzuku et al. [14] reported that the electrochemically reactive $LiNiO_2$ showed larger integrated intensity ratio of 0 0 3 peak to 1 0 4 peak ($I_{0\,0\,3}/I_{1\,0\,4}$) and a clear split of the 1 0 8 and 1 1 0 peaks in their XRD patterns. The degree of cation mixing (displacement of nickel and lithium ions) is low if the value of $I_{0\,0\,3}/I_{1\,0\,4}$ is large and the 1 0 8 and 1 1 0 peaks are split clearly. The value of $(I_{0\,0\,6} + I_{1\,0\,2})/I_{1\,0\,1}$, called the R-factor, is known to be smaller as the unit cell volume of $Li_yNi_{2-y}O_2$ gets smaller. The R-factor increases as y in $Li_yNi_{2-y}O_2$ decreases for y near 1. This indicates that the R-factor increases as the degree of cation mixing becomes larger [15].

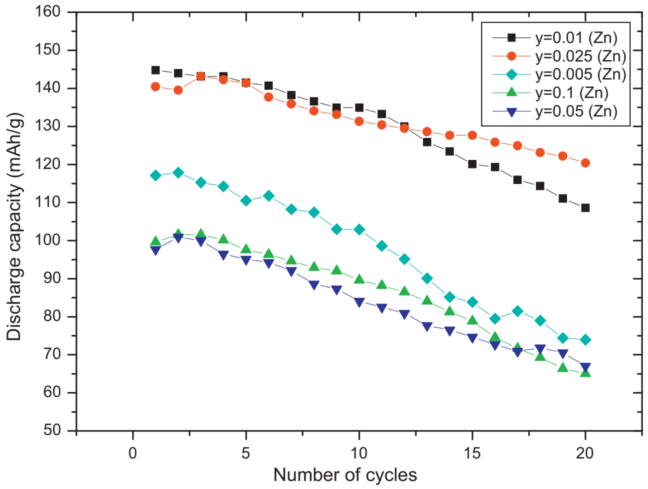

Fig. 1. Variations of discharge capacity at 0.1 C-rate with the number of cycles for $LiNi_{1-y}Zn_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05 and 0.1) calcined at 750 °C for 30 h.

Table 1 shows data calculated from XRD patterns of $LiNi_{1-y}Zn_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05, and 0.1) 750 °C for 30 h under oxygen stream. When Zn is substituted, $LiNi_{0.99}Zn_{0.01}O_2$ with the highest $I_{0\,0\,3}/I_{1\,0\,4}$ value has the largest first discharge capacity (144.8 mAh/g) while $LiNi_{0.975}Zn_{0.025}O_2$ with the smallest R-factor has smaller first discharge capacity 140.5 mAh/g than $LiNi_{0.99}Zn_{0.01}O_2$, but $LiNi_{0.975}Zn_{0.025}O_2$ shows better cyclability than $LiNi_{0.99}Zn_{0.01}O_2$.

Fig. 2 shows variations of discharge capacity at 0.1 C-rate with the number of cycles for $LiNi_{1-y}Ti_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05, and 0.1) calcined at 750 °C for 30 h. As the fraction of Ti increases, the first discharge capacity decreases while cyclability improves. For similar values of y, $LiNi_{1-y}Ti_yO_2$ had in general better electrochemical properties than $LiNi_{1-y}Zn_yO_2$.

Table 2 shows data calculated from XRD patterns of $LiNi_{1-y}Ti_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05, and 0.1) 750 °C for 30 h under oxygen stream. $LiNi_{0.995}Ti_{0.005}O_2$ with the smallest R-factor has not only the largest first discharge capacity (169.8 mAh/g) but also relatively good cycling performance.

Fig. 3 shows the FT-IR absorption spectrum of $LiNiO_2$. IR modes correspond to vibrations involving primarily atomic motion of cations against their oxygen neighbors [16]. The strong peaks at 555 and 509 cm^{-1} are considered to correspond to MO_6 group [16] and the peak at 412 cm^{-1} is considered to correspond to O–M–O chemical bond. The bond between Li and oxygen, O–Li–O bond, is not observed. This bond was reported to appear below the wavenumber 400 cm^{-1} [16]. The peaks at 1515, 1450, and 871 cm^{-1} are reported to correspond to Li_2CO_3 peak [17]. This shows that Li_2CO_3 is contained in the $LiNiO_2$ sample even if it is not observed from XRD pattern.

Fig. 4 shows the FT-IR absorption spectra of $LiNi_{1-y}Zn_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05, and 0.1). The peaks of Li_2CO_3 are observed. The samples $LiNi_{1-y}Zn_yO_2$ ($y = 0.05$ and 0.1) show a weak peak at 447 cm^{-1}. This peak is considered to be related to the Li_2ZnO_2 phase contained in these samples.

Fig. 5 shows the FT-IR absorption spectra of $LiNi_{1-y}Ti_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05, and 0.1). The peaks of Li_2CO_3 are

Table 1
Data calculated from XRD patterns of $LiNi_{1-y}Zn_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05, and 0.1) 750 °C for 30 h under oxygen stream.

Samples	Unit cell volume (Å^3)	$I_{0\,0\,3}/I_{1\,0\,4}$	R-factor
$y = 0.1$	102.715	0.91	0.76
$y = 0.05$	102.244	1.05	0.72
$y = 0.025$	102.173	1.07	0.49
$y = 0.01$	102.203	1.08	0.54
$y = 0.005$	102.244	1.05	0.57

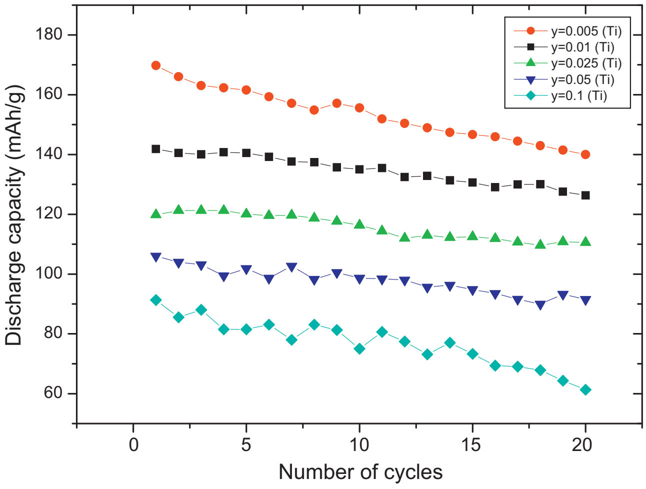

Fig. 2. Variations of discharge capacity at 0.1 C-rate with the number of cycles for $LiNi_{1-y}Ti_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05 and 0.1) calcined at 750 °C for 30 h.

observed. As the substituted Ti content increases, the peak at 570 cm^{-1} becomes weaker and the peak at 440 cm^{-1} becomes stronger. With the increase in the substituted Ti content, the peaks at 505 and 440 cm^{-1} move to the larger wavenumber side. The peak at 505 cm^{-1} becomes split as the substituted Ti content increases. This is considered because the stable ionic state is +4 and the substituted Ti does not exist as O–M–O single bonds but the substituted Ti exists as O–M=O or O=M–O double bonds.

When Zn and Ti are substituted for Ni in $LiNiO_2$, it is observed that the first discharge capacity and cyclability are closely related to the *R*-factor value as those of $LiNiO_2$ not substituted are. Dahn et al. [15] reported that lower unit cell volume does indicate lower *R*-factor value and higher value of y for $Li_yNi_{2-y}O_2$. The first discharge capacity and cyclability were less related to $I_{0\,0\,3}/I_{1\,0\,4}$ value than to unit cell volume and *R*-factor of the samples. Subramanian and Fey [18] reported that $LiNi_{0.7}Co_{0.2}Ti_{0.05}M_{0.05}O_2$ with M = Zn showed small $I_{0\,0\,3}/I_{1\,0\,4}$ value and small first discharge capacity. However, capacity increased with charge–discharge cycling without formation of impurity. In our work, as the fraction of substituted Zn increases, the quantity of impurities (ZnO and Li_2ZnO_2) increases, and discharge capacity decreases with charge–discharge cycling. For $LiNi_{1-y}Ti_yO_2$, as the value of y increases, the first discharge capacity decreases while cycling performance is improved.

Table 2
Data calculated from XRD patterns of $LiNi_{1-y}Ti_yO_2$ ($y = 0.005$, 0.01, 0.025, 0.05, and 0.1) 750 °C for 30 h under oxygen stream.

Samples	Unit cell volume ($Å^3$)	$I_{0\,0\,3}/I_{1\,0\,4}$	*R*-factor
$y = 0.1$	102.747	0.70	0.76
$y = 0.05$	102.453	0.95	0.64
$y = 0.025$	102.075	1.15	0.55
$y = 0.01$	102.232	1.14	0.53
$y = 0.005$	102.251	1.06	0.5

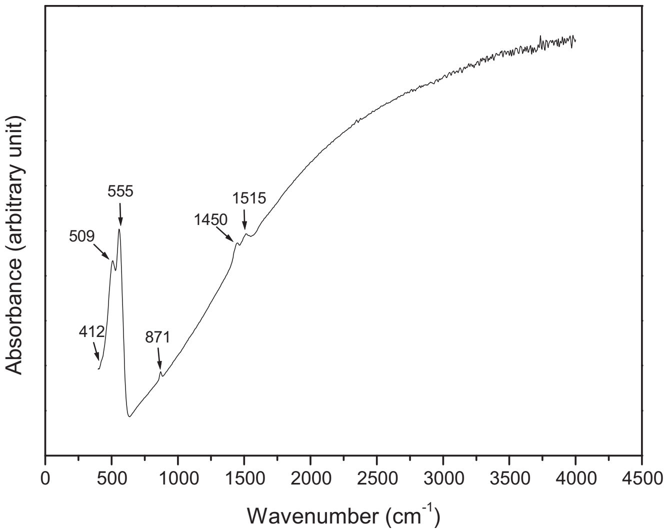

Fig. 3. FT-IR absorption spectrum of $LiNiO_2$.

Kim and Amine [12] suggested that the Ti^{4+} may compensate for the charge deficit caused by Ni^{2+} ions in the transition metal layer and prohibit the migration of Ni^{2+} into the lithium layer, facilitating smooth lithium transport. Kang et al. [19] reported that, although Ti is substituted for Ni in $LiNiO_2$, Ni^{2+} still exists and Ni^{2+} is partially stabilized in lithium sites. Comparison of Figs. 1 and 2 shows that $LiNi_{1-y}Ti_yO_2$ have better electrochemical properties than $LiNi_{1-y}Zn_yO_2$. Fig. 6

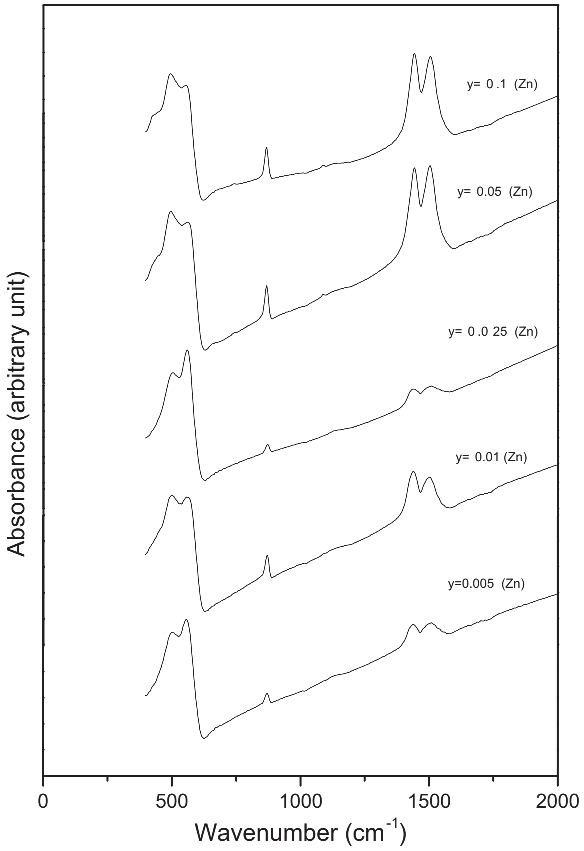

Fig. 4. FT-IR absorption spectra of $LiNi_{1-y}Zn_yO_2$.

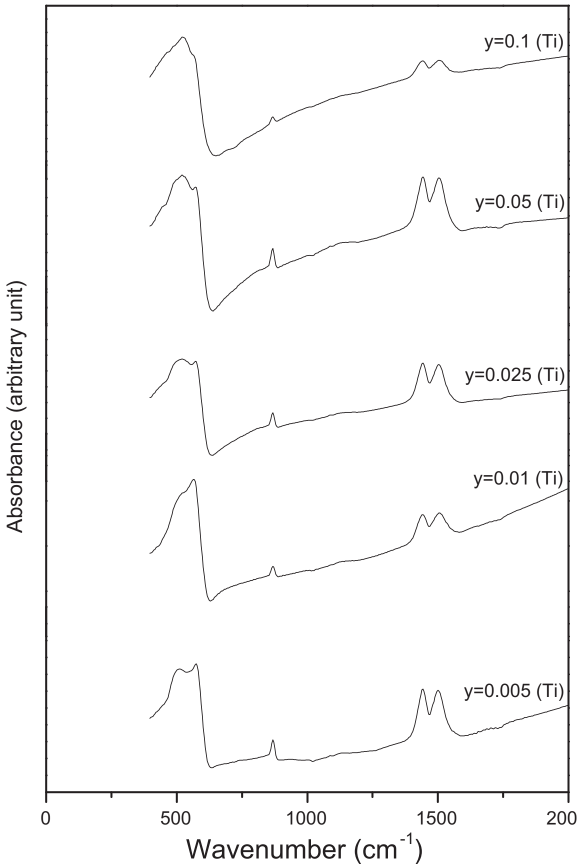

Fig. 5. FT-IR absorption spectra of $LiNi_{1-y}Ti_yO_2$.

shows schematic illustration of atom distribution for $LiNi_{1-y}Zn_yO_2$ and $LiNi_{1-y}Ti_yO_2$. It is considered that Zn ions occupy the lithium sites since Zn ion has the same oxidation number as Ni^{2+} and an ionic radius of 0.74 Å similar to that of Ni^{2+} (0.69 Å) [20], resulting in larger cation mixing. The movement of lithium may be obstructed when Zn^{2+} occupies the lithium sites in the same way as Ni^{2+} in the lithium sites does. The number of Ni^{2+} in the Li layer is considered to be smaller, as suggested by Kim and Amine [12], and accordingly the number of Ni^{2+} in the transition metal layer is larger, compared with those in the Zn-substituted samples. The smaller cation mixing of the Ti-substituted samples is considered to lead to their better electrochemical properties than the Zn-substituted samples.

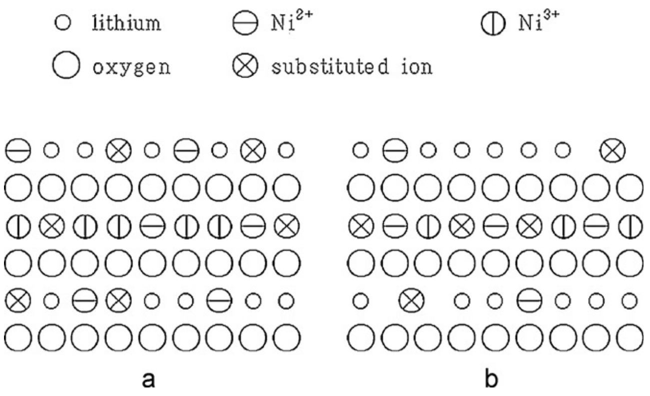

Fig. 6. Schematic illustration of atom distribution for (a) $LiNi_{1-y}Zn_yO_2$ and (b) $LiNi_{1-y}Ti_yO_2$.

4. Conclusions

$LiNiO_2$ and $LiNi_{1-y}M_yO_2$ (M = Zn and Ti, y = 0.005, 0.01, 0.025, 0.05, and 0.1) were synthesized with solid-state reaction method by calcination at 750 °C for 30 h under oxygen stream after preheating at 450 °C for 5 h in air. $LiNi_{0.995}Zn_{0.005}O_2$ among the Zn-substituted samples and $LiNi_{0.995}Ti_{0.005}O_2$ among the Ti-substituted samples showed the best electrochemical properties. $LiNi_{0.995}Ti_{0.005}O_2$ with the smallest R-factor has not only the largest first discharge capacity (169.8 mAh/g) but also relatively good cycling performance. For similar values of y, $LiNi_{1-y}Ti_yO_2$ had in general better electrochemical properties than $LiNi_{1-y}Zn_yO_2$. Electrochemical properties seemed to be closely related to R-factor but less related to I_{003}/I_{104} value. In the FT-IR absorption spectra of $LiNiO_2$ and $LiNi_{1-y}M_yO_2$ (M = Zn and Ti, y = 0.005, 0.01, 0.025, 0.05, and 0.1), Li_2CO_3 was detected even if it is not observed from XRD pattern, with the samples $LiNi_{1-y}Zn_yO_2$ (y = 0.05 and 0.1) showing Li_2ZnO_2 additionally. The smaller cation mixing of the Ti-substituted samples is considered to lead to their better electrochemical properties than the Zn-substituted samples.

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