X-ray Absorption Near Edge Structure Study on Valence Changes of Ni and Co in $\text{Li}_{1-x}\text{Ni}_{0.82}\text{Co}_{0.15}\text{M}_{0.03}\text{O}_2$ (M = Nb, Ti) Cathode Materials

Shinjiro HAYAKAWA,^{a,*} Yuta KUBOUCHI,^a Tetsutaro HAYASHI,^b Toshiaki ONAKADO,^b Hirofumi NAMATAME,^c and Takeshi HIROKAWA^a

^aDepartment of Applied Chemistry, Hiroshima University (Higashi-hiroshima, Hiroshima 739-8527, Japan)

^bNiihama Center Analytical Technology Dep., Sumitomo Metal Mining Co. LTD (Niihama, Ehime 792-0002, Japan)

^cHiroshima Synchrotron Radiation Center, Hiroshima University (Higashi-hiroshima, Hiroshima 739-0046, Japan)

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X-ray absorption near edge (XANES) measurements at K-edges of Ni and Co were carried out on the Li deintercalated $\text{Li}_{1-x}\text{Ni}_{0.82}\text{Co}_{0.15}\text{M}_{0.03}\text{O}_2$ (M = Nb, Ti) cathode materials for Li secondary batteries. Samples were prepared by two different ways of Li deintercalation. One was cathode materials removed from the coin cell charged in the different degree of Li deintercalation and the other was chemically processed with hydrochloric acid in the aqueous solution. Comparisons of XANES spectra between LNCO and Ti or Nb doped LNCO were made, and it was found that the formation of Ni^{4+} was greatly reduced in the charged cathode materials with the dope of Ti or Nb. The similar results were obtained within samples prepared by the real charge and the chemical charge. Valence of Co was invariable during the charge, and was supposed to be trivalent.

Key Words : XANES, Li Secondary Battery, Niobium, Titanium

1 Introduction

Layered LiCoO_2 ¹⁾ and LiNiO_2 (LNO)²⁾ are well known cathode materials for the secondary lithium-ion batteries. To improve their capacities while compensating their weak points, use of a solid solution $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ (LNCO) has been invented.^{3,4)} When pursuing larger capacity safety problem has become greater issue, and the addition of the second or the third metal to LNO or LNCO has been extensively investigated.⁵⁻⁷⁾ To improve the thermal stability of LNCO, partial substitution of Ni with Nb⁸⁾ or Ti⁹⁾ was found to be effective. However, roles of the doped Nb and Ti are still unknown.

K-edge X-ray absorption fine structure (XAFS) spectroscopy are widely utilized to evaluate valence and local structure of Ni and Co, and the edge shift in the near edge region can be utilized as a measure of valence change during Li deintercalation.¹⁰⁻¹⁴⁾ We have employed X-ray absorption near edge structure (XANES) measurements to investigate effects of doped Nb and Ti on the valence of Ni and Co during the Li deintercalation.

2 Experimental

Ti doped LNCO was prepared in the following procedure.⁹⁾ The starting material was powder of mixed oxides of nickel and cobalt. Appropriate amount of $\text{Li}(\text{OH})$ and TiO_2 (anatase) were added, and the mixture was calcined at 730 °C in O_2 atmosphere. Nb doped LNCO was prepared from the co-precipitated hydroxide of nickel, cobalt and niobium.¹⁰⁾ The precipitation was made by mixing an aqueous sulfate solution of nickel and cobalt, a KOH solution containing NbCl_5 , and a NaOH solution simultaneously. The temperature of the mixed solution was kept 40 °C, and pH was 12. The co-precipita-

tion was washed with small amount of water before the addition of an appropriate amount of $\text{Li}(\text{OH})$. The mixture was calcined at 730 °C in O_2 atmosphere. To prevent doped metals from substituting Li site and to ensure the capacity of the cathode materials, excess Li was added in both cases.¹⁵⁾ The excess Li was up to 10% compared to the stoichiometric fraction.

To prepare samples of various degree of Li deintercalation, two types of methods were employed. One was electrochemical method (real charge). A cathode pellet (10 mm in diameter) was prepared by pressing *ca.* 75 mg of the mixture of LNCO ($\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$) or doped LNCO ($\text{LiNi}_{0.82}\text{Co}_{0.15}\text{M}_{0.03}\text{O}_2$), polytetrafluoroethylene (PTFE), and acetylene black. A coin type cell (CR2032) was assembled with the cathode pellet mentioned above, a Li metal disk as anode, a porous polypropylene separator (Cell Guard #2400), and an electrolyte consisting of 1 M solution of LiClO_4 in 1:1 volume mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The cell was charged to the certain amount of Li deintercalation. The charged pellets were subsequently removed from the cell in an Ar filled glove-box, and each sample had been kept in an evacuated polymer bag until the XAFS measurement.

The other method (chemical charge) used chemical deintercalation of Li.¹⁶⁾ The reaction was performed with 2 g of samples, and they were processed with the certain amount of hydrochloric acid in an aqueous solution at the room temperature. The end point of the reaction was chosen when the pH of the solution became stable. The reacted sample was filtered and washed with small amount of acetone. The amount of Li desorption was evaluated from the analysis of the remained solutions by

using inductively coupled plasma atomic emission spectroscopy (ICP-AES) or atomic absorption spectroscopy (AAS). The processed LNCO and Ti or Nb doped LNCO were also analyzed with the ICP-AES method, and the extraction of Ni, Co, Ti and Nb were investigated. The extraction of Ni was found with the Ti or Nb doped LNCO, and the maximum fraction of Ni extraction was *ca.* 0.2 for Ti ($x = 0.55$) and Nb ($x = 0.70$).

The pristine and deintercalated samples with the chemical charge were investigated with X-ray diffraction (XRD), and the obtained XRD patterns were consistent with the single phase of α -NaFeO₂ structure. The lattice parameters were evaluated with Rietveld analysis. All of the samples exhibited expansion of c-axis with the Li deintercalation because of the expansion of the oxygen layer. However, the thickness of the Ni-layer in the direction of c-axis was reduced. The change of the lattice parameters were slightly suppressed with the dope of Nb or Ti.

XANES measurements were carried out on the BL12A of Photon Factory, Tsukuba, Japan. Synchrotron radiation from the bending magnet was monochromatized with a Si (111) double crystal monochromator, and the transmission method was employed to obtain XANES spectra of Ni and Co. Incident X-ray energy was not calibrated, and Ni metal and NiO were measured as reference samples. Samples for XANES measurements were prepared to realize adequate optical density for X-rays around Co and Ni K-edges. Cathode pellets prepared by the real charge were exposed to the ambient condition, and they were pressed to be in the adequate thickness. Appropriate amount of samples treated with the chemical charge were weighed, and they were pelletized with 200 mg of boron nitride as a binder.

3 Results and Discussion

Figure 1 shows Ni K-edge XANES spectra of LNCO and Ti or Nb doped LNCO. As Balasubramanian *et al.* have demonstrated, Ni K-edge position (the value of the energy at half-step height) of LNCO could be utilized as the relative measure of oxidation state.¹⁰⁾ The similar calibration curve was made from the Ni K-edge positions of Ni metal (8337.94 eV), NiO (8341.10 eV), and non-doped LNCO (8342.90 eV). The non-doped LNCO was utilized as the reference sample of Ni³⁺. The averaged oxidation states of Ni derived from the K-edge energies and the calibration curve were shown in Table 1. The evaluated values could be utilized as a relative measure of oxidation or reduction of Ni with the Li deintercalation. However, the absolute oxidation state should be discussed carefully.

The edge shift was observed with the Li deintercalation in the non-doped LNCO. The result indicated the averaged oxidation state of Ni changed from 3.05 to 3.66, and the certain amount of Ni⁴⁺ was created as the charge compensation of Li deintercalation.

In the case of Ti doped LNCO, the initial oxidation states of Ni were 3.04 and 2.35 for samples made by real charge and chemical charge, respectively. The doped Ti⁴⁺ was considered to reduce some of Ni³⁺ in the initial

Fig. 1 Ni K-edge XANES spectra of a) $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$, b) $\text{Li}_{1-x}\text{Ni}_{0.82}\text{Co}_{0.15}\text{Ti}_{0.03}\text{O}_2$, c) $\text{Li}_{1-x}\text{Ni}_{0.82}\text{Co}_{0.15}\text{Nb}_{0.03}\text{O}_2$ as a function of Li deintercalation.

state, and the averaged oxidation state of Ni could be slightly smaller compared to the non-doped LNCO. The difference of the oxidation state between the real charge and chemical charge could be attributed to the deintercalation of excess Li when the cell was assembled with the electrolyte. The averaged oxidation states of Ni increased after the Li deintercalation in both samples. However, the magnitude of the edge shift was slightly reduced compared to that observed with the non-doped LNCO.

In the case of Nb doped LNCO, the initial oxidation states of Ni were 2.69 and 2.82 for samples made by real

Table 1 Ni K-edge position and the averaged oxidation state of non-doped and Ti or Nb doped LNCO.

Sample	Parameters		E_{edge} (eV)	Valence
	method ^a	x		
Non-dope LNCO	cc	0.00	8342.90	3.05
	cc	0.60	8343.91	3.66
Ti-doped LNCO	rc	0.00	8342.89	3.04
	rc	0.50	8343.40	3.35
	cc	0.00	8341.75	2.35
	cc	0.55	8343.91	2.79
	cc	0.70	8342.60	2.86
Nb-doped LNCO	rc	0.00	8342.53	2.82
	rc	0.50	8342.50	2.81
	cc	0.00	8342.32	2.69
	cc	0.70	8342.60	2.86
	cc	0.70	8342.60	2.86

^a cc (chemical charge), rc (real charge)

Fig. 2 Co K-edge XANES spectra of a) $\text{Li}_{1-x}\text{Ni}_{0.82}\text{Co}_{0.15}\text{Ti}_{0.03}\text{O}_2$, b) $\text{Li}_{1-x}\text{Ni}_{0.82}\text{Co}_{0.15}\text{Nb}_{0.03}\text{O}_2$ as a function of Li deintercalation.

charge and chemical charge, respectively. It was clear that the spectra were identical with the sample made by the real charge and the doped Nb prohibited the change of the oxidation state of Ni. In the case of the sample made by the chemical charge, the slight edge shift was observed.

Figure 2 shows Co K-edge XANES spectra of Ti and Nb doped LNCO. The spectral shapes were almost identical for all of the samples except for the slight energy shift of the main peak. Nakai *et al.* have reported edge shift in Co K-edge XANES spectra of LiCoO_2 after the Li deintercalation¹³⁾ while the edge shift was not observed in those obtained with LNCO.^{10,13)} The results indicate that the charge compensation was mainly took place around Ni in LNCO, and the obtained results confirmed the valence of Co was kept trivalent during the Li deintercalation with Ti or Nb doped LNCO. The slight high energy shift of the main peak was attributed to the shorter bond length of Co-O according to the results of extended XAFS analysis.^{10,14)} The results were consistent with the reduced thickness of the Ni layer derived from Rietveld analysis of the XRD pattern.

All of the results demonstrated doped Ti and Nb disturbed formation of Ni^{4+} during the Li deintercalation, and it might be related to the improvements in the thermal stability of the cathode material. As the valence of Co was invariant, large portion of the charge compensation might be achieved in the oxygen site.¹²⁾ However, the greater effects with the doped Nb suggest the other possibility. The doped Nb might be initially Nb^{4+} , and the formation of Nb^{5+} could contribute to the portion of the charge compensation.

4 Conclusion

Valence changes of Ni in $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ (LNCO) and those of Ni and Co in $\text{LiNi}_{0.82}\text{Co}_{0.15}\text{M}_{0.03}\text{O}_2$ ($\text{M} = \text{Nb}, \text{Ti}$) were investigated with the K-edge XAFS spectroscopy. The edge shift of Ni XANES spectra was utilized as a relative measure of the oxidation state during the Li deintercalation, and it was found that the oxidation of Ni during the Li deintercalation was disturbed or prohibited with the doped Ti and Nb. The edge shift of Co XANES spectra was not observed in all of the samples, and the valence of Co was kept in trivalent. The effects of doped Ti and Nb were similar for the samples prepared by the real charge and chemical charge. The large portion of the charge compensation during the Li deintercalation might be achieved in the oxygen site in the doped LNCO.

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