

# Characterization of $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ positive active materials for lithium ion batteries

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## Abstract

Layered  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  materials were prepared by a solid-state reaction at 950 °C for 10 h in air and characterized by various methods. The cell performance depended on the composition. The rate performance deteriorated as Co content ( $1 - 2x$ ) decreased. On the other hand, it improved as excess Li content ( $y$ ) increased. The change of cell performance associated with composition variations was closely related to both the structural disorder (cation mixing) and the electrical conductivity (volume resistivity). The degree of cation mixing depended greatly on Co content ( $1 - 2x$ ). On the other hand, the volume resistivity depended greatly on excess Li content ( $y$ ). In other words, the cell performance was improved by the reduction of cation mixing and volume resistivity. Only Ni K-edge X-ray absorption near edge structure (XANES) spectra showed edge shifts to higher energy due to the oxidation of Ni as either Co content ( $1 - 2x$ ) or excess Li content ( $y$ ) increased. The unit cell size decreased as either Co content ( $1 - 2x$ ) or excess Li content ( $y$ ) increased. They are probably caused by the change from  $\text{Ni}^{2+}$  ( $r_{\text{Ni}} = 0.69 \text{ \AA}$ ) to the smaller  $\text{Ni}^{3+}$  ( $r_{\text{Ni}^{3+}} = 0.56 \text{ \AA}$ ). From these results, it is assumed that the reduction of volume resistivity is closely related to the increase of  $\text{Ni}^{3+}$  concentration in  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ .

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## 1. Introduction

Recently, many researchers have investigated new cathode materials to find possible alternatives to  $\text{LiCoO}_2$  widely used in lithium ion batteries. On the other hand,  $\text{LiCoO}_2$  has any problems such as the higher cost, the lower thermal stability as the charged cathode material. By the way, the optimum cathode material should have lower cost as well as greater safety and performance. One of the promising cathode materials is  $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$  [1–11]. These layered  $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$ -based cathode materials have many advantages such as higher thermal stability, lower solubility to solvents and smaller volume change and gas evolution on charging. In a recent paper, Lu et al. reported that  $\text{Li}[\text{Ni}_{0.25}\text{Co}_{0.5}\text{Mn}_{0.25}]\text{O}_2$  and  $\text{Li}[\text{Ni}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}]\text{O}_2$  are attractive electrode ma-

terials for Li-ion cells in that they appear to be much less reactive with electrolyte at high temperatures than  $\text{LiCoO}_2$  [1]. Especially, there is great interest in Co less composition in cost performance of all  $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$ . In this study, we have characterized several  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  materials with various metal compositions.

## 2. Experimental

Several  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  materials with different metal compositions were prepared by heating the stoichiometric amounts mixture of each starting raw material at 950 °C for 10 h in air.

For the obtained samples, we have examined various properties such as crystal structure (XRD), electrical conductivity (powder resistivity), specific surface area (BET), valence of transition metal (XANES) and electrochemical property (cell performance), etc.

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The specific surface area was measured by the single-point BET method.

Occupation parameter  $g(\text{Li})$  and lattice parameters were measured by powder X-ray diffraction (XRD). XRD was conducted using a Cu target. Profile refinement of the collected data was made using the Rietveld program RIETAN2000.

The volume resistivity was measured under 40 MPa applied pressure with the powder resistivity measurement system by the four-probe method (Mitsubishi Chemical).

Ex situ Ni, Mn and Co K-edge XAFS experiments were carried out at KEK-PF BL-9A [12]. Si(1 1 1) double-crystal monochromator was used with detuning to  $\sim 60\%$  intensity. Pristine powders of cathode materials were pressed into BN-diluted pellets and measured in transmission mode.

Electrochemical tests were carried out using the 2032 coin-type cells. The positive electrode consisted of 75 wt.% metal oxide powder, 20 wt.% acetylene black and 5 wt.% PTFE. Lithium metal was used as the negative electrode.

The rate performance of  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  materials was examined by various current densities in the range of 3.0–4.3 V at 25 °C.

### 3. Results and discussion

#### 3.1. Specific surface area of $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$

Since the electrochemical property depends greatly on the specific surface area of positive active materials, the specific surface area is an important property considered in characterizing these materials. So, the BET specific surface area was measured for the prepared  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  samples. It was found from the result that these samples are about the same value (ca.  $1 \text{ m}^2 \text{ g}^{-1}$ ). Therefore, we considered that the effect due to the difference of specific surface area was negligible.

#### 3.2. Cell performance of $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$

In order to examine the cell performance of  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ , we investigated the rate performance using the coin-type cell.

Fig. 1 shows that the relationship between composition and rate performance for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $0.33 \leq x \leq 0.475$ ,  $0.00 \leq y \leq 0.20$ ). It was observed that the rate performance deteriorated rapidly as Co content ( $1 - 2x$ ) decreased. On the other hand, it improved rapidly as  $y$  increased up to 0.10, and then saturated above 0.10. It should be noted that the cell performance dramatically deteriorates as Co content ( $1 - 2x$ ) decreases when excess Li content ( $y$ ) is at around 0–0.05.

#### 3.3. Structural disorder (cation mixing) of $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$

‘Cation mixing’ is a partial interchange of occupancy of Li and transition metal ions among the sites, which gives rise

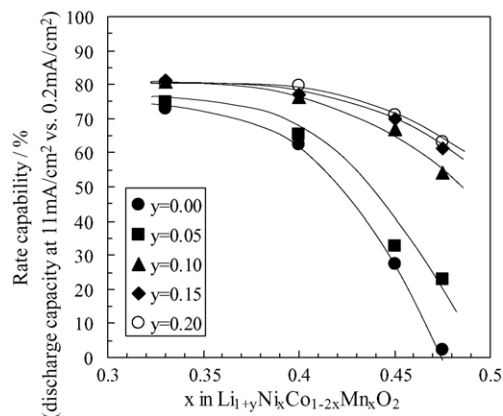


Fig. 1. Relationship between composition and rate performance for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $0.33 \leq x \leq 0.475$ ,  $0.00 \leq y \leq 0.20$ ).

to disordering in the structure [4,13–16]. It is considered that the structural disorder (cation mixing) is an important character for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  cathode materials, because it is known to deteriorate the electrochemical performance of these layered compounds [4]. It has been reported that more transition metal atoms (probably Ni) are found in Li sites (3a) when the Ni content ( $x$ ) increases in  $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}$  [2]. So, in order to examine the relationship between structural disorder and composition, we carried out XRD analysis for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  cathode materials. Fig. 2 shows that the relationship between composition and occupation parameter  $g(\text{Li})$  for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $y = 0.05$  and  $0.10$ ). Occupation parameter  $g(\text{Li})$  means the occupancy of Li atoms in Li sites (3a). Occupation parameter  $g(\text{Li})$  decreased rapidly as Co content ( $1 - 2x$ ) decreased. This result shows that the more transition metal atoms were found in Li sites (3a) as Co content ( $1 - 2x$ ) decreased. This tendency is similar to that reported in similar oxide cathode materials [2]. On the other hand, it was observed that  $g(\text{Li})$  increased slightly when excess Li content ( $y$ ) increased from 0.05 to 0.10. This result shows that the transition metal atoms in Li sites (3a) slightly decreased with increasing excess Li content ( $y$ ) from

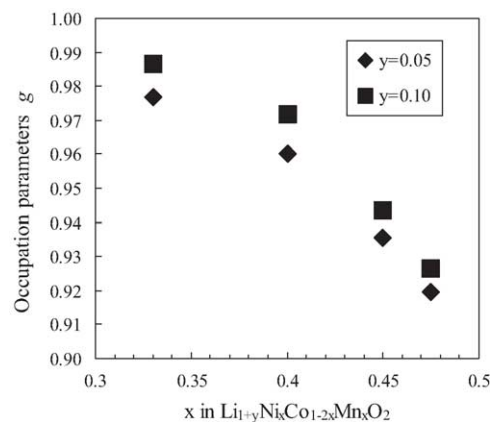


Fig. 2. Relationship between composition and occupation parameter  $g(\text{Li})$  for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $y = 0.05$  and  $0.10$ ).

0.05 to 0.10. Therefore, it is considered that the cation mixing of  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  depends greatly on Co content ( $1-2x$ ) rather than excess Li content ( $y$ ). In other words, it shows that there existed a strong relationship between Co content ( $1-2x$ ) and structural disorder (cation mixing). On the other hand, it seems that there is not much correlation between excess Li content ( $y$ ) and structural disorder (cation mixing).

On the basis of the data presented in Figs. 1 and 2, we reviewed the relationship between structural disorder (cation mixing) and cell performance. These results showed that the amount of the change in the occupation parameter  $g(\text{Li})$  was not in good agreement with the difference in the cell performance. As a consequence, it has been suggested that the change of cell performance cannot be completely explained by only the structural disorder.

### 3.4. Powder conductivity of $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$

In order to examine the electrical conductivity of  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ , the volume resistivity of powder samples was measured.

Fig. 3 shows the relationship between excess Li content ( $y$ ) and volume resistivity for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $0.33 \leq x \leq 0.475$ ,  $0.00 \leq y \leq 0.20$ ). The volume resistivity increased as Co content ( $1-2x$ ) decreased. On the other hand, it reduced rapidly as excess Li content ( $y$ ) increased up to 0.10, and then reduced gradually as  $y$  increased over 0.10.

Fig. 4 shows the relationship between volume resistivity and rate performance for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $0.33 \leq x \leq 0.475$ ,  $0.00 \leq y \leq 0.20$ ). The rate performance improved as the volume resistivity reduced.

Therefore, in considering both the electrical conductivity and the structural disorder, it is easy to explain the reason why the cell performance improved as Co and excess Li contents increased in  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ .

By the way, it is interesting to note that the reason why the electrical conductivity improved as Co or ex-

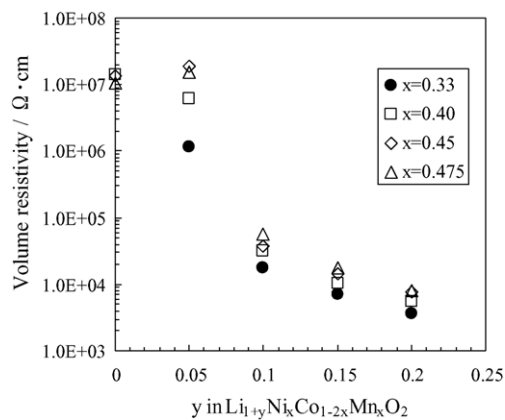


Fig. 3. Relationship between excess Li content and volume resistivity for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $0.33 \leq x \leq 0.475$ ,  $0.00 \leq y \leq 0.20$ ).

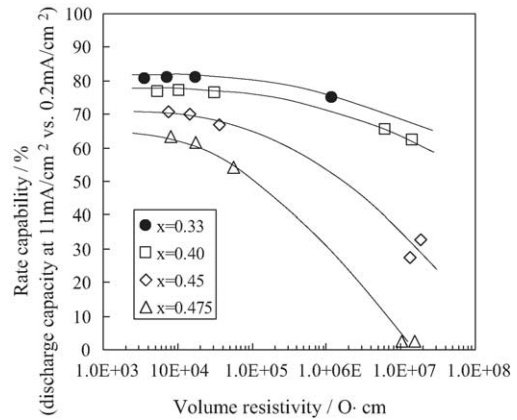
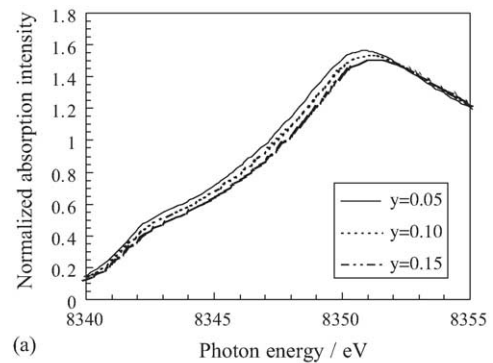
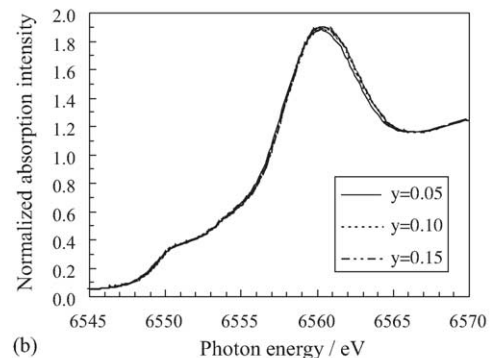


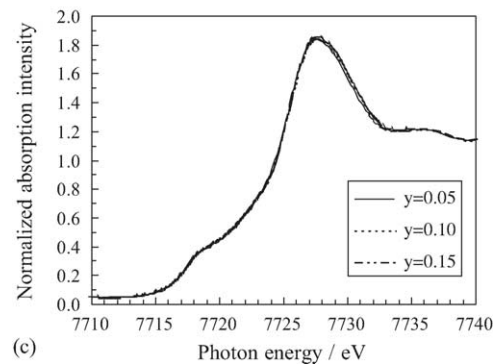
Fig. 4. Relationship between volume resistivity and rate performance for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $0.33 \leq x \leq 0.475$ ,  $0.00 \leq y \leq 0.20$ ).



(a)



(b)



(c)

Fig. 5. Ni (a), Mn (b) and Co (c) K-edge XANES spectra for  $\text{Li}_{1+y}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  ( $y=0.05, 0.10$  and  $0.15$ ) cathode materials.

cess Li content increased. We expected that it should be caused by the change of transition metal (Ni, Mn, Co) valence in  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ . So, in order to examine the expectation, we analyzed XANES spectra and lattice parameter.

### 3.5. XANES spectra of $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$

It has been previously suggested that the oxidation states of Ni, Co and Mn are +2, +3 and +4, respectively, in the  $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  series [1,2,4,7,11]. In order to obtain the information for the oxidation states of transition metal (Ni, Co, Mn) in  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ , the K-edge X-ray absorption near edge structure (XANES) spectra were measured. Fig. 5 shows XANES spectra for  $\text{Li}_{1+y}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  ( $y=0.05, 0.10$  and  $0.15$ ) cathode materials at Ni (a), Mn

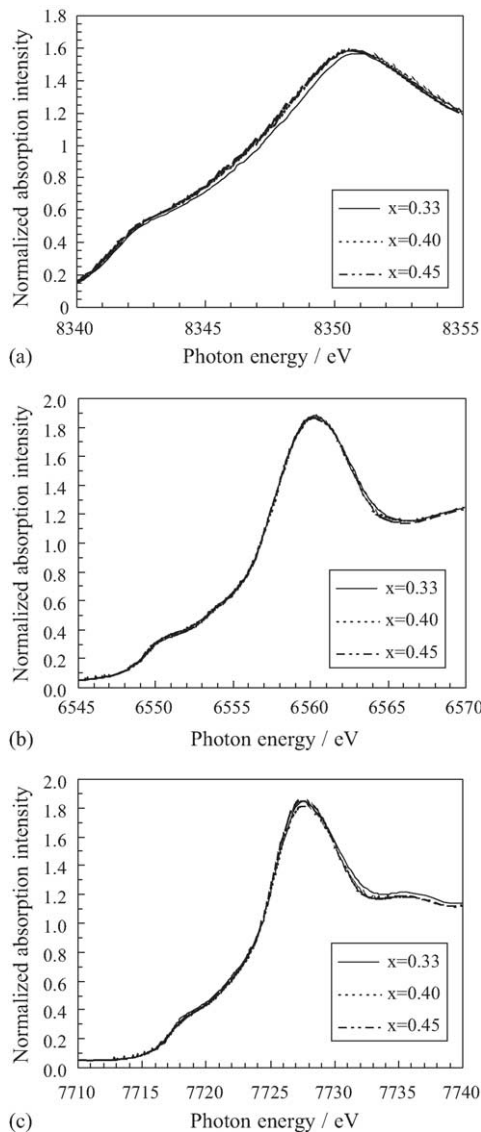


Fig. 6. Ni (a), Mn (b) and Co (c) K-edge XANES spectra for  $\text{Li}_{1.05}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $x=0.33, 0.40$  and  $0.45$ ) cathode materials.

(b) and Co (c) K-edges. Only Ni K-edge XANES shifts to higher energy due to the oxidation of Ni as excess Li content ( $y$ ) increased. These results can be interpreted as part of Ni ion was oxidized from  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$  on doping of  $\text{Li}^+$  ion.

Fig. 6 shows the K-edge XANES spectra for  $\text{Li}_{1.05}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $x=0.33, 0.40$  and  $0.45$ ) cathode materials in Ni (a), Mn (b) and Co (c). Again, it was

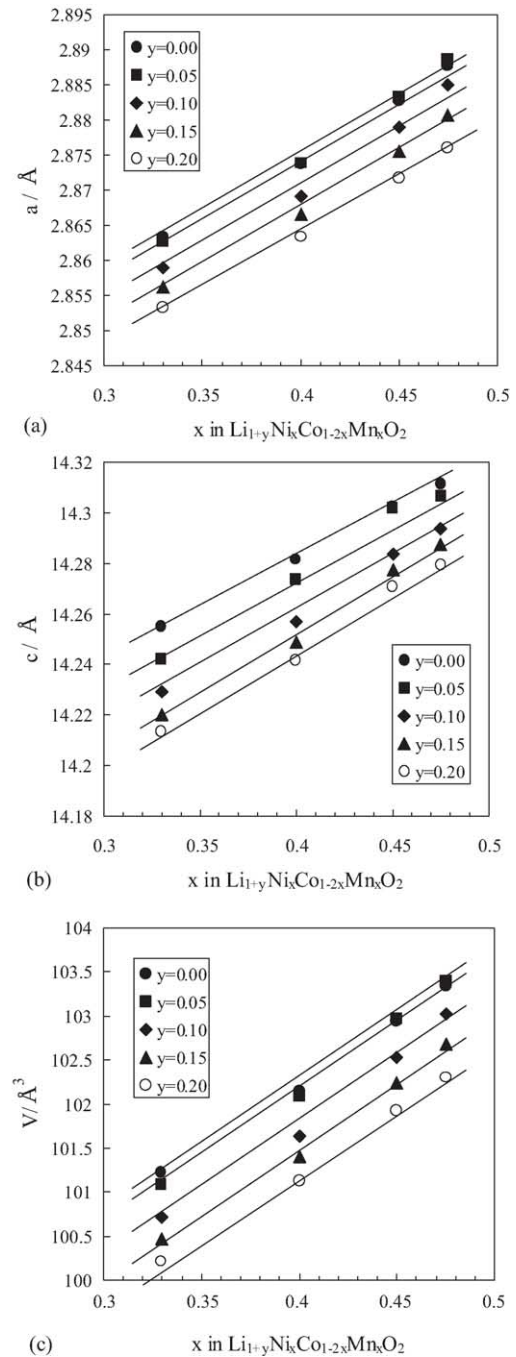


Fig. 7. Composition dependence of lattice parameters for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $0.33 \leq x \leq 0.475$ ,  $0.00 \leq y \leq 0.20$ ) cathode materials in  $a$  axis (a),  $c$  axis (b) and  $V$  (c).

only Ni that showed a slight edge shift to higher energy due to the oxidation of Ni as Co content ( $1 - 2x$ ) increased. These results indicate that part of Ni ion was oxidized from  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$  with increasing Co content.

These results indicate that the increased oxidation states of Ni with increasing either Co content ( $1 - 2x$ ) or excess Li content ( $y$ ) might be related to the increased electrical conductivity. In addition, it might contribute to the decreased 'cation mixing', because of the decreased  $\text{Ni}^{2+}$  ion which is possible to substitute for Li (3a) sites.

### 3.6. Lattice parameter of $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$

In order to examine the unit cell size of  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ , the lattice parameters were measured by XRD. Fig. 7 shows that the composition dependence of lattice parameters for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $0.33 \leq x \leq 0.475$ ,  $0.00 \leq y \leq 0.20$ ) cathode materials in  $a$  axis (a),  $c$  axis (b) and  $V$  (c). The unit cell size increased as Co content ( $1 - 2x$ ) decreased. It is assumed that this result is caused by the substitution of the larger  $\text{Ni}^{2+}$  ( $r_{\text{Ni}^{2+}} = 0.69 \text{ \AA}$  [17]) for  $\text{Co}^{3+}$  ( $r_{\text{Co}^{3+}} = 0.545 \text{ \AA}$  [17]). Because the  $\text{Mn}^{4+}$  ( $r_{\text{Mn}^{4+}} = 0.53 \text{ \AA}$  [17]) is much the same size as the  $\text{Co}^{3+}$ . This result is in agreement with the tendency reported in similar oxide cathode materials [2]. On the other hand, the unit cell size decreased as excess Li content ( $y$ ) increased. It is assumed that this result is caused by the change from two  $\text{Ni}^{2+}$  ( $r_{\text{Ni}^{2+}} = 0.69 \text{ \AA}$ ) to the smaller two  $\text{Ni}^{3+}$  ( $r_{\text{Ni}^{3+}} = 0.56 \text{ \AA}$  [17]) due to substituting a  $\text{Li}^+$  ( $r_{\text{Li}^+} = 0.76 \text{ \AA}$  [17]) for a transition metal ion (3b sites). These results can be explained by the following interpretation. In order to keep the electroneutrality, the substitution of a  $\text{Li}^+$  for a transition metal ion changes two  $\text{Ni}^{2+}$  to two  $\text{Ni}^{3+}$ . The rate of increase of the unit cell size due to the substitution of a larger  $\text{Li}^+$  ( $r_{\text{Li}^+} = 0.76 \text{ \AA}$ ) for a transition metal ( $r_{\text{M-ion}} = 0.59 \text{ \AA}$ ; where  $r_{\text{M-ion}}$  means the average ionic radii of  $\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$  and  $\text{Mn}^{4+}$ ) is smaller than the rate of decrease of the unit cell size to due to the change from two  $\text{Ni}^{2+}$  ( $r_{\text{Ni}^{2+}} = 0.69 \text{ \AA}$ ) to the smaller two  $\text{Ni}^{3+}$  ( $r_{\text{Ni}^{3+}} = 0.56 \text{ \AA}$ ).

## 4. Conclusion

In this study, we have characterized several  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  which are Co-less and/or Li rich composition. The cell performance depended on the composition. It appeared that the change of electrochemical property (cell performance) associated with composition variations were closely related to both the structural disorder (cation mix-

ing) and the electrical conductivity (volume resistivity) for  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ .

From results on XANES spectra, only Ni K-edge showed an edge shift to higher energy due to the oxidation of Ni as either Co content ( $1 - 2x$ ) or excess Li content ( $y$ ) increased. These results indicate that part of Ni was oxidized from  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$ . The results of lattice parameter measurement showed the unit cell size decreased as either Co content ( $1 - 2x$ ) or excess Li content ( $y$ ) increased. It is assumed that these results were caused by the change from  $\text{Ni}^{2+}$  to the smaller  $\text{Ni}^{3+}$ . In summary, these experimental results indicate that the reduction of volume resistivity is closely related to the increase of  $\text{Ni}^{3+}$  concentration in  $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ .

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