

## Ordering Structure of Transition Metal in Layered Oxides as a Cathode Material for Li Secondary Battery

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### Introduction

Recently,  $\text{Li}(\text{Mn}, \text{Ni}, \text{Co})\text{O}_2$  has been attracting much attention as a cathode active material for a lithium secondary battery. Because a complexity of the transition-metal ordering [1, 2], however, a relationship between the electrochemical property and the structure is still ambiguous. In addition, cathode properties of these materials depended significantly on the synthetic processes, according to previous work [3]. Therefore, it can be considered as an important issue to investigate an effect of the synthetic process on the crystal structure.

From such background, we prepared  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  by various methods and estimate their crystal structures. The local structures, i.e. transition-metal orderings, were analyzed by X-ray absorption fine structure (XAFS) measurements as well as pair distribution function (PDF) methods using neutron scattering data. Based on the results, we discussed a relationship between the local structures and the battery characteristics.

### Experimental

$\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  were synthesized by a conventional solid-state method and a solution method. As for both the methods, a final sintering was carried out at 950 °C in air for 15 h although a cooling rate from the sintering temperature to room temperature was changed. Phases of the obtained samples were identified by powder X-ray diffraction, and the metal compositions were estimated by using an inductively coupled plasma (ICP) emission spectrometer. In order to study cathode properties of these samples, charge-discharge cycle tests were performed. Neutron scattering measurements (HIPPO, LANSCE) were also carried out to investigate the crystal structure in detail. As a local structure analysis, we measured XAFS spectra at Photon Factory (BL7C and BL9A) and then analyzed the data with REX2000 and FEFF programs.

### Results and Discussion

From X-ray diffraction patterns, it was confirmed that all the prepared  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  had a layered rock-salt structure (S. G.;  $R\text{-}3m$ ). As for these samples, cycle performances were also estimated. As a result, it was

found that the sample prepared by the solution method had higher discharge capacity and better cycle performance than that obtained by the solid-state method. In addition, it was also demonstrated that the cooling rate in the sintering process made a significant influence on the cycle performance of  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ .

In order to clarify an effect of the preparation method on the local structure, we analyzed EXAFS spectra by assuming some different transition-metal ordering models. As an example, Fig. 1 shows the Fourier transform of EXAFS data for the sample prepared by the solution method. From the fitting results, it was clarified that the transition metals of the  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  were arranged in a different way depending on the preparation process. Such a tendency was also observed in PDF analyses using neutron scattering data.

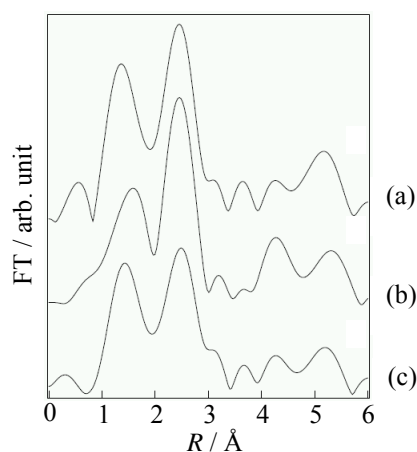


Fig. 1 Fourier transforms of EXAFS spectra for  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  prepared by the solution method; (a) Mn K-edge, (b) Ni K-edge, (c) Co K-edge.

### References

- [1] Y. Koyama et al., *J. Electrochem. Soc.*, **151**, A1545 (2004).
- [2] N. Yabuuchi et al., *J. Electrochem. Soc.*, **152**, A1434 (2005).
- [3] Y. Idemoto et al., *Solid State Ionics*, **179**, 625 (2008).

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