7C/2008G621

Heat-Treatment Effect on Cathode Characteristics, and Average and Local Structures of $LiNi_{0.5}Mn_{0.5}O_2$ as a Cathode Active Material for Li-Ion Battery

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1 Introduction

$LiCoO_2$-based materials with the layered rock-salt structure have been widely used as a cathode material for the lithium-ion battery, but they have some problems, such as high cost and high toxicity of Co. Therefore, developments of Co-free cathode active materials are highly expected. As one of the candidates, $LiNi_{0.5}Mn_{0.5}O_2$ with the similar crystal structure as the $LiCoO_2$ has drawn much attention, and it was already found that its cathode properties depended on the preparation process [1].

From such background, we focused on an effect of a post annealing on $LiNi_{0.5}Mn_{0.5}O_2$ in this work. As for the samples after the annealing, we investigated cathode properties, average crystal structures and local structures.

2 Experiment

$LiNi_{0.5}Mn_{0.5}O_2$ was synthesized by a conventional solid-state method. A mixture of starting materials was fired at 950 °C for 15 h in air. As a post annealing process, a high P_{O2} treatment was performed at 450 °C for 48 h in pure O_2 with a pressure of 2.0 MPa. In addition, the sample was heated at 600 °C for 48 h under the Ar condition. These obtained samples were characterized by X-ray diffraction measurements, inductively coupled plasma analyses (ICP), and charge-discharge cycle tests. In order to clarify the heat-treatments effects on the average structures, the Rietveld analysis was carried out using neutron diffraction data [HERMES(JRR-3)].

The annealing effects were also investigated from the viewpoint of local structures by using X-ray absorption fine structure (XAFS) techniques. XAFS spectra of the Ni and Mn *K*-edges were recorded with a transmission method by BL7C at Photon Factory in KEK, and then investigated with REX-2000 program. Theoretical parameters used in curve fittings of EXAFS data were calculated by FEFF8.

3 Results and Discussion

From X-ray diffraction patterns of a pristine $LiNi_{0.5}Mn_{0.5}O_2$ and the samples heat-treated in Ar reducing and high P_{O2} conditions, it was clarified that all the samples had a single phase of the layered rock-salt structure. It was also found by ICP that the metal compositions did not depend on the heat-treatment condition. Charge-discharge cycle tests clarified that the capacity retention was improved by these heat-treatments.

In order to clarify their crystal structures, we carried out the Rietveld analyses using the neutron diffraction patterns. From the results, it was suggested that the oxygen content was slightly lower than a stoichiometric composition of 2 in the pristine specimen. After the high P_{O2} annealing, the oxygen deficit became negligible by a gaseous oxygen uptake. On the other hand, the reducing heat-treatment increased the oxygen-deficit amount.

In addition, we discussed local structures based on EXAFS analyses. Figure 1 shows Fourier transformations of k^3-weighted EXAFS spectra of the pristine and heat-treated $LiNi_{0.5}Mn_{0.5}O_2$. For the purpose of local-distortion studies, curve fittings for the first coordination peaks (the TM-O shell) were performed, and the results are given in Table 1. In these analyses, the coordination numbers were fixed based on the oxygen contents refined by the Rietveld analyses. From the Debye-Waller factors, it was indicated that the distortion around Ni was relaxed by annealing under the reducing condition. Such a change in the local distortion is considered to have a positive influence on the cycle performance of $LiNi_{0.5}Mn_{0.5}O_2$.

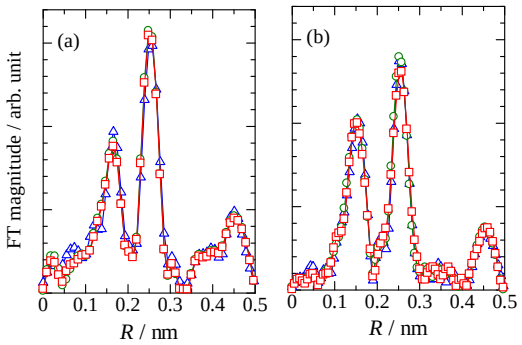

Fig. 1: Fourier transformations of EXAFS spectra of (a) Ni *K*- and (b) Mn *K*-edge of the prepared $LiNi_{0.5}Mn_{0.5}O_2$. (circle; pristine, triangle; reduced, square; oxidized)

Table 1: Interatomic distances (R) and Debye-Waller factors (σ) for Ni *K*- and Mn *K*-edge EXAFS spectra.

Sample	Ni-O		Mn-O	
	R / nm	σ / nm	R / nm	σ / nm
Pristine	0.2058	0.0130	0.1973	0.0128
Reduced	0.2066	0.0125	0.1973	0.0125
Oxidized	0.2057	0.0132	0.1975	0.0130

References

[1] Y. Idemoto, et. al., *Electrochemistry*, **79** (2011) 15.

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