

 MLF Experimental Report	提出日 Date of Report 2010/6/14
課題番号 Project No. 2009A0013 実験課題名 Title of experiment Heat-treatment effects on crystal structures of Li(Mn, Ni, Co)O ₂ as cathode active materials for lithium ion battery 実験責任者名 Name of principal investigator Yasushi Idemoto 所属 Affiliation Tokyo University of Science	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/(BL No.) SuperHRPD/BL08 実施日 Date of Experiment 2009/6/10 - 2009/6/11

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.
<p>LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ and LiNi_{0.8}Co_{0.2}O₂-based cathode active materials powder</p>

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。) Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.
<p>Experimental method</p> <p>LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ and LiNi_{0.8}Co_{0.2}O₂-based cathode active materials for the Li-ion battery were prepared with a conventional solid-state method and a solution method using a citric acid. Some of the products were heat-treated at 950 °C for 6 hours under Ar reducing conditions. All the obtained samples were characterized by powder X-ray diffraction and ICP measurements. Thermodynamic stabilities of the samples were estimated based on the Hess's law, from their dissolution enthalpies determined by the calorimetry technique. Cathode performances of the materials were examined by CV and charge-discharge cycle tests.</p> <p>In order to investigate the crystal structures in detail, neutron diffraction patterns of the samples were measured with SuperHRPD, and then the Rietveld analyses were carried out by using a Z-code package. In the experiment, the diffraction patterns were collected in vacuum at room temperature, and the measurement time was about 8 hours for each sample with a weight of 1 gram.</p>

2. 実験方法及び結果(つづき) Experimental method and results (continued)

Results

From the neutron diffraction patterns measured using SuperHRPD, it was confirmed that $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ -based materials had a single phase of the layered rock-salt structure (S. G.; $R-3m$). On the other hand, it was demonstrated that some specimens of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ system had an impurity phase of Li_2CO_3 although such an extra phase could not be detected by laboratorial X-ray diffractions. The Li_2CO_3 amounts seemed to depend on the preparation process, that is, a synthesis method and a heat-treatment condition. Because cycle performances of Li-ion batteries using samples with the extra phase as the cathode were inferior, it can be concluded that the Li_2CO_3 had a negative influence on the cathode characteristics.

In order to discuss the crystal structures in more detail, we performed the Rietveld analysis using the diffraction data on some $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ -based samples, which were prepared by means of the solution method and then heat-treated under controlled gas conditions. The Rietveld analysis could be performed successfully by assuming the space group as $R-3m$. An occupancy of the Ni at the Li site (i.e., an amount of a cation mixing) was below 10 %, regardless of the specimens. In the analyses, a site occupancy of the oxygen was also refined. As a result, it was suggested that the sample heat-treated in air had no oxygen vacancy in the case of $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ system.