

Dependence of crystal structure and thermodynamic stability on different synthetic method and Li content for $\text{Li}_x(\text{Ni},\text{M})\text{O}_2$ ($\text{M}=\text{Mn},\text{Co}$) as a cathode active material for Li ion battery

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As a cathode active material for lithium ion battery, LiCoO_2 with a layer structure is the most widely used. Due to high cost and high toxicity of the Co, however, nickelate-based materials have drawn much attention. From such background, we have studied $\text{Li}_x(\text{Ni},\text{M})\text{O}_2$ ($\text{M}=\text{Mn},\text{Co}$); especially $\text{Li}_x\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$, which have lower Co content. As a result, we found that their cathode performance depended on the synthetic process. However, less information on their crystal structures make the synthetic process effects ambiguous at this moment.

In this work, we investigated crystal structures of $\text{Li}_x\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ prepared by two different methods. We investigated the crystal structures by Rietveld analysis using neutron diffraction and nuclear densities by MEM. Based on the results, we discussed relationship between thermodynamic stability, crystal structure and cathode performance, and then tried to reveal how the synthetic process affected them.

$\text{Li}_x\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ were prepared by two methods; that is, conventional solid-state method and solution method using citric acid as an additive. Their cathode performances were studied by CV and charge-discharge cycle tests. In order to clarify crystal structure at the charged state, chemical delithiation using $0.5\text{N}-(\text{NH}_4)_2\text{S}_2\text{O}_8$ was also performed. Thermodynamic stabilities of the samples were evaluated from their heats of dissolution which were measured by a twin-type multi-calorimeter. The crystal struc-

tures were determined by neutron diffraction using HERMES[1] of IMR at JRR-3M in JAERI. The data was refined using the Rietan-FP[2]. The nuclear densities were determined with PRIMA program[3].

From XRD patterns, it was found that main phases of $\text{Li}_x\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ ($x=0.98\sim 1.08$) synthesized in this work had the -NaFeO_2 -type layer structure (S. G.: R-3m) although Li_2MnO_3 was slightly observed as a secondary phase depending on preparation process. Cycle performance tests revealed that the samples with the same analytical composition exhibited different cathode performance depending on synthetic method, that is, the samples synthesized by solid state reaction exhibit more stable cycle performance than those prepared by solution method. From formation enthalpies of the samples evaluated by the calorimetry, it could be concluded that higher thermodynamic stability induced better cathode performance.

In order to discuss effects of the synthetic processes on their crystal structure, the Rietveld analysis using the neutron diffraction was carried out. As a result, it was found that cation mixing that is, Ni content at Li site and Li content at Ni site was essentially independent of the synthetic process. However, local distortion around the transition metal site, which was evaluated from the results of the Rietveld analysis, was larger in the samples exhibiting worse cycle performance. Such a distortion also became larger by a chemical delithiation although the crystal structure kept the layer structure even after the delithiation. In the case

of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ [4], similar results to $\text{Li}_x\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ were also obtained.

[1] K. Ohoyama, T. Kanouchi, K. Nemoto, M. Ohashi, T. Kajitani, Y. Yamaguchi, *Jpn. J. Appl. Phys.* 37, 3319 (1998) .

[2] F. Izumi, and T. Ikeda, *Mater. Sci. Forum*, 321, 198 (2000).

[3] F. Izumi and R. A. Dilanian, "Recent Research Developments in Physics, " Vol.3, Part II, Transworld Research Network, Trivandrum (2002), pp.699-726.

[4] Yasushi Idemoto, Yu Takanashi, Naoto Kitamura, *J. Power Sources*, 189(1), 269 (2009).