

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

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Many lithium-intercalated transition metal oxides have been studied as positive electrode materials in high energy density rechargeable batteries. In recent years, the layered-structured $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ has been extensively studied as a candidate to replace the LiCoO_2 cathode materials. But, it is not clear that relationship between thermodynamic stability, structure stability and cycle performance. We had been reported that the relationship between thermodynamic stability, structure stability and cathode performance of $\text{LiMn}_{2-y}\text{MyO}_4$ ($\text{M}=\text{Cr}, \text{Al}, \text{Mg}, \text{Co}, \text{Ni}, \text{Zn}$), $\text{Li}_x\text{Mn}_{1-y}\text{MyO}_2$ ($\text{M}=\text{Mn}, \text{Al}, \text{Cu}$). In this study, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, $\text{LiMn}_{0.3}\text{Co}_{0.3}\text{Ni}_{0.3}\text{M}_{0.1}\text{O}_2$ ($\text{M}=\text{Al}, \text{Ti}, \text{Fe}$) and $\text{LiMn}_{1/3}\text{Co}_{1/3-0.1}\text{Ni}_{1/3}\text{Al}_{0.1}\text{O}_2$ were prepared by the solid-state and solution reaction. We investigated the relationship between the thermodynamic stability, crystal structure, properties, and electrode performance depend on synthesis method, substitution and Li content.

The samples were prepared by two methods. The samples synthesized by solid-state reaction using each simple oxide as starting materials. Another samples synthesized by solution reaction using each metal acetate dissolved in distilled water and mixed with aqueous solution of citric acid. Li^+ extraction from $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ were carried out 0.5mol dm^{-3} $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution by a batch method. Li content was controlled by immersing time. The heat of dissolution was measured by a twin-type multi-calorimeter. The enthalpy change per mole of atoms for the formation reaction,

ΔH_{HR} , were calculated from the heat of dissolution by applying Hess' law. We considered a similar experiment about Li^+ extraction samples. The crystal structure was determined by powder neutron diffraction using HERMES of IMR at the JRR-3M. The data were refined using the Rietan-2000. The nuclear densities determined by powder neutron diffraction and the electron densities determined by powder XRD were calculated by MEM using the PRIMA.

All samples were determined to single phase with a well-defined layer structure ($R\text{-}3m, 166$) by XRD. The intensity ratio of (003) and (104) peaks in the XRD patterns is greater than 1.2 and there is a clear splitting of the (006) and (102), (108) and (110) doublet peaks in the all compounds, which confirms there is little cation mixing in the layered structure. The lattice parameter, a , decrease and c increase with the decreasing Li content. $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$, which obtained by solution reaction, was more high discharge capacity and good cycle performance than that obtained by solid-state reaction. One of these factors controlled cycle performance, we investigated the thermodynamic and structure stability. From the crystal structure analysis, the cation mixing was little change with decreasing Li content. The bond lengths of Li-O increased and M-O ($\text{M}=(\text{Mn}, \text{Co}, \text{Ni})$) decreased with decreasing Li content. From the results of electronic and crystal structure, the change of covalent bond and cation mixing were small by substitution. The chemical diffusion coefficient of Li^+ was little change by each

synthetic method. The enthalpy change per mole of atoms for formation reaction, ΔH_f , of $\text{Li}_x\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ obtained by each synthetic method is linearly changed with Li content. It is thought that there is not structure changes ($0.4 < x < 1.0$), and it corresponds to the crystal structure analysis. From the results, the host structure is structurally and thermodynamically stable of the all amounts of Li content. Moreover, ΔH_f of the sample by solution reaction decreased compared to that of the sample by solid-state reaction. ΔH_f increased with decreasing Li content and $\text{Li}_x\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ and $\text{Li}_x\text{Mn}_{1/3}\text{Co}_{1/3-0.1}\text{Ni}_{1/3}\text{Al}_{0.1}\text{O}_2$, which obtained by solution reaction, was more thermodynamically stable than that obtained by solid-state reaction. It was suggested that these factors should provide an effective cycle performance.