Phase Relationships of Chemically Delithiated
Layered Li$_{1-x}$Ni$_{0.45-y}$Mn$_{0.55+y}$Co$_2$O$_2$

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Introduction
Most of commercial lithium ion cells currently use the layered LiCoO$_2$ cathode, but only 50 % of its theoretical capacity could be practically utilized (140 mAh/g). Also, Co is expensive and relatively toxic. In this regard, layered LiNi$_{1-x}$Mn$_x$Co$_2$O$_4$ oxides are appealing as high capacity and less expensive cathode materials.\(^3\) We present here the phase relationships of chemically delithiated layered Li$_{1-x}$Ni$_{0.45-y}$Mn$_{0.55+y}$Co$_2$O$_2$ (0 ≤ (1−x) ≤ 1, and 0 ≤ y ≤ 1) oxides and a correlation of the phase relationships and chemical lithium extraction rate to structural parameters such as cation disorder between the Li$^+$ and transition metal planes.

Experimental
The LiNi$_{0.50+y}$Mn$_{0.45-y}$Co$_2$O$_2$ (0 ≤ y ≤ 1) samples were synthesized by firing the co-precipitated hydroxides of nickel, cobalt, and manganese with 7 atom % excess LiOH. H$_2$O at 900 °C for 24 h. Chemical extraction of lithium was carried out by stirring the LiNi$_{0.50+y}$Mn$_{0.45-y}$Co$_2$O$_2$ powders in an acetone solution of NO$_2$BF$_4$ under argon atmosphere. While the lithium content in the delithiated product could be varied by varying the amount of NO$_2$BF$_4$, the molar ratio of LiNi$_{0.50+y}$Mn$_{0.45-y}$Co$_2$O$_2$; NO$_2$BF$_4$ was kept constant at 1/2 in 20 ml of acetone for studying the chemical lithium extraction rate. The lithium contents in the LiNi$_{0.50+y}$Mn$_{0.45-y}$Co$_2$O$_2$ samples were determined by atomic absorption spectroscopy. Structural refinements and lattice parameter determinations were carried out by analyzing the X-ray diffraction data with the Rietveld method using the DBWS-9411 PC program.\(^7\)

Results and Discussion
Figure 1 compares the X-ray diffraction patterns of the end members Ni$_{0.45+y}$Mn$_{0.55-y}$Co$_2$O$_2$ for 0 ≤ y ≤ 1. The structure of the end member changes from P3 to O1 to O3 as the cobalt content y in Li$_{1-x}$Ni$_{0.50+y}$Mn$_{0.45-y}$Co$_2$O$_2$ decreases. For example, Co$_2$O$_4$ (y = 1) Ni$_{0.42}$Mn$_{0.50}$Co$_2$O$_4$ (y = 0.33) and Ni$_{0.45}$Mn$_{0.40}$Co$_{0.15}$O$_2$ (y = 0.05) have, respectively, the P3, O1, and O3 structures. Figure 2 shows the variation of the degree of cation disorder in the parent LiNi$_{0.50+y}$Mn$_{0.45-y}$Co$_2$O$_2$ oxides with the Co content. The degree of cation disorder increases with decreasing Co content y. While the absence of any transition metal ions in the lithium planes in the case of well ordered compositions such as LiCoO$_2$ leads to a ready sliding of the MO$_2$ sheets to give P3 or O1 phases, the presence of transition metal ions in the lithium planes prevents such a gliding and maintains the initial O3 structure for the end members. The prevention of gliding is due to the electrostatic repulsion across the shared faces of the polyhedra in the P3 structure. Figure 3 compares the lithium contents remaining after 15 min of chemical lithium extraction time for various values of y in Li$_{1-x}$Ni$_{0.45-y}$Mn$_{0.55+y}$Co$_2$O$_2$. The lithium content increases or the lithium extraction rate decreases with decreasing Co content due to an increasing degree of cation disorder. The variation in the chemical lithium extraction rate is in agreement with the electrochemical rate capability.

References