Phase Relationships of Chemically Delithiated
Layered Li_{1-x}MO_2 (0 ≤ (1-x) ≤ 1) Oxides

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Introduction

The layered LiMO_2 (M = Mn, Co, and Ni) cathodes differ significantly in their reversible capacity values. For example, LiCoO_2, LiNi_{0.85}Co_{0.15}O_2, and LiNi_{0.5}Mn_{0.5}O_2 deliver ~ 140, 180, and 160 mAh/g respectively although they all have the same O3 type structure. The factors that limit the capacities are not fully understood in the literature. With an aim to develop a better understanding of the layered oxides and the factors that limit their capacities, our group has been focusing on the structural and chemical characterizations of the Li_{1-x}MO_2 (0 ≤ (1-x) ≤ 1) samples obtained by chemical delithiation. We present here the phase relationships of the various cation-substituted Li_{1-x}MO_2 oxides with lithium content.

Experimental

The chemical lithium extraction was carried out by stirring the LiMO_2 powders in an acetonitrile solution of NO_2BF_4 for 2 days under argon atmosphere:

LiMO_2 + x NO_2BF_4 → Li_{1-x}MO_2 + x NO_2 + x LiBF_4

The products were characterized by X-ray diffraction using Rietveld analysis. The lithium and oxygen contents were determined, respectively, by atomic absorption spectroscopy and a redox isometric titration.

Results and discussion

Figure 1 shows the phases formed as a function of lithium content (1-x) for the various Li_{1-x}MO_2 systems. Factors such as the nature of M^{2+}, cation disorder between the M^{2+} and Li^{+} planes, and the presence of residual Li^{+} ions in the Li^{+} plane influence the phase relationship. While Li_{1-x}CoO_2 and the cobalt-rich compositions generally show the formation of P3 and O1 type phases from the initial O3 type phase due to a gliding of the MO_2 sheets, the nickel-rich compositions tend to maintain the initial O3 type structure, but with a smaller lattice c parameter in some cases (designated as O3’ type phase). However, the substitution of a small amount of a non-transition metal ion like Al^{3+} (> 10%) for Co^{3+} suppresses the formation of P3 type phase. While the maintenance of the initial O3 type structure in the nickel-rich samples is due to the cation disorder, it is due to the inability to extract all the lithium and the consequent presence of residual Li^{+} ions in the Li^{+} planes in Li_{1-x}Co_{0.85}Al_{0.15}O_2.

Figure 2 compares the variations of the oxidation state and the oxygen content with lithium content (1-x) for the various chemically delithiated Li_{1-x}MO_2 samples. The systems tend to lose oxygen from the lattice at deep lithium extraction due to chemical instability. The chemical instability decreases in the order Li_{1-x}CoO_2 > Li_{1-x}Ni_{0.3}Mn_{0.7}O_2 > Li_{1-x}Ni_{0.5}Mn_{0.5}O_2 = Li_{1-x}Ni_{0.75}Mn_{0.25}O_2, which is consistent with the observed charge voltage profiles.

In order to see whether the possible incorporation of protons during the chemical lithium extraction could influence the phase relationships and oxygen content analysis data, we have examined the samples by FTIR spectroscopy (Figure 3). While both Ni(OH)_2 and the LiH_2Ni_{0.5}Mn_{0.5}O_2 sample obtained in an aqueous acid medium show characteristic absorption bands (~3500 cm\(^{-1}\)) corresponding to O-H groups, both the parent LiNi_{0.5}Mn_{0.5}O_2 and Ni_{0.3}Mn_{0.7}O_2 obtained with NO_2BF_4 do not, ruling out the incorporation of protons during chemical delithiation in acetonitrile medium.

Figure 1. Phase relationships of the Li_{1-x}MO_2 samples obtained by chemical delithiation. The hatched region refers to the inaccessibility of the phases.

Figure 2. Variations of the (a) oxidation state of the transition metal ion M^{2+} and (b) oxygen content with lithium content (1-x) in Li_{1-x}MO_2.

Figure 3. Comparison of the FTIR spectra of Li_{1-x}Ni_{0.5}Mn_{0.5}O_2 with that of Ni(OH)_2.

References