

In-situ XRD Study of the Phase Evolution in Undoped and Cr-doped $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as 5-volt Cathode Materials for Li-ion Batteries

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The phase evolution during lithium de-intercalation/intercalation within $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel (denoted LMN) has been previously studied using both ex-situ [1-2] and in-situ [3-6] X-ray diffraction techniques. Conflicting results have been reported. In the ordered LMN, three distinct cubic phases were detected relating to each of the Ni^{2+} , Ni^{3+} , and Ni^{4+} oxidation states in the ordered LMN material. These phases transformed from one to another by means of two distinct two-phase regions that correspond to the wide voltage plateaus observed in the electrochemical profile of the cathodes. In contrast, the disordered LMN material showed a smooth peak shift to higher angles with no clear two-phase region until nearing the end of charging, which is consistent with the fact that the plateaus in the voltage profiles are less pronounced [4]. On another hand, a structural change has been reported upon delithiation of disordered $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ at $x=0.5$ with loss of the glide symmetry. However, a different phase diagram has been reported in [4] for this same disordered LMN, with a solid solution for large values of x , followed with a two phase region at $x\sim 0.6$, due to the onset of a second cubic phase, phase II, and another two-phase region at $x<0.4$, where phase II coexists with another cubic phase, phase III. In [5], the three phases are found to co-exist in a finite range of concentrations. However, the authors did not specify if their measurements were made on ordered or disordered LMN. We can simply note that their result is in agreement with the phase diagram found in [4] for LMN in the ordered phase, since the three phases are found to co-exist only in this case in [4]. Moreover, the phase diagram is reported to depend on the morphology of the particles [6].

In this work, we have investigated the structural evolution of a $\text{Li}_x\text{Mn}_{1.45}\text{Ni}_{0.45}\text{Cr}_{0.1}\text{O}_4$ sample and a commercial $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ in the $Fd\bar{3}m$ phase as a function of the Li content (x) using in-situ XRD analyses. Results of both charge (Li extraction) and discharge (Li insertion) reactions have been reported in order to better understand the influence of Cr-substitution to the spinel. The phase diagram

for both samples shows the existence of three phases that form alternatively solid solutions and two-phase regions (Fig. 1). The results have been understood on a basis of a model that takes strain effects into account, also explaining the fact that the phase diagram is sample dependent, hence the different results reported in the literature. The analysis of the phase diagram confirms the faster dynamics of the Li-insertion/de-insertion in the Cr-doped sample, evidenced by the improved capacity retention at high C-rates. The other benefit of the Cr-substitution is the increase of the stability of the lattice. The drawback is a decrease in the energy density that is not due to a loss of capacity, but a smaller redox potential of the nickel vs. Li^+/Li .

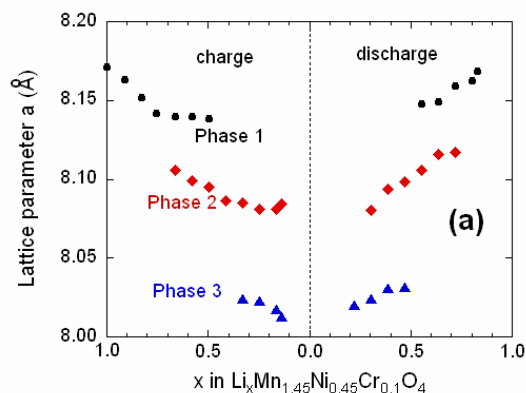


FIG. 1. Variation of the lattice parameters of the different cubic phases in the undoped sample as a function of the Li concentration x during a cycle at C/24 rate for e-Cr-doped sample.

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