

Surface-Facet Dependent Reactivity between $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and Carbonate Electrolytes

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$\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ operates at 4.7 V vs. Li/Li^+ and has a theoretical capacity of 147 mAh g^{-1} which make the material an attractive cathode for high-energy and high power applications such as electric and plug-in hybrid vehicles[1]. The high operating voltage, however, is above the oxidation stability window of conventional carbonate based electrolytes, which leads to severe side reactions and reduces cycle life. In addition, lithium is reinserted in the electrode during storage at charged states, resulting in self-discharge [2]. Several factors can be expected to influence the rate of relithiation, particularly state of charge, temperature and electrolyte choice [3]. We have recently shown that surface facets play an important role in lithium transport properties and side reactivities with the electrolyte [4]. In this presentation we report the detailed studies on side reactions between the electrolyte and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ crystals with different surface facets.

Large, well crystallized $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ samples were synthesized by a molten salt technique previously described by our group [2]. By tuning the synthesis conditions, plate shaped crystals with dominant (112) surface facets and octahedron shaped crystals with (111) facets were obtained. The samples were chemically delithiated and then stored in 1.2 M LiPF_6 in EC:DEC (1:1) (% v/v) electrolyte at 8°C, 20°C and 45°C, each for 45 days. Analyses were performed periodically to monitor the aging process, with the electrolyte recuperated and the solid sample washed with DMC and dried. SEM studies on the aged particles showed no obvious electrolyte residue, but EDX analysis revealed the presence of fluorine and phosphorous species, possibly from the decomposition of the LiPF_6 salt.

The octahedron crystals used in our study have a well ordered crystal structure and they were found to transform through two two-phase transitions during delithiation. The initial cubic phase (phase I) has a lattice parameter of 8.17 Å. As lithium is extracted from the structure, a second (phase II) and then a third (phase III) cubic phase with lattice parameters of 8.09 and 8.01 Å, respectively, appear.

Figure 1 shows the XRD patterns of the aged crystals during the various stages of storage at 8°C and room temperature. The fresh delithiated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ is composed of phase III exclusively. After storage at 8°C, the ratio of the peaks from phase II and III only changed slightly, indicating low amount of lithium reinsertion into the material (Fig 1a). At room temperature, however, the intensity of the peak from phase II continues to increase over time, suggesting substantial relithiation during storage (Fig 1b). Similar phenomena were also observed during the aging of the plate crystals. The evolution of the XRD pattern, therefore, can be used as a measure for side reaction, particularly with regard to relithiation.

We will discuss the possibility of using some other techniques, including XPS, laser induced breakdown spectroscopy (LIBS), Raman and FTIR, as quantitative

tools to determine relithiation kinetics. The influence of temperature and surface facets on side reaction kinetics will also be presented.

References

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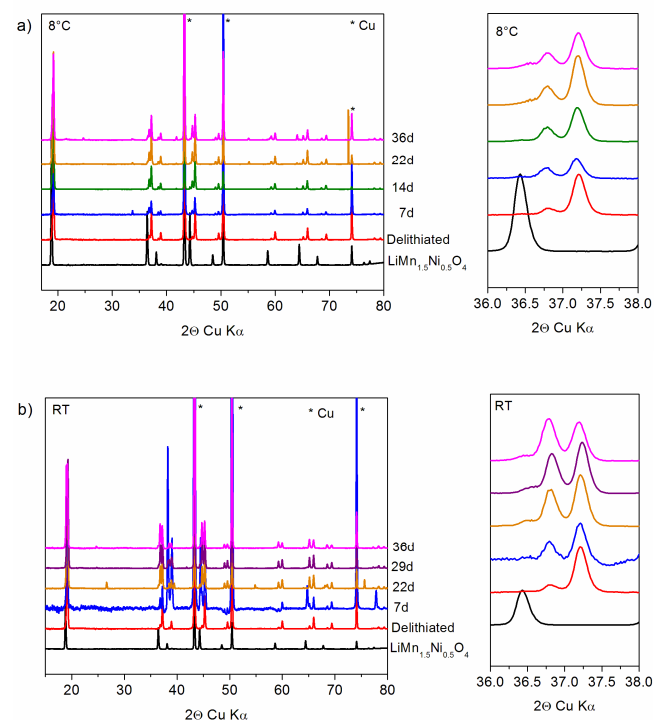


Figure 1. XRD patterns (left) and evolution of the (311) peak (right) of delithiated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ octahedrons during the 36-day storage in 1 M LiPF_6 in EC:DEC electrolyte at: a) 8°C and b) room temperature.

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