

**Microstructural and Electrochemical
Characterizations of Layered Li-Excess Nickel-
Manganese Oxide as Li-Ion Battery Cathode
Synthesized by Co-precipitation and High-
Temperature Calcination**

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Li-ion batteries (LIBs) are foreseen to play a very important role in energy storage for the next decade. Research for advanced Li-ion secondary batteries has been following the direction toward higher energy and power densities. Various cathode materials, such as LiCoO_2 , $\text{LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$, spinel LiMn_2O_4 , olivine LiFePO_4 ,⁴ and $\text{Li}_{1+x}(\text{M},\text{Mn})_{1-x}\text{O}_y$, having different or similar lattice structures have been developed. Among these materials, the class of layered Li-rich Mn-transition metal oxides ($\text{Li}_{1+x}(\text{M},\text{Mn})_{1-x}\text{O}_y$) has lately drawn escalated attention due to their potential high capacities beyond 200 mAh g^{-1} . In these oxides, the excess Li ion gives rise to the presence of inter-grown Li_2MnO_3 slabs within $\text{Li}(\text{M},\text{Mn})\text{O}_2$ matrix to form a layered “composite” structure. These Li_2MnO_3 slabs may be transformed to electrochemical active MnO_2 layers by removal of Li^+ upon charging above 4.5 V (versus Li/Li^+) and stabilizing the layered structure under high depth of lithiation/de-lithiation during the charge/discharge cycles.

$\text{Li}_{1+x}(\text{M},\text{Mn})_{1-x}\text{O}_y$ oxides have often been synthesized via a two-step precipitation-calcination process where either carbonates or hydroxides of the constituent transition metals are first co-precipitated in a continuously stirred tank reactor (CSTR), and the precipitates are mixed with either Li carbonate or hydroxide and then calcined at high temperatures to produce the cathode oxides. Such a process is commercially viable and capable of producing spherical secondary oxide particles with diameters within the range of $5\sim 10 \mu\text{m}$ comprised of nano-sized grains and pores. The spherical geometry and the selected particle dimension are intended for high electrode packing density.

There have been many studies devoted to tailoring the powder properties in these processes. However, very wide ranges of thermal conditions, ranging from $700 \text{ }^\circ\text{C}$ to $1000 \text{ }^\circ\text{C}$ with a holding time between 3 and 24 hr, have been employed for calcination. Clearly, insufficient thermal treatment may result in incomplete reaction and hence low specific capacity. On the other hand, unnecessary prolonged heating not only results in an increase in manufacturing cost, but also leads to excess sintering that could result in microstructures unfavorable to rate performance. Therefore, understanding the dynamics of the microstructural evolution during the heat treatment process and its relation to electrochemical performance would be valuable to the manufacturing of practical composite $\text{Li}_{1+x}(\text{M},\text{Mn})_{1-x}\text{O}_y$ materials.

In this study, spherical composite oxide $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$ powder has been synthesized by high-

temperature calcination of mixture of Li_2CO_3 and $(\text{Ni}_{0.25}\text{Mn}_{0.75})\text{CO}_3$, which is synthesized by a continuous co-precipitation method. The evolution in microstructure of the oxide during calcination is studied mainly by transmission X-ray microscopy (TXM), complemented by X-ray diffraction and thermogravimetry, and it can be divided into three major stages. In particular, the second stage occurs between 400 and $800 \text{ }^\circ\text{C}$, and involves complete $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$ formation and the development of a unique radially-distributed linear pore structure. TXM 3D-elemental analysis gives statistical evidence showing heterogeneity in Ni and Mn distribution, which causes capacity loss and might be a common problem encountered in the two-step precipitation-calcination process. The electrochemical performance of the resulting $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$ powder exhibits complex dependence on microstructure. The radially distributed pore pattern and small grain size produced by intermediate heating history favor the rate performance of the composite oxide cathode by reducing charge-transfer resistance and enhancing apparent Li ion solid-state diffusivity. Large grain size resulting from prolonged heating, on the other hand, reduces the formation of spinel MnO_2 domain upon de-lithiation of the Li_2MnO_3 component of the composite oxide.

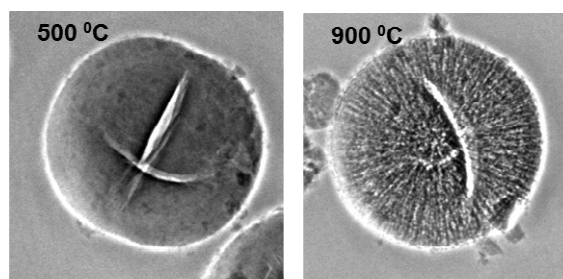


Figure 1. Transmission X-ray micrographs showing interior microstructures of $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$ particles calcined at different temperatures