Growth Mechanism of Ni$_{0.3}$Mn$_{0.7}$CO$_3$ Precursor with Continuous Stirred Tank Reactor (CSTR) for High Capacity Cathodes

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Co-precipitation is a promising method for the synthesis of precursors for lithium ion battery cathodes because it leads to homogeneous composition, narrow particle size distribution, and high packing density materials. Carbonate co-precipitation, as a process to produce transition metal (Mn, Ni, Co) precursors,$^{[1-3]}$ has many advantages compared to hydroxide process: First, in the carbonate matrix, the oxidation state of the cations is kept as 2 for all transition metals. Second, the experimental conditions under which carbonates are usually made are less harsh than those of the hydroxide process. Last but not least, carbonate is a tunable process for better morphology control.

In this study, the nucleation and growth process of carbonate precursor Ni$_{0.3}$Mn$_{0.7}$CO$_3$ during co-precipitation reaction in continuous stirred tank reactor (CSTR) was investigated. Theoretical calculations were conducted to optimize pH condition in the carbonate co-precipitation reaction. It was predicted that pH zone range from 7.5 to 8.5 is the optimum pH condition for the carbonate co-precipitation.

Evolution of particle size, morphology, composition and structure were characterized as a function of reaction time. It was found that the stoichiometry of the seed particles in the early stage of the reaction was richer in nickel and a small amount of Ni(OH)$_2$ impurity phase was observed by x-ray diffraction. The carbonate composition stabilized after several hours of co-precipitation. However, continuous growth of the precursor particles lasted for the whole synthesis process with an average particle size around 30 $\mu$m. Fig. 1 is the average particle size evolution as a function of reaction time. A linear relationship was observed between the average particle size and the reaction time. The calculated growth rate was around 1 $\mu$m/hour. The collected precursors were washed and dried, then mixed with Li$_2$CO$_3$ to produce the lithiated final materials Li$_{1.5}$(Ni$_{0.3}$Mn$_{0.7}$)O$_{2+\gamma}$.

The paper will discuss the relationship between the electrochemical results of the lithiated materials and the physical and morphological properties of the precursors by which those materials were prepared.

Fig. 1. Evolution of average particle size as a function of reaction time. The insets are scanning electron microscopy images of samples collected at different reaction time.

References


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