

Synthesis of Multi-component Olivine by a Novel Mixed Transition Metal Oxalate Coprecipitation Method and Electrochemical Characterization

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The multi-component olivine cathode material, $\text{LiMn}_{1/3}\text{Fe}_{1/3}\text{Co}_{1/3}\text{PO}_4$, was prepared via a novel coprecipitation method of the mixed transition metal oxalate, $\text{Mn}_{1/3}\text{Fe}_{1/3}\text{Co}_{1/3}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$. The stoichiometric ratio and distribution of transition metals in the oxalate, therefore, in the olivine product, was affected sensitively by the environments in the coprecipitation process, while they are the important factors in determining the electrochemical property of electrode materials with multiple transition metals. The effect of the pH, atmosphere, temperature, and aging time was investigated thoroughly with respect to the atomic ratio of transition metals, phase purity, and morphology of the mixed transition metal oxalate. The electrochemical activity of each transition metal in the olivine synthesized through this method clearly was enhanced as indicated in the cyclic voltammetry (CV) and galvanostatic charge/discharge measurement. Three distinctive contributions from Mn, Fe, and Co redox couples were detected reversibly in multiple charge and discharge processes. The first discharge capacity at the C/5 rate was 140.5 mAh g^{-1} with good cycle retention. The rate capability test showed that the high capacity still is retained even at the 4C and 6C rates with 102 and 81 mAh g^{-1} , respectively.

Keywords: lithium rechargeable battery, cathode material, multi-component olivine, mixed oxalate, coprecipitation

Structural Evolution of Layered $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ upon Electrochemical Cycling in a Li Rechargeable Battery

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Recently $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ has been consistently examined and investigated by scientists because of its high lithium storage capacity, which exceeds beyond the conventional theoretical capacity based on conventional chemical concepts. Consequently, $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ is considered as one of the most promising cathode candidates for next generation in Li rechargeable batteries. Yet the mechanism and the origin of the overcapacity have not been clarified. Previously, many authors have demonstrated simultaneous oxygen evolution during the first delithiation. However, it may only explain the high capacity of the first charge process, and not of the subsequent cycles.

In this work, we report a clarified interpretation of the structural evolution of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$, which is the key element in understanding its anomalously high capacity. We identify how the structural evolution of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ occurs upon the electrochemical cycling through careful study of electrochemical profiles, ex-situ X-ray diffraction (XRD), HR-TEM, Raman spectroscopy, and first principles calculation. Moreover, we successfully separated the structural change at subsequent cycles (mainly cation rearrangement) from the first charge process (mainly oxygen evolution with Li extraction) by intentionally synthesizing sample with large particle size. Consequently, the intermediate states of structural evolution could be well resolved. All observations made through various tools lead to the result that spinel-like cation arrangement and lithium environment are created and embedded in layered framework during repeated electrochemical cycling.

Keywords: Li rechargeable battery, Li-excess layered material, $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$, structural evolution, cathode