

Local Structure, Morphology and Electrochemistry of Mn⁴⁺-Based Nanosized Spinel

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The increasing demands on high energy and high power Li-ion batteries lead the researchers to explore high voltage cathode materials. Nowadays research is turned to the improvement of their electrochemical performance by elaboration of nanosized composites and by metal substitution. A more detailed knowledge on the small-scale effects in these materials is needed.

In this contribution we provide data on the local structure, morphology and electrochemistry of nanosized Mn⁴⁺-based spinels. Two groups of spinels are examined: LiNi_{0.5}Mn_{1.5}O₄ and Li₄Mn₅O₁₂. The spinels were prepared using acetate-oxalate precursors, which were obtained mechanochemically at room temperature from metal acetates and oxalic acid. Acid treatment of the samples was used in order to modify their structure and morphology. XRD, HRTEM, ⁷Li NMR and Mn⁴⁺ EPR are used for structural characterization. The electrochemical performance was tested in model lithium cells.

At 400 °C the acetate-oxalate precursor method yields a XRD single LiNi_{0.5}Mn_{1.5}O₄ phase with a mean particle size of about 20 nm. Low-temperature LiNi_{0.5}Mn_{1.5}O₄ displays a statistical cation distribution over the 16d spinel sites (*s.g.* *Fd3m*). At 600 °C a cationic redistribution takes place leading to a 1:3 cationic ordering (*s.g.* P₄32). At this temperature the particle size distribution becomes broader, but the mean particle size remains unchanged. Using acid treatment, LiNi_{0.5}Mn_{1.5}O₄ with an ordered structure and very close particle size distribution is obtained. Cationic distribution and size effects determine the electrochemical performance of LiNi_{0.5}Mn_{1.5}O₄.

At 400 °C, acetate-oxalate precursor method yields single a Li₄Mn₅O₁₂ phase with close particle distribution around 30 nm. According to HRTEM studies, the structure of nanosized Li₄Mn₅O₁₂ can be described as an integration of monoclinic Li₂MnO₃-like domains into a spinel matrix, $(1-a)\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4 \cdot a\text{Li}_2\text{MnO}_3$ and $x < 0.33$. Acid treatment leads to disappearance of the “Li₂MnO₃”-like domains, while the spinel matrix remains stable.

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