Mehanochemical Synthesis of Nanosized $Li_{1+x}Co_{1-x}O_2$

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In the last 15 years lithium cobaltate, $LiCoO_2$, has been considered as a material of great scientific importance due to its application as a cathode material in high-power lithium ion batteries. There are four structural modifications of $LiCoO_2$, the best electrochemical performance is established for $LiCoO_2$ with layered *O3*-type structure. Commercial $LiCoO_2$ consists of particles with dimensions of about 5 μm and displays a limited rate capability. To overcome this drawback, there is a need to elaborate specific methods for the preparation of nanosized $LiCoO_2$.

In this contribution we have studied the mechanochemical interaction of CoOOH and LiOH in order to prepare nanosized $LiCoO_2$ with a layered *O3*-type structure. The Li-to-Co ratio in the precursor mixture was varied from 1 to 2. The interaction of CoOOH and $LiOH.H_2O$ was monitored by DTA and TGA analysis. XRD powder analysis, TEM and ^6Li MAS NMR spectroscopy were used for structural characterization of lithium cobaltates.

The mechanochemical treatment of the CoOOH - LiOH mixture leads to a lattice expansion along the *c*-axis of the layered structure accompanied with a preservation of the intralayer distance between the metal ions. In addition, a partial transformation of CoOOH into lithium-containing Co_3O_4 spinel takes place. Thermal treatment at 400 ^oC yields *O3*-type $LiCoO_2$ with small amounts of spinel-type $LiCoO_2$ (less than 2 %). The spinel modification of $LiCoO_2$ is able to accommodate extra Li forming $Li_{1+x}Co_{1-x}O_2$ oxides with a Li-to-Co ratio higher than 1. The layered modification of LiCoO2 exhibits a Li-to-Co ratio equal to 1 and remains rigid with respect to the insertion of Li^+ in the CoO_2-layers. Both phases display thin particles with sizes varying between 10 and 50 nm. There is no intergrowth between the two structural modifications.

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