# High-Pressure Synthesis of $Li_{1+x}Co_{1-x}O_2$ with Extra Lithium in the Co-Site

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Cathode materials for lithium-ion batteries are based on lithium-transition metal oxides that can intercalate large amounts of lithium reversibly at potentials higher than 4V vs. Li. In terms of battery applications, oxides with layered and spinel crystal structures are of considerable interest. Despite of the high cost and toxicity of Co, $LiCoO_2$ with a layered crystal structure is still used as the main cathode material in lithium-ion cells. Recently, complex solid solutions of monoclinic $Li[Li_{1/3}M_{2/3}]O_2$ (M = Mn, Ti, Zr) with other layered compounds $LiMO_2$ (M ≡ Cr, Co, Ni) were reported as promising cathode materials.

In this contribution we report new data on the formation of novel $Li_{1+x}Co_{1-x}O_2$ compositions with a Li-to-Co ratio higher than 1 ($x \approx 0.12$). For the preparation of $Li_{1+x}Co_{1-x}O_2$, we have considered a new synthetic procedure involving a solid-state reaction between $Li_2O_2$ and $Co_3O_4$ spinel under high-pressure in an oxygen-rich atmosphere, intending to incorporate more than one Li in the structure and to stabilize Co ions in higher oxidation states. The new structural feature of these compositions as compared to the well-known layered $LiCoO_2$ is the incorporation of Li in the Co-site in addition to the nearly pure Li-site. The structure and the lithium distribution in these compositions were characterized by powder XRD analysis and $^6$Li MAS NMR spectroscopy.

The target compositions were prepared by solid state reaction between $Li_2O_2$ and $Co_3O_4$ spinels under high-pressure (up to 3 GPa) using a piston cylinder type apparatus. The use of $Li_2O_2$ ensures an oxygen-rich atmosphere during the formation of $Li_{1+x}Co_{1-x}O_2$. When the Li-to-Co ratio in the precursor mixture is lower than 1.2, $LiCoO_2$ with a layered crystal structure is obtained. The incorporation of extra Li in $LiCoO_2$ leads to an increase in the mean Co(Li)-O bond length. By increasing the Li-to-Co ratio in the precursor mixture, a new structural modification is obtained. The crystal structure is described in terms of a spinel modification, where Li and Co occupies the *16c* and *16d* spinel positions ($Li_2Ti_2O_4$–type structure). The structural formula determined from the Rietveld refinement is $[Li]_{16c}[Li_xCo_{1-x}]_{16d}O_2$. The accommodation of $Li^+$ in the $Li_{1+x}Co_{1-x}O_2$ spinel is limited up to x=0.12. The different environment of Li in layered $LiCoO_2$ and $Li_{1+x}Co_{1-x}O_2$ spinel is demonstrated by $^6$Li NMR spectroscopy.

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