



On the incorporation of extra Li in lithium cobaltate $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$

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ABSTRACT

Novel $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ compositions were prepared by two synthesis methods: solid-state reaction between Li_2O_2 and Co_3O_4 under high pressure and mechanochemically assisted reaction between CoOOH and $\text{LiOH}\cdot\text{H}_2\text{O}$. Variation of the Li-to-Co ratio in the precursor mixture from 1.0 to 1.5 resulted in the formation of $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ compositions with $x \sim 0.12$. The structure and cationic distribution in $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ were monitored by XRD powder analysis, TEM analysis and ^6Li MAS NMR spectroscopy. Pure $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ with $\text{Li}_2\text{Ti}_2\text{O}_4$ -type spinel structure was obtained under high pressure only. Mechanochemically assisted synthesis at 400 °C yielded layered LiCoO_2 with a small amount of spinel-type $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$. The spinel modification of LiCoO_2 is able to accommodate extra Li, so that the Li-to-Co ratio is higher than 1. The layered modification of LiCoO_2 is more rigid with respect to the accommodation of more than one lithium atom.

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1. Introduction

The studies of the composition and the crystal structure of lithium cobaltates began about 50 years ago [1]. Johnston et al. were the first to report on lithium interacting with CoO forming compounds with a composition $\text{Li}_x\text{Co}_{1-x}\text{O}$. In the concentration range of $0 < x < 0.2$, the lithium and cobalt ions occupy statistically the octahedral sites of the close-packed oxygen lattice leading to the formation of a single phase with a rock-salt type structure. At $x = 0.5$, a rhombohedral phase is obtained due to the consecutive arrangement of Li and Co ions in the octahedral sites. As a result, discrete lithium and cobalt layers composed of edge-sharing trigonally distorted octahedra are developed [2]. Between the layers, the LiO_6 - and CoO_6 -octahedra share common edges so that three CoO_2 -layers are needed to describe the unit cell of LiCoO_2 . Following the notation proposed by Delmas et al. [3], this structural modification of LiCoO_2 is designated as O3-form.

At low temperature (about 400 °C), a new modification of LiCoO_2 with a spinel-related structure has been prepared by solid-state reaction between lithium carbonate and cobalt oxide [4–6]. This modification is noted as low temperature (LT), as opposed to the rhombohedral high-temperature modification (HT). Analogous to O3- LiCoO_2 , the structure of the LT- LiCoO_2 can be derived from the close oxygen packing, whereas the Li and Co ions occupy the two octahedral sites in a 3:1 (or 1:3) ratio thus leading to a spinel modification (structural type $\text{Li}_2\text{Ti}_2\text{O}_4$). Based on a neutron diffraction study, it was shown that about 6% of the cobalt ions are located in the lithium sites

[5]. Nevertheless, the refinement of the diffraction data of these solids in both R3m layered structure and Fd3m spinel structure was found to give comparable fits to the data [5]. The mechanochemical synthesis is considered as an appropriate method for the preparation of LiCoO_2 with spinel structure [7–9]. Above 600 °C, the spinel phase is transformed to the layered O3-modification.

Recently, two metastable polytypes of LiCoO_2 have been prepared by ion-exchange reaction [10–14]. Their structures are composed of the same LiO_2 and CoO_2 -layers, but the mode of the layer stacking along the c_{hex} axis is different: O2- LiCoO_2 with ABBA oxygen packing [10–12] and O4- LiCoO_2 with ABCBACBCAB oxygen packing [13,14]. This difference is a consequence of the occupancy of the energetically unfavorable positions, where the Li^+ and Co^{3+} octahedra share common faces. The stacking of the layers is fixed by the type of distribution of the Li^+ ions, which is a result from the competition between the intra-plane $\text{Li}^+ - \text{Co}^{3+}$ electrostatic repulsions and the in-plane $\text{Li}^+ - \text{Li}^+$ electrostatic repulsions [15]. Based on first-principles investigations of the phase stability in the O2- LiCoO_2 system, it has been shown for the first time that the reduction of the in-plane $\text{Li}^+ - \text{Li}^+$ electrostatic repulsions can be achieved by simultaneous occupancy of both sites instead of the energetically most favorable site [16].

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 [17–19]. This is a consequence of its ability to intercalate lithium reversibly at a potential of about 4 V. The best electrochemical performance is established for the O3-modification [17–19]. This modification is capable to accommodate a small excess of Li in the Co layers at the expense of creation of oxygen vacancies. As a result, over-stoichiometric oxides with the composition $\text{Li}_{1+t}\text{Co}_{1-t}\text{O}_{2-t}$ (where $t \sim 0.04$)

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are formed [20]. When $O3\text{-LiCoO}_2$ contains over-stoichiometric Li^+ ions, the mechanism of the electrochemical reaction in the initial stage of Li extraction is changed [21]. The formation of over-stoichiometric $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_{2-t}$ with oxygen vacancies is a specific feature for lithium cobaltate. Layered LiNiO_2 is isostructural with the $O3$ -modification of LiCoO_2 . Under high pressure in an oxygen atmosphere, novel compositions $\text{Li}[\text{Li}_x\text{Ni}_{1-x}]\text{O}_2$, $0 \leq x \leq 0.33$, with a layered structure are formed over the whole concentration range [22,23]. The crystal structure of $\text{Li}[\text{Li}_x\text{Ni}_{1-x}]\text{O}_2$ changes from trigonal $R\text{-}3m$ to monoclinic $C2/m$ at a Li-to-Ni ratio of 2 (or $x = 1/3$) [23]. A new structural feature of these compositions as compared to the well-known $\text{Li}[\text{Ni}]\text{O}_2$ is the development of mixed $[\text{Li}_x\text{Ni}_{1-x}]\text{O}_2$ -layers in addition to the nearly pure Li-layers. The replacement of Ni^{3+} by Li^+ in the nickel-rich layers is compensated by the appearance of Ni^{4+} ions. As far as we know, there are no data on the formation of $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ where the compensation of Li^+ charge is achieved by Co^{4+} ions.

The purpose of this contribution is to study the incorporation of extra Li in lithium cobaltate from a fundamental point of view. For the preparation of the $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ compositions, we have employed two synthetic routes: solid-state reaction between Li_2O_2 and Co_3O_4 under high pressure and mechanochemical assisted reaction between CoOOH and $\text{LiOH}\cdot\text{H}_2\text{O}$. In the precursors, the Li-to-Co ratio was varied between 1 and 1.5. While the high pressure in an oxygen atmosphere allows stabilizing transition metal ions in a high oxidation state [22,23], the mechanochemical synthesis is known to produce defective layered compositions [9]. XRD powder analysis, TEM and ^6Li MAS NMR spectroscopy were used for structural characterization of mixed $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ -compositions.

2. Experimental

The starting reagents were $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Aldrich, ACS reagent, $\geq 98\%$), $\text{LiOH}\cdot\text{H}_2\text{O}$ (Aldrich, 99.95% trace metals basis) and Li_2O_2 (Aldrich, 90%).

The target compositions $\text{Li}[\text{Li}_x\text{Co}_{1-x}]\text{O}_2$ were prepared by a solid-state reaction between Li_2O_2 and Co_3O_4 spinels at 3 GPa and 700°C for 2.5 h. Co_3O_4 was obtained by thermal decomposition of cobalt carbonate at 500°C . The cobalt carbonate was precipitated by the addition of NaHCO_3 at $\text{pH} = 8$ while passing CO_2 through an aqueous solution of the Co nitrate (0.5 M). This method allows preparing a single Co carbonate phase with calcite-type structure. The Li-to-Co ratio in the precursor mixture was 1.0, 1.25 and 1.5. High-pressure synthesis was performed using a 1/2 inch end-loaded piston-cylindrical apparatus at the Bayerisches Geoinstitut, Bayreuth. The samples were placed in 1 cm long, 5 mm diameter Pt capsules with caps, which were welded from one side and close fitted from the other. The details of the high-pressure procedure are given elsewhere [22].

Mechanochemically assisted reaction between CoOOH and $\text{LiOH}\cdot\text{H}_2\text{O}$ followed by heating at 400°C was also applied for the preparation of $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ compositions. The mechanochemical synthesis proceeded in a planetary monomill Fritsch Pulverisette 6 using agate balls (diameter = 10 mm) and agate container (volume $\approx 75\text{ cm}^3$). The conditions were as follows: milling in air atmosphere, the weight ratio of powder samples to balls was 1:13, 200 rpm rotation speed and ball milling duration was for 10 h and 20 h. CoOOH was obtained by oxidation of freshly precipitated $\beta\text{-Co}(\text{OH})_2$ with oxygen at room temperature, according to the method described by Delaplane et al. [24].

The lithium and cobalt content in the samples was determined by ICP analysis. The mean oxidation state of cobalt was determined by iodometric titration against a standardized sodium thiosulfate solution. Iodometric titration was performed on 10–20 mg of sample in Ar atmosphere. For each composition titrations were repeated several times in order to obtain accurate and consistent results.

X-ray phase analysis was performed using a Philips X'Pert powder diffractometer with monochromatic $\text{CoK}\alpha_1$ radiation, and Si being the internal standard. In addition, a Bruker Advance D8 diffractometer with detector Sol-X and $\text{CuK}\alpha$ radiation was used. The scan range was $15 \leq 2\theta \leq 120^\circ$ with a step increment of 0.02° . A Fullprof computer software was used for the refinements [25]. The diffractometer zero point, the Lorentzian/Gaussian fraction of the pseudo-Voigt peak function, scale factor, the unit cell parameters, the oxygen parameter, the thermal factor for the trigonal and spinel positions, the line half-width parameters and the preferred orientation were refined.

The TEM investigations were performed on a TEM JEOL 2100 instrument at accelerating voltage of 200 kV. The specimens were prepared by grinding and dispersing them in ethanol by ultrasonic treatment for 6 minutes. The suspensions were dripped on standard holey carbon/Cu grids. The measurements of lattice-fringe spacing recorded in HRTEM micrographs were made using digital image analysis of reciprocal space parameters. The analysis was carried out by the Digital Micrograph software.

Solid-state $^6,7\text{Li}$ NMR spectra were recorded at 88.32 and 233.23 MHz (14.1 T) on a Bruker AV600II + spectrometer. MAS NMR spectra were recorded with single pulse excitation (1 μs) and a 0.2 s recycle delay. The number of scans acquired depended on the lithium content of the sample, typically 128–1024 for ^7Li and 10,000–300,000 for ^6Li . The samples were loaded into 4 mm zirconia rotors and spun at 11.0 kHz. Chemical shifts are quoted in parts per million, from external tetramethylsilane, TMS (Ξ scale). The unified scale relies on Ξ values, stated as percentages [$\Xi \equiv 100x (v_x/v_{\text{TMS}})$], where v_x is the absolute frequency for the 0 ppm position in the X spectrum, and v_{TMS} is the absolute frequency for ^1H of TMS. The solid-state NMR spectra were fitted using DMFIT software [26].

3. Results

3.1. High-pressure synthesis of $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$

Fig. 1 shows the XRD patterns of $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ compositions obtained under high pressure. When the Li-to-Co ratio in the precursor mixture is lower than 1.5, LiCoO_2 with a layered crystal structure is obtained (Fig. 1). For $\text{Li}/\text{Co} = 1.0$, the unit cell parameters of LiCoO_2 obtained under high-pressure match those of LiCoO_2 obtained at atmospheric pressure (Table 1). By increasing the Li-to-Co ratio from 1.0 to 1.5, there is an increase of the a -parameter, while the c -parameter decreases. At $\text{Li}/\text{Co} = 1.5$, a new structural modification is formed. The XRD pattern is satisfactorily fitted by the Rietveld analysis on the basis of the model of the spinel structure including Li and Co in $16d$ and $16c$ spinel positions ($\text{Li}_2\text{Ti}_2\text{O}_4$ -type structure, Fig. 1 and Table 2). This phase is isostructural to the low-temperature modification of LiCoO_2 having a spinel-related structure. An important difference between spinel-type Li–Co phase obtained under high pressure and the metastable LT- LiCoO_2 is the amount of Li: for the high-pressure phase the Li-to-Co ratio is higher than 1 (Table 1), while $\text{Li}/\text{Co} \sim 1$ has been established for LT- LiCoO_2 [5]. The fitting procedure becomes slightly better when small part of Co and Li exchanged their positions (about 2%, Table 2). The total occupancy of $16c$ and $16d$ positions was constrained to 1. As a result, the analysis of XRD patterns gives the following structural formula: $\text{Li}_{1.12}\text{Co}_{0.88}\text{O}_2$. The exact amount of Li incorporated in the Co position is a difficult task due to lower scattering factor of Li. However, it is clear that the Li-to-Co ratio in the precursor is higher than that of target $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ (Tables 1 and 2). When the Li-to-Co ratio in the precursor is 1.5, the refinement procedure gives a Li-to-Co ratio of 1.27 for the target composition. This means that the incorporation of Li in LiCoO_2 by formation of $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ spinel is limited. In addition, the Li-to-Co ratio is somewhat lower than that determined by chemical analysis: 1.27 vs. 1.35, respectively. To check for possible contamination of the target $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$ with unreacted lithium salts, Fig. 1 presents the

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