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# Synthesis of lithium cobalt oxide by single-step soft hydrothermal method

Kiran Kumar Bokinala [a,b,c], M. Pollet [b,*], A. Artemenko [b], M. Miclau [a], I Grozescu [a,c]

[a] National Institute for R&D in Electrochemistry and Condensed Matter, Timisoara 30024, Romania
[b] CNRS, Université de Bordeaux, ICMCB, 87 Avenue du Dr. A. Schweitzer, Pessac F-33608, France
[c] Universitatea Politehnica, Timisoara, Romania

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ABSTRACT

Lithium cobalt double oxide $LiCoO_2$ was synthesized at 220 °C by soft hydrothermal method using $Co(OH)_2$ and LiOH as precursors, LiOH/NaOH as mineralizers and $H_2O_2$ as oxidant. The soft hydrothermal synthesis method offers the dual advantage of a much lower synthesis time and a higher purity in comparison with other synthesis methods. The compound was identified by X-ray diffraction and its purity was checked by magnetic and electron magnetic resonance measurements. The grain morphology was studied by Scanning Electron Microscopy and an exponential growth of particle size with synthesis time was observed.

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## 1. Introduction

Lithium cobalt double oxide $LiCoO_2$ is well known for its high performance as cathode part of Li-ion batteries; it offers both a high output voltage and a high specific energy [1–7]. $LiCoO_2$ owes its efficiency to its layered structure which alternates Li and $CoO_2$ layers; in its thermodynamically stable form, it crystallizes with *R*-3*m* space group (O3-polytype [8]) with both direct solid state or hydrothermal synthesis methods [9]; other polytypes are also known like O2- [10] and O4-polytypes [11] and for the Li deficient cases, O1- [12], O6- [13], and T2-polytypes [14]. Among the several synthesis methods already proposed to produce $LiCoO_2$, all present at least one of the following weaknesses: high temperature synthesis, multiple steps, long preparation time, long synthesis times, specific care, limited yield and/or presence of impurities in the final product. For standard solid-state synthesis method for instance, the synthesis temperature of the initial mixture of $Li_2CO_3$ and $Co_3O_4$ reaches 850 °C [15] and $Co_3O_4$ impurities are present [16]. In order to reduce the synthesis temperature of lithium cobaltate, a sol–gel method based on an inorganic carboxylic route was successfully developed, but $Co_3O_4$ phase was still observed after the thermal treatment at 700 °C [17]. More recently a microwave assisted synthesis with double-containment was reported [18].

The hydrothermal synthesis method has already been extensively used to synthesise a wide range of oxide materials [19–22]; it was shown to be advantageous as it requires lower synthesis parameters, it is less expensive and it leads to the good oxygen stoichiometry. The problem of the impurities can be overcome by varying the ratios of precursors: In the specific case of $LiCoO_2$, cobalt impurities can be avoided by increasing the Li to Co ratio. So far, $LiCoO_2$ has been prepared by hydrothermal subcritical as well as in supercritical conditions with 50% concentrations of hydrogen peroxide as an oxidant [23,24]. It is actually challenging to find synthesis conditions which allow to reduce the concentration of hydrogen peroxide and to tune the grain size. In order to optimize the synthesis conditions of $LiCoO_2$ using hydrothermal method, we studied the influence of the precursors' concentration, the molality of the solution and the synthesis temperature on the resultant phase as well as the influence of the reaction time on the surface morphology and the purity of the samples.

## 2. Experimental

A previous report [25] on the stability diagram of Co–Na–$H_2O$ system with NaOH and $Co(OH)_2$ as precursors and NaOH as mineralizer has revealed the systematic presence in the product of secondary phases of precursor and $HCoO_2$ for any synthesis temperature lower than 220 °C whatever the NaOH amount; furthermore, the stability diagram of Na–Co–$H_2O$ system indicates an optimal concentration of $Co(OH)_2$ precursor in the solution of 13 mmol/L at 220 °C. These two parameters were used as initial parameters for the present study. Powders of $Co(OH)_2$ and LiOH were selected as precursors. High concentrations of ionic mineralizers (LiOH and NaOH) were used to improve the solubility of $Co(OH)_2$ and 5% hydrogen peroxide as oxidant were

* Corresponding author.
*E-mail addresses:* pollet@icmcb-bordeaux.cnrs.fr (M. Pollet), marinela.miclau@gmail.com (M. Miclau).

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added. The precursors were first dissolved in water and the 5% $H_2O_2$ were added to the solution; this latter was transferred into a 70 mL Teflon-line autoclave with a filling degree of 85%. Samples were heated at 220 °C varying the reaction time from 5 to 80 h and the mineralizers concentration from 1 to 4 m. After cooling to room temperature (RT), the samples were washed and dried at RT.

XRD patterns were recorded with a PANalytical X'Pert Pro powder diffractometer in the Bragg–Brentano geometry, using Cu $K_\alpha$ radiation in the range $2\theta = 5–80°$ at RT and analyzed using FULLPROF program [26]. The surface morphology was studied using Scanning Electron Microscopy (Hitachi S4500 field emission microscope). Elemental analysis was carried out by inductively coupled plasma absorption electron spectroscopy (ICP-AES) on a Varian 720-ES. Zero field cooled (ZFC) and field cooled (FC) DC-magnetization data at an applied field of 0.01 T were collected on a superconducting quantum interference device magnetometer (Quantum Design Magnetic Property Measurement System) in the 4–200 K temperature range. EPR measurements were performed with an X-band Bruker spectrometer operating at 9.4 GHz. An Oxford Instruments ESR 9 He cryostat operating in the temperature range 4–300 K was used for the temperature dependence studies of EPR spectra intensities. To perform both quantitative and qualitative analysis the same amount (0.025 g) of powder of $LiCoO_2$ samples was used in the cavity.

## 3. Results and discussion

Fig. 1 summarizes the result of varying the NaOH: LiOH mineralizer's ratio in the solution, the temperature (220 °C), the reaction time (24 h), the hydrogen peroxide concentration (5%) and concentration of $Co(OH)_2$ (13 mmol/L) were kept constant.

Using only LiOH as mineralizer, $LiCoO_2$ crystallizes only from 0.5 m as a minority phase in a solution containing mostly $Co_3O_4$; with the increase of LiOH concentration, $LiCoO_2$ yield increases however with some impurities of CoO for LiOH $\leq$ 2 m; when LiOH $\geq$ 2 m, the only product visible from XRD is $LiCoO_2$. The inductive coupled plasma (ICP) analysis confirmed the close to stoichiometric ratio Li:Co = 1:1.

Our previous work (without hydrogen peroxide, below 150 °C and with a 3 M NaOH solution only) has only revealed a partial evolution of $Co(OH)_2$ precursor (space group: *P*-3*m*1; JCPDS 01-074-1057) to $Co(OH)_2$ hexagonal (JCPDS 00-001-0357). At 150 °C and 4 M NaOH, $Co(OH)_2$ hexagonal disappears and it is replaced with CoOOH. The transformation of $Co(OH)_2$ precursor continues with increasing the NaOH molarity and temperature; CoOOH was found to crystallize in the three layered polytype ($3R_1$) and to become the majority phase for 180 °C and 3 M NaOH. Similar results were observed for other cobalt oxyhydroxide samples prepared in oxidative conditions (air or hydrogen peroxide). The same oxidation of $Co(OH)_2$ to (3 $R_1$)-CoOOH was also reported during the synthesis of nano-sized lithium cobalt oxide by sonochemical synthesis [30]. If temperature is increased, $Co_3O_4$ forms.

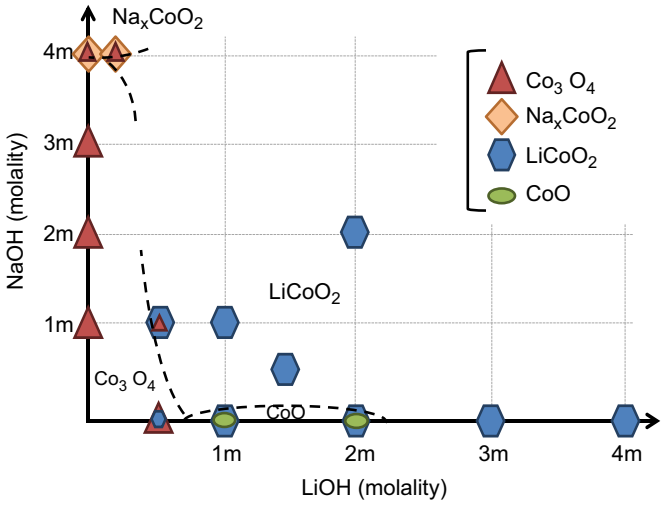


**Fig. 1.** The effect of ionic mineralizers on resultant phases obtaining at 220 °C and after 24 h.

The several steps for the reaction can be written as [30]

$$2Co(OH)_2 + H_2O_2 \xrightarrow[LiOH]{220\ degC} 2HCoO_2 + 2H_2O \quad (1)$$

$$LiOH \Rightarrow Li^+ + OH^- \quad (2)$$

$$HCoO_2 + Li^+ + OH^- \Rightarrow LiCoO_2 + H_2O \quad (3)$$

The total reaction is

$$2Co(OH)_2 + 2LiOH + H_2O_2 \xrightarrow[5\ h,15\ h,24\ h,60\ h]{220°C} 2LiCoO_2 + 4H_2O (1+2+3)$$

The role of NaOH is actually multiple: First, just like LiOH, it acts as mineralizer; second, NaOH is slightly more oxidative than LiOH and it might help stabilizing higher valence state of cobalt (CoO traces are disappearing on adding NaOH); third, probably in relationship with point 2, it promotes the crystallization of $LiCoO_2$: the crystallinity of $LiCoO_2$ obtained with 1 M LiOH and 1 M NaOH is higher than with 4 M of LiOH only and the FWHM evolution *vs* NaOH content clearly evidence a narrowing of the diffraction peaks. It is worth noting that for equimolar ratios of LiOH and NaOH, only $LiCoO_2$ forms while $Na_xCoO_2$ could also be expected. Several points can be highlighted that explain this result: (i) whatever the conditions used, we were not able to stabilize the stoichiometric compound $NaCoO_2$, meaning that the formed compound always contains a minimum amount of $Co^{4+}$; as mentioned above, NaOH is more likely to stabilize higher valence state of cobalt however, our phase diagram shows that $Co^{4+}$ might be accessible only for strong excess in NaOH; (ii) $HCoO_2$ was shown to be formed at low temperature [ref to the stability diagram of Co–Na–$H_2O$]; in solution it appears as $CoO_2^-$ which is expected to have a short time life [27] and to fast react with its environment; as lithium has a higher electron affinity than sodium (respectively 0.618 eV and 0.548 eV), one can expect a faster combination with $Li^+$ than with $Na^+$; (iii) both compounds are lamellar, however $LiCoO_2$ basically has a more pronounced 3D character (ordered rock salt structure) than $Na_xCoO_2$ what can favour its growth.

Fig. 2 highlights some typical features in the crystal shapes depending on the mineralizers concentration and the reaction time. For the lowest concentrations of mineralisers and with 24 h of synthesis duration, only desert-rose shape could be observed (Fig. 2a). Keeping constant the overall mineralizer concentration but increasing the LiOH to NaOH ratio results in the growth of small spherical particles (Fig. 2b). Further increasing the reaction time leads to the growth of concave cuboctohedrons (Fig. 2c). Also, the effect of higher mineralizer concentration on the crystal shapes was studied.

Some SEM micrographs for the samples synthesized from $[Co(OH)_2] = 13$ mmol/L and equimolar LiOH and NaOH mineralizers amount (2 M) are shown in Fig. 3 for several reaction time.

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