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Low-temperature cobalt oxide as rechargeable cathodic material for lithium batteries

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Abstract

The present paper describes a novel synthesis of $LiCoO_2$ obtained from a solution technique. Low-temperature $LiCoO_2$ compound has been prepared by the reaction of lithium and ammonium hydroxyde with a cobalt nitrate aqueous solution. An appropriate heat treatment of the corresponding precipitate performed at 400 °C in air leads to a crystallized layered $LiCoO_2$. Preliminary structural and electrochemical experiments are reported and evidenced that lithium extraction occurs at a lower potential (3.7 V) than for its high-temperature analogue with a maximum depth of charge of 0.5 Li/Co when used in a conventional electrolyte.

Keywords: Rechargeable cathodic materials; Cobalt oxide; Lithium insertion

1. Introduction

In recent years, consistent attention has been devoted to novel types of rechargeable cathode materials usable in secondary lithium batteries and especially in 'rocking-chair' batteries. $LiCoO_2$ has then been extensively studied as the positive electrode owing to its open layered structure and its high theoretical energy density of 1070 Wh/kg and an average discharge voltage of 3.9 V [1–3]. But the benefit of high operating potential raises the problem of the system stability which reduces the maximum rechargeable capacity to about 0.5 Li per mole of oxide.

Numerous works have emphasized the influence of the synthesis way upon the electrochemical performance of lithium intercalation compounds and their interest [4–6]. In particular, considerable improvement has been obtained by using low-temperature techniques such as sol–gel processes and precipitation reactions in obtaining high performance cathodic materials [7]. These solutions techniques have been proved to give rise to new structures to modify various parameters like morphology, electronic conductivity, surface active area, number of defects, size of consistency domains, etc., which are of the utmost importance for electrochemical properties. In addition to the great versatility of these low-temperature techniques, the possibility to take advantage of the wide temperature range available for heat treatment of such materials is of particular interest.

In the present paper, we report on an attempt to extend low-temperature (LT) techniques to the $LiCoO_2$ synthesis in order to lower its working potential and then to improve its cycle life. We will describe the synthesis and characterization of this new kind of LT $LiCoO_2$ and preliminary results on its electrochemical properties investigated from voltammetric and chronopotentiometric measurements.

2. Experimental

Low-temperature $LiCoO_2$ was obtained by a precipitation process in aqueous solution which leads to a more homogeneous mixture and allows the formation of the compound at low temperature. A lithium and ammonium hydroxide solution is mixed to a nitrate cobalt solution. The mixture is slowly evaporated at 60 °C under vacuum and the recovered precipitate is dried at 110 °C for 15 h. A thermal treatment at temperature ≥400 °C for 2 h in air leads to the formation of $LiCoO_2$. However, it is possible to obtain $LiCoO_2$ at 300 °C with the presence of a few impurities of Co_3O_4 and some residual nitrates. Samples are prepared at 400, 600 and 800 °C for 2 h.

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Thermal analysis measurements are performed in air at a heating rate of 10 °C/min using a Netzsch STA 409 analyser with the simultaneous recording of weight losses (gravimetric thermal analysis) and temperature variations (differential scanning calorimetry). The oxidation state of cobalt is determined by a chemical titration in return using ferrous sulfate and potassium bichromate. X-ray diffraction experiments are performed with a CGR Theta60 X-ray system using Co Kα1 radiation.

The electrochemical characteristics of LT $LiCoO_2$ were determined with three-electrode electrochemical cells. The working electrode consisted of 10 mg of active material mixed with graphite (20 wt.%). The mixture is pressed on to a stainless-steel grid, 1 cm in diameter. The counter and reference electrodes consisted of lithium wires in separated compartments. The electrolyte used was 1 M $LiClO_4$ in propylene carbonate. Propylene carbonate, double-distilled, was obtained from Fluka and used as-received. Anhydrous lithium perchlorate was dried under vacuum at 200 °C for 12 h. Electrochemical measurements were made with a potentiostat PAR 273 coupled to an IBM 386 computer.

3. Results and discussion

The simultaneously recorded thermal analysis curves of the precipitate are shown in Fig. 1. This compound should contain lithium and ammonium nitrate, cobalt(II) hydroxyde and water. A first weight loss in the temperature range from 80 to 180 °C corresponds to the departure of water. The first exothermic peak at 210 °C associated with an important weight loss involves the decomposition of ammonium nitrate into N_2O. Melting of lithium nitrate which gives rise to an endothermic peak located at 260 °C probably enhances the reactivity of lithium with a cobalt-based compound. A final important weight loss observed around 400 °C corresponds to the departure of the remaining nitrates and to the formation of crystallized $LiCoO_2$ simultaneously.

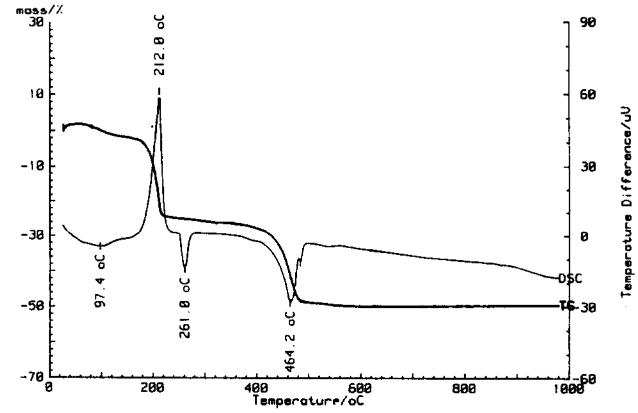

Fig. 1. Simultaneous thermal analysis and differential thermal analysis of the dried precipitate.

The X-ray diffraction patterns for the compound $LiCoO_2$ are presented in Fig. 2 as a function of the heat treatment. For each compound, all the peaks could be indexed to the trigonal space group $R\bar{3}m$ without impurities. $LiCoO_2$ structure can be described as a layered structure consisting of alternating cobalt and lithium layers, where lithium and cobalt atoms are both in octahedral sites of CoO_6 ad LiO_6 with common edges [8]. The X-ray experiments present broader peaks when the temperature of the synthesis decreases. On the diagrams corresponding to the low-temperature compounds, the peaks indexed 001 are slightly shifted leading to a parameter *c* of 13.9 Å for $LiCoO_2$ obtained at 400 °C, 14.02 Å for $LiCoO_2$ obtained at 600 °C, and 14.07 Å for the one obtained at 800 °C, respectively. These results show a lower crystallinity and probably more disorder in the atoms arrangement for the compounds obtained at low temperature.

Cyclic voltammograms of LT $LiCoO_2$ obtained at 400, 600 and 800 °C are performed in the potential range from 4.2 to 3.2 V wherein no electrolytic de-

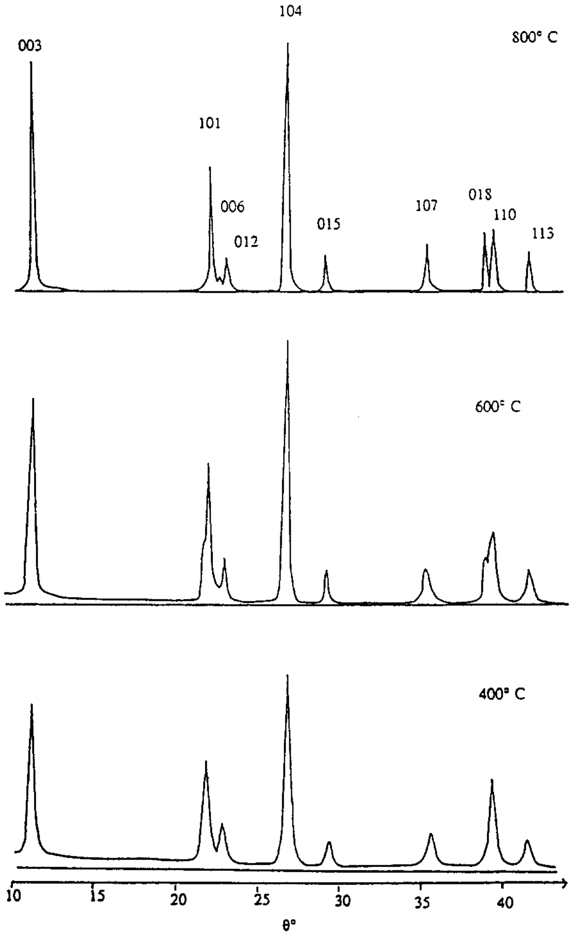

Fig. 2. X-ray diffraction patterns for $LiCoO_2$ as a function of the heat treatment.

composition occurs (ν=25 μV/s, Fig. 3). For the 800 °C heat-treated compound, well-defined anodic and cathodic peaks are observed at 3.97 and 3.93 V, respectively, separated by only 50 mV which clearly illustrates the reversibility of the material upon deintercalation and intercalation of Li^+ ions, in agreement with previous reports [2,3,9] on high-temperature (HT) $LiCoO_2$ prepared by solid-state reactions. The coulombic efficiency for the oxidation/reduction process is about 85% while the anodic process involves extraction of 0.37 Li^+/Co.

Conversely, the 400 °C LT $LiCoO_2$ material exhibits broader anodic and cathodic peaks with a difference between the peak potentials above 200 mV, these latter being located at 3.75 and 3.47 V. These features show that the 400 °C LT $LiCoO_2$ is a less oxidizing system than the 800 °C compound, but is characterized by a lower degree of reversibility even when a similar coulombic efficiency in the order 80% is found (Δx=0.40). Despite the low scanning rate applied, the presence of an important dissymmetry in the shape of the anodic peak seems to indicate that an additional oxidation reaction takes place beyond 3.75 V though the corresponding X-ray diffraction pattern does not reveal any impurity. A significant discrepancy appears between the present results and those reported by Gummow et al. [5] on LT $LiCoO_2$ also prepared at 400 °C but using solid-state reactions of Li_2CO_3 with $CoCO_3$. Indeed, these authors observed from voltammetric experiments an anodic and cathodic peaks located at 4.1 and 3.2 V, respectively. The higher scanning rate used by these latter could not explain such a discrepancy in the results which could rather signify that two different host structures $LiCoO_2$ would be involved in both cases.

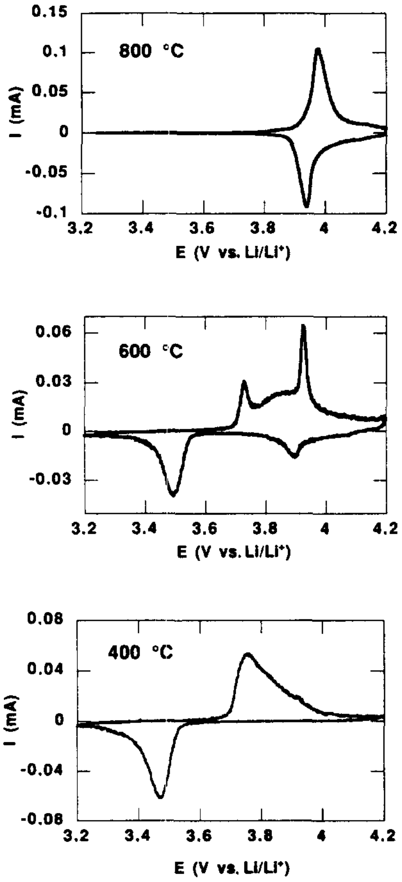

Fig. 3. Cyclic voltammograms of $LiCoO_2$ obtained at 400, 600 and 800 °C, at scan rate of 25 μV/s within cycling limits from 3.2 to 4.2 V.

The medium-temperature phase obtained at 600 °C exhibits on one hand two anodic peaks at 3.73 and 3.92 V separated by a strong anodic current, and on the other hand two cathodic peaks at 3.9 and 3.49 V. In fact, the corresponding voltammogram includes all the extraction/insertion processes already evidenced in both 800 and 400 °C heat-treated forms. The '600 °C' compound combines the more extended potential range for lithium insertion/de-insertion with an apparent lower rechargeability. This phenomenon raises the problem of the presence of other phases which would not be revealed by X-ray investigation.

The voltammetric characteristics of the three materials have been studied as a function of the potential scan at a constant sweeping rate of 25 μV/s. The results are summarized in Table 1 for the 400 and 800 °C LT materials. For the 400 °C LT $LiCoO_2$, when the potential scan is limited to a low value (3.76 V, Δx=0.2), a high efficiency $>$90% is achieved for the lithium de-insertion/insertion processes. For more extended cycling (4.2 V, Δx=0.4) this efficiency decreases to about 75% to reach only 60% (4.4 V, Δx=0.5). Whereas slightly higher results are obtained for the '800 °C' material, quite similar values are found for the '600 °C' compound exhibiting the poorest behaviour. Upon cycling up 4.6 V, the 44% efficiency obtained for the 800 °C was expected because of the electrolyte breakdown at high potential.

Typical charge/discharge curves for 400 °C LT $LiCoO_2$ are shown in Fig. 4. We find again the main electrochemical feature of the LT material, i.e., its lower potential for lithium extraction/insertion 3.7 V/3.55 V against 3.95 V/3.85 V for the 800 °C, with an efficiency of 75% in good agreement with that observed on LT $LiCoO_2$ prepared by solid-state reactions [4,5]. From the second charge, a significant polarization appears.

The influence of the current density on the oxidation process for a depth of charge of 0.5 F/mol is illustrated in Fig. 5. The lithium extraction process is never significantly affected in terms of faradaic yield which indicates high kinetics of lithium transport inside the host structure. However, the significant and regular polarization leading to a translation of the whole charge curve of the '400 °C' material towards higher voltage values as the current density increases, suggests a lower

Table 1
Voltammetric data of $LiCoO_2$ obtained at 400 and 800 °C for different cycling limits (scan rate = 25 μV/s)

800 °C $LiCoO_2$			400 °C $LiCoO_2$		
Anodic potential limit (V vs. Li/Li^+)	$\Delta x_{oxidation}$ (F/mol)	Q_{red}/Q_{ox} (%)	Anodic potential limit (V vs. Li/Li^+)	$\Delta x_{oxidation}$ (F/mol)	Q_{red}/Q_{ox} (%)
4.6	0.56	44	4.4	0.49	60
4.4	0.38	80	4.2	0.41	73
4.2	0.37	82	4	0.4	74
4.1	0.34	84	3.85	0.35	78
4	0.26	85	3.76	0.19	93

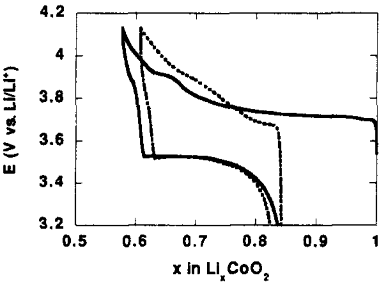

Fig. 4. Charge/discharge curves of $LiCoO_2$ synthesized at 400 °C for the first two cycles at constant-current density of 50 μA/cm².

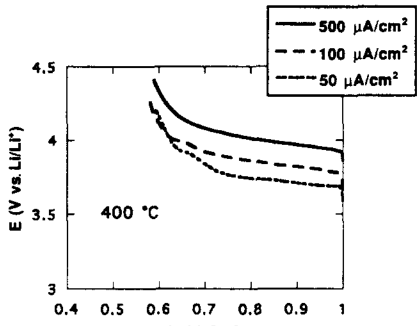

Fig. 5. Influence of the current density on the oxidation process of $LiCoO_2$ obtained at 400 °C.

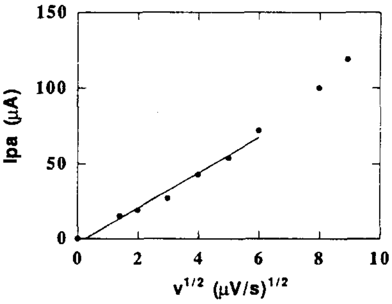

Fig. 6. Variation of anodic peak current vs. scanning rate for $LiCoO_2$ obtained at 400 °C.

electronic conductivity in the '400 °C' compound rather than a concentration polarization.

An average value for the chemical diffusion coefficient of Li^+ ions in '400 °C' $LiCoO_2$ can be calculated using the data drawn from the voltammetric study by using the following relation between the anodic peak current and the scanning rate: $i_p = 0.4463$ F. A $(\Delta C)(F/RT)^{1/2} \nu^{1/2} D^{1/2}$ where F, A, ΔC and ν are, respectively, the Faraday constant, the geometric area (1 cm²), the variation of the lithium content (mol/cm³) and the scan rate (V/s). A molar volume $V_m = 19$ cm³/mol was used.

For scan rates in the range from 2 to 60 μV/s a linear relation i_p versus $\nu^{1/2}$ is found (Fig. 6) which proves that the oxidation reaction is controlled by the diffusion process of Li^+ ions. Thus, a mean value for the chemical diffusion coefficient of Li^+ ions, $D_{Li} \approx 10^{-12}$ cm²/s can be determined from the slope of the obtained line. A close value is calculated from chronopotentiometric measurements. This relatively low value contrasts with the constant faradaic yield found for any current densities used in the range from 50 to 500 μA/cm²; no literature data are available for the LT $LiCoO_2$, but much higher values are given for the HT compound [10,11]. The formation of an Li^+ ion-conducting layer on the surface of the electrode [12], i.e., a thick polymer film resulting from the reaction of electrolyte with the strong oxidizing agent Co^{4+}, could explain this apparent low value which would include the slow lithium diffusion through this additional solid phase. In addition, for a composite electrode, the effect of electrode porosity and particle size of material can influence the chemical diffusion measurements [13,14], especially when the kinetics of lithium transport in the host lattice is very high.

Cyclic galvanostatic charge/discharge experiments have been performed as a function of the depth of charge and cycle number. The cycling properties of 400 °C $LiCoO_2$ are illustrated in Fig. 7. Starting from a high value close to 95% for $x = 0.1$, its cycling efficiency is still high, near 90% for $x = 0.3$ but decreases thereafter with the cycle number. A sharp decrease appears when larger lithium contents are involved. For instance, for $x = 0.37$, the initial ratio near 75% immediately drops to 20% after four cycles. This poor cycle life probably stems from the significant polarization observed during

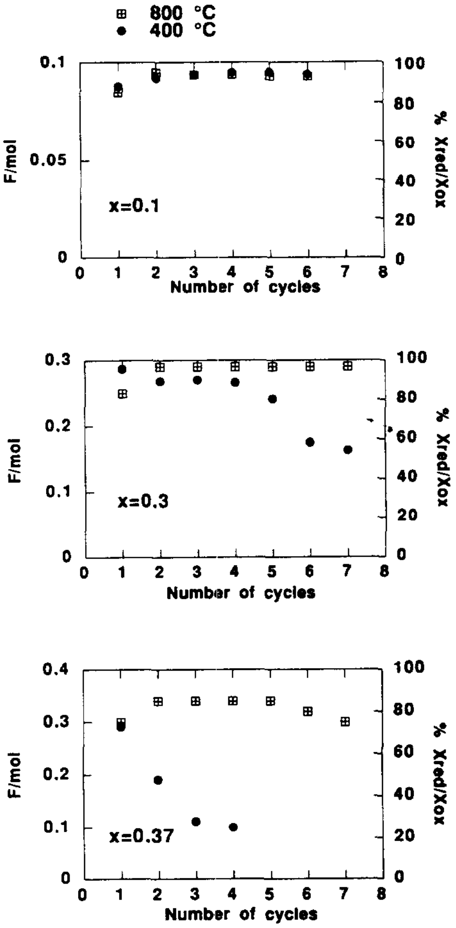

Fig. 7. Evolution of the faradaic yield of $LiCoO_2$ obtained at 400 and 800 °C, as a function of the number of cycles; effect of the depth of charge x.

the subsequent charges which indicates a notable unstability of the delithiated compound.

Moreover, when 0.5/0.6 Li^+ ions are extracted from the LT $LiCoO_2$ prepared via solid-state reactions, and described as a quasi-spinel structure, less than 20% of the initial faradaic yield is recovered after the third cycle [5,15].

With a lower working voltage allowing to avoid electrochemical decomposition of electrolyte (at least for $x < 0.5$), the present results give evidence for the intrinsic unstability of the delithiated structure of 400 °C LT $LiCoO_2$, especially when more than 0.3 Li^+ ions are extracted from the crystalline network.

However, due to the notable differences found in the electrochemical behaviour of LT and HT $LiCoO_2$ compounds, the question arises about how the ordering of Li^+ and Co^{2+} ions in particular sites of the host structure affects the electrochemical reactivity of $LiCoO_2$.

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