High performance LiCoO$_2$ positive electrode material

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Abstract

LiMO$_2$ (M = Co, Ni) and LiMn$_2$O$_4$ compounds synthesized at low temperature (LT) show very different electrochemical properties compared with their high-temperature (HT) analogues. These powders are in general characterized by a higher surface area and smaller grain size. When used as cathode materials in lithium secondary batteries, such LT compounds should show an enhanced electrochemical behaviour under heavy drain. We have developed a new synthesis method of LiMO$_2$ and LiMn$_2$O$_4$ characterized by monodispersive grain size powders, high surface area, good crystallinity, and a chemical composition close to the stoichiometry. We have carried out a comparison of the electrochemical properties of LiCoO$_2$ powders obtained by the classical method and this new synthesis route. In spite of a slightly lower discharge capacity, the new powder showed higher performances in terms of rate capacity.

Keywords: Electrodes; Lithium; Cobalt oxide

1. Introduction

The lithium-ion battery shows excellent characteristics in terms of energy density, cycle life and safety [1–4]. This newly commercialized system is expected to take an increasing share in the secondary batteries market designed for portable items applications such as camcorders, telephones and computers and, very likely, as a future power source for the electric-vehicle propulsion.

During the charge and discharge operations, the lithium ion is transferred from one electrode to the other through an intercalation/de-intercalation process. The carbon–lithium is used as the negative pole which reversibly stores lithium between the carbon layers. The positive electrode consists of either layered structure Li$_x$MO$_2$ (M = Co, Ni) or cubic spinel Li$_x$Mn$_2$O$_4$.

The coulombic capacity of a lithium-ion battery is limited mainly by two factors:

(i) the lowest amount of remaining lithium x in Li$_x$MO$_2$ or Li$_x$Mn$_2$O$_4$ at the end of charge which allows to preserve the dimensional stability of the positive and, therefore, its reversibility, and

(ii) the highest amount of lithium in the negative, y in Li$_y$C$_6$ that prevents the growth of dendritic lithium which is known to strongly affect the cycleability of this electrode.

The reversible variation of the electrodes composition Δx and Δy depends on the nature of the transition metal used in the positive electrode [2,5,6], on the type of carbonaceous materials [7,8] and also on the composition of the electrolyte [9].

The kinetics of the electrode reactions are basically dominated by the interfacial properties between the solid-state electrodes and the organic liquid electrolyte. When a high discharge current is applied, a series of electrode polarization and ohmic drop in the electrolyte appears resulting on an overall decrease in the cell potential. In a cell designed for high rate operation, these changes should be kept as low as possible in order to reach the highest corresponding energy output. This implies that the lithium concentration within the electrode should be kept as homogeneous as possible. As a matter of fact, a high lithium-diffusion coefficient is required but also a higher active electrode surface in order to reduce the local current density and therefore the electrode polarization.

The electrode activity is monitored by the ion and electron sites available in the electrode. It is believed that in the Li$_x$MO$_2$ and Li$_x$Mn$_2$O$_4$ phase, a good crystallinity and chemical composition are important parameters to achieve a higher electrode activity. The surface area is directly dependent on the synthesis

conditions, especially the lithium and metal precursors and the conditions of the heat treatment.

Several techniques have been proposed to synthesize high surface area and low grain-size powders especially at temperature lower than 600 °C [10–15]. However, the electrode activity of such powders was not sufficient to achieve a high capacity under heavy drain.

In this paper, we present a new synthesis method that leads to a rather good compromise between the electrode activity and its active surface area. A comparative study of the electrochemical behaviour of this new powder and the conventional one is presented using two techniques: slow scan cyclic voltammetry and rate-capacity determination.

Experimental

2.1. Synthesis techniques and characterization

A detailed description of the new synthesis techniques used to prepare high surface area $LiCoO_2$ powders can be found in Ref. [16]. One of these routes consists in adding to a suspension of cobalt acetate a determined amount of lithium acetate solution under strong stirring. The mixture is then heat-treated at 550 °C under air for at least 2 h.

The powder was characterized by chemical analysis, X-ray diffraction, scanning electron microscopy (SEM) and BET. The Li:Co ratio was 1.03. The X-ray diffraction pattern was characteristic of the $R\bar{3}m$ phase.

The SEM graph is given in Fig. 1(a). It shows a narrow grain-size distribution in the 1 μm range. Fig. 1(b) shows the micrograph obtained with a conventional $LiCoO_2$ powder (prepared at $T>800$ °C with $Li_2CO_3 + CoCO_3$ as precursors) [17]. The grain-size distribution is broader and is averaged at about 5 μm. The surface area measured on both $LiCoO_2$ gives 13.2 m^2/g for the low-temperature (LT) $LiCoO_2$ and 0.63 m^2/g for the high-temperature (HT) sample.

2.2. Composite electrode preparation and electrochemical cell

LT and HT $LiCoO_2$ powders were mixed with acetylene black (AB), a fine powder of natural graphite (NG) and poly(ethylene oxide) (PEO) used as binder. The specific composition of the mixture was $LiCoO_2$:AB:NG:PEO = 80:7:7:6 (wt.%). Acetonitrile (AN) was added to the mixture to form a suspension by mechanical stirring. AN was then evaporated at about 40 °C in air and the resulting powder was pressed under 2 t/cm² to form a pellet of 13 mm in diameter and 20 to 30 mg in weight. The pellets were then dried at 120 °C under primary vacuum for 15 h and transferred into an argon-filled dry box. The electrochemical test
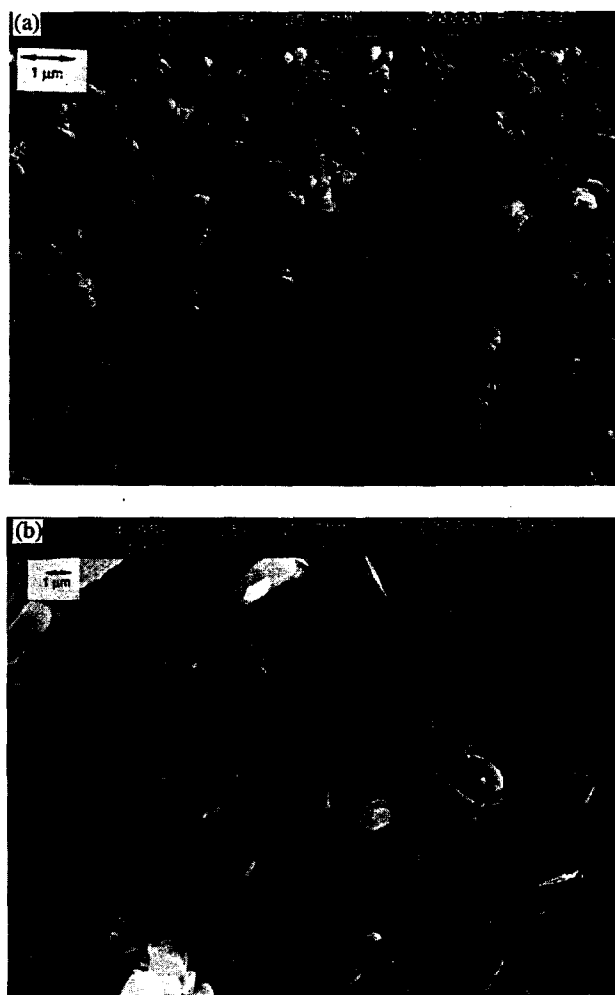

Fig. 1. Scanning electron micrographs of (a) low-temperature $LiCoO_2$ (10 000×), and (b) high-temperature $LiCoO_2$ (5000×).

cell consisted in a coin-type one (CR 2430). Lithium foil was used as the negative pole. The separator was made from a Celgard 2400 film and the electrolyte consisted in a 1 M solution of $LiClO_4$ in a propylene carbonate–ethylene carbonate–dimethoxyethane (1:1:2 vol.) solution.

Potential step voltammetry at a sweep rate of 20 mV/h was applied in the 2.7–4.2 V range and discharge rate capacity tests were carried out at $C/5$ to $2C$ rates down to potential of 2 V, on cells preliminary charged at $C/20$ rate up to 4.2 V.

3. Results and discussion

3.1. Step voltammetry

The voltammograms obtained from the LT and the HT compound are presented in Fig. 2(a) and (b), respectively. In the case of LT $LiCoO_2$, the main oxidation peak is observed at 3.94 V, while the main
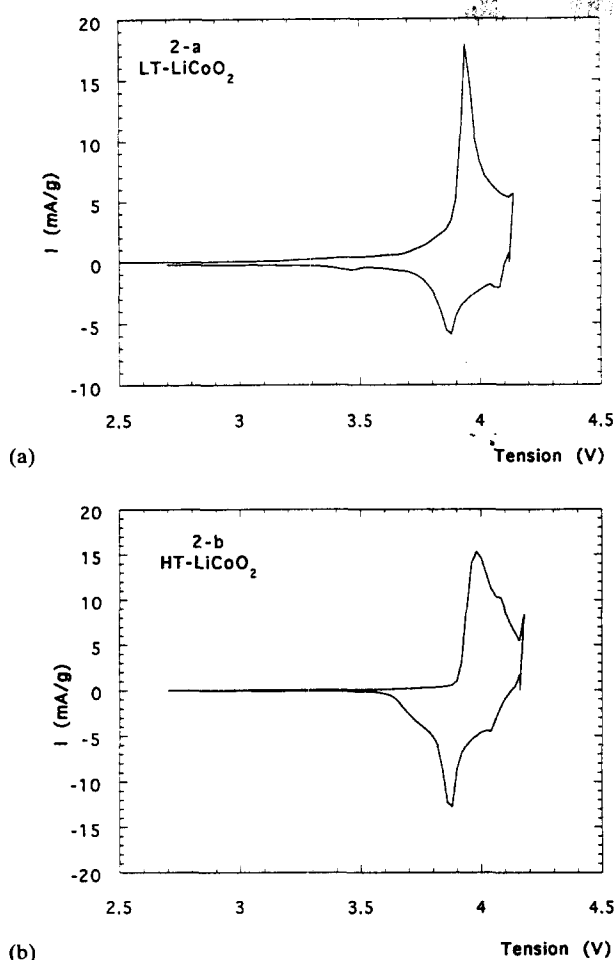
(a)

(b)

Fig. 2. Voltammogram of (a) low-temperature $LiCoO_2$ (20 mV/h), and (b) high-temperature $LiCoO_2$ (20 mV/h).

Table 1
Capacity and energy densities and average cell potential at different discharge rates

$LiCoO_2$	Q (mAh/g)	E (V)	W (Wh/kg)
Low-temperature			
C/5	104.8	3.83	401.6
C/2	104.4	3.75	364
C	92.9	3.58	303.3
2C	55	3.33	165.5
High-temperature			
C/5	120.7	3.87	458.3
C/2	104.1	3.77	383.8
C	75.3	3.56	262.6
2C	30.9	3.31	99.9

reduction peak appears at 3.88 V. For the HT compound, these peaks appeared at potentials close to 3.98 and 3.88 V, respectively. Other minor peaks can be observed at 4.1 V in oxidation and/or reduction. This observation was made possible owing to the use of very low voltage sweeping rate. These higher voltage peaks could not

be ascribed to a specific effect but they might be due to an anion adsorption on the surface impurities.

In Fig. 2(a) (LT $LiCoO_2$), a small reduction peak around 3.4 V is present. This peak has been previously observed as the main reduction peak in powders obtained at LT but using different precursors or drying and/or heat treatment as described in this work [10,18]. The 3.4 V peak was attributed to a cation disorder in the structure. Nevertheless, the results obtained with this new LT $LiCoO_2$ are in contrast with those previously reported concerning the relative intensities of the 3.4 and 3.88 V reduction peaks. This tends to prove, also considering the similarity in shape of the HT and the LT $LiCoO_2$ voltammograms, that this new LT $LiCoO_2$ has a higher cation order and therefore a better crystallinity.

3.2. Rate capacity

Fig. 3(a) to (d) shows a direct comparison, for a given discharge rate, between the two powders, in terms of cathode utilization. The percentage is calculated considering that the 100% utilization would correspond to the best performance obtained for an infinite discharge rate. This estimation allows to consider only the active part of the material that is actually involved in the intercalation/de-intercalation process. Table 1 gives the values of the capacity and energy densities and average cell potential during discharge at different rates.

It can be clearly observed that the higher the discharge, the greater is the difference in cathode utilization between the two materials, the LT compound showing the best performances. Since the rate is higher, the average potential of the LT product becomes slightly lower than that of the HT $LiCoO_2$ compound. Nevertheless, as shown in Fig. 3(c) and (d), even when this potential is lower, it is more stable than for the HT compound, and it leads to a higher cathode utilization.

The higher crystallinity of HT $LiCoO_2$ may account for the higher initial discharge potential. For deeper discharge rates, the lithium-ion concentration gradient increases due to a lower active surface area. This results in a quick electrode polarization and, consequently, the cell voltage falls below that of the LT $LiCoO_2$-based cell.

4. Conclusions

An LT $LiCoO_2$ has been synthesized using a new method. This new method permitted to obtain mono-dispersive, high-specific surface area and low grain-size powders. Some characteristics and electrochemical properties of this new powder have been compared with a classical HT product. It showed a good crystallinity
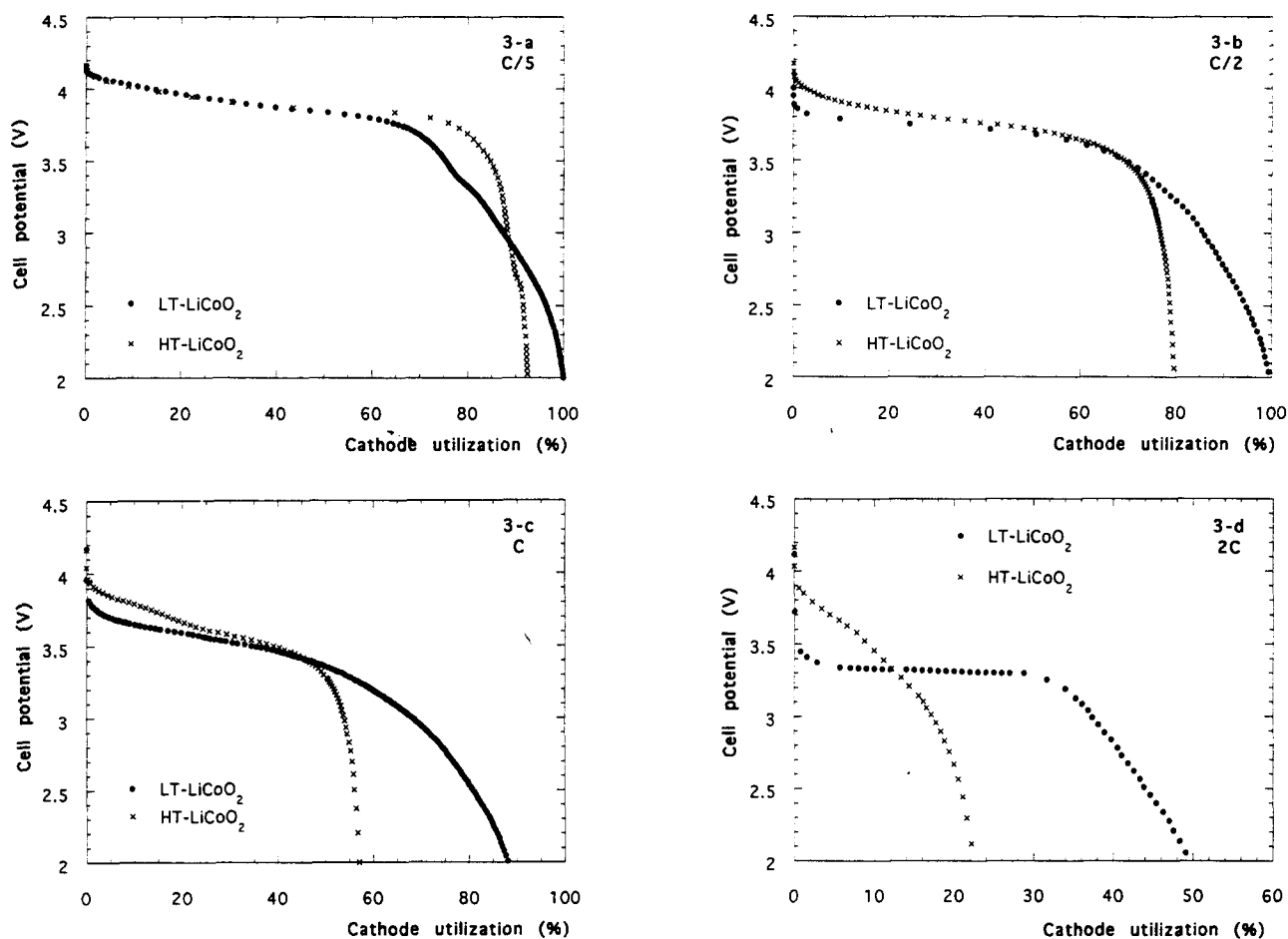
Fig. 3. Cathode utilization of (●) low-temperature LiCoO$_2$ and (×) high-temperature LiCoO$_2$ at different discharge rates: (a) C/5; (b) C/2, (c) C and (d) 2C.

and chemical composition close to the stoichiometric LiCoO$_2$. This powder also showed, in terms of rate capacity in discharge, greater performance than the HT product, especially under high-current drains.

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