Journal of the European Ceramic Society **18** (1998) 1405–1411

PII: S0955-2219(98)00019-3
0955-2219/98/$—see front matter

Preparation and Properties of Li-Co-O Compounds

Ermete Antolini

ENEA C.R.E. Casaccia, Erg Tea Echi, Via Anguillarese 301, 00060 Santa Maria di Galeria, Roma, Italy

(Received 14 November 1997; accepted 23 January 1998)

Abstract

Lithium cobalt oxide compounds are promising materials in various industrial applications, as water electrolysis cells, rechargeable lithium batteries, molten carbonate fuel cells and humidity ceramic sensors. This paper presents an overview of the preparation and properties of Li–Co–O compounds: lithiated Co_3O_4*,* $LiCoO_2$ *and* $LiCoO_2$*–CoO solid solutions. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Co_3O_4 is an electrode material which arouses great interest in the chlor-alkali industry because of its good electrocatalytic properties, ready availability and low cost.[1] Co_3O_4 is also an interesting catalyst material for that regarding CO oxidation in a gas phase.[2] Doping this compound with lithium its electrocatalytical activity considerably increases: as shown in Table 1, the oxygen evolution potential decreases with increasing Li-doping.[3] $LiCoO_2$ is an attractive electrode for rechargeable lithium cells because lithium can be extracted from, and reintroduced into, the structure with a concomitant change in the oxidation state of the cobalt ions.[4,5] $LiCoO_2$ is also a promising cathode material for molten carbonate fuel cells because of its low dissolution in the electrolyte.[6] Finally, the effect of water vapour and gas adsorption on the electrical properties of solid solutions $Li_xCo_{1-x}O$ have been studied with the aim of developing humidity ceramic sensors.[7]

In consideration of their promising application in different industrial fields, this paper presents an overview of the preparation, stability and properties of Li–Co–O compounds: lithiated Co_3O_4, $LiCoO_2$ and $LiCoO_2$–CoO solid solutions.

2 Lithiated Co_3O_4

Co_3O_4 has the structure of a normal spinel in which the Co^{2+} ions are in tetrahedral sites and the Co^{3+} ions occupy octahedral sites. Lithium ions may occupy sites or interstices in the spinel lattice of Co_3O_4. Substitution of lithium can occur either at the tetrahedral sites, replacing Co^{2+} ions or at the octahedral sites, replacing Co^{3+} ions. The mechanism of lithium doping and the structure obtained depend on temperature and precursors of the reaction. By solid state reaction of cobalt and lithium salts in an oxygen atmosphere, lithium cobalt spinel oxides of the type $Li_xCo_{3-x}O_4$ are obtained, where the lithium ions substitute for Co ions on octahedral sites (8a) (synthesis temperature 600°C)[8] or tetrahedral sites (16d) (synthesis temperature 800°C).[9] Charge compensation is achieved by Co^{4+} ions in octahedral spinel sites. When lithium ions occupy octahedral sites, the cubic unit cell parameter a_o varies almost linearly with x up to 0·4, as shown in Fig. 1.[8] Electrochemically or by a reaction with *n*-butyllithium,[10] lithium can be inserted in free octahedral (16c) interstices of the Co_3O_4 lattice to get $Li_yCo_3O_4$ intercalation compounds. Table 1 shows the dependence of resistivity and oxygen evolution potential on lithium content in Co_3O_4.[3]

Zhecheva *et al.* referred that by solid state reaction between cobalt and lithium salts in air at 500–750°C spinels of the types $Li_yLi_xCo_{3-x}O_4$ were obtained, where the indices x and y referring to Li^+ occupying, respectively, sites and interstices in the spinel lattice.[11–13]

At low concentrations (up to 2·6 Li^+ at%) the lithium ions are uniformly distributed in the bulk of the crystallites. With increasing total lithium amount, the Li concentration in the core of the crystallites does not change significantly and the lithium ions accumulate in the outer parts of the

Table 1. Resistivity and oxygen evolution potential of Li-doped Co_3O_4 (Rasiyah and Tseung[3]) * 5 mol dm^{-3}, 70°C, 1 A cm^{-2}

Li (a/o)	*Resistivity (Ω cm)*	*Oxygen evolution potential (V)**
0	104	1·69
4	10	1·56
7	1	1·535
10	1	1·52

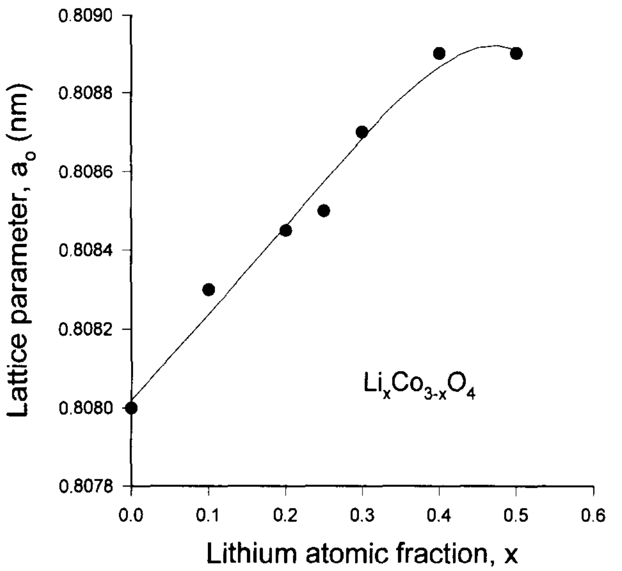

Fig. 1. Variation of unit cell parameter a_o with x of $(Co^{2+})[Co_{2-3x}{}^{3+}\ Co_{2x}{}^{4+}Li_x{}^{+}]O_4$ (Appaindairajan *et al.*[8]).

crystallites. The system can be considered as consisting of coherently intergrown crystal regions with different Li content having small thermodynamical and crystallochemical differences, i.e. lithiated Co_3O_4 spinel and quasi-spinel $LiCoO_2$ (see later) structures.

The features of $Li_yLi_xCo_{3-x}O_4$ are the following:

1. the concentration of lithium ions occupying regular spinel sites in the core of the crystallites decreases with rising preparation temperature;
2. the amount of lithium ions in spinel interstices increases with rising preparation temperature;
3. from 2·6 to 9·4 Li^+ at%, the crystallites consist of a Co_3O_4 core with relatively small lithium amount, and a lithium-rich external domain. The lithium content of these regions does not depend of total lithium content of the system;
4. the phase transition from a spinel to a rock salt structure (as $Co_3O_4 \rightarrow CoO$ transition) of $Li_yLi_xCo_{3-x}O_4$ takes place with the formation of two phases: $LiCoO_2$ and $Li_xCo_{1-x}O$.

Then, from experimental results it seems that, above the critical values of xo and yo in $Li_yLi_xCo_{3-x}O_4$, two-phase system formed by quasi spinel $LiCoO_2$ and spinel $Li_{yo}Li_{xo}Co_{3-xo}O_4$ is energetically improved with respect to entropically improved (more desordered system) single phase spinel $Li_yLi_xCo_{3-x}O_4$ ($y > yo, x > xo$), likely by the layered-spinel resonance of $LiCoO_2$.

The thermal decomposition of CoOOH in $LiNO_3$ melt at 300°C is a new route for the preparation of mixed lithium cobalt spinel oxide,[14] in which the lithium ions are distributed nearly statistically in the tetrahedral and octahedral sites of the spinel lattice. In Fig. 2 various methods to obtain lithium cobalt spinel oxide are reported.

Finally, recent works report the formation of lithiated Co_3O_4 at very low temperatures (< 300°C) by solid state reaction in air of Li_2CO_3 and Co_3O_4[15] or $CoCO_3$.[16]

3 Low Temperature $LiCoO_2$

Gummow *et al.*[17] prepared low temperature lithium cobalt oxide (LT–$LiCoO_2$) at 400°C by reaction of Li_2CO_3 and $CoCO_3$. The temperature was held at this value for approximately 1 week to form a single phase product. When lithium cobalt oxide is prepared at 400°C it has a cubic rock salt structure with overall composition $Li_{0.98}Co_{1.02}O_2$. The structure of LT–$LiCoO_2$ is not ideally layered, and 6% of the cobalt ions reside in the octahedral (3a) sites of the lithium layers. LT–$LiCoO_2$ has an essentially ideal cubic closed packed oxygen array ($c/a = 4{\cdot}90$). Because the cation distribution in this compound is intermediate between layered and spinel type structure and because of the strong resemblance of the X-ray and neutron diffraction patterns to that of a lithiated spinel structure

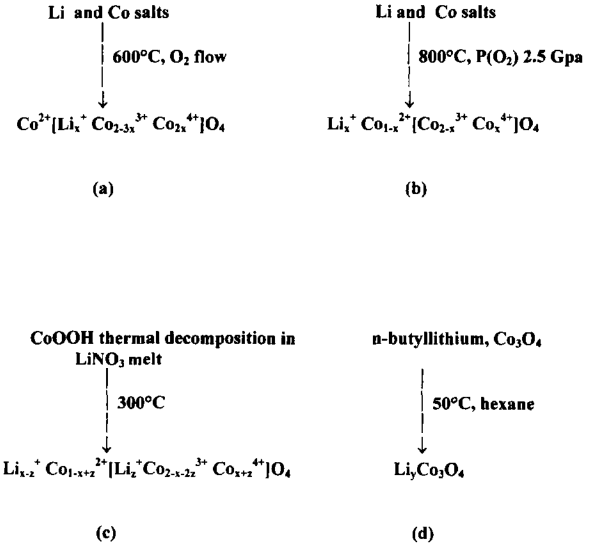

Fig. 2. Various preparation methods of lithiated cobalt spinel oxide, where lithium ions occupy (a) octahedral sites, (b) tetrahedral sites, (c) both octahedral and tetrahedral sites, (d) and interstices.

$Li_2[Co_2]O_4$, it is referred as a quasi-spinel phase.[18,19]

On the basis of the formation of mixed lithium cobalt spinel oxide previously analyzed, at 400°C the formation of quasi spinel $LiCoO_2$ takes place by a two step process. First, single phase $Li_yLi_xCo_{3-x}O_4$ is obtained as:

$$\begin{aligned} &3(x+y)/2(3-x)Li_2CO_3 + Co_3O_4 \\ &+ (5x-3y)/4(3-x)O_2 \rightarrow 3/(3-x) \qquad (1) \\ &Li_yLi_xCo_{3-x}O_4 + 3(x+y)/2(3-x)CO_2 \end{aligned}$$

For $x = xo$ and $y = yo$, quasi spinel $LiCoO_2$ formation occurs:

$$\begin{aligned} &(3-2xo-yo)/2Li_2CO_3 + Li_{yo}Li_{xo}Co_{3-xo}O_4 \\ &+ (1/2 - xo + 1/2yo)/2O_2 \rightarrow (3-xo)LiCoO_2 \\ &+ (3-2xo-yo)/2CO_2 \end{aligned} \qquad (2)$$

The system is formed by two phases: LT–$LiCoO_2$ and $Li_{yo}Li_{xo}Co_{3-xo}O_4$. The amount of LT–$LiCoO_2$ phase increases with increasing lithium content of the sample up to obtain single phase LT–$LiCoO_2$ for a Li:Co atomic ratio of 1.

Efforts to obtain ideal $Li[Co_2]O_4$ spinel structure from a starting mixture with Li/Co atomic ratio = 0·5 and ideal lithiated $Li_2[Co_2]O_4$ spinel structure (with lattice constant ratio $c/a = 4{\cdot}899$) at low temperature have till now been unsuccessful.[19] $Li_{0.5}CoO_2$, obtained by chemical delithiation of $LiCoO_2$ synthesized at 400°C, shows a spinel-type structure,[19] but, as lithium is removed from $LiCoO_2$, Co^{3+} is oxidized to Co^{4+}, which is known to be an unstable oxidation state.

4 High Temperature $LiCoO_2$

At 700–900°C layered rock salt structure lithium cobalt oxide (HT–$LiCoO_2$) with trigonal symmetry, R3m, as $CsCl_2I$, is obtained.[20] This structure is based on a closed-packed network of oxygen atoms with the Li^+ and Co^{3+} ions ordering on alternating (111) planes of the cubic rock salt structure. This (111) ordering introduces a slight distortion of the lattice to hexagonal symmetry. The c/a ratio of 4·989 is significantly larger than that of an ideal ccp lattice ($c/a = 4{\cdot}899$).

Solid-state synthesis of HT–$LiCoO_2$ may start from many different precursors in the Li/Co atomic ratio about 1: Li_2O_2 and CoO,[20] Li_2CO_3 and Co_3O_4,[21] Li_2CO_3 and Co,[22] $LiOH.H_2O$ and $CoCO_3$,[4] Li_2CO_3 and $CoCO_3$.[5] Independent of cobalt precursors, $LiCoO_2$ synthesis proceeds through the reaction between Li precursors and Co_3O_4.[22–24] A calcination temperature above 700°C has generally been used. Using acetates as starting materials also yield HT–$LiCoO_2$ below 500°C.[23] Well-crystallized, layered $LiCoO_2$ was prepared by heating cobalt-organic acid complexes (such as oxalic, succinic, malic and tartaric acid) at 900°C in air.[25] Synthesis of $LiCoO_2$ powders by ultrasonic spray decomposition of $LiNO_3$ and $Co(NO_3)_2$ was reported by Ogihara *et al.*[26] Ultrafine HT–$LiCoO_2$ was synthesized by the sol-gel method using polyacrilic acid as a chelating agent.[27] For Li/Co atomic ratio of the precursors < 1, formation of undoped Co_3O_4 and $LiCoO_2$ was detected.[28,29] Unlike low temperature reaction, Li_2CO_3 reacts with Co_3O_4 to get layered $LiCoO_2$, without formation of lithium doped Co_3O_4:

$$\begin{aligned} &3/2Li_2CO_3 + Co_3O_4 + 1/4\,O_2 \rightarrow 3LiCoO_2 \\ &+ 3/2CO_2 \end{aligned} \qquad (3)$$

A difference in the electrical conductivity, depending on Li/Co atomic ratio, was also denoted. Increasing conductivity was observed when decreasing the Li/Co atomic ratio from stoichiometric $LiCoO_2$.[28] This improvement has been suggested to stem from the occurrence of a secondary phase (Co_3O_4). Co_3O_4 in itself has higher conductivity than $LiCoO_2$.[28] An increasing of sample conductivity was also observed by increasing the Li/Co atomic ratio above 1,[24,30,31] as shown in Fig. 3.[31] Solid-state NMR measurements showed that only a small amount of Li (< 20% of the excess) enters the structure ionically while reducing the formal Co valence.[31] Most of the excess consists of unreacted Li_2CO_3.[24,31] Another small portion of the excess Li (about 10%) appears to enter interstitial sites in close proximity to paramagnetic Co^{2+} ions.

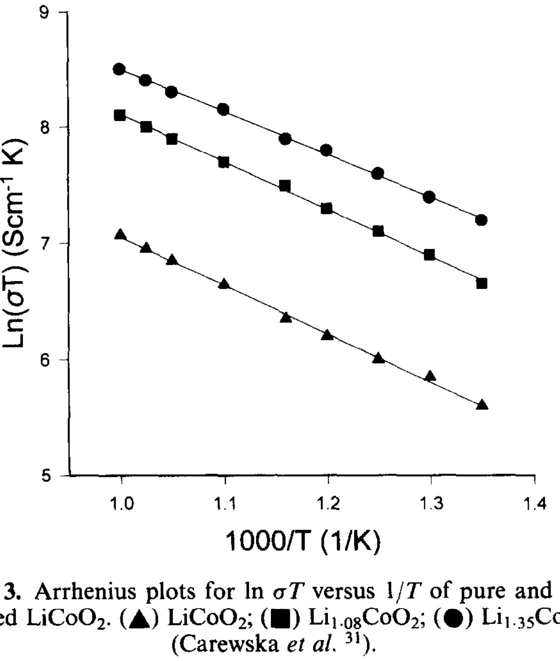

Fig. 3. Arrhenius plots for ln σT versus $1/T$ of pure and Li-doped $LiCoO_2$. (▲) $LiCoO_2$; (■) $Li_{1.08}CoO_2$; (●) $Li_{1.35}CoO_2$ (Carewska *et al.* [31]).

Recently, $LiCoO_2$ powders were prepared at temperatures as low as 100°C through the use of a two days ion exchange reaction between CoOOH and an excess of $LiOH.H_2O$.[32] Low temperature fabricated $LiCoO_2$ powders were well crystallized with lattice parameters agreeing with 850°C prepared samples.

Figure 4 shows different methods to obtain lithium cobalt oxide.

4.1 Comparison of the electrochemical properties of LT-LiCoO$_2$ and HT-LiCoO$_2$

The electrochemical properties of LT–$LiCoO_2$ differ considerably from HT–$LiCoO_2$. Electrochemical extraction of lithium from LT–$LiCoO_2$ takes place on a constant voltage plateau at 3·6 V (on open-circuit) against pure lithium.[17] This behaviour contrasts markedly with that of a Li/HT–$LiCoO_2$ cell in which the open-circuit voltage varies between 3·2 and 4·5 V over the compositional range $0{\cdot}1 < x < 1{\cdot}0$.[33] Figure 5 shows the electrochemical (OCV) curve of a Li/HT–Li_xCoO_2 cell and that of an Li/LT–Li_xCoO_2 cell. The Li/HT–Li_xCoO_2 cell shows a curve typical of a single-phase reaction for $x < 0{\cdot}2$ with the voltage increasing steadily to 4·5 V at $x = 0{\cdot}1$. Although delithiation of LT–Li_xCoO_2 beyond $x \approx 0{\cdot}3$ was not achieved by chemical means, Fig. 5 shows that it was possible to delithiate LT–Li_xCoO_2 to $x = 0{\cdot}1$, by slow electrochemical extraction in a non-aqueous environment. After an initial rapid increase in voltage to $x \approx 0{\cdot}95$, which was attributed to a single-phase reaction process and the generation of a defect rocksalt phase $Li_{0{\cdot}95}CoO_2$, the Li/LT–Li_xCoO_2 cell shows a two-phase, constant-voltage plateau at 3·6 V from $x = 0{\cdot}95$ to $x = 0{\cdot}1$. The two-phase behaviour of the LT–$LiCoO_2$ electrode is consistent with a phase transition between a rock salt structure in which the cations occupy only octahedral sites and a spinel-type structure in which the cations occupy both octahedral and tetrahedral sites. Unfortunately, Li/LT–$LiCoO_2$ cells lose capacity on cycling; this poor performance is attributed to the structural instability of the quasi-spinel LT–$LiCoO_2$ structure on repeated extraction and re-insertion of lithium.

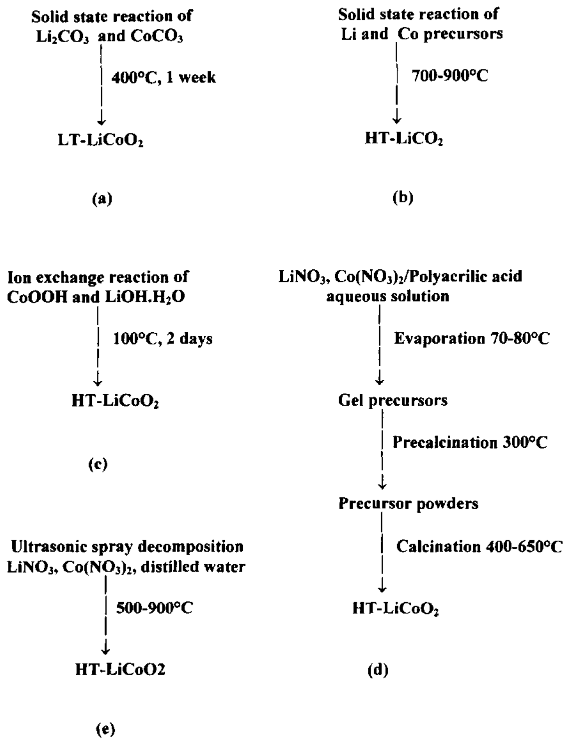

Fig. 4. Various preparation methods of $LiCoO_2$. (a) LT–$LiCoO_2$; (b) HT–$LiCoO_2$ obtained by solid state reaction; (c) ion exchange reaction; (d) sol–gel method; and (e) ultrasonic spray decomposition.

Moreover, during lithium extraction from HT–$LiCoO_2$ the c/a ratio change from 4·99 at $x = 1$ to 5·12 at $x = 0{\cdot}5$.[34] The expansion of the c-axis was attributed to a decrease in the electrostatic binding energy of the lithium-depleted layers. Unlike HT–$LiCoO_2$, LT–$LiCoO_2$ has an essentially ideal cubic-close-packed oxygen array ($c/a = 4{\cdot}90$) which surprisingly is maintained during lithium extraction,[17] as inferred from the values of the lattice parameters reported in Table 2.

4.2 LiCoO$_2$–CoO solid solutions

For temperatures higher than 900°C, $LiCoO_2$ begins to decompose by lithium oxide and oxygen loss, as the following reaction:[21]

$$LiCoO_2 \rightarrow 1/(2-y)Li_yCo_{2-y}O_2 + (1-y)/(2-y)\ Li_2O + (1-y)/2(2-y)O_2 \qquad (4)$$

where $Li_yCo_{2-y}O_2$ ($y < 1$, layered rock salt structure, as $CsCl_2I$) is the solid solution of CoO in $LiCoO_2$. $LiyCo_{2-y}O_2$ is also directly formed by solid solution of CoO in $LiCoO_2$, as:

$$yLiCoO_2 + 2(1-y)CoO \rightarrow Li_yCo_{2-y}O_2 \qquad (5)$$

In the $Li_yCo_{2-y}O_2$ structure Co^{2+} ions are present both in Li^+ layer and in Co^{3+} layer. Crystallographic data of this compound are not reported in literature. Then, at temperatures ≥1000°C, solid solution of $Li_yCo_{2-y}O_2$ in CoO takes place, as:

$$Li_yCo_{2-y}O_2 + (y-2x)/xCoO \rightarrow y/xLi_xCo_{1-x}O \qquad (6)$$

where $Li_xCo_{1-x}O$ (rock salt structure, as NaCl) is the solid solution of $Li_yCo_{2-y}O_2$ in CoO. Li^+ and Co^{3+} ions partially substitute the normal sites of Co^{2+}, to keep charge neutrality conditions. As a consequence, while stoichiometric CoO is an insulator, $Li_xCo_{1-x}O$ solid solutions become p-type

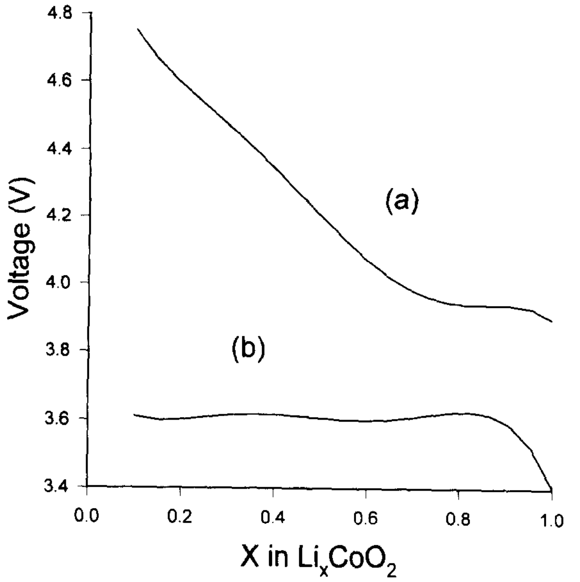

Fig. 5. Electrochemical (open-circuit-voltage) curve of: (a) Li/HT-Li_xCoO_2; (b) Li/LT-Li_xCoO_2 (Gummow *et al.* [17]).

Table 2. Lattice parameters of HT-$LiCoO_2$, LT-$LiCoO_2$ and delithiated products (Gummow *et al.*[17])

Sample	*a (Å)*	*c (Å)*	*c/a*
HT-$LiCoO_2$	2·8179(1)	14·0597(8)	4·99
HT-$Li_{0.86}CoO_2$	2·8159(3)	14·124(2)	5·02
LT-$LiCoO_2$	2·8297(6)	13·868(4)	4·90
LT-$Li_{0.71}CoO_2$	2·8304(4)	13·866(2)	4·90
LT-$Li_{0.40}CoO_2$	2·8273(2)	13·851(1)	4·90

semiconductors. Figure 6 shows two preparation routes of $Li_xCo_{1-x}O$. The cubic lattice constant of $Li_xCo_{1-x}O$ linearly decreases with lithium content in the solid solution, as shown in Fig. 7.[7] The values of x goes up to 0·2.[20] Figure 8 shows the dependence of the electrical resistivity of $Li_xCo_{1-x}O$ solid solutions with different x on relative humidity at 25°C.[7] The electrical resistivity increased with increasing relative humidity. As the samples were p-type semiconductors, the increase in the electrical resistivity may be caused by the electron transfer from the H_2O molecule adsorbed on the surface of the sample to the conduction band. The solubility of the $LiCoO_2$ in CoO decreases with temperature,[28] so $Li_xCo_{1-x}O$ for thermal treatment at 800–850°C or during slow cooling demixed with $CoO \rightarrow Co_3O_4$ transition, as:

$$Li_xCo_{1-x}O + (1-2x)/6O_2 \rightarrow xLiCoO_2 + (1-2x)/3Co_3O_4 \qquad (7)$$

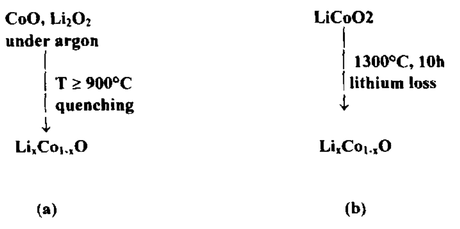

Fig. 6. Two preparation routes of $Li_xCo_{1-x}O$.

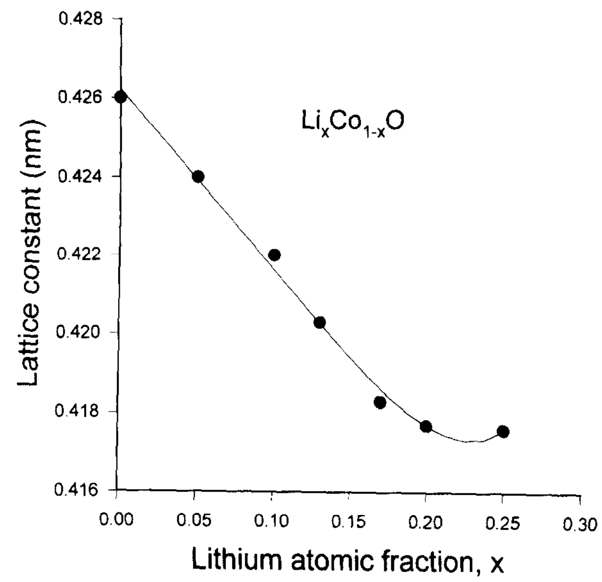

Fig. 7. Dependence of the lattice constant on $_x$ of $Li_xCo_{1-x}O$. (Sato *et al.*[7]).

For this reason, it is possible to obtain single phase $Li_xCo_{1-x}O$ at room temperature only on quenching the compound from the firing temperature. Thermal treatments at temperatures higher than 1100°C partially stabilize $Li_xCo_{1-x}O$ against demixing during cooling.[29] The stability of the solid solution increases with firing temperature because the sintering of the material is a hindrance to oxygen uptake from the atmosphere, required for the reaction (7). Following thermal treatment at 1000°C, for Li content up to 20 at% single phase $Li_xCo_{1-x}O$ is obtained.[20] At 1300°C, in the presence of CoO a strong preferred orientation of $Li_xCo_{1-x}O$ crystallographic structure was revealed.[35] For lithium atomic fraction higher than 20 at% Li^+, two solid solutions, $Li_yCo_{2-y}O_2$ and $Li_xCo_{1-x}O$, are formed. For 47 at% Li^+, $Li_yCo_{2-y}O_2$ single phase is obtained.[28] $Li_yCo_{2-y}O_2$ is not stable at temperature lower than 900°C, and a progressive change to stoichiometric $LiCoO_2$ and Co_3O_4 occurs:

$$Li_yCo_{2-y}O_2 + (1-y)/3O_2 \rightarrow yLiCoO_2 + 2(1-y)/3Co_3O_4 \qquad (8)$$

As Moore and White,[28] the conductivity of $Li_xCo_{1-x}O$ is higher then $Li_yCo_{2-y}O_2$.

4.3 Particle size and sintering of Li–Co–O compounds

Sintering of lithiated Co_3O_4 samples is difficult, as at high temperatures these compounds decompose in an irreversible way. Literature data on lithiated Co_3O_4 are not available.

For that regarding $LiCoO_2$ powders, in order to achieve a larger current capacity and reliability of the battery, it is necessary to obtain submicron particles of uniform morphology with narrow size distribution and homogeneity. This is because the

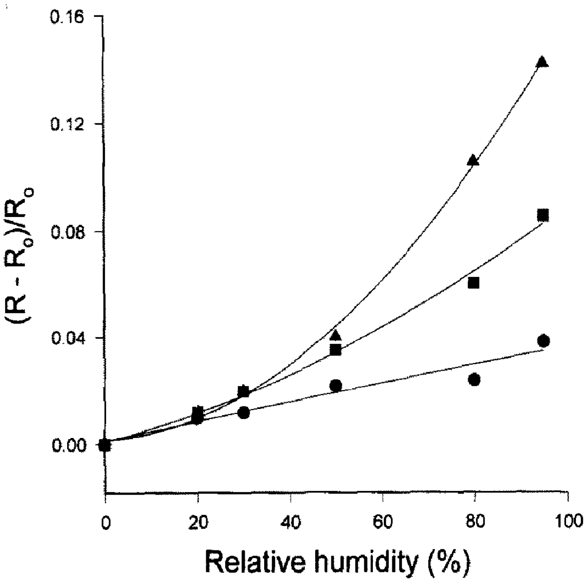

Fig. 8. Dependence of the electrical resistivity of different Li_x-$Co_{-x}O$ solid solutions on relative humidity at 25°C. (•) $x = 0{\cdot}170$; (■) $x = 0{\cdot}130$; (▲) $x = 0{\cdot}052$ (Sato *et al.*[7]).

performance of the battery depends on packing density, specific surface area, and homogeneity of $LiCoO_2$ powders. Generally $LiCoO_2$ powders prepared by solid state reaction show inhomogeneity, irregular morphology, large particle size and broad particle-size distribution. Lundblad and Bergman[24] found that CO_2 and O_2 partial pressure of the calcination atmosphere have a significant effect on primary particle size of $LiCoO_2$ obtained by solid-state reaction. The smallest particles are obtained if the CO_2 pressure is kept low and the O_2 pressure is kept high.[24] After thermal treatment at 700°C for 5 h, Lundblad and Bergman[24] obtained $LiCoO_2$ primary particles with a size of 100–300 nm. A drastic increase of particle size results from a heat treatment at 800°C for 3 h. In this case, the primary particles, with a size of 500–3000 nm, are more flaky with a diameter to thickness ratio of about 5:1. Ogihara *et al.* synthesised $LiCoO_2$ using ultrasonic spray decomposition. This technique allows to obtain very small particles with uniform size distribution. As-prepared particles were spherical and submicrometer. Average particle size and its geometrical standard deviation were 560 nm and 1·33, respectively.[26] $LiCoO_2$ particle size, obtained by ultrasonic spray decomposition, decreased with increasing the decomposition temperature; the particle morphology was not affected by the temperature decomposition. Sun *et al.* prepared by the sol–gel method at the low calcination temperature of 550°C $LiCoO_2$ powders, composed of very uniformly sized ultrafine particulates with an average particle size of 30–50 nm and a specific surface area of 2·3–17 $m^2 g^{-1}$.[27] At temperatures ≥800°C the presence of a liquid phase of unreacted Li_2CO_3 supports the sintering process of $LiCoO_2$.[24] Marini *et al.* found that the sintering process of $LiCoO_2$/CoO mixtures takes place at lower temperature, with respect to single phase CoO.[29] Figure 9 shows the difference of the plaque diameter change of pure CoO sample $(l/lo)_{Co\text{–}O}$ and $LiCoO_2$/CoO sample $(l/lo)_{Li\text{–}Co\text{–}O}$ following thermal treatment at various temperatures of Co/Li_2CO_3 mixtures. Plaque diameter change is achieved by combining the expansion due to cobalt oxidation and the shrinkage due to the sintering of cobalt oxide powder. As shown in Fig. 9, going from 900 to 1000°C the difference of plaque diameter change of pure and lithiated samples remarkably increased. The intense shrinkage of lithiated sample is due to the movement of lithium ions along grain boundary of the material, which promotes the sintering process.[36]

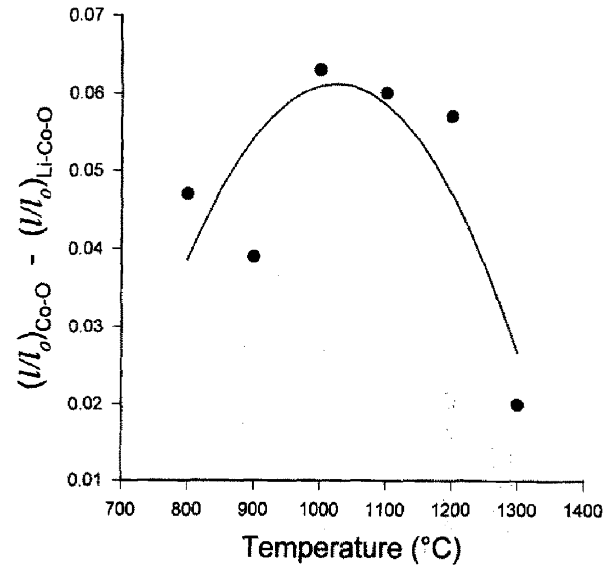

Fig. 9. Difference of plaque diameter change of Co–O and Li–Co–O samples as a function of temperature (Marini *et al.*[29]).

For that regarding $LiCoO_2$–CoO solid solutions, Sato *et al.* found that $Li_xCo_{1-x}O$ porosity following sintering at 1050°C is independent of lithium atomic fraction.[7]

5 Conclusions

Thermal treatment of Li and Co precursors in the presence of oxygen gives rise to different Li–Co–O compounds, depending on temperature and time of the thermal treatment, Li/Co ratio, oxygen pressure and preparation route. Generally, by increasing temperature it goes from lithiated Co_3O_4 to quasi spinel $LiCoO_2$, to layered $LiCoO_2$, and finally to solid solution of CoO in $LiCoO_2$ (layered ordered $Li_yCo_{2-y}O_2$), and/or to solid solution of $LiCoO_2$ in CoO (rock salt desordered $Li_xCo_{1-x}O$), the ratio of these compounds depending on lithium atomic fraction. The electrical conductivity increases going from stoichiometric to lithiated Co_3O_4 and CoO, going from stoichiometric $LiCoO_2$ to lithiated $LiCoO_2$, and going from $Li_yCo_{2-y}O_2$ to $Li_xCo_{1-x}O$.

The electrochemical properties of LT–$LiCoO_2$ differ considerably from HT–$LiCoO_2$. Whereas electrochemical extraction from HT–$LiCoO_2$ in room temperature lithium cells takes place as a single-phase reaction above 3·9 V for $x \leq 0{\cdot}9$, electrochemical extraction from LT–$LiCoO_2$ occurs as a two-phase reaction at an open-circuit voltage of 3·6 V for $0{\cdot}1 < x < 0{\cdot}95$.

References

1. Boggio, R., Carugati, A., Lodi, G. and Trasatti, S., Mechanistic study of Cl_2 evolution at Ti-supported Co_3O_4 anodes. *J. Appl. Electrochem*, 1985, **15**, 335–349.
2. Poillerat, G., Electrocatalyse sur oxydes metalliques. *J. de Phys. IV, Coll. C1*, 1994, **4**, 107–115.
3. Rasiyah, P. and Tseung, A. C. C., A mechanistic study of oxygen evolution on Li-doped Co_3O_4. *J. Electrochem. Soc.*, 1983, **130**, 365–368.
4. Reimers, J. N. and Dahn, J. R., Electrochemical and in-situ X-ray diffraction studies of lithium intercalation in Li_xCoO_2. *J. Electrochem. Soc.*, 1992, **139**, 2091–2097.
5. Ohzuku, T. and Ueda, A., Solid-state redox reactions of $LiCoO_2$ for 4 Volt secondary lithium cells. *J. Electrochem. Soc.*, 1994, **141**, 2972–2977.
6. Veldhuis, J. B. J., Eckes, F. C. and Plomb, L., The dissolution properties of $LiCoO_2$ in molten 62:38 mol% Li:K carbonate. *J. Electrochem. Soc.*, 1992, **139**, L6.
7. Sato, T., Hsien-Chang, C., Endo, T. and Shimada, M., Preparation and electrical properties of $Li_xM_{1-x}O$ (M = Ni, Co). *J. Mater. Sci. Lett.*, 1986, **5**, 552–554.
8. Appandairajan, N. K., Viswanathan, B. and Gopalkrishnan, J., Lithium-substituted cobalt oxide spinels $Li_xM_{1-x}Co_2O_4$ ($M = Co^{2+}$, Zn^{2+}; $0 \leq x \leq 0{\cdot}4$). *J. Solid State Chem.*, 1981, **40**, 117–121.
9. Shimada, M., Ohashi, M. and Koizumi, M., Preparation of lithium-doped Co_3O_4. *Adv. Ceramics*, 1986, **15**, 135–142.
10. Thackeray, M. M., Baker, S. D., Adendorff, K. T. and Goodenough, J. B., Lithium insertion into Co_3O_4: a preliminary investigation. *Solid State Ionics*, 1985, **17**, 175–182.
11. Zhecheva, E., Stoyanova, R. and Angelov, S., Doping of Co_3O_4 with lithium by a solid-state reaction in air. I. Oxidation degree, coordination of cations. *Mater. Chem. Phys.*, 1990, **25**, 351–360.
12. Zhecheva, E., Stoyanova, R. and Angelov, S., Doping of Co_3O_4 with lithium by a solid-state reaction in air. II. Distribution of lithium in the solid solution. *Mater. Chem. Phys.*, 1990, **25**, 361–373.
13. Stoyanova, R., Zhecheva, E. and Angelov, S., Doping of Co_3O_4 with lithium by a solid-state reaction in air. III. EPR evidence of intrinsic disorder reactions in the tetrahedral interstitials. *Mater. Chem. Phys.*, 1990, **26**, 239–244.
14. Zhecheva, E. and Stoyanova, R., Low-temperature preparation of a lithium–cobalt spinel ($Li_{0{\cdot}35}Co_{2{\cdot}65}O_4$) by thermal decomposition of CoOOH in a $LiNO_3$ melt. *Mater. Res. Bull.*, 1991, **26**, 1315–1322.
15. Antolini, E., Formation of lithium–cobalt spinel oxide ($Li_xCo_{3-x}O_4$) by solid-state reaction of a Li_2CO_3–Co_3O_4 powder mixture. *Mater. Res. Bull.*, 1997, **32**, 9–14.
16. Lundblad, A. and Bergman, B., Synthesis of LiCoO2 starting from carbonate precursors I. The reaction mechanism. *Solid State Ionics*, 1997, **96**, 173–181.
17. Gummow, R. J., Thackeray, M. M., David, W. I. F. and Hull, S., Structure and electrochemistry of lithium cobalt oxide synthesized at 400°C. *Mater. Res. Bull.*, 1992, **27**, 327–337.
18. Gummow, R. J., Liles, D. C., Thackeray, M. M. and David, W. I. F., A reinvestigation of the structures of lithium cobalt oxides with neutron-diffraction data. *Mater. Res. Bull.*, 1993, **28**, 1177–1184.
19. Gummow, R. J., Liles, D. C. and Thackeray, M. M., Spinel versus layered structures for lithium cobalt oxide synthesised at 400°C. *Mater. Res. Bull.*, 1993, **28**, 235–246.
20. Johnson, W. D., Heikes, R. R. and Sestrich, D., Formation of lithium cobalt oxide. *J. Phys. Chem. Solids*, 1958, **7**, 1–12.
21. Fernandez-Rodriguez, J. M., Hernan, L., Morales, J. and Tirado, J. L., Low-temperature hydrothermal transformation of $LiCoO_2$ and $HCoO_2$. *Mater. Res. Bull.*, 1988, **23**, 899–904.
22. Antolini, E. and Ferretti, M., Synthesis and thermal stability of $LiCoO_2$. *J. Solid State Chem.*, 1995, **117**, 1–7.
23. Carewska, M., Di Bartolomeo, A. and Scaccia, S., Themoanalytical study of synthesis of mixed lithium cobalt oxides. *Thermochimica Acta*, 1995, **269/270**, 491–506.
24. Lundblad, A. and Bergman, B., Synthesis of $LiCoO_2$ starting from carbonate precursors II. Influence of calcination conditions and leaching. *Solid State Ionics*, 1997, **96**, 183–193.
25. Yoshio, M., Tanaka, H., Tominaga, K. and Noguchi, H., Synthesis of $LiCoO_2$ from cobalt-organic acid complexes and its electrode behaviour in a lithium secondary battery. *J. Power Source*, 1992, **40**, 347–353.
26. Ogihara, T., Yanagawa, T., Ogata, N., Yoshida, K., Mizuno, Y., Yonezawa, S., Takashima, M., Nagata, N. and Ogawa, K., Preparation of $LiCoO_2$ fine powders by ultrasonic spray decomposition and its application to lithium secondary battery. *Denki Kagaku*, 1993, **61**, 1339–1341.
27. Sun, Y. -K., Oh, I. -H. and Hong, S. A., Synthesis of ultrafine $LiCoO_2$ powders by the sol–gel method. *J. Mater. Sci.*, 1996, **31**, 3617–3621.
28. Moore, R. J. and White, J., Equilibrium relationship in the systems Li–Co–O and Li–Ni–O. *J. Mater. Sci.*, 1974, **9**, 1401–1408.
29. Marini, A., Berbenni, V., Massarotti, V., Capsoni, D. and Antolini, E., Phase composition, microstructure and sintering in the system Co-Li_2CO_3. *J. Solid State Chem.*, 1995, **116**, 23–32.
30. Giorgi, L., Carewska, M., Patriarca, M., Scaccia, S., Simonetti, E. and Di Bartolomeo, A., Development and characterisation of novel cathode materials for molten carbonate fuel cell. *J. Power Source*, 1994, **49**, 227–243.
31. Carewska, M., Scaccia, S., Croce, F., Arumugam, S., Wang, Y. and Greenbaum, S., Electrical conductivity and ^{67}Li NMR studies of $Li_{1+y}CoO_2$. *Solid State Ionics*, 1997, **93**, 227–237.
32. Amatucci, G. G., Tarascon, J. M., Larcher, D. and Klein, L. C., Synthesis of electrochemically active $LiCoO_2$ and $LiNiO_2$ at 100°C. *Solid State Ionics*, 1996, **84**, 169–180.
33. Plichta, E., Slane, S., Uchiyama, M., Salomon, M., Chua, D., Ebner, W. B. and Lin, H. W., An improved Li/Li_x-CoO_2 rechargeable cell. *J. Electrochem. Soc.*, 1989, **136**, 1865–1873.
34. Honders, A., der Kinderen, J. M., van Heeren, A. H., de Wit, J. H. W. and Broers, G. H. J., Bounded diffusion in solid solution electrode powder compacts. II. The simultaneous measurement of the chemical diffusion coefficient and the thermodynamic factor in Li_xTiS_2 and Li_xCoO_2. *Solid State Ionics*, 1985, **15**, 265–275.
35. Ferretti, M. and Antolini, E., Effect of CoO presence on the structure of $Li_xCo_{1-x}O$ obtained by $LiCoO_2$ decomposition. *Mater. Lett.*, 1997, **31**, 335–337.
36. Antolini, E. and Ferretti, M., Thermal treatment of Co/Li_2CO_3 mixtures at 1200°C. *Mater. Lett.*, 1995, **24**, 89–95.