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Li_2O evaporation from $Li_xCo_{1-x}O$ solid solutions at 1200°C

Ermete Antolini*

Scuola di Scienza dei Materiali, Via 25 Aprile 22, 16016 Cogoleto, Genova, Italy

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Abstract

Lithium loss from $Li_xCo_{1-x}O$ solid solutions at 1200°C was investigated by diffractometric (XRD) and gravimetric measurements. The results of XRD analysis indicated that the time dependence of Li_2O evaporation from the solid solutions was 0.2 for a nominal Li 10% sample, while for a nominal Li 20% sample, the time dependence changed from 1 to 0.2 following 5 h of isothermal treatment. This dimensionless parameter is related to the evaporation mechanism. The behaviour of the nominal Li 20% sample was related to the presence of layered $Li_yCo_{2-y}O_2$ solid solution in the external part of the particles. Lithium content of the solid solution attained a constant value of 0.06, independent of nominal lithium content of the sample. Then, the solid solution with x about 0.06 seems to be stable against lithium loss. Experimental weight loss, due to both lithium loss and $Li_xCo_{1-x}O$ stabilization against phase transition, was compared with calculated weight loss using the parameters obtained from XRD analysis. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Li_2O evaporation; $Li_xCo_{1-x}O$ solid solution

1. Introduction

Cubic rock salt (NaCl-type) oxides of the general formula $Li_xCo^{2+}_{1-2x}Co^{3+}_xO$, or $Li_xCo_{1-x}O$, correspond to a solid solution of $LiCoO_2$ in CoO [1]. Li^+ and Co^{3+} ions partially substitute the normal sites of Co^{2+}, to keep charge neutrality conditions. The cubic lattice constant of $Li_xCo_{1-x}O$, with x in the range 0-0.2, linearly decreases with lithium content in the solid solution [2]. By increasing the $LiCoO_2$ to CoO molecular ratio, the formation of a solid solution of CoO in $LiCoO_2$, with layered rock salt structure ($CsCl_2I$ type), can also occur. The solubility of $LiCoO_2$ in CoO decreases with decreasing temperature [3], so solid solution demixing takes place during slow cooling with CoO → Co_3O_4 transition, according to:

$$\begin{aligned} &Li_yCo_{1-y}O + [(1-2y-\xi(1-2z)]/6O_2 \\ &\quad \rightarrow \xi Li_zCo_{1-z}O + (y-z\xi)LiCoO_2 \\ &\quad + [(1-2y-\xi(1-2z)]/3Co_3O_4 \end{aligned} \tag{1}$$

with $z<y$ and $\xi<1$. For this reason it is possible to obtain a single phase solid solution at room temperature only on quenching the sample from the firing temperature. Layered $Li_yCo_{2-y}O_2$ demixing also takes place during cooling in the same way as in cubic solid solutions. Thermal treatments at temperatures higher than 1000°C partially stabilize the solid solution against demixing during cooling [4]. The stability of the solid solution increases with firing temperature because the sintering of the material, occurring during annealing, is a hindrance to oxygen uptake from the atmosphere, required for the reaction (1). Solid solutions of $LiCoO_2$ in CoO have been studied for developing humidity ceramic sensors [2], and as a cathode material for molten carbonate fuel cells [5]. Many studies were performed on Li_2O evaporation from solid solutions of lithium oxide in nickel oxide $Li_xNi_{1-x}O$ [6–10]. For $Li_xNi_{1-x}O$, i.e. in the absence of a phase transition, Li-doped NiO being stable during cooling, lithium loss from solid solutions with $x \leqslant 0.2$ can be determined by XRD measurements (there is a linear relation of the lattice constant and lithium content of the solid solution) or by weight loss of the samples following annealing, using simple relations [11,12]. In the case of $Li_xCo_{1-x}O$, instead, the determination of lithium loss from the lattice constants obtained by XRD analysis,

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* Tel.: +39-10-918-2880; fax: +39-10-918-2368.
E-mail address: ermantol@libero.it

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performed following thermal treatment, is not possible owing to a phase transition. Weight loss following annealing must take into account this phase transition. Perhaps, for this reason no studies on Li_2O evaporation from $Li_xCo_{1-x}O$ are present in literature. In this work we have investigated lithium loss from $Li_xCo_{1-x}O$ solid solutions at 1200°C. The solid solutions were slowly cooled (2°C/min) to avoid sample failure.

2. Experimental

Cobalt powder (Matthey reagent 99.8%) and lithium carbonate (Merck 547), in the nominal lithium atomic fractions 0.10 and 0.20, were used as starting materials. Mixtures of these powders were suspended in water with a binder, cast, dried and heated at 2°C/min to 1200°C. The samples were held at 1200°C for various times in the range 0–40 h, then cooled at 2°C/min to room temperature. Thermal treatment was performed in air using a Bicasa BE 35 furnace.

XRD measurements were carried out by a Philips PW 1729 powder diffractometer equipped with a Philips PW 1771 vertical goniometer using filtered Co K_α radiation.

3. Results and discusson

Starting from a Co and Li_2CO_3 powder mixture, during dynamic thermal treatment in air up to 1200°C, the following reactions occur:

$$3Co + 2O_2 \rightarrow Co_3O_4 \quad \text{(Co oxidation)} \tag{2}$$

$$Co_3O_4 + 3/2Li_2CO_3 + 1/2O_2 \rightarrow 3LiCoO_2 + 3/2CO_2 \quad \text{(}LiCoO_2\text{ formation)} \tag{3}$$

$$Co_3O_4 \rightarrow 3CoO + 1/2O_2 \quad \text{(spinel-to-rocksalt phase transition, T 918°C)} \tag{4}$$

$$LiCoO_2 + (1-2x)/xCoO \rightarrow 1/xLi_xCo_{1-x}O \quad \text{(cubic }Li_xCo_{1-x}O\text{ formation)} \tag{5}$$

$$CoO + 1/2(1-y)LiCoO_2 \rightarrow 1/2\ 1(1-y)Li_yCo_{2-y}O_2 \quad \left(\text{layered }Li_yCo_{2-y}O_2\text{ formation}\right) \tag{6}$$

$$Li_yCo_{2-y}O_2 \rightarrow (2-y)/(2-z)Li_zCo_{2-z}O_2 + (y-z)/(2-z)Li_2O + {}^1/_2(y-z)/(2-z)O_2 \quad \left(Li_2O\text{ loss from }Li_yCo_{2-y}O_2\right) \tag{7}$$

$$Li_xCo_{1-x}O \rightarrow (1-x)/(1-y)Li_yCo_{1-y}O + (x-y)/2(1-y)Li_2O + (x-y)/4(1-y)O_2 \quad \text{(}Li_2O\text{ loss from }Li_xCo_{1-x}O\text{)} \tag{8}$$

The formulae $Li_xCo_{1-x}O$ and $Li_yCo_{2-y}O_2$ are equivalent, with $y = 2x$. We write the formulae $Li_xCo_{1-x}O$, to designate the cubic phase and as $Li_yCo_{2-y}O_2$ to designate the layered structure. Phase compositions of the samples following different time of isothermal treatment at 1200°C, obtained from XRD analysis, are reported in Table 1. The presence of $Li_xCo_{1-x}O$, $LiCoO_2$ and Co_3O_4 phases was detected in all the samples, but the compositions only submitted to the dynamic step of the thermal treatment, where $Li_xCo_{1-x}O$ was not revealed. According to Moore and White [1], we can infer that single phase cubic or two phase cubic and layered solid solutions are formed during the dynamic step up to 1200°C. $LiCoO_2$ and Co_3O_4 are formed during the cooling by phase transition, according to relation (1). Phase transition decreases with increasing thermal treatment time at 1200°C, owing to sintering of the body. From now on we will designate x, y and z as the lithium atomic content in the solid solution before lithium evaporation and phase transition (x), after lithium loss and before phase transition (y), and following lithium loss and phase transition (z). For x and $y > 0.09$, for the reason later indicated, the Li atomic fraction represents the sum of lithium content in both cubic and layered solid solutions. Table 2 shows the lattice parameters and lithium atomic fraction z of $Li_zCo_{1-z}O$. The values of z have been calculated from the relation of lattice parameter and lithium atomic fraction in the solid solution reported in Ref. [2]. These values are quite constant around 0.060–0.065, independent of nominal lithium content and thermal treatment time of the samples. This behaviour can be attributed to the presence of particles with non-homogeneous $Li_yCo_{1-y}O$, i.e. an inner solid solution with $y \cong$

Table 1
Phase compositions (wt.%) from XRD analysis, and mass change of the samples, following different times of the thermal treatment at 1200°C

Sample Li (at %)	Time (h)	$LiCoO_2$ (%)	Co_3O_4 (%)	$Li_xCo_{1-x}O$ (%)	Mass change (%)
10	0	13	87	0	18.3
10	1	10	83	7	17.3
10	3	9	77	14	16.3
10	5	8	72	20	15.3
10	10	7	61	32	14.2
10	40	2	20	78	12.3
20	0	23	77	0	12.5
20	1	20	72	8	11.0
20	3	15	68	17	10.2
20	5	10	63	27	9.0
20	10	7	58	35	7.5
20	40	2	23	75	3.0

Table 2
Lattice constants and lithium atomic fractions of the solid solutions following different isothermal treatments at 1200°C

Nom. Li (at.%)	Thermal treatment time (h)	Lattice constant (Å)	z in $Li_zCo_{1-z}O$ (at.%)
10	0	–	–
10	1	4.234	6.5
10	3	4.234	6.5
10	5	4.234	6.5
10	10	4.236	6.0
10	40	4.236	6.0
20	0	–	–
20	1	4.234	6.5
20	3	4.234	6.5
20	5	4.234	6.5
20	10	4.235	6.3
20	40	4.236	6.0

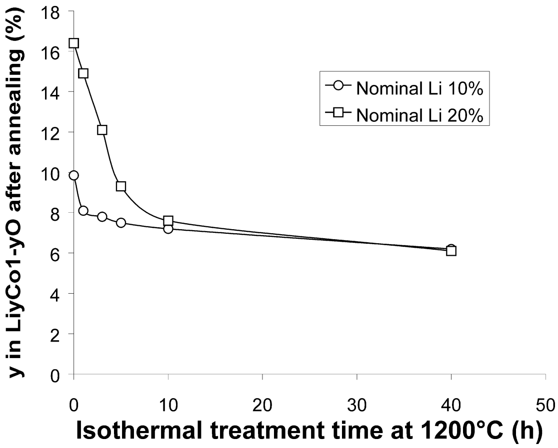

Fig.1. Dependence of remaining lithium atomic fraction y in $Li_yCo_{1-y}O$ on isothermal treatment time at 1200°C of nominal 10 and 20% Li samples.

0.06 and one or more outer solid solutions (cubic and/or layered) with $y > 0.06$, as reported in a previous work on the formation of lithium oxide cobalt oxide solid solution [13]. Phase transition starts from the lithium-rich surface of the particle, in contact with O_2. The last step of the phase transition involves $Li_yCo_{1-y}O$ with y 0.06. Li_2O evaporation from the solid solution occurs as reaction (8) proceeds. Neglecting lithium loss during cooling, from the phase amounts, φ, of the different compounds and z values reported in Tables 1 and 2, it is possible to calculate lithium atomic fraction y (mean value of the non-homogeneous solid solution) in $Li_yCo_{1-y}O$ at the end of isothermal treatment and before phase transition. The lithium atomic fraction y can be expressed as:

$$y = n_{Li}/(n_{Li} + n_{Co}) \tag{9}$$

where n_{Li} and n_{Co} are total quantity mol of lithium and cobalt ions present in the samples. As n_{Li} and n_{Co} do not change during the phase transition, we can write:

$$n_{Li} = z n_{Li_zCo_{1-z}O} + n_{LiCoO_2} \tag{10}$$

$$n_{Co} = (1 - z) n_{Li_zCo_{1-z}O} + n_{LiCoO_2} + 3n_{Co_3O_4} \tag{11}$$

where $n_i = \varphi_i/M_i$ (M_i is the molecular weight) denotes the quantity mol of $Li_zCo_{1-z}O$, $LiCoO_2$ and Co_3O_4, respectively. From Eqs. (9)–(11) it follows:

$$y = \left(z n_{Li_zCo_{1-z}O} + n_{LiCoO_2}\right)/\left(n_{Li_zCo_{1-z}O} + 2n_{LiCoO_2} + 3n_{Co_3O_4}\right) \tag{12}$$

Fig. 1 shows the dependence of lithium atomic fraction y in $Li_yCo_{1-y}O$ following isothermal treatment and before phase transition, on annealing time at 1200°C for nominal 10 and 20 Li at.% samples. For both the compositions, y initially decreases, then attains a constant value around 0.06. The fractional lithium loss (lithium ions evaporated to total lithium ions present in the solid solution at the beginning of isothermal treatment ratio) from the solid solution was obtained from y values, as the relation:

$$y_{ev}/y_{to} = (y_{to} - y_t)/[y_{to}(1 - y_t)] \tag{13}$$

where y_{ev} is the evaporated lithium atomic fraction, and y_{to} and y_t are the lithium atomic fractions in the solid solution without isothermal treatment and following an isothermal treatment of t h, respectively. Figs. 2 and 3 show normal and log-log plots of fractional lithium loss vs. isothermal treatment time, respectively. Unlike lithium oxide evaporation from $Li_xNi_{1-x}O$ solid solution [6], in this case Li_2O evaporation is not governed by a parabolic law (time dependence $n = 0.5$), but, as can be seen in Fig. 3 for a nominal Li 10% sample we have a straight line with slope, denoting the time dependence of lithium loss, about 0.2, for nominal Li 20% sample the plot breaks into two straight lines with different slopes. The slopes of these lines are about 1 and 0.2, respectively. The change of slope occurs for isothermal treatment time of 5 h, corresponding to Li atomic fraction in the solid solution of 0.093, similar to the starting value of the nominal 10% Li sample. On this basis, we can hypothesize that single phase cubic solid solution is present in the sample up to Li atomic fraction 0.09 (mean value), then, for $x > 0.09$ the formation of layered solid solution also occurs. Considering the formation of Co-saturated $Li_yCo_{2-y}O_2$ solid solution, i.e. with y 0.82 [1], the amount of layered structure is about 20%. So, the behaviour of the 20% Li sample can be explained taking into account the presence of this amount of layered $Li_yCo_{2-y}O_2$ solid solution in the external part of the particle, where lithium loss occurs in a different way with respect to cubic $Li_xCo_{1-x}O$ solid solution.

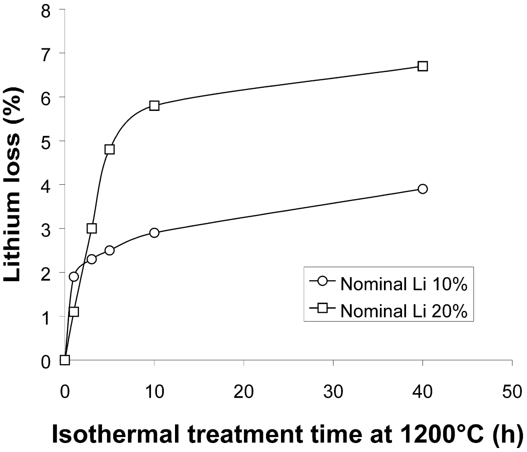

Fig. 2. Lithium loss vs. isothermal treatment time at 1200°C of nominal 10 and 20% Li samples.

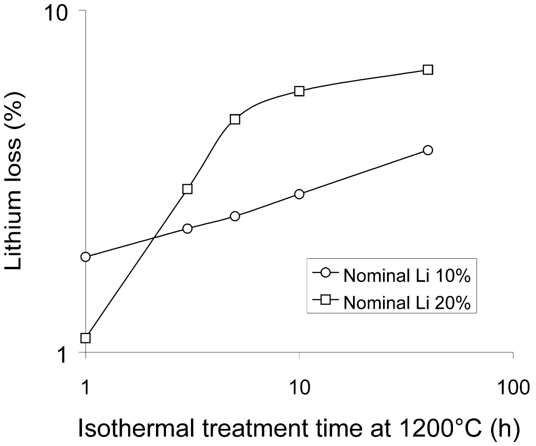

Fig. 3. Log–log plot of lithium loss vs. isothermal treatment time at 1200°C of nominal 10 and 20% Li samples.

Total mass change following thermal treatment Δm_{tot} for different isothermal times is reported in Table 1. This value includes all the weight changes related to Eqs. (1)–(7). Because the mass changes following the dynamic step up to 1200°C are the same for all samples, we have calculated weight loss only due to $Li_2O + O_2$ evaporation during isothermal treatment and phase transition during cooling $(\Delta m^t)_w$, using the following relation:

$$\left(\Delta m^t\right)_w = \left(\Delta m_{tot}^{to} - \Delta m_{tot}^{t}\right)/\left(1 + \Delta m_{tot}^{to}\right) \tag{14}$$

where Δm_{tot}^{to} and Δm_{tot}^{t} are total mass change without isothermal treatment and following an isothermal time of t h, respectively. Fig. 4 shows $(\Delta m^t)_w$ vs. isothermal treatment time for nominal 10 and 20% Li compositions. Without isothermal treatment, lithium loss at 1200°C is zero, and the degree of phase transition is 1. With increasing annealing time, both lithium loss and a decrease of the degree of phase transition give rise to weight loss. To compare XRD and mass change measurements, we have calculated weight loss from XRD data (phase amount and lithium atomic fraction in the solid solution after annealing) $(\Delta m^t)_X$. In the hypothesis of equimolecular evaporation of lithium and oxygen, i.e. in the absence of both interstitial Li^+ and vacancies in $Li_xCo_{1-x}O$ lattice, the relation of $(\Delta m^t)_X$ and phase amount φ and Li atomic fraction z, taking into account of the relations (1) (phase transition) and (8) ($Li_2O + O_2$ evaporation) is:

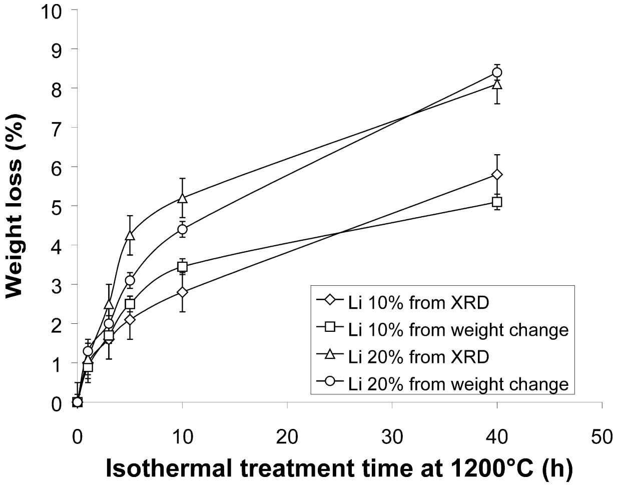

Fig. 4. Weight loss, calculated by both diffractometric and gravimetric measurements, vs. isothermal treatment time at 1200°C of nominal 10 and 20% Li samples. Error bar of weight loss from diffractometric measurements ±0.5; error bar of weight loss from gravimetric measurements ±0.2.

$$\left(\Delta m^t\right)x = \left[(x-y)/(1-y)M_{LiO} + \xi(1-2z)(1-x)/6(1-y) M_{O_2}\right]/\left[M_{Li_xCo_{1-x}O} + (1-2y)(1-x)/6(1-y)M_{O_2}\right] \tag{15}$$

where x and y are Li atomic fraction in the solid solution before and after lithium evaporation during the isothermal treatment, respectively, z is Li atomic fraction in the solid solution after phase transition, ξ is the molar ratio of solid solution amount before and after phase transition (obviously $1-\xi$ is the degree of phase transition), and M_{LiO}, M_{O_2} and $M_{Li_xCo_{1-x}O}$ are the formula weights of LiO, O_2 and $Li_xCo_{1-x}O$, respectively. ξ is defined as:

$$\xi \equiv n_{Li_zCo_{1-z}O}/n_{Li_yCo_{1-y}O} \tag{16}$$

where $n_{Li_yCo_{1-y}O}$ and $n_{Li_zCo_{1-z}O}$ are the amount of solid solution before and after phase transition, respectively. Assuming constant lithium amount during phase transition, it has:

$$y n_{Li_yCo_{1-y}O} = z n_{Li_zCo_{1-z}O} + n_{LiCoO_2} \tag{17}$$

From Eqs. (16) and (17) it obtains:

$$\xi = y/\left(z + n_{\mathrm{LiCoCO_2}}/n_{\mathrm{Li_zCo_{1-z}O}}\right) \tag{18}$$

So, we can obtain ξ from XRD data. Fig. 4 shows the dependence of weight loss, from weight and XRD measurements, on isothermal time. A suitable agreement of $(\Delta m^t)_X$ and $(\Delta m^t)_w$ can be denoted.

To confirm the results of this work, the data reported in Ref. [13], regarding the formation of $Li_xCo_{1-x}O$ from decomposition of $LiCoO_2$ at 1300°C, showed the stability of the solid solutions with Li about 0.065. XRD patterns following thermal treatment at 1300°C for 10 and 20 h revealed no substantial difference: in both spectra the reflections of $Li_xCo_{1-x}O$, x 0.065, with traces of Co_3O_4 and $LiCoO_2$ were present. It is known that Co^{3+} ions are unstable at high temperatures: $(Co^{3+})_2Co^{2+}O_4 \rightarrow 3Co^{2+}O$ at 918°C, and $LiCo^{3+}O_2 > 1/(2-y)\ Li_y(Co^{3+})_y(Co^{2+})_{2-2y}O_2$ for temperatures higher than 900°C, with reduction of Co^{3+} to Co^{2+}. In the cubic rock salt structure each cation is close to 12 other cations. Therefore, for $x \leqslant 00.7$ each lithium ion has 12 surrounding Co^{2+}. The positive charge to achieve neutrality is delocalised on 12 Co, resulting in a high stability of this configuration, i.e. of the solid solution.

4. Conclusions

Following thermal treatment at 1200°C, lithium loss occurs from $Li_xCo_{1-x}O$ solid solutions. The time dependence of Li_2O vaporization from nominal Li 10% sample was 0.2, whereas the time dependence of Li_2O vaporization from nominal 20% Li sample changes from 1 to 0.2 following 5 h of isothermal treatment time. The behaviour of nominal Li 20% sample is due to the presence of layered $Li_yCo_{2-y}O_2$ solid solution in the external part of the particles. Lithium atomic fraction remaining in the solid solution following annealing attains a constant value of about 0.06, independent of the nominal lithium content.

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