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# A Review Study of the Preparation of Porous Lithium-Doped Nickel Oxide

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**Abstract**

*The effect of both the kind and composition of starting powders and the thermal treatment of the green compacts on the preparation of porous $Li_xNi_{1-x}O$ plaques, used as cathode material in molten carbonate fuel cells, are reviewed.*

*Es wird eine Übersicht gegeben über den Einfluß, den die Art und Zusammensetzung der Ausgangspulver und die Wärmebehandlung der Grünlinge auf die Herstellung von porösen $Li_xNi_{1-x}O$-Platten, die als Kathodenmaterial in geschmolzenen Karbonat Brennstoffzellen eingesetzt werden, hat.*

*Les effets de la variété des composés de Ni utilisés, de la composition du mélange de Ni–$Li_2CO_3$ et du traitement termique sur la préparation des solutions solides de $Li_xNi_{1-x}O$, utilisées comme cathodes dans les piles à combustibile à carbonates fondues, sont passés en revue.*

## 1 Introduction

Pure, stoichiometric NiO is a green compound with rocksalt structure. It is an insulator with a specific resistance $>5\times10^{12}$ ohm m. The sintering of NiO powders, as reported by Iida,[1] may be divided into three stages: in the first stage, below 1200°C, grain growth and densification show no appreciable increase; in the second stage, from 1200° to 1400°C, densification takes place rapidly whereas grain growth is slow; in the third stage, above 1500°C, densification proceeds slowly but grain growth is rapid. Verwey *et al.*[2] observed that when NiO and $Li_2O$ are heated together at 1200°C in air, the following reaction takes place:

$$(1/2)x\mathrm{Li_2O} + (1-x)\mathrm{NiO} + (1/4)x\mathrm{O_2} \rightarrow \mathrm{Li}_x^{+}\mathrm{Ni}_{1-2x}^{++}\mathrm{Ni}_x^{+++}\mathrm{O} \quad (1)$$

Verwe *et al.* prepared compositions for values of $x<0{\cdot}3$ and studied the electrical conductivity and lattice parameters of these materials as a function of composition. These materials crystallized with the cubic rocksalt structure of NiO, the length of the unit-cell edge decreasing slightly with increasing lithium content as a consequence of the difference in ionic radius between $Ni^{++}$ and $Ni^{+++}$ ions. Lithium-doped NiO, Ni(Li)O, is a black compound; it is a semiconductor, with specific resistances down to $10^{-3}$ ohm m at room temperature.[3]

Because of their electrical conductivity and their stability in molten carbonates at 650°C (the slight dissolution of Ni(Li)O in molten Li/K carbonates[4] can be decreased by increasing the basicity of the melt, i.e. by increasing the $Li_2CO_3/K_2CO_3$ ratio[5,6] or by adding of a small amount of basic alkaline earth oxides to the melt[7]), Ni(Li)O solid solutions are at present used as cathode material in molten carbonate fuel cells (MCFC).[8] The cathode structure was recognized early as one of the principal factors determining cell performance; porosity (in the range 60–70%), pore size distribution, and mean pore size (6–12 μm) all play an important role. The cathode structure ideally has a broad pore size spectrum, which provide small pores for the electrochemical reaction and large pores mainly for gas diffusion.[9] In-situ formation is the method commonly used to obtain MCFC cathodes:[10] a porous metallic nickel plaque is assembled into a cell in the form of a plaque, which becomes oxidized and lithiated in situ soon after the cell is brought to operating temperature. The lithium is supplied by the electrolyte; the oxygen is supplied by the gas phase.

However, a number of problems are associated with the in-situ oxidation of a sintered nickel structure. The in-situ oxidation of the nickel plaque causes the original nickel microstructure to break into clusters of much smaller particles with no interconnections, leading to a cathode that is structurally weak and friable. Another problem is a

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30–40% volume expansion during the oxidation and lithiation of the nickel. Moreover, during in-situ oxidation the lithium for doping is supplied by the $Li_2CO_3$–$K_2CO_3$ electrolyte, resulting in an early consumption and compositional variation of electrolyte. The ex-situ formation of the cathode[11] allows the problems of the in-situ technique to be overcome. This method foresees the assembling into a cell of the cathode in its final form (porous Ni(Li)O plaque). The advantages of this way of obtaining the electrode are (a) porosity and pore size distribution control, (b) no volume variation, and (c) no electrolyte consumption. This paper examines efforts in evaluating the effect of both the kind and composition of the starting powders and the thermal treatment of the green compacts on the preparation of porous Ni(Li)O plaques, usable as cathodes in molten carbonate fuel cells.

## 2 Ni(Li)O Solid Solution Preparation

### 2.1 By reagent-grade NiO and $Li_2CO_3$[12]

The reaction leading to $Li_xNi_{1-x}O$ solid solution formation is a two-step process:

$$(x/2)Li_2CO_3 \rightarrow (x/2)Li_2O + (x/2)CO_2 \qquad (2)$$

$$(x/2)Li_2O + (1-x)NiO \rightarrow Li_xNi_{1-x}O \qquad (3)$$

Carbonate decomposition takes place at temperatures higher than 640°C.[13] The bulk diffusion of lithium oxide into nickel oxide takes place at a fast rate at temperatures higher than 750°C.[14] At these temperatures the solution of lithium oxide into nickel oxide is in competition with the evaporation of lithium oxide, therefore the lithium amount in the final solid solution is lower than the lithium amount in the starting mixture.

### 2.2 By Ni and $Li_2CO_3$ powders[13]

Thermal treatment in air of Ni and $Li_2CO_3$ powders in the temperature range 500 to 700°C gives rise to the Ni(Li)O solid solution, according to the following reaction:

$$(1-x)Ni + (x/2)Li_2CO_3 + (x/4)O_2 \rightarrow Li_xN_{1-x}O + (x/2)CO_2 \qquad (4)$$

The fundamental aspects of the reactive process taking place into the powdered system analysed can be summarized as follows: (a) lithium carbonate decomposition takes place in the entire temperature range of nickel oxidation, leading to solid solution formation at lower temperatures than those required both for bulk diffusion of lithium oxide into nickel oxide and for spontaneous carbonate decomposition; (b) all lithium oxide in the mixture participates to the solid solution formation independent of whether it was produced by nickel-modulated or spontaneous carbonate decomposition; (c) defect, i.e. nickel vacancy concentration increases with increasing the relative amount of lithium oxide produced by spontaneous carbonate decomposition that enters the solid solution.

**Table 1.** Effect of the starting materials on porosity and mean pore diameter of $Li_xNi_{1-x}O$ ($x = 0{\cdot}06$) cathodes thermal treated at 850°C for 0·5 h[15]

| *Starting materials* | *Pressing pressure (MPa)* | *Porosity (%)* | *Mean pore diameter (μm)* |
|---|---|---|---|
| $Li_2CO_3$/NiO | 34·5 | 41·8 | 0·38 |
| $Li_2CO_3$/NiO | 6·9 | 44·2 | 0·43 |
| $Li_2CO_3$/NiO | 0·7 | 50·3 | 0·66 |
| $Li_2CO_3$/Ni(123) | 17·2 | 55·0 | 2·17 |
| $Li_2CO_3$/Ni(255) | 34·5 | 57·0 | 3·72 |
| $Li_2CO_3$/Ni(123) | 6·9 | 64·7 | 3·29 |
| $Li_2CO_3$/Ni(255) | 6·9 | 67·8 | 6·13 |
| $Li_2CO_3$/Ni(123) | 1·7 | 69·0 | 3·96 |
| $Li_2CO_3$/Ni(255) | 1·7 | 74·9 | 7·33 |
| $Li_2CO_3$/Ni(255) | 0·7 | 78·8 | 7·91 |

## 3 Effect of NiO Source

The aim is to evaluate the effect of the starting components on porosity and median pore diameter of ex-situ cathodes. Baumgartner & Zarnoch[15] fabricated cathodes using, as initial ingredients, $Li_2CO_3$ with either NiO or powdered Ni. Two grades of Ni powder were used: Ni INCO Type 123 (INCO, NY) is spherical in particle morphology with a 3–4 μm particle size and a 2·1 g/cm³ apparent density and Ni INCO Type 255 (INCO, NY) is a branched chain of Ni particles 2–3 μm in particle size and 0·5–0·65 g/cm³ in apparent density. Table 1 shows that both the porosity and mean pore diameter of Ni(Li)O plaques increase as the starting material is changed from NiO to Ni INCO Type 123 to Ni INCO Type 255.

## 4 Ni(Li)O Formation from Ni–$Li_2CO_3$ Powder Mixture

In this section efforts in evaluating the effect of both $Li_2CO_3$ content in the starting mixture and the thermal treatment of the green compact on the microstructure of Ni(Li)O plaques from Ni–$Li_2CO_3$ powder mixtures are examined. All the green compacts were prepared by the tape casting technique.

### 4.1 $Li_2CO_3$ as pore former

In addition to serving as a lithium source, lithium

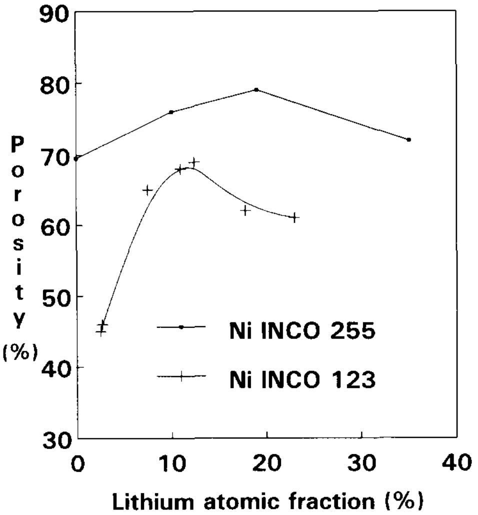

**Fig. 1.** Porosity values of $Li_xNi_{1-x}O$ plaques following thermal treatments (+) at 900°C (Ni INCO Type 123/$Li_2CO_3$ mixtures)[16] and (■) at 950°C (Ni INCO Type 255/$Li_2CO_3$ mixtures)[7] as a function of lithium atomic fraction.

carbonate acts as pore former:[16,17] as shown in Fig. 1, where the porosity values of Ni(Li)O plaques from mixtures with different Ni powder thermal treated at 900°C (Ni INCO Type 123) and 950°C (Ni INCO Type 255) are plotted as a function of lithium atomic fraction. In this figure the sample porosity initially exhibits a substantial increase, associated with the liberation of carbon dioxide during $Li_2CO_3$ decomposition, followed by a decrease with lithium incorporation above 10–12 cation % for the data from Ref. 16 and above 20 cation % for the data from Ref. 17. In Table 2 the values of Hg and true porosity for samples with different lithium content heat treated at 950°C are shown: this result indicates that $Li_2CO_3$ presence in the starting mixture gives rise to the formation of micropores, but does not affect the number of mesopores and macropores of the resulting Ni(Li)O plaques.

## 4.2 Effect of $Li_2CO_3$ decomposition pathway on the dilatation of resulting Ni(Li)O plaques[18,19]

There are two pathways for $Li_2CO_3$ decomposition: (1) $Li_2CO_3$ decomposition catalysed by the presence of nickel and (2) spontaneous $Li_2CO_3$ decomposition.[13] Weight changes following isothermal treatment are reported as a function of time in Fig. 2. As can be seen, at the temperature of 550°C (Fig. 2(a)) all the samples show a monotonic weight increase, while at 650°C (Fig. 2(b)) the weight change curves of lithium-containing samples go through a maximum. A monotonic weight increase is just that which is to be expected in the case of a modulate carbonate decomposition, while a maximum in the weight change curve can be explained by the coexistence of independent processes of nickel oxidation and lithium carbonate decomposition. At $T = 550°C$ there is a limit to the relative amount of lithium carbonate whose decomposition can be modulated by nickel oxidation, which results in $x$Li = 0·17. Plaque diameter changes (PDC) are reported as a function of time in Fig. 3(a) (550°C) and (b) (650°C). A comparison of Figs 2 and 3 shows that spontaneous carbonate decomposition causes a plaque dilatation higher than the nickel-modulated $Li_2CO_3$ decomposition. According to this experience, to limit plaque dilatation, a good preparation

**Table 2.** Mercury porosity (*P*Hg) and true porosity from density measurements (*P*) as a function of nominal cationic fraction ($x$Li)[17]

| *xLi* | *PHg* (%) | *P* (%) |
|---|---|---|
| 0·00 | 68·3 | 69·5 |
| 0·10 | 68·2 | 76·3 |
| 0·19 | 69·4 | 79·4 |

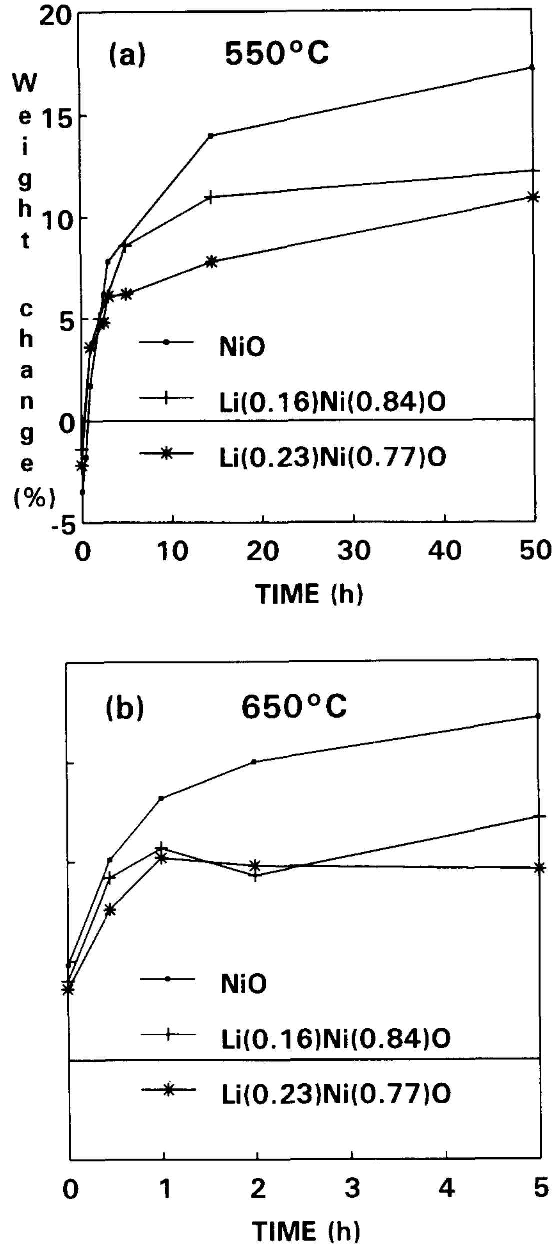

**Fig. 2.** Weight change of Ni/$Li_2CO_3$/binder mixtures following thermal treatments at (a) 550°C and (b) 650°C as a function of isothermal time.[18,19]

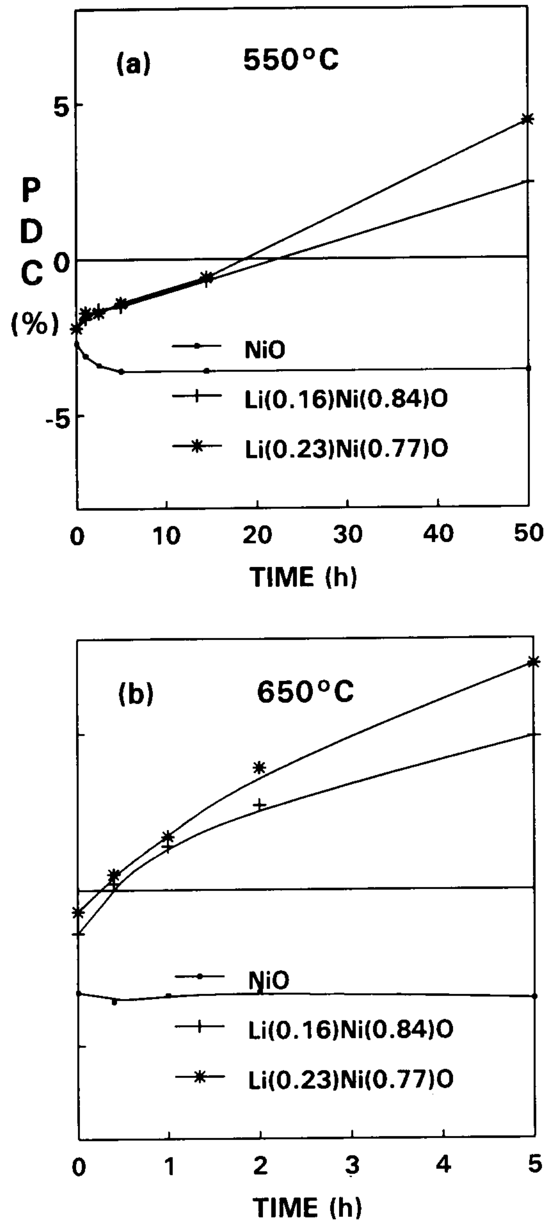

**Fig. 3.** Plaque diameter change (PDC) of Ni/$Li_2CO_3$/binder mixtures following thermal treatments at (a) 550°C and (b) 650°C as a function of isothermal time.[18,19]

procedure for $Li_xNi_{1-x}O$ solid solutions should foresee (1) the use of mixtures with lithium content lower than $x$Li = 0·17; (2) solid solution formation at temperatures lower than 640°C, and (3) solid solution homogenization at temperatures around 700°C.

### 4.3 Sintering of a Ni(Li)O plaque in the presence of a $Li_2CO_3$ reactive liquid phase

Ni INCO Type 255/$Li_2CO_3$ samples were subjected to thermal treatments in the temperature range from 700° to 900°C,[20] in order to establish the nature of the decrease of the sample porosity after thermal treatments at 900/950°C of high-carbonate-content Ni/$Li_2CO_3$ mixtures, as observed in previous studies[16,17] (see Fig. 1). In this work it was found that the presence of an undecomposed $Li_2CO_3$ reactive liquid phase at temperatures >723°C ($Li_2CO_3$ melting temperature) in the high-carbonate-content samples gives rise to a sintering process. As shown in Fig. 4, the relative density of the samples containing more than 20 at.% of lithium ions has increased on going from a treatment temperature of 700°C to one of 900°C. Figure 5 shows the plaque diameter change as a function of time at 700 and 750°C for the sample with nominal lithium atomic fraction $x = 0{\cdot}44$: at 700°C solid-state $Li_2CO_3$ decomposition gives rise to plaque dilatation, while at 750°C the presence of a liquid phase of undecomposed $Li_2CO_3$ promotes material sintering.

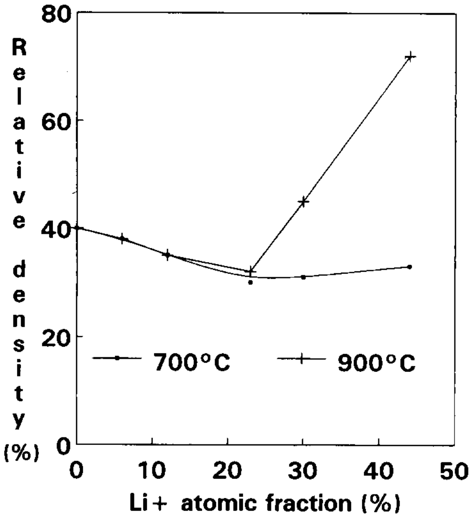

**Fig. 4.** Relative density of $Li_xNi_{1-x}O$ solid solutions following thermal treatments at (■) 700°C and (+) 900°C of Ni/$Li_2CO_3$ mixtures as a function of lithium atomic fraction.[20]

However, the presence of a $Li_2CO_3$ reactive liquid phase in the $Li_2CO_3$/Ni(Li)O mixtures is not enough to promote densification of the resulting lithium-rich solid solution. It has been found[21] that the material densification depends on the way the $Li_2CO_3$/$Li_xNi_{1-x}O$ mixtures are obtained. These mixtures have been prepared by two different

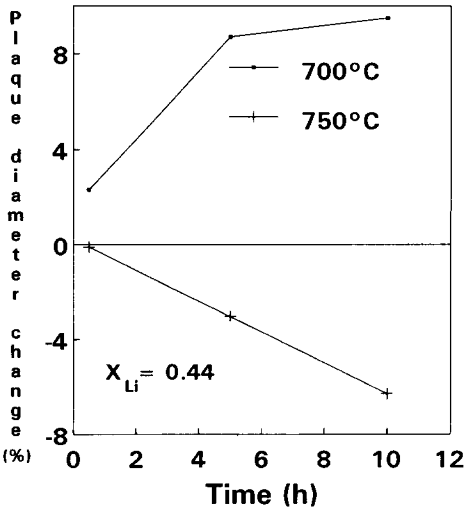

**Fig. 5.** Plaque diameter change of Ni/$Li_2CO_3$/binder mixture with $x$Li = 0·44 following thermal treatments at (■) 700°C and (+) 750°C as a function of isothermal time.

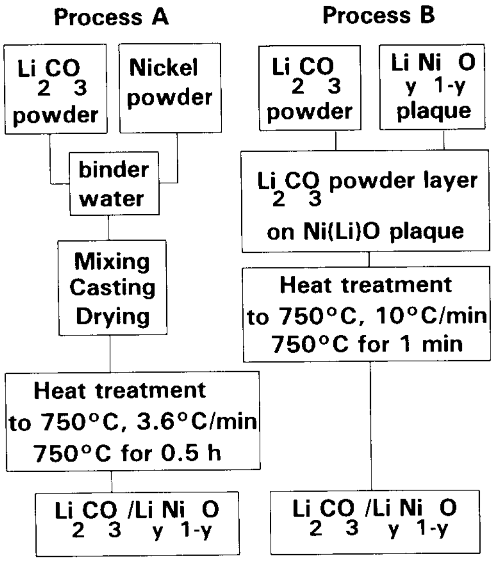

**Fig. 6.** Processing route methods A and B for the preparation of $Li_2CO_3/Li_yNi_{1-y}O$ mixtures.[21]

processing route methods, as indicated in Fig. 6. In Fig. 7 the dependence of the density of samples obtained by different methods on isothermal time can be seen: the density of the samples obtained with the process (A) increased with isotherm time, while that of the sample obtained with the process (B) slightly decreased with time. This means, in order that material densification occurs, that the presence of a reactive liquid phase is not enough, but that an intimate contact is necessary between $Li_2CO_3$ and lithium-doped NiO grains.

## 4.4 Sintering of Ni(Li)O cathodes by $Li_2O$ evaporation

It is known that the lithium atomic fraction $x$ in $Li_xNi_{1-x}O$ affects the sintering process of lithium oxide–nickel oxide solid solutions[16,17] and that lithium oxide evaporation from $Li_xNi_{1-x}O$ with $x = 0{\cdot}13$ takes place in a considerable way at temperatures higher than 1000°C.[22] More recent work[23,24] indicated that for $x > 0{\cdot}2$ $Li_2O$ evaporation from Ni(Li)O takes place at lower temperatures (750–850°C). In the entire range of $Li_2O$ evaporation both morphological particle change and an increase of cation vacancies concentration were evident. An intense shrinkage, due to the sintering process, in lithiated nickel oxide, with respect to the undoped NiO, was observed at 1200°C.[25] Like the effect of the gradient in the chemical potential of oxygen on the sintering process of NiO,[26] this behaviour was attributed to the existence of a gradient in the chemical potential of the lithium ion between the surface and the interior of the particles, due to lithium oxide evaporation, which acts as the driving force of the mass transport by volume diffusion. The linear dependence of shrinkage on the lithium loss shown in Fig. 8 supports the hypothesis that the driving force for the sintering process is the lithium oxide evaporation. In the light of the behaviour of these solid solutions, it is possible to fabricate Ni(Li)O cathodes with predetermined lithium contents and degrees of sintering by pre-arranging the amount of $Li_2CO_3$ in the starting mixture.

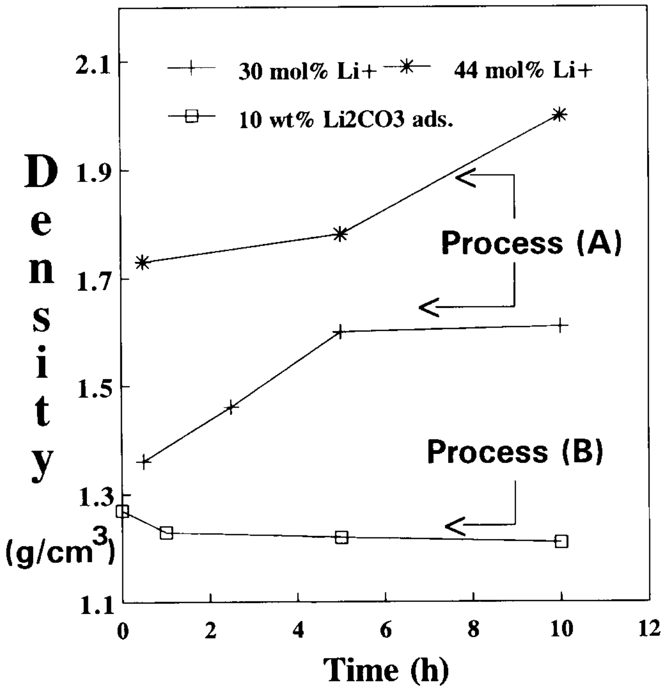

**Fig. 7.** Density of $Li_2CO_3/Li_yNi_{1-y}O$ plaques following thermal treatment 750°C as a function of isothermal time.[21]

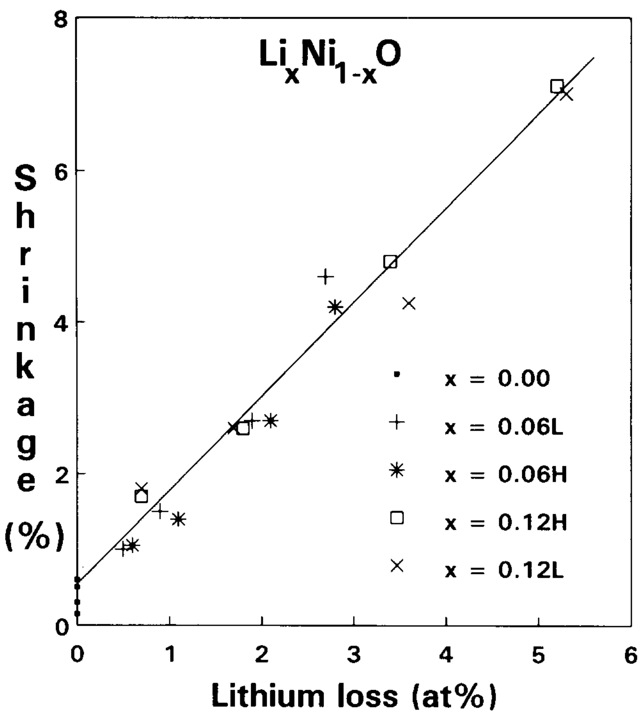

**Fig. 8.** Shrinkage versus lithium loss for $Li_xNi_{1-x}O$ solid solutions with different $x$ values. L = lower density sample, H = higher density sample.[25]

The aforesaid effects of lithium content and thermal treatment are shown in a schematic way in Fig. 9, where the radial variation of the plaque is

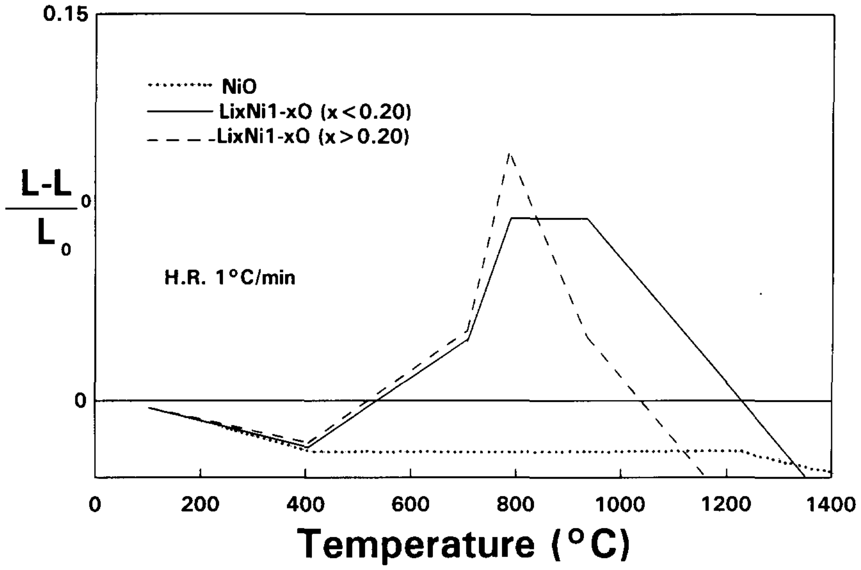

Fig. 9. Plaque diameter change versus temperature during the thermal treatment of Ni/$Li_2CO_3$ mixtures. ·····, NiO; ——, $Li_xNi_{1-x}O$, $x < 0{\cdot}20$; ----, $Li_xNi_{1-x}O$, $x > 0{\cdot}20$. Heating rate 1°C/min.

plotted as a function of temperature at constant heating rate. For the undoped NiO sample, after the initial shrinkage due to particle rearrangement following binder burnout, there is no radial variation up to 1200°C; for the $Li_xNi_{1-x}O$ sample with $x < 0{\cdot}20$ plaque dilatation by carbon dioxide evolution up to 700°C, no effect between 700 and 900°C, and shrinkage by lithium oxide evaporation at temperatures higher than 900°C are visible. For $Li_xNi_{1-x}O$ with $x > 0{\cdot}20$ it can be denoted that plaque dilatation will occur by $CO_2$ evolution up to 723°C, subsequent shrinkage by liquid-phase sintering between 723 and 900°C, and shrinkage by $Li_2O$ evaporation at temperatures higher than 900°C. In Fig. 10 it can be seen that, varying in a suitable way the starting composition of the mixture and the thermal treatment, cathodes having about the same lithium atomic fraction $x$, but different total porosity ($P$) and/or microstructure, can be obtained.

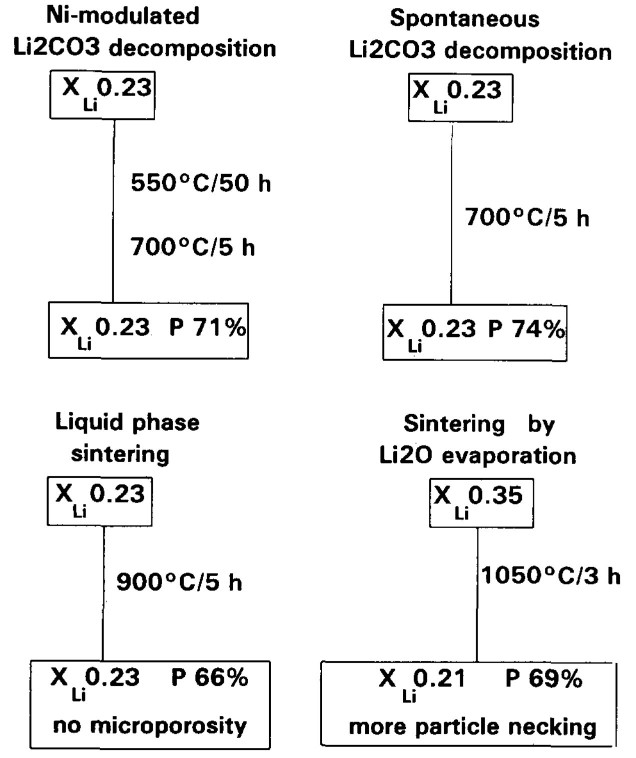

Fig. 10. Schematic representation of the ways of obtaining $Li_xNi_{1-x}O$ solid solutions with about same $x$ but different porosity ($P$) and microstructure by varying nominal lithium atomic fraction and thermal treatment.

## 5 Conclusion

On the basis of these results, Ni(Li)O plaques with desired requirements of total porosity, pore size distribution, grain size and lithium content can be tailored, by submitting to the appropriate thermal treatments the nickel–lithium carbonate starting mixture, containing the right amount of $Li_2CO_3$.

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