

New synthesis method of $\text{LiM}_{1-x}\text{M}'_x\text{O}_2$ elaborated by soft chemistry for rechargeable batteries (M and M' = Ni, Co or Mn)

C. Nayoze, F. Ansart*, C. Laberty, J. Sarrias, A. Rousset

CIRIMAT-LCMIE, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 4, France

Received 3 July 2000; received in revised form 24 November 2000; accepted 18 December 2000

Abstract

Synthesis of $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ by soft chemistry leads to a “new” material, which is more reactive and has a different morphology from oxide prepared by the direct solid-state method. The preparation of material by soft chemistry consists in a coprecipitation of powders, followed by a thermal treatment. This method allows a better control of structure, morphology and specific surface area (S_w). This one is directly linked to the manganese presence which can increase it by a factor 10. Concerning the morphology, the presence of manganese in sample leads to an oxide network favorable for a good lithium intercalation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Soft chemistry; Lithium batteries; Cathode; Morphology; Microstructure

1. Introduction

The layer transition metal oxides LiNiO_2 , LiCoO_2 and their related phases seem to be among the most promising cathode materials for lithium ion and rechargeable batteries. However, the pure phases have some disadvantages, e.g. the cyclability of LiNiO_2 is strongly dependent on the synthesis and operating conditions, whereas LiCoO_2 requires rather high potentials upon cycling. Different problems are present with the use of LiNiO_2 despite its desirable high discharge capacity. First, the poor capacity retention when charged and discharged at full depth of discharge. A second problem is relative to slow kinetics of LiNiO_2 , particularly near the end of discharge. Third is the difficulty and complicated synthesis where only relatively few precursors can be used.

Recently, a series of the $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ oxides has been studied [1–4]. These materials showed a higher capacity and energy than conventional lithium cobaltite, LiCoO_2 .

$\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ oxides undergo three distinct phase transitions during oxidation [5,6], but the incorporation of some Co stabilizes the structure: no phase transition occurs.

Recently, new synthesis methods of material [7–10] have been studied in order to improve the A_xMO_2 properties and reactivity (A = Li or Na and M = Cr, Mn, Fe, Co or Ni). Then, these wet synthesis methods have the advantage to

control the morphology and size, compared to conventional one.

The objectives of our research were initially, to synthesize $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ oxides (x ranging from 0 to 1) at intermediary temperatures (650–750°C) and then to move to possible additional substitutions of cobalt by nickel and/or manganese.

After calcinations, mixed oxides should meet several requirements: a strong dispersion, i.e. a large ratio surface/volume so that the material is as most reactive as possible, an homogeneous distribution of elementary particles, a specific surface S_w as high as possible and an homogeneous network for a good lithium intercalation with a maximum of diffusion paths.

In this paper, after an experimental description of the synthesis technique and of the characterization methods, the influence of parameters on morphology and structure is studied in the second part. The last part corresponds to a discussion concerning a possible optimization of cathode materials elaboration method.

2. Experimental

To define the method of optimal synthesis, the lithium cobalt oxide LiCoO_2 was used as standard. Then, a series of $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ oxides (x ranging from 0 to 1) was prepared by soft chemistry using oxalic precursors. The method consists of two main stages. In the first stage, a solution of cobalt, nickel and manganese nitrates is precipitated with

* Corresponding author. Tel.: +33-5-61-556108; fax: +33-5-61-556163.
E-mail address: ansart@ramses.ups-tlse.fr (F. Ansart).

Table 1
Experimental conditions

Lithiated precursors	Transition metal salts	Solvents	Complex agents
Nitrates	Nitrates	Deionized water	Ammonium oxalate
Hydroxides	Nitrates	Ethanol	Oxalic acid
Hydroxides	Nitrates	Ethanol + ethylene glycol	Oxalic acid

lithium-based precursors at room temperature, in oxalic acid solution. The metallic salts are dissolved in ethanol. These alcoholic solutions, for which the dielectric constants are sharply lower than those for water, usually help to obtain oxalate particles smaller than those formed in aqueous medium alone. In order to obtain oxalate precursor, we used only ethanol and lithium hydroxide as lithium-based precursor. Concerning the oxalate preparation, Table 1 summarizes the syntheses made in various solvents and complex agents. In addition, the control of the operational parameters (T , pH, speed and time of stirring, thermal processing) is essential.

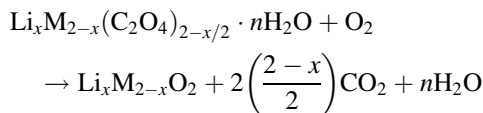
To obtain a good lithium intercalation, it is necessary to have lithium in excess. This leads us to optimize the initial ratio lithium/metal = 4/1. After the oxalic precursors precipitation, a filtration allows to separate the solid phase from the filtrate containing the lithium in excess. Lithium chemical analyses in the filtrate have been performed by atomic absorption spectrometry. In each case, the difference with the initial lithium content has been confirmed to be the final lithium content in the oxalate.

In the second stage, the oxalic precursors are decomposed under air flow, heated for 10 h and slowly cooled to room temperature. The three steps are as follows.

1. A dynamic step where the samples were heated from room temperature to Dwell temperature at a rate of 220°C/h.

2. An isothermal step during which the samples were maintained for 10 h at Dwell temperature.
3. A dynamic step during which the samples were cooled from the maximum temperature to room temperature at a rate of 220°C/h.

The global chemical reaction corresponds as follows:



The flow-chart of the procedure is summarized in Fig. 1.

3. Synthesis and characterization methods

For each synthesis, studies of composition, morphology and structure have been performed. Chemical analysis was done by atomic absorption and ionic chromatography. Chemical references are LiNO_3 for atomic absorption spectrometry and LiCl for ionic chromatography. Structures of the oxides were characterized by powder X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation (SIEMENS D501). The specific surface areas (S_w) were measured by the BET method using nitrogen by a Micrometrics Model 2100^E Accusorb. The powders were observed by scanning electron microscopy (SEM) with a JEOL JSM 6400 device.

XRD patterns analysis of the oxalates prepared with lithium nitrate used as lithiated precursor, solvents as deionized water and ammonium oxalate revealed the presence of Co_3O_4 only. It is noted that no LiCoO_2 phase is detected. The use of ethanol or ethylene glycol as solvent induce a phase mixture constituted by LiCoO_2 and Co_3O_4 (10% for the lithium precipitation in ethylene glycol versus 60% in ethanol). SEM studies of the different oxides and oxalates show that oxalate is needle shaped 1 or 2 μm long. After

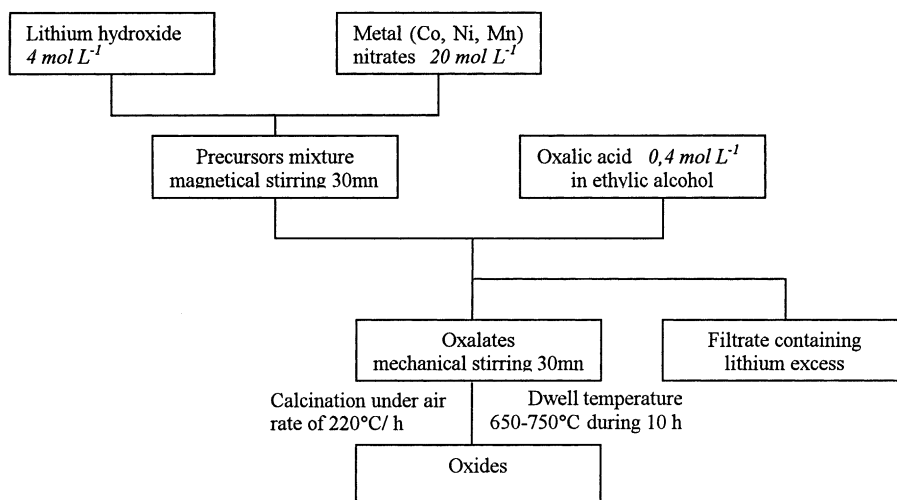


Fig. 1. Flow-chart of the synthesis procedure.

calcination, oxide is constituted by particles (1 μm). The XRD patterns of the oxalates prepared with lithium hydroxide revealed that the ethanol–ethylene glycol mixture does not allow obtaining of a pure phase. However, pure phase LiCoO_2 is obtained by using only ethanol as solvent.

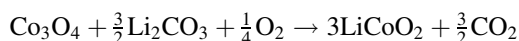
Oxalate morphology is the same as in the previous case. Aggregates size is smaller and network seems to be in favor of the lithium intercalation because of the number of diffusion paths. Thus, a mixture of ethanol/oxalic acid induce 70% of lithium precipitation with a pure phase LiCoO_2 .

4. Results and discussion

4.1. $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$

XRD patterns analysis of these compounds revealed the presence of pure phase at 700°C (see Fig. 2). Below this temperature, Li_2CO_3 phase appears and is transformed into oxide above this temperature. Furthermore, presence of Co_3O_4 can be underlined for short times of calcination. These results suggest that LiCoO_2 formation (with or without nickel substitution) occurs according to the following procedures.

- At the beginning of the process, cobalt ions are oxidized into Co_3O_4 .
- In the same time, Li_2CO_3 is obtained by the reaction of LiOH with CO_2 and by the heat treatment of lithium oxalate under air.
- When all Co_3O_4 is formed, the formation of LiCoO_2 prevailed according to the reaction:



SEM micrographs of the oxalates and oxides present different morphologies. Oxalates exhibit needles 1–7 μm long from an homogeneous repartition for $x = 0$ to a complex network for $x = 1$. But after calcination, this network changes into aggregates of 1–15 μm particles (see Fig. 3a and b). This oxide network only changes for $x = 0.2$ ($\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{O}_2$) in very compact aggregates of 10 μm .

4.2. $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$

Like the previous cobalt-based compounds, thermal treatment is optimized at 700°C with an isothermal step of 10 h. Below this temperature, reaction is not complete and Li_2CO_3 is still present (Fig. 4). Furthermore, the morphology is quite different. The oxides have the same morphology as the oxalates from which they are derived. One can identify needles. The particles are homogeneous in size. Fig. 5a and b show the micrographs of $\text{LiNi}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}\text{O}_2$ and its oxalic precursor. Other studies have shown that manganese can really stabilize the oxalate morphology (different sizes of needles). This result is interesting because the initial network is not affected, so the oxalate reactivity can be partially conserved.

The S_w of the different oxides are reported in Figs. 6 and 7. It is very important to compare the S_w of the different compounds with the nature of the transition metals because it is directly bound to reactivity. The S_w of the oxides considerably varies with the nature of the transition element. As a result, for a calcination temperature, LiCoO_2 has a more important S_w than LiNiO_2 (see Fig. 6). The substitution of cobalt by a very small amount of manganese increase drastically the S_w at 700 and 750°C with a factor 10. Same results have been observed with LiNiO_2 samples.

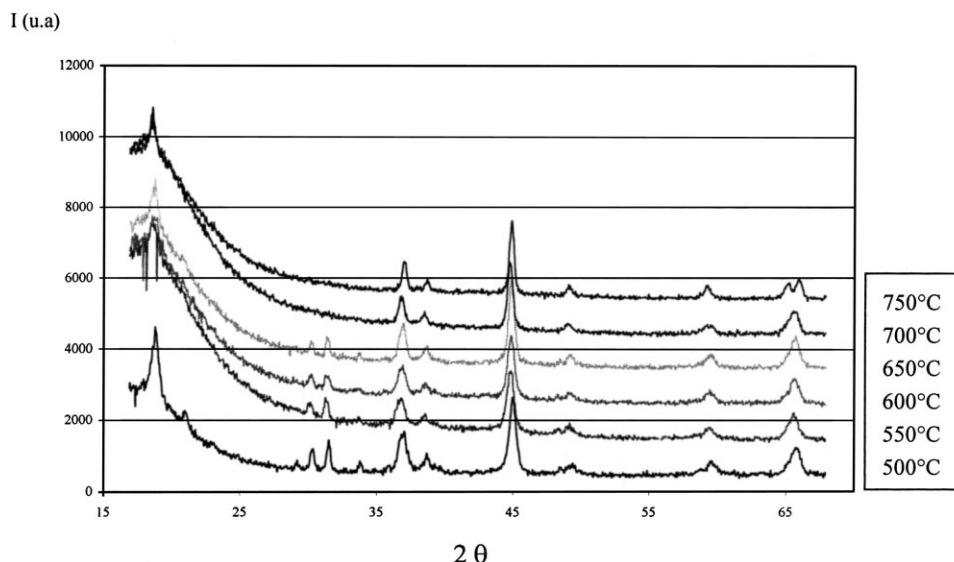
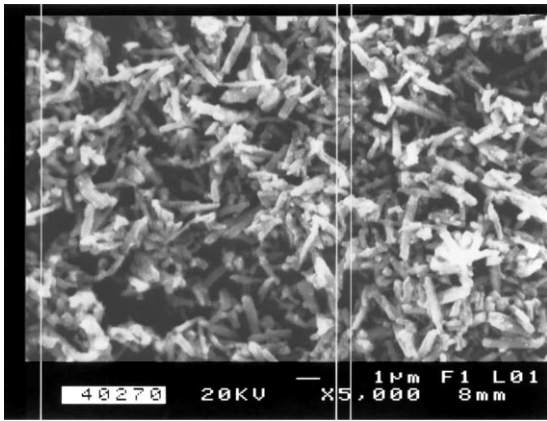
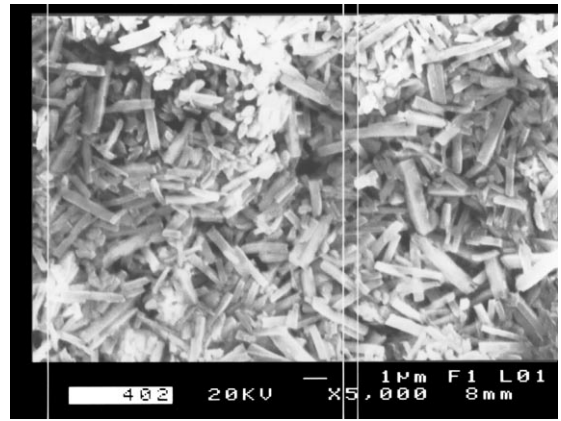


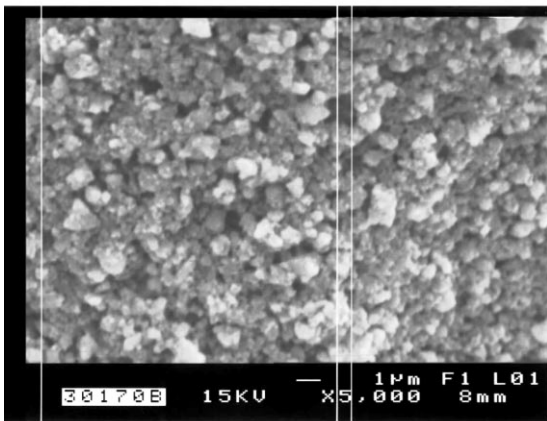
Fig. 2. Diffraction patterns of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ as a function of calcination temperatures.



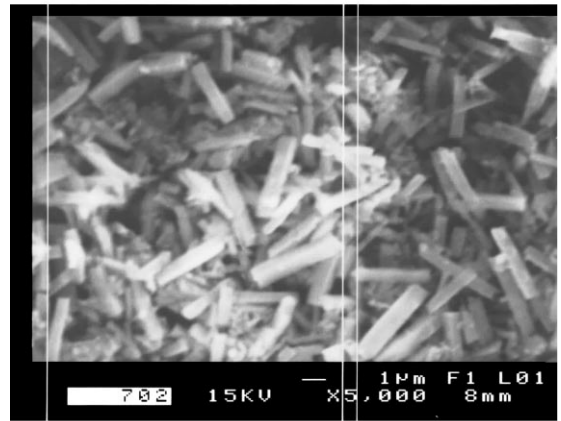
a) oxalate before calcination



a) oxalate before calcination



b) oxide



b) oxide

Fig. 3. SEM micrographs of the oxalate and the corresponding oxide.

Fig. 5. SEM micrographs of the oxalate and the corresponding oxide $\text{LiNi}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}$.

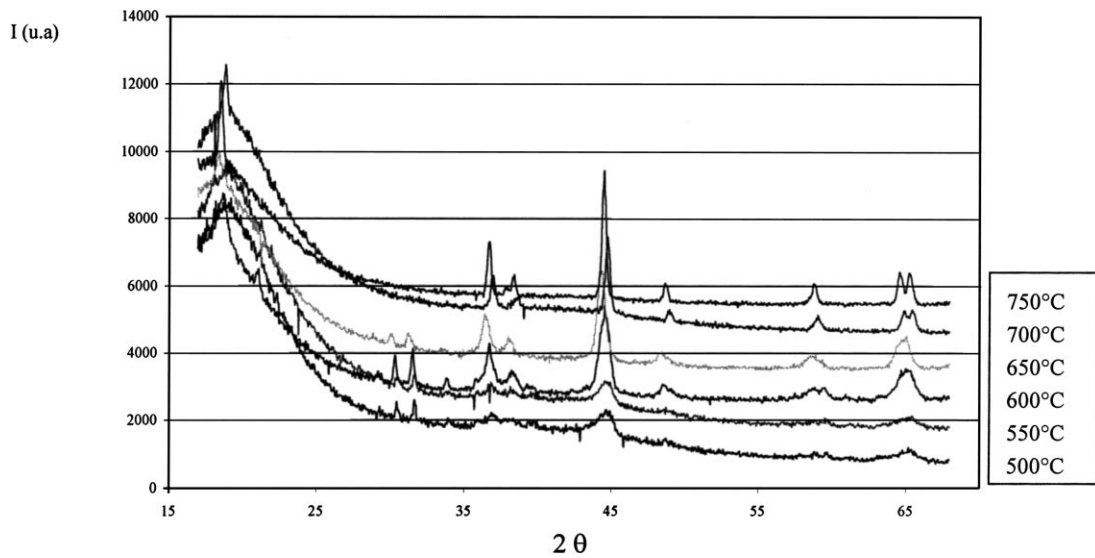


Fig. 4. Diffraction patterns of $\text{LiNi}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}$ as a function of calcination temperatures.

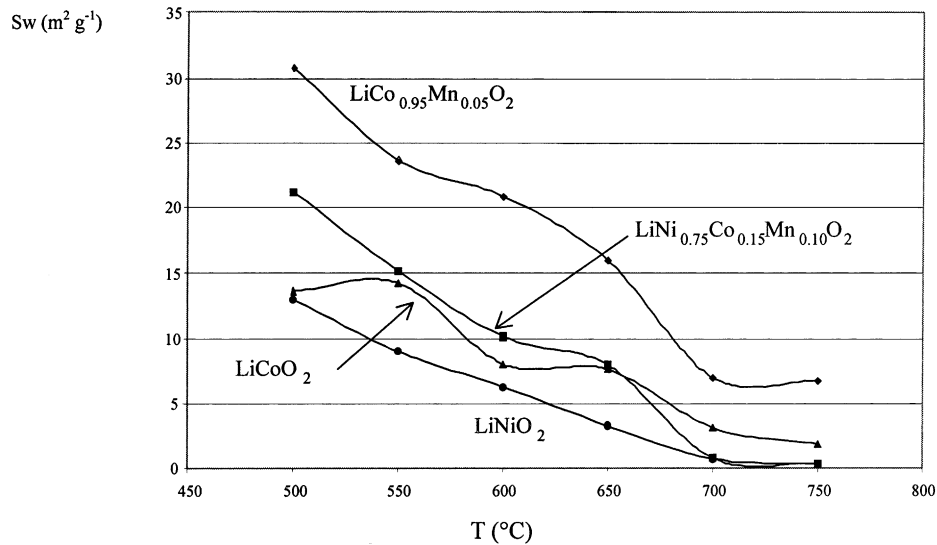


Fig. 6. Specific surface area (S_w) as a function of temperature.

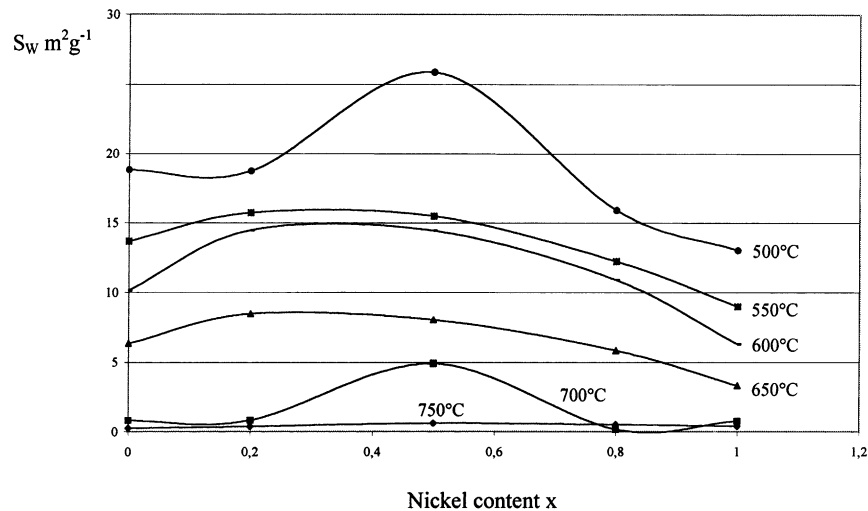


Fig. 7. Specific surface areas (S_w) vs. nickel content in $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$.

5. Conclusions

Considering $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ family with $0 < x < 1$, the oxide chosen to define the optimal synthesis method by soft chemistry, is LiCoO_2 . Other composition materials have been synthesized by this method. Thus, various types of lithium salts, metal salts, solvents and complex agents were used, with the control of the experimental conditions (pH, temperature, duration and stirring speed, etc.). It proved that the synthesis must be done by oxalic way, with lithium hydroxide mixed with metal salt nitrates in a ratio 4:1, in an ethylic solution. This ratio is necessary to have a pure phase and a good lithium intercalation. This procedure allows a better mixture of elements and thus a better particles repartition and homogeneity. Such reactions yield materials of higher reactivity. So, this coprecipitation method shows that ethanol as solvent has a good influence on the morphology

control and lithium hydroxide in obtaining a pure oxide after thermal treatment. Lithium intercalation can be important with this type of oxide morphology due to the presence of diffusion paths.

Measurements of surface specific area have shown good values for $\text{LiCo}_{0.95}\text{Mn}_{0.05}\text{O}_2$ at a calcination temperature of 700 $^\circ\text{C}$ and these values are larger than that of LiCoO_2 at all temperatures (at $T = 700$ or 750 $^\circ\text{C}$ with a factor 10). In fact, presence of manganese seems essential to the improvement of S_w which is a parameter directly linked with reactivity. Generally, the more reactivity of a material is important, the more performances are successful. This result has been correlated with other studies specifically concerning manganese. This criterion is significant because the substitution of cobalt by manganese, in few proportion, induces a material cost reduction because cobalt is an expensive metal and manganese does not modify the material structure.

References

- [1] C. Delmas, I. Saddoune, A. Rougier, J. Power Sources 43 (1993) 595.
- [2] H. Arai, S. Okada, Y. Sakurai, J. Yamaki, J. Electrochem. Soc. 144 (1997) 3117.
- [3] R. Alcantara, P. Lavela, J.L. Tirado, R. Stoyanova, E. Zhecheva, J. Electrochem. Soc. 145 (1998) 730.
- [4] E. Levi, M.D. Levi, G. Salitra, D. Aurbach, R. Oesteu, U. Heider, L. Heider, Solid State Ionics 126 (1999) 97.
- [5] T. Ohzuku, A. Ueda, M. Naragayama, J. Electrochem. Soc. 140 (1993) 1862.
- [6] W. Li, J.N. Reimers, J.R. Dan, Solid State Ionics 67 (1993) 123.
- [7] M. Tabuchi, K. Ado, H. Kobayashi, H. Sakaebe, H. Kageyama, C. Masquelier, M. Yonemura, A. Hirano, R. Kanno, J. Mater. Chem. 9 (1999) 199.
- [8] B. Garcia, P. Barboux, F. Ribot, A. Kahn-Harari, L. Mazerolles, N. Baffier, Solid State Ionics 80 (1995) 111.
- [9] S. Bach, M. Henry, N. Baffier, J. Livage, J. Solid State Chem. 88 (1990) 325.
- [10] P. Barboux, J.M. Tarascon, F.K. Shoccohi, J. Solid State Chem. 94 (1991) 185.