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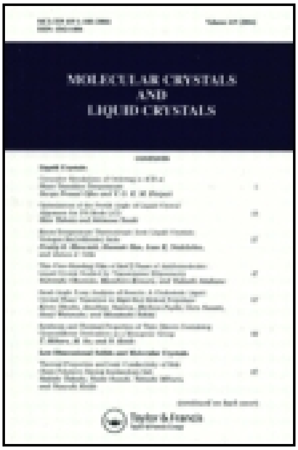

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Low Temperature Synthesis of $LiNiO_2$ and $LiCoO_2$: Comparison, Stability and Reaction Mechanism

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Low Temperature Synthesis of $LiNiO_2$ and $LiCoO_2$: Comparison, Stability and Reaction Mechanism

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Abstract

A thorough study concerning the formation of $LiNiO_2$ by a low temperature exchange reaction under hydrothermal conditions has been made. $LiNiO_2$ with low degree of cationic mixing and good electrochemical performances was prepared from NiOOH. $LiCoO_2$ is obtained from CoOOH using the same procedure. The synthesized products (LT-$LiNiO_2$) present electrochemical properties similar to those of $LiNiO_2$ prepared by conventional powder synthesis (HT-$LiNiO_2$) in spite of the difference in BET surface area : 20 m^2/g for LT-$LiNiO_2$ and 0.7 m^2/g for HT-$LiNiO_2$. We found the thermal and moisture stability of our LT-$LiNiO_2$ prepared material to be much lower than that of HT made material. Furthermore, this instability was found to be 1) intrinsic to the material and not due to the synthetic method 2) enhanced by decreasing the $LiNiO_2$ particle size, and 3) much lower than that of $LiCoO_2$. A complete mechanism is proposed to describe the correlation between the stability of the Ni based lithiated oxides in reducing conditions and their stability over moisture. Finally, in view of electrochemical applications, cobalt substituted products should be used in order to ensure the stability both against reduction-delithiation and hydrolysis.

Introduction

Among the various electrochemical systems and technologies used for secondary batteries, the Li-ion rechargeable cells are the most promising in view of application for electronics **[1]**. This interest has prompted the search for Li-M-O materials showing high reversible insertion capacity versus Li and good cycling behavior upon cycling. $LiMn_2O_4$, $LiNiO_2$ and $LiCoO_2$ are actually the best candidates for large scale productions of " rocking-chair " cells using graphite as negative electrode **[2]**. Despite the cost and toxicity of cobalt, $LiCoO_2$ is up to now the only cathode material found in

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commercialized rechargeable Li-ion cells (Sony). In contrast, $LiNiO_2$ is cheaper and less toxic but the Li-Ni-O system is characterized by the existence of a $Li_{1-y}Ni_{1+y}O_2$ solid solution making its synthesis difficult. This Li/Ni mixing results in the presence of Ni^{2+} within the Li layers, detrimental to the electrochemical performances of the material (low capacity and high polarization). **[3,4]**

To alleviate this issue, many attempts have been made to prepare these phases at lower temperatures using several routes such as mecanochemical syntheses, sol-gel processes, use of metallorganic precursors and exchange processes in molten salts or organic media. **[5-7]** The resulting materials showed low reversible capacities and needed further heating treatments involving temperatures as high as those used in the conventional solid state synthesis in order to enhance their electrochemical performances. In previous papers **[8,9]** we demonstrated the possibility of synthesizing $LiMO_2$ (M= Co, Ni) from MOOH by a low temperature ion exchange reaction under hydrothermal conditions. A study was also made on the influence of several parameters during the $LiNiO_2$ synthesis. Among them, the composition of the initial mixture and especially its water content, was found to be crucial for the success of the synthesis. The so-obtained optimized LT-$LiNiO_2$ shows electrochemical performances that compare favorably with those of HT-$LiNiO_2$. However, given the difficulty in preparing pure β-NiOOH and the effect of the impurities on the result of the synthesis, other precursors such as γNiOOH have been used as well. **[10]**

In this present paper we focused on the chemical and electrochemical properties of LT-$LiMO_2$ (M= Co, Ni) and more specifically on their thermal and moisture stability.

Experimental

$LiNiO_2$ was synthesized by cationic exchange under hydrothermal conditions using NiOOH (home made) and $LiOH{\cdot}H_2O$ (Prolabo > 98 %) as starting products. The reaction parameters such as temperature, reaction time, pressure, and reagents ratio were optimized as described elsewhere.**[9]** All the reactions were thus performed at 160°C for two days under a 60 bar air pressure in an autoclave device. The starting reaction mixture consisted of $NiOOH/LiOH{\cdot}H_2O/H_2O$ in a weight ratio of 1/10/10. LT-$LiNi_{1-y}Co_yO_2$ was obtained in the same way using β-$Ni_{1-y}Co_yOOH$ as starting product. X-ray Diffraction (XRD) analyses were performed with a Philips PW 1710/1729 diffractometer using CuK_α radiation (1.5418 Å). Infrared spectra were obtained using a Nicolet 510 FT-IR spectrophotometer. Electrochemical tests were made with Swagelok™ cells. The positive electrode was usually prepared by mixing $LiNiO_2$ powder with 20 %wt black carbon (SP) or using

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the Bellcore's plastic technology PLiON™. Cells were tested on a MacPile Macintosh controlled (Bio-Logic, Claix, France). Cycling data were collected between 3.0 and 4.1 V at a rate of C/35. TGA analysis was carried out using a Setaram TGDTA92 thermobalance. Specific surface areas were measured with a Micromeritics Gemini 2375 system according to the BET multi-point. The grinding treatments were performed with a Fritsch P7 planetary miller.

Results and discussion

Once the synthesis parameters optimized **[10]**, the $LiNiO_2$ materials obtained by cationic exchange showed electrochemical performances that compare favorably with those of HT made material **(Figure 1)**.

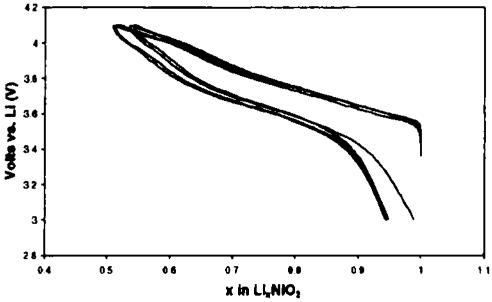

Figure 1 : Electrochemical curves of LT-$LiNiO_2$ made by cationic exchange from γ-NiOOH

The effects of thermal treatments on the electrochemical properties of LT-$LiNiO_2$ were already described **[10]**, and it was shown that heating induced cationic mixing and reduction of nickel even at low temperatures (200°C). Thus, we decided to study in detail the origin of these changes.

Stability of LT-$LiNiO_2$ upon heating

Thermogravimetric analyses were performed on LT-$LiNiO_2$ both under oxygen and argon up to 600°C. In both cases there is a large weight loss centered at about 180°C **(Figure 2)**. The XRD pattern collected after the first weight loss already shows that the starting product is degraded and indicates the presence of some Ni^{2+} ions in the interlayer space (i.e. increase in y value in $Li_{1-y}Ni_{1+y}O_2$) and suggests that a partial reduction-delithiation of the material takes place as well. This weight loss was related to water departure by performing an "in-situ" IR experiment as a function of temperature that

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showed that the absorption bands of water gradually diminished in intensity with temperature to disappear above 200 °C.

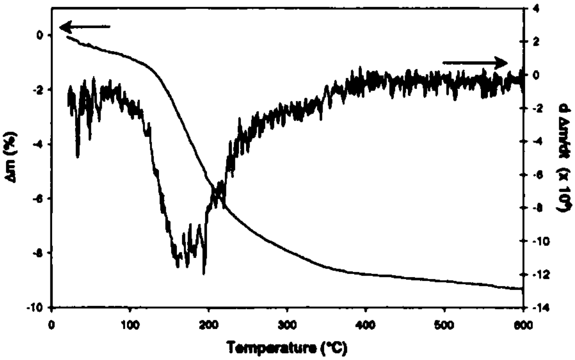

Figure 2 : Thermogravimetric analysis of LT-$LiNiO_2$

Since the synthesis of $Li_{1-y}Ni_{1+y}O_2$ proceeds in aqueous media and through a H^+/Li^+ exchange, the presence of adsorbed water and intercalated protons besides Li^+ resulting in a formula $(H,Li)_{1-y}Ni_{1+y}O_2$ must be considered. Such a formula for our exchanged materials will result in a weight loss in the TGA measurements according to the departure of protons. However, it is difficult to distinguish between the water losses resulting from adsorbed water and the departure of protons. On the other hand, we can ensure that protons cannot be only taken into account to explain this feature since it will result in a H^+ content higher than one per nickel. Although the presence of large amount of Li_2CO_3 in our samples make unfeasible their chemical analysis, electrochemical studies showed that their H^+ content could be considered to be very low. **[10]** An heating treatment under air at 400°C applied to HT-$LiNiO_2$ did not show any variation in its XRD pattern, thus indicating that it remains unaltered. The presence of adsorbed water and/or protons in LT-$LiNiO_2$ then appears to govern its different behaviors with respect to HT-$LiNiO_2$. However, the way water molecules would be "bonded" to the structure is not clear. The fact that the cell parameters of LT-$LiNiO_2$ are similar to those of HT-$LiNiO_2$ despite the large amount of water measured on the LT-$LiNiO_2$ sample, would be in favor of adsorbed rather than intercalated water.

Stability of ground HT-$LiNiO_2$ upon heating

Since LT-$LiNiO_2$ material have much higher surface area than HT-$LiNiO_2$ (20 m^2/g and 0.7 m^2/g, respectively), we ground HT-$LiNiO_2$ (13 m^2/g) and studied its evolution upon heating under air. The XRD patterns of the heated product and of the non-heated one **(Figure 3)** clearly show that a

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degradation (e.g. increase in y value) of the ground sample takes place at 400°C although the non ground one is unaltered. This demonstrates a direct effect of the surface area on the stability of LiNiO$_2$ and that this instability is intrinsic to the material and not due to the synthetic method.

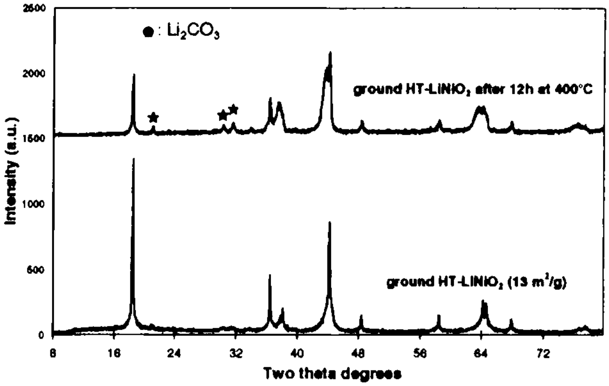

Figure 3 : XRD evolution of ground HT-LiNiO$_2$ upon heating under air

Stability of LiMO$_2$ (M= Co, Ni) upon moisture

Since we previously showed the role of water on the stability of LiNiO$_2$, we studied the stability of LiMO$_2$ (M= Co, Ni) upon moisture and the effect of the surface area. For that, a small batch of powder is poured in water and left for one day. The amount of lithium loss in solution is measured and XRD patterns of the resulting powders are taken. This study showed that 1) ground HT-LiNiO$_2$ is less stable in water than not ground HT-LiNiO$_2$ 2) HT-LiNiO$_2$ is partially delithiated/reduced in water 3) LT-LiCoO$_2$ (29 m^2/g) is perfectly stable in water as well as HT-LiCoO$_2$ (0.3 m^2/g) 4) the stability in water is enhanced when Ni is partially substituted for Co (**Figure 4**).

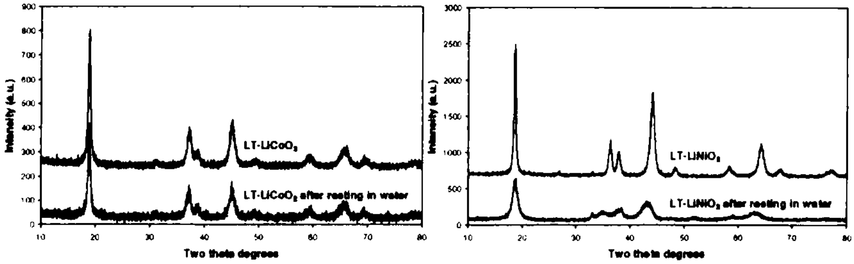

Figure 4 : Evolution of LT-LiNiO$_2$ and LT-LiCoO$_2$ after resting in water for one day at 25°C. Note the degradation of LT-LiNiO$_2$.

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From these results, a complete scheme of reaction can be proposed to describe the thermal and moisture instability of $LiNiO_2$ (**Figure 5**).

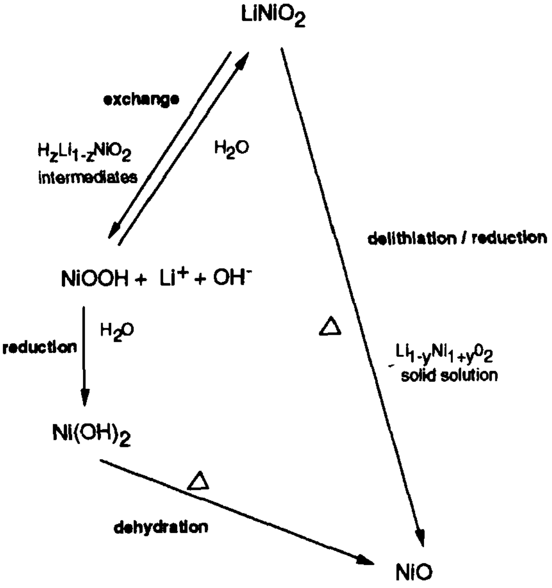

Figure 5 : Decomposition paths for $LiNiO_2$ in water and upon heating

In view of $LiNiO_2$ application in lithium-ion batteries the need for stabilization means is clear. For that, Ni for Co partial substitution seems to be a more versatile approach compared to a storage of $LiNiO_2$ in dry atmosphere. Furthermore, starting from β-$Ni_{1-y}Co_yOOH$, our LT synthetic method was successfully applied to the preparation of $LiNi_{1-y}Co_yO_2$ that show good electrochemical performances (**Figure 6**).

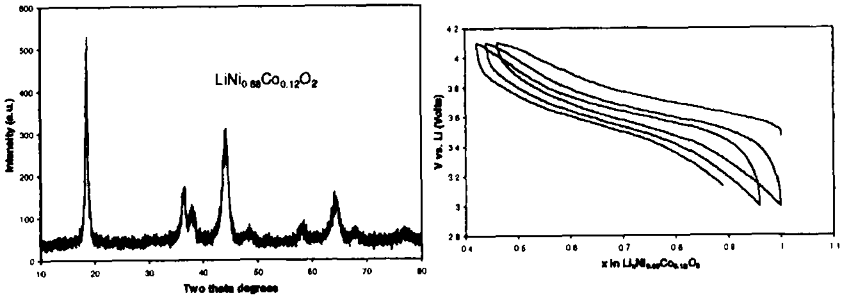

Figure 6 : XRD pattern and electrochemical curve of LT-$LiNi_{0.88}Co_{0.12}O_2$

Conclusion

We have studied the synthesis of $LiNiO_2$ by a low temperature ion-exchange reaction starting from NiOOH. The effect of the composition of the starting product was stressed. $LiNiO_2$ with a low degree of cationic mixing and therefore good electrochemical performances was prepared either from pure β-NiOOH, γ-NiOOH, or a mixture of both where the γ phase is the majority. The synthesis was successfully extended to $LiNi_{1-y}Co_yO_2$ as well. The stability of both LT and HT-$LiNiO_2$ upon moisture or heating was tested. The fact that $LiNiO_2$ was found to be unstable upon delithiation/reduction and hydrolysis stresses the importance of cobalt substitution in this phase in view of its practical application in Li-ion batteries. Up to now, cobalt substitution was known to enhance the resistance of the samples against reduction upon heating, thus simplifying the synthetic process. Another very important advantage of the cobalt substitution, as documented herein, is also to enhance the stability of the $LiNiO_2$ phase towards moisture.

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