Synthesis and Electrochemical Properties of $LiNiO_2$ Prepared *via* an Aqueous Solution Technique

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$LiNiO_2$ cathode materials have been prepared using a soft chemistry route. Precipitation of hydroxide is followed by drying and heating in the temperature range 650-900 °C under oxygen flow and leads to shorter preparation time than with powders mixing methods usually used. The sample $LiNiO_2$ obtained at 700° C shows the best electrochemical behaviour. This has been attributed to a low lithium deficiency.

The sol-gel process and a precipitation technique have been applied to prepare cathode materials such as $LiMn_2O_4$ and $LiCoO_2$ with a spinel structure and original electrochemical features.[1,2] $LiNiO_2$ is more attractive than $LiCoO_2$ for Li-ion batteries due to its lower cost and higher discharge capacity but, this compound shows structural and compositional variations depending on their preparation conditions.[3-5] Due to the difficulty to oxidize Ni^{2+} into Ni^{3+}, Li deficient compounds $Li_{1-x}Ni_{1+x}O_2$ ($x<1$) are generally obtained. The Li deficiency is associated with the presence of Ni^{2+} ions in Li layers (3a sites) which may disturb Li intercalation-deintercalation process and significantly affect $LiNiO_2$ charge-discharge characteristics.[6] More homogeneous cathode materials can be expected from the use of an aqueous solution technique involving a more intimate and more reactive mixing of the various reagents. The possibility to take advantage of a wide temperature range available for heat treatment is particularly attractive in the field of $LiNiO_2$ synthesis to control and to limit Li deficiency. In the present work, a new synthesis way of $LiNiO_2$ by using precipitation reactions is evaluated to yield a high performance $LiNiO_2$ cathode material. Preliminary results on its electrochemical properties are reported.

$LiNiO_2$ samples were obtained by a precipitation process in aqueous solution. A solution of 1M LiOH and 3M NH_4OH is mixed to a 1M $Ni(NO_3)_2$ solution with stirring in a ratio Li/Ni=1. A gelatinous green precipitate is obtained and the remaining water and ammonia are slowly removed in a rotary evaporator at 70 °C under primary vacuum. The resulting powder is then dried in air for 12 h at 100 °C. At this stage the samples probably consist of LiOH, $Ni(OH)_2$ and $LiNO_3$ intimely mixed and NH_4NO_3. $LiNiO_2$ is obtained after calcination under oxygen in a tubular furnace for 18 h at 650 °C or for 5 h in the temperature range 700-900 °C. After heating, the samples are quenched to room temperature in air. Chemical analysis give for the sample obtained at 650 °C the formula $Li_{0.9}Ni_{1.1}O_2$ and for the others $Li_{0.97}Ni_{1.03}O_2$ (error=±0.02). Rietveld analysis performed on $LiNiO_2$ obtained at 700 °C confirms chemical analysis and leads to the formula: $[Li_{0.966}Ni_{0.034}]_{3b}[Ni]_{3a}[O_2]_{6c}$. An other synthesis way using the same reagents but with a large excess of lithium have been reported for preparing highly stoichiometric oxides.[7] The electrochemical characteristics of $LiNiO_2$ were determined by using a three-electrode electrochemical cell. Other details are given in reference.[2]

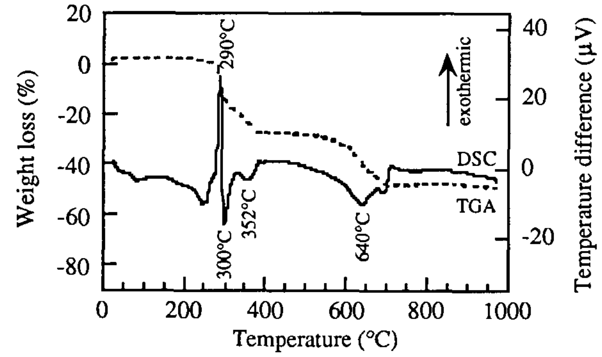

Figure 1. Thermal analysis under air of the lithium-nickel precipitate (heating rate 10 °C/min).

The simultaneous recorded thermal analysis curves of weight losses (TGA) and temperature variations (DSC) of the precipitate, are shown in Figure 1. The first exothermic peak at 290 °C associated with an important weight loss (15%) involves the decomposition of NH_4NO_3 into N_2O. Melting of $LiNO_3$ which gives rise to an endothermic peak near 300 °C probably enhances the reactivity of Li with a nickel-based compound. A second and important weight loss (10%) ranging from 300 to 400 °C can be ascribed to the transformation of $Ni(OH)_2$ to nickel oxide (endothermic peak near 352 °C) with water departure. A final significant weight loss correlated with the ill-defined endothermic peak at 640 °C corresponds to the departure of the remaining nitrates and to the formation of crystallized $LiNiO_2$.

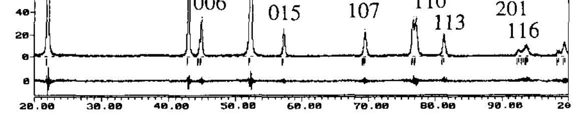

Figure 2: Observed (···), calculated (__) and difference plots for the compound $LiNiO_2$ prepared at 700 °C for 5 h (λ $CoK_{\alpha1}$).

Figure 2 shows observed , calculated and difference patterns for the compound $LiNiO_2$ prepared at 700 °C for 5 h. Final convergence was obtained with the following R factors:[8]

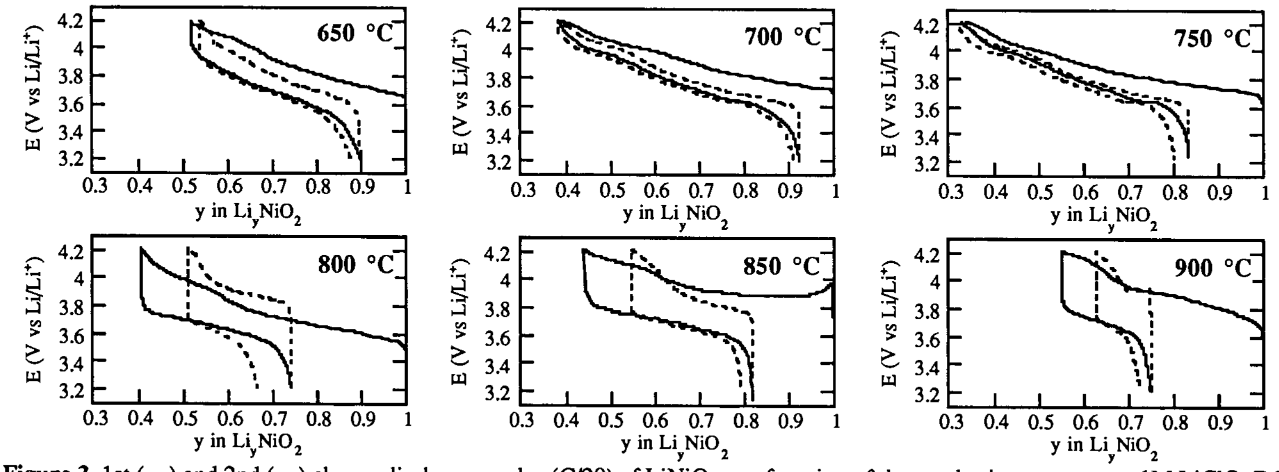

Figure 3. 1st (—) and 2nd (---) charge-discharge cycles (C/20) of $LiNiO_2$ as a function of the synthesis temperature, 1M $LiClO_4$/PC.

R_b=7.51, R_f=3.59, R_p=12.2 and R_{wp}=17.5. All the peaks can be indexed in the trigonal space group R$\bar{3}$m without impurities. $LiNiO_2$ structure can be described as a layered structure consisting of alternating Li and Ni layers where Li and Ni atoms are respectively in octahedral (3a) and (3b) sites in a cubic close-packed oxygen array. X-ray experiments show a slight fitness of diffraction lines when the temperature of synthesis increases which indicates a better crystallinity. 2.87 Å and 14.14 Å are a and c calculated parameters of the 650 °C sample. For the other samples, whatever the temperature the a and c parameters remain nearly unchanged: a=2.88 Å, c=14.20 Å for the 700 °C sample which is close to those found for all solid state prepared materials.[3]

The electrochemical results are presented in Figure 3. The best results are obtained for the temperatures 700 and 750 °C and particularly for the 700 °C sample. Indeed, the charge voltage in both cases gradually increases from 3.6 to 4.2 V and corresponds to an initial extraction of about 0.65 Li^+ ions from the structure. The subsequent discharge occurs without any noticeable polarization and gives rise to an important faradaic yield of 0.54 F/mole. This corresponds to a specific capacity of 160 Ah/kg while the second cycle confirms the reversible behaviour of these compounds. From the first cycle, near 0.1 Li^+ ions remain irreversibly trapped in the oxide. The poor electrochemical features of the sample crystallized at 650 °C are expected on account of its large Li deficiency. This is due to a disordered cationic distribution at the Li sites which is minimized at 700 and 750 °C. Oxides obtained at 800, 850 and 900 °C give rise to a poor electrochemical behaviour accompanied with a high polarization phenomenon, and especially low reversible capacities. The initial charge capacity decreases from 0.6 to 0.45 when temperature increases from 800 to 900 °C. For instance, a discharge capacity of only 0.2 F/mole is recovered with the 900 °C sample while 300 mV separate the reduction-oxidation process. The poor performance for heat-treated compounds ($T \geq 800$ °C) probably accounts for the presence of Ni^{2+} in the phase.[3,9,10] For high temperature treatments, the instability of Ni^{3+} leads to the decomposition of $LiNiO_2$ into an oxide which presents a large amount of extra nickel in the Li planes[11] hindering the Li ordering which is assumed to be responsible for the monoclinic distorsion during deintercalation. In addition, the thickness of the interslab space is known to decrease making the Li reintercalation and diffusion more and more difficult.

References and Notes

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