

## **THERMAL BEHAVIOUR OF CHEMICALLY DEINTERCALATED $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$**

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The thermal behaviour of chemically deintercalated samples obtained by HCl treatment of non-stoichiometric Li/Ni mixed oxides is studied. A multi-step reduction of Ni with  $\text{O}_2$  evolution is observed between room temperature and  $800^\circ\text{C}$ . Two cation redistribution processes are shown by the exothermal occurrence of a spinel phase at  $300^\circ\text{C}$  and the endothermal reduction to a rock-salt phase with random distribution of Li and Ni cations in octahedral sites at  $800^\circ\text{C}$ .

**Keywords:** Li/Ni mixed oxides, non-stoichiometric oxides

### **Introduction**

The structure and reactivity of lithium/transition-metal mixed oxides has been studied in depth in recent years due to the interest in their intercalation-deintercalation and cation-exchange chemistry. Many of these oxides have NaCl-related structures, which include ordered variants, as rhombohedral  $\text{LiMO}_2$  (M: V, Cr, Co and Ni) [1], and phases with a random cation-distribution as  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  [2]. The products of chemical and electrochemical deintercalation of these oxides sometimes show an interesting thermal behaviour due to their possible conversion in other structural variants [3]. Thus,  $\text{LiV}_2\text{O}_4$  shows a rhombohedral structure at room temperature and normal cubic spinel structure at  $300^\circ\text{C}$  [4].

Non-stoichiometric mixed oxides of general formula  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  were first prepared by heating mixtures of Ni(II) carbonate and lithium carbonate at  $800^\circ\text{--}900^\circ\text{C}$  in  $\text{O}_2$  atmosphere [5]. Changes in the experimental conditions – temperature,  $\text{O}_2$  flow rate – have a direct effect in the chemical composition of the products. These oxides have rhombohedral,  $\alpha\text{-NaFeO}_2$ -related

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structure ( $\text{CdCl}_2$  derived), with  $\alpha$  close to  $60^\circ$ . Electrochemical lithium deintercalation in  $\text{LiNiO}_2$  has been carried out in a galvanostatic cell, with variable current density [6]. The product had  $\text{Li}_{0.5}\text{NiO}_2$  composition, maintaining the rhombohedral structure of the original sample, which is transformed into the normal cubic spinel phase  $\text{LiNi}_2\text{O}_4$  above  $250^\circ\text{C}$ . Chemical deintercalation in aqueous media of  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  was recently reported [7].

This work reports a study on the thermal behavior of chemically deintercalated  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ . The conditions for the formation of NaCl and spinel related phases are discussed.

### Experimental

Li/Ni mixed oxide samples were obtained by annealing mixtures of Ni(II) hydroxycarbonate and lithium carbonate at  $875^\circ\text{C}$  for 18 h under a constant  $\text{O}_2$  flow-rate. The products were washed with absolute ethanol, dried at  $100^\circ\text{C}$  and stored in a vacuum desiccator with  $\text{P}_4\text{O}_{10}$ . Chemical deintercalation was carried out by adding 100 ml 1:50 v/v 36% HCl to 2.5 g of sample at room temperature and stirring during 20 h. The solid products were washed with distilled water and dried at  $100^\circ\text{C}$ .

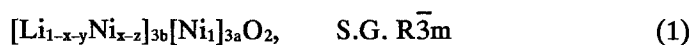
TG traces were recorded on a Cahn 2000 electrobalance at a 10 deg/min heating rate under a static air atmosphere. The gaseous products formed in the thermal decomposition were analysed on a Quadruvac Q100 mass spectrometer provided with a Faraday QF200 detector. Thermally transformed samples were obtained by interrupting TG experiments at selected temperatures. DSC traces were obtained in static air atmosphere at a 10 deg/min heating rate with a Mettler TA3000 apparatus previously calibrated with an indium metal sample.

Li/Ni ratios were determined by atomic absorption spectrometry. The average oxidation state of Ni was determined by back-titration with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  by a procedure described elsewhere [7]. XRD patterns were obtained with a Siemens D500 diffractometer using  $\text{CuK}\alpha$  radiation and a graphite monochromator.

### Results and discussion

The mixed oxide samples obtained by the ceramic method had variable Li/Ni ratios and average oxidation state of Ni, depending on the value of  $\text{O}_2$  flow-rate used in the preparation. The XRD patterns of all samples were in-

dexable in the  $R\bar{3}m$  s.g. with variable  $a$  and  $\alpha$  values. As reported earlier [7], Li/Ni ratios close to unity imply a higher divergence of  $\alpha$  from the value corresponding to a NaCl structure ( $60^\circ\text{C}$ ). After HCl treatment, lithium and nickel deintercalation of variable magnitude was detected in the resulting solids, simultaneously to a partial dissolution. Analogous behavior has been described in the acid treatment of  $\text{LiMn}_2\text{O}_4$  (spinel structure) to yield  $\lambda\text{-MnO}_2$  [8]. The resulting solid samples are characterized by higher Ni average oxidation states than the original samples. In addition, deintercalated samples maintain the parent rhombohedral structure, as a result of the topotactic nature of the process. The approximate cation distribution of these solids, as determined by Rietveld analysis [7] may be adjusted to the general formula:



where  $y$  and  $z$  are the deintercalated amounts of Li and Ni, respectively.

Four chemically deintercalated samples, henceforth referred to as A–D, were obtained by consecutive periods of HCl treatment of  $\text{Li}_{0.77}\text{Ni}_{1.23}\text{O}_2$ . The chemical analysis data show that the metal (Li + Ni)/oxygen (M/O) and Li/Ni ratios decrease from sample A to D (Table 1) while they fit to the general formula (1) with  $x \approx 0.23$ . The rhombohedral parameter  $\alpha$  takes values lower than those observed in the original sample and decreases with  $(y + z)$  (Table 1).

**Table 1** Chemical composition and unit cell parameters of the original and chemically delithiated samples. Evolution of metal/oxygen ratio with temperature

Sample	M/O			$a/\text{\AA}$	$\alpha/^\circ$	M/O 300°C	M/O 800°C
	Li/Ni	25°C	Formula				
Original	0.63	1.00	$\text{Li}_{0.77}\text{Ni}_{1.23}\text{O}_2$	5.76(6)	60.0(1)	–	–
A	0.38	0.83	$\text{Li}_{0.45}\text{Ni}_{1.20}\text{O}_2$	5.77(2)	59.6(3)	–	1.01
B	0.32	0.75	$\text{Li}_{0.36}\text{Ni}_{1.14}\text{O}_2$	5.75(9)	58.9(0)	0.76	1.00
C	0.26	0.72	$\text{Li}_{0.30}\text{Ni}_{1.14}\text{O}_2$	5.75(0)	58.8(8)	0.76	1.00
D	0.24	0.71	$\text{Li}_{0.27}\text{Ni}_{1.14}\text{O}_2$	5.75(2)	58.8(8)	0.76	0.99

The TG curves of A–D samples (Fig. 1) show weight loss effects between  $320^\circ\text{--}550^\circ\text{C}$  which have an endothermic nature, as shown by the DSC traces (Fig. 2a–c). In these plots, a complex endotherm showing two or three overlapping endothermic peaks is observed between  $320^\circ$  and  $550^\circ\text{C}$ . It should be noted that the DSC trace of the non-deintercalated sample shows no thermal effect, in contrast to previous work on nearly-stoichiometric

$\text{LiNiO}_2$  [1]. The products obtained at  $800^\circ\text{C}$  show a decrease of the average oxidation state of nickel and an increase of the M/O ratio (Table 1) while the Li/Ni ratio remains constant during thermal treatment. It is worth noting that the weight loss observed in the TG curves is higher for samples with lower M/O ratios. These facts imply a Ni reduction process. The spectrometric analysis of the evolved gases (Fig. 2d) agree with this interpretation, as  $\text{O}_2$  is detected in the temperature intervals in which the endothermic effects occur.

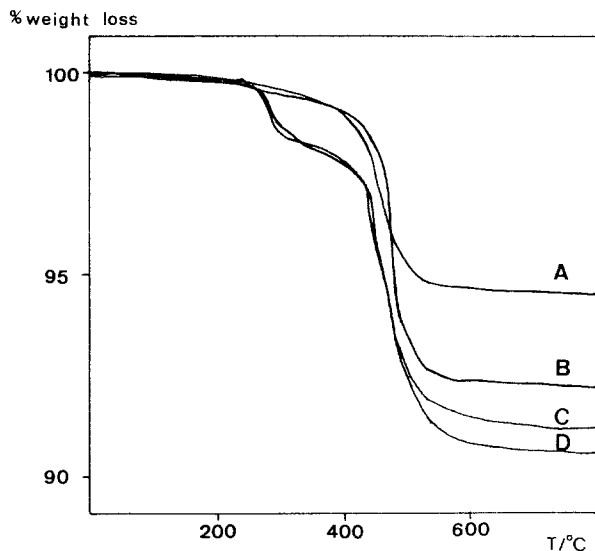


Fig. 1 TG curves of A-D samples

On the other hand, the XRD patterns of the samples obtained at  $800^\circ\text{C}$  (Fig. 3) show the presence of mixtures of rhombohedral and NaCl-related phases. In the latter phases, a random distribution of Li and Ni in the octahedrally coordinated sites is expected, as found in  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  for  $x < 0.3$  [2]. Only for samples with enhanced lithium deintercalation (samples C and D), the pattern is indexable in the cubic phase exclusively. The range in which the solid solution maintains the NaCl structure may be the origin of this behaviour. Thus it can be concluded that from room temperature to  $800^\circ\text{C}$ , the reduction process is accompanied by a redistribution of cations between the octahedrally coordinated sites, leading to random distribution when Li contents allow a rock-salt structure.

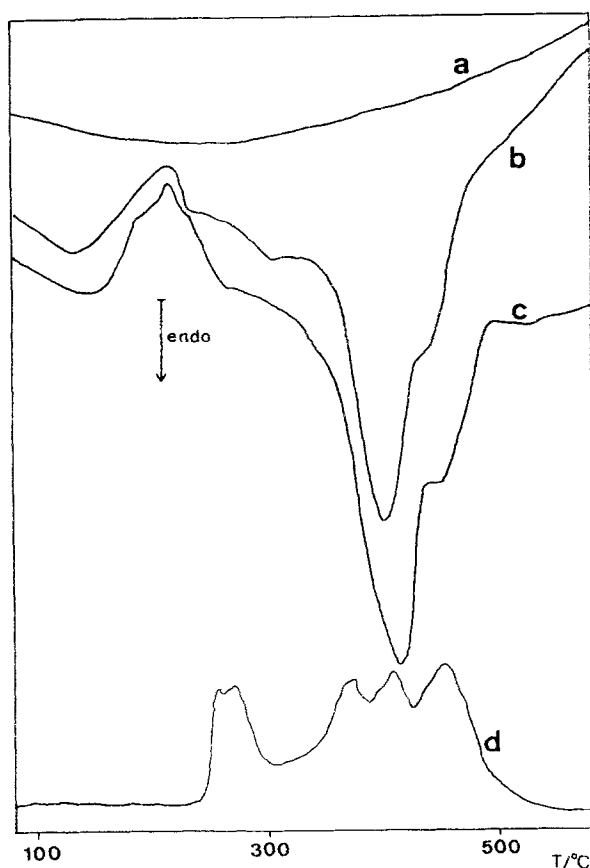


Fig. 2 DSC curves of A–D samples (a, b, c) and spectrometry results (d)

As the degree of deintercalation increases, the TG traces (Fig. 1) show a progressive increase in the intensity of an additional weight loss effect, centered between 150° and 300°C. This effect is also associated to an O<sub>2</sub> release as shown by the spectrometry measurements (Fig. 2d). The experimental O/M (Table 1) ratios are also in agreement with a low-magnitude reduction of Ni in the samples. On the other hand, the DSC traces of samples A–D show the progressive development of an exothermic effect with peak temperature at 240°C (see for example Fig. 2b and c). If nickel reduction is assumed to be endothermic, an additional exothermic process should take place simultaneously, leading to a net exotherm. The DRX patterns of samples prepared by interrupting the TG experiments at 300°C of samples C and D (Fig. 3, sample C) give new light on the nature of this process. Besides the reflections corresponding to a rhombohedral phase, the

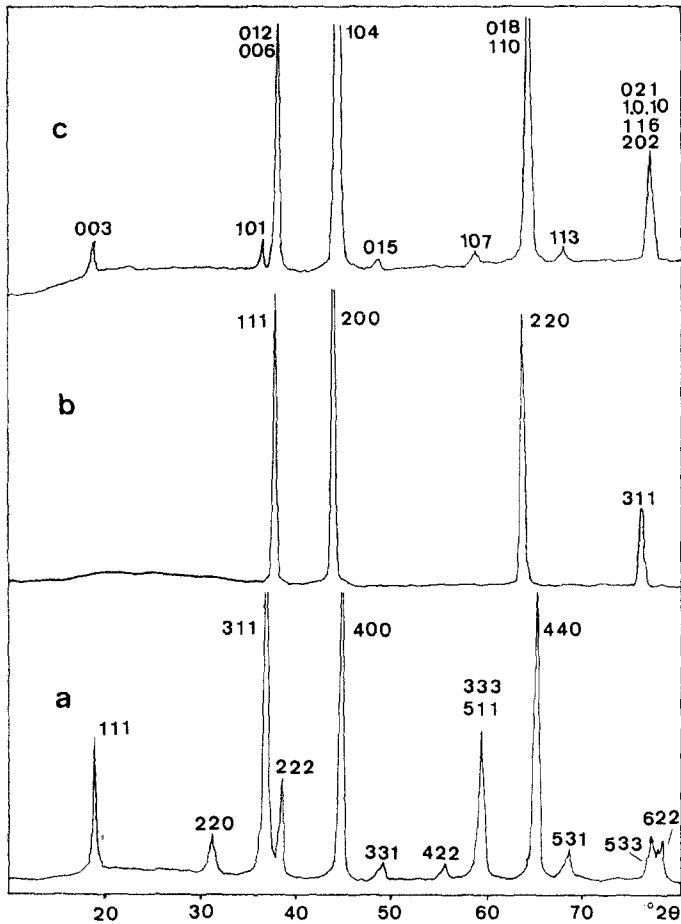


Fig. 3 DRX patterns of sample C prepared by interrupting the TG experiment at 300°C

DRX patterns show the occurrence of several reflections which are indexable in the  $Fd3m$  s.g. with a unit cell parameter close to 8 Å. This spinel-related phase is similar to that obtained by thermal treatment of electrochemically deintercalated  $\text{LiNiO}_2$  [6]. Thus, it can be concluded that the phase transition leading to the spinel phase is exothermic. Although the nature of the accompanying reduction may be endothermic, a net exotherm is observed in the DSC traces. In addition, the degree of formation of the spinel phase is enhanced for high oxidation states of Ni and low Li/Ni ratios in the chemically deintercalated samples.

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**Zusammenfassung** — Es wird das thermische Verhalten von Proben untersucht, die durch Einwirkung von HCl auf nichtstöchiometrische Li/Ni-Mischoxide erhalten wurden. Im Bereich zwischen Raumtemperatur und 800°C wird eine mehrstufige Reduktion von Ni unter Freisetzung von Sauerstoff beobachtet. Durch das exotherme Auftreten einer Spinellphase bei 300°C und die endotherme Reduktion zu einer Steinsalzphase mit einer Random-Verteilung der Li- und Ni-Kationen an oktaedrischen Stellen bei 800°C wurden zwei Kationen-Neuverteilungsprozesse aufgezeigt.