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# Thermal behavior and the decomposition mechanism of electrochemically delithiated $\text{Li}_{1-x}\text{NiO}_2$

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## Abstract

Thermal behavior of  $\text{Li}_{1-x}\text{NiO}_2$  ( $R\bar{3}m$  or  $C2/m$ ) up to  $400^\circ\text{C}$  was studied using thermogravimetry (TG), differential scanning calorimetry (DSC), and high-temperature X-ray diffraction measurements and its decomposition mechanism was proposed. Delithiated  $\text{Li}_{1-x}\text{NiO}_2$  was thermally decomposed to  $\text{LiNi}_2\text{O}_4$  spinel ( $Fd\bar{3}m$ ) at the temperature range of  $180\text{--}250^\circ\text{C}$ . For  $x \leq 0.5$ ,  $\text{Li}_{1-x}\text{NiO}_2$  was decomposed to  $\text{LiNiO}_2$  and  $\text{LiNi}_2\text{O}_4$  and the fraction of the spinel in the decomposed product increased almost linearly with  $x$ . For  $0.5 < x \leq 0.8$ ,  $\text{Li}_{1-x}\text{NiO}_2$  was converted into  $\text{LiNi}_2\text{O}_4$  spinel and this reaction was accompanied by oxygen evolution.  $\text{Li}_{1-x}\text{NiO}_2$  of all compositions turned into a rock-salt phase ( $Fm\bar{3}m$ ) with oxygen liberation at temperatures above  $270^\circ\text{C}$ . The temperature for the decomposition of  $\text{Li}_{1-x}\text{NiO}_2$  to a spinel or a rock-salt phase decreased with  $x$  in  $\text{Li}_{1-x}\text{NiO}_2$ . The thermal behavior of  $\text{Li}_{1-x}\text{NiO}_2$  could be interpreted as an overlap of the exothermic rearrangement of cations (nickel and lithium ions) to form a spinel or a rock-salt phase and the endothermic oxygen evolution reaction. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium nickel oxide; Thermal behavior; Decomposition mechanism

## 1. Introduction

$\text{LiNiO}_2$  has been studied extensively as a cathode material because of its higher specific capacity (of  $200\text{ mAh/g}$ ) than that of  $\text{LiCoO}_2$  used commercially [1,2]. However,  $\text{LiNiO}_2$  has a few disadvantages compared to  $\text{LiCoO}_2$  as a cathode material for lithium secondary batteries. Its major disadvantages are: (i) difficulty in synthesis of an electrochemically active form because of its tendency for non-stoichiometry [2]; (ii) capacity fading with cycling resulted from the structural instability [1] and (iii) poor thermal stability due to the instability of nickel ions in the high oxidation state of +3 or +4 [3,4].

In particular, the thermal stability of the  $\text{LiNiO}_2$  has been considered as one of the most important properties that must be improved in order to apply this oxide to the lithium rechargeable batteries because the thermal instability of delithiated  $\text{Li}_{1-x}\text{NiO}_2$  causes safety hazard. Dahn et al. [3] have reported that the delithiated  $\text{Li}_{1-x}\text{NiO}_2$  is metastable and liberates oxygen at elevated temperatures and that the temperature at which oxygen evolution occurs depends

on  $x$  in  $\text{Li}_{1-x}\text{NiO}_2$ . Ohzuku et al. [5] have reported that  $\text{Li}_{0.15}\text{NiO}_2$  undergoes a few exothermic reactions at about  $200^\circ\text{C}$  and it has been suggested by other workers [4,6] that these exothermic reactions are caused by random redistribution of Ni and Li cations. However, the detailed decomposition mechanism of  $\text{Li}_{1-x}\text{NiO}_2$  including a formation of spinel or rock-salt phase, oxygen evolution and their dependence on the composition and temperature have remained ambiguous.

As part of a larger study to develop nickel-based lithium transition metal oxides with enhanced thermal stability, we examined the thermal behavior of a set of  $\text{Li}_{1-x}\text{NiO}_2$  by thermogravimetry (TG), differential scanning calorimetry (DSC), and high-temperature X-ray diffraction measurements and studied the detailed decomposition mechanism.

## 2. Experimental

$\text{LiNiO}_2$  was synthesized by reacting stoichiometric amount of  $\text{LiNO}_3$  (Aldrich Chemical Co.) and  $\text{Ni}(\text{OH})_2$  (Aldrich Chemical Co.). The mixture of  $\text{LiNiO}_2$  and  $\text{Ni}(\text{OH})_2$  was well mixed, pressed into pellets and precalcined at  $600^\circ\text{C}$  for 12 h in a stream of oxygen. The precalcined product was powdered, pressed into pellets and

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Table 1  
Composition and Rietveld refinement results for LiNiO<sub>2</sub>

$R_{WP}^a$	$a$ (Å)	$c$ (Å)	$z(O)$	Composition <sup>b</sup>	Cationic distribution
8.34	2.8813	14.201	0.2415	Li <sub>0.951</sub> Ni <sub>1.049</sub> O <sub>2</sub>	[Li <sub>0.948</sub> Ni <sub>0.052</sub> ] <sub>3a</sub> [Li <sub>0.003</sub> Ni <sub>0.997</sub> ] <sub>3b</sub> O <sub>2</sub>

<sup>a</sup>  $R_{WP} = [M / \sum(wI_O^2)]^{1/2}$ , where the quantity minimized is  $M = \sum w(I_O - I_C)$ , with  $I_O$  and  $I_C$  being the observed and calculated intensities and  $w$  a weight related to the error.

<sup>b</sup> Determined from the oxidation state of nickel ion obtained by iodometric titration.

reacted at 800°C for 24 h under oxygen flow. The reaction product was ground and stored in a desiccator. The crystal structure of LiNiO<sub>2</sub> was characterized by neutron diffraction measurement. The neutron powder diffraction data were analyzed by the Rietveld profile analysis using the general structure analysis system (GSAS) suite of program [7]. The classic reliability factors, defined in the caption for Table 1, were used.

Electrochemical lithium extraction was carried out with cells which have been described previously [8]. A composite electrode was prepared by mixing 88 wt.% LiNiO<sub>2</sub>, 6 wt.% acetylene black as a conducting material, and 6 wt.% polyvinylidene fluoride–hexafluoropropylene copolymers (Kynar FLEX 2801, Elf-Atochem America) as a binder dissolved in *n*-methyl-2-pyrrolidone. The mixed slurry was coated onto Al foil and dried for >24 h. Lithium foils were used as a reference electrode and a counter electrode and 1 M LiClO<sub>4</sub> in propylene carbonate (PC) was used as an electrolyte. All electrochemical measurements were conducted at room temperature in a glove box filled with purified argon.

In order to obtain a charged sample, the cell was charged to a desired composition at a constant current of 20-h rate. After a relaxation of several days, the electrode was taken from the cell. It was then washed with tetrahydrofuran and dried thoroughly in a vacuum. The structural change of the electrode with temperature was analyzed by high-temperature X-ray diffraction measurement after heating the electrode to a desired temperature. Thermal behavior of the charged compounds was measured with TG (TGA 2050, TA Instruments) and DSC (DSC 2010, TA Instruments) in an air atmosphere at a heating rate of 5°C/min.

### 3. Results and discussion

#### 3.1. LiNiO<sub>2</sub> powder characterization

The neutron diffraction pattern of the LiNiO<sub>2</sub> could be indexed assuming a space group of R $\bar{3}m$  and the Rietveld refinement results of the pattern using the GSAS suite of programs are listed in Table 1. More details including a neutron diffraction measurement and an assumption and constraints during the refinements were described previously [8]. The lattice parameters are in good agreement with previously reported values for stoichiometric LiNiO<sub>2</sub> [1,2].

#### 3.2. Thermal decomposition of Li<sub>1-x</sub>NiO<sub>2</sub>

Fig. 1 shows TGA results for the washed composite electrodes containing a series of Li<sub>1-x</sub>NiO<sub>2</sub>, an acetylene black and a PVDF–HFP copolymer at a heating rate of 5°C/min in an air atmosphere. The LiNiO<sub>2</sub> was quite stable and showed no significant weight loss over the entire temperature range. However, one or two steps of weight loss were observed in the delithiated Li<sub>1-x</sub>NiO<sub>2</sub> samples. For  $x \leq 0.5$ , a weight loss was observed only at temperatures above 330°C. And for the samples with  $x > 0.5$ , the weight loss was observed at around 220°C as well as at temperatures above 270°C.

It has been reported that Li<sub>0.5</sub>NiO<sub>2</sub> converts to spinel LiNi<sub>2</sub>O<sub>4</sub> (cubic, Fd3m) near 200°C [9]. For the  $x = 0.5$  sample, it was not necessary to release oxygen to form a spinel and, therefore, no weight loss was involved. However, for  $x > 0.5$ , the conversion of Li<sub>1-x</sub>NiO<sub>2</sub> to spinel was apparently accompanied by oxygen release, because there were more than four oxygen atoms for three cations in such samples. At higher temperatures Li<sub>1-x</sub>NiO<sub>2</sub> of all compositions converted to members of the series of Li<sub>y</sub>Ni<sub>1-y</sub>O (cubic, Fm3m) with rock-salt structure [3,4,6] and further weight loss was observed. The temperature at which the decomposition of Li<sub>1-x</sub>NiO<sub>2</sub> to a spinel or a rock-salt phase occurred decreased with  $x$ .

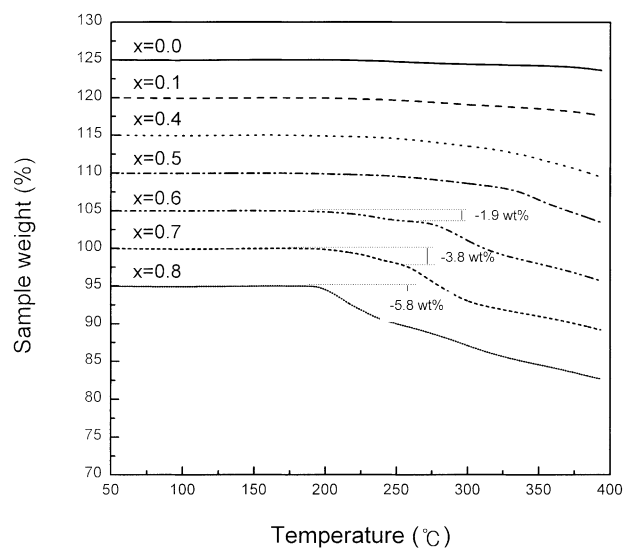


Fig. 1. TGA results for Li<sub>1-x</sub>NiO<sub>2</sub> composites in an air atmosphere at a heating rate of 5°C/min. The data have been offset vertically by 5% sequentially for clarify.

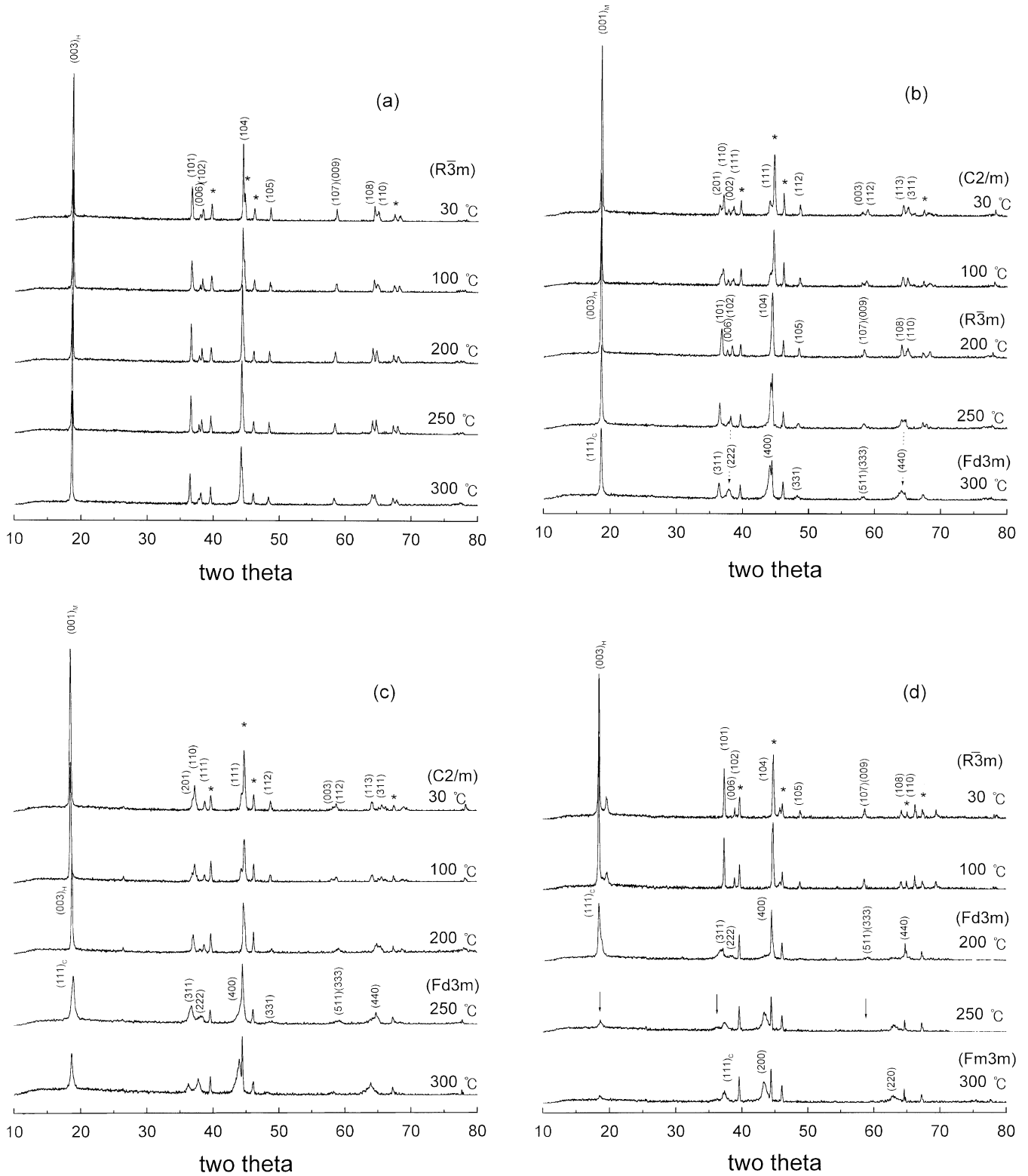


Fig. 2. X-ray diffraction patterns of (a)  $\text{Li}_{0.9}\text{NiO}_2$ ; (b)  $\text{Li}_{0.7}\text{NiO}_2$ ; (c)  $\text{Li}_{0.5}\text{NiO}_2$ , and (d)  $\text{Li}_{0.2}\text{NiO}_2$  at various temperatures after heating at a rate of  $5^\circ\text{C}/\text{min}$  (asterisk indicate Al foil and sample holder, Pt).

Delithiated  $\text{Li}_{1-x}\text{NiO}_2$  ( $R\bar{3}m$  or  $C2/m$ ) was thermally decomposed to a  $\text{LiNi}_2\text{O}_4$  spinel and a  $\text{Li}_y\text{Ni}_{1-y}\text{O}$  with rock-salt structure depending on  $x$  and the decomposition temperature. Therefore, the thermal decomposition of  $\text{Li}_{1-x}\text{NiO}_2$  to a spinel phase and to a rock-salt phase must be distinctly interpreted in order to understand the detailed thermal behavior of  $\text{Li}_{1-x}\text{NiO}_2$ .

### 3.3. Thermal decomposition to a spinel phase

Fig. 2 shows the X-ray diffraction patterns of  $\text{Li}_{1-x}\text{NiO}_2$  with  $x = 0.1, 0.3, 0.5$  and  $0.8$  at various temperatures measured during heating at a rate of  $5^\circ\text{C}/\text{min}$ . For  $\text{Li}_{0.9}\text{NiO}_2$ , the trigonal phase of  $R\bar{3}m$  was maintained over the entire temperature range excluding the small decrease in the distances between  $(0\ 0\ 6)$  and  $(1\ 0\ 2)$  peaks and  $(1\ 0\ 8)$  and  $(1\ 1\ 0)$  peaks in  $300^\circ\text{C}$ . However, monoclinic  $\text{Li}_{0.7}\text{NiO}_2$  converted to the trigonal phase at  $200^\circ\text{C}$  and then turned into the cubic phase with spinel structure at  $300^\circ\text{C}$  as indicated by the coalescence of the  $(0\ 0\ 6)$  and  $(1\ 0\ 2)$  peaks and  $(1\ 0\ 8)$  and  $(1\ 1\ 0)$  peaks of the trigonal  $R\bar{3}m$  phase. Based on a  $2 \times 2 \times 2$  cubic rock-salt lattice, these peaks correspond to the  $(2\ 2\ 2)$  and  $(4\ 4\ 0)$  peaks in the cubic structure with space group  $\text{Fd}\bar{3}m$ , respectively. For  $\text{Li}_{0.2}\text{NiO}_2$ , trigonal two phases were turned into the spinel phase at  $200^\circ\text{C}$ . The temperatures at which the spinel ( $\text{Fd}\bar{3}m$ ) phases were observed decreased with  $x$  and were in good accordance with the TG results mentioned above. The decomposition to a rock-salt phase observed at  $200^\circ\text{C}$  for  $\text{Li}_{0.2}\text{NiO}_2$  will be discussed in the Section 3.4.

In order to investigate the effect of  $x$  in  $\text{Li}_{1-x}\text{NiO}_2$  and the temperature on the decomposition to a spinel, the heat flow involved in the spinel formation was measured and the results were shown in Fig. 3. The  $\text{LiNiO}_2$  was quite stable and no significant heat flows into or from the composites were observed over the entire temperature range. The

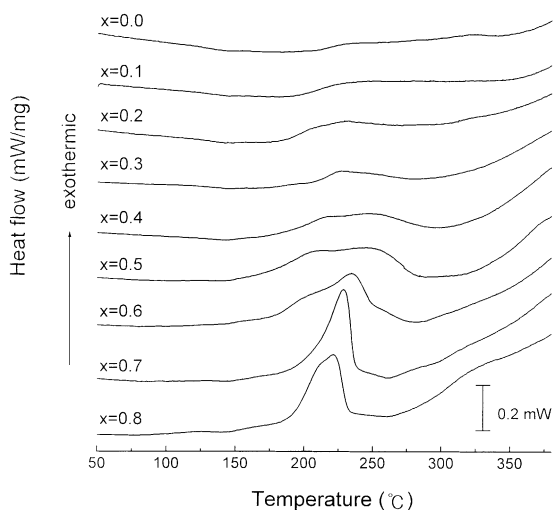
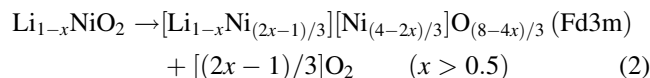
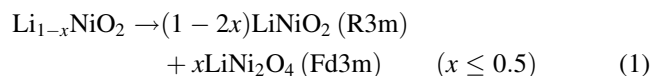


Fig. 3. DSC results for  $\text{Li}_{1-x}\text{NiO}_2$  composites in air atmosphere at a heating rate of  $5^\circ\text{C}/\text{min}$ .

delithiated  $\text{Li}_{1-x}\text{NiO}_2$ , however, showed some exothermic peaks at around  $220^\circ\text{C}$  which increased as the degree of deintercalation increased. As reported previously [9,10], these exothermic peaks were attributed to a spinel formation and it was confirmed by the high-temperature X-ray diffraction measurements as shown in Fig. 2. The cooperative displacements of one quarter of the Ni ions into neighboring Li ion layers and the Li ions in octahedral sites into neighboring tetrahedral sites take place during the  $\text{LiNi}_2\text{O}_4$  spinel formation from the trigonal layered  $\text{Li}_{0.5}\text{NiO}_2$ . This cationic redistribution has been referred to a main cause for the exothermic heat flow observed during the spinel formation [4].

Fig. 4 shows the area under the peaks, which is directly proportional to  $\Delta H$  for the spinel formation reaction, observed at around  $220^\circ\text{C}$  of DSC curves in Fig. 3 as a function of  $x$ . For  $x \leq 0.5$ , the peak area increased linearly with  $x$  in  $\text{Li}_{1-x}\text{NiO}_2$  and it showed that the amount of a spinel phase in the decomposed products was proportion to  $x$ . However, the  $\text{Li}_{1-x}\text{NiO}_2$  with  $x > 0.5$  showed a different tendency of  $\Delta H$  decreased with  $x$  and it might be explained by overlapping between the exothermic spinel formation and the endothermic oxygen evolution reaction occurred simultaneously in this composition range.

The thermal decomposition behavior of  $\text{Li}_{1-x}\text{NiO}_2$  to a spinel at around  $220^\circ\text{C}$  could be expressed as following equations:



Eq. (2) indicates that the amount of the spinel decreases with  $x$  for  $x > 0.5$  and it also leads to the small decrease in  $\Delta H$

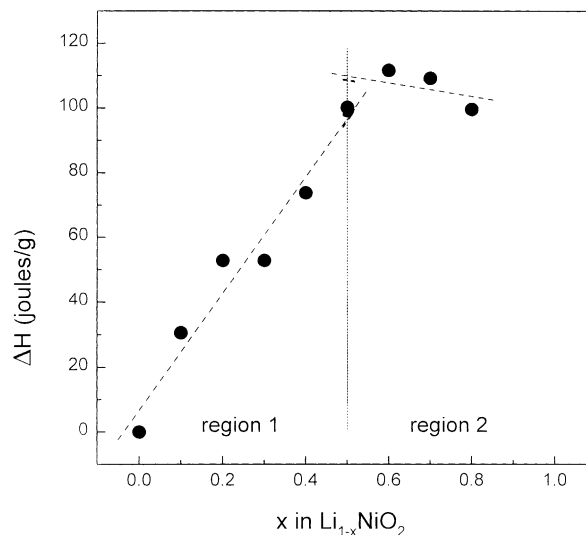


Fig. 4.  $\Delta H$  during the decomposition of  $\text{Li}_{1-x}\text{NiO}_2$  composites to a spinel phase.

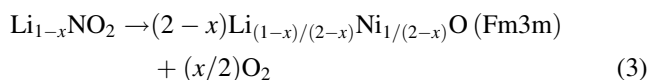
with  $x$  for the samples at this composition range as shown in Fig. 4. The calculated weight losses of the  $\text{Li}_{1-x}\text{NiO}_2$  composite electrodes containing a 88 wt.% of  $\text{Li}_{1-x}\text{NiO}_2$  during the conversion to a spinel were 2.0, 4.1 and 6.1 wt.% for  $x = 0.6, 0.7$  and  $0.8$ , respectively, and were in good agreement with the measured values shown in Fig. 1. Small differences between the two might be caused by a relatively fast heating rate of  $5^\circ\text{C}/\text{min}$  in present work.

### 3.4. Thermal decomposition to a rock-salt phase

Fig. 2(d) showed that the (1 1 1), (3 1 1) and (5 1 1) peaks of the spinel disappeared at  $300^\circ\text{C}$  and only (2 2 2), (4 0 0) and (4 4 0) peaks remained. They could be indexed as (1 1 1), (2 0 0) and (2 2 0) peaks assuming a cubic cell with a rock-salt structure of Fm3m. During the conversion from a spinel to a rock-salt structure, both lithium and nickel ions move randomly to other layers and there is no difference between the cation layers in the resulting structure.

It has been reported [3,4,6] that the decomposition of  $\text{Li}_{0.2}\text{NiO}_2$  to a rock-salt phase is accompanied by the oxygen evolution and exothermic reaction caused by random redistribution of cations across the cation layers. These were confirmed by the weight losses observed in TG curves shown in Fig. 1 and exothermic heat flows in DSC curves in Fig. 3, at the temperatures above  $270^\circ\text{C}$ , respectively. The delithiated  $\text{Li}_{1-x}\text{NiO}_2$  of all composition showed a similar thermal behavior of weight loss and exothermic heat flow at temperatures higher than their decomposition temperature into a spinel and it could be explained by the formation of a rock-salt phase.

The decomposition of trigonal or monoclinic  $\text{Li}_{1-x}\text{NiO}_2$  to a rock-salt phase was expressed as following reaction [4] and took place at less elevated temperature as the degree of deintercalation increased.



## 4. Conclusions

Thermal behavior of electrochemically delithiated  $\text{Li}_{1-x}\text{NiO}_2$  and its decomposition mechanism were closely examined by TG, DSC, and high-temperature X-ray diffraction measurement.

Delithiated  $\text{Li}_{1-x}\text{NiO}_2$  with the structure of hexagonal (R3m) or monoclinic (C2/m) was decomposed to  $\text{LiNi}_2\text{O}_4$  spinel (cubic, Fd3m) at the range of  $180\text{--}250^\circ\text{C}$  and the decomposition temperature decreased in  $x$  in  $\text{Li}_{1-x}\text{NiO}_2$ . For  $x \leq 0.5$ ,  $\text{Li}_{1-x}\text{NiO}_2$  was decomposed to  $\text{LiNiO}_2$  and  $\text{LiNi}_2\text{O}_4$  and the fraction of the spinel phase in the decomposed products increased linearly with  $x$ . For  $0.5 < x \leq 0.8$ ,  $\text{Li}_{1-x}\text{NiO}_2$  was converted into  $\text{LiNi}_2\text{O}_4$  spinel and released oxygen.  $\text{Li}_{1-x}\text{NiO}_2$  of all compositions turned into  $\text{Li}_{(1-x)/(2-x)}\text{Ni}_{1/(2-x)}\text{O}$  (cubic, Fm3m) with rock-salt structure at temperatures above  $270^\circ\text{C}$  and this reaction was accompanied by oxygen evolution. The temperature at which the decomposition to a rock-salt phase took place also decreased with  $x$  in  $\text{Li}_{1-x}\text{NiO}_2$ . The thermal behavior observed in TG and DSC could be explained as an overlap of the exothermic rearrangement of Ni and Li cations to form a spinel or rock-salt phase and the endothermic oxygen evolution reaction.

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