INFLUENCE OF THERMAL TREATMENT ON LiNiO$_2$ PHASE

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Abstract
The LiNiO$_2$ phase was prepared by the mechanical homogenization of powder precursors and annealing of mixture at temperatures from 700 to 800°C for various times in an air or pure oxygen atmosphere. XRD phase analysis showed a formation of the secondary phase during thermal treatment. Infrared spectra of annealed samples are simplified by the loss of two characterictic bands. The crystallographic symmetry of the formed phase was not determined but we believe on the basis of analysis of XRD records that it is close to hexagonal symmetry. No significant mixing of cations (Li and Ni) in individual cationic layers was observed after thermal treatment. The content of Li in LiNiO$_2$ phase decreases with annealing time by sublimation whereas one was stopped at Li/Ni ratio of 0.9
Keywords: LiNiO$_2$, Li ion cell, cathodic materials

INTRODUCTION

The research and development of a new materials for Li – ion primary or secondary cells has been pointed on layered LiCoO$_2$, LiNiO$_2$ and spinel (LiMn$_2$O$_4$) phases in the last decade of 20-th century. The most used cathodic material is hexagonal LiCoO$_2$ which is characterized by excellent properties from the point of view of high capacity and low capacity losses [1]. Some limitations due to its expensive technology, toxicity and cycle life failure are known for LiCoO$_2$. Further cathodic material used in the practice, is spinel LiMn$_2$O$_4$, which is cheaper and low toxic. Disadvantages of this material are lower electrochemical capacity (at 4 V) and higher capacity losses during charge/discharge cycles [2,3]. The hexagonal LiNiO$_2$ phase appertains to progressive materials which are taken for perspective alternatives of hexagonal LiCoO$_2$. For preparation of sufficiently stoichiometric and pure LiNiO$_2$ phase, the preparation conditions must be very precisly kept [4,5]. Low temperature preparation techniques of LiNiO$_2$ phase, namely the sol-gel or combustion method, have been developed [6], the one of the most used methods of preparation represents the conventional ceramic method based on reaction of mixed powder precursors at higher temperature. For practical use of LiNiO$_2$ phase as the cathodic material, the lattice ordering and the rise of layered structure (hexagonal lattice) with pure Li and Ni layers is a very important criterion. The electrochemical deintercalation of Li$^+$ ions and following reversible intercalation at origin lattice sites can be carried out in ordered LiNiO$_2$ only. From the viewpoint of intercalation process, the preparation of LiNiO$_2$ structure with pure cationic (Ni and Li) layers is needed because the presence of Ni^{II} in LiO$_6$ layers causes suppressing reversible intercalation of Li$^+$ ions into origin sites in the Li-layer and electrochemical capacity fading [7,8]. During electrochemical inter/deintercalation Li$_x$NiO$_2$, the phase transformation from hexagonal to monoclinic lattice has been observed in composition region of $0.5 < x < 0.75$. From detailed study of

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this transformation, it appears that Li-vacancy ordering is responsible for the presence of hexagonal/monoclinic transformation. In ref. [9] has been shown that the Jahn-Teller distortion of the lattice does not cause transformation to monoclinic phase. The spinel $LiNi_2O_4$ phase with cubic arrangement of lattice arise by annealing of deintercalated $Li_{0.5}NiO_2$ phase at a temperature of 300^oC [10].

In this paper, the question on the change of phase composition of prepared $LiNiO_2$ phases after a long-time annealing of the precursor in air and in pure oxygen at the temperature of 800^oC have been studied.

EXPERIMENTAL PROCEDURE

$LiNiO_2$ phase was prepared by mechanical milling of the stoichiometric amount of NiO (>99 %) and LiOH (analytical grade) in an planetary mill (FRITSCH 5, Germany). Milling was performed in an agate chamber in distilled water. The homogeneous mixture was annealed after drying at temperatures of 700, 750 and 800^oC for 9, 24, 48, 62 hours in O_2 or at 800^oC for 24, 48 and 62 hours in air. The gas flow-rate was 50 ml/min. Gas atmosphere was purified by bubbling over the H_2SO_4 (conc.) and mixture of $CrO_3+H_2SO_4$ (conc.). The Li content was determined by atomic absorption spectrometry, and the total Ni content by chelatometry [11]. The oxidation state of Ni was determined by bichromatometry [4] whereas the equivalence point was given by potentiometry (Pt indication and calomel reference electrodes). Phase purity and the ordering of $LiNiO_2$ phase were analysed using X-ray diffraction analysis (XRD) (MIKROMETA, Czech Republic) and IR spectroscopy (SPECORD M80, Germany) by the KBr method using a 1:400 ratio. The lattice constants of hexagonal $LiNiO_2$ phase were calculated using $Cu_{K\alpha1}$ diffraction lines from deconvoluted XRD spectra.

RESULTS AND DISCUSSION

In Figures 1a,b,c are shown the XRD diffraction spectra of $LiNiO_2$ phase prepared at 800^oC in air and in pure oxygen. The XRD spectrum of the sample prepared by annealing of the precursor during 9 hours in O_2 (Fig.1a) represents the spectrum of hexagonal $LiNiO_2$ phase. In the spectrum, a splitting of the line at 2θ angle $\sim 38^o$, which matchs reflections from (006) and (012) planes of hexagonal lattice, can be seen. This splitting is clearly visible on a derivative curve. No additional diffraction lines were observed in the spectrum in the region of 2θ from 62 to 66° (Fig.2), in which are located a reflection from (018) and (110) planes. A different situation can be seen in Fig.1b, where is shown the XRD spectrum of $LiNiO_2$ phase prepared by annealing in O_2 for 62 hours. Besides diffraction patterns of hexagonal $LiNiO_2$ phase, patterns of other minority phases are clearly seen in the spectrum. From comparison of spectra in Fig.1a and 1b, it appears that the origin spectrum of the hexagonal phase was split into dublets which are sufficiently separated mainly at the most intensive (003) and (104) lines. A similar shape also has the spectrum of $LiNiO_2$ phase prepared by annealing at 800^oC for 62 hours in air (Fig.1c), but one that is not as noticeable as in the spectrum in Fig.1b. In Figure 2 is shown the diffraction line splitting of (018) and (110) plane reflections. Thus, the line splitting was found in all reflections but on a basis of measured intensity of peaks, it shown that the content of secondary phase is not exceeding of 20 at.%. The spinel cubic phase during annealing was not formed because a diffraction line at the angle of $2\theta \sim 31^o$ (besides the sample prepared at 800^oC for 24 hours in air) was not observed in the XRD spectrum and nor did other diffraction lines represent lines of the spinel phase. From analysis of XRD spectra and its comparison results that very similar diffraction line splitting has been found in monoclinic Li_xNiO_2 phase (0.5<x<0.75), which was created by the electrochemical deintercalation of Li^+ ions. The possibility of formation

of monoclinic Li_xNiO_2 phase by thermal process has not yet been shown because of the low stability of this phase at higher temperatures, and the $LiNi_2O_4$ spinel or disordered (NaCl type) phases are formed during thermal treatment of monoclinic phase. The second possibility to explain the diffraction line splitting is the formation of a new additional hexagonal secondary phase. In [14] has been shown that a hexagonal phase can exist at a wide region of Li concentrations in a Li_xNiO_2 phase. Hexagonal axes (a,c) increase with Li content in the phase. This fact is in accordance with the observed placing of diffraction lines of secondary phase, because all peaks are shifted to lower diffraction angles.

800 °C/9 hours

800 °C/62 hours

↘ a)   ⇧ b)

800 °C/62 hours air

⇐ c)
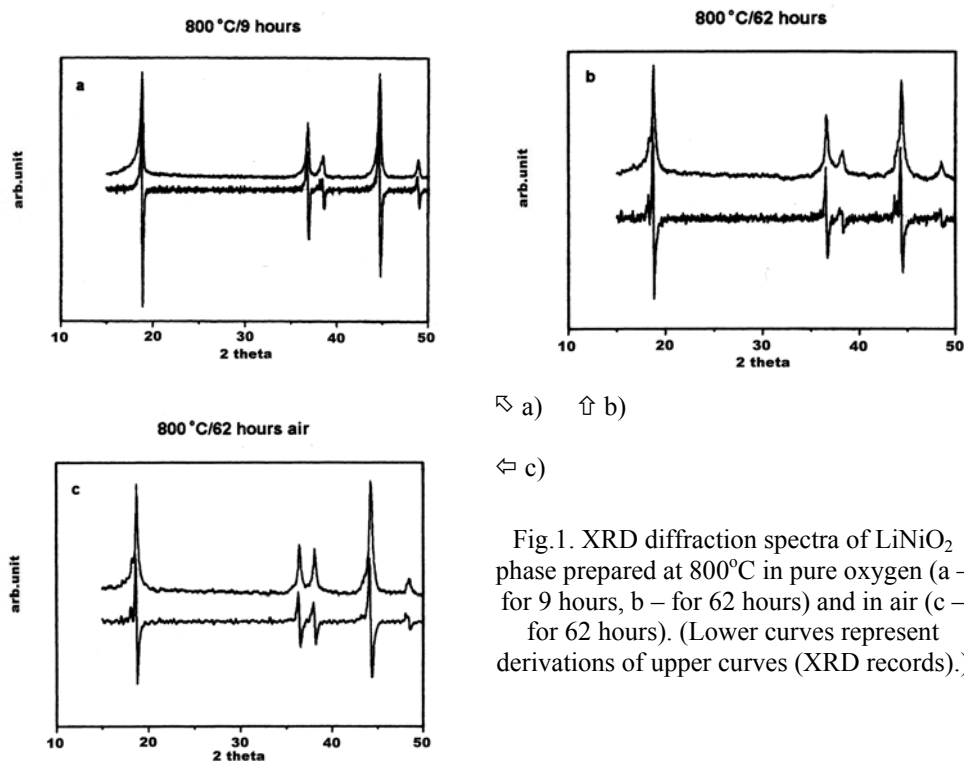
Fig.1. XRD diffraction spectra of $LiNiO_2$ phase prepared at 800°C in pure oxygen (a – for 9 hours, b – for 62 hours) and in air (c – for 62 hours). (Lower curves represent derivations of upper curves (XRD records).)

The results of analysis of XRD spectra and chemical analyses are summarized in Tab.1. States 1-3 represent samples prepared at 700, 750 and 800°C for 9 hours in O_2, 4-6 (respectively 7-9) were obtained at 800°C for 24, 48 and 62 hours in O_2 (or in air). The decrease of the Li/Ni ratio can be seen in the table as a result of the sublimation of Li from $LiNiO_2$ phase with annealing time, whereas one was stopped at a Li/Ni ratio of 0.9. The final stoichiometric formula of $Li_{1-x}Ni_{1+x}O_2$ phase was determined, according to the method described in ref.[4], from an intensity ratio of I_{003}/I_{104} and acknowledgement of the Li/Ni ratio. It need be mentioned that formulas obtained by such a manner are not fully valid because we do not know the stoichiometry of the secondary phase and real Li/Ni ratio. Samples annealed in air had practically the same content of Ni^{III} at applied annealing times. In the case of samples prepared in oxygen flow, the continuous decrease of Ni^{III} content with annealing time was observed, but values of the Ni^{III} content were higher than in the samples annealed in air. It is clear that the oxidation potential of an air atmosphere, is lower

than one of an oxygen atmosphere and this fact causes the preferential reduction of Ni^{III} during thermal treatment. No significant mixing of cations (Li and Ni) in individual pure Li or Ni layers was observed after annealing at a temperature of $800^{o}C$.
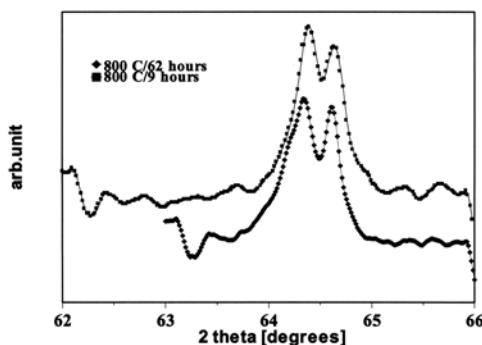

Fig.2. XRD diffraction spectra of $LiNiO_2$ in region of 2θ from 62 to 66° (reflections from (018) and (110) planes).

Tab.1. Results of XRD analysis of $LiNiO_2$ diffraction spectra.

Li/Ni	Ni^{III}/Ni [%]	c_{hex} [Å]	a_{hex} [Å]	$[Li_{1-x-u}Ni_{x+u}]_{3b}[Li_u Ni_{1-u}]_{3a} O_{2-\delta}$	State *
1.10	63.7	14.154	2.884	$[Li_{0.98}Ni^{II}_{0.02}][Li_{0.07}Ni_{0.32}^{II}Ni_{0.61}^{III}]O_{1.78}$	1
1.06	88.6	14.162	2.882	$[Li_{0.97}Ni^{II}_{0.03}][Li_{0.06}Ni_{0.08}^{II}Ni_{0.86}^{III}]O_{1.92}$	2
1.04	90.9	14.190	2.882	$[Li_{0.98}Ni^{II}_{0.02}][Li_{0.04}Ni_{0.08}^{II}Ni_{0.89}^{III}]O_{1.93}$	3
0.95	77.6	14.161	2.883	$[Li_{0.95}Ni^{II}_{0.05}][Li_{0.02}Ni_{0.18}^{II}Ni_{0.80}^{III}]O_{1.92}$	4
0.90	75.6	14.176	2.882	$[Li_{0.90}Ni^{II}_{0.10}][Li_{0.05}Ni_{0.16}^{II}Ni_{0.79}^{III}]O_{1.92}$	5
0.90	64.0	14.192	2.883	$[Li_{0.95}Ni^{II}_{0.05}][Ni_{0.33}^{II}Ni_{0.67}^{III}]O_{1.86}$	6
0.98	51.1	14.152	2.888	$[Li_{0.79}Ni^{II}_{0.21}][Li_{0.20}Ni_{0.28}^{II}Ni_{0.52}^{III}]O_{1.76}$	7
0.95	51.5	14.191	2.888	$[Li_{0.97}Ni^{II}_{0.03}][Ni_{0.47}^{II}Ni_{0.53}^{III}]O_{1.78}$	8
0.88	54.1	14.211	2.892	$[Li_{0.94}Ni^{II}_{0.06}][Ni_{0.45}^{II}Ni_{0.55}^{III}]O_{1.80}$	9

*see text

Figure 3 show the IR spectrum of hexagonal $LiNiO_2$ phase in a wavenumber region of 650-300 cm^{-1} prepared at $800^{o}C$ for 9 hours in O_2. From the deconvolution of spectrum results that the spectrum is composed of four bands which are located at 560, 500, 410 and 310 cm^{-1}, as can be seen in the figure. These peaks are characteristic for vibrations of NiO_6 octahedrons where high frequency bands represent stretching vibrations along Ni-O bonds, and low frequency bands represent bending vibratons of O-Ni-O bonds [6]. It can be mentioned that stretching vibrations along Li-O bonds located at 250 cm^{-1} were not recorded in spectra [12]. The analysis of IR spectra from the viewpoint of the integral intensity (INI) dependence of each separated peak on Ni^{III} (resp.Ni^{II}) fraction prepared $LiNiO_2$ phases was done in the following part of this work. All spectra were normalized in order to have the intensity of the peak maximum equal 1. The integral intensity of each peak was expressed as a fraction of the total band INI. Some error in determination of INI could be done in the estimation of base line location. The assumption concerning constant absorption coefficients of the given band were accounted in the analysis. Obtained

dependences of the integral intensity of separated peaks are shown in Fig.4 a, b. INI of the peak at 560 cm^{-1} and the weak peak at 310 cm^{-1} increase with Ni^{III} content in LiNiO$_2$ phase. Similarly, the summation of INI of peaks at 490 and 400 cm^{-1} increases with Ni^{II} content in this phase. From the above dependences, it shows that a band at wavenumber 560 cm^{-1} disappears with a decreasing of Ni^{III} content in LiNiO$_2$ phase, whereas the difference between original integral intensity and lowered INI is transferred to INI of low frequency bands at 490 and 400 cm^{-1}.
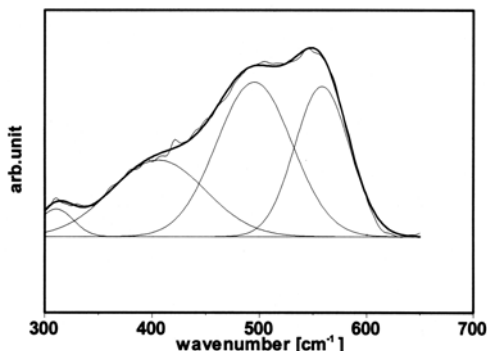

Fig.3. Deconvolution of the IR spectrum of hexagonal LiNiO$_2$ phase in wavenumber region of 650-300 cm^{-1} prepared at 800°C for 9 hours in O$_2$.
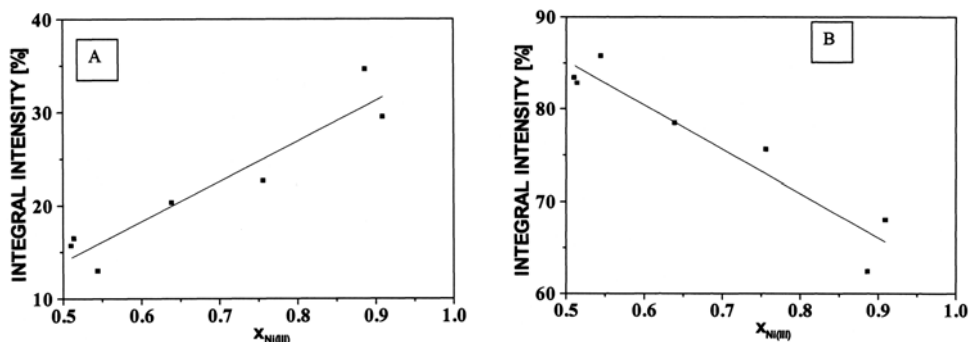

Fig.4. Dependences of integral intensities (INI) on Ni^{III} content in LiNiO$_2$ phase (A – INI of band at 560 cm^{-1}, B – summation of INI of bands located at 490 and 400 cm^{-1}).

An IR band located at wavenumber of 310 cm^{-1}, similar as in the case of a high frequency band, disappears from the spectrum with a decrease of Ni^{III} content. The group factor analysis of hexagonal LiNiO$_2$ phase (D$_{3d}^5$ symmetry) yields four infrared active modes [13]. The presence of two weak bands at $\approx$ 1500 cm^{-1} and 860 cm^{-1} has not yet been credibly explained. According to ref. [9], Ni^{III}O$_6$ octahedrons present in the hexagonal phase are distorted (Jahn-Teller distortion) with four short bonds and two prolonged bonds. From these facts is the result that INI of band at 560 cm^{-1} represents stretching vibrations along shorter Ni^{III} – O bonds and a summation of INI of bands at 490 and 400 cm^{-1} represents both stretching vibrations of the two longer Ni^{III} – O bonds (Ni^{II} – O bonds too) and bending of O - Ni^{III}- O (shorter bonds), O - Ni^{II} – O vibrations. A weak band at 310 cm^{-1} characterizes probably bending vibrations of longer O – Ni^{III}- O bonds in distorted

$Ni^{III}O_6$ octahedrons. The estimate of the number of bonds which share in the increase of integral intensities of each separated band could not be done because forces of oscillators (and absorption coefficients) are different for $Ni^{II}O$ and $Ni^{III}O$ (shorter) bonds.

CONCLUSIONS

Results obtained in this work can be summarized as follows:

1. An IR spectrum is simplified by the loss of two spectral bands which could be possibly assigned to a change of symmetry of the annealed $LiNiO_2$ phase. Because of a decreasing of the number of bands, we may believe that a disordered NaCl-type of $LiNiO_2$ phase was formed. This is a discrepancy with measured XRD spectra of $LiNiO_2$ phases in which diffraction line splitting was observed. Mainly the presence of a new peak at a reflection from the (003) plane, which is not present in XRD spectrum of NaCl cubic structure, makes us doubt the creation of a disordered $LiNiO_2$ secondary phase.
2. During annealing in air, a preferential reduction of Ni^{III} was found.
3. The content of Li in $LiNiO_2$ phase decreases with annealing time by sublimation, while one was stopped at a Li/Ni ratio of 0.9
4. No significant mixing of cations (Li and Ni) in individual cationic layers was observed after thermal treatment.

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