Preparation and Structural Stability of LiNiO$_2$ in Separate Synthesis Methods at Different Temperatures

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Abstract: The LiNiO$_2$ has been the most widely used cathode material in commercial lithium ion batteries because of its high discharge capacity, low cost and environmentally acceptable properties. However, it is difficult to obtain stoichiometric LiNiO$_2$ by solid-state reaction method at high temperature in air atmosphere. This is due to the instability of trivalent nickel species and disordering of cationic distribution at lithium sites. In this paper, we have synthesized the LiNiO$_2$ cathode material by sol-gel and solid state reaction methods at different temperatures (between 750 ºC and 800 ºC) for obtaining the sample in good phase formation. The sol-gel synthesis method is mainly used because the chemical reaction is easy and also it requires only a low reaction temperature. Further it yields a high degree of homogeneity compared to the conventional solid state synthesis. The crystal structure, bonding nature and vibrational features of the compound are investigated. The crystalline powders are characterized for their phase identification using x-ray diffraction analysis (XRD). All the samples synthesized by these two methods possessed the α-NaFeO$_2$ structure of the rhombohedral system (space group, $R\bar{3}m$) with no evidence of any impurities. The morphological features of the powders are characterized by field effect scanning electron microscopy (FESEM). The grain sizes of the samples are found to be approximately 1.5-2 μm. The FT-IR spectroscopic data of LiNiO$_2$ reveal the structure of the oxide lattice constituted by LiO$_6$ and NiO$_6$ octahedra. From this study we conclude that the LiNiO$_2$ synthesized by sol-gel method is structurally stable and it can be used as cathode in lithium ion batteries.

Keywords: Layered structure, XRD, FESEM, FTIR

Introduction

Layered lithium metal oxides such as LiCoO$_2$ and LiNiO$_2$ have been of great interest as cathode materials for secondary lithium batteries. Presently LiNiO$_2$ has been intensely investigated because of its comparatively low cost, less toxicity, lower price, large reversible capacity and environmental advantages over LiCoO$_2$[1-3]. However, it still has problems, *i.e.*, irreversible phase transformation, difficulty in synthesis and safety concerns, which need to be settled for the wider usage in practical lithium batteries. The discharge capacity of LiNiO$_2$ measured experimentally was certified to have about 140-150 mAh g^{-1} due to the synthesis of non-stoichiometric[4-5] LiNiO$_2$. In the present work we have to synthesize LiNiO$_2$ cathode material by two different synthesis methods using different temperatures for better phase formation. Firstly we prepared the material by the solid state reaction with the calcination

temperatures 700 ºC, 750 ºC and 800 ºC for 24 h and secondly the sol-gel method with the calcination temperatures 800 °C for 2 h, 4 h, 6 h, 8 h and 16 h for better phase formation.

Experimental

Synthesis of LiNiO₂ powders by solid state reaction method (SSR)

The cathode compositions were synthesized by a solid state reaction from stoichiometric amounts of Li_2CO_3 (Himedia 99.9%) and NiO (Himedia 99.9%). A slight excess amount of lithium (1%) was used to compensate for any loss of the metal which might have occurred during the calcining at high temperatures. The appropriate stoichiometric amount of the chemicals are ground in an agate mortar and calcined at 700 ºC, 750 ºC and 800 ºC for 24 h in air using a muffle box furnace.

Synthesis of LiNiO₂ powders by sol-gel method (SG)

This sol-gel method is mainly used because the chemical reaction is easy, requires only a low reaction temperature and has a high degree of homogeneity. The $LiNO_3$ (Himedia, 99%) and Nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ (MERCK, ≥99.5%) were used as raw materials. The saturated solutions of these materials were prepared separately and these solutions were mixed. The oxalic acid was added to the solution, with a molar ratio of 1:1 maintained between the oxalic acid and the total metal ions required to form $LiNiO_2$ compound. Here, oxalic acid plays the role of a chelating agent. The 20 g sample of oxalic acid was dissolved in 20 mL distilled water and then mixed with 5 g pure $LiNiO_2$ particles under dynamic stirring for 6 h. The solution mixture was heated in the temperature range of 150 °C with a continuous stirring until a thick gel was obtained. The resulting gel was heated to 400 °C for 2 h to decompose the nitrates. The powder thus obtained was calcined at 800 °C for 2 h, 4 h, 6 h, 8 h and 16 h.

The structural characteristics were determined by x-ray diffraction using a Rigaku Cu-Kα diffractometer with diffraction angles of 20° and 80° in increments of 0.02°. The morphologies of the synthesized materials were studied by field emission scanning electron microscopy (FESEM) was taken from Carl Zeiss, EVO MA 15, Oxford Instruments, Inca Penta FET x 3.JPG. The Fourier transform infrared spectra were recorded using Nicolet 6700 and following the KBr pressed pellet technique to determine the structures of all the calcined cathode materials.

Results and Discussion

X-Ray diffraction

X-ray crystallography is a standard technique for solving crystal structures. The information contained in a diffraction pattern is finding the peak positions, crystal system, cell parameters, qualitative phase identification, peak intensities, unit cell contents, quantitative phase fractions, peak shapes, peak widths, crystallite size, non-uniform micro strain *etc*.

The XRD patterns of the $LiNiO_2$ cathode materials prepared by SSR method at different temperatures (700º C, 750º C and 800º C for 24 h) are shown in Figure 1. The XRD patterns of $LiNiO_2$ prepared by sol-gel method at 800°C for different time periods (2h, 4h, 8h and 16h) are presented in Figure 2. All the patterns can be indexed as a rhombohedral structure (JCPDS # 740919) which belongs to the space group $R\bar{3}m$. It means that pure-phase $LiNiO_2$ is obtained and no remarkable secondary phase is observed. Moreover, the crystal structural parameters do not change with varying the sintering temperature[6].

From the XRD patterns, lattice parameters and crystallite sizes can be calculated**.** The changes in the lattice parameters with the variation of the sintering temperature and time periods are presented in Tables 1 and 2. The low temperature $LiNiO_2$ tends to exhibit higher lattice parameters due to the presence of defects and impurities[7]. Such defects are introduced

during sample preparation and vary according to method and reagents used. Literature suggests that lattice parameter and particle size are directly related, *i.e.* as particle size increases it causes a corresponding decrease in lattice parameter. However, from the experimental technique employed here, particle size increases as temperature increases, though lattice parameter continues to increase steadily.
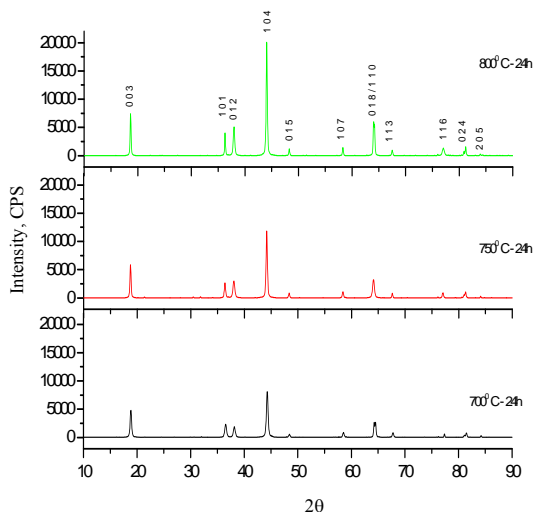

Figure 1. X-ray diffraction pattern for $LiNiO_2$ prepared by solid state reaction method at different temperature for 24 h
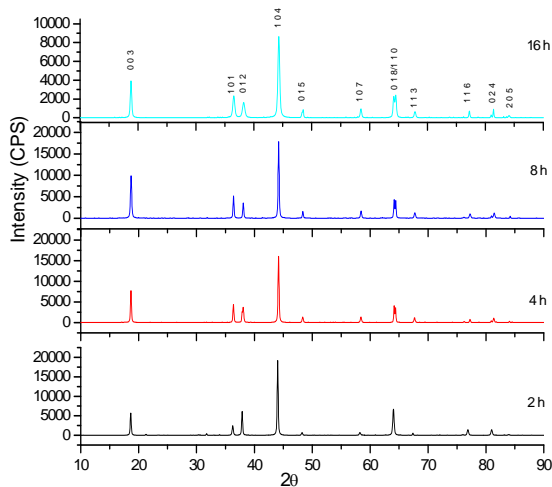
Figure 2: X-ray diffraction pattern for $LiNiO_2$ prepared by sol-gel method at 800° C for different time periods

Crystallite size

The crystallite size is an important structural parameter of the materials. The width of the Bragg reflection in a standard X-ray diffraction pattern provides information on the average crystallite size. The XRD peak broadening can measure the crystallite size in a direction perpendicular to the crystallographic plane, if the broadening arises entirely as a result of the

size effect. The variations of the crystallite size of the materials synthesized by two methods are shown in Figures 3 and 4. The crystallite size can be evaluated measuring the full width at half maximum (FWHM) according to the Scherrer formula:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where   D is the crystallite size (nm),

          K the shape factor (0.9),

          λ the wavelength of the x-rays ($\lambda = 1.54056$ Å for Cu-Kα radiation),

          β the FWHM (radians)

and θ the Bragg's diffraction angle (°).

Lattice constant

Lattice constant is calculated by using the formula in equation. For a hexagonal system, we have the following equation;

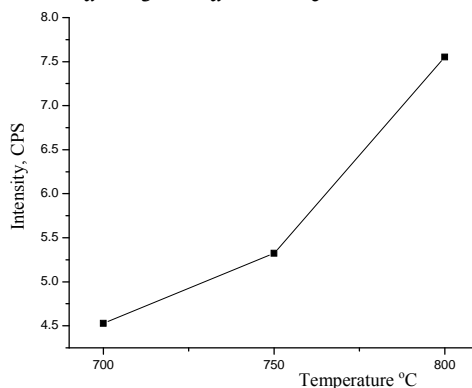$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$

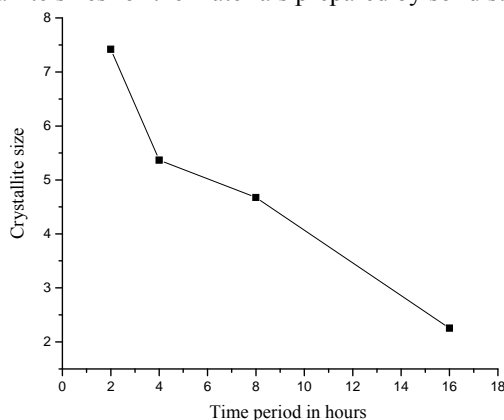**Figure 3.** Crystallite sizes for the materials prepared by solid state reaction method

Figure 4. Crystallite sizes for the materials prepared by sol-gel method

The calculated lattice parameters *a, c, c/a* and unit-cell volume of the compounds synthesized by solid state reaction method and sol-gel method are shown in Figures 5 and 6 respectively. The calculated lattice parameters *a, c, c/a* and unit-cell volume and crystallite

size of the compounds synthesized by both methods are summarized in Tables 1 and 2. The c/a value shows a similar trend with that of the variation of intensity ratio of the XRD peaks. Similar phenomena are reported in the lithium excess layered cathode materials. Thus, the decrease of lattice parameter could be attributed to the reduction of Ni^{3+} (r_{Ni3+} = 0.56 Å) ions to Ni^{2+} (r_{Ni2+} = 0.69 Å) ions to compensate the charge valence caused by decrease of lithium in the cathode material. The structural integrity of layered cathode material can be estimated by the *c/a* ratio. The c/a ratio > 4.9 also reveals the well-defined layered structure, since the higher value of c/a indicates well defined layered structure[8-10].
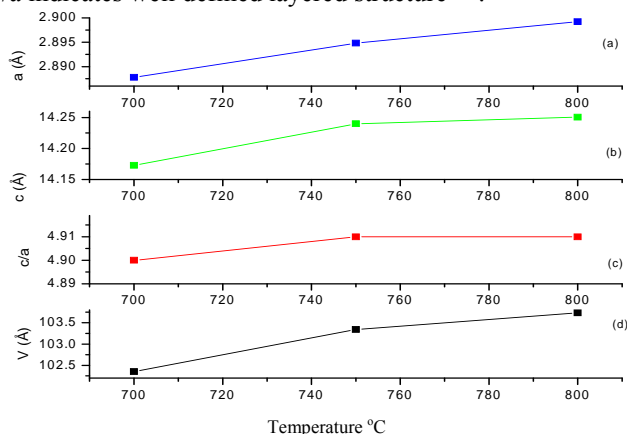

Figure 5. (a) a-axis lattice parameter (b) c-axis lattice parameter (c) c/a values and (d) unit cell volume of $LiNiO_2$ prepared by solid state reaction method
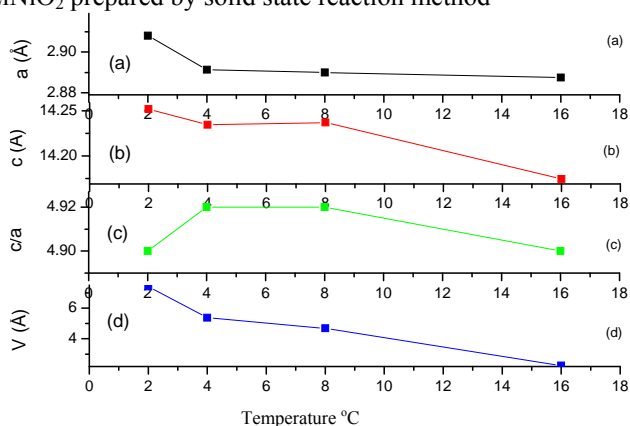

Figure 6 (a). a-axis lattice parameter (b) c-axis lattice parameter (c) c/a values and (d) unit cell volume of $LiNiO_2$ prepared by sol-gel method

Table 1. Calculated lattice data of $LiNiO_2$ prepared by solid state reaction method at different temperatures for 24 hours

| Calcination temperature ºC	a Å	c Å	c/a	Volume (Å)^3	Crystallite size, nm
700	2.8878	14.1728	4.90	102.35	4.52
750	2.8948	14.2398	4.91	103.34	5.32
800	2.8992	14.2504	4.91	103.73	7.55

Table 2. Calculated lattice data of LiNiO$_2$ prepared by sol-gel method at 800 °C

Time in hours	a Å	c Å	c/a	Volume (Å)^3	Crystallite size, nm
2	2.9080	14.2520	4.90	103.92	7.41
4	2.8914	14.2345	4.92	103.06	5.36
8	2.8900	14.2371	4.92	102.98	4.67
16	2.8875	14.1747	4.90	102.35	2.25

Scanning Electron Microscopic studies

The scanning electron microscope images of the surface of the samples under measurement are recorded by scanning it with a high energy beam of electrons. The SEM gives topographical information as well as chemical composition. The advantages of SEM are: (i) the particles can be individually examined, (ii) visual means of identifying sub-micron specimens and (iii) particle shape can be measured.

The scanning electron micrographs of LiNiO$_2$ (SSR and SG) calcined samples are illustrated in Figure 7. The powder of LiNiO$_2$ consists of quite small particles of uniform size. The compounds prepared by sol-gel method are composed of very uniform and small nano crystallites with particle size about 2 - 3 μm. The SSR samples consist of particles of similar shape and size. The particles are generally in the form of smooth-edged polyhedra and their average size is approximately 3-5 μm. This unique morphology is advantageous for electrode materials, because it allows the electrochemical performance to be improved.
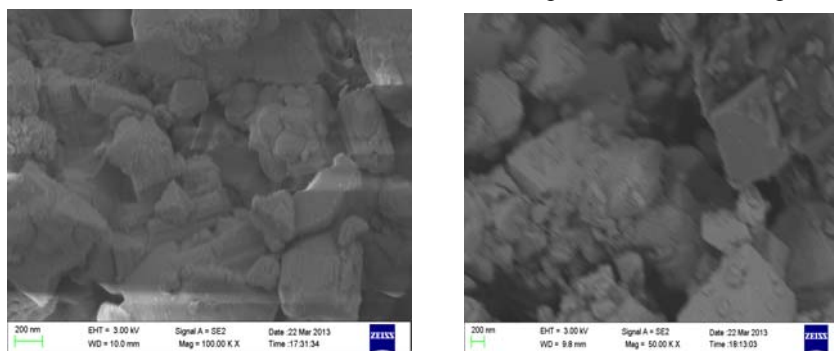
Figure 7. The SEM micrographs of LiNiO$_2$ synthesized by (a) SSR and (b) SG methods

Fourier transform infrared spectra

The structure of LiNiO$_2$ samples synthesized by solid state reaction and sol-gel methods are further characterized by FTIR. The Figure 8 shows the FTIR spectra of the LiNiO$_2$ samples (SSR) calcined at 750 °C and 800º C for 24 h in air atmosphere. According to the factor group analysis, the infrared spectra of LiNiO$_2$ compounds with $R\overline{3}m$ space group yield four infrared active modes. In the Figure 8, we observe the mode of vibrations for LiNiO$_2$ in the 400-1000 cm^{-1} region, which is largely associated with the vibrations of NiO$_6$ and LiO$_6$ octahedral units. The typical absorption peaks observed at 468.89 cm^{-1}, 477.39 cm^{-1}, 498.64 cm^{-1}, 614.81 cm^{-1} and 865.55 cm^{-1} are in agreement with those for LiNiO$_2$ prepared by solid-state reaction at high temperature. The peaks at 468.89 cm^{-1}, 498.64 cm^{-1}, 614.81 cm^{-1} and 865.55 cm^{-1} can be considered as typical peaks for identifying LiNiO$_2$. The LiNiO$_2$ crystal can be considered to be composite metallic oxidant in which Li ion layer is sandwiched between Ni and O layers. The absorption peak at 498.64 cm^{-1} corresponds to the symmetric stretching and shrinking vibration peak of M-O-M (M=Li, Ni). The double peaks at 865.55 cm^{-1}

and 878.21 cm^{-1} are attributed to the bond energy of Ni-O and Ni=O trending to be close because of homogenization of valence electrons[11].

The results obtained in the case of FTIR spectra of LiNiO$_2$ by sol-gel synthesis are almost the same as those for LiNiO$_2$ by solid state reaction method and they are shown in Figure 9. The typical absorption peaks at 461.81 cm^{-1}, 475.98 cm^{-1}, 491.56 cm^{-1}, 623.31 cm^{-1}, 865.55 and 885.38 cm^{-1} are observed. The absorption peak at 491.56 cm^{-1} corresponds to the symmetric stretching and shrinking vibration peak of M-O-M (M=Li, Ni). The double peaks at 865.55 cm^{-1} and 885.38 cm^{-1} are attributed to the bond energy of Ni-O and Ni=O trending to be close because of homogenization of valence electrons[12].
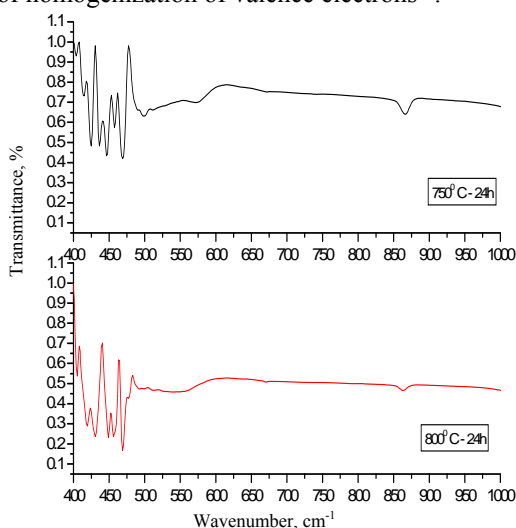
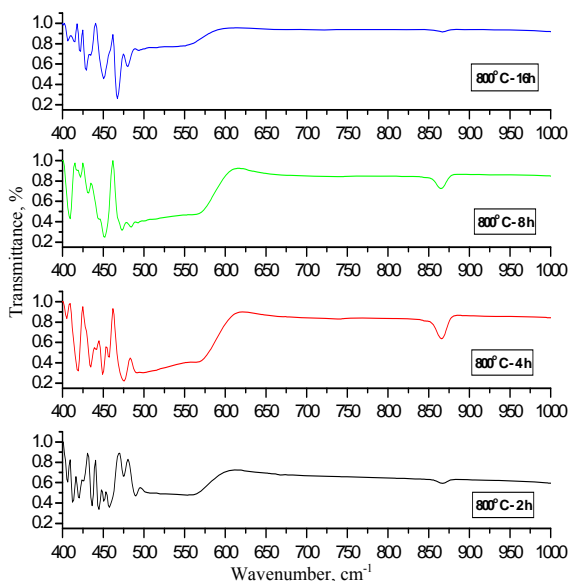**Figure 8.** FT-IR spectra of LiNiO$_2$ (SSR) synthesized at two different temperatures

Figure 9. FT-IR spectra of LiNiO$_2$ (SG) synthesized at 800 ºC for 2 h, 4 h, 8 h and 16 h

Conclusion

The LiNiO$_2$ cathode materials have been prepared by two different synthetic methods, solid state reaction and sol-gel. The X-ray diffraction patterns of all the samples showed the presence of a layered α-NaFeO$_2$ structure with $R\overline{3}m$ space group. The results of SEM analysis indicate that the synthesized LiNiO$_2$ materials have a layered structure and spherical shape. The typical absorption peaks in FTIR spectra are in good agreement with those for LiNiO$_2$ prepared by solid state reaction and sol-gel method at high temperature according to the reports of earlier researchers.

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