Effect of Calcination Temperature on the Physical Properties of Layered LiNiO₂ Prepared by Solid-State Reaction Method

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Abstract: A layered structure compound LiNiO₂ material is synthesized by the solid-state reaction method under air atmosphere in the temperature range from 750 °C to 850 °C using Li₂CO₃ and NiO as the starting materials for 20 hours. The physical properties of the synthesized powder are investigated by X-ray diffraction (XRD), Field effect scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopic (FT-IR) techniques. The results of XRD patterns possessed the α-NaFeO₂ structure of the rhombohedral system (space group, R₃m) with no evidence of any impurities. The morphological features of the powders are characterized by field effect scanning electron microscopy (FESEM). The particles of LiNiO₂ powder are generally in the form of a smoothly edged polyhedron and their average grain size is approximately 2 - 3 μm. The FT-IR spectroscopic data of LiNiO₂ reveal the structure of the oxide lattice constituted by LiO₆ and NiO₆ octahedra. In general, from this study, we conclude that the LiNiO₂ synthesized by solid state reaction method at different temperatures to increase in the sintering temperature. The lattice constant is increased, while the sintering temperature is increased. The maximum and minimum intensity ratios of XRD spectra shows that the optimum calcination condition is 800°C for 20 h. At 750-850°C, the particle size distribution is in the range of 2 - 3 μm.

1. INTRODUCTION

The lithium-ion battery is one of the most promising energy storage technologies currently available and widely used in portable electronics applications [1,2]. The main reason behind such rapid growth is its high energy density and cycling performance that no other energy storage devices can match [3]. Recent demands for energy and environmental sustainability have further spurred great interest in a larger scale lithium-ion battery system for vehicles and grid load leveling as well as complimentary energy storage for renewable energy resources, such as solar and wind powers [4,5]. Lithium transition metal oxides such as LiCoO₂ [6], LiNiO₂ [7], LiMnO₂ [8] and LiMn₂O₄ [9] have been extensively investigated as cathode materials for rechargeable lithium-ion batteries. The Co-containing lithium oxide, LiCoO₂, has been the most intensively studied for use in commercial rechargeable batteries, because of its large diffusivity and high operating voltage [10]. However, it has the drawback that cobalt is expensive and toxic as a result, it creates pressure to replace the cobalt with other materials [11]. It has a layered structure (R₃m).

The Ni-containing lithium oxide, LiNiO₂, with an (R₃m) structure is considered to be a promising cathode material, due to its large discharge capacity and low cost. However, due to the size similarity of Li and Ni (Li⁺ = 0.72 Å and Ni²⁺ = 0.69Å), the LiNiO₂ is practically obtained in the non-stoichiometric composition, Li₁₋ₓNi₁₊ₓO₂ [12], and the Ni²⁺ ions in the lithium planes obstruct the movement of the Li⁺ ions during charge and discharge studies [13].

In the present paper, LiNiO₂ cathode material are synthesized by a solid state reaction method at (750°, 800° and 850° C) different temperatures for 20 h. Finally, the structure and microstructure are systematically examined.
2. EXPERIMENTAL

The cathode material compositions are synthesized by a solid-state reaction method from stoichiometric amounts of Li$_2$CO$_3$ (Merck 99.9%), and NiO (Merck 99.9%).

$$0.5\text{Li}_2\text{CO}_3 + \text{NiO} \rightarrow \text{LiNiO}_2 + \text{gas} \uparrow$$

A slight excess amount of lithium (5%) was used to compensate for any loss of the metal which might have occurred during the calcination at high temperatures. The mixture of the starting materials is sufficiently mixed and after grinding the powder it is then heat treated in air at 500 °C for 5 h. The powder is again ground, mixed and calcined again at diverse temperatures 750 °C/20 h, 800 °C/20 h and 850 °C/20 hours are chosen as the research objects to explore the impact of calcination temperature on the mechanical properties of LiNiO$_2$.

The powder X-ray diffraction (XRD) data of the sample are collected on a Rigaku Cu-Kα diffractometer with diffraction angles of 20° and 80° in increments of 0.02°. The unit cell lattice parameter is obtained by the least square fitting method from the d-spacing and (hkl) values. Further, the crystallite size of the sample is obtained by applying the Scherrer’s equation from XRD pattern. The particle morphology of the powders is observed using a field effect scanning electron microscopy image taken from CarlZeiss, EVOMA 15, Oxford Instruments, Inca Penta FETx3.JPG. Fourier transform infrared (FT-IR) spectra are obtained on a Shimadzu FT-IR-8900 spectrometer using a KBr pellet technique in the wave number range between 400 and 1200 cm$^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Structures and morphologies of LiNiO$_2$

Figure 1 (a to c) shows XRD patterns of the synthesized materials calcined at various temperatures for 20 h. As can be seen, the diffraction peaks of all the samples agree well with the (0 0 3), (1 0 1), (0 1 2), (1 0 4), (0 1 5), (1 0 7), (0 1 8) (1 1 3) and (1 1 6) crystal planes of the stoichiometric layered structure with a hexagonal unit cell and $R\bar{3}m$ space group. However, some weak diffraction peaks can be also found from Figure 1. It suggested that the impurity phase appeared in the products prepared at 750 °C and 850 °C. The reason is that at 750 °C and 800°C the calcination temperature is not high enough to achieve perfect crystallization of LiNiO$_2$. At 850 °C, no impurity peaks could be observed, suggesting that single phase layered LiNiO$_2$ with hexagonal structure and $R\bar{3}m$ space group is obtained [14]. It indicates that the optimal calcination temperature is to be from 850 °C. Table 1 shows that the lattice parameters $a$, $c$, $c/a$ and the unit cell volume of the LiNiO$_2$ sample with different temperatures. Both $a$ and $c$ increase the hexagonal unit cell volume also increases correspondingly.

![X-ray diffraction patterns for LiNiO$_2$ prepared by solid-state reaction method at 750°, 800° and 850° C / 20 hours](image-url)

(a) (b) (c)
Table 1: Lattice parameters, unit cell volume, $I_{003}/I_{104}$ and crystallite size of LiNiO$_2$ with different temperatures

<table>
<thead>
<tr>
<th>LiNiO$_2$</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>Unit cell volume (Å$^3$)</th>
<th>$I_{003}/I_{104}$</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750 °C</td>
<td>2.885</td>
<td>14.199</td>
<td>4.921</td>
<td>102.366</td>
<td>0.403</td>
<td>72.15</td>
</tr>
<tr>
<td>800 °C</td>
<td>2.897</td>
<td>14.232</td>
<td>4.913</td>
<td>103.426</td>
<td>1.104</td>
<td>56.34</td>
</tr>
<tr>
<td>850 °C</td>
<td>2.893</td>
<td>14.241</td>
<td>4.923</td>
<td>103.264</td>
<td>0.991</td>
<td>37.52</td>
</tr>
</tbody>
</table>

Figure 2: (a) and (b) a-axis and c-axis lattice parameter (c) c/a values and (d) unit cell volume of LiNiO$_2$ prepared by solid state reaction method at different temperatures.

Figure 2 (a to c) shows the relation between the lattice parameters of the LiNiO$_2$ material with different temperatures. As lattice parameters $a$ and $c$ linearly increase, shrinkage along directions and the reduction of the lattice volume [15]. The trigonal distortion, $c/a$, increases from 4.920 for 750 °C to 4.923 for 850 °C, well above the 4.9 is clearly suggesting the formation of layered structure. Figure 3 shows the crystallite size of LiNiO$_2$ material for different temperatures (750 °C, 800 °C and 850 °C) and the values are 72.15, 56.34 and 37.52 nm. So, we can understand that the values of crystallite size are inversely proportional to the synthesized temperatures. Figure 4 shows the intensity ratio of $I_{003}/I_{104}$ as a function of different temperatures in LiNiO$_2$. The ratio increase is obtained from 750 °C to 800 °C and a slight decrease when further heated to 850 °C. Since this ratio is sensitive to the cation distribution in lattice parameters [16].

Figure 3: Crystallite size of LiNiO$_2$ material for different temperatures (750 °C, 800 °C and 850 °C)

Figure 4: The peak intensity ratio of $I_{003}/I_{104}$ as a function of LiNiO$_2$ with different temperatures
Figure 5 (a to c) shows the FESEM images of the LiNiO$_2$ material at different temperatures for 20h. It is evident that with the increasing calcination temperature, the particle size became larger. When the calcination temperature is 750 °C, the particles dispersed uniformly [17]. The particle size of the products prepared at 750 °C, 800 °C and 850 °C are about 2 μm, 2.5 μm and 3 μm, respectively. On the other hand, when the temperature is 850 °C, the products are badly agglomerated. The agglomeration size of the products prepared at 750 °C and 800 °C were in the range of 2 μm and 2.5 μm, respectively. It’s obvious that the particles agglomerated seriously at relatively higher temperature, especially for the materials prepared at 850 °C [18].

The FT-IR spectra of LiNiO$_2$ cathode material synthesized at different temperatures 750 °C, 800 °C and 850 °C are depicted in Figures 6 (a to c). The FT-IR spectra of the powders display the predominance of the stretching modes and the IR resonance frequency of LiO$_6$ octahedra located nearly between 400 and 460 cm$^{-1}$. The band observed around 532 cm$^{-1}$ may be assigned to the asymmetric stretching modes of N-O bonds in NO$_6$ octahedra and the other band around 608.13 cm$^{-1}$ may be attributed to the O-N-O bending modes [19]. The broadening of FT-IR bands may be due to the cation mixing in the crystal layers [20].

### 4. CONCLUSIONS

Pure Layered LiNiO$_2$ is rapidly synthesized by solid-state reaction method at different temperatures. However, 750 °C, 800 °C, minor amount of impurities emerged in the results. The reason is that at 750 °C, 800 °C, the calcination temperature is not high enough to achieve perfect crystallization of LiNiO$_2$. At 850 °C is no impurity peaks could be observed, suggesting that single phase layered LiNiO$_2$ with hexagonal structure and $R3m$ space group is obtained. It is indicated that the optimal calcination temperature is 850 °C, the crystallinity of products became better and the particle size tardily agglomerated to a comparatively large scale.
References

[7] Tze Qing Tan, Mohd Sobri Idris, Rozana Aina Maulat Osman, M.V. Reddy, B.V.R. Chowdari, Structure and electrochemical behaviour of LiNi0.4Mn0.4Co0.2O2 as cathode material for lithium ion batteries, Solid State Ionics 278 (2015) 43–48.