Effect of Calcination Temperature on the Physical Properties of Layered LiNiO_2 Prepared by Solid-State Reaction Method

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Abstract: A layered structure compound LiNiO_2 material is synthesized by the solid-state reaction method under air atmosphere in the temperature range from 750 °C to 850 °C using Li_2CO_3 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 $\alpha\text{-NaFeO}_2$ 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 particles of LiNiO_2 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 LiNiO_2 reveal the structure of the oxide lattice constituted by LiO_6 and NiO_6 octahedra. In general, from this study, we conclude that the LiNiO_2 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 LiCoO_2 [6], LiNiO_2 [7], LiMnO_2 [8] and LiMn_2O_4 [9] have been extensively investigated as cathode materials for rechargeable lithium-ion batteries. The Co-containing lithium oxide, LiCoO_2 , 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 ($R\bar{3}m$).

The Ni-containing lithium oxide, LiNiO_2 , with an ($R\bar{3}m$) 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 ($\text{Li}^+ = 0.72 \text{ \AA}$ and $\text{Ni}^{2+} = 0.69 \text{ \AA}$), the LiNiO_2 is practically obtained in the non-stoichiometric composition, $\text{Li}_{1-y}\text{Ni}_{1+y}\text{O}_2$ [12], and the Ni^{2+} ions in the lithium planes obstruct the movement of the Li^+ ions during charge and discharge studies [13].

In the present paper, LiNiO_2 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_2CO_3 (Merck 99.9%), and NiO (Merck 99.9%).

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-K α 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.

Figure 1: X-ray diffraction patterns for LiNiO_2 prepared by solid-state reaction method at 750°, 800° and 850° C / 20 hours

Table 1: Lattice parameters, unit cell volume, I_{003}/I_{104} and crystallite size of LiNiO_2 with different temperatures

LiNiO_2	a (Å)	c (Å)	c/a	Unit cell volume (Å) ³	$I_{(003)}/I_{(104)}$	Crystallite Size (nm)
750 °C	2.885	14.199	4.921	102.366	0.403	72.15
800 °C	2.897	14.232	4.913	103.426	1.104	56.34
850 °C	2.893	14.241	4.923	103.264	0.991	37.52

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 increases, 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 $2\ \mu\text{m}$, $2.5\ \mu\text{m}$ and $3\ \mu\text{m}$, 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 $2\ \mu\text{m}$ and $2.5\ \mu\text{m}$, respectively. It's obvious that the particles agglomerated seriously at relatively higher temperature, especially for the materials is prepared at 850°C [18].

Figure 5: FESEM images for LiNiO_2 is prepared by solid-state reaction method at (a) 750° , (b) 800° and (c) 850°C / 20 hours

Figure 6: FT-IR images for LiNiO_2 is prepared by solid-state reaction method at 750° , 800° and 850°C / 20 hours

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 $460\ \text{cm}^{-1}$. The band observed around $532\ \text{cm}^{-1}$ may be assigned to the asymmetric stretching modes of N-O bonds in NO_6 octahedra and the other band around $608.13\ \text{cm}^{-1}$ 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 $R\bar{3}m$ 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

- [1] K. Ozawa, Lithium-ion rechargeable batteries with LiCoO₂ and carbon electrodes: the LiCoO₂/C system, *Solid State Ionics*, 69 (1994) 212-221.
- [2] Z.S Peng, C.R Wan, C.Y Jiang, Synthesis by sol-gel process and characterization of LiCoO₂ cathode materials, *J. Power Sources* 72 (1998) 215-220.
- [3] J. R. Dahn, U. von Sacken, M. W. Juskow, H. Al-Janaby, Rechargeable LiNiO₂ / Carbon Cells, *J. Electrochem. Soc.* 138 (1991) 2207-2211.
- [4] M.Y. Song, R. Lee, Synthesis by sol-gel method and electrochemical properties of LiNiO₂ cathode material for lithium secondary battery, *J. Power Sources*, 111 (2002) 97-103.
- [5] A.R. Armstrong, P.G. Bruce, Synthesis of layered LiMnO₂ as an electrode for rechargeable lithium batteries, *Nature*, 381 (1996) 499 - 500.
- [6] K.S. Tan, M.V. Reddy, G.V.S. Rao, B.V.R. Chowdari, High-performance LiCoO₂ by molten salt (LiNO₃:LiCl) synthesis for Li-ion batteries, *J. Power Sources* 147 (2005) 241-248.
- [7] Tze Qing Tan, Mohd Sobri Idris, Rozana Aina Maulat Osman, M.V. Reddy, B.V.R. Chowdari, Structure and electrochemical behaviour of LiNi_{0.4}Mn_{0.4}Co_{0.2}O₂ as cathode material for lithium ion batteries, *Solid State Ionics* 278 (2015) 43-48.
- [8] G.X. Wang, P. Yao, S. Zhong, D.H. Bradhurst, S.X. Dou H.K. Liu, Electrochemical study on orthorhombic LiMnO₂ as cathode in rechargeable lithium batteries, *J. Appl. Electrochem.*, 29 (1999) 1423-1426
- [9] Paulos Taddesse Shibeshi, V. Veeraiah, Structural, electrical and electrochemical characterization of LiLa_{0.01}Cr_{0.13}Mn_{1.86}O₄ cathode material for lithium-ion battery, *J. Phys. Chem. Solids*. 75 (2014) 1075-1079.
- [10] M.Y. Song, D.S. Lee, Electrochemical Properties of Cathode Materials LiNiO₂ and LiNi_{1-y}MyO₂ (M = Zn²⁺, Al³⁺ and Ti⁴⁺). *Trends Appl Sci Res.* 1 (2006) 15-24.
- [11] Y. Takahashi, S. Tode, A. Kinoshita, H. Fujimoto, I. Nakane, S. Fujitani, Development of Lithium-Ion Batteries with a LiCoO₂ Cathode Toward High Capacity by Elevating Charging Potential, *J. Electrochem. Soc.* 155 (2008) A537-A541.
- [12] T. Titipun, T.Somchai, Synthesis of Li_{1-x}Ni_{1+x}O₂ using malonic acid as a chelating agent, *Ceram int.* 31 (2005) 241-247.
- [13] N.Murali, K.Vijaya Babu, K.Ephraim Babu, V.Veeraiah, Structural and Morphological Characterization of Mg Doped LiNiO₂ Cathode Materials for Lithium-Ion Batteries, *Chem. Sci. Trans.* 2015, 4(4), 1031-1036.
- [14] R. Moshtev, P. Zlatilova, S. Vasilev, I. Bakalova, A. Kozawa, Synthesis, XRD characterization and electrochemical performance of overlithiated LiNiO₂, *J. Power Sources*, 81 (1999) 434-441.
- [15] Sung Nam Kwon, Jihong Song, Daniel R. Mumm, Effects of cathode fabrication conditions and cycling on the electrochemical performance of LiNiO₂ synthesized by combustion and calcination, *Ceram int.* 37 (2011) 1543-1548.
- [16] P. Kalyani, N. Kalaiselvi, Various aspects of LiNiO₂ chemistry: A review, *Sci. Tech. Adv. Mater.* 6 (2005) 689-703.
- [17] C.H.Han, J.H.Kim, S.H.Paeng, D.J.Kwak, Y.M.Sung, Electrochemical characteristics of LiNiO₂ films prepared for charge storable electrode application, *Thin Solid Films* 517 (2009) 4215-4217.
- [18] P.N.Jung, K. T.Jung, T.H.Kwon, G.B.Cho, S.C.Huh, B.K.Choi, K.W.Kim, T.H.Nam, Microstructure and electrochemical properties of magnetron-sputtered LiCoO₂/LiNiO₂ multi-layer thin film electrode, *Mater. Res. Bull.* 48 (2013) 4993-4996.
- [19] R. Sathiyamoorthi, P. Shakkthivel, S. Ramalakshmi, Yong-Gun Shul, Influence of Mg doping on the performance of LiNiO₂ matrix ceramic nanoparticles in high-voltage lithium-ion cells, *J. Power Sources*, 171 (2007) 922-927.
- [20] S.Tao, Q.Wu, Z.Zhan, G.Meng, Preparation of LiMO₂ (M=Co, Ni) cathode materials for intermediate temperature fuel cells by sol-gel processes, *Solid State Ionics*, 124 (1999) 53-59.