



Combustion Synthesis of Lanthanum Substituted LiNiO_2 Using Hexamine as a Fuel

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Abstract: Lithium nickelate and its lanthanum substituted compound have been successfully prepared by combustion synthesis process using LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Hexamine is used as fuel. The physicochemical properties of the powders were investigated by thermal analysis (TGA/DTA). The crystalline powders were characterized for their phase identification using x-ray diffraction analysis (XRD). FT-IR spectroscopy was used to study the local structure of the oxide environment. The morphological features of the powders were characterized by scanning electron microscopy (SEM). DTA analysis reveals the evolution of an exothermic peak at 465 °C indicating the rapid decomposition of the hexamine and dissociation of nitrate salts, forming the final compound lithium nickelate. The XRD pattern reveals the rhombohedral structure of LiNiO_2 with trigonal symmetry comprising of two interpenetrating close packed FCC sub-lattices. The lattice constant values 'a' and 'c' are in good agreement with the reported data. In the FT-IR spectra, vibrational bands are identified in the range of 400-800 cm^{-1} representing the NiO_2 layer. LiNiO_2 exhibits a very fine crystalline structure with an irregular morphology. The La substituted LiNiO_2 powder has shown a smooth-edged polyhedral structure with an average particle size of 5-10 μm .

Keywords: Lithium nickelate, Combustion synthesis, Hexamine, Fuel.

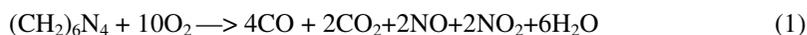
Introduction

Today's world of modernization and miniaturization lays a greater emphasis on more power from smaller and lighter battery devices. In this regard lithium batteries find a greater demand for powering smaller, lighter and portable consumer electronic devices¹⁻².

The layered oxide LiMO_2 (Ni, Co *etc.*) have been proposed as the cathode materials for lithium secondary batteries³⁻⁵. Of these, LiNiO_2 is one of the most promising cathode materials because it has high operating voltage, high discharge capacity, high energy density, low production cost and less environmental pollution compared to LiCoO_2 cathode material⁶⁻⁸.

Stoichiometric LiNiO_2 is difficult to synthesize and its multi-phase reactions during electrochemical cycling lead to structural degradation⁹. During the charge process, LiNiO_2 undergoes a sequential change in crystal structure from the hexagonal phase to the monoclinic phase, to the hexagonal phase to monoclinic and again hexagonal structure. To overcome these difficulties, the nickel ion has been substituted by various metal ions like Co, Ga, Al^{3+} , Mn^{3+} and Ti^{3+} , or an equal amount of Ti^{4+} and Mg^{2+} , Cu^{2+} to attain structural safety and better electrochemical properties¹⁰⁻¹².

It has been reported that the substitution of foreign metal ions stabilizes the crystal structure of the material during the intercalation/deintercalation of lithium ions, even in an overcharged state and thereby improves LiNiO_2 cyclability¹³. Substitution of rare earths inhibits the destruction of crystal structure and improves the charge transfer resistance¹⁴. Hexamine also called hexamethylene tetramine is a heterocyclic organic compound widely used in organic synthesis. The combustion reaction of hexamine can be represented as



Hexamine was tried as a fuel for the preparation of LiMn_2O_4 nanoparticles¹⁵, alumina nanofibers¹⁶, zinc oxide¹⁷, dispersed bimetallic carbides and nitrides¹⁸. Recently the rare earth boride, cerium hexaboride has been synthesized using this compound as the fuel¹⁹. To our knowledge, no one has tried hexamine as the fuel for the synthesis of lithium nickelate by combustion synthesis route. Hence, an attempt has been made to synthesize fine crystalline La substituted LiNiO_2 powder by this method. The results on the synthesis and the characterization of these compounds are reported in this paper.

Experimental

Lanthanum substituted LiNiO_2 powder was synthesized using a novel combustion method. Initially aliquot amounts of analytical grade lithium nitrate LiNO_3 and nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were thoroughly mixed with hexamine. The mixture was then dissolved in deionized water to obtain a precursor solution. The solution was preconcentrated in a quartz crucible until the evaporation of free water and ignited at higher temperature. During ignition flame and fumes were evolved leaving behind a fluffy mass. By changing the stoichiometric ratio with the addition of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, substituted compounds of lithium nickelate with the nominal composition of $\text{LiNi}_{0.5}\text{La}_{0.25}\text{O}_2$ was prepared. The synthesized powders were placed in a high alumina crucible and calcined at 700 °C for 5 h using an electrical resistance furnace.

The thermal behavior of the as synthesized lithium nickelate was studied by thermogravimetry and differential thermal analysis TGA/DTA using a thermal analyser STA 1500 PL thermal sciences, version V4.30 analyzer. The phase formation and the structural features of the synthesized compounds were characterized by XRD (Philips 8030 x-Ray Diffractometer). FT-IR spectra of synthesized samples (in KBr discs) were taken with a thermo electron corporation, USA Model: Nexus 670 (FTIR), Centaurms 10x (Microscope). The elemental impurities present in the synthesized compounds were determined by CHNS analyzer (Elementar Model Vario EL III). The morphology of the synthesized crystals was scrutinized by SEM (HITACHI Model S-3000H).

Results and Discussion

The TGA and DTA curves of combustion synthesized precursor powders are shown in Figure 1. The curves exhibit discrete regions of weight loss on product transformation. The weight loss is mainly due to the chemical dissociation of water present in the reacting salts. This process occurred in the temperature between 143 °C and 306 °C. The weight loss in the temperature range of 306-468 °C may be attributed to the decomposition of the fuel hexamine and the nitrate salts. Beyond 468 °C, there is a surge in the curve indicating the transformation of precursor salts in to a single-phase lithium nickelate compound.

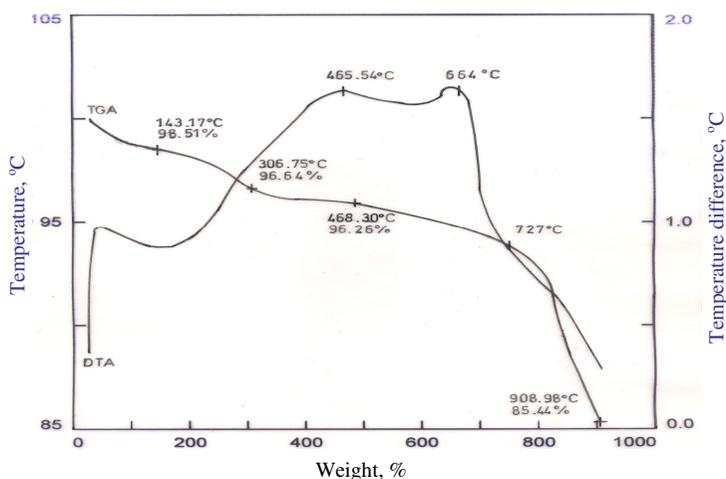


Figure 1. TGA and DTA curves for LiNiO₂

DTA analysis reveals the evolution of an exothermic peak at 465 °C, indicating the rapid decomposition of hexamine and dissociation of nitrate salts. The remaining compounds transform in the temperature range 465-664 °C by chemical dissociation reactions. The observed exothermic peak is thus representing the possible reaction between Li₂O and NiO forming the final compound lithium nickelate.

The XRD patterns of the parent LiNiO₂ and LiNi_{0.75}La_{0.25}O₂ are presented in the Figure 2. In the ideal stoichiometric LiNiO₂, the Li⁺ and Ni³⁺ cations are supposed to be orderly arranged along the (111) direction of the rock salt cubic lattice leading to a 2D layer structure, isostructural with a-NaFeO₂ compound. Hence, LiNiO₂ has a rhombohedral structure with trigonal symmetry comprising of two interpenetrating close packed FCC sub-lattices: one consists of oxygen anions and the other consists of Li and Ni cations on alternating (111) planes. The lattice constant values 'a' and 'c' are calculated from the XRD data and presented in the Table 1. It is noticed that there is a variation in the lattice constant values, which may be due to the substitution of La³⁺ ions.

The fourier-transform IR (FT-IR) spectra of the synthesized samples are presented in the Figure 3. Generally, the FTIR spectral data of LiM_xO_y reveal the local structure of the oxide lattice constituted by LiO₆ and MO₆ octahedra. The relative IR absorbance is sensitive to the short-range environment of oxygen coordination around the cations in the oxide lattices, crystal geometry and the oxidation states of the cations involved. It is less likely to get affected by the grain size and the morphology of long-range order of the crystal lattice^{20,21}. Since, LiO₂ and NiO₂ layers are separated in lithium nickelate, four vibrational bands are identified in the range 400-800 cm⁻¹ for the NiO₂ layer.

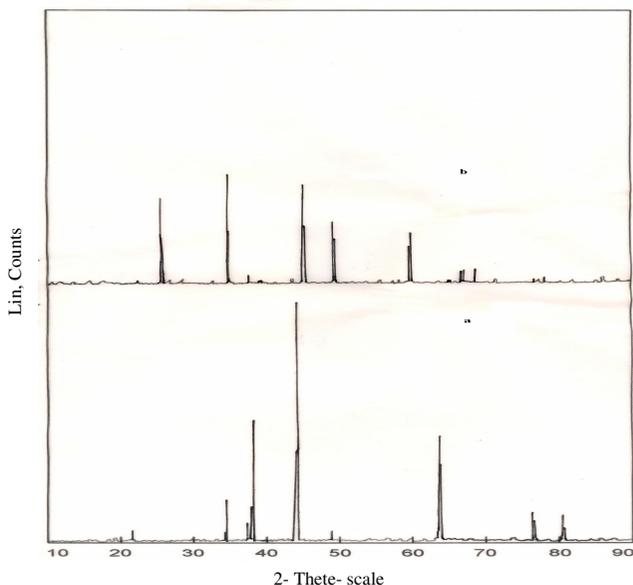


Figure 2. XRD pattern of (a) LiNiO_2 ; (b) $\text{LiNi}_{0.75}\text{La}_{0.25}\text{O}_2$

Table 1. Lattice constant values calculated from XRD data

Sample	a Å°	c Å°
LiNiO_2	2.905	14.24
$\text{LiNi}_{0.75}\text{La}_{0.25}\text{O}_2$	2.83	14.3591

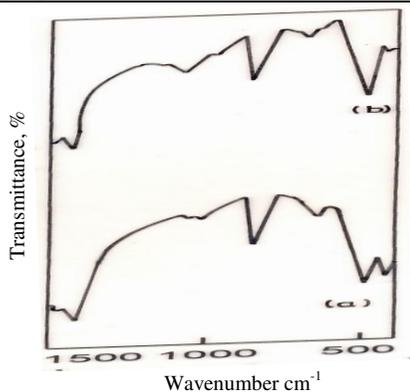


Figure 3. FTIR spectra of (a) LiNiO_2 ; (b) $\text{LiNi}_{0.75}\text{La}_{0.25}\text{O}_2$

The band observed around 496.8 cm^{-1} may be ascribed to the asymmetric stretching of Ni-O bonds in NiO_6 octahedra. The other band around 430 cm^{-1} and a weak band at 647.6 cm^{-1} may be attributed to the bending modes of O-Ni-O bond^{22,23}. Peaks around 860 and 1430 cm^{-1} are responsible for the presence of Ni-O bond. Upon the introduction of La^{3+} ions, the bands of NiO_6 octahedra are found to shift towards higher frequency region due to shortening in the Ni-O distance.

The impurity elements present in the synthesized compounds are determined using a CHNS analyzer and presented in Table 2. The data on the elemental analysis show that the

sample contains minor concentration of carbon as impurity. The percentage of carbon is found to be very low in the case of La substituted sample in comparison with the parent LiNiO₂ compound. The presence of carbon may be due to the usage of the fuel hexamine.

Table 2. Analysis of impurity elements in the products

Sample	N	C	H
LiNiO ₂	0.000	5.904	0.000
LiNi _{0.75} La _{0.25} O ₂	0.000	4.182	0.000

The morphological features of the synthesized powders are examined using a scanning electron microscope. The SEM micrographs are presented in figures 4a-4b. The Figures show that the parent LiNiO₂ exhibits a very fine crystalline structure with an irregular morphology. Obviously morphological changes occur by the presence of La³⁺ ions in the substituted compound. The La substituted LiNiO₂ powder has shown a smooth-edged polyhedral structure with an average particle size of 5-10 μm.

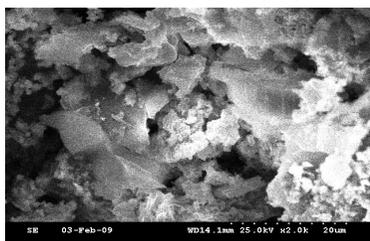


Figure 4a. SEM micrograph of LiNiO₂

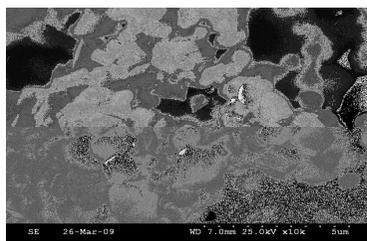


Figure 4b. SEM micrograph of LiNi_{0.75}La_{0.25}O₂

Conclusion

Lithium nickelate and lanthanum substituted lithium nickelate crystals are successfully synthesized using combustion synthesis process. The compounds possess good physiochemical properties. The synthesis process is found to be an economically viable one, which can be extended for the bulk preparation of these materials.

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