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Structural characterization of LiNiO2 and LiNi0.96Mg0.04O2 cathode materials

N. Murali, K. Vijaya Babu, K. Ephraim Babu and V. Veeraiah^{*}

*Department of Physics, Andhra University, Visakhapatnam-530 003, INDIA

Email: v_veeraiah@yahoo.co.in

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ABSTRACT

The layered compounds $LiMO_2$ (M=transition metals) remain most promising because of their theoretical capacity is much higher than that of their competitors such as spinel or olivine material. The goal of this paper is to synthesize a cathode material composed of $LiNiO_2$ and $LiNi_{0.94}Mg_{0.04}O_2$ that has an increased capacity and cycling life. To do this, we synthesis the compounds of $LiNiO_2$ and $LiNi_{0.96}Mg_{0.04}O_2$ with varying amount of Mg by using solid state reaction method at high temperature. Each unique compound will be characterized using XRD, FESEM and FTIR to reveal the structural properties of the material.

Keywords: Solid-state reaction method, Layered structure, Lattice constant, FTIR, FESEM.

INTRODUCTION

The batteries have been around since the early twentieth century and have provided humans access to electrical power almost anywhere in the world [1]. They are widely used device that converts stored chemical energy into electricity. Two basic types of batteries exists which known as the primary batteries or non-rechargeable batteries and secondary batteries which can be recharged and used multiple times. The battery consist three elements anode, cathode and an electrolyte. The traditional cathode materials used in today's the lithium ion battery industry are a group of 3-d transition metal oxides like LiCoO₂, LiNiO₂ and $LiMn_2O_4$ [2]. The lithium ion battery consists of three main components positive, negative and electrode separated by a separator dipped in electrolyte [3]. The Negative electrode is normally an electron donor group which is electropositive in nature like lithium metal. The Positive electrode is normally an electron acceptor which is strongly electronegative (e.g. $LiMO_2$ (M= Co, Ni, Mn, etc compounds) [4]. The layered LiMO₂ are traditional cathode materials that have been thoroughly studied experimentally and theoretically. The layered structure can he envisioned as two interpenetrating fee lattices, one consisting of oxygen. And the other consisting of alternating (111) planes of Li and Transition Metal (TM) ions [4]. In the R3m space group the Li and the metal ions remain fixed in the ideal rock salt positions, but the whole (111) oxygen planes may relax in the (111) direction giving rise to different slab spaces that affect lithium mobility.

The solid state reaction method [5, 6], sol-gel method [7], coprecipitation method [8], combustion method [9] etc, have been reported for the synthesis of LiNiO₂. To address this issue, we have investigated magnesium doped LiNiO₂, that is LiMg_xNi_{1-x}O₂. Doping with magnesium is expected to stabilize the

lithium ions on their crystallographic sites and thus to prevent insertion of nickel ions in lithium layers (10). Among all these methods of solid-state reaction method is easy to synthesis and low cost, and then we used in this work.

MATERIALS AND METHODS

Preparation And Experimental Techniques: The cathode compositions are synthesized by a solid-state reaction method from stoichiometric amounts of Li_2CO_3 (Merck 99.9%), MgO (Merck 99.9%) and NiO (Merck 99.9%).

 $\begin{array}{c} 0.5 \text{ Li}_2\text{CO}_3 + \text{NiO} \rightarrow \text{LiNiO}_2 + \text{gas} \uparrow \\ 0.5 \text{ Li}_2\text{CO}_3 + 0.94 \text{ NiO} + 0.06 \text{ MgO} \rightarrow \text{LiNi}_{0.94}\text{Mg}_{0.06}\text{O}_2 + \text{gas} \uparrow \end{array}$

A slight excess amount of lithium (5%) was used to compensate for any loss of the metal which might have occurred during the calcined at high temperatures. The mixture of the starting materials with the composition of LiNiO2 and LiNiO.96Mg0.04O2 was sufficiently mixed and grinding the powder was then heat-treated in air at 500° C for 5 h, it was ground, mixed and calcined at 750° C for 20 h. Then, this powder was cooled at rate of 5° C min⁻¹. finally, the powder was ground and mixed calcined again at 800° C for 20 h in air using a muffle box furnace. It is found that the solid-state reaction method between Li₂CO₃, NiO and MgO is a convenient way to produce LiNiO₂ and LiNi_{0.96}Mg_{0.04}O₂. Depending on the Li₂CO₃ wt %, it was possible to obtain LiNiO₂ with the correct stoichiometry and without the presence of the LiCO₃ impurity phase.

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

X-Ray Diffraction: The powder X-ray diffraction is a technique used to characterize the crystallographic structure, crystallite size (grain size) and preferred orientation in polycrystalline powdered solid samples. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction data. The Powder diffraction is also a common method for determining strains in crystalline materials.

Crystallite size: The crystallite size can be evaluated measuring the full width at half maximum (FWHM) according to the Scherrer's 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-K α 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

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

Figure 1 shows the XRD diffraction pattern of $LiNiO_2$ material calcined at 800 °C for 20 h. The analysis confirms the formation of the layered structure without any impurity phase. The X-ray pattern is

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comparable with the standard JCPDS data. Although the 20 values are comparable with the standard pattern of LiNiO₂ [11], there are considerable differences in the intensity of lines (003) and (111). The intensities and positions of the peaks we observe a good agreement between the results and those reported by other workers [6, 12]. From the XRD pattern of the powder sample the lattice parameter and crystallite size are also calculated. The lattice parameters vary slightly corresponding to the variation in the d values of LiNiO₂ and LiNi_{0.96}Mg_{0.04}O₂ as expected (Fig.2).



Figure 1: XRD pattern of LiNiO₂





A single phase of orthorhombic structure with the space group R3c has been confined by XRD analysis. The orthorhombic lattice constant of LiNiO₂ based on the (111) peak is calculated as a = 2.8963 Å 1204

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corresponding to c =14.2316 Å and the orthorhombic lattice constant of $LiNi_{0.96}Mg_{0.04}O_2$ based on the (111) peak is calculated as a = 2.8867 Å corresponding to c =14.2399 Å. The sharp peaks indicate the increase in crystallinity and ordering of local structure and release of lattice strain(Table 1).

Fable 1 : Lattice constants	(a, c) and c/a	ratio for	LiNiO ₂ a	und LiNi0.9	$Mg_{0.04}O_2$
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Compound	a Å	c Å	c/a	Crystallite size (nm)	Cell volume
LiNiO ₂	2.8963	14.2316	5.779	42.96	103.3939
LiNi _{0.96} Mg _{0.04} O ₂	2.8867	14.2399	5.969	40.21	102.7676

Scanning Electron Microscope: The scanning electron microscope (SEM) uses high energy beam of electron in a raster scan pattern to produce the magnified image of the sample. The SEM is mainly a reflection instrument and use radiation reflected from the sample for producing the magnified image. Particles up to nanometer size could be viewed using Scanning Electron Microscope (Figure 3)



Figure 3: SEM Micrographs of LiNiO₂ and LiNi_{0.96}Mg_{0.04}O₂

The particle morphology of the cathode materials is one of the most important factors to influence their electrochemical performance. The SEM images of the pure LiNiO_2 and the magnesium substituted sample [13]. The morphological changes are clearly observed as a result of magnesium substitution. It can be seen that the particles of LiNiO_2 powder material have fairly uniform particle size distribution, indicating well developed crystallinity. This is confirmed by XRD pattern (sharper, higher and well defined diffraction peaks). The grain size of the compounds are shown in table 2.

Table 2: Varia	tion of gr	ain size w	ith composition
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Compound	Grain size (µm)
LiNiO ₂	2.20
LiNi _{0.96} Mg _{0.04} O ₂	1.47

Ft-Ir Spectroscopy Studies: The Fourier Transform Infrared spectroscopy is a versatile technique for the qualitative and quantitative characterization of materials. It deals with vibrational motion of atoms in a molecule. The molecules absorb IR radiations of specific energy when their motion is associated with the dipole change [14]. The energy of the absorbed IR radiation is unique for particular bond (functional groups) and useful for qualitative and quantitative analysis of that functional group present in the molecule [15, 16].

The room temperature FTIR spectra of the synthesized samples are performed and the results are shown in figure 3. Two distinct peaks are observed in each FTIR spectrum at different wavelength regions. The two

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strong frequency bands appeared at wave numbers 864.13 and 492.98 cm⁻¹ are responsible for the formation of LiNiO₂ which might be attributed to asymmetric stretching modes of Li-Ni-O. On the other hand, due to the formation of LiNiO₂ and LiNi_{0.9}Mg_{0.04}O₂ materials, these two peaks are shifted slightly towards higher wave numbers 865.55 and 507.14 cm⁻¹ and 464.64 and 453.31 cm⁻¹ respectively, which may be attributed to the asymmetric stretching modes of Li-Ni-O (Table 3). This is consistent with the assumption deduced from XRD results. Also, it is in good agreement with the larger lattice parameter of magnesium contained samples calculated from the XRD patterns.



Figure 4: FTIR spectra of LiNiO₂ and LiNi_{0.96}Mg_{0.04}O₂

Table 3: FTIF	R wave numb LiNiO ₂	er variation of the two compound ${\rm LiNi}_{0.96}{\rm Mg}_{0.04}{\rm O}_2$	ounds
	864.13	865.55	
	492.98	507.14	
	467.48	464.64	

The substitution of Mg in $LiNiO_2$ sample is effective in improving its crystallinity and we hope it will be a good cyclability and capacity retention performances in further studies

453.31

461.81

APPLICATIONS

The substitution of Mg in $LiNiO_2$ sample is effective in improving its crystallinity and we hope it will be a good cyclability and capacity retention performances in further studies.

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CONCLUSIONS

LiNiO₂ and LiNi_{0.96}Mg_{0.04}O₂ samples are successfully synthesized by solid-state reaction method. XRD results suggest that the synthesized samples adopt rhombohedral layered structure and belong to R3c space group. No additional phase or impurity is detected. The grain sizes of all samples are between 0.43 and 0.53 μ m. The FTIR analysis confirms that the Mg ions are inserted into the lattice of the crystal during the formation LiNi_{0.96}Mg_{0.04}O₂ compounds. From this study it is understood that the substitution of Mg in LiNiO₂ sample is effective in improving its crystallinity and we hope it will be a good cyclability and capacity retention performances in further studies.

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