RESEARCH ARTICLE

SYNTHESIS, DIELECTRIC AND IMPEDANCE STUDIES OF LiNi$_{1-X-0.02}$Mg$_{0.02}$Zn$_X$O$_2$ (X = 0.0 and 0.02) CATHODE MATERIALS FOR LITHIUM-ION BATTERIES.

N. Murali [* 1,2], J. M. Sailaja[2], S.J. Margarette[2], and V. Veeraiah[2].
1. Advanced Analytical Laboratory, DST-PURSE Programme, Andhra University.
2. Department of Physics, Andhra University, Visakhapatnam-530 003, INDIA.

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Manuscript Info	*Abstract*
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Zn-Mg co-substituted layered structure cathode materials LiNi$_{1-x-0.02}$Zn$_x$Mg$_{0.02}$O$_2$ (x = 0.00 and 0.02) is prepared by a solid state reaction method. These materials are characterized by structural, morphological and electrochemical impedance studies. The X-ray diffraction (XRD) data revealed that the formation of phase and possessed the α-NaFeO$_2$ structure of the rhombohedral-hexagonal system (space group, $R\bar{3}m$) with no evidence of any impurities. The morphology and uniform distribution of the synthesized samples are studied with Field Effect Scanning Electron Microscopy (FESEM). The substitution of Mg and Zn for Ni can enlarge the particle size and improve the crystallinity. Electrochemical impedance studies (EIS) in the frequency range from 42 Hz to 1 MHz with temperature variation from 30° to 100° C are studied by high ionic conductivity for amount of x = 0.02 doping material. The temperature dependent non-Debye type of dielectric relaxation has been studied and the Nyquist plots showed the negative temperature coefficient of resistance behavior of these compounds.

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Introduction:-

In the past decades, the lithium metal oxides have played an important role a portable electrical device, high energy storage capacity and excellent rechargebility. Among them, LiCoO$_2$ is still continuing as the most used cathode material because of its easy synthesis, relatively good cyclic stability and stable discharge voltage [1-2]. But LiCoO$_2$ is very toxic, has a high cost and some safety issues. However, in order to minimize these problems, research efforts are focused on the substitution of LiCoO$_2$ with LiNiO$_2$ and LiMnO$_2$. The LiNiO$_2$ is an isostructural compound with lithium cobalt oxide, but has not been pursued in the pure state for battery cathode even though nickel is more readily available than cobalt [3]. The advantages of LiNiO$_2$ over LiCoO$_2$ include better cycling performance, rate capability and thermal stability. The discharge capacity of LiNiO$_2$ measured experimentally is certified to have about 140-150 mAhg^{-1} due to the synthesis of non-stoichiometric LiNiO$_2$. It is difficult to synthesize stoichiometric LiNiO$_2$ because of the loss of lithium from the host structure during high temperature calcination due to the high vapor pressure of lithium [4-5]. Another typical problem is its capacity fade is observed even for stoichiometrically synthesized LiNiO$_2$ due to the formation of the NiO$_2$ phase of the phase transition of the LiNiO$_2$ structure when charging up to a high voltage (4.0 V vs. Li$^+$/Li) during deintercalation of Li-ions [6-7]. Furthermore studies reveal

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Corresponding Author:- N. Murali
Address*:- Advanced Analytical Laboratory, DST-PURSE Programme, Andhra University.*

that the electrochemical properties of LiNiO$_2$ are extremely dependent on synthesis conditions and hence the optimization of preparation conditions is essential for LiNiO$_2$ in order to minimize all the constraints.

In the present work, we synthesized LiNi$_{1-x-0.02}$Mg$_{0.02}$Zn$_x$O$_2$ (x = 0.0 and 0.02 cathode materials at 850º C for 20 h. The effect of Mg and Zn content on the structure and morphology studies are investigated. The main emphasis has been focused on the study of conduction mechanism and dielectric behavior. From the conductivity studies, various important parameters such as activation energy, electric modulus, relative dielectric constant etc., are estimated and the results are presented.

Preparation and Experimental Techniques:-
The cathode compositions are synthesized by a solid state reaction method from stoichiometric amounts of Li$_2$CO$_3$ (Merck 99.9%), ZnO (Merck 99.9%), MgO (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 occurred during the calcination at high temperatures. The mixture of the starting materials is sufficiently mixed and grinded, the powder of it is then heat treated in air at 500º C for 5 h and it is again ground and mixed, and calcined again at 750º C for 20 h. Then, this powder was cooled at the rate of   5º C/ min. Finally, the powder was ground and mixed, and calcined again at 850º C for 20 h in air using a muffle box furnace. For electrical study, pellets with diameter of 10 mm and thickness of 1.1 to 1.25 mm are used.

The phase identification and crystal structure characteristics are determined by X-ray diffraction using a Rigaku Cu-Kα diffractometer with diffraction angles of 20º and 80º at the wavelength of 1.5406 Å. The morphologies of the synthesized materials are studied by field effect scanning electron microscopy (FESEM) from Carl Zeiss, EVO MA 15, Oxford Instruments. The Fourier transform infrared spectra are recorded using Nicolet 6700 and following the KBr pressed pellet technique to determine the structures of the calcined cathode materials. These materials are prepared by adding PVA and ground in an agate mortar and pestle for one hour and then pressing by Hydraulic press at 5 tones for 6 minutes and then sintering the pellets at 850° C / 20 hours. The surface layers of the sintered pellet are carefully polished and washed with acetone and then the pellet is coated with silver paste on the opposite faces which act as electrodes. The impedance study on these pellets is performed by a Hioki 3532-50 LCR Hitester in the frequency range 42 Hz to 1 MHz at temperature range from room temperature to 100° C.

Results and Discussion:-
X-ray Diffraction Studies:-
The X-ray diffraction analysis of the synthesized cathode materials is carried out in order to investigate the relation between crystallographic properties [8]. It is can be observed that the entire fingerprint peaks (003), (101), (006), (102), (104), (108), (110) and (113) are legibly identifiable, thereby suggesting the existence of α-NaFeO$_2$ structure. Figures 1 (a) shows the XRD patterns of LiNi$_{1-x-0.02}$Mg$_{0.02}$Zn$_x$O$_2$ (x = 0.0 and 0.02). All the diffraction patterns of synthesized materials of Mg and Zn substituted LiNiO$_2$ can be indexed to a phase-pure hexagonal structure with the space group of $R\overline{3}m$ (166). They have indicated that the Li+ and Ni+ ions occupy the octahedral 3a and 3b sites respectively, which match well with the diffraction file JCPDS card No. 74-0919 and no remarkable secondary phase is observed [13].

It can be seen that the crystal lattice parameters of the substitution compounds are increased than those of pristine LiNiO$_2$ since the atomic radii of the substituted Mg and Zn are higher than that of the Ni. The hexagonal parameters, a and c of synthesized samples are calculated from unit cell software (1995) [9]. The calculated lattice parameters, unit cell volume, crystallite size and c/a are summarized in Table 1. The lattice parameters a and c of the cathode materials increased with the increase of Zn composition [10-11]. The increase of lattice parameter could be attributed to reduction of Ni^{3+} (rNi^{3+} = 0.56 Å) ions to Ni^{2+} (rNi^{2+} = 0.69 Å) 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 and the intensity ratio of I$_{(003)}$/I$_{(104)}$. The c/a ratio values are 4.98 to 5.02 and the higher c/a values indicates well ordered hexagonal structure [12-13]. The Bragg intensity ratio of I$_{(0\ 03)}$/I$_{(104)}$, which is a signature of the cation-mixing [14], is given by 1.22 and 1.24 for synthesized samples, respectively. The separations of (0 0 6) / (0 1 2) and (1 0 8) / (1 1 0) peaks in the XRD spectra, which represent the layered character of the structure and good electrochemical properties is observed.
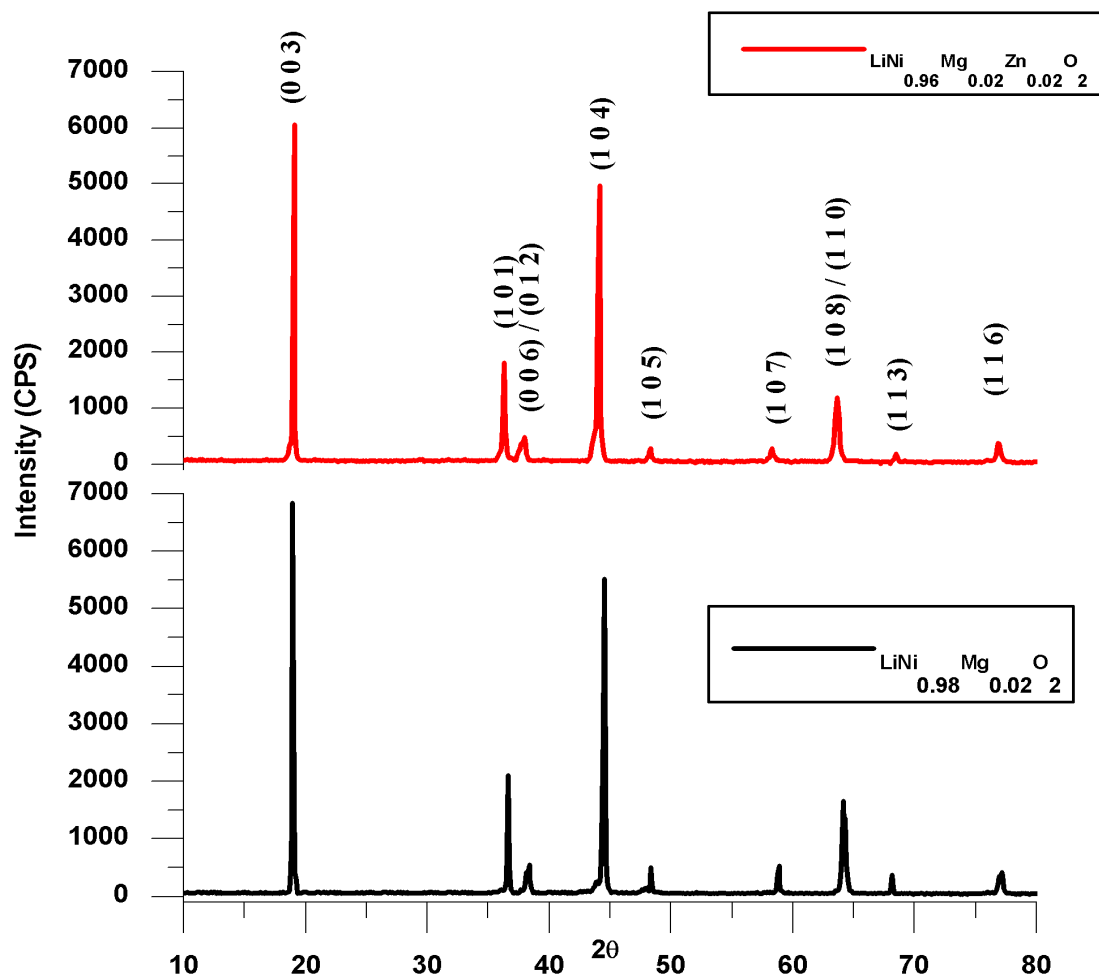
Figure 1:- XRD pattern of $LiNi_{1-x-0.02}Mg_{0.02}Zn_xO_2$ (x = 0.0 and 0.02)

Table 1:- Lattice constants, c/a value, cell volume and crystallite sizes of synthesized samples

Names	a (Å)	c (Å)	c/a	V (Å)^3	I_{003}/I_{104}	Crystallite size (nm)
$LiNi_{0.98}Mg_{0.02}O_2$	2.870	14.28	4.98	101.78	1.22	8.546
$LiNi_{0.96}Mg_{0.02}Zn_{0.02}O_2$	2.871	14.41	5.02	102.85	1.24	8.107

Field Effect Scanning Electron Micrograph Studies:-

The FESEM micrographs of $LiNi_{1-x-0.02}Mg_{0.02}Zn_xO_2$ (x = 0.0 and 0.02) obtained are shown in Figures 2(a) and (b). This unique morphology is advantageous for electrode materials because it allows the electrochemical performance to improve [15-16]. The grain sizes of the synthesized samples are found to be 3.19 and 3.64 μm, respectively. The average grain size increases with the increasing Zn content. Also the materials have some spherical shaped grains with uniform distribution [17]. Extended grains without voids are clearly seen to increase in Zn content in these figures.
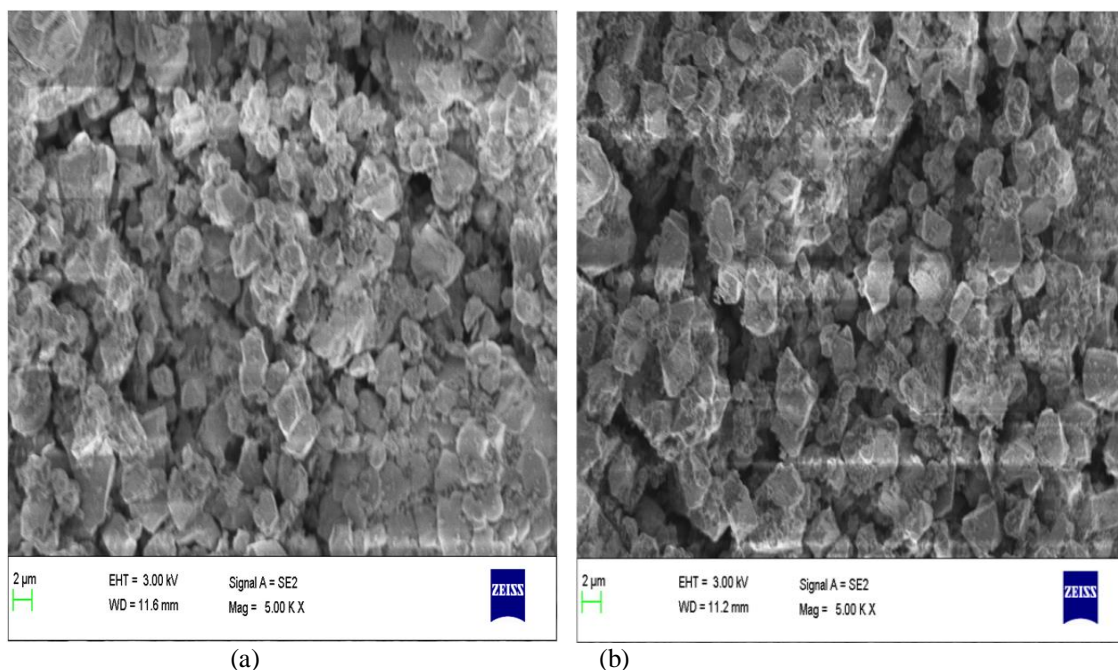
(a)   (b)

Figure 2:- (a) and (b): FESEM micrographs for $LiNi_{1-x-0.02}Mg_{0.02}Zn_xO_2$ (x = 0.0 and 0.02)

Dielectric and Impedance Studies:-

The electrochemical systems can be studied using Electrochemical Impedance Spectroscopy (EIS) with methods based on measuring the impedance response of a system over a range of frequencies. By using the electrochemical impedance spectroscopy technique, information on the electrochemical reactions in the system and transport of reactants/products is obtained. This technique is applied on an electrochemical system which is in equilibrium or under steady state conditions [18-19]. The Arrhenius plots of AC conductivity for $LiNi_{1-x-0.02}Mg_{0.02}Zn_xO_2$ (x = 0.0 and 0.02) are shown in Figures 3(a) and (b).

The conductivity in the cathode takes place at low frequencies and it increases with an increase in the temperature as expected. The frequency dependence of the dielectric constant (ε_r) of $LiNi_{1-x-0.02}Mg_{0.02}Zn_xO_2$ (x = 0.0 and 0.02) are shown in Figures 4 (a) and (b). The recommended cathode materials for Li-ion batteries should have a low dielectric constant and high resistance. We observe that the dielectric constant of the synthesized cathode materials is 5.0×10^3 and 5.0×10^5 for $LiNi_{1-x-0.02}Mg_{0.02}Zn_xO_2$ (x = 0.0 and 0.02) respectively and they are found to be very small [20-21].

Higher values of Z' and Z" at low frequency regions are due to the higher polarization caused by space charge [22]. It is also observed that the values of Z' and Z" gradually decrease with the increase of both frequency and temperature, indicating an increase in AC conductivity with the rise in temperature and frequency values and they are listed in Table 2. The modulus formalism is a very convenient tool to interpret the dynamical aspects of electrical transport phenomena. The major advantage of the electric modulus formalism is to suppress the electrode effect. This can also be used to study conductivity relaxation times. The complex modulus is defined as the inverse of the complex permittivity [23]. It is observed that the electric modulus increases with frequency and reaches a maximum (M_{max}) peak value. The modulus peak maximum shifts to higher frequencies as temperature increases, but the shapes do not change in the temperature range considered [24].
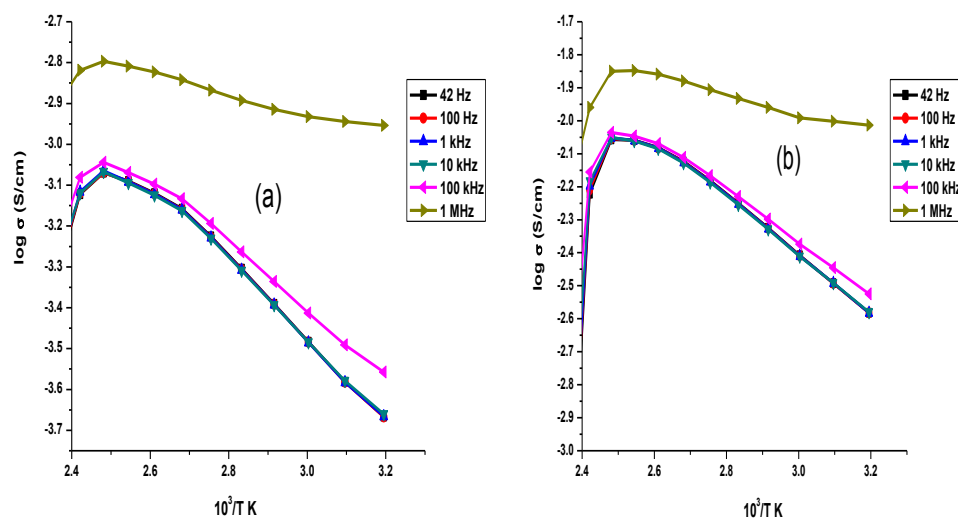
Figure 3:- (a) and (b): Arrhenius plots of AC conductivity for $LiNi_{1-x-0.02}Mg_{0.02}Zn_xO_2$ (x = 0.0 and 0.02)

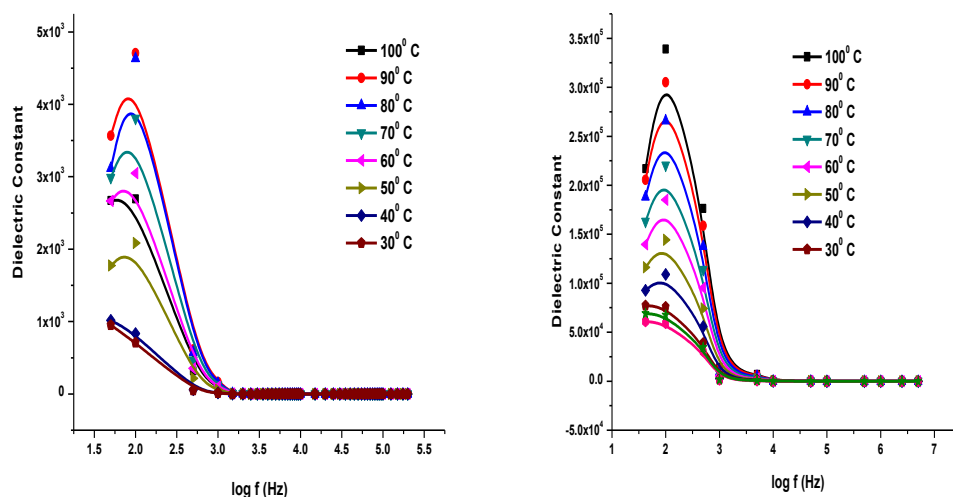**Figure 4:-** Frequency dependence of the dielectric constant (ε_r) plots of $LiNi_{1-x-0.02}Mg_{0.02}Zn_xO_2$ (x = 0.0 and 0.02)

Table 2:- AC conductivity values for $LiNi_{1-x-0.02}Mg_{0.02}Zn_xO_2$ (x = 0.0 and 0.02)

Temperature (°C)	AC conductivity (S/cm)	
	$LiNi_{0.98}Mg_{0.02}O_2$	$LiNi_{0.96}Mg_{0.02}Zn_{0.02}O_2$
30	2.02×10^{-6}	2.32×10^{-6}
40	2.15×10^{-6}	2.62×10^{-6}
50	2.62×10^{-6}	3.22×10^{-6}
60	3.29×10^{-6}	3.91×10^{-6}
70	4.07×10^{-6}	4.74×10^{-6}
80	4.96×10^{-6}	5.63×10^{-6}
90	5.96×10^{-6}	5.59×10^{-6}
100	6.95×10^{-6}	7.53×10^{-6}
110	7.59×10^{-6}	8.29×10^{-6}
120	8.14×10^{-6}	8.73×10^{-6}

Conclusions:-

The LiNi$_{1-x-0.02}$Mg$_{0.02}$Zn$_x$O$_2$ (x = 0.0, 0.02) cathode materials are synthesized by solid state reaction method. The structure and morphology of the synthesized materials are characterized by XRD and FESEM. The AC conductivity of the compounds is determined at various temperatures. The plots of log σ against reciprocal temperature obey Arrhenius rule. The activation energy calculated from the Arrhenius plots is found to be in the range from 0.14 to 0.89 eV. The ionic conductivity of the compounds is found to be varying from 8.14x10^{-6} to 8.73x10^{-6} S/cm with increase in temperature from 30° C to 120° C.

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