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# Synthesis and electrical properties of layered structure Li [$Ni_{0.5}$ $Co_{0.25}$ $Mn_{0.25}$] $O_2$ cathode material

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**Abstract:** Li [$Ni_{0.5}Co_{0.25}Mn_{0.25}$] $O_2$ is one of the potential cathode materials, due to its high energy density and low cost. Li [$Ni_{0.5}Co_{0.25}Mn_{0.25}$]$O_2$ cathode material has been synthesized by mixed hydroxide method. The XRD pattern exhibited predominant peak at $2\theta$ =18.39° with (003) orientation along with other characteristic orientations (104), (101), (105), (108) which is attributed to hexagonal layered structure with R3m space group and the estimated lattice parameters a= 2.84 Å, c=14.43 Å. The electrical transport plays an important role in the performance of the electrode in the lithium microbattery. The electrical conductivity of the Li [$Ni_{0.5}Co_{0.25}Mn_{0.25}$] $O_2$ sample is measured using Four Probe technique. The electrical conductivity is observed to be increased from $10^{-4}$ S/m to$10^{-2}$ S/m by increasing temperature from 303 K to 473 K with estimated activation energy of 0.25 eV. The ac electrical measurements also carried out at various temperatures from 303 K to 473 K in the frequency range 1 Hz - 1 M Hz.
**Keywords:** Li [$Ni_{0.5}$ $Co_{0.25}$ $Mn_{0.25}$] $O_2$, structural, ac, dc electrical conductivity properties.

## 1. Introduction and Experimental:

The layered structured Li [$Ni_{0.5}$ $Co_{0.25}$ $Mn_{0.25}$] $O_2$ is one of the best suited cathode material with good electronic conductivity and structural stability for application in lithium ion batteries [1]. The electrochemical properties of Li [$Ni_{0.5}$ $Co_{0.25}Mn_{0.25}$] $O_2$ compound the electrical conductivity will be increased. In recent years extensive efforts have been committed to decrease the particle size as much as possible to improve the effective surface area, thereby more electrochemical reactions occurs. In the present study Li [$Ni_{0.5}$ $Co_{0.25}Mn_{0.25}$] $O_2$ has been prepared by mixed hydroxide method. Conductivity studies on the lithiated cathode materials are significant in order to gain a better imminent on the conduction mechanism especially in its usage for lithium ion batteries. Hence, the present study has been aimed to concentrate on electrical properties of Li [$Ni_{0.5}$ $Co_{0.25}Mn_{0.25}$] $O_2$ powder synthesized by mixed hydroxide method.

Li [$Ni_{0.5}Co_{0.25}Mn_{0.25}$] $O_2$ with R3m space group is prepared by using mixed hydroxide method. For that LiOH.$H_2O$ (98%+Aldrich), $Co(NO_3)_2.6H_2O$(98%+Aldrich), $Ni(NO_3)_2.6H_2O$(98%+Fluka), and Mn $(NO_3)_2.4H_2O$ (97%+,Fluka) are used as the initial materials. The precipitate was filtered and washed twice with additional distilled water to remove any residual Li salts (LiOH and $LiNO_3$). The precipitate was then dried in air at 180

$^{o}$C for 12 h. The dried precipitate was mixed with stoichiometric amount of $LiOH.H_2O$ and ground and sintered at 900$^{o}$C for 3h. The structure of the prepared sample is studied by the X-ray diffraction technique (Siefert computerized X-ray diffractometer, model 3003 TT) using $CUK_{\alpha 1}$ radiation ($\lambda$=0.15406nm) in the 2$\Theta$ range 15-70$^{o}$. The impedance measurements were performed using a phase sensitive multimeter(Model:PSM 1700,UK) in the range of 1Hz to 1MHz at different temperatures. The dc electrical conductivity measurements were made on this powder employing the standard four-probe technique (Model: PID-200 SES instruments Pvt Ltd, Roorkee).

## 2. Results and Discussion:

### Structural analysis:

Fig.1.shows the XRD pattern of Li $[Ni_{0.5}\ Co_{0.25}\ Mn_{0.25}]\ O_2$ powder. All the peaks are indexed based on the $\alpha$-$NaFeO_2$ structure (space group R 3m). The XRD spectrum exhibited predominant peak (003) predominant orientation at 2$\theta$=18.39$^{o}$along with other characteristic orientations (101), (104), (105), (108) at 36.50$^{o}$,44.25$^{o}$,48.44$^{o}$, 64.19$^{o}$ which is attributed to hexagonal layered structure with R3m space group and the estimated lattice parameters a= 2.84 Å, c=14.43 Å. The estimated crystallite size is about 26nm.

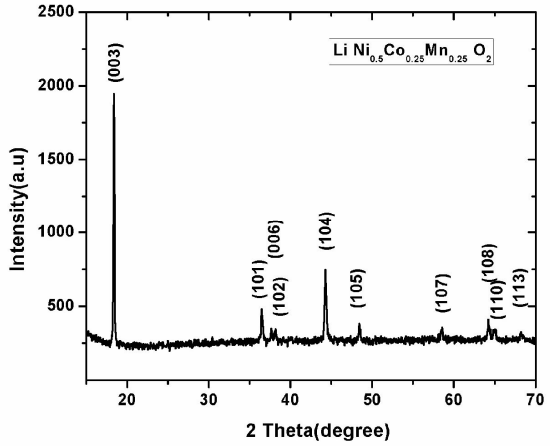


**Fig.1. XRD spectrum of Li $[Ni_{0.5}\ Co_{0.25}\ Mn_{0.25}]\ O_2$ powder**

### Electrical studies: dc conductivity

The dc electrical conductivity of Li $[Ni_{0.5}Co_{0.25}Mn_{0.25}]\ O_2$ was found to be strongly dependent on the temperature. Investigations are aimed to observe the dependence of the electrical conductivity by the varying the temperature. It is observed that, the conductivity increases with respect to temperature.

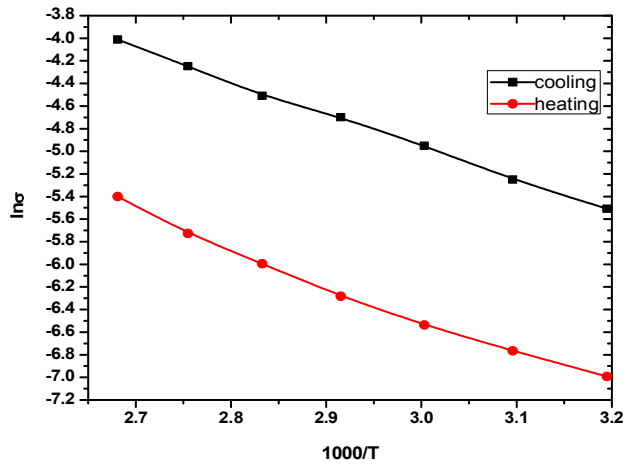


**Fig.2. Temperature dependence of dc conductivity of Li $[Ni_{0.5}\ Co_{0.25}\ Mn_{0.25}]\ O_2$.**

The electrical conductivity is increased from 3.87 x $10^{-4}$ S/m to 1.09 x $10^{-2}$ S/m by increasing temperature from 303 K to 473 K. The plots of logarithmic conductivity versus reciprocal of temperature are shown in Fig.2. The dc electrical conductivity data matched the following Arrhenius equation describing the migration of electrons by thermal activated process[2].The temperature dependence of ionic conductivity obeys Arrhenius rule. From the slope of the graph activation energy can be calculated. The estimated activation energy has been found to be 0.25 eV.

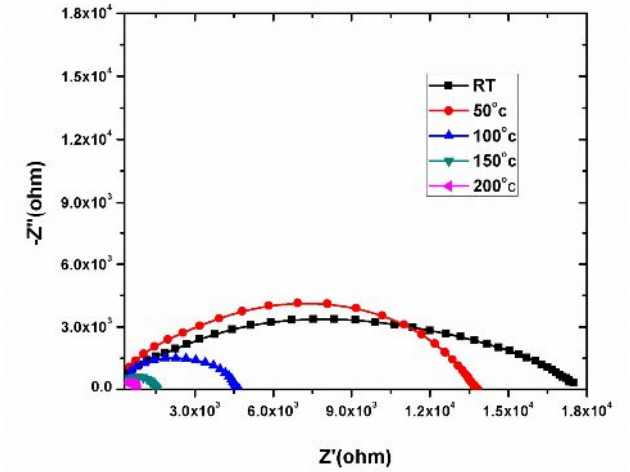


**Fig.3. Cole-Cole plots of Li [$Ni_{0.5}$ $Co_{0.25}$ $Mn_{0.25}$] $O_2$.**

**Electrical Studies: ac conductivity**

Fig.3. shows that the typical real (Z') and imaginary (Z") parts of Li [$Ni_{0.5}Co_{0.25}Mn_{0.25}$] $O_2$ impedance data plotted in complex impedance plane at 303-473k. The plots clearly show that there is an inclined straight line at lower frequency region followed by a semi circular arc at the higher frequency region. Low frequency semi circle is not easy to identity because of the constant phase angle of diffusion impedance is interacting with charge-transfer impedance [3-4]. The intersection of the semicircular arc on the real X-axis gives the bulk resistance ($R_b$) of synthesized Li [$Ni_{0.5}Co_{0.25}Mn_{0.25}$] $O_2$**.** The bulk electrical resistances ($R_b$) of the material are obtained, from the cole-cole plots with the intercept of the high frequency side on the X axis. The bulk resistance decreases with increasing temperature. The conductivity of the sample is calculated and it is observed that the evaluated ac conductivity value of the sample is 1.39 x$10^{-2}$ S/m at 473 K. From the slope of the graph activation energy is 0.25 eV. The electrochemical performance was studied by cyclic voltametry and charge-discharge measurements. The Li [$Ni_{0.5}Co_{0.25}Mn_{0.25}$] $O_2$ cathode material delivered an initial discharge capacity of about 140 $mAhg^{-1}$ with good cyclic stability.

## Conclusions:

The layered structure Li [$Ni_{0.5}$ $Co_{0.25}$ $Mn_{0.25}$]$O_2$ cathode material has been synthesized by mixed Hydroxide method. The formation of hexagonal layered structure Li [$Ni_{0.5}$ $Co_{0.25}$ $Mn_{0.25}$] $O_2$ with R3m space group has been confirmed from the XRD analysis. The dc electrical conductivity of the sample has been found to be varied from 3.87x$10^{-4}$ s/m to 1.09x$10^{-2}$s/m by increase of the temperature from room temperature to 473 K. The ac electrical measurements also carried out at room temperature to 473 K in the frequency range 1 Hz-1 MHz with estimated activation energy is found to 0.25 eV.

## 3. References:

1. Liao P.Y, Duh J.G. and Sheu H.S., In Situ Synchrotron X- Ray Studies of LiNi1-x-yCoyMnxO2 Cathode Materials, Electrochemical and Solid-State Letters., 2007, 10(4), A88-A92.
2. Vander Ven A, Aydinol M.K, Ceder G, Kresse G. and Hafner J., First-principles investigation of phase stability in LixCoO2, Phy.Rev., 1998,B 58,2975.
3. Nakamura T. and Okano Y., Electromagnetic properties of Mn–Zn ferrite sintered ceramics, Journal of Applied Physics., 1996,79,7129.
4. Koops C.G., on the dispersion of resistivity and dielectric constant of some semiconductors at audio frequencies, Phys,Rev., 1951,83,121.

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