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Impedance and Conductivity Analysis of Zn Doped $Li_4Mn_5O_{12}$

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Abstract : Cubic spinel shaped $Li_4Mn_{5-x}Zn_xO_{12}$ (x= 0.0, 0.25, 0.5 and 0.75) has been synthesized by single step molten salt method at 800°C for 10hr. Sample has been characterized by XRD, SEM, impedance and conductivity analysis at different temperature. Results have shown good conductivity for 0.1 mole Zn doped $Li_4Mn_5O_{12}$.

Keywords: Li-ion battery, molten salt method, conductivity and impedance analysis.

I. INTRODUCTION

Batteries play a vital role to fulfill the requirements of storing electrical energy. At present Li-ion batteries are available commercially, graphene and Cobalt based Li electrodes are used as anode and cathode material for rechargeable Li-ion batteries. An alternate material is indispensable for cobalt as the capitalization cost is very high and toxic [1]. In this scenario, Manganese based compounds ($LiMn_2O_4$, $LiMn_2O_3$ and $Li_4Mn_5O_{12}$) has shown an immense satisfaction as an alternate to cobalt due to its harmless nature, low cost, wide operating potential window, long shelf life and high cell voltage [2]. Thackery *et al.,* [3] have reported the merits of $LiMn_2O_4$ accompanied with changes in symmetry and also Jahn – Teller distortion due to its reduction in oxidation state of Mn^{4+} during cycling, which can be reduced by aliovalent substitution in Mn sites [1]. Also the Increase in oxidation state leads to good cycling stability in 3V region.

II. BACKGROUND and RELATED WORK

Choi *et al.,* [4] has made an attempt by anionic substitution of F^- in O^{2-} sites which suppress the disproportionate of $Li_4Mn_5O_{12}$ and also exhibits good capacity. Further Yan jing Hao *et al.,* [5] have confirmed the $Li_4Mn_5O_{12}$ electrode as a symmetric supercapacitor with good capacity behavior. Jiang *et al.,* [6] has synthesized $Li_4Mn_5O_{12}$ nano-crystallites by the combined action of low temperature spray-drying with solid phase reaction for first time. $Li_4Mn_5O_{12}$ has been synthesized by employing high energy ball milling technique by Julien *et al*., [7] and exhibited the capacity of 158 mAh/g. Moreover by using molten salt method $Li_4Mn_5O_{12}$ nanowires have been synthesized by Yang Tian *et al*., [8] with good charge/discharge curves between 2.3 and 3.3 V. Followed by the researches, researchers (Yan Zhao *et al.,* [9], Yan-jang Hao *et al.,* [10], Robertson *et al.,* [11]) have carried out extensive work on $Li_4Mn_5O_{12}$. In the present work, an attempt has been made to prepare Zn doped $Li_4Mn_5O_{12}$ in order to increase the conductivity by molten salt method.

III. MATERIALS AND METHOD

$Li_4Mn_{5-x}Zn_xO_{12}$ (x=0.0, 0.25, 0.5 and 0.75) has been prepared by molten salt method using $LiOH.H_2O$, MnO_2 and ZnO as starting precursors with LiCl - KCl as flux. The stoichiometric quantities of starting compounds are grounded and mixed well with flux. Obtained slurry has been calcined at 800ºC for 10 h and then allowed to cool to room temperature. The resultant products have been washed for several times with distilled water and then with ethanol to remove the residual

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molten salts and then dried. Powder XRD pattern using CuKα radiation has been used to identify the phase structure and to calculate the lattice parameter. The investigation of the morphology of the prepared samples has been examined by scanning electron microscope and Electrical conductivity of the prepared materials by using HIOKI 3532 LCR HI-TESTER in the frequency range of 42Hz – 1MHz at various temperatures.

IV. RESULT AND DISCUSSION

XRD pattern has carried out to confirm the nature of the material, which is shown in Fig. 1a. It was observed that the formation of highly crystalline nature of the material without any impurity. All the diffraction peaks are matched well with the standard JCPDS card no. 46-0810 indicating the formation of pure $Li_4Mn_5O_{12}$. Observed peaks were indexed to (111), (311), (222), (400), (331), (511), (440) and (531) plane in the form of spinel cubic structure with Fd3m space group. XRD spectrums of doped samples are shown in Fig. 1(b-d), whose peaks also matched well with parent material, confirms that Zn entered into Mn lattice without any changes in its structure. Lattice parameter of all the samples were calculated and given in Table 1. Lattice constant of doped materials are found to be higher than pure material due to the difference in ionic radii of Mn^{4+} (0.535Å) and Zn^{4+} (0.74 Å) which follows vegard's law [12]. Similarly, due to the difference in atomic density of Mn^{4+} and Zn^{4+} the lattice density of doped materials were found to be higher than pure $Li_4Mn_5O_{12}$ [12].

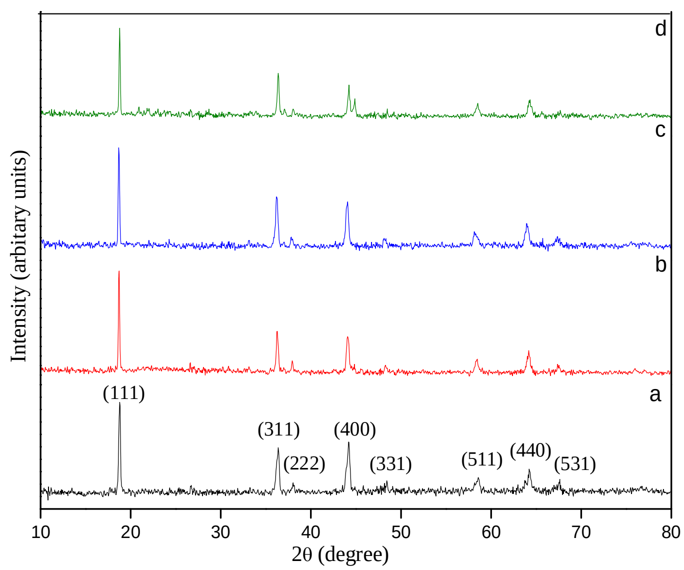

Fig.1. XRD spectrum of (a) $Li_4Mn_5O_{12}$, (b) $Li_4Mn_{4.75}Zn_{0.25}O_{12}$
(c) $Li_4Mn_{4.50}Zn_{0.50}O_{12}$, (d) $Li_4Mn_{4.25}Zn_{0.75}O_{12}$

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Table 1

Compounds	Lattice Parameter (Å)	Cell Volume (Å)^3	Lattice density x 10^{23} (g/cm^3)
$Li_4Mn_5O_{12}$	8.193	550.049	11.941
$Li_4Mn_{4.75}Zn_{0.25}O_{12}$	8.212	553.79	11.92
$Li_4Mn_{4.5}Zn_{0.5}O_{12}$	8.23	557.441	11.90
$Li_4Mn_{4.25}Zn_{0.75}O_{12}$	8.19	549.353	12.14

Morphology of the samples had studied by SEM analysis and shown in Fig. 2. Particles were measured in micron size (by length) displaying uniform 3D polyhedral shape, without any agglomeration due to molten salt. Sizes of the particles were reduced by increasing the concentration of the dopant. Few particles are in the range of 0.4 to 0.6 µm. Histogram of the particle sizes are given in Fig. 3.

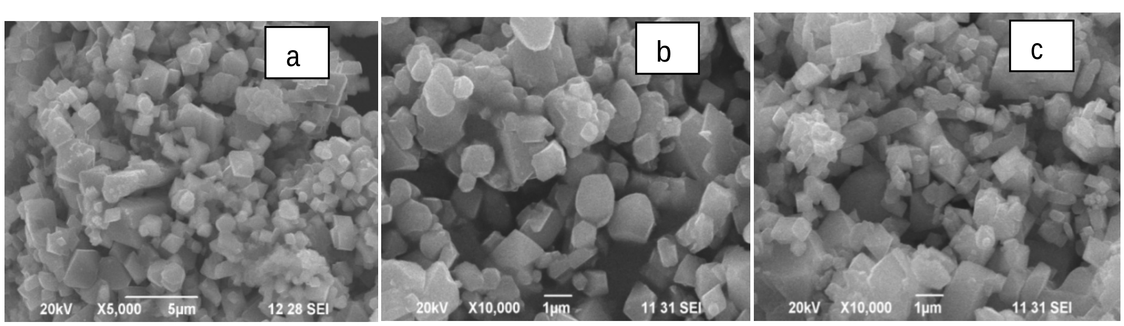

Fig.2. SEM images of (a) $Li_4Mn_5O_{12}$, (b) $Li_4Mn_{4.50}Zn_{0.50}O_{12}$ and (c) $Li_4Mn_{4.25}Zn_{0.75}O_{12}$

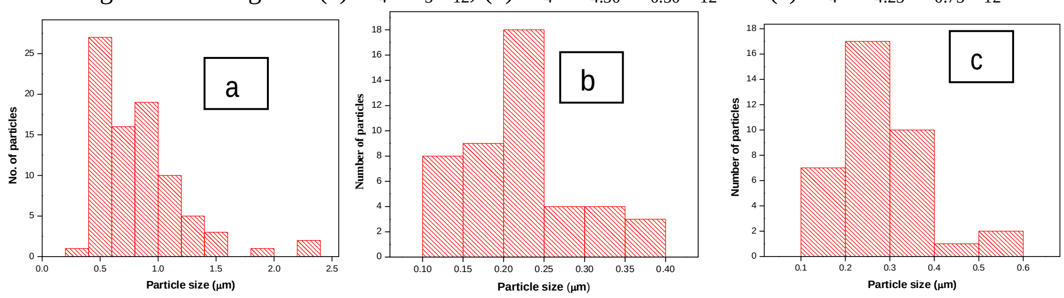

Fig.3. Histogram of (a) $Li_4Mn_5O_{12}$, (b) $Li_4Mn_{4.50}Zn_{0.50}O_{12}$, (d) $Li_4Mn_{4.25}Zn_{0.75}O_{12}$

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Cole-Cole plot of $Li_4Mn_{5-x}Zn_xO_{12}$ were studied by electrical properties at four different temperatures such as 353 K to 413 K. Fig.4(a-d) indicates the formation one semi-circle due to the parallel combination of R-C reveals that the conduction process occurs through bulk of the material i.e. grain interior [13]. Bulk resistance (Rb) of the material can be obtained by intercepting the semi-circle on the x-axis. Rb values decreases with increase in temperature i.e. negative temperature coefficient of resistance (NTCR) property, indicates the semi-conducting nature of the material [13]. The center of the circle falls below the real axis elucidates the non-Debye nature of the material. Conductance spectra of all the samples are shown in Fig.5 (a-d) dc conductivity of all the samples were calculated and given in Table 2. Compared to pure material Zn doped sample shows high conductivity except $Li_4Mn_{4.25}Zn_{0.75}O_{12}$.

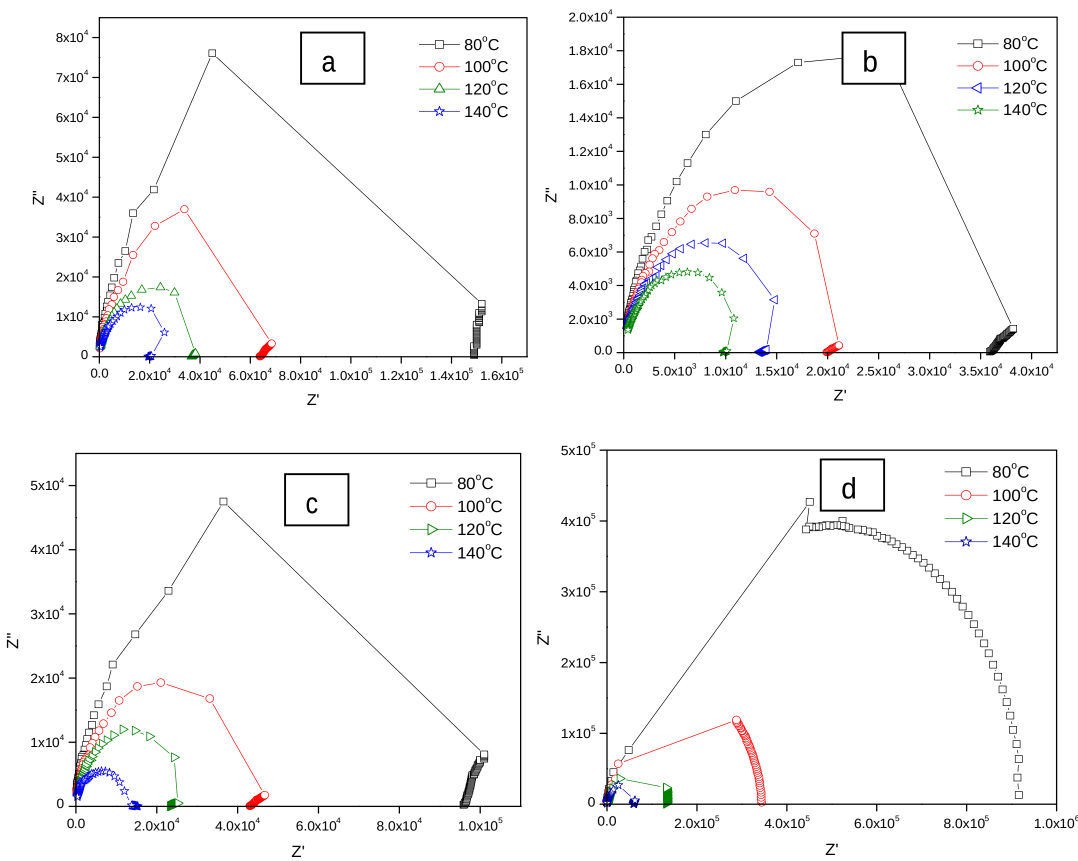

Fig.4. Cole-Cole plot of (a) $Li_4Mn_5O_{12}$, (b) $Li_4Mn_{4.75}Zn_{0.25}O_{12}$, (c) $Li_4Mn_{4.50}Zn_{0.50}O_{12}$, (d) $Li_4Mn_{4.25}Zn_{0.75}O_{12}$

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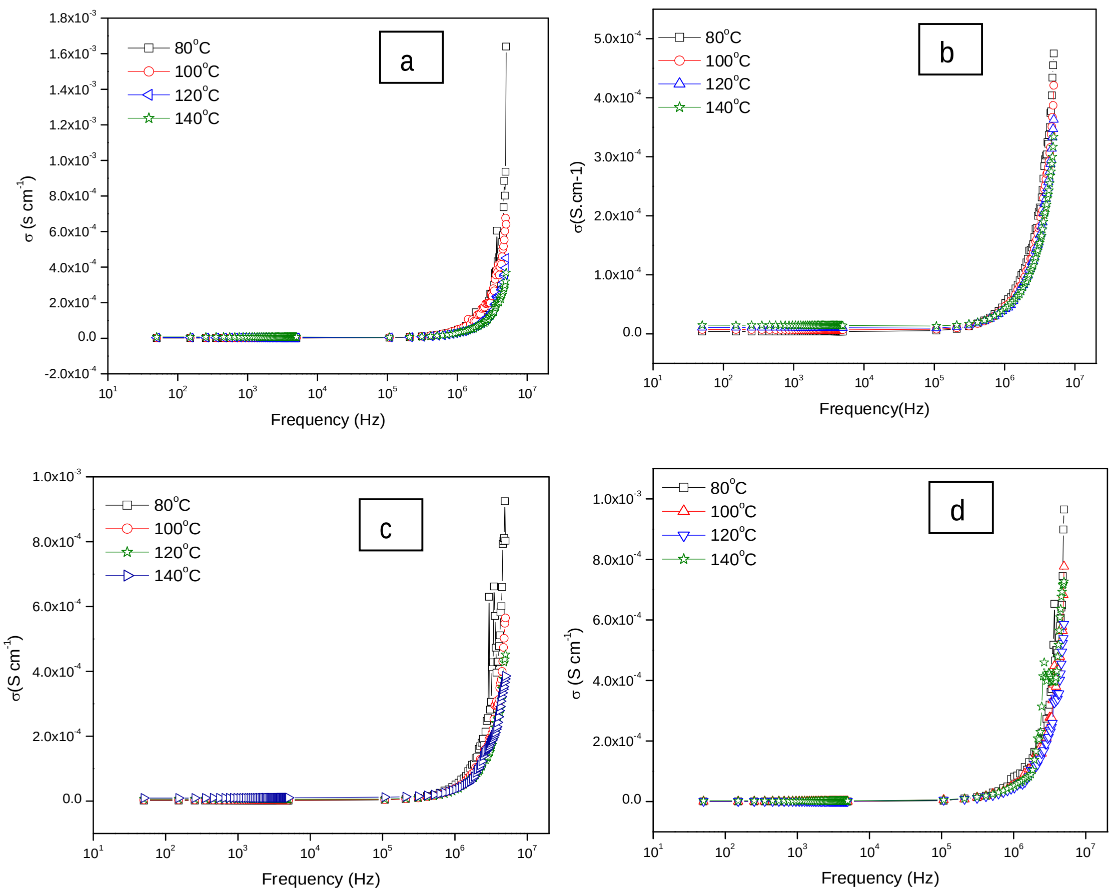
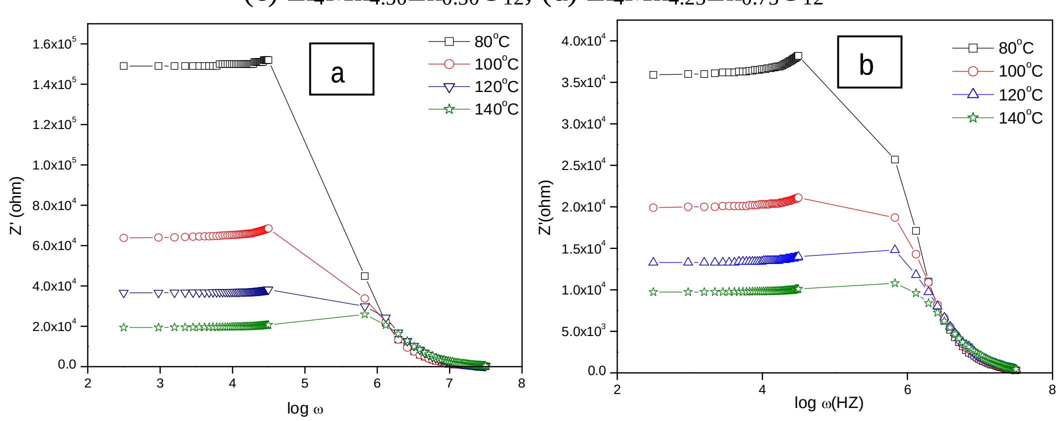


Fig.5.conductance spectra of (a) $Li_4Mn_5O_{12}$, (b) $Li_4Mn_{4.75}Zn_{0.25}O_{12}$, (c) $Li_4Mn_{4.50}Zn_{0.50}O_{12}$, (d) $Li_4Mn_{4.25}Zn_{0.75}O_{12}$



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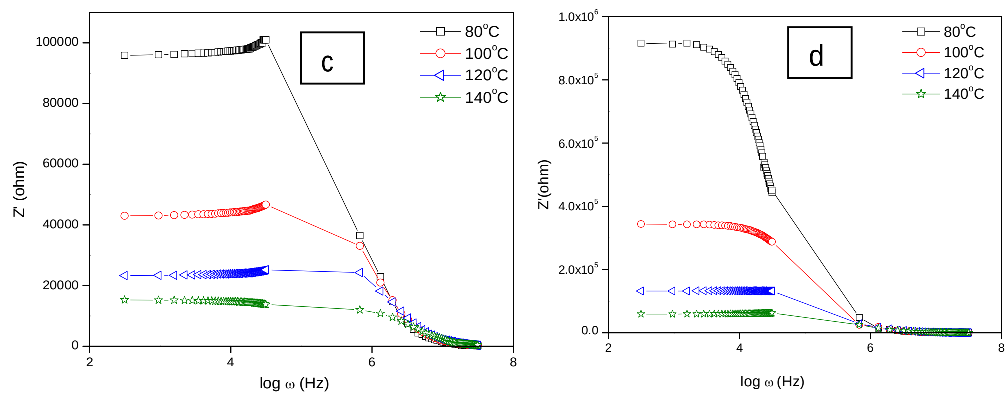

Fig.6. Variation in Z' with frequency of (a) $Li_4Mn_5O_{12}$, (b) $Li_4Mn_{4.75}Zn_{0.25}O_{12}$, (c) $Li_4Mn_{4.50}Zn_{0.50}O_{12}$, (d) $Li_4Mn_{4.25}Zn_{0.75}O_{12}$ at different temperature

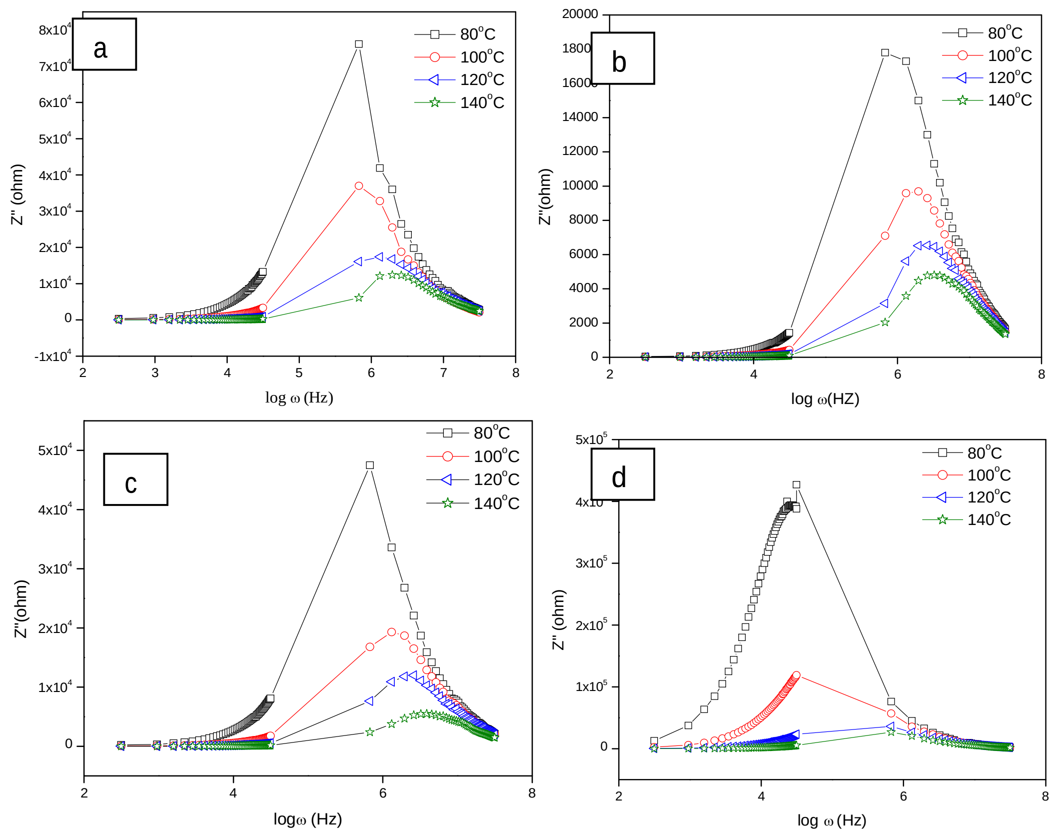

Fig.7. Variation in Z'' with frequency of (a) $Li_4Mn_5O_{12}$, (b) $Li_4Mn_{4.75}Zn_{0.25}O_{12}$, (c) $Li_4Mn_{4.50}Zn_{0.50}O_{12}$, (d) $Li_4Mn_{4.25}Zn_{0.75}O_{12}$ at different temperature

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Variation in real part (Z') and imaginary part (Z") of impedance with frequency at different temperature is shown in Fig.6 (a-d) and Fig.7 (a-d). Conduction process increases with increase in temperature and frequency is elucidated from the Z' curve [13]. At high temperature all the curves merged together, broadening of Z" peak with temperature indicates the temperature dependence of the material, which is responsible for conduction process [13].

Table 2

Material	**Temp.(K)**	**Rb x 10^4 (ohm)**	**σ x 10^{-6} (S.cm^{-1})**	**ω_p x 10^4 (Hz)**	**N x 10^{-9} (S cm^{-1}kHz^{-1})**	**μ x 10^{21} (cm^{2}V^{-1}s)**
$Li_4Mn_5O_{12}$	353	14.85	1.678	6.058	9.77	1.072
	373	6.378	1.54	10.615	5.43	1.77
	393	3.808	3.54	38.37	3.629	6.102
	413	2.017	6.23	41.95	6.141	6.349
$Li_4Mn_{4.75}Zn_{0.25}O_{12}$	353	3.587	1.536	6.92	7.83	1.22
	373	1.982	5.331	25.49	7.79	4.27
	393	1.365	8.63	34.23	9.90	5.44
	413	0.994	10	41.14	10.03	6.22
$Li_4Mn_{4.5}Zn_{0.5}O_{12}$	353	9.635	3.387	19.19	6.40	3.30
	373	4.332	4.387	25.43	6.43	4.26
	393	2.376	6.434	38.38	6.58	6.10
	413	1.459	10	45.39	8.65	7.22
$Li_4Mn_{4.25}Zn_{0.75}O_{12}$	353	9.157	2.543	9.09	9.86	1.61
	373	3.394	2.81	14.14	7.41	2.36
	393	1.346	3.066	15.97	7.54	2.54
	413	6.112	3.676	17.05	8.90	2.58

V. CONCLUSION

The following conclusions have been drawn on the present work and are

1. Zn doped $Li_4Mn_5O_{12}$ synthesized at single step molten salt method and Cole-Cole plot inferred that the conduction process is due to the bulk of the material and NTCR property of the material.
2. $Li_4Mn_{4.75}Zn_{0.25}O_{12}$ exhibited enhanced conductivity than other materials ($Li_4Mn_5O_{12}$, $Li_4Mn_{4.5}Zn_{0.5}O_{12}$ and $Li_4Mn_{4.25}Zn_{0.75}O_{12}$).
3. The optimum concentration of the dopant is found to be 0.25 mole which has significant impact on the efficiency of the material.
4. It can be confirmed that $Li_4Mn_{4.9}Zn_{0.1}O_{12}$ is a better alternate material for $LiCoO_2$.

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