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Structural and Electrical Properties of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$ as a Cathode Material for Rechargeable Li-ion Batteries

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Abstract: *The composite material nickel doped lithium manganese oxides has been prepared by simple molten salt method to enhance the electrical property. X-ray diffraction pattern of the material revealed the formation of cubic spinel structure with fd3m space group. The presences of functional groups were identified by FT-IR spectrum. The formation of sub-micron sized polyhedral shape of the particles was studied with the help of SEM analysis. Electrical studies were carried out using HIOKI LCR meter for wide range of temperatures (100^{o}C-400^{o}C) and maximum conductivity has been obtained as 7.01 x 10^{-5}S.cm^{-1} at 400^{o}C.*
Keywords: *Li-ion batteries, cathode, Ni doped, polyhedral shape, conductivity analysis.*

I. Introduction

A lithium-ion based energy storage device plays a significant role in modern technology. With high power density and energy density they are widely used in electronic equipments such as hybrid electric vehicles (HEV), laptops, camcorders and electric vehicles (EV) [1-3]. Efforts have been taken to study the performance of the batteries by considering the materials for electrode. Commercially, graphite and lithium cobalt oxide are used as anode and cathode in rechargeable Li-ion battery. Synthesis of cathode materials with good electrical performance in Li-ion battery is a tough task because of the lack of perfect stoichiometric ratio of the materials to be used [4]. Researchers are undergoing sincere efforts for synthesizing best cathode material in Li-ion battery.

Further researchers have shown great interest for synthesizing Spinel lithium manganese oxide due to its environmental friendly, low cost, long shelf life, high safety and high cell voltage. Different forms of $LiMnO_2$, $LiMn_2O_4$, $Li_4Mn_5O_{12}$ (or Li $[Mn_{1.67}Li_{0.33}]$ O_4) and $Li_2Mn_4O_9$ have been synthesized and studied by various researchers [5-12]. Among the forms $LiMnO_2$ and $LiMn_2O_4$have shown the occurrence of Jahn –Teller distortion and loses its potential as cathode material [13]. In this scenario, Thackeray *et al*. [14] have inferred the suitability of $Li_4Mn_5O_{12}$ as cathode material due to the absence of Jahn-Teller distortion. Research work has been carried out to synthesize $Li_4Mn_5O_{12}$via solid state [15], hydrothermal [16], sol-gel [17], spray-drying [18], molten salt [11], etc to improve its electrochemical performance. Moreover, preparation of $Li_4Mn_5O_{12}$ in definite ratio seems to be difficult as it disproportionates into $LiMn_2O_4$ and Li_2MnO_3 at high temperature [13]. Yang *et al*. [11] have prepared $Li_4Mn_5O_{12}$ nanowires by simple molten salt method and inferred the good electrochemical performance. Further, Sharmila *et al*. [19-20] have synthesized anode material of $Li_4Ti_5O_{12}$ and studied the performance.

In this paper, an attempt has been made to improve the electrochemical performance by doping the lithium manganese oxide with 0.1 mole of Ni in Mn sites. Samples are prepared by Molten salt method as there is no requirement of organic additive and also lack of formation of agglomeration.

II. Experimental Method

2.1 Synthesis

Stoichiometric amount of $LiOH.H_2O$, MnO_2 and $NiCl_2.H_2O$ were mixed together and grained well for 30 minutes. Molten salt such as LiCl and KCl were added in the molar ratio 60:40 and again grained. The obtained homogenous mixture was heated in muffle furnace at 800^{o}C for 10hrs. The resultant powder was washed thoroughly with distilled water several times and finally with ethanol to remove the residual salts.

2.2 Characterization

To identify the structure of the material, XRD has been recorded on X'Pert PRO diffractometer equipped with CuKα radiation (λ=0.1540 nm) in the range of 2θ=10-80^o with a step size of 0.0500^o. FT-IR spectrum has been recorded for the identification of functional groups and Scanning electron microscopy has been utilized to study the surface morphology of the material. To study the electrical properties, pellet of the samples have been made and impedance was measured for wide range of temperature (100-400^{o}C) using computer controlled HIOKI 3532 LCR HITESTER in the frequency range of 50 Hz-10 KHz.

III. Results And Discussion

Fig. 1 shows the XRD pattern of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$ by molten salt method and the results are in good agreement with the standard JCPDS card No. 46-0810. All the peaks confirmed the high crystalline nature and indexed to cubic spinel structure with fd3m space group. The Bragg's angle at 18.75, 36.33, 38.01, 44.17, 48.35, 58.47, 64.24, 67.57, 76.03 and 77.10 corresponds to (111), (311), (222), (400), (331), (511), (440) and (531) planes respectively. Lattice constant, cell volume and lattice density were calculated as 8.1915 (Å), 549.66 $(Å)^3$ and 11.9564 (g/cm^3) and are similar to the earlier results obtained [21-22]. The average grain size of the material was found to be 40.13 nm using Debye-Scherer formula [15 & 23].

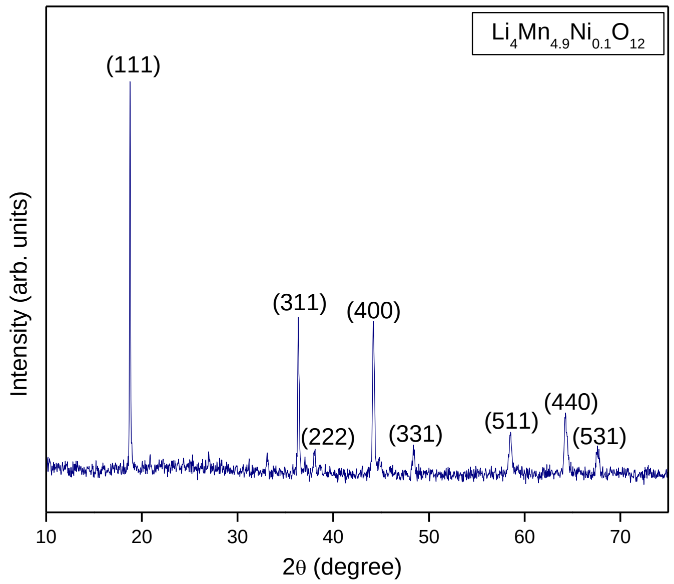

Fig.1 XRD pattern of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$

Fig. 2 shows the Fourier-transform Infrared spectrum (FT-IR) and the band around 730 cm^{-1} attributed to Mn-O vibrations in MnO_6 octahedron [24]. The weak to moderate band around 980 and 1063 cm^{-1} are ascribed to γOH...O and δOH [25].

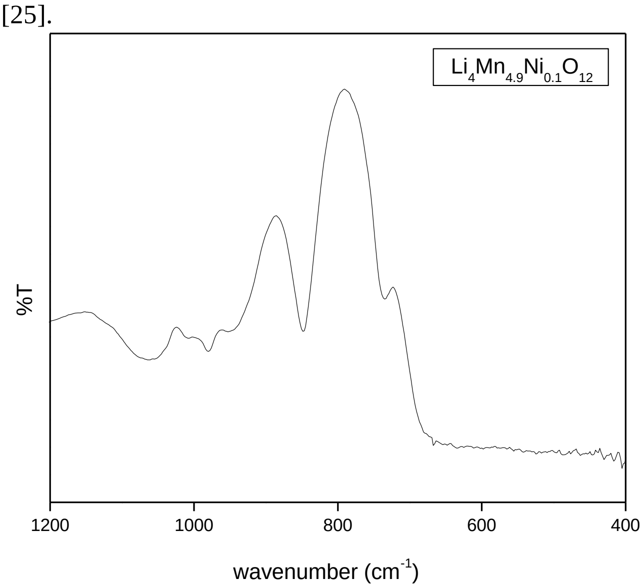

Fig.2 FT-IR spectrum of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$

SEM image has been depicted in Fig. 3a and it is clear from the image that the particles were distributed uniformly and exhibited polyhedral shape without any agglomeration. The sizes of the particles are in the range of 0.8-1μm by length and it coincides with the existing results obtained by the researchers [19 & 26]. Histogram of the particle size distribution as shown in Fig. 3b.

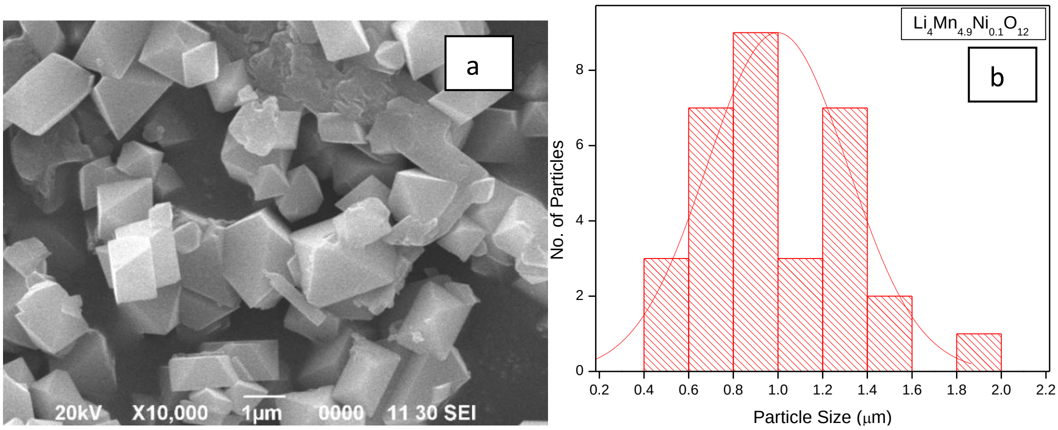

Fig. 3 a) SEM images of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$ b) Histogram of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$

Electrical properties of the material have been studied by Complex Impedance Spectroscopy (CIS). Fig. 4 elucidates the cole-cole plot or Nyquist plot of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$ at different temperatures. The formation of single semi-circle at all the temperatures indicating the absence of grain boundary effect and the conduction process occurs only through the bulk conduction of the material [27]. The formation of single semi-circle confirmed the parallel combination of bulk resistance (R_b) and bulk capacitance (C_b) of the sample. C_b can be calculated from the relation $2\pi\gamma_{max}R_bC_b=1$ and found to be in the order of pF. The conduction process occurred due to the interior grains [28]. R_b values decrease with increase in temperature and negative temperature co-efficient of resistance (NTCR) of the sample confirmed the semi-conducting nature of the material [29]. Using the formula $\sigma= (l/R_bA)$ Scm^{-1}, ionic conductivity has been calculated, where 'l' is the thickness of the sample and 'A' is the area of the sample. The calculated values were given in Table 1. Due to thermally activated mobility of charge carriers, conductivity of the sample increases with increase in temperature [30].

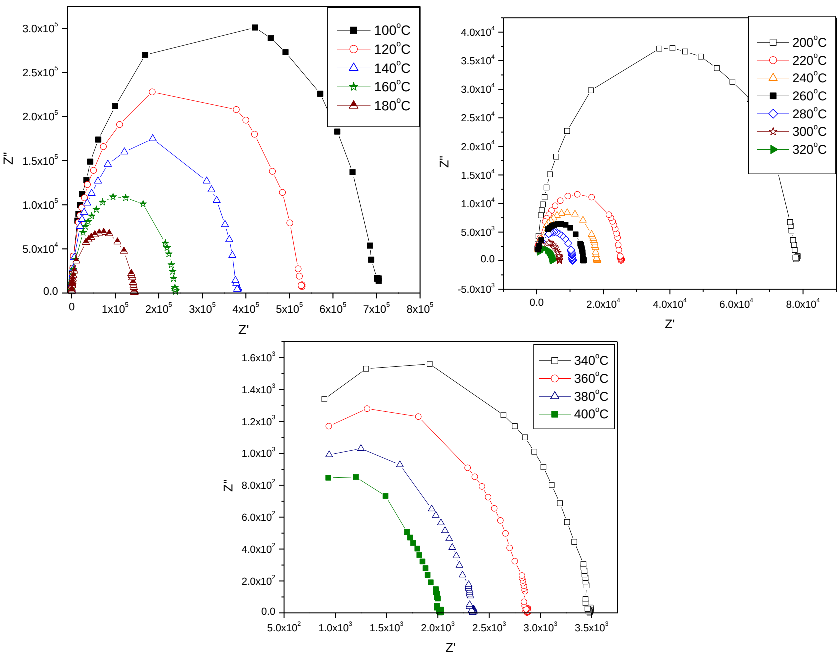

Fig. 4 Cole-Cole plot of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$ at different temperature

The variation of the real part of impedance (Z′) with frequency at different temperatures were shown in Fig. 5. The value of Z′ decreases with increase in temperature at low frequency region signifying the increase of conduction process. At high frequency all the curves merge together irrespective of the temperature due to the release of space charges [31]. Z′ becomes independent of frequency at particular region for all the temperatures which explained the existence of frequency relaxation process of the sample [31].

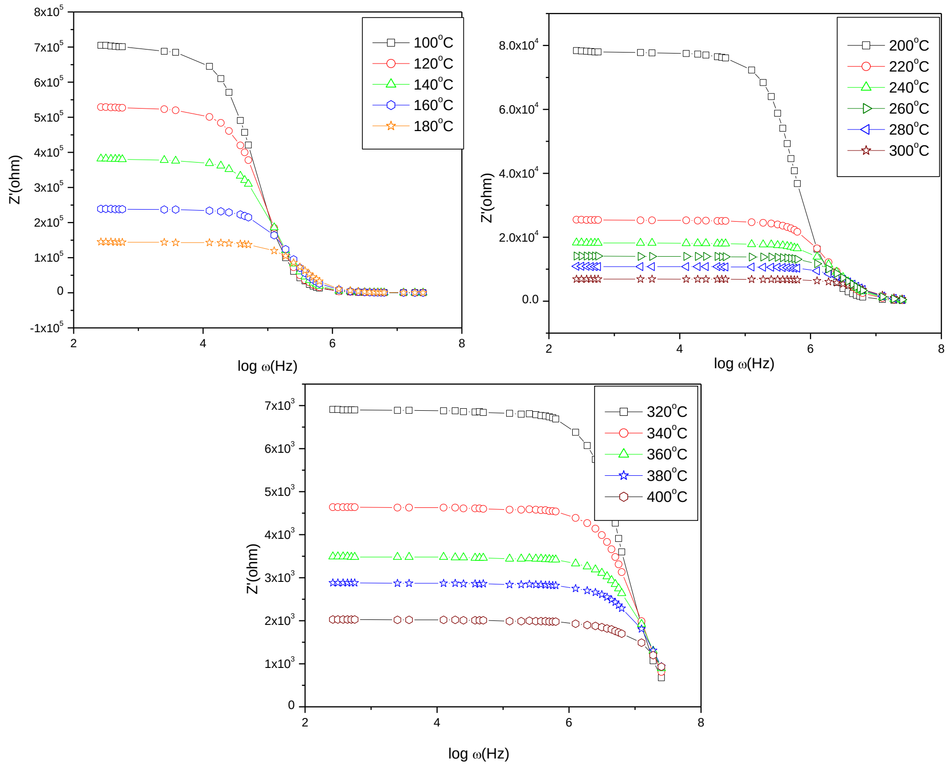

Fig. 5 Variation of Z' vs frequency at different temperature

Fig. 6 shows the variation of imaginary part of impedance (Z") with frequency at different temperatures. It clearly shows that the curve increases gradually at low frequency region and attains maximum value for all the temperatures. Due to the presence of immobile electrons, this broadening of peak occurs which indicates the temperature dependent relaxation process [32-33]. By increasing the temperature, the peak shift towards the high frequency region elucidates the existence of space charges [34].

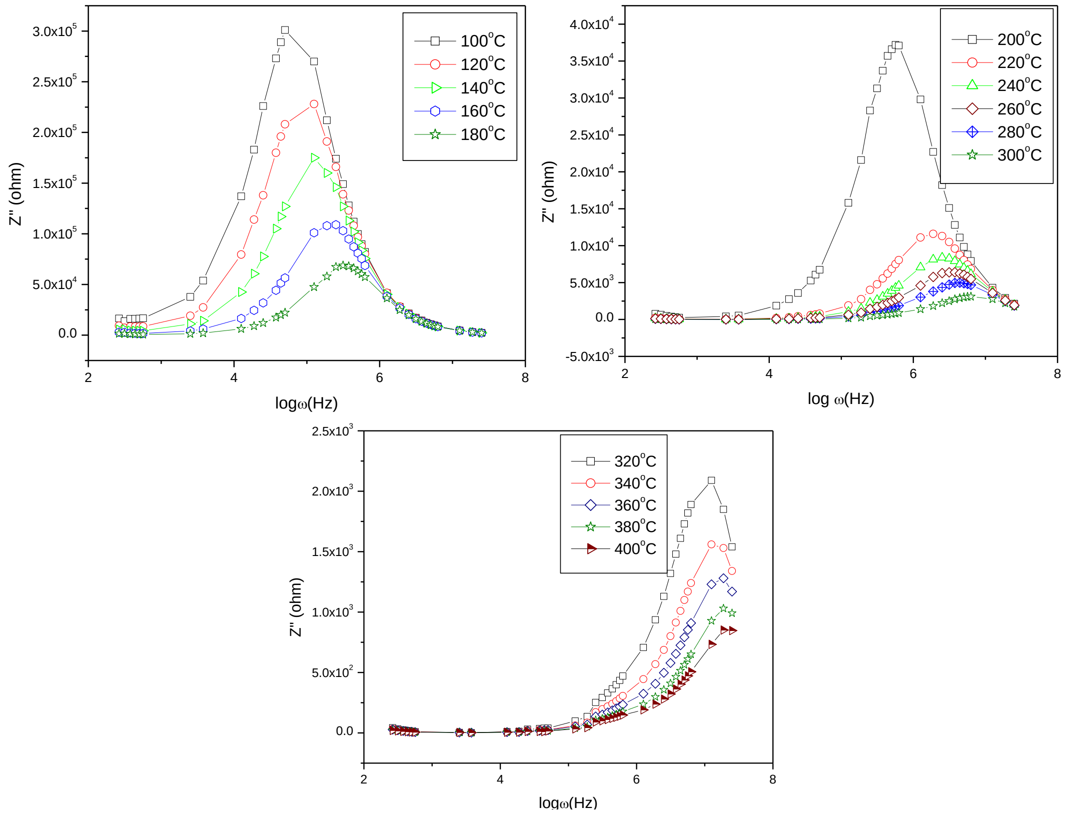

Fig. 6 Variation of Z" vs frequency at different temperature

The conductivity of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$ at different temperatures was shown in Fig. 6. Two regions have been observed from the curve: (i) frequency independent plateau at low frequency and (ii) a dispersive region at high frequency [35]. The low frequency region corresponds to dc conductivity of the material. The conductivity was found to increase with increase in temperature elucidating the Jonscher's universal power law of $\sigma(\omega) = \sigma_{dc} + A\,\omega_p^n$, where 'n' represents frequency exponent, 'ω'is the hopping frequency and σ_{dc} represents dc conductivity of the material. With the help of non- linear curve fitting method mobility and charge carrier concentration can be obtained from the graph. All the values are given in Table 1. The obtained parameters are closer to the calculated values of col-cole plot. It satisfies the Arrhenius relation: $\sigma_{dc} = \sigma_0 \exp(Ea/KT)$, where σ_0 is the pre-exponential factor and Ea is the activation energy. It can be obtained by plotting a graph between 1000/T vs dc conductivity. Very small amount of energy in the order of eV can be required for this conduction process. Maximum conductivity has been observed at 400°C.

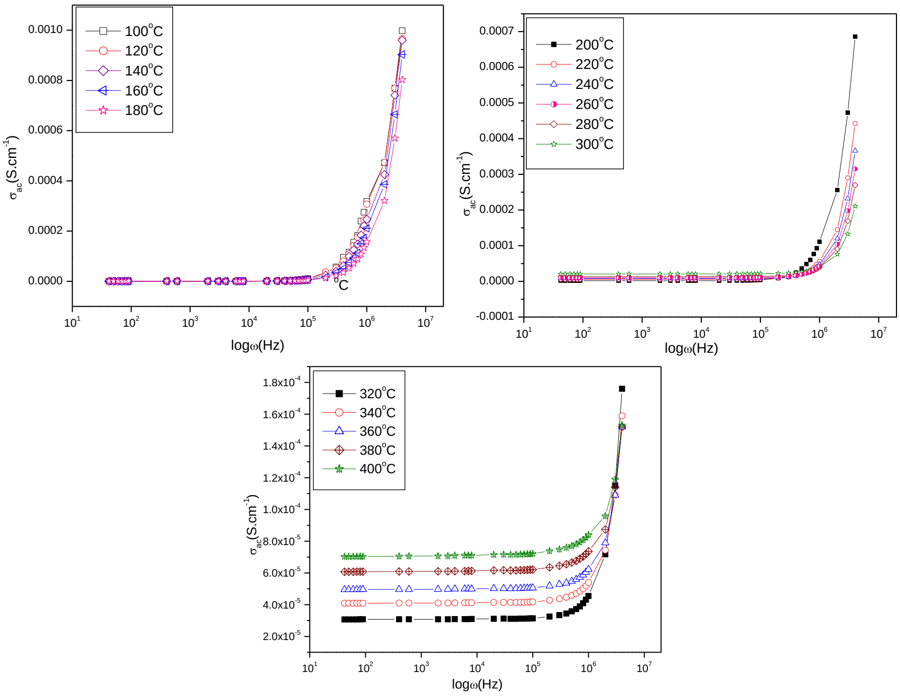

Fig. 7 Conductance Spectra of $Li_4Mn_{4.9}Ni_{0.1}O_{12}$ at different temperatures

Table 1 Electrical Parameters

Temp. (°C)	$R_b(\Omega)$	C_b (pF)	γ_{max} Hz	σ_{dc} ($S.cm^{-1}$)		ω x 10^4 Hz	N x 10^{-9} ($S.cm^{-1}$ kHz^{-1})	μ x$cm^2V^{-1}s$
				Cole-Cole	Conductance			
100	7.043 x 10^5	2.826	8 x 10^3	2.125 x 10^{-7}	2.14 x 10^{-7}	0.168	47.51	2.81 x 10^{19}
120	5.288 x 10^5	1.505	2 x 10^4	2.83 x 10^{-7}	2.76 x 10^{-7}	0.105	103.3	1.66 x 10^{19}
140	3.824 x 10^5	2.082	2x 10^4	3.913 x 10^{-7}	3.94 x 10^{-7}	0.613	26.54	9.27 x 10^{19}
160	2.407 x 10^5	1.653	4 x 10^4	6.217 x 10^{-7}	6.25 x 10^{-7}	0.830	32.60	11.98 x 10^{19}
180	1.44 x 10^5	2.211	5 x 10^4	1.039 x 10^{-6}	1.15 x 10^{-6}	1.971	26.43	27.19 x 10^{19}
200	7.819 x 10^4	2.262	9 x 10^4	1.914 x 10^{-6}	1.96 x 10^{-6}	5.913	92.94	13.21 x 10^{19}
220	2.531 x 10^4	2.097	3 x 10^5	5.913 x 10^{-6}	5.323 x 10^{-6}	23.08	11.83	28.12 x 10^{19}
240	1.796 x 10^4	2.216	4 x 10^5	8.33 x 10^{-6}	8.323 x 10^{-6}	40.154	11.04	47.08 x 10^{20}
260	1.378 x 10^4	1.925	6 x 10^5	1.086 x 10^{-5}	1.011 x 10^{-5}	48.36	11.14	56.71 x 10^{20}
280	1.062 x 10^4	2.141	7 x 10^5	1.409 x 10^{-5}	1.41 x 10^{-5}	68.63	11.37	77.56 x 10^{20}
300	6.648 x 10^3	2.395	1 x 10^6	2.251 x 10^{-5}	2.09 x 10^{-5}	108.48	11.06	11.84 x 10^{21}
320	4.647 x 10^3	1.713	2 x 10^6	3.22 x 10^{-5}	3.08 x 10^{-5}	163.61	11.16	17.26 x 10^{21}
340	3.47 x 10^3	2.294	2 x 10^6	4.313 x 10^{-5}	4.10 x 10^{-5}	217	11.59	22.13 x 10^{21}
360	2.856 x 10^3	1.858	3 x 10^6	5.24 x 10^{-5}	4.99 x 10^{-5}	262.31	12.04	25.91 x 10^{21}
380	2.339 x 10^3	2.269	3 x 10^6	6.39 x 10^{-5}	6.11 x 10^{-5}	314.94	12.66	30.16 x 10^{21}
400	2.009 x 10^3	2.642	3 x 10^6	7.44 x 10^{-5}	7.01 x 10^{-5}	366.40	12.87	34.04 x 10^{21}

IV. Conclusion

0.1 mole of Ni doped lithium manganese oxide has been successfully prepared by simple molten salt method at 800^{o}C. XRD pattern revealed the cubic spinel structure formation without any impurity. The presence of MO_6 octahedral functional group was confirmed from FT-IR analysis. Sub-micron sized polyhedral shaped particles are identified from SEM analysis without any agglomeration. The negative temperature coefficient of resistance and temperature dependence of the material was studied from impedance analysis. The ac conductivity of the material found to obey universal Jonscher's power law. 0.1 mole of Ni doped $Li_4Mn_5O_{12}$ exhibits excellent conductivity especially at high temperature (400^{o}C). Results of the study revealed that doping Ni with optimum concentration will lead to the enhancement of the electrical properties of the material and also suggesting the possible application in Li-ion batteries with good electrochemical performance.

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