Preparation and Characterization of Pure and Ti^{4+}doped $Li_4Mn_5O_{12}$ Spinels as Cathodes for Li-ion Batteries

S.Sharmila[1], B.Janarthanan[2], J.Chandrasekaran[3]

Abstract

An attempt was made to synthesize $Li_4Mn_{5-x}Ti_xO_{12}$ (x=0.0, 0.1, 0.3 and 0.5 mole) via single step molten salt method. Structural, morphological and electrical studies were carried out to analyze its structure, shape, size and conductivity of the material. XRD pattern revealed the formation of spinel structure with fd3m space group. SEM analysis exhibited the formation of polyhedral shape with micron sized particles. Conductivity of the samples was improved by Ti^{4+} doping with three different concentrations and 0.3 moles were identified as optimum concentration with 1 x $10^{-5}$$Scm^{-1}$ at 413 K.

Keywords - dc conductivity, $Li_4Mn_5O_{12,}$ polyhedral shape, rechargeable Li-ion batteries, spinel structure.

I. Introduction

To improve the electrochemical performance of rechargeable Li-ion batteries, extensive research work was being undertaken worldwide in recent years. Due to high energy density, power density, capacity and long cycle life, Li-ion battery received so much attention of the researchers. Commercially, $LiCoO_2$ was used as a cathode material due to its good cyclability, stability, and high theoretical capacity (274 mAh g^{-1}). However, toxic nature and high cost of cobalt has led to a search for an alternative material. Lithium manganese oxides have generated much interest due to low cost, eco-friendly nature and moderate theoretical capacity [163 mAh g^{-1}]. Different forms of manganese oxides are available such as $LiMnO_2$, $LiMn_2O_4$, $LiMn_2O_3$, $Li_4Mn_5O_{12}$ (or Li [$Mn_{1.67}Li_{0.33}$] O_4) and $Li_2Mn_4O_9$. Among these $Li_4Mn_5O_{12}$ the end member of the family has become the most attractive material nowadays. $Li_4Mn_5O_{12}$ has many advantages like low cost, wide operating potential window, long shelf life and high cell voltage [1], which is also free from Jahn –Teller distortion during cycling due to +4 oxidation state of Mn [2-3]. The main drawback of $Li_4Mn_5O_{12}$ (LMO) is in obtaining stoichiometric ratio, which may disproportionate into $LiMn_2O_4$ and $LiMnO_2$ at high temperature [2] and also its poor electrochemical performance.

It can be solved by three ways, namely (i) structure modifications (ii) using carbon additives (iii) or by doping like Mg^{2+}, Zr^{4+}, Ti^{4+}, Sn^{4+}, Co^{2+}, Ni^{3+}, Zn^{2+}, La^{3+}, F^-, etc., in Li, Mn or O sites [4-7]. W.Choi *et al.* [3] synthesized LMO by the substitution of F^- in O^- site with different concentrations to suppress the disproportionate problem and obtained good capacity for $Li_4Mn_5O_{11.85}F_{0.1}$ material. Y.Zhang *et al.* [2] reported LMO by hydrothermal method at low temperature (110°C) without any disproportion. LMO/AC was reported by Y.J. Hao e*t al.* [8] via sol-gel method at low temperature and obtained a remarkable result. Structural stability and electrochemical performance of LMO were improved by Co doping in Li and Mn sites with different concentrations by A.D. Robertson *et al.* [9]. Y.P.Jiang *et al.* [10] presented LMO crystallites by the combination of spray drying and solid phase reactions. The particles obtained at 250°C ball milled were in small size with good uniformity and exhibited high initial discharge capacity and good cyclability. Ti substituted LMO were examined by M-L-P.Le *et al.* [11] they presented the structural, magnetic and electrochemical behavior via the solid solution method. To the best of the present researcher(s) knowledge less number of research works have been carried out, till date, by researchers via conventional solid state reaction [11-14], mechanochemical method [15], molten salt method [16] to enhance the electrochemical performance of LMO.

In the present study an attempt has been made by the researcher(s) to prepare LMO by simple molten salt method to enhance the conductivity and impedance performance by the substitution of Ti^{4+} in Mn^{4+} sites. Ti was selected as a dopant due to its low cost and different oxidation state. Molten salt method has been chosen to prepare the material because of its simple step, easy mode of preparation, no requirements of organic additives and low cost. Prevention of agglomeration of particles is the other reason.

II. Experimental

2.1 Synthesis Method

Spinel $Li_4Mn_5O_{12}$ were prepared using $LiOH.H_2O$ and MnO_2 as the starting precursors by molten salt method with LiCl and KCl as flux. The stoichiometric quantities of precursors were ground well for ½ hr individually and

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mixed with molten salt (60:40) for ½ hr to get a homogenous mixture. The resultant mixture was heated at 800^{o}C for 10hr. Obtained powder was washed with distilled water and, finally with ethanol to remove the residual salts. Same procedure was employed to prepare Ti doped $Li_4Mn_5O_{12}$ with TiO_2 as the precursor. Samples were named as LP, LT1, LT3 and LT5 based on Ti concentrations as 0, 0.1, 0.3 and 0.5 respectively.

2.2 Characterization

Structure of the materials was examined by Powder X-ray diffraction (XRD) 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}. Morphology of the samples was studied by scanning electron microscopy (SEM). The electrical conductivity of the materials was identified using computer controlled HIOKI model 3532 LCZ meter within the frequency range of 40 Hz-5MHz at three different temperatures such as 393 K, 413 K and 433K.

III. Results and discussion

Structural formation and crystalline nature of the synthesized $Li_4Mn_{5-x}Ti_xO_{12}$ (x=0, 0.1, 0.3 and 0.5) samples were characterized by X-ray powder diffraction pattern. Fig. 1 shows that the observed diffracted peaks at 2θcorresponds to (111), (311), (222), (400), (331), (511), (440) and (531) planes, which are in good agreement with standard JCPDS card no.46-0810 with high crystalline nature. The diffracted peaks explains the formation of cubic spinel structure with fd3m space group with pure phase indicating that the dopant Ti^{4+} entered into the lattice structure without any changes in its structural characteristics. In this crystal structure, manganese ions are distributed randomly at 16d octahedral sites, partial lithium ions are located at 8a tetrahedral sites and remaining lithium ions in 16d octahedral sites, and the oxygen ions in 32e sites [17].

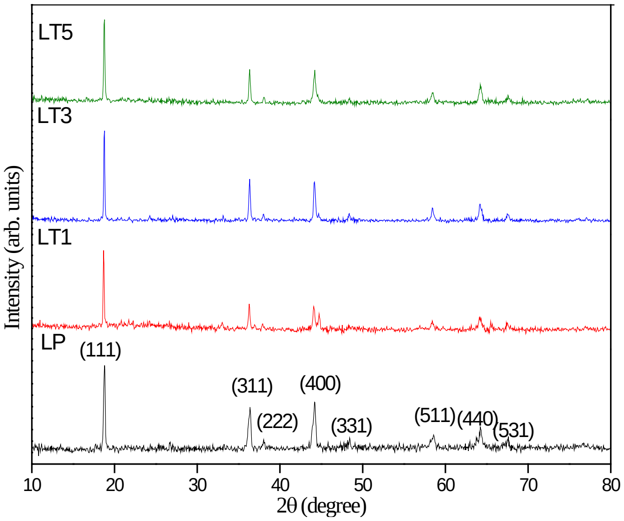


Fig. 1 XRD pattern of LP, LT1, LT3, LT5

Lattice constant values for all the samples were calculated and given in Table 1. Lattice parameter 'a', found to be high for doped $Li_4Mn_5O_{12}$ compared with the pure sample, shows that the substitution effect follows Vegard's law [18]. Due to the difference in ionic radii of Mn^{4+} (0.053nm) and Ti^{4+} (0.056nm), lattice expansion occurs causing an increase in lattice parameter of Ti doped material [18]. By increasing the concentration of dopant above 0.1, 'a' starts to decrease. Similarly, the atomic density of Mn^{4+} (7.47 g/cm³) is larger than Ti^{4+} (4.50 g/cm³). As a result, lattice density of pure $Li_4Mn_5O_{12}$ becomes larger than LT1, LT3 and LT5. Using Debye-Scherer formula, the grain size was calculated and it increased for doped samples, above 0.3 moles and there was a decrease as compared to the parent material. Specific surface area of pure and doped samples were calculated using the formula d=6/ϱs cm²/g and given in Table 1, which was found to be decreasing with the increase in concentration and for 0.5 mole it increased due to small grain size [19].

TABLE 1

XRD parameters of $Li_4Mn_{5-x}Ti_xO_{12}$ (x= 0, 0.1, 0.3 and 0.5)

Sample	a (Å)	Cell Volume (Å)³	Lattice Density (g/cm³)	Grain Size (nm)	Surface area (cm²/g)
$Li_4Mn_5O_{12}$	8.1934	550.049	11.941	34.81	144
$Li_4Mn_{4.9}Ti_{0.1}O_{12}$	8.2135	554.104	11.837	41.24	122
$Li_4Mn_{4.7}Ti_{0.3}O_{12}$	8.2007	551.518	11.858	45.44	111
$Li_4Mn_{4.5}Ti_{0.5}O_{12}$	8.1982	551.016	11.835	30.57	165

Fig.2 morphologically explains the shape and size of the samples. It clearly infers that the particles are distributed uniformly without agglomeration and also exhibits that the particles are in micron size with well developed polyhedral shape. The particle sizes were calculated and found that there was no more variation in its size due to the addition of dopant. Maximum numbers of particles are in the range of 0.4-0.6 µm for both $Li_4Mn_5O_{12}$ and $Li_4Mn_{4.9}Ti_{0.1}O_{12}$ sample. By increasing the concentration of Ti to 0.3 moles the size of the particles was reduced to 0.2 µm. Histograms of the sizes of the particles are shown in Fig. 3.

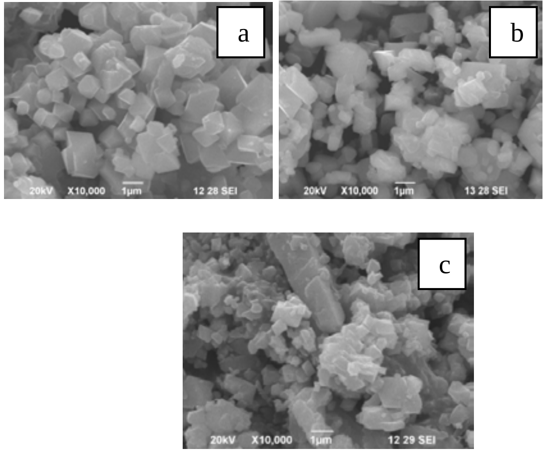


Fig.2. SEM images of a) $Li_4Mn_5O_{12}$ b) $Li_4Mn_{4.9}Ti_{0.1}O_{12}$ and c) $Li_4Mn_{4.7}Ti_{0.3}O_{12}$

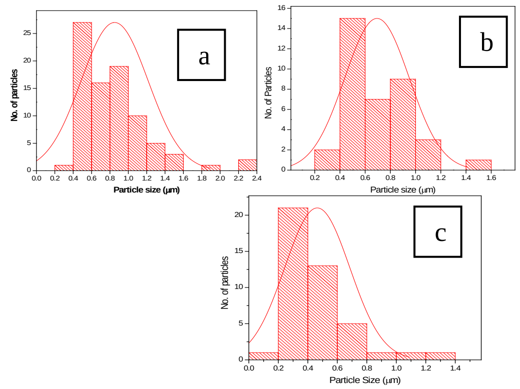
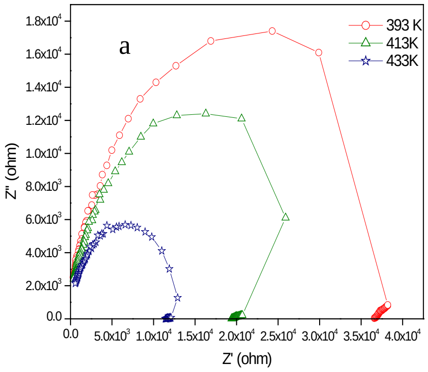


Fig.3. Histogram of a) $Li_4Mn_5O_{12}$ b) $Li_4Mn_{4.9}Ti_{0.1}O_{12}$ c) $Li_4Mn_{4.7}Ti_{0.3}O_{12}$

The origin of conducting mechanism -- and the electrical conductivity of the material can be identified using impedance measurements [20]. The parallel cells combination of R-C explains the AC impedance. With the help of Z' and Z", cole-cole plot or Nyquist plot can be obtained. Fig.4 represents the cole-cole plot of $Li_4Mn_{5-x}O_{12}$ at three different temperatures (393K, 413K, and 433K). All samples exhibit the formation of single semi-circle at high frequency due to the parallel combination of bulk resistance (R_b) and bulk capacitance (C_b), revealing that the conduction process occurs through the bulk of the material [21]. Bulk resistance (R_b) of the sample can be obtained based on the interception of the semi-circle on X- axis. Using the relation $2\pi\gamma_{max}R_bC_b=1$, C_b values can be calculated. The calculated values are given in Table 2 which is in the order of pF clearly indicating that the conduction process occurs due to the bulk of the material [19-20]. Non-Debye nature of the material and relaxation phenomena can be identified by the depressed semi-circle below the real axis [20].



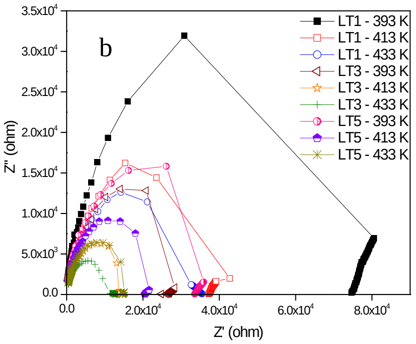


Fig.4 Cole-Cole plot of (a) LP (b) LT1, LT3, LT5

Ionic conductivity of the material can be calculated by the relation $\sigma = (l/R_bA)$ Scm^{-1}, where 'l' is the thickness of the sample, 'R_b' represents bulk resistance; and A is the area of the sample and the values are indicated in Table 2. Fig.4 elucidates that the radius of the semicircle decreases with increase in temperature leading to decrease in bulk resistance, i.e. negative temperature co-efficient of resistance (NTCR) indicating that the material is in semi-conducting nature. Among these samples, LT1 has high R_b, which leads to less conductivity. Ionic conductivity of the material increases with increase in temperature due to thermally activated charge carriers via hopping mechanism [22-23].

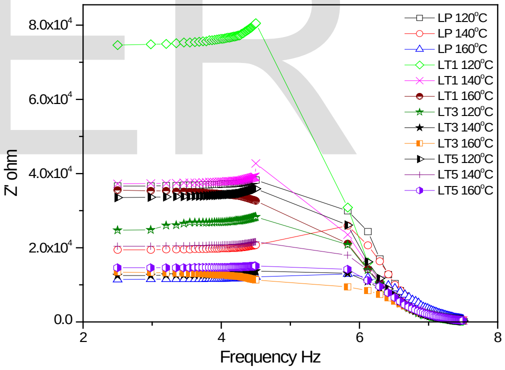


Fig.5 Variation of Z' with frequency of LP, LT1, LT3, LT5

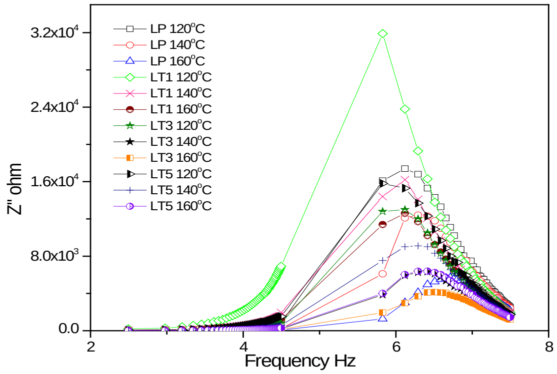


Fig.6 Variation of Z" with frequency of LP, LT1, LT3, LT5

Variation of Z' with frequency for doped and pure samples is shown in Fig.5. LT1 exhibits high Z' than doped and pure samples which have low conductivity. By increasing the content of dopant and temperature, the value of Z' reduces and conductivity increases. At all the temperatures and at high frequency, merging of Z' appears which is a clear evidence for releasing of space charge [24]. These releases indicate that the material exhibits temperature depending on electrical relaxation phenomena.

Similarly, variation of Z" with frequency at three different temperatures are shown in Fig. 6. All the spectra exhibit single peak and its center does not lie at the same frequency indicating the non-Debye relaxation. With rise in temperature, there is a broadening of peak which also indicates the relaxation phenomena of the material [23]. Due to the presence of space charges, shifting in peak occurs while increasing the temperature.

Fig.8 explains the variation of conductivity with temperature. With increase in temperature, conductivity also increases and it can be elucidated by Arrhenius equation: $\sigma = \sigma_0 \exp(-E_a/kT)$, where σ_0 corresponds to pre-exponential factor, E_a is the activation energy and k represents Boltzmann constant. LT3 and LT5 require less activation energy than LP for migration of ions [25]. LT1 needs more energy than others, which obviously has low conductivity. The activation energy is found to be in the order of 0.19, 0.30, 0.17 and 0.14 eV for LP, LT1, LT3 and LT5 respectively.

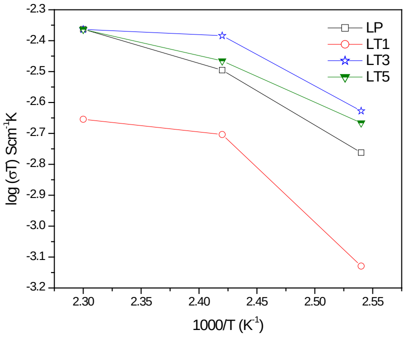


Fig.7 Log (σT) vs 1000/T of LP, LT1, LT3, LT5

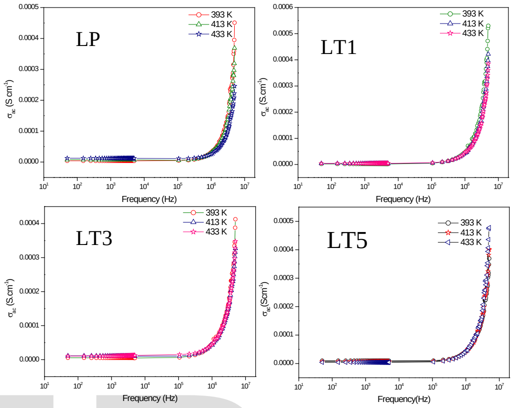


Fig.8 Conductance spectra of LP, LT1, LT3, LT5

TABLE 2
Electrical Parameters of $Li_4Mn_{5-x}Ti_xO_{12}$ (x= 0, 0.1, 0.3 and 0.5)

Material	Temp. (K)	R_b x 10^4 Ω	C_b x 10^{-11} pF	D x 10^{20} cm^2s^{-1}	γ_{max} x 10^5 Hz	Conductance (S cm^{-1})		ω_p x 10^4 Hz	N x 10^{-9} (S.cm^{-1} kHz^{-1})	μ x 10^{21} $cm^2V^{-1}s$
						σ_{dc}	cole-cole			
LP	393	3.66	2.08	1.66	2.08	4.4 x 10^{-6}	4.34 x 10^{-6}	30.93	5.58	4.92
	413	1.99	2.57	3.61	3.10	7.74x10^{-6}	7.99 x 10^{-6}	66.97	4.77	10.13
	433	1.18	1.64	4.84	8.20	1 x 10^{-5}	1.34 x 10^{-5}	89.81	4.82	12.96
LT1	393	7.48	1.99	0.716	1.06	2.12x10^{-6}	2.27 x 10^{-6}	11.78	7.10	1.86
	413	3.77	2.02	1.908	2.08	4.79x10^{-6}	4.52 x 10^{-6}	21.26	9.31	3.21
	433	3.55	2.14	2.139	2.08	5.12x10^{-6}	4.8 x 10^{-6}	33.99	6.52	4.90
LT3	393	2.7	2.82	2.275	2.08	6 x 10^{-6}	6.18 x 10^{-6}	38.94	6.05	6.19
	413	1.35	2.85	3.985	4.12	1 x 10^{-5}	1.23 x 10^{-5}	43.13	9.57	6.52
	433	1.25	2.47	4.178	5.14	1 x 10^{-5}	1.33 x 10^{-5}	46.96	9.22	6.77
LT5	393	3.38	4.40	2.081	1.06	5.49x10^{-6}	5.32 x 10^{-6}	33.46	6.44	5.32
	413	2.13	2.40	3.303	3.10	8.29x10^{-6}	8.44 x 10^{-6}	33.9	10.10	5.13
	433	1.49	2.58	4.178	4.12	1 x 10^{-5}	1.20 x 10^{-5}	54.35	7.96	7.85

Fig.8 shows the conducting behavior of pure and doped $Li_4Mn_5O_{12}$ at different temperatures with respect to frequency. At low frequency plateau, the curve corresponds to dc conductivity of the material and at high frequency a dispersion region corresponds to ac conductivity. Conductivity of the material increased with temperature and obeyed Jonscher's Power law: $\sigma(\omega) = \sigma_{dc} + A\omega_p^n$.

With the help of non-linear curve fitting method, conductivity values were calculated. Using Almond and West formalism, hopping frequency ω_P were obtained [26]; from these values charge carrier concentration (N) and mobility (μ) were calculated and they are given in Table 2. LT3 sample shows high conductivity at all temperatures than other samples, which shows that 0.3 mole of Ti is the optimum concentration for doping. Charge carrier values remaining constant for all the temperatures in the order of 10^{-9} suggest that moving Li ions are responsible for conductivity [27].

IV. CONCLUSIONS

Pure and doped Lithium manganese oxides were successfully synthesized via single step molten salt method. XRD pattern exhibits good crystalline nature with high purity of the material. The size of the particles was found to be in the range of 0.2 – 0.6 μm in length with polyhedral shapes without any agglomeration. R_b values were found to be decreasing with increase in temperature for all the samples indicating NTCR property. Conductivity of $Li_4Mn_5O_{12}$ were found to be increased by the substitution of Ti as dopant in Mn sites. Among different concentrations of Ti, 0.3 mole exhibited excellent conducting property (1 x 10^{-5} S cm^{-1}) at 413K which shows 0.3 moles as the optimum concentration for doping. Basing on these results, we suggest that $Li_4Mn_{5-x}Ti_xO_{12}$ be taken as a good alternative material for $LiCoO_2$.

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