Structural, Morphological, Electrical and Electrochemical Properties of Gadolinium Doped $Li_2Mn_4O_9$ for Li-ion Battery Applications

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Abstract--- Pure and gadolinium doped $Li_2Mn_4O_9$ cathode material is prepared by simple solid state method. The structural, morphological, electrical and electrochemical properties of both materials are studied. The coral reef structures are identified from the SEM analysis in micron size. The chemical composition of Mn, O and Gd are verified by Electron Dispersive Spectroscopy. 0.5 mole of Gd doped material exhibits good electrical conductivity at 393 K than other two samples. The cyclic voltameter studies are done for $Li_2Mn_4O_9$. Electrical studies confirm that Gd doped $Li_2Mn_4O_9$ is a feasible cathode material for lithium ion batteries because it enhanced the conductivity of the material.

Keywords--- $Li_2Mn_4O_9$, Solid State Method, DC Electrical Property and Cyclic Voltammogram.

I. Introduction

The demand for energy sources are increasing twice as fast as to the overall energy use. Three billion people lives in the societies that are without the access of enough energy to meet their needs as per UNESCO [AGECC, 2010]. The ever widening energy needs and the subsiding fossil fuel resources urge the pursuit of the sustainable energy alternatives. Now-a-day the researches are trying to find the alternative energy sources especially on lithium ion batteries to accelerate their electrical and electrochemical properties to meet the demand. Lithium based rechargeable batteries were first proposed in 1980 and successfully used by "SONY Energetic" [1]. The spinel ($LiMn_2O_4$) and defect spinel ($Li_4Mn_5O_{12}$ and $Li_2Mn_4O_9$) are the emerging cathode materials for the rechargeable lithium batteries [2] due to its low cost, less environmental impact, outstanding cyclic capability, high power and a large cell voltage. The defect spinel are free from Jahn-Teller distortion among different Li-Mn-O system [3].

$Li_4Mn_5O_{12}$ shows good capacity in the 3V region than 4V region since, the oxidation state of Mn increases, its capacity decreases. $Li_4Mn_5O_{12}$ and $Li_2Mn_4O_9$ exhibit a better cyclic capability than LiMn2O4 spinel in 3V region [4]. $Li_2Mn_4O_9$ structure has a cation vacancies on both tetra and octahedral sites, which is also the end member of the family with the formula [Li0.89]8a[Mn1.78]16d[O4]32e [5]. The neutron diffraction results indicated that the composition of the lithium manganese spinel is dependent on the synthesis conditions. If the firing temperature is at 750-900^oC leads to oxygen vacancies. Therefore it is good to keep the synthesis temperature below 750 ^oC to prepare $Li_2Mn_4O_9$. $Li_2Mn_4O_9$ nano composites which exhibits excellent rate capability and cycling stability with 92% and 99% capacity retention after 100 cycles at 0.5C and 1C rate respectively [6].

Kilroy et al., reported $Li_2Mn_4O_9$ with the carbonate precursors and obtained maximum value of z as 0.88, which also had a good capacity retention and stability at 4.5 V to 2.5 V[7]. MM Thackeray et al., [8] identified the occupancy of lithium at the tetrahedral 8a sites. The refined composition, the distribution of the manganese and lithium cation on the octahedral 16d sites. Strobel et al., the double vacancy scheme for LiMnO spinal prepared by low temperature solid state reaction depending upon the distribution of cation vacancies in the lattices[9]. An extra Li insertion/ extraction step is clearly visible in the 0.1 M of HCl treated $Li_2Mn_4O_9$ with the tetrahedral vacancies only which is also very stable. S.Choi et al., [10] using solution based chemical synthesis to access the spinal

limo249 at low temperature. At an intermediate firing temperature the Li rich $Li_2Mn_4O_9$ is formed but Mn2 O3 impurity is formed at a temperature 700. For the sample fired at an optimum temperature of 400^0C a reverse capacity of about 130 mAh/g in the range 3.8-2 v with excellent cyclability could be achieved for the $Li_2Mn_4O_9$ sample fired at temperature of $400\ ^0$C

The focus of the present work is to synthesis $Li_2Mn_4O_9$ using single step solid state method and to substitute Gd into Mn sites of $Li_2Mn_4O_9$ in order to improve the electrochemical performance and thereby checking the suitability of the material as the cathode in lithium ion battery. Gadolinium is chosen as the dopant since it possess different oxidation states, low resistivity, improve workability and resistance to high temperature oxidation. The solid state method is preferred because of its low cost, less time, simple and no organic additives are required.

II. Experimental Method

Synthesis

$Li_2Mn_4O_9$ is prepared using simple solid state method. The stoichiometric amounts of $LiOH.2H_2O$ and MnO_2 are mixed using mortar and pestle. The mixture ground for ½ hr and annealed at different temperatures 500, 600 and 700^oC for 7 hrs in muffle furnace. Obtained sample is crushed and utilized for the characterization. Same procedure is used to prepare Gd doped $Li_2Mn_4O_9$ sample with Gd2O3as the starting precursor. Samples are named as $Li_2Mn_4O_9$ (L), $Li_2Mn_{3.75}Gd_{0.25}O_9$ (LG2) and $Li_2Mn_{3.5}Gd_{0.5}O_9$ (LG5).

The powder XRD (XPERT-3) with CuKα radiation (λ=1.5nm) is used to identify the crystal structure in the range $2\theta = 10\text{-}80^o$. The morphology of the prepared samples is analyzed by SEM. The elemental compositions of the materials are confirmed by Electron dispersive spectroscopy. The electrical conductivity is measured using HIOKI 3532 LCR HITESTER in the frequency range 50 Hz to 50 kHz at various temperatures such as 60, 80, 100 and 120^oC.

For the preparation of electrodes, the active material $Li_2Mn_4O_9$, activated carbon along with Poly Vinylidene Fluoride as a binder are taken in the weight ratio of 70:20:10 with N-methyl-2-pyrrolidone (NMP) as the dispersing solvent to form the uniform slurry. After mixing for 15 minutes, the slurry is coated on a stainless steel coin and dried at 60 ^{o}C for an hour, followed by vacuum drying at 120^oC overnight. The CR2032 coin type cell is assembled in a glove box under an inert atmosphere with pure lithium metal as an anode and prepared by electrode as cathode. A glass microporous membrane is used as separator and non-aqueous 1M $LiPF_6$ in 1:1 ratio of ethyl carbonate and Dimethyl Carbonate as the electrolyte. The fabricated coin cells are charged to 4.4V and then discharged to 3V *vs* Li/Li^+. Cyclic Voltammetry studies are carried out at a scan rate of 0.1 mV/s in VMP3 Bio Logic Electrochemical Workstation.

III. Results and Discussions

Structural Properties

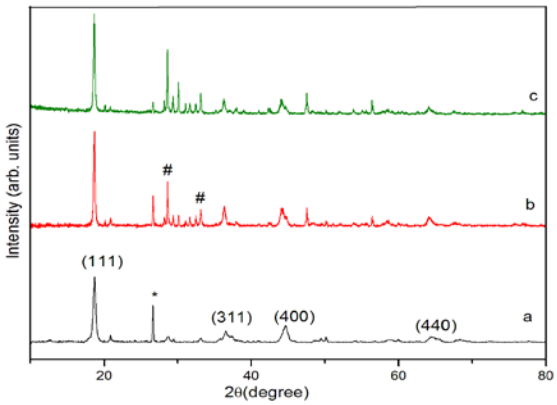

Fig. 1: XRD Spectrum of a) L b) LG2 c) LG5

X-ray diffraction pattern is recorded for the pure and Gd doped $Li_2Mn_4O_9$ samples to analyze the structure of the material. Fig.1 (a-c) shows XRD pattern of the pure and Gd doped $Li_2Mn_4O_9$. All the diffraction peaks are well defined and the sharp showing highly crystalline structure of the prepared material. All the diffracted peaks have

quite resemblance with the earlier reports (rossouw1990) and JCPDS card no. (88-1608). Obtained peaks at 18.8, 36.53, 44.6 and 64.4 are indexed to (111), (311), (400) and (440) plane respectively. All the diffraction peaks can be indexed as fd3m space group with the face centered cubic spinel structure. But some extra peak can be observed as impurity in the Fig. 1(a) at 26.6° in the parent sample and identified as SiO_2, which is also confirmed from the EDAX analysis. This may be due the fewer amounts of impurities present in the source. Similarly, in Fig.1the (b and c) additional peaks have been observed in the range of 26° to 33° attributed to Gd_2O_3 and GdO_2 (86-2477, 85-0373) indicating some dopants may not entered into the lattice structure of $Li_2Mn_4O_9$. This can also be confirmed from SEM analysis by the formation of some particles on the surface morphology. In contrast the intensity of the (111) plane is increased with increasing the concentration of dopant.

Table 1: XRD Parameters

Material	Lattice constant(Å)	Cell Volume $(Å)^3$	Lattice density(g cm^{-3})	Grain size(nm)
$Li_2Mn_4O_9$	8.164	544	24.35	41
$Li_2Mn_{3.75}Gd_{0.25}O_9$	8.210	553	22.77	46
$Li_2Mn_{3.5}Gd_{0.5}O_9$	8.214	554	21.45	74

XRD parameters are calculated and given in the Table 1. Using Debye Scherer formula the lattice parameter, grain size, cell volume and lattice density are calculated. The lattice parameter is found increasing with the increase of concentration, this may be due to lattice expansion caused by higher ionic radius of Gd (107.8 pm) than Mn (72pm) which found to obey Vegard's law [12-13]. Similarly, the difference in atomic density causes the decrease in lattice density. The grain size of doped $Li_2Mn_4O_9$ is high compared with pristine $Li_2Mn_4O_9$ due to lattice expansion of the material.

Morphological Analysis

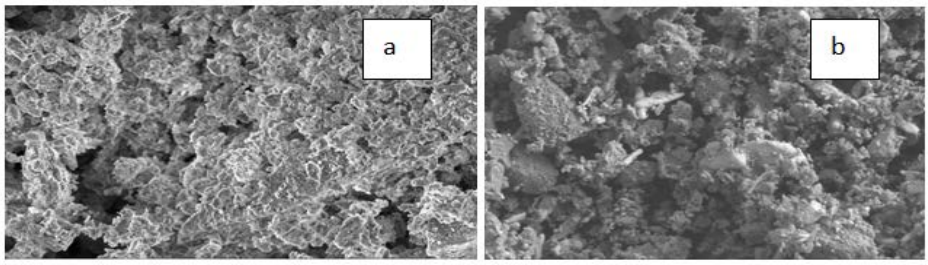

Fig. 2: SEM Images of a) L b) LG5

Fig. 2 (a-b) shows the SEM images of $Li_2Mn_4O_9$ and $Li_2Mn_{3.5}Gd_{0.5}O_9$. The coral reef structure is identified for the pristine and doped material. Pristine $Li_2Mn_4O_9$ exhibits the morphology of the particles in micron size without any agglomeration. Some secondary phase formation of GdO_2 is observed in LG5 which is also confirmed the XRD results. The elemental composition of the material has identified from EDAX spectrum. Fig. 3(a-b) shows the EDAX analysis of the material.

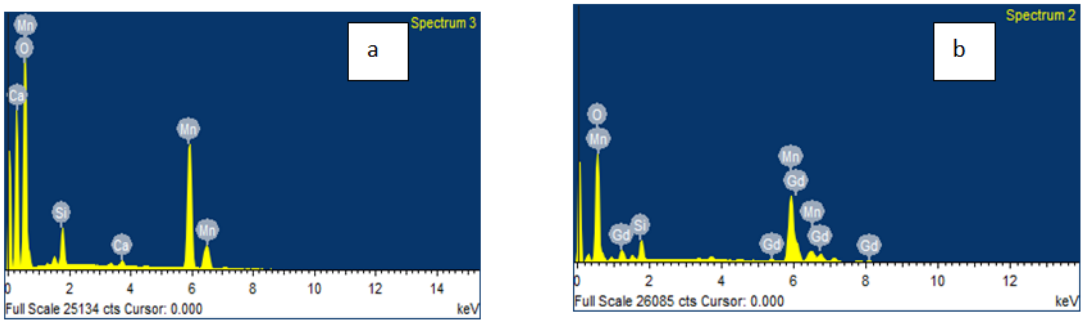

Fig. 3: EDAX Spectrum of a) L b) LG5

The presence of manganese and oxygen except Lithium is confirmed in electron dispersive spectroscopy. Elements below the carbon can't be detected by this method. The atomic percentage of Gd calculated for $Li_2Mn_{3.5}Gd_{0.5}O_9$ is 3.53% which is very close to the theoretical value of 3.33%.

Electrical Properties

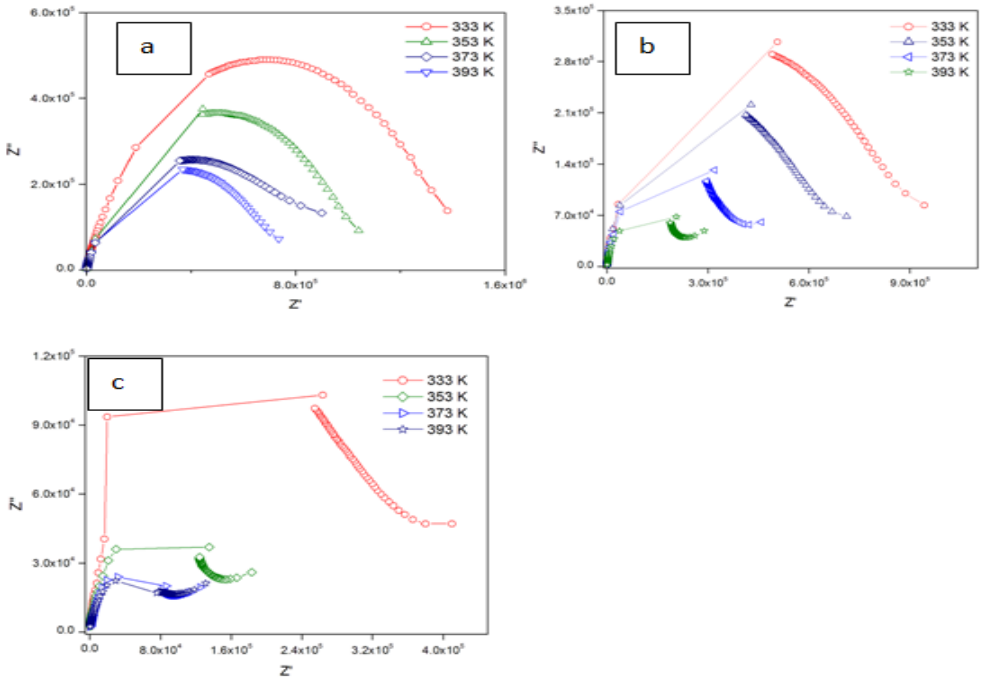

Fig. 4: Cole-Cole Plot of a) L b) LG2 c) LG5

Cole-Cole plot is the wonderful tool to study the changes in the electrical behavior of the material due to the surface modification or dopant. The electrical transport properties are studied at low temperature from 60 to 120°C. Fig. 4 (a-c) shows the cole-cole plot of pristine and doped material. For pure $Li_2Mn_4O_9$ the single semi-circle has been observed at all temperatures indicating the absence of grain boundary effect, also infers the conduction through the bulk of the material [12,13]. A small linear part has been observed while adding the dopants at high temperature (100 and 120°C). The plot envisages one semicircle at high frequency and a straight line at low frequency. Due to the migration of Li+ ions at electrode/electrolyte interface, a semicircle has observed at high frequency region; middle frequency corresponds to charge-transfer process. At low frequency region, straight lines are observed due to the diffusion of lithium ions into electrode material [14]. Due to the parallel combination of resistance and capacitance, a semicircle is observed for all the three samples at all temperature. By increasing the temperature, the radius of the semi-circle is reduced and elucidates the reduction in bulk resistance (R_b) inferring the semiconductor behavior of the material. The value of bulk capacitance are calculated for all temperatures using the relation $2\pi\gamma_{max}R_bC_b=1$ and is given in the Table 2. The values obtained are in the order of pF which proves that conduction process is through the bulk of the material [15-16].

Table 2: Electrical Parameters

Material	Temp. (K)	R_b x 10^5	C_b (pF)	σ_{dc} (10^{-7})	ωp x 10^4 (Hz)	N x 10^{-9} (S cm^{-1} kHz^{-1})	$\mu \times 10^{20}$ ($cm^2V^{-1}s^{-1}$)
L	333	13.8	38.7	1.05	0.305	10.75	0.609
	353	10.3	30.9	2.56	0.319	26.66	0.60
	373	8.94	3.56	2.856	0.92	10.84	1.619
	393	7.32	5.19	3.608	0.67	19.79	1.139
LG2	333	9.43	33.8	2.76	3.98	2.169	7.952
	353	7.1	44.9	3.56	3.7	3.196	6.961
	373	4.21	75.6	6.15	5.95	3.64	10.54
	393	2.58	5.77	10.18	9.6	3.953	16.09
LG5	333	3.78	84.3	7.69	15.74	1.529	31.43
	353	1.59	9.36	16.9	27.65	2.035	51.90
	373	0.863	17.3	17.5	64.45	0.958	114.1
	393	0.751	19.8	19.06	68.81	1.033	115.3

The ionic conductivity of material is calculated using the equation $\sigma = l/R_b\ A$ (S cm^{-1}), where R_b is the bulk resistance of the sample, l is the thickness of the sample, A is the area of the sample and given in the Table 2. Due to thermally activated mobile charge carriers the conductivity increases with the increase of temperature [17].

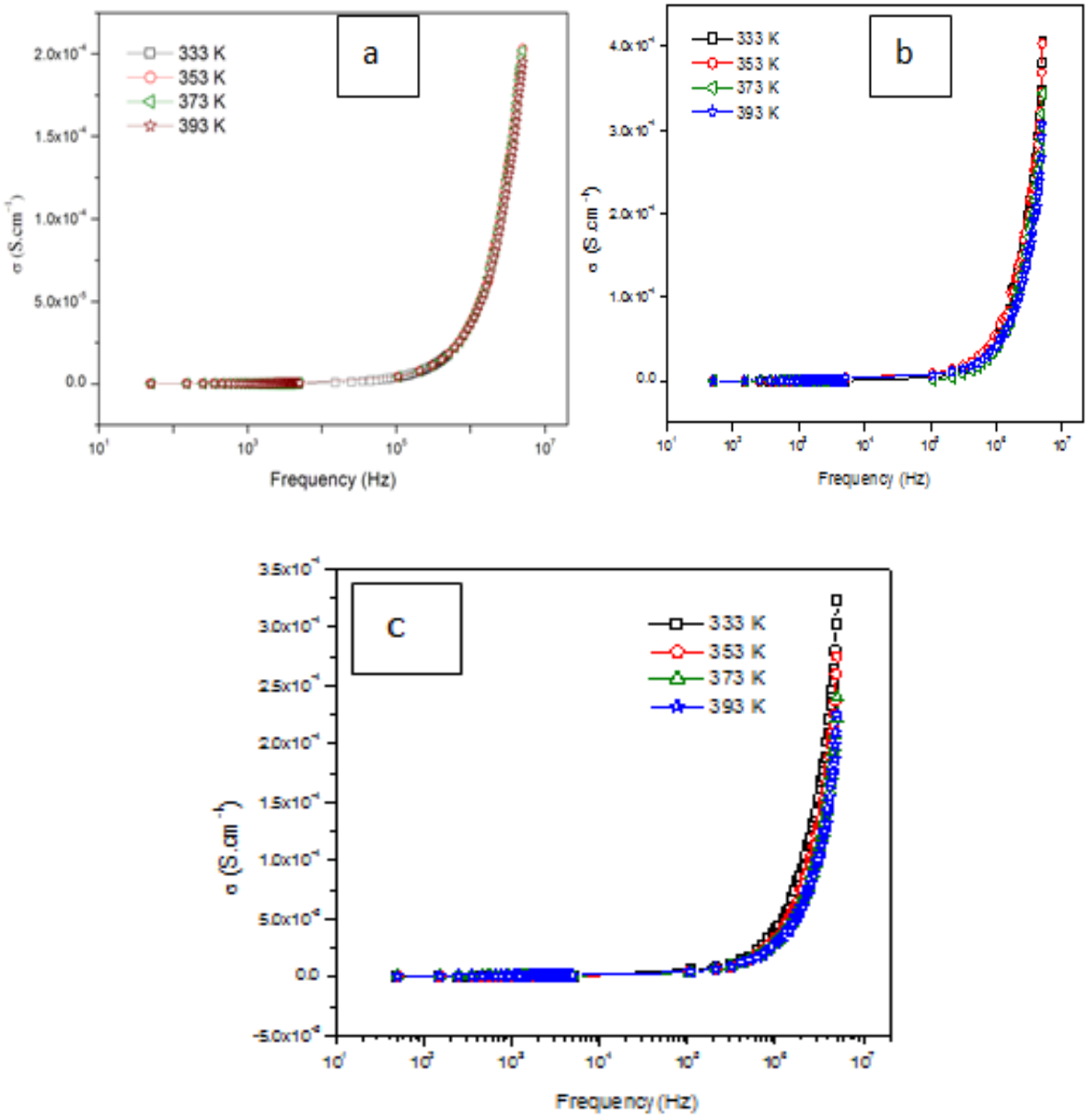

Fig. 5: Conductance Spectrum of a) L b) LG2 c) LG5

The electrical conductance of pristine and doped $Li_2Mn_4O_9$ is shown in the Fig 5 (a-c). Two different conductance behaviors are revealed in the measured range of frequencies for all the samples. At low frequency the frequency independent plateau corresponds to σ_{dc} conductivity at high frequency region and the frequency dependent reveals to σ_{ac} conductivity of the material. The conduction spectra is found to obeys the Jonscher's law $\sigma(\omega)=\sigma dc+A\omega$. Non-liner curve fitting method is used to calculate the hopping conduction, charge carrier concentration and mobility of the material. It has been observed as the conductivity increases with the increase of temperature for all the sample and high temperature has been observed for 0.5 mol of Gd doped $Li_2Mn_4O_9$ at 393 K. Diffusion co-efficient is calculated and found to increase with the increase of temperature and indicates the migration of more oxygen ions [13].

Electro Chemical Performance

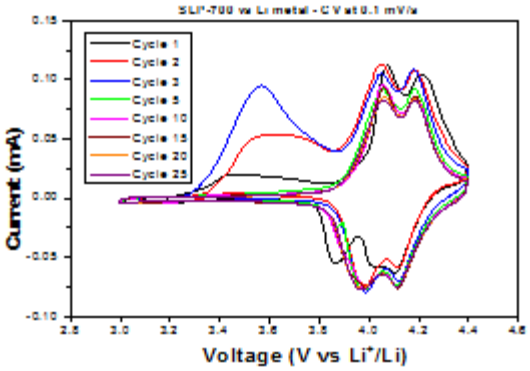

Fig. 6: Cyclic Voltammogram of $Li_2Mn_4O_9$

The electrochemical behavior of the pristine $Li_2Mn_4O_9$ is characterized by cyclic voltammogram and shown in the Fig. 6. CV is recorded for 25 cycles in the voltage range 3 to 4.5 V at the scan rate 0.1mV/s. Two set of anodic and cathodic peaks is observed for pristine $Li_2Mn_4O_9$ around 4 to 4.2 V. The cathodic peak corresponds to Li insertion and anodic peak corresponds to de-insertion of Li+ ions. By increasing the cycle the number the intensity of the redox peak decreases slightly which indicates the chances of decreasing the cyclability of the material.

IV. Conclusion

Defect spinel pure and Gd doped Li_2Mn4O_9 microcystals are successfully prepared by solid state method. The structure and morphology of the material is studied from XRD, SEM and EDAX analysis. Bulk resistance decreases with increases in the temperature and the least value is obtained for 0.5 mol Gd doped $Li_2Mn_4O_9$ shows the NTCR property of the material. Similarly, high conductivity (19.06 x 10^{-7} $S.cm^{-1}$) is obtained for $Li_2Mn_{3.5}Gd_{0.5}O_9$ at 393 K. CV results shows good electrochemical behavior of $Li_2Mn_4O_9$ material.

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