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Effect of Heat Treatment Time on Performance of $LiMn_2O_4$ Nan particles Produced by Sol-Gel Method

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Abstract: ***$LiMn_2O_4$ nanomaterials was synthesized by sol gel technique and calcined at 800^0C temperature for different heat treatment time. The crystal structure and phase identification was done by X-Ray diffraction study; XRD revealed that the crystallite size decreased with increasing annealing time. Morphological, elemental analyses were carried out by FE-SEM and EDS showed the grain size in the range of 100-130 nm. XPS spectra confirmed Mn valency in +4 and +3 states. Dielectric study exhibited available free charge carriers at low frequencies within the material. Cyclic Voltammetry results showed that the sample annealed at 10h has improvement in Li^+ intercalation and de-intercalation.***

Keywords: $LiMn_2O_4$, FE-SEM, Cyclic Voltammetry, XPS

I. INTRODUCTION

People are becoming more dependent on fossil fuel for daily life activities. It has a negative impact on the environment, so there is a need for alternative energy. In order to store energy efficiently and operate the system properly, alternative energy systems require batteries [1]. Roughly, lithium consumption in the United State alone is approximately 6 million tons and a total of 40 million tons across the globe.[2]. Recently, lithium has been in great demand for electronic industry especially in the production of Li-ion batteries [3]. The demand for eco friendly, harmless, reliable and small power sources with high energy density, for both electronic devices and zero emission vehicle can be fulfilled by Li-ion batteries [4,5]. But one of the problems with Li polymer batteries is progressive capacity fading with repeated cycles [6]. Cathode material decides the limit of a battery. The hopeful active materials for lithium-ion secondary batteries are Lithium transition metal oxides [7].

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The principle positive cathode materials for Li –ion batteries are $LiNiO_2$ [8], $LiCoO_2$ [9] and $LiMn_2O_4$ [10]. Spinel $LiMn_2O_4$ is safe, low cost, has high voltage profile and non toxic in characteristics, in correlation with $LiCoO_2$, $LiNiO_2$[11]. However, the effect of calcination time on particle size of $LiMn_2O_4$ is less studied.
In the present work, $LiMn_2O_4$ nanomaterial was synthesized by sol-gel method and calcined at 800^0C for different heat treatment time. The effect of calcination time on structural and dielectric parameters was studied.

II. EXPERIMENTAL

2.1 Synthesis $LiMn_20_4$ material was synthesized by sol–gel method with precursor materials $Li(CH_3COO)\cdot H_2O$, $Mn(CH_3COO)_2.4H_2O$ and citric acid as starting materials. Mn acetate was first stirred in deionized water to provide a saturated solution. Li acetate has been slowly added to this precursor with slow stirring. Saturated citric acid aq. solution is added in the molar ratio of 1:2:3 (Li:Mn:Citric acid). The pH was controlled by adding ammonia hydroxide solution at 7. The solutions were then heated under constant stirring at 80^0C for 5 h to form the gel. Obtained precursor gel was kept in hot air oven at 120^0C overnight to get a dry mass. The dried mass was grinded and calcined at 800^0C for 4, 5, 6, 8 and 10 hours respectively to obtain nano powders of $LiMn_2O_4$.
For cyclic Voltammetry (CV), aqueous electrochemical cell was prepared by three electrodes submersed in Li_2SO_4 aqueous electrolyte. For Cyclic Voltammetry electrochemical cell was prepared with working electrodes (WE) $LiMn_2O_4$ (cathode), Pt-counter electrode (CE) (anode), AgCl - reference electrode (RE). The WE was made by mixing 90% LMO, 5% carbon black, 5% polyvinylidene fluoride and N-Methyl Pyrrolidone was added for making slurry which is coated on 2 mm thick SS foil. CV is taken at the scan rate of 0.01 mV S^{-1} with in the scanning potential range of 0.2–1.2 V. CV measurements was taken on CHI 660E model electrochemical workstation

2.2 Characterization studies:

All synthesized materials were studied by x-ray diffraction to know phase formation and for crystal structure by X'pert PRO MPD, PANalytical, Philips with Cu-Kα radiation at a scan rate of 2^0min^{-1}. The morphology and grain size of $LiMn_2O_4$ was observed by Field Emission Scanning Electron Microscope (FE-SEM).

To identify the existence of functional groups in the materials and to confirm the existence of phases,

FT-IR was performed. XPS data was taken for $LiMn_2O_4$ for identification of Mn valency. The electrical and dielectric properties of $LiMn_2O_4$ pellets were studied considering the impedance data. The impedance data of the samples were collected in the temperature range of 30- 300^o in oxygen atmosphere using Novacontrol, Alpha-A High Performance Frequency Analyzer in the frequency range of 50-1MHz.

III. RESULTS AND DISCUSSION

3.1 XRD analysis: XRD patterns of LMO calcined at different heat treatment times were depicted in Fig.1. From figure, well defined peaks observed in all samples suggest crystallized cubic spinel LMO (JCPDS 35-0782) [12]. Initially some secondary peaks seen in the figure, those could be assigned to Mn_2O_3 are start to decrease with increase in time and disappear at 10 hours calcination time. This may shows that at lower calcinations time unstable Mn^{2+} easily oxidizes and forms Mn_2O_3 minor peaks. With increasing calcination time, Li ions were occupied by tetrahedral 8a sites, while Mn^{3+}/Mn^{4+} ions start to occupy octahedral 16d sites. The crystal sizes calculated using scherrer's formula were 76, 72, 69, 65 and 61 nm respectively for 4, 5, 6, 8 and 10 hours of calcinations. This shows that sample calcined for 10 hours time has lower crystalline size.

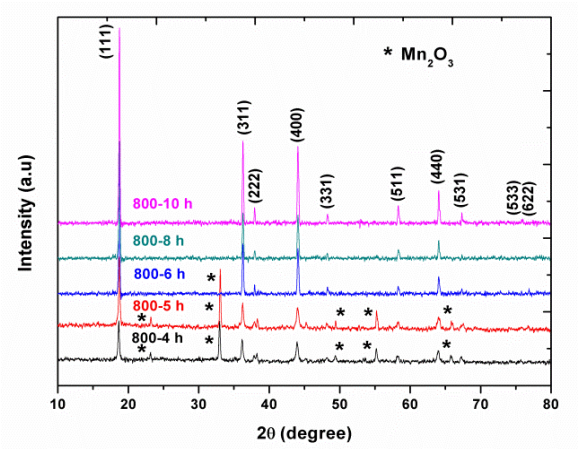

Fig 1: XRD patterns of $LiMn_2O_4$ nanoparticles calcined at different times

3.2 FE-SEM and EDS study The structural morphology, grain distribution were studied through FE SEM depicted in Fig.2(a-e). With increasing annealing time, well defined polyhedral structures of the particles were observed. The mean grain size of the materials was observed between 100-130 nm. Fig.3 (a-e) shows EDS profiles of LMO annelaed at different times corroborates existence of Mn and O.

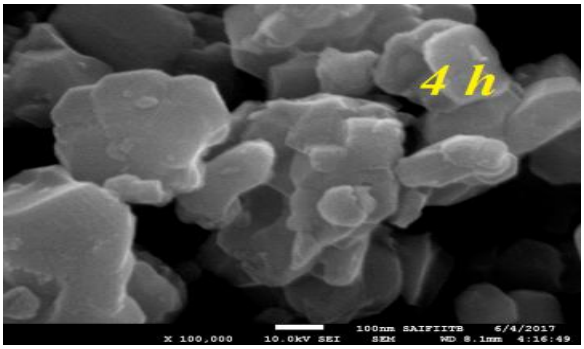

Fig 2(a)

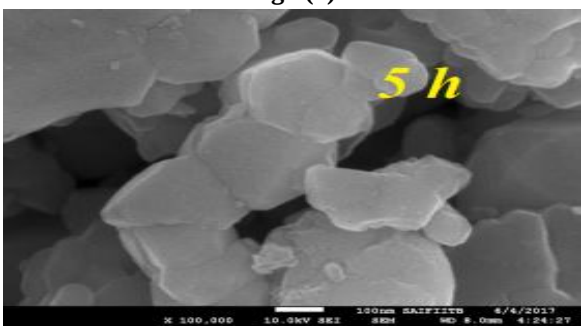

Fig 2(b)

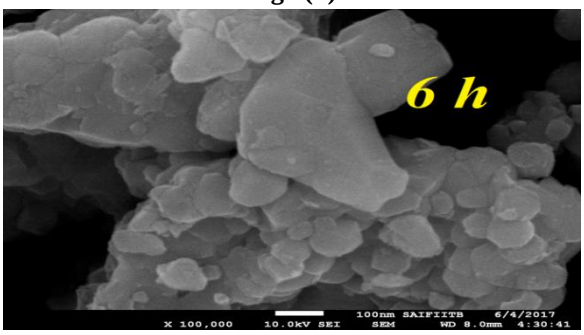

Fig 2(c)

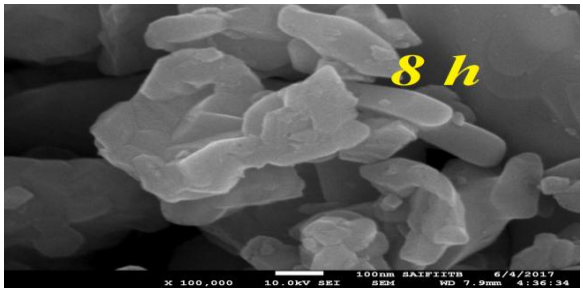

Fig 2(d)

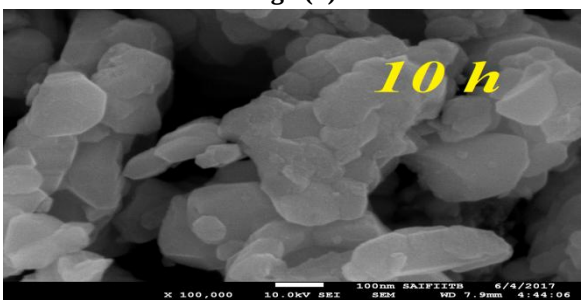

Fig 2(e)

Fig 2 (a-e): FE-SEM images of $LiMn_2O_4$ calcined at different time intervals.

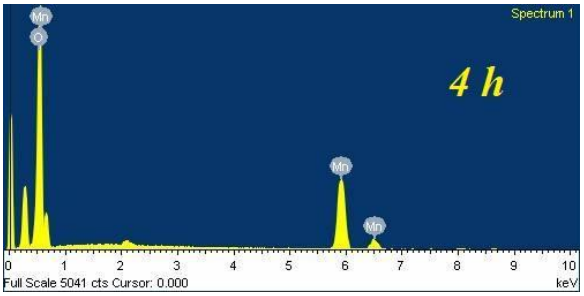

Fig 3(a)

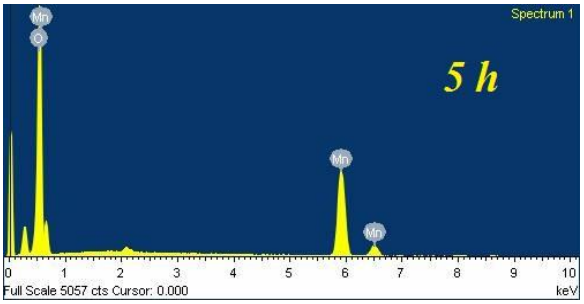

Fig 3(b)

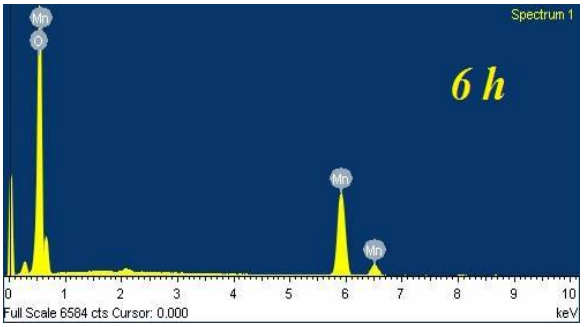

Fig 3(c)

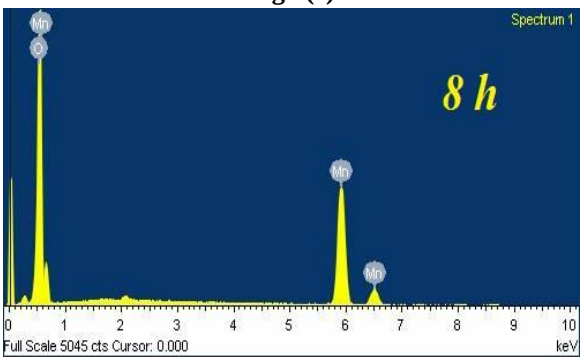

Fig 3(d)

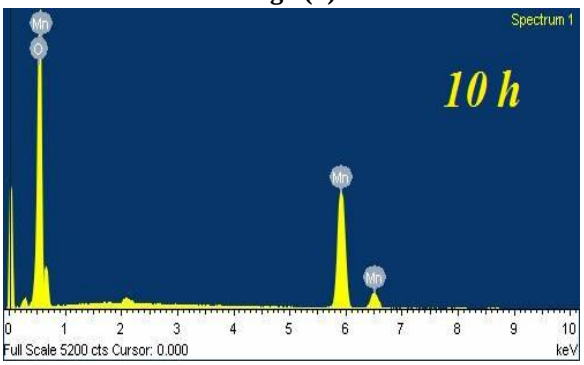

Fig 3(e)

Fig 3 (a-e): EDS profiles of $LiMn_2O_4$ calcined at different time intervals.

3.3 XPS analysis:

XPS survey scan and Mn2p spectra of $LiMn_2O_4$ annealed at different times were shown in Fig.4(a-c). Fig 4b shows two major peaks corresponding to $Mn2p_{3/2}$ and $2p_{1/2}$ [13]. Curve fitting was done on $Mn2p_{3/2}$ peak for the sample which is annealed at 10h, which is shown in fig 4c. From figure 4c, the fitting parameters were given as Mn^{4+}~48.8% , Mn^{3+}~48.9%, Mn^{2+}~2.3%. These values indicate that the sample annealed at 10h duration is the optimized sample.

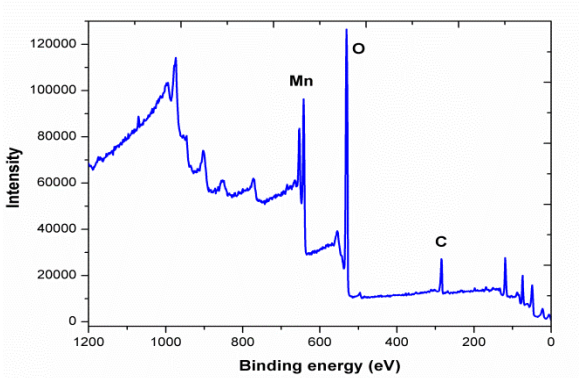

Fig: 4(a) XPS survey scan of $LiMn_2O_4$ calcined for 10h

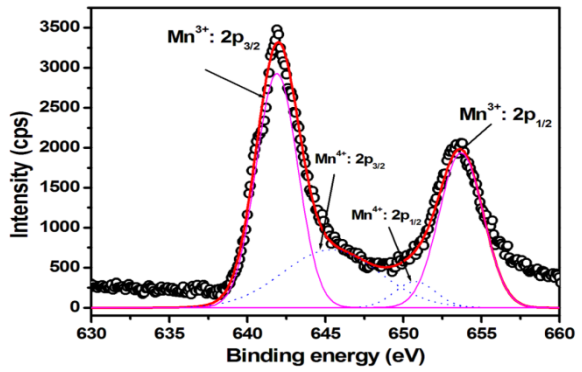

Fig:4(b) Mn 3+ and Mn4+ peaks in $LiMn_2O_4$

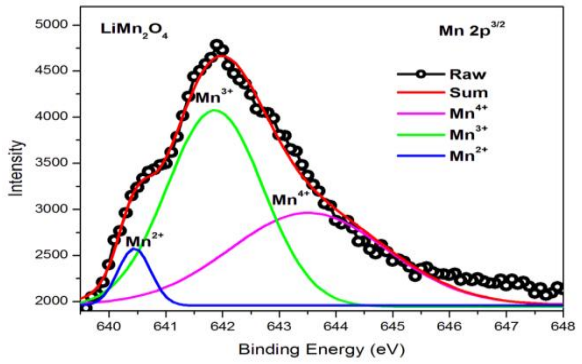

Fig:4 (c) Curve fitting of $Mn2p_{3/2}$

3.4 Cyclic Voltammetry:

Cyclic Voltammetry graphs were shown in Fig.5(a-e). From the figure it is observed that, with increase in annealing time, the peak potential difference of anodic and cathodic peaks in reduction, oxidation decreased, which suggests that lithium intercalation and de-intercalation become easier in $LiMn_2O_4$ [14].

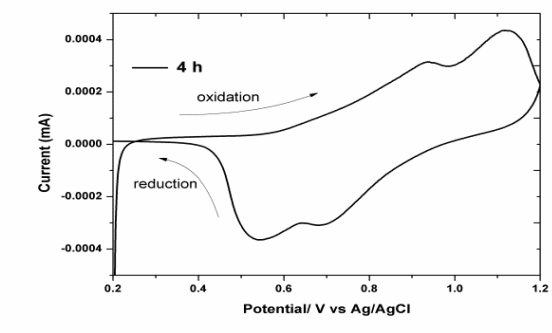

Fig 5(a)

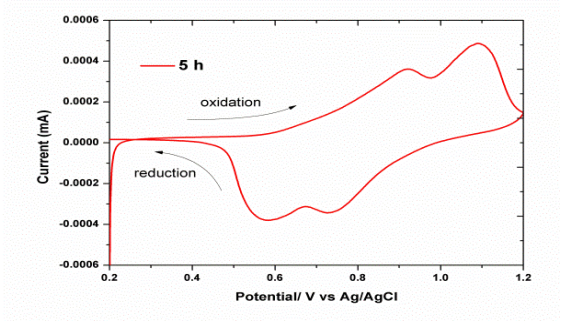

Fig 5(b)

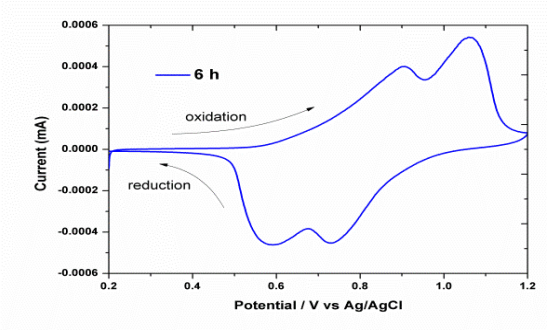

Fig 5(c)

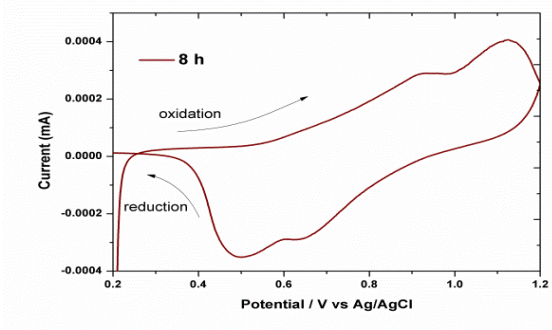

Fig 5(d)

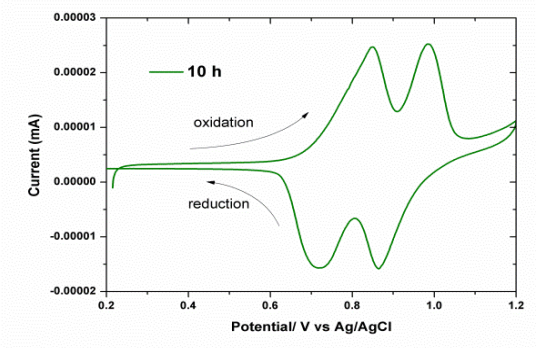

Fig 5(e)

Fig 5.(a-e) Cyclic Voltammograms of $LiMn_2O_4$ calcined at different times

IV. CONCLUSIONS

$LiMn_2O_4$ material was produced following sol gel method successfully and annealed at 800^0C for different time intervals. XRD results showed that with increase in time the crystallinity increased. FE-SEM micrographs confirmed the particle size between 100-130 nm. XPS study revealed the Mn valency as 3^+ and 4^+ states. From Cyclic Voltammetry results it is found that with increase in time of annealing the peak potential difference decreased, which indicates the improvement in lithium ion intercalation and de-intercalation processes.

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Compliance with Ethical Standards:

- Authors declare that they have no conflict of interest

Highlights for review

- Effect of calcination time on $LiMn_2O_4$ performance
- Cubic spinel structure of $LiMn_2O_4$
- Cyclic Voltammograms of $LiMn_2O_4$
- XPS study of $LiMn_2O_4$

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Titles of the figures:

Fig 1 XRD graphs of $LiMn_2O_4$ nanoparticles calcined at 800^0C

Fig 2(a-e): FE-SEM images $LiMn_2O_4$ calcined at different times

Fig 3(a-e): EDS profiles of $LiMn_2O_4$

Fig 4 (a) XPS survey scan of $LiMn_2O_4$ calcined for 10h (b) Mn 3^+ and $Mn4^+$ peaks in $LiMn_2O_4$ (c) Curve fitting of $Mn2p_{3/2}$

Fig 5(a-e): Cyclic Voltammograms of $LiMn_2O_4$ calcined at different times

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