# Synthesis and Characterization of MnFe$_2$O$_4$ Nanoparticles and its Electrochemical Performance Evaluated as Anode for Li-ion Battery Applications

**K.Gurushankar, T.Theivashanthi, M.S.Revathy, Durgadevi**

*Abstract: In the last decade, large number of research has been made to increase the capacity of anodes by changing the graphite with Si or Sn and conversion based materials such as MnFe$_2$O$_4$, Co$_3$O$_4$, Fe$_2$O$_3$ and NiO etc.,. In the present work, MnFe$_2$O$_4$ nanoparticles has synthesized by simple solid-state method. The crystal structure of MnFe$_2$O$_4$ evaluated by powder X-ray diffraction (XRD) and its morphology invetigated by Scanning Electron Microscopy (SEM), and its electrochemical performance has been carried out by Cyclic Voltammetry (CV), charge-discharge and electrochemical impedance analysis (EIS). The results of charge-discharge performance showed an excellent discharge capacity of 860 mA hg$^{-1}$ when tested as anode for Li-ion battery applications.*

*Keywords : MnFe$_2$O$_4$, XRD, Cyclic Voltammetry.*

## I. INTRODUCTION

There is a huge drive all over the world to develop rechargeable batteries for energy storage and electro mobility. In this regard, improvement of materials for their applications in energy storage devices great demand therefore considerable amount of research has been focused in recent years and lot of technologies have been developed for nickel cadmium, nickel–metal hydride, lead acid, lithium ion battery etc [1,2]. Among all other renewable energy sources, LIBs are promising as obvious choice for storing energy from renewable resources such as solar and wind. After launching of SONY company rechargeable LIB with high charge/discharge current rates were established to be more capable for their application in different portable electronic devices like cellular phones, laptops and digital electronics [3]. Three major key components play a pivotal role in a LIB system: cathode, anode and electrolyte. Lithium batteries energy density increased by three following ways

(1) either using high voltage
(2) Cathode active materials as electrodes

(3) Developing high capacity anode and cathode electrode materials.

Several efforts have been made to develop nanostructured electrode materials which can deliver high energy density and power density to produce large scale of LIB for next generation applications [4]. In recent years, there has enormous research effort aimed at exploring nanostructured electrode materials in LIBs, such as Silicon (Si), Tin (Sn), conversion based oxides and LiMn$_2$O$_4$, Li-rich NMC, LiFePO$_4$ to replace the current commercial graphite (anode) and LiCoO$_2$ (Cathode).

There is a big challenge facing nowadays to develop nanostructured electrodes for energy storage devices and to control the structure and morphology of electrode design for producing efficient transport pathways of ions and electrons in high-performance energy devices. Alternatively, the graphite anodes and shows a low theoretical capacity of 372 mA hg$^{-1}$ produced current battery technology, cannot meet the requirement of high power and high energy for the next generation rechargeable batteries. Also, new anode materials are desired for various fields like high power, high capacity, good cycling stability, as well as low cost and non-toxic nature. In the last decade, lot of research has been carried out to increase the capacity of anodes by changing the now used graphite with Si or Sn and conversion based materials such as MnFe$_2$O$_4$, Co$_3$O$_4$, Fe$_2$O$_3$, NiO etc.,. However, the realization of high capacity and high rate capability for these anodes has been hindered by the severe volume changes during the reaction with lithium ions, and its low conductivity. In order to overcome those problems,

Recently nanostructured materials have been developed and demonstrated with improved electrochemical performance. Therefore, plenty of efforts have been paid for great attention on fabricating electrode materials with good durability, high energy density. Magnetic nanoparticles draw more importance among scientific community for battery applications because when they are reduced to nano size, they exhibit some remarkable properties including superparamagnetism.

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## II. MATERIALS AND METHODS

### A. Synthesis of MnFe₂O₄ nanoparticles by solid state method

The precursors for Manganese and Iron (salts) are added in molar ratio of 2: 1 with an activating agent. Iron (III) nitrate and manganese nitrate are used as starting materials for metal precursor. Citric acid is used as an activating agent. Weighed amounts of high purity metal nitrates were mixed with 100 ml amount of deionized water to get a nitrate solution. The chelating agent citric acid is added with precursor solution with proposed ratio under continuous stirring. The solution temperature maintained constantly at 80° C using a hot plate. After 1 hour, the temperature is increased to reach 100°C, all the water contents are evaporated and it becomes a sol-gel. Due to auto combustion $CO_2$, $H_2O$ and $N_2$ are released and it forms a stable fine powder. The fine powder was then further performed by heating in a furnace to a temperature of 800°C for five hours. The synthesis is performed without any additional treatment, and organic solvents. The product is washed by using distilled water and ethanol several times to remove the residual materials, centrifuged, dried at 80°C overnight. Finally the synthesized product was stored in without moisture container and characterized with different characterization techniques like XRD, FESEM, FT-IR, and UV-Visible Spectroscopy.

Electrochemical performances of the samples were evaluated by 2032 coin cell type. The anode material electrode was prepared by mixing the active material with SP-carbon and polyvinylidene difluoride (PVDF) with a weight ratio of 80:10:10 in (NMP solution) to ensure the homogeneity and the mixture was coated into a Cu foil. Before going to test the electrode the material was kept in to the vacuum oven for 12 hrs at 120 °C to remove the excess solvent and moisture. The electrolyte was composed of EC: DEC: DMC with the weight ratio of 2:1:2 and the coin cell were assembled into an argon-filled dry glove box. Then the cells charge-discharge performance was measured by using a VMP3 Biologic battery tester. The typical active material loading was 1.0–2.0 mg/cm², Cyclic Voltammetry (CV) measurements were carried out at a scan rate of $0.1mVs^{-1}$ between 0.001–3.0V at room temperature. The electrochemical charge-discharge measurements were performed at a C/5 rate in a voltage range of 0.001–3.0V. Electrochemical impedance spectroscopy (EIS) technique was performed at discharged condition of 0.01 V vs $Li/Li^+$ at room temperature within the frequency range of 400 kHz to 50 mHz with a perturbation of 20 mV amplitude used for as prepared cell and after cycling over to analyze the electrode kinetics.

## III. RESULTS AND DISCUSSION

### A. Structural studies

Fig. 1.shows the XRD pattern of MnFe₂O₄ powder prepared by solid state method using citric acid as a chelating agent, which is having cubic geometry. From the results of MnFe₂O₄, the XRD pattern is in agreement with standard JCPDS data (card No. 74-2403) as already reported by Gasparov et al [5]. All the diffraction peaks in the XRD pattern of the synthesized products can be perfectly matched to the (111), (220), (311), (400), (422), (511) and (440) faces of the MnFe₂O₄ cubic spinel ferrite type structure. The peak broadening could be attributed to the nanocrystalline nature of the prepared samples. No additional peaks for impurities are observed in the XRD pattern, which confirms the purity of MnFe₂O₄.
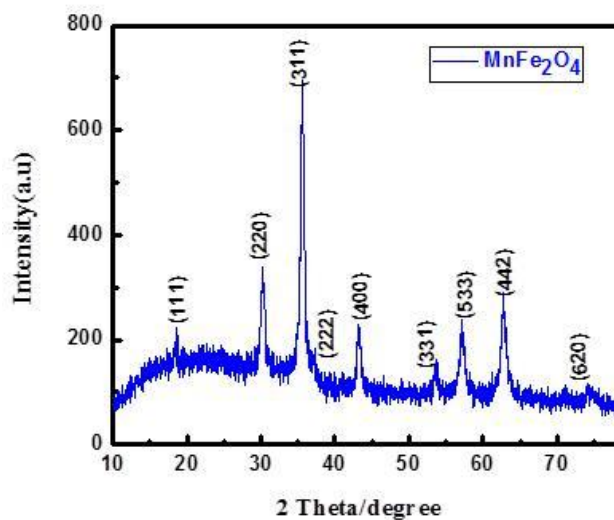


**Fig. 1. XRD pattern of MnFe₂O₄ powder**

In this segment, SEM images demonstrated the structural features, change in morphology, and texture and elemental composition of the manganese ferrite powder. SEM micrographs of MnFe₂O₄ with different magnifications are shown in the Fig. 2 (a-c). From the SEM photographs, it is clearly understood that the products are having spongy sheet like structure consisting of grains with average size of 200-300 nm. The grains are look like without agglomeration in the samples. Moreover, the presence of agglomerates in the powder may suggest high temperature calcination.

Fig. 2 (c) shows voids and pores in the surface of the samples; this could be the reason for release of large amounts of gas during the auto combustion process. The samples have a spongy structure and one can see that the formation of multigrain agglomerations consisted of very fine crystallite. Chemical composition analyses through EDAX were also carried out on powder samples. Manganese ferrite compound also noticed in Figure (d&e). The EDAX spectrum (e) of the samples shows that all elements are nearly expected elemental composition.
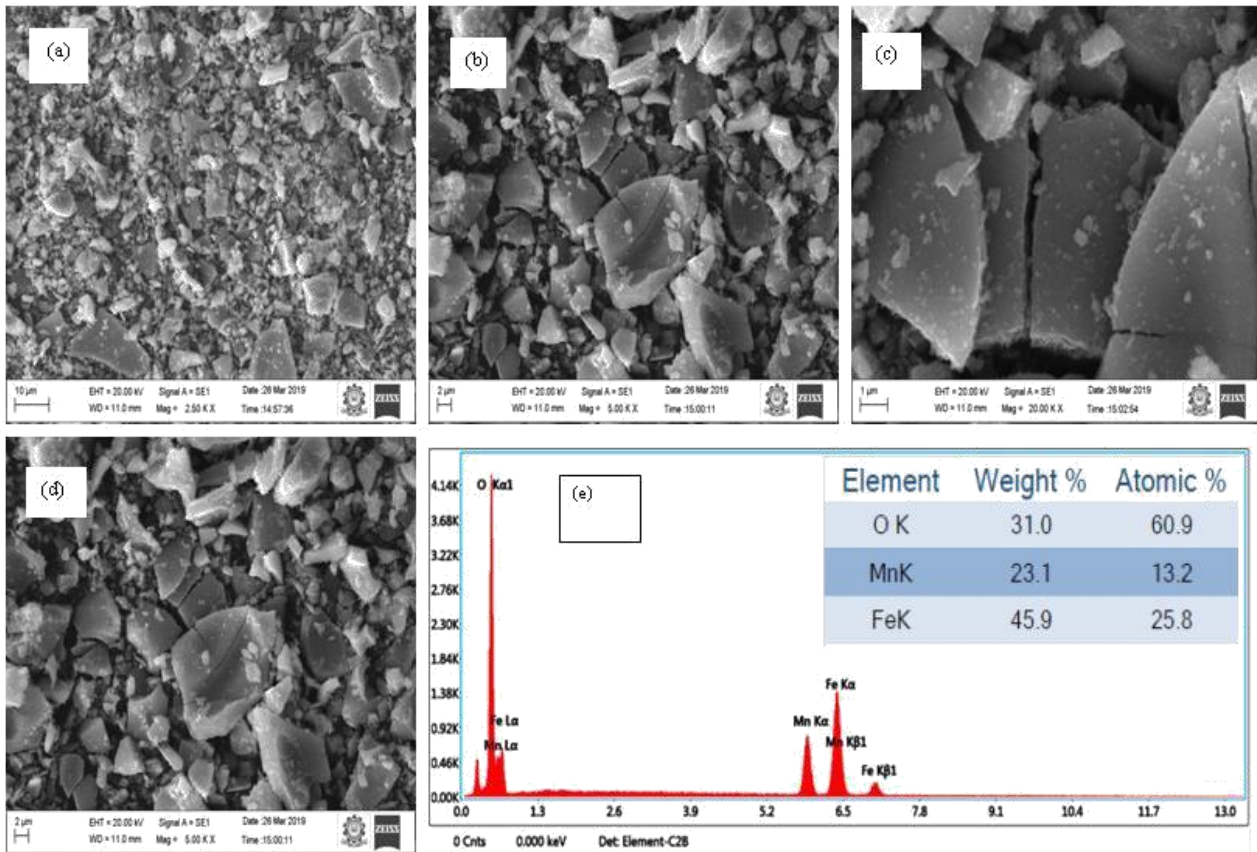
**Fig. 2. a),b),c),d) SEM images and e) EDAX spectrum of Manganese ferrite.**

**B. FTIR Study**

Fig.3. shows the FT-IR spectra of the as-prepared sample of manganese ferrite. Ferrite bands are likely to appear at 550-600 $cm^{-1}$, which is assigned to the tetrahedral compounds and the appearance of the bands at 542, 512, and 458 $cm^{-1}$ indicate that iron (III) oxide band present in the $MnFe_2O_4$ system. The presence of water within the nanocrystalline ferrite is exposed by the characteristic bands at 3323 and 1648 $cm^{-1}$, identified as O–H stretching and bending modes of vibration, respectively. The characteristic bands (1039 and 1191 $cm^{-1}$) can be recognized for the presence of manganese ions in the structure.

**C. Evaluation of Electrochemical Performance MnFe2O4 used as anode for Li ion batteries**

- *Cyclic Voltammetry studies*

The Li storage property of $MnFe_2O_4$ as anode material for Li-Ion Batteries (LIBs) are calculated using a two-electrode cell, where $MnFe_2O_4$ serves as the working electrode and lithium metal foil serves as the counter as well as reference electrode. This $MnFe_2O_4$ composite Cyclic Voltammetry (CV) studies were performed in the potential window of 3.0–0.001 V at a scan rate of 0.1 mV/s for initial four cycles at room temperature using biologic battery testing system. The first cycle have reduction peaks at 1.561 V and 0.561 V, which could be attributed to the formation of SEI layer and the reduction of $MnFe_2O_4$ to metallic Mn and Fe. Besides, the anodic peak at around 1.595 V which is related to the

oxidation of metallic manganese and iron to $Mn^{2+}$ and $Fe^{3+}$ [6]. These sharp redox peaks indicated the excellent charge-transfer kinetics in the beginning of the electrode reaction, which is conducive to the lithium intercalation/deintercalation [7, 8].
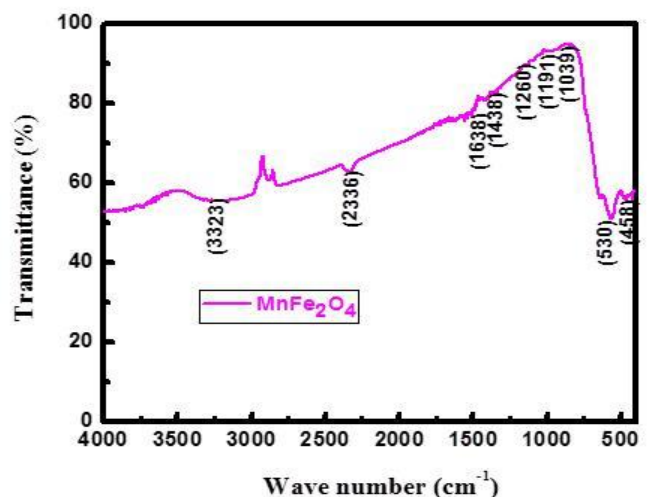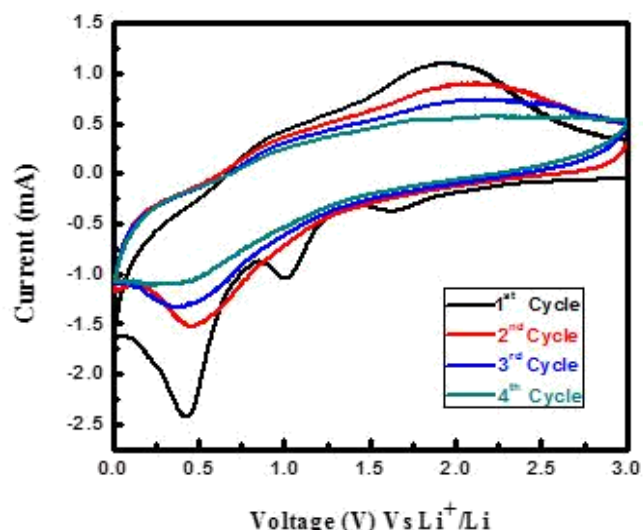


**Fig. 3. FTIR of MnFe2O4 powder**

**Fig. 4. Cyclic Voltammogram of MnFe2O4**

In CV, after first cycle is over, the overlapping of 2nd ,3rd & 4th cycle curves indicate good reversible behavior as well as good cycling performance of our electrode.

- *Cycling (charge-discharge) studies for Li ion battery anode*

In order to investigate the influence of Li storage properties for MnFe₂O₄ charge-discharge experiments were conducted by galvano statically with cutoff voltage window between 0.001-3.0V at C/10 rate. Figure 5(a) shows that MnFe₂O₄ charge-discharge curves performed at C/10 rate with the range of voltage between 0.001-3.0V for the first and fifth cycles charge-discharge curve. Fig.5(b) shows that corresponding discharge capacity versus cycle number plot of Fig. 5(a). At C/10 rate the first cycle discharged capacity is ~860 mAhg$^{-1}$ and after five cycles over the discharge capacity is 846 mAhg$^{-1}$. Therefore the capacity retention for after five cycles is around 98%.
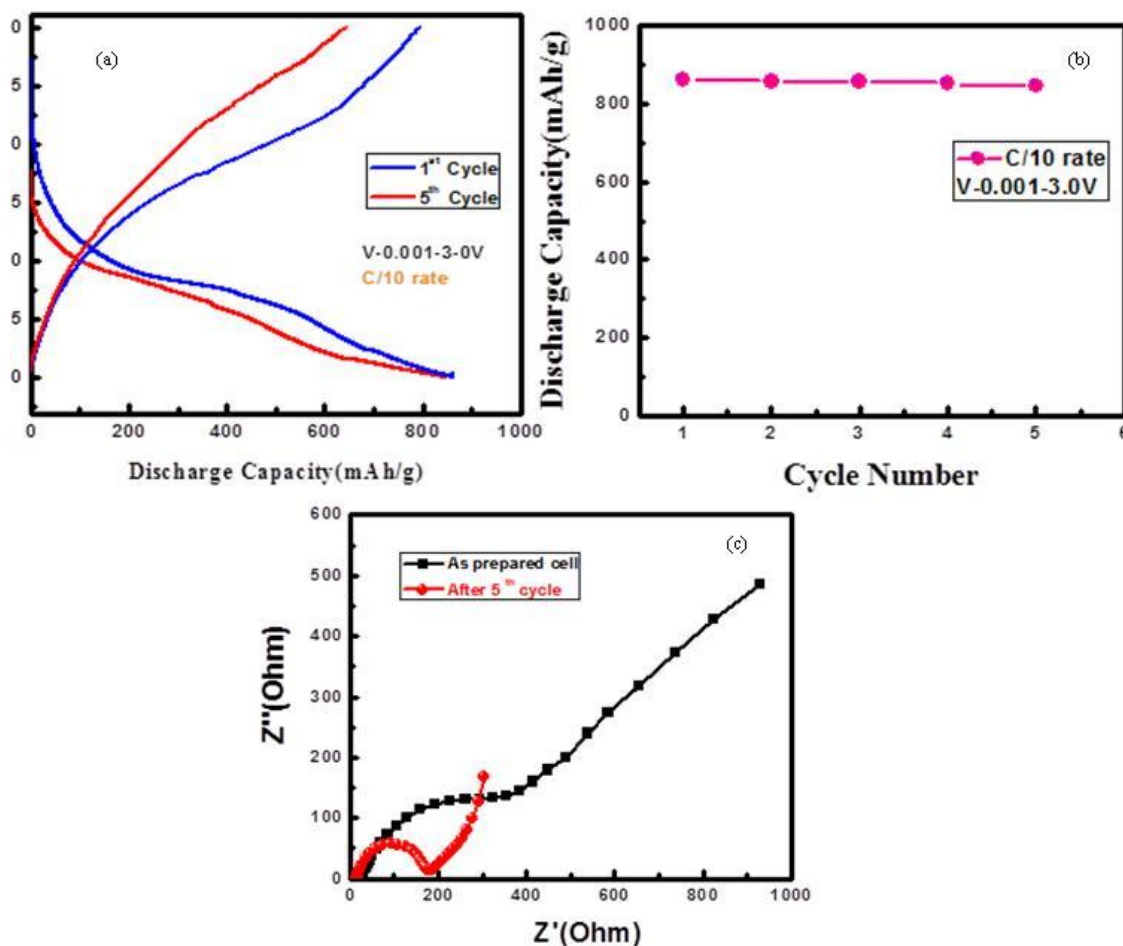


**Fig. 5. (a) Voltage vs Discharge capacity (b) Discharge capacity vs cycle number, (c) EIS study- Nyquistic plot**

- *Electrochemical Impedance Spectroscopy (EIS) studies*
Electrochemical impedance spectroscopy (EIS) technique was performed at discharged condition of 0.001 V vs Li/Li$^{+}$ at room temperature within the frequency range of 400 kHz to 50 mHz with a perturbation of 20mV amplitude used for as prepared cell and after five cycling over to analyze the electrode kinetics. Fig. 5 (c) shows the Nyquist plots as prepared cell, after completing the 5th discharge cycles. The

diameter of the semicircle can be assigned to charge transfer resistance (R$_{ct}$) [9]. The inclined straight line can be attributed to Warburg diffusion of Li$^{+}$ ions into the bulk of the active material [10]. Compare than as prepared cell electrode impedance the 2nd cycle impedance R$_{ct}$ value is low, indicating the enhanced electron transfer due to the good conductivity of electrode.

## IV. CONCLUSION

In conclusion, successfully we synthesized $MnFe_2O_4$ nanoparticles by simple synthesis method using citric acid as chelating agent. Finally the synthesized product was characterized by different techniques such as XRD, FTIR & SEM. The pure cubic crystalline phase of $MnFe_2O_4$ is confirmed by using XRD analysis. The optical studies like FT-IR confirmed the metal ions & metal oxide present in the sample. Further the morphology is analyzed using SEM analysis shows that the sample having spongy likes sheet structure consisting of grains with average size of 200- 300 nm. Finally the electrochemical measurements showed when tested as anode for Li ion battery applications the initial cycle shows 860 mA h $g^{-1}$ discharge capacity at C/10 rate. After 5 cycles over the discharge capacity showed 845 mA h $g^{-1}$ at C/10 rate. The $MnFe_2O_4$ nanoparticles are good for the storage and intercalation/deintercalation of lithium ions which leads to higher specific capacity and better cycling properties of anode. Moreover, the EIS spectra indicating that less resistance of our $MnFe_2O_4$ electrode will improve the enhanced electron transfer due to the good conductivity of electrode. These primary results are showing that the promising prospect of $MnFe_2O_4$ used as anode materials for lithium-ion batteries.

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