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## RESEARCH ARTICLE

### SYNTHESIS AND ELECTROCHEMICAL STUDY OF MANGANESE FERRITE ( $\text{MnFe}_2\text{O}_4$ ) NANOPARTICLES

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#### ABSTRACT

Manganese ferrite ( $\text{MnFe}_2\text{O}_4$ ) nanoparticles, were synthesized by Sol-Gel technique, to investigate its applicability as electrode material for supercapacitor. The cubic spinal structure of  $\text{MnFe}_2\text{O}_4$  was confirmed from X-ray diffraction (XRD) pattern and an average particle size calculated from Scherer equation was 15 nm. The scanning electron microscope (SEM) photograph reveals agglomerated nanosized grains of the product. Electrochemical properties were investigated via cyclic voltammetry and galvanostatic charge/discharge in 1M KCL electrolyte. The  $\text{MnFe}_2\text{O}_4$  electrode exhibits maximum specific capacitance of  $197\text{Fg}^{-1}$  at the scan rate of  $1\text{mVs}^{-1}$ . An electrochemical Impedance study of the product was also carried out to investigate its electrochemical characteristics. The  $\text{MnFe}_2\text{O}_4$  nanoparticles seem to be promising material for supercapacitor.

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## INTRODUCTION

Supercapacitor has emerged as new technology in energy storage, which can store much more energy than conventional capacitors and offer much higher power density (Conway BE, 1991). As a result, supercapacitors may become an attractive power solution for an increasing number of applications i.e., back-up power sources for electronic devices, load-levelling, engine start or acceleration for hybrid vehicles and electricity storage generated from solar or wind energy (Miller et al., 2008). Supercapacitors can be divided into three general classes: Electric/electrochemical double layer capacitor (EDLC), Pseudocapacitors, and Hybrid capacitors (Choi et al., 2015). Each class is characterized by its unique mechanism for storing charge. These are, respectively, non-Faradaic, Faradaic, and a combination of the two. Faradaic processes, such as oxidation-reduction reactions, involve the transfer of charge between electrode and electrolyte. A non-Faradaic mechanism, by contrast, does not use a chemical mechanism. Rather, charges are distributed on surfaces by physical processes that do not involve the making or breaking of chemical bonds

(Zheng et al., 1995). There are three major types of electrode materials for supercapacitors: carbon-based materials, metal oxides/hydroxides and conducting polymers (Brezesinski et al., 2011). Carbon-based materials such as activated carbon, mesoporous carbon, carbon nanotubes, graphene and carbon fibres are used as electrode active materials in EDLCs, while conducting polymers such as polyaniline, polypyrrole and polythiophene or metal oxides such as  $\text{MnO}_2$ ,  $\text{V}_2\text{O}_5$ , and  $\text{RuO}_2$  are used for pseudocapacitors. The energy density and power density of pseudocapacitors are usually several times larger than those of EDLCs (Hung et al., 2014). The first discovered electrode material for pseudocapacitor is  $\text{RuO}_2$  (Lei and Chen 2015). It was demonstrated that its specific capacitance reached  $700\text{Fg}^{-1}$  (Wang YG et al., 2005). Whereas, the high cost limited its wide application. In order to prepare affordable electrode, other materials such as cobalt oxide (Xu et al., 2010) nickel oxide (Fu et al., 2009) and manganese oxide (Xu et al., 2007) were investigated. For more practical applications, supercapacitors with higher operating voltage and higher energy density without sacrificing cycle life (Vellacheri et al., 2014) are desired. However, in aqueous electrolyte, the operating voltage, which plays an important role in improving the energy density, according to the equation:  $E=1/2 \text{ CV}^2$ , is restricted by water decomposition voltage. Therefore, developing novel supercapacitors with high performances and

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operating voltages in aqueous electrolyte is still in great demand (Zhang *et al.*, 2012).

Further it is found that in the nano-regime, Manganese Ferrite ( $MnFe_2O_4$ ) undergoes a cation rearrangement and the multiple oxidation states of Mn-species influences electrical properties substantially (Deraz NM, Alarifi A, 2012 and Wang B *et al.*, 2013). In the present work we report the Sol-Gel synthesis of Manganese Ferrite nanoparticles and investigation of electrochemical performances of Manganese Ferrite based supercapacitor by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy.

## MATERIALS AND METHODS

### Synthesis of Manganese Ferrite ( $MnFe_2O_4$ )

A nanocrystalline  $MnFe_2O_4$  was synthesised by sol-gel citrate method. The starting chemicals used for the synthesis are Manganese (II) nitrate tetra hydrate  $Mn(NO_3)_2 \cdot 4H_2O$  (Acros Organics) Ferric nitrate  $Fe(NO_3)_3 \cdot 9H_2O$  (S.D. Fine Chem. Ltd.), Citric acid (S. D. Fine. Chem.Ltd.), Polyvinylidene fluoride (PVDF) and N-methyl-2- pyrrolidone ( $C_5H_9NO$ ) (Srichem Sisco Research Laboratories Pvt. Ltd.). All the chemicals used were of AR grade. Citric acid was added into the mixture of stoichiometric amounts of precursors  $Mn(NO_3)_2 \cdot 4H_2O$ ,  $Fe(NO_3)_3 \cdot 9H_2O$ . Citric acid acts as a chelating agent and assists for the removal of nitrates. The mixture was then allowed to disperse in 20 ml ethanol. The solution then kept on magnetic stirrer with hot plate at  $80^0C$  and vigorously stirred for 3 hours. The gel formed was then kept in pressure bomb at  $120^0C$  for 12 hours. The final product was obtained by further heating it in the furnace at  $650^0C$  for 6 hours. The morphology and size of the resulting nanomaterial was examined using Scanning Electron Microscopy (SEM). The phase of the nanomaterial was identified by X-ray Diffraction (XRD) with the step of  $0.01^0$  over  $20^0$  to  $80^0$  20 range.

### Electrode preparation and electrochemical measurement

The working electrode was prepared by mixing the monocrystalline powder as active material (80 wt. %), activated by carbon black conductor (10wt %) and polyvinylidene fluoride binder (PVDF 10 wt. %) in n-methyl-2-pyrrolidone solvent. Then the mixture was uniformly coated on the rectangular gold plate with  $1mg/cm^2$  and was dried at room temperature for 12hrs. All electrochemical measurements i.e. Cyclic Voltammetry (CV) and Galvanostatic charge-discharge (GCD) were performed in 1 M KCl electrolyte through a conventional three electrode arrangement on CHI6002C electrochemical analyser. The fabricated electrode ( $1mg/cm^2$ ) was used as the working electrode, a platinum foil was used as the counter electrode and Ag/AgCl saturated calomel electrode.

The specific capacitance,  $C$  ( $F \cdot g^{-1}$ ) of the electrode calculated from CV curve using following equation,

$$C = \frac{1}{m.s. \cdot V} \int I_{(V)} dV \quad \dots\dots (1)$$

Where  $m$  (g) is the mass of electroactive material loaded on the electrode,  $s$  ( $V \cdot s^{-1}$ ) is the scan rate for the measurement and  $\int I_{(V)} dV$  is the area under the cyclic voltammogram.

The specific capacitance  $C$ , ( $F \cdot g^{-1}$ ) of the electrode calculated from the GCD curve as,

$$C = \frac{i}{-\frac{v}{t} \times m} = \frac{i}{-slope \times m} \quad \dots\dots (2)$$

Where  $i$  is the current applied. ( $\Delta V/\Delta t$ ) is the slope of the discharge curve after IR drop, and  $m$  is the mass of the active material on one electrode.

## RESULTS AND DISCUSSION

### Crystal structure analysis

The XRD pattern of the sol-gel synthesised nonocrystalline  $MnFe_2O_4$  powder prepared at room temperature is shown in Fig 1. XRD shows crystalline single phase of ferrite ( $MnFe_2O_4$ ) to be very close to the JCPDS card no.75-0034&74-2403. All peaks are related to cubic spinal structure of Manganese Ferrite. Five diffraction peaks obtained indexed to the crystal plane (220), (311), (400), (422), (333), (440). Broad peaks of the sample shows ultra-fine grained nature and small size nanoparticles. The crystallite size was calculated by using Debye-Scherrer formula (Sharma *et al.*, 2014).  $D = \frac{k\lambda}{\beta \cos \theta}$ , average crystallite size is 15 nm for the prominent peak corresponding to (311) plane.

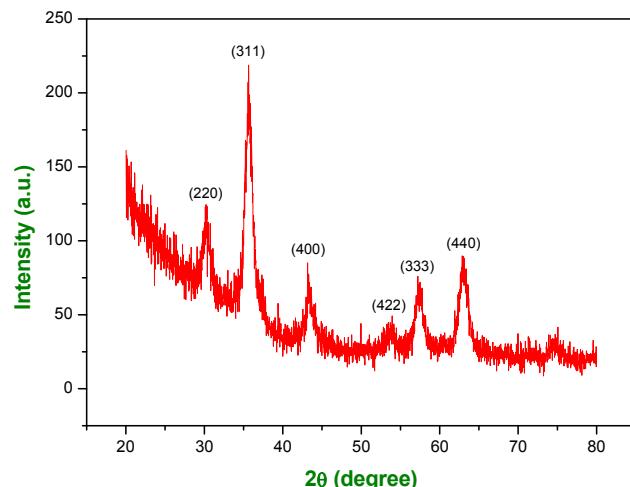
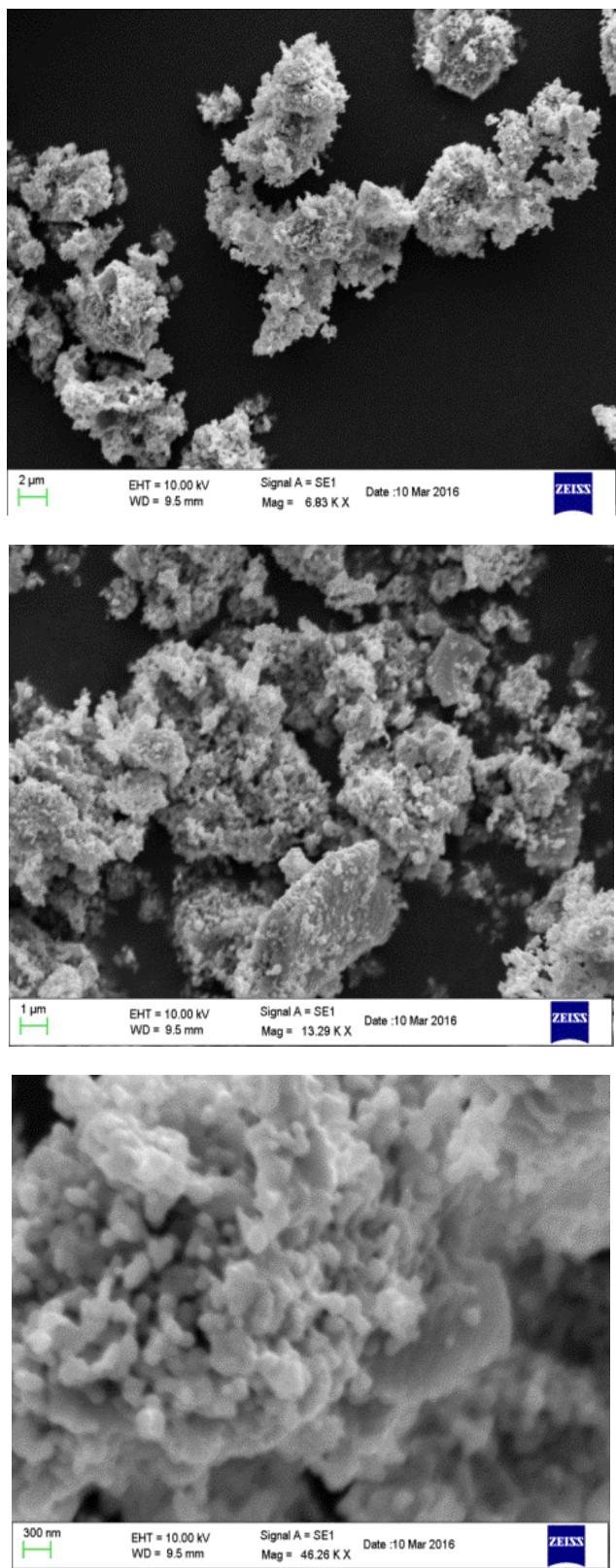


Fig.1. XRD pattern for cubic spinel  $MnFe_2O_4$  nano-particles

### Surface morphological analysis

SEM micrographs of  $MnFe_2O_4$  nanocomposite with different magnifications are shown in Fig. 2. Surface morphology of  $MnFe_2O_4$  mainly consists of nanosized grains (about 300nm diameter) agglomerated in larger grains. It was found that the grains are present individually in the powder also particles are uniformly distributed and surface defects are minimal.

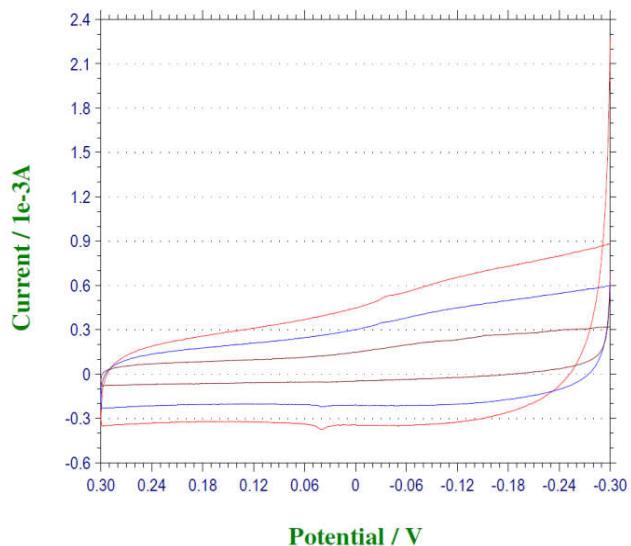


**Fig.2. SEM images showing the morphology of nanocomposite MnFe<sub>2</sub>O<sub>4</sub>**

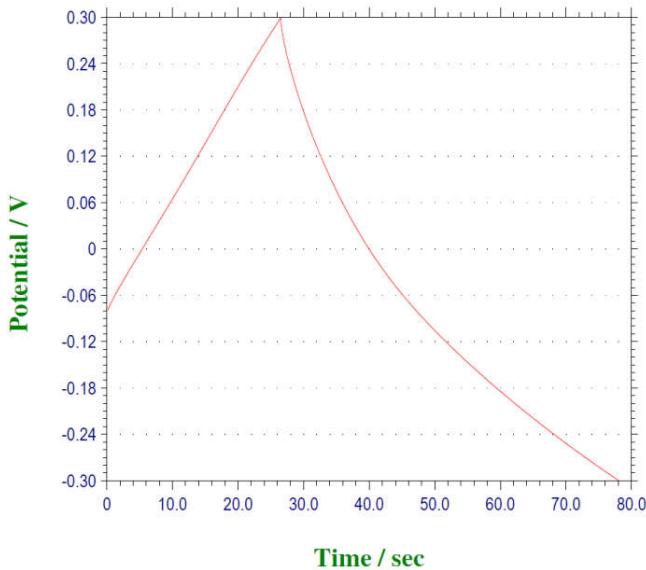
#### Electrochemical analysis

Cyclic Voltammetry (CV) is an electrochemical technique to study the capacitive behaviour of nanomaterials. The cyclic voltammetry (CV) response of the MnFe<sub>2</sub>O<sub>4</sub> electrodes at

different scan rates of 1, 3 and 5 mV s<sup>-1</sup> is as shown in Fig.3. Voltammetry testing was carried out at potentials between -0.3 V and 0.3 V in 1 M KCl aqueous electrolyte solution. The CV curve shows the nearly rectangular shape, expected for an ideal capacitor. Some weak oxidation and reduction peaks are observed in the potential range between 0.04 and -0.04 V versus Ag/AgCl, represents the faradic pseudocapacitive behaviour. The specific capacitance calculated from the CV curves using equation 1. Maximum capacitance obtained was 197 Fg<sup>-1</sup>, at the scan rate of 1 mV s<sup>-1</sup>.



**Fig.3. Cyclic voltammogram of MnFe<sub>2</sub>O<sub>4</sub> electrode at scanrates 1 mVs<sup>-1</sup>, 3 mVs<sup>-1</sup>, 5 mVs<sup>-1</sup>**



**Fig.4. GCD curve of electrode at current 1mA**

It indicates good performance of nanostructured MnFe<sub>2</sub>O<sub>4</sub> electrode (Kuo *et al.*, 2006). The specific capacitance of the nanostructure electrodes decreases with the increase of scan rates. This is because at higher scan rates, there is limited accessibility of ions inside every pore of the electrode, and only the outermost portion of the electrode is utilized for the ion diffusion. However, at a higher scan rate of 5 mV s<sup>-1</sup> the

specific capacitance remains almost 148.4 F g<sup>-1</sup>. Fig.4. shows the galvanostatic charge–discharge behaviour of the composite electrode between 0.3 and 0.3 V at the current of 1 mA. The stability of the active material in 1 M KCl was examined using chrono-potentiometry. The shape of the curve shows the good charge–discharge reversibility. The discharge specific capacitance of 141.8 Fg<sup>-1</sup> is obtained from equation 2, which is approximately same as that obtained from CV curve. This indicates excellent electrochemical capability of  $MnFe_2O_4$  electrode.

## Conclusion

$MnFe_2O_4$  was successfully prepared by using sol-gel method. The XRD pattern of  $MnFe_2O_4$  exhibits cubic spinal structure with an average crystalline size 15 nm. The SEM photographs reveal porous nature of the material. Electrochemical properties of sample were investigated in detail by CV and GCD.  $MnFe_2O_4$  electrode shows maximum specific capacitance of 197 Fg<sup>-1</sup> at the scan rate of 1mVs<sup>-1</sup>. Material also shows better capability rate of charge-discharge. It can be believed that this kind of composites show great potential as an electrochemical supercapacitors.

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