



## Size dependent magnetic and capacitive performance of MnFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles

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### ABSTRACT

MnFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) are prepared by simple chemical oxidation method with optimized experimental conditions. The particle size is reduced by introducing the ferric ions as a size reducing agent during the chemical reaction. The saturation magnetization of the MnFe<sub>2</sub>O<sub>4</sub> MNPs are tuned between 45 and 67 emu/g. The shift in the particle size distribution is confirmed from the transmission electron microscope (TEM) micrograph. The highest specific capacitance of 415 F/g is achieved for the smaller sized MnFe<sub>2</sub>O<sub>4</sub> MNPs prepared with higher concentration of ferric ions. The results suggest that the ferric ions could be used for the size control of ferrites through chemical oxidation method and the sized reduced MnFe<sub>2</sub>O<sub>4</sub> MNPs could be a suitable choice for the electrochemical supercapacitor applications.

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### 1. Introduction

Supercapacitor are bound to be interesting due to their high-power density, simple and low-cost fabrication process compared to batteries [1]. Based on the working mechanism, supercapacitors are classified as pseudo, electric double layer and hybrid capacitor. Among these pseudocapacitors mechanism are widely studied due to the opportunities to evaluate various metal oxides for the suitable selection based on the morphology, valance state of metal ions, surface area [2,3]. However, the low electronic conductivity of metal oxides limiting the utilization as an electrode material which leads to the composites of metal oxides with the addition of good electronic conductivity materials named as hybrid capacitor. The selection of metal oxide compound with a multi valance metal ions within the compound would improve the electronic conductivity through the metal ions [4]. Further the specific capacitance of electrode materials can be improved by developing novel morphology with high surface area or by developing smaller sized particles with higher surface area. Recently ferrite based magnetic

nanoparticles (MNPs) are found to be interesting due to the easy preparation, high theoretical capacitance value, size tuning and chemical stability. Among ferrites, MnFe<sub>2</sub>O<sub>4</sub> is important because of the multivalent metal ions with spinel structure and the chemical preparation process. MnFe<sub>2</sub>O<sub>4</sub> is belongs to inverse spinel ferrites where Mn<sup>2+</sup> and Fe<sup>2+</sup> occupies tetrahedral site and Fe<sup>3+</sup> occupies octahedral sites. The transition between the divalent and trivalent ions in the inverse spinel structure would improve the electronic conductivity during the redox reaction process. Chemical oxidation process is an important and attractive method for the synthesis of MNP due to the opportunity to tune the size by controlling experimental parameters such as reaction temperature, time, fraction of oxidation or reducing agent and addition of nucleating agent [5]. Though the morphology dependent electrochemical characteristics of nanomaterials has been studied [6–8], the size dependent electrochemical properties is not studied much as size of the nanomaterials also playing a major role in the electrochemical characteristics [8].

In this work, the MnFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles sizes were tuned by the addition of ferric ions during the chemical reaction process. The effect of ferric ions on the particle size, magnetic and size dependent electrochemical characteristics of the MnFe<sub>2</sub>O<sub>4</sub> are discussed in detail.

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## 2. Experimental and characterization

MnFe<sub>2</sub>O<sub>4</sub> are prepared by chemical oxidation method [5] with 0.1 M of FeCl<sub>2</sub>·4H<sub>2</sub>O, 0.05 M of MnCl<sub>2</sub>. The solution was stirred with 400 rpm with at 90 °C. Optimized amounts of NaOH and KNO<sub>3</sub> was added and the reaction is kept for 2 h. For size reduction, 10 to 50% molar of ferric ions (FeCl<sub>3</sub>) were introduced during the reaction. Formed particles were washed several times with double distilled water with magnetic separation. The particles were further kept in a heating oven at 80 °C for 10 h. For working electrode, 80 wt% of MnFe<sub>2</sub>O<sub>4</sub>, 10 wt% of acetylene black and 10 wt% of polyvinylidene difluoride (PVDF) were mixed in presence of N-methyl pyrrolidone (NMP). Then the mixture is stirred for uniform mixing and the slurry was pasted onto a Nickel foam and dried at 80 °C. X-ray diffraction (XRD) was done using Bruker D8 X-ray diffractometer equipped with Cu(K<sub>α</sub>) radiation source. Room temperature magnetic properties were analyzed by Vibrating Sample magnetometer (VSM) (Model 7404, Lakeshore, USA) and TEM (FEI Tecnai F20) measurement were done for the morphology analysis. Cyclic voltammogram (CV) and Galvanostatic Charge/Discharge (GCD) experiments were recorded with Biologic (SP-150) electrochemical workstation in a 2 M KOH aqueous electrolyte using a three-electrode system. KCl saturated Ag/AgCl and platinum wire electrode were used as reference and counter electrodes.

## 3. Result and discussion

The single phase of MnFe<sub>2</sub>O<sub>4</sub> was identified for all MNPs as shown in Fig. 1a. The average grain size of the MnFe<sub>2</sub>O<sub>4</sub> prepared without ferric ion concentration was estimated as 26 nm by using

Scherrer's equation. The grain size of MnFe<sub>2</sub>O<sub>4</sub> prepared with ferric ion concentration of 10, 20 and 50% was estimated as 24, 14 and 13 nm. The surface area of the MNPs was estimated by calculating the X-ray density [9] from the XRD output parameters and the estimated surface area are 44, 47, 82 and 87 m<sup>2</sup>/g for the MnFe<sub>2</sub>O<sub>4</sub> prepared without and with 10, 20 and 50% of ferric ion concentration. The soft magnetic nature was observed from the hysteresis loop and the highest saturation magnetization (M<sub>s</sub>) of 67 emu/g was observed for the MnFe<sub>2</sub>O<sub>4</sub> prepared without ferric ion concentration. The M<sub>s</sub> values of 65, 53 and 45 emu/g was observed for the MnFe<sub>2</sub>O<sub>4</sub> prepared with 10, 20 and 50% of ferric ion concentrations as shown in Fig. 1b. MnFe<sub>2</sub>O<sub>4</sub> prepared without ferric ion concentration showed a coercivity (H<sub>c</sub>) of 90 Oe and the reduced coercivity of 70, 42 and 17 Oe was observed for the MnFe<sub>2</sub>O<sub>4</sub> prepared with 10, 20 and 50% of ferric ion concentration. Very less coercivity value indicates that the particles are in superparamagnetic regime. The reduction in the M<sub>s</sub> and H<sub>c</sub> are due to the particles size reduction achieved with the ferric ions. All the samples showed a spherical morphology with the particles size ranges from 30 to 75 nm for the MNPs prepared without ferric ions and the particle size range decreased to lower region of 10 to 25 nm when we used 50% ferric ions. By using log-normal fit, the average particle size was estimated as 50 and 14 nm for the MnFe<sub>2</sub>O<sub>4</sub> prepared without and with 50% ferric ions. Spherical shape and interlayer atomic fringes of the MNPs are clearly seen from Fig. 1c.

Further, to evaluate the size dependent electrochemical characteristics of the MnFe<sub>2</sub>O<sub>4</sub>, two separate working electrodes were prepared with 50 and 14 nm MnFe<sub>2</sub>O<sub>4</sub> and the electrochemical experiments were done. The increase in the integrated area of the CV curves with increasing scan rate is observed as shown in

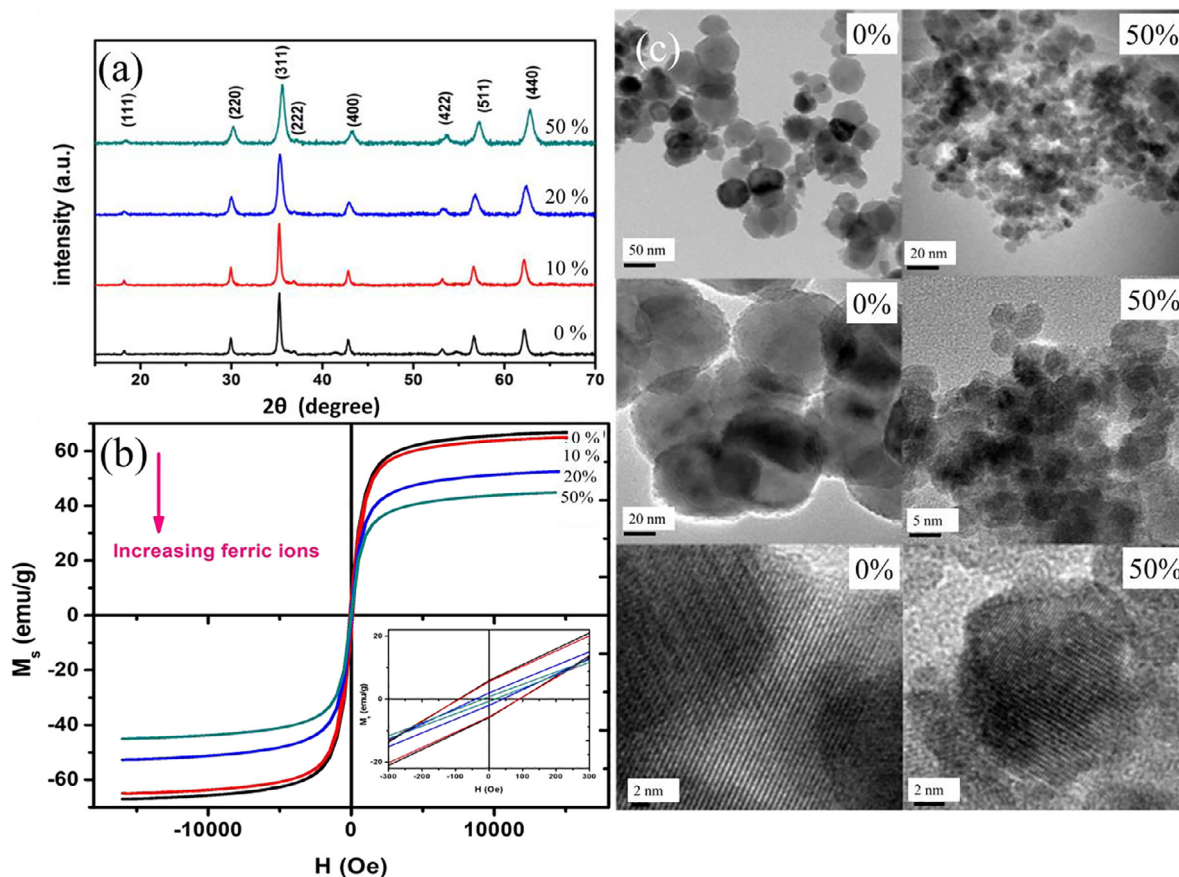
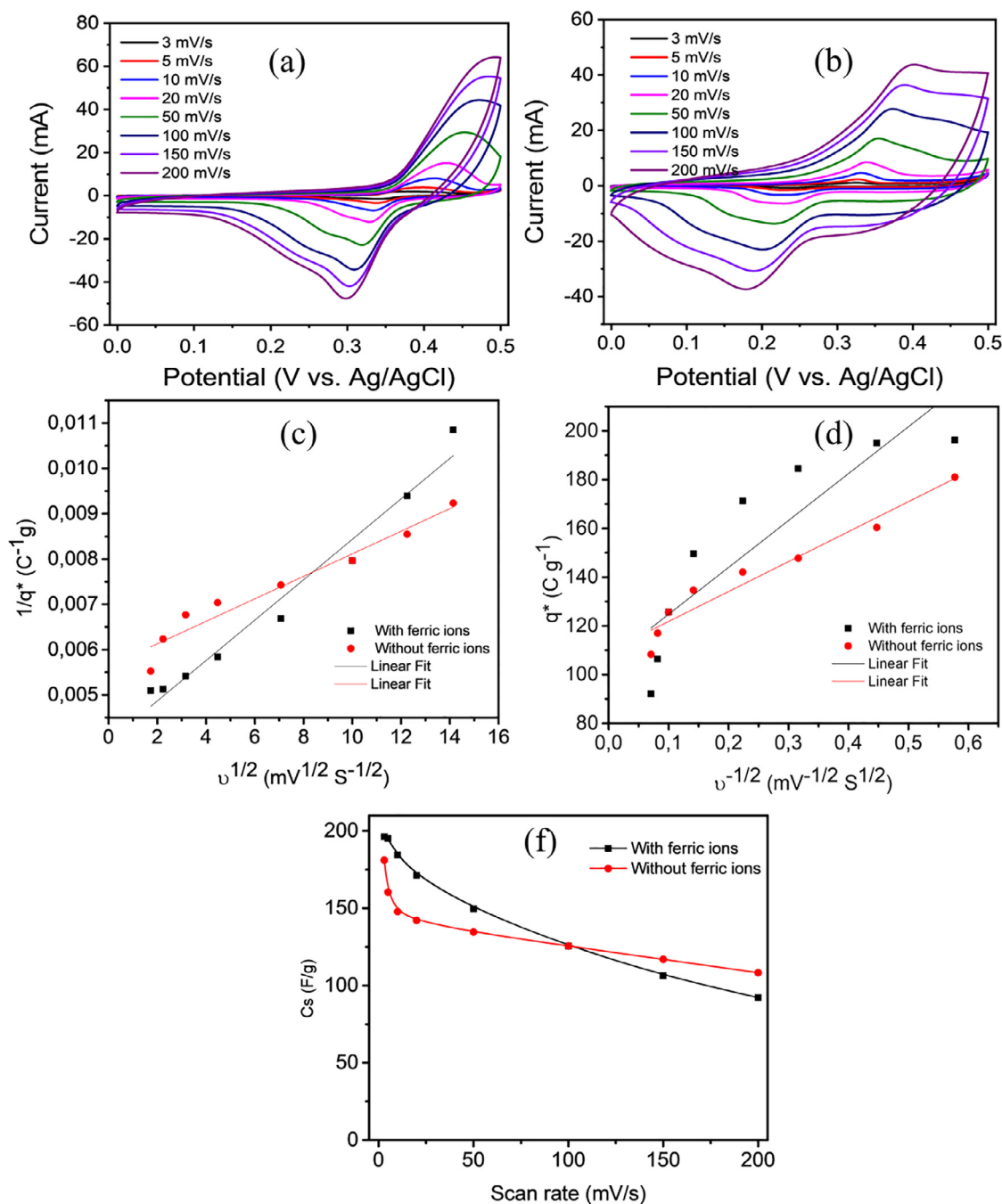


Fig. 1. (a) XRD pattern (b) VSM hysteresis loop and (c) TEM Micrograph of MnFe<sub>2</sub>O<sub>4</sub> with and without ferric ions.



**Fig. 2.** (a-b) Cyclic voltammogram, (b-c) Transatti plot and (d) Specific capacitance vs. scan rate for MnFe<sub>2</sub>O<sub>4</sub> prepared with and without ferric ions.

Fig. 2(a & b) which indicates that the higher capacitive current density of the electrode material. The presence of multivalent metal ion in MnFe<sub>2</sub>O<sub>4</sub> electrode material is the advantageous for the fast pseudocapacitance redox reactions during the electrochemical reactions between the Fe<sup>3+</sup>/Fe<sup>2+</sup> or Mn<sup>2+</sup>/Mn<sup>3+</sup>. The electronic conductivity of the electrode will be high for these kind of multivalent metal oxides due to divalent and trivalent metal ions present with the spinel structure.

The amount of total charge, charge stored in inner surface and outer surface of the MnFe<sub>2</sub>O<sub>4</sub> are estimated from the Transatti plot analysis of  $1/q^*$  vs  $v^{-1/2}$  and  $q^*$  vs  $v^{-1/2}$  for 50 nm and 14 nm particles as shown in Fig. 2 (c & d). The 50 nm MnFe<sub>2</sub>O<sub>4</sub> electrode showed a maximum charge stored in inner surface compared to the charge stored in outer surface. In contrast, the 14 nm particles

showed the maximum charge contribution is from the outer surface than the charge stored in inner surface of the electrode materials. As the surface area of the 14 nm particles are high compared to 50 nm particles, it will be advantageous to have the maximum charge contribution from the outer surface for the smaller sized MnFe<sub>2</sub>O<sub>4</sub>.

The highest specific capacitance ( $C_s$ ) of 196 F/g was observed for 14 nm particles and it decreased with increasing scan rate, reaches 92 F/g with higher scan rate of 200 mV/s as shown in Fig. 2e. Whereas the 50 nm particles showed the highest  $C_s$  value of 185 F/g and showed the same decreasing trend. The decreasing  $C_s$  value with increasing scan rate is due to the restriction of charge transfer kinetics between the electrode and electrolyte interface and the internal resistance.

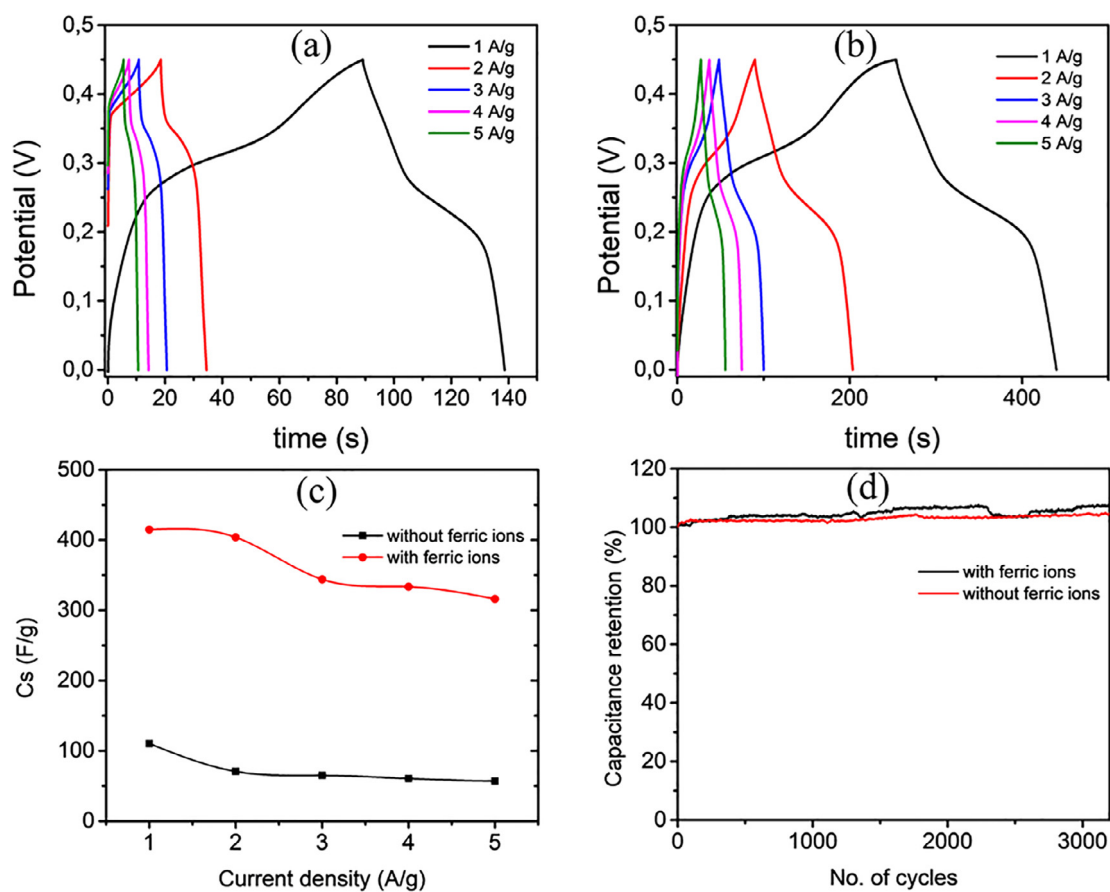


Fig. 3. (a-b) GCD curved, (c) Specific Capacitance vs. Current density and (d) cyclic stability plot of  $\text{MnFe}_2\text{O}_4$  prepared with and without ferric ions.

In GCD, the symmetric shape in charge/ discharge time is observed with a small IR drop at the initial stages of discharge time as shown in Fig. 3a and the IR drop is due to the resistance between the electrode materials and the electrolyte. The maximum Cs of 110 F/g was estimated for the  $\text{MnFe}_2\text{O}_4$  prepared without ferric ions and the particles prepared with ferric ions showed the highest Cs of 415 F/g. The estimated Cs are decreasing with increasing current density, which is due to the internal resistance and the limitation of active electrode material involved in the redox reactions. The capacity retention of the  $\text{MnFe}_2\text{O}_4$  electrodes were analyzed by cyclic stability experiments up to 3000 cycles at 5 A/g. The cyclic stability was observed as 104 and 106% for the  $\text{MnFe}_2\text{O}_4$  prepared without and with ferric ions.

#### 4. Conclusion

$\text{MnFe}_2\text{O}_4$  were prepared by simple chemical oxidation method and different amounts of ferric ions were used to tune the particles sizes from 50 to 14 nm. The reduction in the particles size was confirmed from TEM and the Ms values were tuned between 45 and 67 emu/g. The maximum Cs of 415 F/g was achieved for the 14 nm particles. The observed results suggesting that ferric ions could be used for the size reduction of  $\text{MnFe}_2\text{O}_4$  and the electrochemical characteristics of the  $\text{MnFe}_2\text{O}_4$  suggesting that it could be suitable candidate for the electrochemical supercapacitor applications.

#### CRedit authorship contribution statement

**Arun Thirumurugan:** Conceptualization, Methodology, Investigation, Writing - original draft. **T. Kavin Kumar:** Resources, Inves-

tigation. **R. Udayabhaskar:** Resources. **Mauricio J. Morel:** Resources. **G. Rajesh:** Resources. **R.V. Mangalaraja:** Resources. **Ali Akbari-Fakhrabadi:** Conceptualization, Resources.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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