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MnFe$_2$O$_4$: Synthesis, Morphology and Electrochemical Properties

Shrikant Kulkarni, Balu Thombare and Shankar Patil$^{(a)}$

$^{1}$Department of Physics, Savitribai Phule Pune University, Ganeshkhind road, Pune 411007, Maharashtra, INDIA
$^{(a)}$Corresponding author: patil@physics.unipune.ac.in

Abstract. MnFe$_2$O$_4$ has been synthesized by simple ammonia assisted co-precipitation method to obtain nanocrystalline powder. X-ray diffraction studies confirmed its crystallinity and phase purity. The MnFe$_2$O$_4$ calcined at 1000°C for 4 h has spinel crystal structure with Fd3m space group and lattice constant 8.511 Å. The electrode was prepared by dip coating method on stainless steel substrate and fired at 600°C for 2 h. Random shape grains of 0.2 to 1.5 micron with pores of 1-2 micron dimensions were observed in SEM images. The electrochemical studies of MnFe$_2$O$_4$ were carried out with 1 mole Na$_2$SO$_4$ electrolyte. The MnFe$_2$O$_4$ electrode shows highest specific capacitance of 27.53 F.g$^{-1}$ and interfacial capacitance of 0.83 F.cm$^{-2}$.

INTRODUCTION

Binary transition metal ferrites with spinel crystal structure and general molecular formula of AB$_2$O$_4$ have been reported for electrochemical supercapacitor applications due to their electrochemical performance. These materials offer robust crystalline structure with three-dimensional possibilities of electron diffusion pathways (Wang Zhang, 2015). Several spinel compounds including Fe$_3$O$_4$, MnFe$_2$O$_4$, NiCo$_2$O$_4$, CoFe$_2$O$_4$ etc. have been considered as potential candidate for electrochemical capacitors. The capacitance values are found in order of MnFe$_2$O$_4$ > CoFe$_2$O$_4$ > Fe$_3$O$_4$, NiFe$_2$O$_4$ etc. (Shin-Liang Kuo, 2007). MnFe$_2$O$_4$ shows specific capacitances of >100 F.g$^{-1}$ and high power densities >10 kW.kg$^{-1}$ in aqueous solutions of alkali/alkaline chlorides and sulfates. Along with these electrochemical properties, MnFe$_2$O$_4$ has very stable structural, electrical and chemical properties in harsh redox environment (Jun Wang, 2004). Therefore, this material attracts lot of attention across the globe.

EXPERIMENTAL

In the present work, MnFe$_2$O$_4$ synthesized using simple ammonia assisted co-precipitation method. Manganese chloride (MnCl$_2$.4H$_2$O; Sigma Aldrich, 99.9% trace metal basis) and ferrous chloride (FeCl$_2$.4H$_2$O; Sigma Aldrich, 99.9% trace metal basis) were taken as raw materials. These chlorides with appropriate molarity were dissolved in Double Distilled Water (DDW; Millipore Elix 3) and stirred for 1 h. The liquor ammonia (NH$_4$OH; Merck 30% GR content) was added to precursor dropwise under continuous stirring till gray colored precipitate formed. This precipitate filtered and washed by DDW repeatedly until filtered water showed neutral pH. Obtained precipitate washed thrice by Ethanol (C$_2$H$_5$OH; Merck make) and dried under IR lamp. Dried precipitate powder was calcined at 1000°C for 4 h and characterized by XRD for crystallinity and phase purity. The electrode was prepared using dip coating technique, in which stainless steel substrate was dipped into paste of MnFe$_2$O$_4$. The paste was prepared using a mixture of Ethyl cellulose (Merck make), $\beta$-terpineol (Merck make), Corn oil (Aldrich make), Amyl acetate (Merck make) and ethanol (Merck make). These organics were mixed together with MnFe$_2$O$_4$ to form a paste. The oxide to organic ratio was kept at 30:70. The viscosity of the paste was adjusted to 60 Poise by adding ethanol and amyl acetate. Substrate was dipped in this paste and revolved at 10 rpm for 30 mins and then took out, dried under hot air shower and fired at 600°C for 2 h. Fired thick film was characterized by SEM (JEOL JSM-6360A) for morphological studied. Cyclic voltammetry studies of this electrode ware carried out using AUTOLAB PGSTAT.
100 potentiostat- galvonostat using 1 mole Na₂SO₄ as electrolyte in the potential range of -0.1 to +0.9 V. The effect of potential scan rate on charge storage properties was studied in the range of 5 mV.s⁻¹ - 100 mV.s⁻¹.

RESULT AND DISCUSSION

As synthesized and calcined powders of MnFe₂O₄ are blackish brown and black in color respectively. The XRD pattern of the powder is presented in Fig. 1 (a) shows MnFe₂O₄ crystallized in cubic spinel crystal structure as all peaks matches well with JCPDS card no. 01-074-2403 corresponding to Jakobsite mineral of MnFe₂O₄. Crystallized manganese ferrite has Fd3m space group with lattice parameters 8.511 Å and all lattice angles 90°. In this spinel structure, oxygen ions are symmetrically located around tetrahedral and octahedral sites occupied by Mn²⁺ and Fe³⁺ ions respectively (X. Zuo, 2004).

![XRD pattern of MnFe₂O₄](image)

![SEM image](image)

![Optical photograph](image)

**FIGURE 1**: (a) XRD pattern of MnFe₂O₄ after calcination at 1000°C for 4 h. (b) SEM image of thick film on stainless steel substrate magnified at 5 kx (c) optical photograph of the thick film surface

Fig. 1 (b) presents SEM images of the thick film taken at 5kx magnification. SEM image shows grains of different shapes and sizes distributed all over the substrate. The grain size was varied from 0.2 to 1.5 microns. Due to irregular grain shapes, lots of voids having dimensions 0.2 to 2 microns are observed between these grains. Overall the surface of the film is porous and very useful for penetration of liquid electrolyte through the voids. The optical photograph of film surface presented in Fig. 1 (c) also confirmed larger voids and promising porous structure of the thick film surface.

Fig. 2 (a) presents cyclic voltammetry studies of the MnFe₂O₄ electrode measured in 1 mole Na₂SO₄ as aqueous electrolyte in the potential range of -0.1 to 0.9 V.

![Cyclic voltammetry](image)

**FIGURE 2**: (a) Cyclic voltammetry studies of MnFe₂O₄ electrode by varying potential scan rate; (b) Effect of potential scan rate on specific capacitance and interfacial capacitance (c) Charge discharge characteristics of MnFe₂O₄ electrode

Cyclic voltammetry studies shows area under the curve increased with scan rate. Broad redox peaks of C-V curves during charging and discharging suggested pseudocapacitive behavior of the electrode governed by faradic redox reaction (R. K. Gupta, 2015), (Jun Yan, 2012). Fig. 2 (b) shows both specific and interfacial capacitance values are decreasing with increase in potential scan rates. This is quite obvious as during lower scan rates, due to slower faradic reactions, more active sites from inner surface of electrode will contributed for charge storage (Vijaykumar V. Jadhav, 2016). The highest specific capacitance of 27.53 F.g⁻¹ and interfacial capacitance of 0.83 F.cm⁻¹.
F. cm\(^{-2}\) were observed at lowest measured scan rate of 5 mV. sec\(^{-1}\). The energy density and power density calculated from highest specific capacitance is 3.82 Wh.kg\(^{-1}\) and 55.06 W.kg\(^{-1}\) respectively. Charge-discharge characteristics of electrode show charging time of 200 seconds and discharging time of 250 seconds. Therefore, coulomb efficiency calculated is 125%. The obtained values of specific capacitance, interfacial capacitance, energy density, power density and coulomb efficiency values with respect to potential scan rate are calculated and presented in Table 1.

**TABLE 1:** Specific capacitance, interfacial capacitance, energy density, power density and coulomb efficiency calculated for MnFe\(_2\)O\(_4\) electrodes with respect to potential scan rate

<table>
<thead>
<tr>
<th>Potential scan rate (mV.s(^{-1}))</th>
<th>Specific capacitance (F.g(^{-1}))</th>
<th>Interfacial capacitance (F.cm(^{-2}))</th>
<th>Energy density (Wh.kg(^{-1}))</th>
<th>Power density (W.kg(^{-1}))</th>
<th>Coulomb efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>27.53</td>
<td>0.83</td>
<td>3.82</td>
<td>55.07</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>11.60</td>
<td>0.35</td>
<td>1.61</td>
<td>23.20</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.59</td>
<td>0.20</td>
<td>0.91</td>
<td>13.17</td>
<td>125</td>
</tr>
<tr>
<td>50</td>
<td>4.25</td>
<td>0.13</td>
<td>0.59</td>
<td>8.51</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>3.31</td>
<td>0.10</td>
<td>0.13</td>
<td>1.84</td>
<td></td>
</tr>
</tbody>
</table>

To summaries, study shows interfacial capacitance and power density values of MnFe\(_2\)O\(_4\) electrode are promising and comparable with the literature. However, lower values of specific capacitance may be result of surface adsorption charge storage mechanism due to larger grain sizes and intrinsically poor electronic conductivity of the electrode (H. Xi, 2012). The specific capacitance can be improved by enhancing specific surface area (SSA) and optimizing electrical conductivity. These two properties are depends upon grain size. Smaller the grain size more the specific surface area, on the contrary, larger the grain size higher the electrical conductivity. Therefore, grain sizes of the electrode material need to be controlled, such that, both of these properties can be tailored for optimum properties.

**CONCLUSIONS**

MnFe\(_2\)O\(_4\) is one of the promising materials for supercapacitor applications. It has been successfully synthesized by co-precipitation method. XRD studies show MnFe\(_2\)O\(_4\) has cubic spinel crystal structure. The electrode was prepared by dip coating technique on stainless steel substrate shows porous microstructure of the film. Cyclic voltammetry studies shows increase in scan rate increases area under the curve, however, the specific and interfacial capacitances decreased rapidly with increase in scan rate. Maximum specific capacitance of 27.53 F.g\(^{-1}\) and interfacial capacitance of 0.83 F.cm\(^{-2}\) was obtained at 5 mV.s\(^{-1}\) potential scan rate. The interfacial capacitance values are comparable with literature, however, specific capacitance values need to be improved by controlling grain size of electrode material such that both specific surface area and electrical conductivity properties get optimized.

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