Journal of Analytical and Applied Pyrolysis 122 (2016) 224–229

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Structural, morphological and electrochemical supercapacitive properties of sprayed manganese ferrite thin film electrode

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ARTICLE INFO

Article history:
Received 31 October 2015
Accepted 23 September 2016
Available online 25 September 2016

Keywords:
Electrochemical supercapacitor
Spray pyrolysis
Spinel ferrite

ABSTRACT

In this work, the structural and, morphological properties and electrochemical supercapacitor electrode application of manganese ferrite ($MnFe_2O_4$) thin films deposited onto glass and stainless-steel substrates using chemical spray method are explored. For confirming the spinel structure and nodule-type morphology of obtained $MnFe_2O_4$ film X-ray diffraction pattern and scanning electron microscopy measurements are used. The Fourier transform infrared spectroscopy spectrum reveals presence of tetrahedral and octahedral peaks. The specific capacitance values, obtained using cyclic-voltammetry plots of as-deposited ferrite electrode in 1 M KOH, NaOH, Na_2SO_3, Na_2SO_4 aqueous solutions at scan rate of 5 mV s^{-1} are respectively 313, 295, 146.02, 180.51 F g^{-1}. The electrochemical impedance spectrum supports for pseudocapacitance behavior in as-deposited $MnFe_2O_4$ film electrode.

1. Introduction

Since decade, because of novel magnetic properties with reduced dimensions, a myriad of research activities in synthesis and characterization of ferrite nanostructures have been undertaken as far as materials science and engineering technology concern, [1,2]. Spinel ferrite (MFe_2O_4 where 'M' is transition metal) nanostructures have been widely explored in literature for various applications including high-density magnetic recording [3,4], ferro-fluid technology [5], biomedical drug delivery [6], and magnetic resonance imaging [7] etc. In manganese ferrite ($MnFe_2O_4$) O^{2-} cations form cubic structure i.e. Mn^{2+} and Fe^{3+} are in two crystallographic positions.[10] Alternatively, spinel ferrite can also be written in $(A^{II+})[B_2{}^{III+}]O_4{}^{II-}$ form, where A^{II+} and B^{III+} are divalent and trivalent cations. They generally occupy tetrahedral (A) and octahedral [B] sites.When divalent cations occupy tetrahedral (A) sites it is considered as normal spinel structure while when they occupy octahedral [B] sites, an inverse spinel structure is dominant. In the normal spinel structure, the bivalent ions (Mn^{2+} in $MnFe_2O_4$) are at the tetrahedral positions and the trivalent ions (Fe^{3+} in $MnFe_2O_4$) are at octahedral positions whereas in inverse spinel structure, bivalent ions are at halfway of the B positions, and trivalent ions are in the rest of the B positions. Ferrite with mixed spinel phase can be obtained at high temperatures (>900 °C) where 20% of the Mn^{2+} ions migrate from A to B positions [8]. Electrochemical supercapacitors (ES), generally used in portable and flexible electronic devices [9–11], have achieved a nodal and considerable market share in the energy storage research field. Depending upon the charge storage kinetics, they are classified as electric double layer capacitors (EDLC) and pseudocapacitors. The pseudocapacitive materials include ruthenium oxide [12–14], copper (II) oxide [15–17], manganese dioxide [18–20], cobalt oxide [21–23] and vanadium pentoxide [24–27] etc., which not only have demonstrated remarkable specific capacitance (SC) values but also have a strong mechanical robustness against various environmental conditions, when used in ES application. Electrodes with MnO_2 nanostructures have achieved as high as 678 F g^{-1} SC at 0.5 A g^{-1} in 0.5 M Na_2SO_4 electrolyte [28]. However, due to their poor chemical stability, nearly 20% capacitance loss after 2000 cycles [18,28] is observed, thereby are not useful in durable SC devices as electrode materials. For example, decrease of the capacitance in MnO_2 electrode can be ascribed to the mechanical swelling effect during

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http://dx.doi.org/10.1016/j.jaap.2016.09.020
0165-2370/

the charge/discharge process. Notably, $MnFe_2O_4$ exhibits expected large SC value among MFe_2O_4 ferrites where, M = Mn, Fe, Co, or Ni and remarkable cycling stability [29,30]. The nanoparticles (NPs) of $MnFe_2O_4$ can be prepared by several physical and chemical methods such as ball-milling [31–33], co-precipitation [34–37], reverse micelle synthesis [38], pulsed laser deposition [39], solid-phase reactions [40], thermal decomposition [41], sol-gel [42,43], microwave-induced combustion [44], combustion [45], microwave hydrothermal [46], mechanochemical [47], and hydrothermal [48] etc. In most of the reported synthesis methods, product is in the form of powder where making films of it is a really difficult task. Film of obtained NPs powder can be made by using a Doctor-blade process where additional experimental steps and chemicals are essential. Moreover, obtained films are relatively thick which have limited scope in ES application as higher electrode mass produces lower SC, which is one of the major parameters of ES devices, when performance is taken into account. Thereby, obtained film electrode should be as thin as possible for potential SC application. In present work, a simple and cost effective chemical spray pyrolysis method is used to obtain $MnFe_2O_4$ thin films directly onto glass and stainless-steel (SS) substrates. Films on glass substrate are used for structural, morphological and phase purity confirmations where as those on SS are applied in electrochemical measurement studies.

2. Experimental details

The glass and SS substrates were used to deposit $MnFe_2O_4$ films. The pieces of SS substrate were scrubbed initially by sand paper for removing oily layer, kept in ultrasonication for 30 min and were transferred in acetone prior to deposition process. The Mn and Fe nitrate salts of chemical formulae $Mn(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were used for depositing $MnFe_2O_4$. To obtain $MnFe_2O_4$ phase 1:2 ratio of Mn^{+2} and Fe^{+3} was preferred. The equal volume solutions of 0.5 M manganese nitrate and 1 M iron nitrate were mixed and resultant solution was used for spraying. Solution of 5 ml was sprayed initially during one time through a glass-nozzle. The substrate-to-nozzle distance was 25 cm. The temperature of substrate was 400 °C and the air-flow rate was 15 lit./min. During the spraying process, the chamber was closed and toxic and hazardous gaseous/fumes produced as byproducts (generated during the chemical reactions) were thrown off by an exhaust which otherwise could be dangerous to a person working in the immediate vicinity. After spray process these films were taken out once temperature was close to room i.e. 25 °C to avoid cracking effect. As discussed earlier, films on glass substrate were used for structural elucidation and morphology evolution studies and those on SS were applied for electrochemical measurements. The electrochemical properties of synthesized $MnFe_2O_4$ films on SS were measured by cyclic-voltammetry (CV) plots. For CV plots three-electrode system; counter (platinum (Pt) foil of $1 \times 1\ cm^2$), reference (Ag/AgCl), and working i.e. $1 \times 1\ cm^2$ $MnFe_2O_4$ film electrode was considered. The back side of substrate was covered with adherent polymer tape so as to avoid direct contact of electrode with electrolyte solution. The WPG100 Won-A-Tech electrochemical analyzer was used for electrochemical analysis having single channel facility and high accuracy of measurement. As-synthesized $MnFe_2O_4$ electrode was used as working electrode in electrochemical impedance spectroscopy (EIS) measurement on Ivium-*n*-Stat electrochemical workstation (Ivium, Netherlands). EIS spectra of $MnFe_2O_4$ in different electrolytes were obtained in the frequency range of 100 kHz–0.01 Hz with AC voltage amplitude of 5 mV where the distance between the working electrode and counter electrode was maintained as ~1 cm.

3. Results and discussion

3.1. Structure, elemental proportion and morphology analyses

The structural elucidation of the synthesized $MnFe_2O_4$ films (on glass substrate) was carried out using X-ray diffraction (XRD) technique. The XRD spectrum was recorded with Reguka-D/MAX 2500 X-ray diffractometer operating X-ray tube voltage 20–80 kV, with

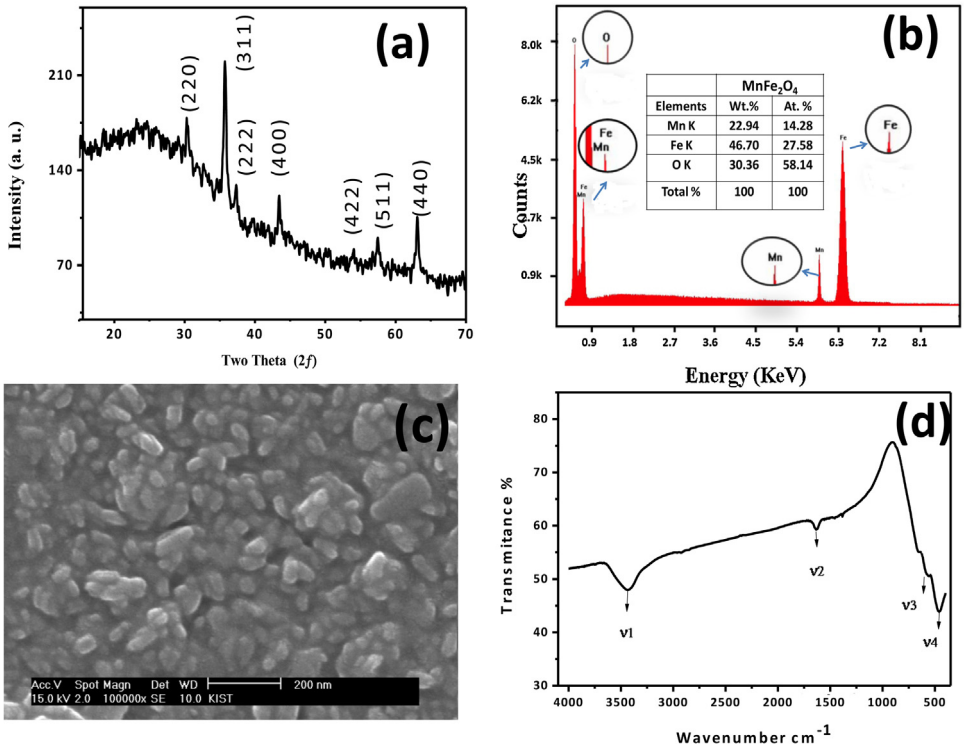

Fig. 1. (a) XRD (2f as deg.), (b) EDAX, (c) FESEM, (d) FT-IR measurements of $MnFe_2O_4$ film deposited on glass substrate.