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Synthesis and electrochemical supercapacitive performance of nickel–manganese ferrite composite films

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ABSTRACT

Thin films of sprayed nickel–manganese ferrite i.e. $Ni_xMn_{1-x}Fe_2O_4$ (x = 0.2, 0.4, 0.6, 0.8) were synthesized onto stainless-steel substrate and envisaged for electrochemical supercapacitor application where surface morphology was influenced by 'x' factor; confirmed from the scanning electron microscopy digital photo-images and energy dispersive X-ray analysis, respectively. The spinel-type rice-like crystallites of $Ni_xMn_{1-x}Fe_2O_4$ were 70–80 nm in lengths and 20–30 nm in diameters. Cyclic-voltammograms of $Ni_xMn_{1-x}Fe_2O$ obtained for different 'x' values i.e. morphologies, were used to figure-out the change of the specific capacitance (SC) for different scan rates in 1 M KOH electrolyte. The 147, 120, 131, 185 F g^{-1} SC values for 0.2, 0.4, 0.6, 0.8 'x' values were obtained at 5 mV s^{-1} scan rate. Electrochemical impedance spectroscopy measurements of $Ni_xMn_{1-x}Fe_2O_4$ film electrodes were performed for knowing the charge transport kinetics where composite i.e. 0.4 and 0.6 'x' valued electrodes confirmed least performance than 0.2 and 0.8 'x' values which could be attributed to availability of number of the surface charges.

1. Introduction

Thin film electrochemical supercapacitor represents the intermediate next generation energy storage device which is considered for high rate of charging/discharging, high power density and excellent chemical and environmental stabilities enabling its versatile use in electrochemical devices including electrical vehicles, power backup etc. [1]. Metal oxides are considered to be promising materials for electrochemical supercapacitors (ES). Among various metal oxide materials reported so far ruthenium oxide (RuO_2) is a major candidate for ES with a moderate value of specific capacitance (SC, 720 F/g) [2]. However, its high-cost and toxicity has made it difficult to find a commercial potential. Hence, alternative inorganic electrode materials including manganese oxide [3], cobalt oxide [4], copper oxide [5], nickel oxide [6] vanadium oxide [7], tungsten oxide [8], iron oxide [9] etc., have intensively been investigated, owing to their readily availability, chemically stableness, mechanically robustness, safe, environmental friendlineness, and remarkably high performances in SC application [10–12]. The SC value of metal oxide can be enhanced, in general, by doping carbon nanotubes, graphene, polymers [13] etc., and in particular, mixing metal oxides of high catalytic activities [14]. The transition metal oxides are good electrode materials for ES application due their higher capacitance and fast redox reaction rate [15]. The iron oxide can react with divalent transition metal oxides MO (M-metal) to form spinel ferrite (MFe_2O_4). Spinel transition metal oxides (AB_2O_4) with two metal elements provide the feasibility to tune the energy density and working voltage by varying the metal content [16,17]. Ferrites such as $MnFe_2O_4$ and $CoFe_2O_4$ have already been corroborated good ES properties [18]. The different chemical methods like solvothermal [18], spray pyrolysis [19], reverse micelle technique [20], solid-state reac-

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Table 1
Volumetric compositions of Ni, Mn and Fe used for $Ni_xMn_{1-x}Fe_2O_4$ films.

Composition	0.5 M Ni $(NO_3)_2$	0.5 M Mn $(NO_3)_2$	1 M Fe $(NO_3)_3$
$Ni_{0.2}Mn_{0.8}Fe_2O_4$	2 ml	8 ml	10 ml
$Ni_{0.4}Mn_{0.6}Fe_2O_4$	4 ml	6 ml	10 ml
$Ni_{0.6}Mn_{0.4}Fe_2O_4$	6 ml	4 ml	10 ml
$Ni_{0.8}Mn_{0.2}Fe_2O_4$	8 ml	2 ml	10 ml

tion [21], method co-precipitation [22], sol–gel technique [23], hydrothermal [24], aerosolization [25], microwave hydrothermal [26], ultrasonic–hydrothermal [27], sonochemistry [28] and ball milling [29,30], etc., are being addressed for fabricating ferrite materials either in powder or directly in thin/thick film categories. Moreover, reports on their direct chemical synthesis and potential ES application with in depth electrochemical properties understanding based on mixed ferrite films by spray pyrolysis are not adequate [31].

In this paper, synthesis of nickel–manganese ferrite i.e. $Ni_xMn_{1-x}Fe_2O_4$ for 0.2, 0.4, 0.6, 0.8 '*x*' values onto stainless-steel (SS) substrate by spray-pyrolysis method has been addressed. These films were air-annealed at 773 K for 5 h (as for higher temperature/time annealing performance was decreased due to compact structure formation) and envisaged in ES application using optimized electrolyte.

2. Experimental details

The SS plates of equal dimensions were used for depositing the composite ferrite films. Initially, SS substrates were etched by sand paper for removing the oxide or un-exfoliated compound on the surface and then kept for ultrasonic cleaning in 0.1 M HCl to remove loosely bounded impurities for 30 min. After this substrates were transferred in acetone before deposition. $Ni(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were used as Ni, Mn and Fe sources, respectively. To obtain the spinel phase of $Ni_xMn_{1-x}Fe_2O_4$, the concentration ratio of Ni^{+2}, Mn^{+2} and Fe^{+3} was monitored to 1:2 (x:1–x:2x) i.e. the value of $x + 1 - x$ always equal to one and concentration Fe^{+3} should twice the addition of Ni^{+2}, Mn^{+2} cations. If $x = 0.2$ then the ratio of Ni^{+2}, Mn^{+2} and Fe^{+3} would be 0.2:0.8:2, respectively and similarly other values of x can be considered the same. Therefore, 0.5 M nickel nitrate, 0.5 M manganese nitrate and 1 M iron nitrate were mixed in appropriate volumetric proportions (Table 1) and used while spraying.

The 5 ml solution of each composition was sprayed through a glass-nozzle on SS substrate. The substrate-to-nozzle distance was 25 cm. The temperature of substrate (hot plate) was 400 °C. The air-flow rate was maintained to 15 l/min to maintain uniform droplet formation. Then these films were annealed for 5 h at 500 °C to remove the nitrate impurities if there is any and to increase the crystallinity. The obtained films were well-adherent and compact to substrate. The mechanism of $Ni_xMn_{1-x}Fe_2O_4$ formation was explained on the basis of initial reactant and final product [32]. Details of spray unit used are schematized in Fig. 1.

After synthesis, the films were characterized for their structures and morphologies by mean of X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements. The elemental compositions were identified, on individual surface, using energy dispersive X-ray analysis (EDAX). The Fourier transform spectroscopy (FTIR) spectra were used to find the presence of metal oxide peaks. The electrochemical performances were measured with the help of electrochemical work station (WPG 100 Won A tech) using three electrodes system. The SC values were obtained from cyclic-voltammetry (CV) and constant current charge–discharge spectra separately. Furthermore, the

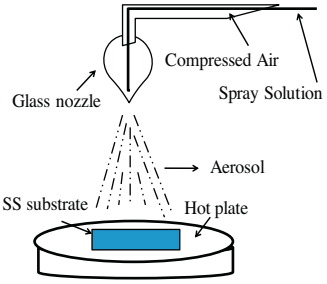

Fig. 1. Schematic diagram for spray pyrolysis setup used for preparing ferrite film electrodes.

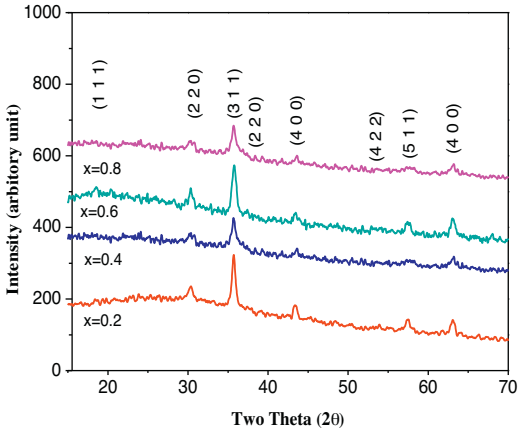

Fig. 2. XRD patterns of sprayed $Ni_xMn_{1-x}Fe_2O_4$ films for different '*x*' values.

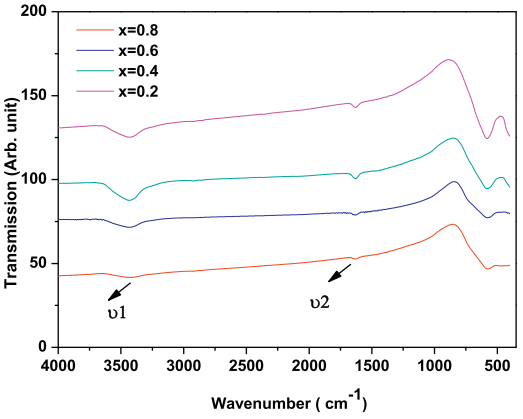

Fig. 3. FTIR spectra of sprayed $Ni_xMn_{1-x}Fe_2O_4$ film electrodes as a function of '*x*'.

electrochemical impedance spectroscopy (EIS) measurement was conducted for knowing the psuedocapacitive behavior of electrode.

3. Results and discussion

3.1. Structural analysis

The structural identification of $Ni_xMn_{1-x}Fe_2O_4$ films was carried out using XRD patterns. The XRD spectra were recorded with Reguka-D/MAX 2500 X-ray diffractometer operating X-ray tube voltage 20–80 kV, with auto-divergent slit and scanning speed of 5° min^{-1}. The Cu-Kα line was used as monochromatic source having wavelength 1.54 Å obtained from Cu target. The Fig. 2 shows the XRD spectra of $Ni_xMn_{1-x}Fe_2O_4$ thin films prepared by spray pyrolysis method. It is worth to mention here is that powders of these ferrite films were scratched using fine blade and were used