Measurement 88 (2016) 66–76

Contents lists available at ScienceDirect

Measurement

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

Spray pyrolysed Mn:Co_3O_4 thin film electrodes via non-aqueous route and their electrochemical parameter measurements

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ARTICLE INFO

Article history:
Received 12 May 2014
Received in revised form 2 December 2014
Accepted 29 February 2016
Available online 16 March 2016

Keywords:
Manganese oxide
Cobalt oxide
Thin films
Spray pyrolysis
Supercapacitor

ABSTRACT

Present work explains the preparation of manganese incorporated cobalt oxide thin film electrodes on stainless steel by spray pyrolysis technique, via non-aqueous (methanolic) media. Structural, morphological and electrochemical characterizations of the prepared samples were made by means of XRD, SEM and electrochemical measurements. Structural elucidation confirms Co_3O_4 has face centred cubic and Mn_3O_4 has tetragonal body centred cubic structure with polycrystalline nature. Surface morphological observation shows the continuous semi porous film growth with spherical grains. Cyclic voltammetry reveals the mixed capacitive behaviour with maximum specific capacitance 605.35 F/g at the scan rate 1 mV/s in 1 M KOH electrolyte. Chronopotentiometric measurement gives energy density 33.5 Wh/kg, power density 2 kW/kg and Columbic efficiency 99.23%. Electrochemical impedance study was carried out in the frequency range 1 mHz to 1 MHz to see the internal resistance. Randles equivalent circuit was developed by using ZsimpWin software to search the circuitry parameters associated with the cell.

1. Introduction

Today's modern society and technology needs eco-friendly high energy and high power storage device like supercapacitors. Supercapacitor is a new energy storage device which has many advantages such as long life, high power density, high energy density, green environmental protection and has attracted enormous research interest in the recent years. It can be applicable in number of charge storage applications like hybrid electric vehicles, laptop, digital camera, mobile phone, military, missiles, etc. It differs from general electrical battery and conventional capacitor. There are two type (1) *EDLSc*: (electric double layer supercapacitor) in which charge separation takes place at the surface of the electrode and electrolyte interface e.g. carbon and (2) *Pseudocapacitor*: in which charge separation takes place at the electrode surface e.g. transition metal oxides (TMOs) and conducting polymers (CPs). Hybrid capacitors are the combination of both EDLSc and pseudocapacitor [1]. The electrodes of these supercapacitors were prepared using variety of materials and numbers of techniques [2]. Amongst these transition metal oxides, it is observed that Co_3O_4 and Mn_3O_4 is cheap in preparation, shows porous morphology, good chemical and physical stability, high specific capacitance (SC). The 3D architecture and porous nature of the material is desired for electrode application because porous nature offers large surface area for electrode–electrolyte interaction and supports electrolyte for easy ionic intercalation in the entire electrode matrix. Some researchers reported porous/3D architecture, nanowires, nano flower, flaks,

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http://dx.doi.org/10.1016/j.measurement.2016.02.063
0263-2241/

and spherical grains of Co_3O_4 and Mn_3O_4 by different techniques via aqueous [3–15] and non-aqueous routes [16–19]. Some researchers reported the electrochemical measurements of Co_3O_4 and Mn_3O_4 prepared via aqueous route using different techniques [20–22,9,23–26,10,27]. Also there are some reports on electrochemical measurements of Mn_3O_4 prepared via aqueous route using different method [9,23–26,10,27]. Pang et al. reported the preparation and electrochemical measurements of Co_3O_4–Mn_3O_4 composite. The observed value of the specific capacitance for Co_3O_4–Mn_3O_4 composite is 412 F/g [28]. From the available literature it is known that there is no single evidence found regarding the preparation of Mn:Co_3O_4 thin films by spray pyrolysis via non-aqueous route and their electrochemical measurements related to supercapacitor applications. Non-aqueous route supports easy thermal decomposition, good morphology, porous nanocrystalline nature [16]. Hence in the present work it is planned to prepare spray pyrolysed thin film electrodes of Mn:Co_3O_4 using methanolic medium by varying Mn content in the spraying solution. The prepared electrodes were used for structural, morphological, optical, elemental and electrochemical measurements.

2. Experimental

Initially, 40 ml, of 0.6 M cobalt nitrate (AR grade, s.d. fine chem.) and manganese nitrate (Aldrich make) solutions were prepared in methanol (AR grade, s.d. fine chem.). Prepared solutions were mixed in different proportions and stirred well. Then after these solutions were sprayed using air as a carrier gas on to the well cleaned stainless steel substrates kept at the constant temperature 623 ± 2 K on the hot plate of the spray pyrolysis technique. Throughout the process spray rate was maintained constant as ~10 ml/min. Prepared samples were nomenclatured as C for 100% Co_3O_4 and M for 100% Mn_3O_4. The other samples were nomenclatured on the basis of % of manganese nitrate solution added in the cobalt nitrate solution like, N_1 = 0.1%, N_2 = 0.4%, N_3 = 0.6%, N_4 = 0.8%, N_5 = 10%, N_6 = 50%, N_7 = 60%, N_8 = 70%, and N_9 = 90%. Samples were characterized by XRD, SEM and electrochemical characterizations like cyclic voltammetry, Chronopotentiometry and Impedance study. Cyclic voltammetry (CV) measurement shows improved capacitive results for the films prepared using non-aqueous route.

The SC (specific capacitance) associated with working electrode was calculated using the following relations reported elsevier [29].

$$C = \frac{\int I dt}{dV/dt} \tag{1}$$

$$SC = \frac{C}{W} \tag{2}$$

where

$\int I dt$ is the area under curve, dV/dt is voltage scan rate, C is the capacitance, W is the weight of the active material dipped in the electrolyte.

Prepared electrodes there after used for structural, morphological and electrochemical characterizations.

2.1. Characterization techniques

Crystal structure, crystallite size and orientation of the planes were decided using X-ray diffractometer (XRD) (Rigaku D/max 2550 Vb^+/PC 18 kW with Cu kα) in the range of diffraction angle (2θ) from 10° to 100°. A scanning electron microscope (SEM) JEOL JSM-6360 was used to perform the surface morphological analysis. Optical absorption of the deposited samples was observed in the wavelength range 350–850 nm with the help of Shimadzu (UV 3600) spectrophotometer. Weight of the deposited material was measured by weight difference method using 1×10^{-6} high accuracy analytical microbalance (Tapson's – 100 TS). An elemental diffraction analysis (EDX) was carried out using AXFORD – SUK (Japan) at 20 kV to measure the percentage content of manganese in the doped cobalt oxide. Electrochemical measurements of the prepared electrodes were carried using computer controlled potentiostat (H CH 600D spl. electrochemical analyzer/workstation) with standard three electrodes cell. In supercapacitive study, cyclic voltammetry of the samples (size 1 $cm^2 \times 1$ cm^2) was carried out in the potential window −0.40 to 0.40 V in 1 M KOH electrolyte using platinum wire as a counter electrode and saturated Ag/AgCl as a reference electrode. CV curves were used to calculate the SC using the relations (1) and (2) [29,30]. The charge–discharge behaviour of the prepared electrode was studied using chronopotentiometric charge–discharge technique for different current densities. Multi frequency impedance measurements were carried out in the frequency range 1 mHz to 1 MHz using AC signal of applied open circuit potential −0.185 V. Electrochemical Impedance spectroscopy (EIS) data was fitted with standard data to search Randle's equivalent circuit using ZsimpWin software.

3. Results and discussion

3.1. Reaction kinetics

The non-aqueous route prepared cobalt oxide and Mn incorporated cobalt oxide thin film formation is as below.

Pure cobalt oxide

$$3Co(NO_3)_2 \cdot 6H_2O + CH_3 - OH \rightarrow Co_3O_4 + 3N_2\uparrow + CH_4 + 1/2\,O_2\uparrow + 18H_2O\uparrow + 7O_2\uparrow \tag{3}$$

Mn incorporated cobalt oxide

$$3Mn(NO_3)_2 6H_2O + 3Co(NO_3)_2\ 6H_2O + CH_3{-}OH \rightarrow Co_3O_4 : Mn_3O_4 + 6N_2\uparrow + CH_4 + 1/2\ O_2\uparrow + 36H_2O\uparrow + 14O_2\uparrow \tag{4}$$

The obtained Mn doped Co_3O_4 thin films are chemically and environmentally stable.

During electrochemical characterization of prepared Co_3O_4:Mn_3O_4 electrodes

Reversible redox reaction

$$Mn_3O_4 - Co_3O_4 + 6OH^- \leftrightarrow 3Mn : Co(OH)_2 + 4O_2 + 6e^- \tag{5}$$