Electrochimica Acta 231 (2017) 460–467

Contents lists available at ScienceDirect

Electrochimica Acta

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

Research Paper

# Hausmannite Manganese oxide cathodes for supercapacitors: Surface Wettability and Electrochemical Properties

Shrikant Kulkarni[a], Dhanya Puthusseri[b], Sanam Thakur[a], Arun Banpurkar[a], Shankar Patil[a,*]

[a] Department of Physics, Savitribai Phule Pune University, Ganeshkhind road, Pune, 411007, India
[b] Centre for Energy Science, Indian Institute of Science Education and Research Pune, Homi J. Bhabha road, Pune 411008, India

ARTICLE INFO

*Article history:*
Received 21 November 2016
Received in revised form 13 January 2017
Accepted 25 January 2017
Available online 31 January 2017

*Keywords:*
Manganese oxide
spray pyrolysis
surface wettability
cyclic voltammetry
supercapacitors

ABSTRACT

$Mn_3O_4$ thick film electrodes have been synthesized by spray pyrolysis method. Effect of its two important synthesis parameters *viz.* solution feed rate and substrate temperature has been studied. Solution feed rate was studied in the range of 150 to 250 cc.min$^{-1}$ while substrate temperature was varied from 325 to 400 °C. X-ray diffraction studies confirms Hausmannite crystal structure and SEM studies show spherical grains, uniformly distributed porous microstructure obtained for deposited $Mn_3O_4$ thick films. The contact angle measurements show these electrodes have very low contact angle in the range of 2–8° and high surface energy. Cyclic voltammetry study showed specific and interfacial capacitance of $Mn_3O_4$ electrodes increased with increase in solution feed rate, due to increased thickness of films. On the other hand, substrate temperature shows effect on film morphology, grain size and porosity, however, does not show any explicit effect on specific and interfacial capacitance. Highest values of specific and interfacial capacitance exhibited by $Mn_3O_4$ are 187.79 F.g$^{-1}$ and 0.82 F.cm$^{-2}$ respectively for sample prepared at 250 cc.min$^{-1}$ solution feed rate and 325 °C substrate temperature. The calculated energy density and power density for the same sample was 26.08 Wh.kg$^{-1}$ and 1.01 kW.kg$^{-1}$ respectively.



## 1. Introduction

Electrochemical supercapacitors (ECS) are one of the most desirable candidates to store energy at high energy density as compared with conventional capacitors. It has high power storage capacity in the range of thousands of Farads and long operational life compared to conventional batteries [1]. Its capability to deliver instantaneous electrical energy made these devices very useful in several applications, such as, portable electronic devices, military, automobiles, space *etc.* [2]. A general assembly in electrochemical supercapacitors consists of an anode, which is a metal electrode, such as platinum, silver *etc.*, electrolyte in liquid phase and cathode material in the form of porous oxides on the conducting substrate. This negative electrode governs the performance of the supercapacitor in terms of the charge storage capacity and charge discharge rate [3]. The cathode required to be dielectric having high electrical resistance as well as large specific surface area (SSA) [4]. Therefore, cathode required to be as porous as possible, having optimum cation vacancies and lattice sites allowing faradic reaction to improve charge storage and slow charge-discharge process of supercapacitors. This work is aimed to develop such an efficient electrodes using manganese oxide.

There are several materials reported to be potential candidate as ECS cathode materials. Transition metal oxides, such as, $RuO_2$, $IrO_2$, are considered to be the best candidate for these applications. However, they are costly due to rare availability [5]. Therefore efforts are being taken to replace Ruthenium and Iridium by oxides of Titanium (Ti) [6], Nickel (Ni) [7], Cerium (Ce) [8], Tin (Sn) [9], Iron (Fe) [10], Manganese (Mn) [11] *etc.*

Among these, $Mn_3O_4$ is one of the promising electrode materials for supercapacitor as it has several advantages over other materials. Manganese salts (chlorides, nitrates, acetates) are very cheap and easily available compared to rare earth salts. Manganese is non-toxic and have ample availability in earth's crust

* Corresponding author.
*E-mail address:* patil@physics.unipune.ac.in (S. Patil).

http://dx.doi.org/10.1016/j.electacta.2017.01.165
0013-4686/

[12]. $Mn_3O_4$ is most stable form of Manganese oxide having good redox performance and theoretical specific capacitance of 1100–1300 F.g$^{-1}$ [13,14]. It has high electrical resistivity in the range of $10^7$–$10^8$ $\Omega$.cm [15,16]. The pseudocapacitive charge storage [17,18] of $Mn_3O_4$ in aqueous solution is;

$$MnO_x(OH)_y + \delta H^+ + \delta e^- \leftrightarrow MnO_x - \delta(OH)_{y+\delta}$$

This implies $Mn_3O_4$ possesses intrinsic properties to become promising candidate as cathode in supercapacitor applications. However, due to high resistivity, $Mn_3O_4$ shows low charge retention capabilities and faster damping capacitance [19]. To take the advantage of inherent properties of $Mn_3O_4$ material need to have an appropriate synthesis method to achieve high specific surface area and appropriate active faradic reaction sites. There are several methods reported in literature by which $Mn_3O_4$ has been synthesized *viz.* microwave assisted hydrothermal synthesis [20], vacuum evaporation [21], Metal Organic Chemical Vapor Deposition (MOCVD) [22], surfactant-assisted dispersion [23], and Pulse Laser Deposition (PLD) [24] *etc.* $Mn_3O_4$ thin films deposited on borosilicate glass substrate using Chemical Bath Deposition (CBD) method shows specific capacitance of 193 F.g$^{-1}$ in 1 mole $Na_2SO_4$ at 10 mV.s$^{-1}$ voltage scan rate [25]. When $Mn_3O_4$ synthesized by Successive Ionic Layer Adsorption and Reaction (SILAR) method on stainless steel substrate, $Mn_3O_4$ shows specific capacitance of 314 F.g$^{-1}$ in 1 mole $Na_2SO_4$ at 5 mV.s$^{-1}$ [26]. $Mn_3O_4$ synthesized by hydrothermal method on graphite paper showed maximum specific capacitance of 322 F.g$^{-1}$ in 1 mole $Na_2SO_4$ electrolyte and scan rate of 5 mV.s$^{-1}$ [27]. However, when $Mn_3O_4$ synthesized by hydrothermal method on glass carbon disk and electrolyte was 2 molar KCl, supercapacitor performance was lowered to 148 F.g$^{-1}$ [28]. Therefore, it is seen that, synthesis method, selection of substrate and electrolyte also played vital role in optimizing performance of $Mn_3O_4$. Correct combination of these methods and parameters will definitely improve supercapacitor performance of $Mn_3O_4$. There are several preliminary tools to identify these combinations theoretically [29]. Selection of substrate is based on the lattice parameters of the targeted material. Similarly, electrode and electrolyte combination is also important to achieve optimum performance of the electrode materials. The electrode materials required to have lower surface tension and higher surface energy, so electrolyte diffuse through pores and electron storage facilitated on inner active surface of the pores. This will enhance the specific surface area of the deposited material and improve charge storage capacity of the cathode. A preliminary tool to identify electrode/electrolyte combination is to evaluate its surface wettability by contact angle measurements. Surface wettability is important property in ECS as the contact between solid electrode and liquid electrolyte decides the surface energy across the interface and hence charge transfer between two. Contact angle (surface wettability) measurement is reliable technique to interpret electrode and electrolyte combination for electrolytic cell [30].

Spray pyrolysis is very simple technique to deposit fine, porous, thin layers of oxide thin films. This method required metal ions precursors to be deposited on hot substrate by sprinkle it through a very fine nozzle with high velocity. These precursors may be acetates, chlorides or nitrates which are very cheap compared to other metal salts. This method is cost effective and very useful for large area and uniform deposition [31,32]. From brief literature survey, and as far as we know, there is only one article recently published on synthesis of $Mn_3O_4$ thin films using spray pyrolysis method [33]. Yadav et al. reported deposition of Hausmannite phase of $Mn_3O_4$ using spray pyrolysis method. They have deposited $Mn_3O_4$ thin films using 0.8 Mole manganese acetate salt on FTO substrate and studied the supercapacitor properties in the context of substrate deposition temperature in the range of 300 to 375 °C. They reports electrochemical properties of these films with reference to Ag/AgCl electrode and 1 Mole $Na_2SO_4$ aqueous electrolyte. This study reported for the working potential range from 0.1 to 0.5 V. It was reported that, film deposited at 350 °C having maximum specific capacitance 394 F.g$^{-1}$ at voltage scan rate of 10 mV.s$^{-1}$.

Present paper discusses about synthesis of $Mn_3O_4$ using spray pyrolysis method on stainless steel substrate by varying two of important synthesis parameters *viz.* solution feed rate and substrate deposition temperature. Effects of these parameters on structural, morphological and surface wettability properties of the electrode are explored and its electrochemical properties are studied for supercapacitor applications.

## 2. Experimental

$Mn_3O_4$ electrodes have been synthesized using spray pyrolysis method. A precursor of 1 mole Manganese chloride tetrahydrate [$MnCl_2.4H_2O$ (Sigma Aldrich 99.99% trace metal basis)] was prepared in freshly prepared DI water (Millipore Elix 3). This solution was added to dispenser syringe to provide precursor solution supply to spray nozzle of locally designed and fabricated spray pyrolysis system. This solution was sprayed at different feed rates ranging from 150 to 250 cc.min$^{-1}$ at temperature of 350° C on preheated stainless steel (SS) substrates having dimensions of $25 \times 75$ mm$^2$ and 1.5 mm thickness. The area of deposition of electrodes was $25 \times 60$ mm$^2$. The distance between the spray nozzle and substrate was kept constant at 50 cm and nozzle air pressure was 1 kgf.cm$^{-2}$. The substrate temperature was varied from 325 to 400° C at the step of 25° C at constant feed rate of 0.2 cc.min$^{-1}$ to study its effect on structural and morphological properties of the electrodes.

Deposited $Mn_3O_4$ electrodes are characterized by X-ray diffraction (Bruker axs D8 Advance) to confirm phase and crystal structure. The microstructure of these electrodes was studied by Scanning Electron Microscopy (SEM: JEOL JSM-6360A). The surface laser micrograph of electrodes were obtained using LASER tomographic thickness measurement unit (Tallysurf CLI 2000, Taylor Hobson, U.K.) to study surface roughness and thickness uniformity of electrodes. Surface wettability of electrodes was studied using contact angle goniometer OCA 20 (DataPhysics, Germany). The contact angle has been determined by sessile drop method and contact angle measured between base line and tangent to drop outline at both ends determined automatically using SCA 20 software. Both OCA and SCA 20 software was from DataPhysics Instruments, Germany. The fitting of drop outline was based on Young-Laplace method which is more reliable as it accounts physical properties of droplets.

The electrochemical characterization of $Mn_3O_4$ electrodes were carried out using a potentiostat (Bio-Logic VMP3). Platinum was used as auxiliary electrode and Hg-$HgSO_4$ was used as reference electrode. Electrolyte used was 1 mole $Na_2SO_4$. The working potential range was −0.1 to 0.9 V and scan rate for all measurements was kept at 5 mV.s$^{-1}$. However, study of scan rate variation was done in the range of 5 to 100 mV.s$^{-1}$ for sample prepared at 150 cc.min$^{-1}$ solution feed rate and 325 °C substrate temperature. Specific capacitance and interfacial capacitance, energy density, power density and coulombic efficiency were calculated using cyclic voltammetry and charge-discharge characteristics of these $Mn_3O_4$ electrodes. The electrochemical behavior of $Mn_3O_4$ films also have been studied by Electrochemical Impedance Spectroscopy (EIS) in the frequency range of 1 Hz to 100 kHz by applying 1 V potential and superimposed frequency perturbation of 0.2 V. The EIS data was fitted and an equivalent circuit was found using '*eisanalyser*' software.