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Sol-gel synthesis of manganese oxide films and their predominant electrochemical properties

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ABSTRACT

In this paper, mesoporous manganese oxide films are easily grown on stainless steel sheet by post chemical bath deposition oxidative annealing by mixing potassium permanganate ($KMnO_4$) with manganese (II) sulphate ($MnSO_4$) in an acidic medium. The prepared films are characterized by X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), proton elastic backscattering spectrometry (EBS) to obtain the phase, morphology and composition respectively. Electrochemical properties of the manganese oxide films are elucidated by cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) in 0.5 M Na_2SO_4 electrolyte. A specific capacitance (SC) of the amorphous MnO_2 film is found to be 360 F g^{-1} at current density of 0.82 A g^{-1} and remains it's 92.7% value after 200 cycles. The film exhibits excellent power density, indicating the superiority for supercapacitor electrode.

1. Introduction

In recent years, supercapacitors have received enormous attentions due to their higher power density than batteries and higher energy density than conventional dielectric capacitors, which make them possibly the alternate energy storage device to fossil fuels for the next generation [1–4]. Mainly, two types of charge storage mechanism have been proposed so far for electrochemical capacitors: electrical double layer capacitors (EDLCs) and pseudocapacitors. Double layer capacitance occurs due to the separation of charges between the electrode and the electrolyte [5], while pseudocapacitance occurs due to fast, reversible Faradic charge transfer between electrode and electrolyte [6]. Various carbon-based materials with larger specific surface area have been reported as double-layer capacitors [7–9]. On the other hand, pseudocapacitor electrode materials are mainly noble and transition-metal oxides such as ruthenium oxide, cobalt oxide, nickel oxide, iridium oxide, vanadium oxide, and manganese oxide [10–15] etc., or conducting polymers [16,17]. Among these materials, amorphous hydrated ruthenium oxide displays a higher specific capacitance of 720–760 F g^{-1} and good cycling [18,19]. But due to its high cost and toxicity, it has got limitations in applications. In this context manganese oxides are the most promising materials due to its low cost, environment friendly in nature and excellent performance [20–22]. Manganese oxide films have been prepared by different methods including sol-gel method [23–29], electrochemical deposition method [30–32], and physical vapor deposition method [33–35] etc. The values of specific capacitance of manganese oxide film are reported as 240 F g^{-1} [30], 243.2 F g^{-1} [32], 328 F g^{-1} [25], etc. in literature. A nanosheet-based MnO_2 film prepared by hydrothermal route exhibits specific capacitance of 385 F g^{-1} at a current density of 0.5 A g^{-1} [36]. Pang et al. have reported a high specific capacitance of 698 F g^{-1} [23,24] and good cycling for sol-gel derived MnO_2 film. However, till date, the performance of MnO_2 thin film as electrode material is still dissatisfying due to their poor optimization.

Herein, we investigate the electrochemical properties of manganese oxide films prepared by simple chemical bath deposition and subsequent oxidative annealing in air.

2. Experimental

All chemicals, $KMnO_4$, $MnSO_4$, and HNO_3 used in this study were of analytical grade and used without further purification. $KMnO_4$ was procured from Merck, and $MnSO_4$, HNO_3 from Loba Chemicals.

The manganese oxide films were deposited by a simple chemical bath deposition (CBD) method as follows. Stable MnO_2

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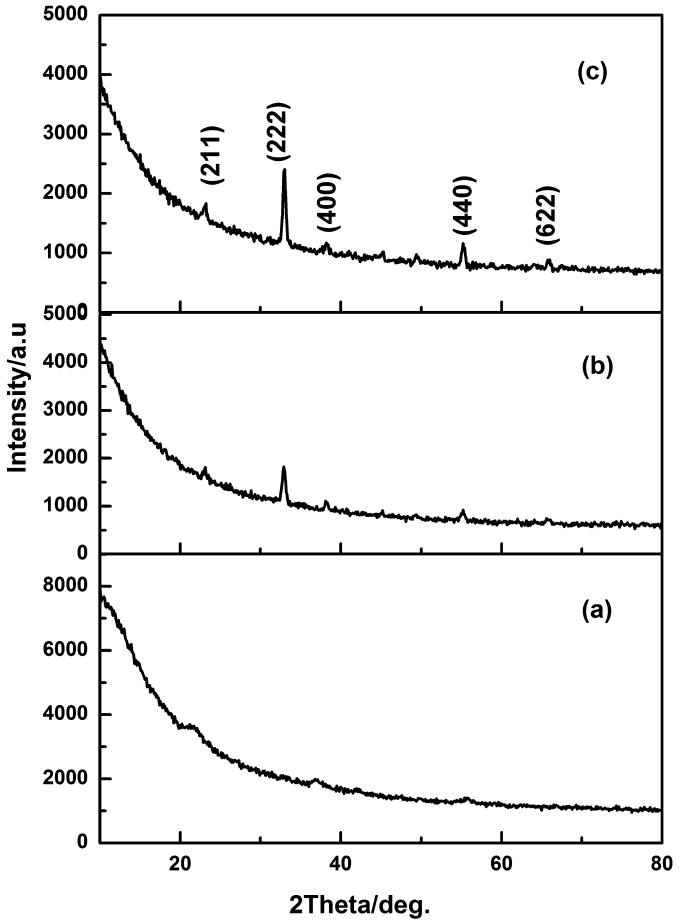

Fig. 1. GI-XRD patterns of the post annealing sol-gel derived films (a) CB373 (b) CB723, and (c) CB873.

colloidal suspensions (sols) were synthesized by reducing Mn (VII) (potassium permanganate) with Mn (II) (manganese sulfate) in acidic aqueous medium (pH 1 by adding conc. HNO_3) following the method adopted by S. Devaraj et al. [37] with modifications. The solution was free from any precipitate. The solution was stirred at 363 K for 5 h till the formation of adhesive black precipitate. A well-polished and 0.06 mm thick stainless steel sheet cleaned in trichloroethylene, acetone, methanol and iso-propanol in an ultrasonic bath subsequently was used as the substrate. Three manganese oxide films were deposited by immersing the substrates in the bath vertically and taking out at a controlled speed one after another using an automated bath deposition system. During the immersion, the heterogeneous reaction occurred and the manganese oxide film formed on the substrates. The color of the as-deposited film was light black. The films were air dried and washed in deionized water and subsequently annealed at temperatures 373 K, 723 K and 873 K for 4 h in air. These are designated as CB373, CB723, CB873, respectively.

The crystallographic study was carried out using ULTIMA IV X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) at glancing incidence condition (GI-XRD) with a grazing incident angle of 0.5^0 in the range $10–80^0$ at 1^0/min scan rate. Surface morphology was carried out by scanning electron microscope (SEM) (from ZEISS) and composition was measured by proton elastic backscattering spectrometry (EBS) in a 3 MV tandetron accelerator (HVE, EUROPA). A well-collimated proton beam (Φ = 2 mm, beam current ~10 nA) of 2 MeV incident energy impinged at normal incidence on the targets mounted on a ladder fixed in a typical scattering chamber. The chamber was pumped down to $\sim 2 \times 10^{-6}$ torr by a turbomolecular pump. A secondary electron suppressor using a ring with negative bias 900 V was positioned in front of the target sample. The backscattered particles were detected at 170° laboratory angle with respect to the beam direction by a silicon surface barrier detector with an energy resolution 20 keV for proton beam. The data were acquired by a PC based multichannel analyzer. The experimental back-scattered spectrum was simulated by SIMNRA [38] to obtain the composition and thickness of the films.

The electrochemical measurements were performed in a computer controlled Autolab100 with FRA through cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS). All the measurements were carried out in three electrode single-cell system using manganese oxide thin films as working electrode, platinum wire as counter electrode and an Ag/AgCl as reference electrode, and 0.5 M Na_2SO_4 solution as the electrolyte. All electrochemical measurements were carried out at room temperature in air. The test cell was designed in such a way that the same electrode area of 0.283 cm^2 of each thin film sample was exposed to the electrolyte for all measurements.

3. Results and discussion

There are two process of formation of films on the stainless steel substrates: nucleation and particle growth and the film formation mechanism has been described elsewhere [25]. The reaction of formation of MnO_2 can be written as,

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+ \quad (1)$$

The GI-XRD patterns of CB373, CB723, CB873, are shown in Fig. 1. The CB373 film has no distinct peak observed, so it is amorphous in nature. The other two films exhibit crystalline structure with planes (2 1 1), (2 2 2), (4 0 0), (4 4 0), (6 2 2), can be indexed to the cubic phase of Bixbyite Mn_2O_3 (JCPDS 71-3820). The SEM micrographs of CB373, CB723, and CB873 are shown in Fig. 2a, b, and c respectively. The films are mesoporous in nature and consisting of irregular agglomerates. It is interesting to notice the evolution of the morphology as annealed temperature rises. Amorphous CB373 film contains large number of channels as compared to those crystalline films. This channel like structure helps cation to invade into the bulk of the film for better oxidation and reduction during electrochemical measurements.

Proton elastic backscattering experiment involving $^{16}O(p, p)^{16}O$ kind of reaction was utilized to determine the composition of the manganese oxide films. Proton beam with incident energy 2 MeV has been chosen for the determination of oxygen accurately due to its 3–4 times higher non-Rutherford cross-section than that compared to Rutherford cross-section [39]. A typical proton elastic

Table 1
Composition and atom density of all the films determined by 2 MeV proton elastic backscattering spectrometry.

Types of films	N_{Mn} (10^{15} at. cm^{-2})	N_O (10^{15} at. cm^{-2})	Total atom density (10^{15} at. cm^{-2})	Active electrode mass (mg cm^{-2})	Composition	Thickness (nm)
Annealed at 373 K for 4 h	2960	5747	8707	0.427	MnO_2	832.8
Annealed at 723 K for 4 h	4012	6018	10030	0.525	Mn_2O_3	1168.4
Annealed at 873 K for 4 h	3179	4248	7427	0.403	Mn_3O_4	829.3

at.: atoms, N_{Mn}: atomic density of manganese, N_O: atomic density of oxygen.