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Electron beam deposition of amorphous manganese oxide thin film electrodes and their predominant electrochemical properties

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HIGHLIGHTS

- MnO_2 powder has been prepared using $KMnO_4$, $MnSO_4$ and HNO_3.
- Manganese oxide film is made by e-beam deposition followed by oxidative annealing.
- Its specific capacitance is 398 F g^{-1} at 1.1 A g^{-1} in 0.5 M Na_2SO_4 electrolyte.
- Its energy density is 85.7 Wh kg^{-1} at 2056.8 W kg^{-1}.
- At the current density of 1.1 A g^{-1} it presents excellent cycling.

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ABSTRACT

Electron beam evaporated manganese oxide films display excellent electrochemical properties on post deposition oxidative annealing in air. The films annealed below 573 K are amorphous, exhibit minor deficiency in oxygen and are characterized by a specific discharge capacitance of 398 F g^{-1} at a discharge current of 1.1 A g^{-1} and 236 F g^{-1} at a discharge current of 5.5 A g^{-1}. In terms of stability, these films retain 99.6% of their specific capacitance even after 400 cycles. The electrochemical properties of these films are explained in terms of their structure and composition which have been measured by X-ray diffraction and proton elastic backscattering spectrometry. In addition, the electrochemical properties are influenced by their morphology; the oxidatively annealed films contain nanometric, spherical and elongated grains which acquire extensive networking during electrochemical measurements.

1. Introduction

Over the past few years, electrochemical supercapacitors have received increasing attention because of their high-power density than conventional batteries, high energy density than dielectric capacitors, long cycle-life and fast charge–discharge rate [1–4]. Supercapacitors are considered as the alternate energy storage devices to fossil fuels for the next generation [5,6]. In this regard, various materials such as conducting polymers, carbon related materials, noble and transition metal oxides have been examined. Among these amorphous hydrated ruthenium oxide (RuO_2. xH_2O) shows remarkably high specific capacitance as 700–1000 F g^{-1} [7]. However it has limited applicability due to its high-cost, and toxicity to environment, other materials have been used [8]. Manganese oxide has emerged as a promising material for batteries [9,10] and supercapacitor [11–16] applications because of its low cost, huge availability and benign nature. MnO_2 exists in different crystallographic structures such as, α, β, γ, δ, λ, among which α-MnO_2 exhibits the highest specific capacitance [11]. The values of specific capacitance of α-MnO_2 material are reported as 152 F g^{-1} [12], 258.7 F g^{-1} [13], 328 F g^{-1} [14], and 356 F g^{-1} [15] in the literature. The specific capacitance of nanosheet-based MnO_2 thin film is reported as 385 F g^{-1} at a current density of 0.5 A g^{-1} [16]. Pang et al. measured a very high specific capacitance of 698 F g^{-1} for sol-gel-derived MnO_2 thin films [17]. The theoretical specific capacitance of MnO_2 is 1370 F g^{-1} [18]. But due to its low electrical conductivity (10^{-5}–10^{-6} S cm^{-1}), high value of capacitance cannot

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be achieved in reality [19]. Manganese oxide films have been prepared by various methods including sol–gel method [14,17], electrochemical deposition method [20,21], and physical vapor deposition method [22,23] etc.

In the present paper, we have studied the predominant electrochemical properties of manganese oxide thin films prepared by e-beam evaporation and subsequent oxidative annealing in air.

2. Experimental

2.1. Preparation of MnO_2 powder

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

We prepare α-MnO_2 powder by some modifications in the synthesis procedure which was adopted by Devaraj et al. [11], and subsequently deposited by electron beam evaporation method. The chemically synthesis of MnO_2 was prepared by drop wise mixing of 0.135 M $KMnO_4$ solution with 0.473 M $MnSO_4$ solution at equal volume (presently 250 ml of each solution was taken), the solution was stirred continuously during mixing. After the mixing concentrated HNO_3 was added into the solution till it attains pH 1. Subsequently the solution was heated at 363 K for 5 h with constant stirring. The purple color of the $KMnO_4$ solution turned into black. The products obtained were washed with deionized water until the solution became colorless and dried at 363 K in an air oven overnight. A black powder was obtained. It was compressed into a 2 mm thick and 20 mm diameter pellet and was subsequently heat treated at 973 K for 4 h in air. The heat treated MnO_2 pellet served as evaporant for e-beam evaporation.

2.2. Deposition of manganese oxides thin film and oxidative annealing

An electron beam evaporation system (Hind Hivac, Model: BC-500) with a 7 kW electron gun was used for manganese oxide thin film deposition. Manganese oxide films were grown on Si (100), polished 0.09 mm thick stainless steel (SS) substrates. Si and SS substrates were successively cleaned in trichloroethylene, acetone, methanol and iso-propanol in an ultrasonic bath. The distance from the target material, placed in graphite boat, to the platen onto which substrates were fixed at about 70 mm. The platen was continuously rotating at speed of 25 rpm during depositions. The thickness of the films was measured by a quartz crystal thickness monitor. The vacuum of the system was created by an oil diffusion pump backing by a rotary pump. The base pressure of the system was 2×10^{-6} torr, while during deposition the average pressure was ~4×10^{-4} torr. The power applied to the electron gun was 0.42 kW during deposition. Manganese oxide films were grown with deposition rate ~3.5 Å s^{-1} on all the substrates and the temperature of the substrates varied in 300 K–343 K range during evaporation.

The films were subjected to oxidative annealing (AA) in a quartz tube furnace in air at 393 K, 573 K and 723 K for 4 h and allowed furnace cooling unto room temperature. These are designated as AA393, AA573 and AA723, respectively.

2.3. Physical characterization

Phase and structure of both the powders and films were determined by a ULTIMA IV X-ray diffractrometer with Cu Kα radiation (λ = 1.5406 Å). The powder XRD was measured at conventional $\theta/2\theta$ scanning condition, while the films were examined at glancing incidence condition (GIXRD) with a grazing incident angle of 0.5° in the range 10–80° at 1°/min scan rate. The morphology of the films was examined by scanning electron microscopy (SEM) (from ZEISS) and atomic force microscopy (AFM) (from NT-MDT). The AFM measurements were performed in semicontact mode and the roughness was evaluated by using image analysis software in terms of rms value.

2.4. Backscattering spectrometry

Proton elastic backscattering spectrometry (EBS) measurements were carried out using a 3 MV Tandetron accelerator (HVE, EUROPA) facility present at this center. A well-collimated proton beam ($\Phi = 2$ mm, beam current <20 nA) of 2 MeV incident energy impinged at normal incidence on the targets mounted on a ladder fixed in a scattering chamber. The chamber was pumped down to ~2×10^{-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 solid angle 1×10^{-3} sr and an energy resolution 20 keV for proton beam. The data were acquired by a PC based multichannel analyzer.

The experimental backscattered spectrum was simulated by SIMNRA [24] to obtain the composition and thickness.

2.5. Electrochemical tests

The electrochemical studies that comprised of cyclic voltammetry (CV), electrical impedance spectroscopy (EIS) and galvanostatic charge–discharge measurements were carried out by an Autolab 100 electrochemical workstation in a cell with area 0.283 cm^2 exposed to electrolyte for all measurements. 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. 0.5 M Na_2SO_4 solution was used as the electrolyte. The measurements were carried out on manganese oxide films grown on SS substrates.

3. Results and discussion

3.1. Characterization of powder

The XRD patterns of the as-prepared powder and those heat-treated at 573 K, 723 K and 973 K for 4 h are shown in Fig. 1. The as-prepared and the samples heated at 573 K, 723 K can be indexed to α-MnO_2 (JCPDS 44-0141) phase. It is a tetragonal crystal system with lattice constant a = 9.845 Å, c = 2.845 Å, which are very similar to JCPDS card values a = 9.7847 Å, c = 2.863 Å. The grain sizes of the crystalline structure calculated using the Scherrer's formula [25] are 6.17, 7.17 and 9.98 nm for the as-prepared, samples treated at 573 K, 723 K respectively. It infers that the prepared samples are in nano crystalline form. The sample transformed to the bixbyite-Mn_2O_3 (JCPDS 24-0508) phase on heating at 973 K for 4 h. The backscattering spectrum of as-prepared powder together with simulated spectrum is shown in Fig. 2. It yields the composition to be Mn:O = 1:2.

The reaction of formation of MnO_2 can be written as:

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5\alpha - MnO_2 + 4H^+ \tag{1}$$

The Brunauer–Emmett–Teller (BET) specific surface area of the phase pure (α-MnO_2) powder was measured by nitrogen adsorption–desorption analysis at 77 K and found to be 98.9 $m^2\ g^{-1}$.