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Electrochemical Synthesis of Manganese Oxide Thin Film for Super Capacitor

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ABSTRACT

In the present investigation, we report synthesis of manganese dioxide (MnO2) thin film on low cost conducting substrate by electrodeposition method for supercapacitor application. The structural and surface wettability study of MnO2thin film was carried out with the help of X-ray diffraction (XRD) and contact angle meter. The supercapacitive properties of MnO2 thin film were carried out by using cyclic voltammetry (CV), charging-discharging (CD) study. The electrodeposited MnO2thin film shows specific capacitance of 430 F/g-at 10 mV/S scan rate. The specific energy and power of MnO2thin film were 7.40 kW/kg and 3.20 Wh/kg respectively. Hence, electrodeposited MnO2thin film is best electrode candidate for energy storage.

Keywords: supercapacitor, electrodeposition, MnO2, XRD, Cyclic voltammetry.

I. INTRODUCTION

In the recent years there is an urgent need of clean, renewable and sustainable energy storage devices. One such devices, supercapacitor or electrochemical capacitor plays key role in development of energy storage devices. It has higher energy density as compared to conventional capacitor and greater power densities than batteries.Supercapacitor have fascinated more attention due to outstanding electrochemical characteristics viz high power density, long capacitance retention ratio, good reversibility, environmental friendless, etc. The supercapacitor or electrochemical capacitor is broadly classified into two types depends on their charge storage mechanism such as electrochemical double capacitor and pseudocapacitor. In electrochemical double layer capacitor (EDLCs) charge storage takes place non faradically. Carbon based electrode material used in EDLCs. In pseudocapacitor charge storage takes place faradically. The conducting polymers and transition metal oxides are used as electrode material in pseudocapacitor. Manganese oxide is mostly studied as electrode material in transition metal oxide

family due to their excellent electrochemical properties such as, non-toxic, cheaper in cost, easy synthesis and variable oxidation states.It is used in catalysis, sensors, supercapacitor, rechargeable batteries and water waste treatment [1-5]. Manganese oxide electrode have been synthesized by various physical and chemical methods. Different synthesis methods gives different microstructures of manganese oxide. In supercapacitor nanocrystalline and hydrophilic electrode is mostly used for supercapacitor application. It provide higher surface area, more interaction of ions from electrode to electrolyte interface and shorten the diffusion path length which strongly improve the supercapacitive performance.

In the present work, efforts have been taken to synthesize manganese oxide electrode by potentiostatic electrodeposition method. There supercapacitive performance was tested by using cyclic voltammetry, charging-discharging studies.

II. EXPERIMENTAL

2.1. Synthesis of Manganese Dioxide (MnO_2) Thin Films:

Manganese Dioxide (MnO_2) thin filmwas carried out using a two-electrode system. Graphite sheet was served as counter electrode. Stainless steel substrate was used as working electrode. For synthesis of Manganese Dioxide (MnO_2) thin film, the aqueous bath contain 0.2M $MnCl_2$ aqueous solution. The Prior to deposition the stainless steel (SS) was used as substrate and it is well polished with zero grade polish paper rough to finish and rinsed with double distilled water and acetone. The MnO_2 thin film was deposited by using potentiostatic electrodeposition method by keeping potential of 1.8 V for 15 minutes, manganese hydroxide was formed. Further oxidation of Mn, the film was annealed at 300˚C for one hour. The colour of Mn changes from yellowish to black brown. Then oxidized film was used for further characterization.

2.2. Characterization techniques:

The as synthesized MnO_2 thin film was characterized by using different characterization techniques. The crystal structure and surface wettability study of MnO_2 thin film was carried out with help of by X-ray diffraction (XRD) techniquesusing Bruker axes D8 Advance Model with copper radiation (Kα of λ = 1.54 A˚) in the 2θ range between 20˚ to 80˚ and Rame-Hart contact angle meter respectively. The electrochemical performance of MnO_2 thin film was studied by using cyclic voltammetry and charging-discharging study. An electrochemical cell consists of three electrode systems, MnO_2thin film as a working electrode, graphite as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. All electrochemical measurement was carried out using aqueous 0.5 M Na_2SO_4electrolyte solution.

III. RESULTS AND DISCUSSIONS

3.1. Structural study:

X-ray diffraction (XRD) is an important tool to analyze the crystal structural information of synthesized thin film. Fig (1) shows the XRD spectra of potentiostatically deposited MnO_2 thin film within2θ range between 20˚ to 80˚. The XRD pattern of MnO_2 thin film electrode shows tetragonal crystal symmetry. The lattice parameter observed in these case are a= b=94.815 AU and c=2.847 AU. The peaks observed in the XRD spectrum of MnO_2 thin film electrode were well matched with JCPDS data (Card No 72.1982). The additional peaks indexed (SS) in the XRD spectra is due to the stainless steel substrate only. Thus, XRD study confirms the crystalline structure of deposited MnO_2 thin film.

3.2. Surface wettability study

The surface wettability study of film determines its ability to interact with ions when dipped into electrolyte, which is determined by measuring the contact angle with liquid electrolyte. If contact angle

is less than 90°, then the film surface is said to be hydrophilic, and for greater than 90°, it is said to be hydrophobic. For more interaction of electrolyte ions with electro active site on the surface of thin film, the contact angle must be as low as possible. Wettability of MnO_2 thin film is studied by measuring contact angle. Fig. (2) shows the images of contact angle with film surface. The observed value of contact angle for MnO_2 thin films is found to be 76°. Thus, wettability study shows hydrophilic nature of MnO_2 thin film. The hydrophilic nature of electrode is feasible for supercapacitor, which allows more interaction of electro active sites of MnO_2 thin film with electrolyte [6].

3.3. Supercapacitive Study:

3.3.1. Cyclic Voltammetry (CV) Study:

Cyclic voltammetry (CV) is a most important tool to give the qualitative information about redox process and specific capacitance associated with electrode. Fig. (4) shows typical cyclic voltammogram of MnO_2 thin film at 10 mV/s scan rate within potential range of +1.2 V to -1.2 V in 0.5 M Na_2SO_4 electrolyte solution. The nature of CV curve is nearly rectangular in shape indicating the ideal pseudocapacitor behaviour of deposited MnO_2 thin film. The specific capacitance of the MnO_2 thin film was calculated by using following formulae,

Specific capacitance (C_s) = C/W ------ (1)

Where, C – capacitance in farad and W – the mass of active electrode materials in gm. The active mass of MnO_2 thin film in gm. The calculated value of specific capacitance of MnO_2 thin film is 430 F/gat 10 mV/s scan rate. The greater value of specific capacitance in present case is nanocrystalline and hydrophilic nature of MnO_2 thin film.

3.3.2. Charging-discharging study:

The electrochemical supercapacitor parameter such as coulombic efficiency, specific energy and power of the electrode was carried out with the help of charging-discharging study. Fig. (4) shows the charging-discharging (CD) study of MnO_2 thin film at 10 mA current density. The nature of charge and discharge curve is triangular in shape. There is a small voltage drop at the starting of discharge curve is due to internal resistance present between the MnO_2 thin film and electrolyte. The electrochemical supercapacitor was calculated by the following formulae:

Coulombic Efficiency=T_d/T_cx100 (2)

Specific power =(V X I_d)/W (3)

Specific energy=(V X I_d X T_d)/W (4)

Where, T_d and Tc is discharging and charging time in sec, V is voltage window volt, I_d is discharging current in A and W is the weight of active material in gm.

The coulombic efficiency of MnO_2 thin film was found to be 94% whereas the specific power and specific energy were observed to be 7.40 kW/kg and 3.20 Wh/kg, respectively.

IV. CONCLUSION

In summary, we have synthesized MnO2 thin film by potentiostatic electrodeposition method for supercapacitor application. The XRD study show the tetragonal crystal structure. The wettability study shows MnO2 thin film is hydrophilic in nature. The MnO2 thin film gives maximum specific capacitance of 430 F/g. The MnO2 thin film shows values of specific energy and specific power isbe 7.40 kW/kg and 3.20 Wh/kg respectively. Thus potentiostatistically deposited MnO2 thin film is suitable material for energy storage devices.

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Figure:

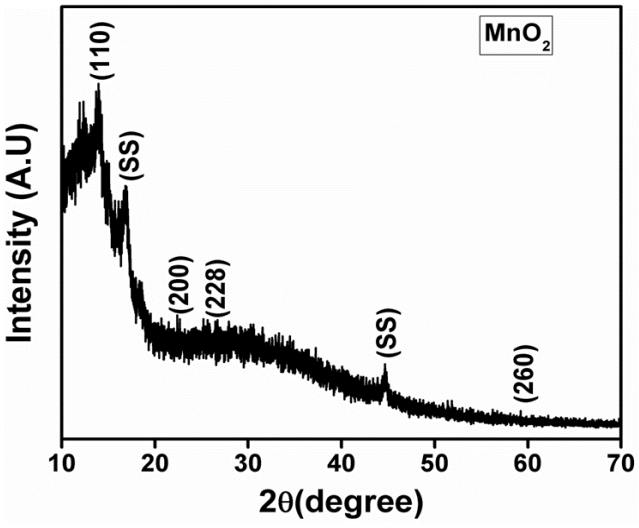

Fig. (1) XRD pattern MnO_2 thin film

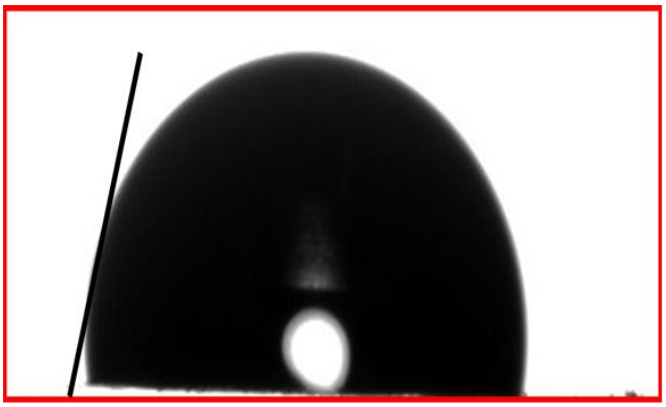

Fig. (2) Surface wettability of MnO_2 thin film

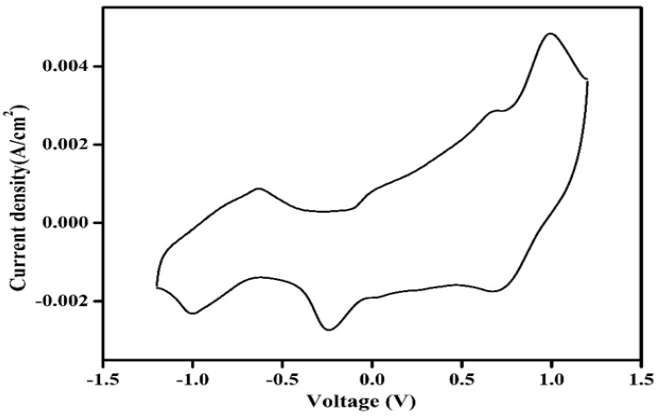

Fig. (3) CV of MnO_2 thin film

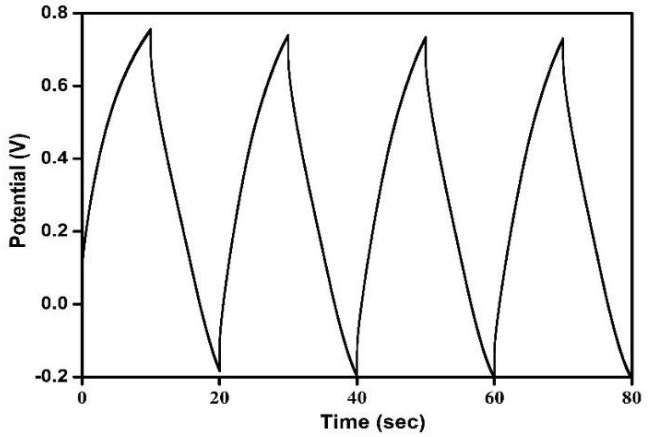

Fig. (4) Charging-discharging study of MnO_2 thin film