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Efficient Sol-Gel deposited MnO2 Electrode for Electrochemical Pseudocapacitor Applications

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ABSTRACT

In the present work, Sol-gel spin coating technique is used to deposit MnO2 thin films on steel substrate, using Manganese Chloride as precursor. The structural, morphological and electrochemical properties of MnO2 thin films were studied by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Cyclic Voltammetry (CV), Galvanostatic charge–discharge (CP), Atomic Force Microscopy (AFM) respectively. The XRD pattern shows the characteristic peaks which are orthorhombic in structure with MnO2 phase. The morphology of the sol-gel derived MnO2 shows uniformly distributed on the surface of substrate also reveals that thin film is highly porous in nature. The EDAX spectrum of MnO2 thin film shows manganese and oxygen elements existed in the sample. In case of CV, the current under the curve increases with increase in scan rate. The maximum specific capacitance is 650 F/g for scan rate 10mV/s.

Keywords : XRD, FESEM, CONTACT ANGLE, AFM, CV, CP.

I. INTRODUCTION

Supercapacitor is a category of electrical energy storage device. The advantages of supercapacitor are high power density, high efficiency, fast charging and discharging speed, long cycle life, and eco friendly. It has become an ultimate option for high power applications, such as hybrid power systems, regenerative energy systems and instant backup power source [1]. The performance of the electrode material is the mainly important thing affecting the nature of supercapacitor [2]. Many researches in this area have been paying attention on the improvement of electrode materials having high specific surface areas [3].

For supercapacitors, a variety of noble and transition metal oxides and conducting polymer were in use as electrode materials with their charge-storage mechanisms based mainly on pseudocapacitance. Amongst these materials, manganese oxide is one of the most attractive materials for supercapacitor electrode because of its environmental friendliness, low cost, and favorable pseudocapacitive characteristics. A lot of types of manganese oxides have been investigated, including nanocrystalline an d amorphous phases. In these oxides, MnO2 thin films for the supercapactive electrode exhibit comparative high specific capacitance. Manganese oxides as supercapacitor electrode materials were fabricated by different methods, such as chemical spray pyrolysis [4], Chemical bath deposition [5], electrodeposition [6] and sol-gel spin coating [7], Sol-gel approach distinguishes from other methods especially by its simplicity and versatility. In the present work attempts are made to deposit thin films of MnO2 using Sol-gel spin coating method.

II. Experimental

2.1 Synthesis and Deposition

Manganese Chloride ($MnCl_2.4H_2O$) was used as precursor for the preparation of MnO_2 thin films electrodes. Initially 0.1 M Manganese Chloride solution of high purity 99.9% was prepared by using 50ml distilled water and 5ml isopropyl alcohol. This solution was stirred for 4 hours at 50^0C in magnetic stirrer. After aging we got a clear and viscous solution which was light pink in color.

The above solution was deposited on to the stainless steel substrate (SS) by spin coating technique. The deposited films were calcinated at 600^0 C for 10 minute. Before deposition, pieces of stainless steel (SS) substrate were polished with zero grade polish paper and then degreased with water and acetone, impressed in 0.1 M H_2SO_4 solution, and kept in ultrasonic bath for 20 minute, after that rinsed in double distilled water, and dried up in air [8].

III. Results and Discussion

3.1 Structural Property

The XRD patterns of MnO2 thin film annealed at 600^0C are shown in Fig 1. Shows the XRD patterns were obtained with source CuKα1 with λ =1.54184. The samples are crystalline in nature.

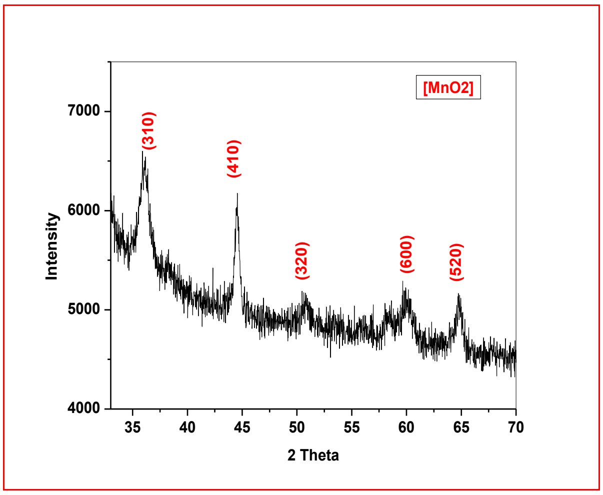

Fig. 1 – XRD pattern of MnO_2

XRD pattern indicates the peaks at 35.93^0 , 44.60°, 50.81°, 59.87°and 64.80° corresponding to plane (310), (410), (320), (600), (520) respectively these planes are corresponding the standard values as per JCPDS data card (82-2169) confirming the formation of orthorhombic MnO2 crystals[9]. By using Scherer's formula the average crystallite size is calculated and it was found to be ˜48 nm.

3.2 Surface Morphology

The FESEM micrographs of the MnO2 are shown in Fig 2. FESEM (FE-SEM FEI Nova Nano SEM 450) was used to explore the surface morphology of prepared film electrode it can be seen that, the grains are well developed and uniformly distributed throughout the substrate surface. It is also observed that films are highly porous in nature. The porous morphologies clearly appear on these deposited films which is favorable for penetration of electrolyte which is good for supercapacitor application [10].

The EDAX (Energy Dispersive Spectroscopy) spectroscopy was used to identify the percentage of the element present in the deposited sample. EDAX analysis is carried out using Bruker XFlash 6130 FESEM instrument. The EDAX spectrum of MnO_2

thin film is shown in figure. 3. As shown in figure, Mn and oxygen elements existed in the sample [11].

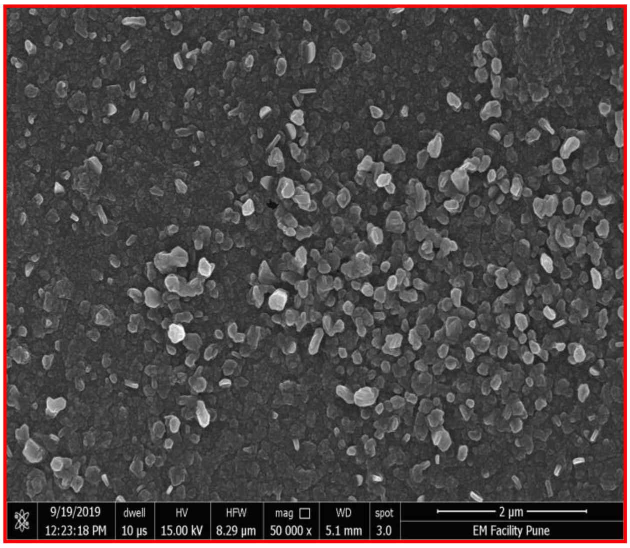

Fig. 2 – FESEM image of MnO_2

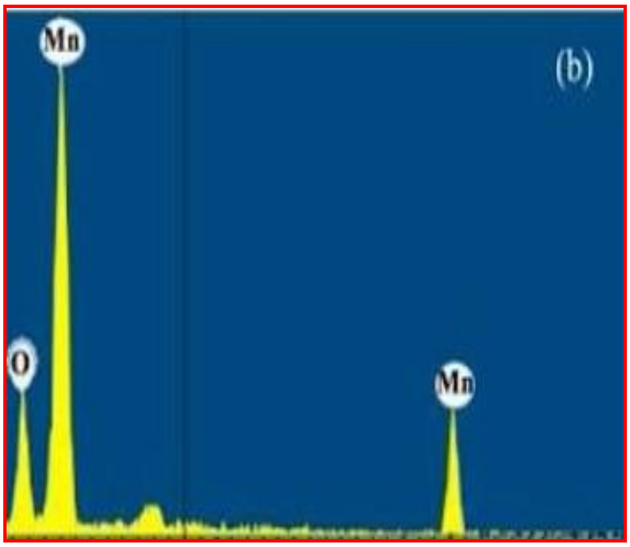

Fig. 3 – EDAX of Mno_2

3.3. Surface wettability test

The surface wettability of the sample was deliberated by water contact angle test, which is the angle at which a liquid/ vapor boundary meets a solid surface. In general, if the water contact angle is less than 90°, the solid surface is hydrophilic, and if it is more than 90°, the solid surface is hydrophobic in nature. If the contact angle is 0^0 then it means it completely wets and if the contact angle is 180^0 then it is non wetting [12]. The Contact angle of MnO_2 electrode with water drop is Right angle 24.50^0 and 26.22^0 signifying that the surface of MnO_2 film is hydrophilic in nature. This is good for supercapacitive performance.

Fig. 4 – Angle of Contact of MnO_2

4. Atomic force microscopy (AFM)

Atomic force microscopy (AFM) image is presented in Fig. 5 shows the topography view of MnO_2. AFM fig shows that rough, irregular nanostructure with extremely porous morphology with several small nanowires of Manganese Oxide is predictable to have a high specific surface area and lead to high specific capacitance when used for super capacitor applications [13]. AFM shows that the thickness of the MnO2 film is about 49.1 nm.

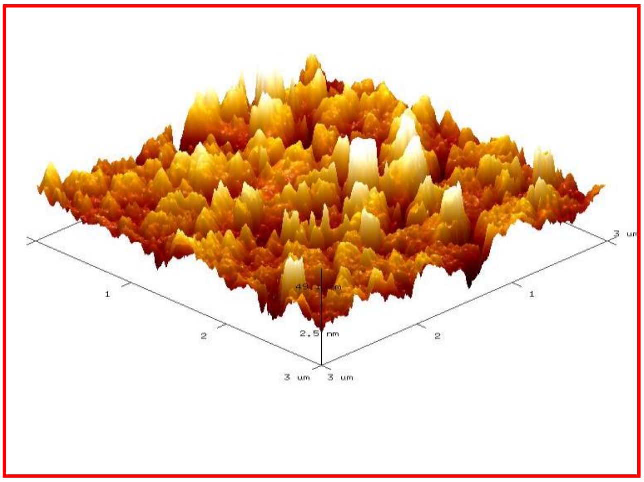

Fig. 5 – Atomic force microscopy (AFM)

5. Electrochemical Property

The CV is an important technique in electrochemistry which provides the qualitative information about the electrochemical processes, whether the process is Faradic or non-Faradic, that takes place in the material. The electrochemical analysis of MnO2 thin film was done with cyclic voltametry (CV) measurements was subjected at various scan rates from 10 mV/s to 100 mV/s in 0.1M KOH (fig.6) shows the CV curves at different scan rates in 0.1 M KOH electrolyte with potential window of -1.2V to 0.6V. The as deposited MnO2 thin film electrode is used as working electrode, Platinum as counter electrode and SCE (Staurated Calomel Electrode) as reference electrode. During the different Scan rates, it was found that the current under the curve gradually increased with scan rate. From this, we can conclude that voltammetric current is directly proportional to the scan rates of CV and it is a good sign of supercapacitive behavior. [14].

To calculate the specific capacitance (SC) of the electrode from the CV curves following formula was used.

$$SC=\frac{c}{m}=\frac{\int_{V_1}^{V_2} I\,dV}{m(V)\frac{dV}{dt}}$$

Where m is the mass of active material, $V1$ and $V2$ are the potential limits, $\frac{dV}{dt}$ is the scan rate potential [15].

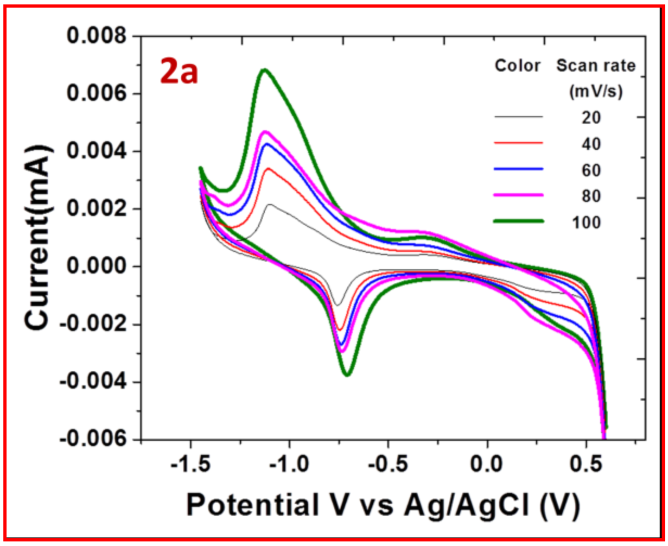

Fig. 6 – Cyclic Voltametery of MnO_2 Electrode.

6. Galvanostatic charge-discharge

The galvanostatic charge-discharge study has been carried out at 1mA. It was observed that the charging and discharging times were almost equal. The charging-discharging curve reveal saw tooth like structure. This may be due to the initial ohmic drop followed by the discharging of electrode.

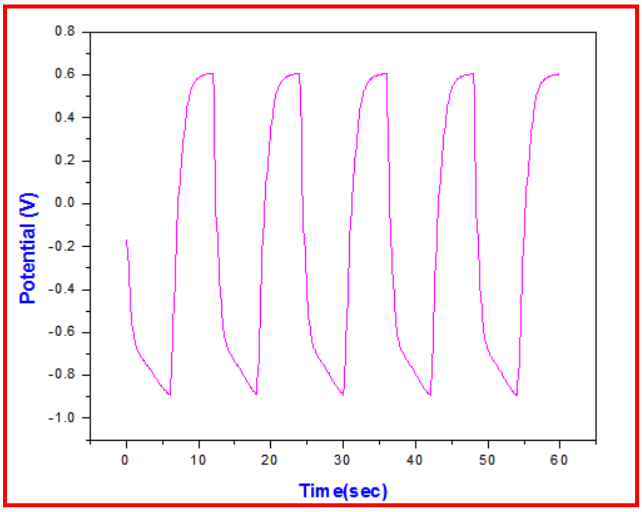

Fig. 7 – Charge Discharge of MnO_2 Electrode

<u>**Specific power, specific energy values**</u>:-

The electrochemical parameters such as specific power (P), specific energy (E) and coulomb efficiency (η %) are calculated using following relations [16];

$P = (V \times I_d)/W$ ------------- (2)

$E = (V \times I_d \times T_d)/W$ ---------- (3)

$\eta\,\% = (T_d\,/T_c) \times 100$ ------ ---(4)

Where Tc, T_d and I_d are charge time, discharge time and discharge current respectively. V is the applied voltage and W is the mass of MnO_2 film electrode. The specific energy (E) was 24 Wh/kg. The specific power (P) of MnO_2 electrode was 15 kW/kg respectively. The columbic efficiency is 97.83%.

IV. CONCLUSION

In this present work, we successfully deposited the MnO_2 electrode using a sol- gel spin coating method on stain less steel (SS) substrate. The structural investigation suggests a crystalline nature of MnO_2. The surface wettability of the MnO_2 sample studied by water contact angle test is supporting for the hydrophilic nature. The maximum specific capacitance is calculated is 650.F/g for scan rate 10mV/s. The specific energy (E) and specific power (P) of MnO_2 electrode was 24 Wh/kg and 15 kW/kg respectively. The columbic efficiency is 97.83%.

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