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Comparative Study of Mno2 and Polypyrrole for Supercapacitor Application.

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ABSTRACT
This paper is related to comparative study of Mno2 and polypyrrole, Mno2 and polypyrrole are separately deposited on two different stainless steel substrate using electrodeposition method, we have studied their super capacitance behaviour using cyclic voltammetry technique and charge discharging curve. We got maximum capacitance value equal to 184.42 F/gm and 29.72 F/gm For MnO2 and Polypyrrole so Mno2 shows better performance than polypyrrole.

Keywords : - Voltammetry, Polypyrrole, Charging Discharging Curve

I. INTRODUCTION

Super capacitors are widely used in an energy storage system. there are two type of supercapacitor ,Activated carbons, for example, have surface areas in excess of 1000m2/g, and the production of EDL (electrical double layers) in these materials provides the basis for the first method. In order to enhance the working potential of the devices, activated carbon capacitors based on carbon materials were manufactured without the utilization of aqueous electrolytes. Second, a faradaic charge exchange procedure is used to provide electrochemical capacitance that permits electrons and ions to go into the electrode material. [1]. Since it exhibits capacitive performance instead of the distinctively peaked redox behaviour that is closely correlated with intercalation, this is referred to as pseudo capacitance.

The several metal oxide and polymer have been studied extensively for high power super capacitance. Manganese dioxide is one of the metal oxide which is used for study of supercapacitor behaviour. Manganege oxide is low cost ,low toxic, high stability material as compared to RuO2 so many researcher mostly use MnO2 for supercapacitor study.

Manganese dioxide gives the very low capacitance as compared to RuO2 so to improve its capacitive behaviour many of researcher have used electrodeposition method. Similarly, some polymer are used to study supercapacitor because they have high conductivity. Polypyrrole is one of the polymer which is used for study of super capacitor as it has high specific capacitance, high conductivity. In the presence of a strong oxidant, pyrrole solution may be used to create conductive polymer films, which have high durability and conductivity. Conductive polymer

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films can be made by chemical oxidation in the presence of a strong oxidant, for example FeCl3 [2, 4, 5], or by electrochemical oxidation from a pyrrole solution in the presence of a supporting salt, the nature of the salt strongly affects the conductivity of the film [2,3]. The electrodeposition technique is more convenient for the synthesis of materials since it has several benefits, such as its simplicity, the quickness of the reaction, and the ability to precisely regulate the experimental conditions.

The aim of our investigation is using electrodeposition method to prepare MnO2 and Polypyrrole thin film separately and study their electro chemical properties. In this paper we have synthesized MnO2 and Polypyrrole film separately by Potentiostatically electrodeposition method and we have studied their morphological structure along with their super capacitive behaviour, and observed that the both thin films are charged–discharged in Na2SO4 electrolyte separately.

II. EXPERIMENTAL METHOD

We first prepared MnO_2 thin film by potentiostatic electrodeposition method. For electrodeposition of MnO_2 we have used 0.1 M $MnSO_4$ and added KOH (0.05M) for adjusting ph. 6.5, then applied 0.95 V voltage for 20 min. A three-electrode electrodeposition approach was used in this study using stainless steel as the working electrode, saturated calomel as the reference electrode, and graphite as the counter electrode. After electro deposition, film was annealed for 200^{0}C, similarly preparation of Polypyrrole thin film was done using potentiostatic electrodeposition method. For electrodeposition of polypyrrole, we used 0.1M Pyrrole and added 5 sulphosalicylic acid for adjusting ph. 2.2, we have applied 0.7 V for electrodeposition for 25 min at room temperature. In this investigation, we found that MnO_2 and Polypyrrole are electrodeposited on two different stainless steel substrate.

A zero grade polish paper was used to prepare the stainless steel substrate prior to electrodeposition, and the surface was then ultrasonically washed with acetone along with ethyl acetate and then etched substrate for few sec in HNO_3 and again ultrasonically cleaned with distilled water. Electrodeposited films are electrochemically characterized by Cyclic Voltammetry, galvanostatic charge discharge technique in 0.5M Na_2SO_4 using autolab Metrohm potentiostat 204.

III. RESULT AND DISCUSSION

a. XRD:

figure1a and 1b shows xrd pattern of MnO2 and Polypyrrole. Both figures shows almost amorphous structure of material, peak are found due to stainless steel which is indexed by square. MnO2 amorphous structure and polypyrrole is more feasible for supercapacitor behaviour.

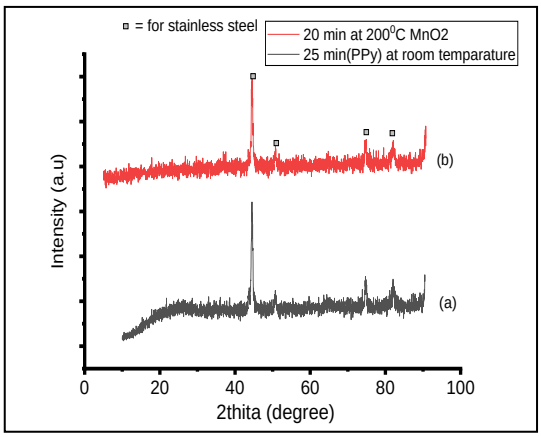

Figure 1 : XRD for a) Polypyrrole b) MnO2

b. FTIR:

FTIR is one of the technique which is used for confirmation of material, the ftir is studied at range 400 to 4000 cm^{-1}, for MnO_2 (figure 2) 3407cm^{-1}, 2924 cm^{-1},2855cm^{-1} peaks are obtained due to streching of water molecule. Peak at 1625 cm^{-1} is attributed for bending of water molecule. 558 cm^{-1} attributes Mn-O vibration so from FTIR of Mno2 graph, it gives the confirmation of MnO_2.similarly for Polypyrrole in figure 2 absorption peak obtained at 3442 cm^{-1}, 2924

cm^{-1} in room temperature is because of O-H and C-H stretches. absorption peak at 1456 cm^{-1} shows streching of C=C while 1635 cm^{-1} and 1372 cm^{-1} demonstrates streching of C=N and C-N bond, peaks at 1034 cm^{-1}, 456.83 cm^{-1} and 607 cm^{-1} are obtained because of C-H in plane vibration and pyrrole ring vibrations, it confirmed that formation of poly pyrrole.

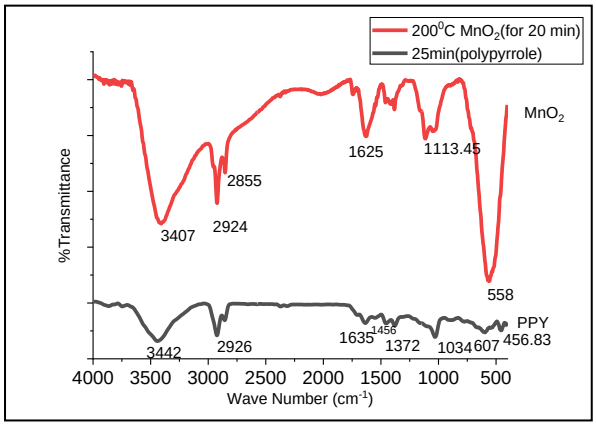

Figure 2 FTIR for Polypyrrole and MnO_2

c. Surface Morphology:

Surface morphology of Polypyrrole and MnO2 were studied using SEM technique. figure 3a shows surface morphology of polypyrrole, it looks like cauliflower structure and it shows polypyrrole uniformly deposited on substrate, similarly figure 3b shows SEM image for MnO_2 it look like granular structure and high Porous.

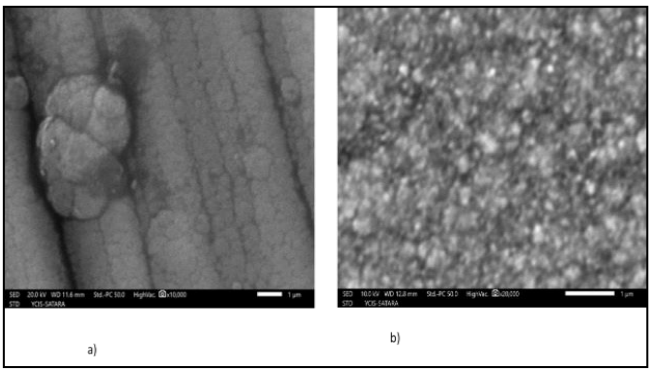

Figure 3 : SEM image for a) Polypyrrole b) MnO_2

d. Electro chemical Characterization:

Electrochemical performance can be studied by Cyclic Voltammetry, galvanostatics charging discharging curve technique using 1M MnSO4 for MnO2 and 0.5 M For polypyrrole.

d.1 Cyclic Voltammetry: Figure 4a and 4b shows the cyclic voltammetry of mno2 and polypyrrole. Figure4a is cyclic voltammetry of polypyrrole for Scan rate 10 mV/sec at Voltage range -0.5 to 0.4 V and figure 4b is cyclic voltammetry of MnO2 at voltage range 0 to 1 V for scan rate 10 mV/sec. from this figure area under the curve of polypyrrole is large as compared to MnO2, But it gives poor capacitance performance due to Na+ ion can reach outer part of electrode layer and cannot enter the interior pores of the nano particles matrix and anionic dopant like 5 sulfosalicylic acid oxidize on the surface of stainless steel [8] and hence capacitance for polypyrrole at 10 mV/sec is 29.82F/gm which is calculated using following equation

$$C_{sp} = \frac{\int I\,dv}{2mV} \qquad \text{.....1)}$$

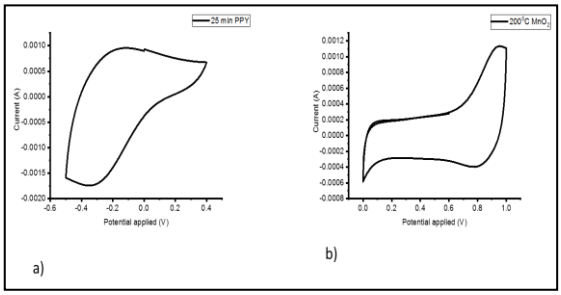

Figure 4. Cyclic Voltammetry for a) Polypyrrole in 0.5 M Na_2So_4 b) MnO_2 in 1 M Na_2So_4

Where $\int I\,dv$, is defined as average charge deduced from CV, active material' mass is represented by m that is deposited on working electrode. Similarly supercapacitance of Mno2 were measured using cyclic voltammetry technique. Fig 4b shows cyclic voltammetry curve of MnO2 for scan rate 10 mV/sec at voltage range 0 to 1 volt. Its area under the curve is lower than PPY, it shows better performance as compared to PPY because at 10 mV/sec the Na+ diffusion from the electrolyte may access to the almost all interior of the nanoparticles matrix, leading to a complete insertion reaction and therefore this

provides a reduction procedure but PPY does not give any reduction process. The maximum supercapacitance calculated using equation 1 is 184.42 F/gm.

In this synthesis, MnO2 shows maximum supercapacitance as compared to Polypyrrole.

d.2 Galvonostatic charging and discharging curve:

Figure 5 shows that charging curve for MnO2 and polypyrrole shows asymmetric nature of curve and MnO2 shows slightly symmetric nature of polypyrrole. initialy both curve slightly drop Voltage before discharge curve, it confirmed that both electrode have low resistance. So supercapacitance for polypyrrole and Mno2 can be calculated using following equation

$$C_{sp} = \frac{I}{m \times dv/dt}$$

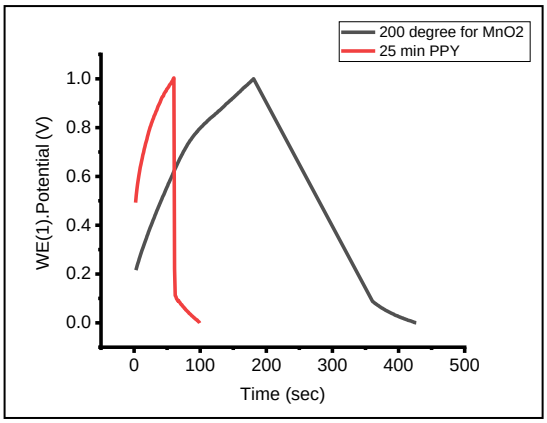

Figure 5. Charging discharging curve for MnO_2 and Polypyrrole

Here, I represent the applied current, deposited material's mass is given by m, and dv/dt is the discharge time calculated from the slope of the galvonostatic charge discharge curve. Maximum capacitance for polypyrrole is 15.96F/gm and for MnO_2 203.92.F/gm at 0.5 ma Current. So capacitance for MnO_2 is greater than polypyrrole. It is possible to compute the energy density of a super capacitor using the following equation:

$$E = \frac{1}{2} C V^2$$

Energy density for MnO2 is 103.045 (wh/kg) and Polypyrrole is 8.019 (wh/kg), so both electrode shows pseudocapacitve behaviour.

IV. CONCLUSION

We have successfully synthesized MnO2 and polypyrrole. From experimental observations, we came to the conclusion that the specific capacitance of Mno2 using cyclic Voltammetry 184.42 g/gm for 10 mV/sec and using galvanostatic charging discharging curve 203.92 F/gm for 0.5 mA current while for Polypyrrole we got specific capacitance is 29.82 F/gm for 10 mv/sec scan rate using cyclic Voltammetry technique and Charging discharging we got 15.96 F/gm at 0.5 mv over all MnO2 shows better specific capacitance as compared to poly pyrrole .ideally polypyrrole has high conductivity but in our research it shows poor Performance . The polypyrrole electrode's low capacitance is because of the high impedance along with low capacitance oxide layer formed at the film–substrate interface by anodic oxidation of stainless steel. So, if researcher used milled steel substrate performance may be improved.

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