International Journal of Scientific Research in Science and Technology
Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)
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Structural, Morphological and Supercapacitive Performance of Electrodeposited PPy/Co_3O_4 Thin Film

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ABSTRACT

The PPy/Co_3O_4 thin film was deposited by electrodeposition method for supercapacitor application. The structural, surface morphological and supercapacitive study of PPy/Co_3O_4 thin film was carried out with the help of X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) study. The structural study of PPy/Co_3O_4 thin film show cubic crystal structure. The supercapacitive study of electrodeposited PPy/Co_3O_4 thin film was carried out with the help of cyclic voltammetry (CV), charging-discharging (CD) and electrochemical impedance Spectroscopy (EIS) study. The PPy/Co_3O_4 thin film gives maximum specific capacitance of 435 $F.g^{-1}$ at 5 $mV.s^{-1}$ in 0.5M Na_2SO_4 aqueous electrolyte solution. The PPy/Co_3O_4 thin film shows coulombic efficiency of 98% while specific energy and specific power was observed to be 80.4 Wh. kg^{-1} and 20.4 kW kg^{-1} respectively. From EIS study, PPy/Co_3O_4 thin film has values of R_s and R_{CT} to be 0.62 Ω and 2.22 Ω respectively at 1V.

Keywords: Supercapacitor, Electrodeposition, PPy/Co_3O_4, XRD, SEM, EIS.

I. INTRODUCTION

Supercapacitor is an electrochemical device having better energy density and power density as compared to conventional capacitor and ordinary batteries. The most of the researchers are trying to develop a new materials which having a good capacity of both delivering energy density and power density in a particular application. Generally, supercapacitors are broadly classified as Pseudocapacitors and electric double layer capacitors (EDLC). The classification is purely based on the types of mechanism of charge storage inside the electrode materials [1].

The Pseudocapacitors are the class of supercapacitors, shown by metal oxide and conducting polymers while the EDLC class of supercapacitors are shown by carbon based materials

[2]. The most studied and better metal oxide for supercapacitive study is ruthenium oxide, but unfortunately ruthenium oxide has some drawbacks such as toxic in nature and too much cost as compare to others. Hence, other metal oxide can replaced for ruthenium oxides such as manganese oxide [3-4], cobalt oxide [5], nickel oxides [6] etc. Amongst of all oxides, cobalt oxide has some features such as availability of source of materials, less toxic than ruthenium oxide, better cycling stability etc. In spite of this, it has less conducting. Conductivity of cobalt oxide electrodes can be improved with the help of some dopant or any other methods such as annealing, making hetero structure with conducting polymer. So by keeping this view in mind we have developed a PPy/Co_3O_4 layered heterostructures by electrochemical deposition method.

In the present study, efforts have been taken to prepare a PPy/Co_3O_4 hetero structure based thin film. The electrochemically prepared PPy/Co_3O_4 thin film have been characterized for structural and morphological study by means X-ray diffraction (XRD) study and Scanning electron microscopy (SEM) study, respectively. The supercapacitive study was carried out in 0.5 M Na_2SO_4 electrolyte solution with the help of cyclic voltammetry, charging-discharge study and electrochemical impedance spectroscopy study.

II. EXPERIMENTAL

2.1. Synthesis of PPy/Co_3O_4 thin film:

The PPy/Co_3O_4 thin film was synthesized following procedure reported earlier literature [7]. Before deposition, the SS substrates was polished with emery polish paper rough to finish and rinsed with double distilled water and acetone. Firstly for deposition of PPy thin film, the bath contains aqueous 0.12 M pyrrole solution was mixed with aqueous 0.12 M H_2SO_4 solution and PPy thin films were deposited on stainless steel (SS) substrates using electrodeposition method at constant current density of 5 mA cm^{-2} for 10 minutes. The PPy thin film deposited on SS substrate was used for further deposition of layered PPy/Co_3O_4 thin film. The cobalt was deposited on PPy at constant current density of 5 mA for 10 minutes and anodically oxidized in 0.5 M KOH solution. The deposited layered PPy/Co_3O_4 thin film was used for further characterization.

2.2. Characterization Techniques:

The structural study of PPy/Co_3O_4 thin film was carried out with the help of XRD using Bruker axes D8 Advance Model with cu radiation (K_α of $\lambda = 1.54$ A°) within 2θ range between 20° to 80°. The surface morphology of PPy/Co_3O_4 thin film was carried out by using SEM (Model: JSM-6160). The supercapacitive performance of PPy/Co_3O_4 thin film was studied by using CV, CD and EIS techniques by using electrochemical workstation (CHI 660 A). The electrochemical cell consists of three electrode systems. PPy/Co_3O_4 thin film was used as a working electrode, graphite was used as a counter electrode and saturated calomel electrode (SCE) was used as a reference electrode. All measurements were carried out in 0.5 M Na_2SO_4 electrolyte solution.

III. RESULTS AND DISCUSSION

3.1. XRD Study:

XRD is an imperative tool to analyze the crystal structure of the prepared film. Fig. 1 show XRD spectra of PPy/Co_3O_4 thin film in 2θ range between 20° to 80°. The XRD spectra of PPy/Co_3O_4 thin film shows all peaks corresponds to Co_3O_4 thin film. The peak indexed in XRD spectra was well matched with JCPDS data (Card No 42-1467) having cubic crystal structure [5]. The most intense peak was found to be (220). The Co_3O_4 thin film deposited on PPy layer was found to be polycrystalline in nature also the peak broadening indicates the formation of nanostructure. The most intense peak (220) indicating the overall growth of Co_3O_4 material is along the direction perpendicular to the (220) plane

(i.e. along [220] direction). The peak marked with SS in XRD spectra is stainless steel substrate only and no additional peak was observed in the XRD of PPy/Co_3O_4 thin film. The low intensity peak in XRD spectra reveals the nanostructured formation of layered PPy/Co_3O_4 thin film.

3.1.2. SEM study:

Fig. 2 (A-B) shows SEM micrographs of PPy/Co_3O_4 thin films at two different magnifications. The SEM micrographs indicating that the substrate was well covered with thin layered structure of polypyrrole followed by Co_3O_4. At higher magnification in Fig. 2(B), it is observed that the nano-grains like structure of Co_3O_4 is formed on polypyrrole layer. Also, it shows some voids within the layered structure of Co_3O_4. Such morphology provides more active sites for electrochemical reactions. The electrochemical reactions may be due to both polypyrrole and Co_3O_4 thin films. Polypyrrole improves conductivity of thin film Co_3O_4 enhances supercapacitive performance because of availability of more reactive sites.

3.2. Supercapacitive Study:

3.2.1. Cyclic Voltammetry (CV) Study:

CV techniques is an important tool to measure the specific capacitance of the electrode material. Fig. 3(A) shows the CV curves of PPy/Co_3O_4 thin film at scan rate of 5 and 10 mV/s within potential limit between -1.00 to +1.00 V vs SCE, respectively. The nature of CV curve nearly rectangular in shape. Also as scan rate increases, area under curve increases and cathodic and anodic peak shift towards more positive and negative direction indicating the ideal pseudocapacitive behaviour of PPy/Co_3O_4 thin film. The specific capacitance of the PPy/Co_3O_4 thin film was evaluated using following formulae,

$$\text{Specific capacitance } (C_s) = \frac{C}{W} \quad \text{---------- (1)}$$

Where, C is capacitance in farad and W is the mass of the active electrode material.

The calculated value of specific capacitance of PPy/Co_3O_4 thin film was found to be 435 $F.g^{-1}$. The high value of specific capacitance of PPy/Co_3O_4 thin film is may be due to porous and nanostructured surface behaviour of PPy/Co_3O_4 thin film, which is confirmed from XRD and SEM study. This increase in specific capacitance is attributed to synergistic effect of PPy and Co_3O_4 thin film. It is believed that nanostructured electrode material provide high surface area of electron intercalation and de-intercalation into from electrode/electrolyte interface to store more charge. It improves the capacitive character [8].

3.2.2. Charging-discharging study:

Fig. 3 (B) shows charge-discharge curves of PPy/Co_3O_4 thin film at current density of 5 mA/cm^2. The exponential increment in potential was observed in charging curve reveals charge storage capability of PPy/Co_3O_4 thin film. The potential drop at the starting of discharge curve is due to internal resistance of the electrode. The discharge curve also shows that slow decrement in potential indicate good capacitive behaviour of PPy/Co_3O_4 thin film. The supercapacitive parameters such as, coulombic efficiency, specific energy and specific power of PPy/Co_3O_4 thin film were calculated by following formulae:

$$\text{Coulombic Efficiency } (\eta) = \frac{T_d}{T_c} \text{x} 100 \quad \text{---------- (2)}$$

$$\text{Specific power (P)} = \frac{V \text{ X } I}{W} \quad \text{---------- (3)}$$

$$\text{Specific energy (E)} = \frac{V \text{ X } I \text{ X } T_d}{W} \quad \text{---------- (4)}$$

Where, T_d and T_c is discharge and charge time in sec, V is voltage in volts, I is current in A, W is the mass of the electrode in gm.

The coulombic efficiency of PPy/Co_3O_4 thin film was found to be 98%. The values of specific energy and specific power of PPy/Co_3O_4 thin film were observed to be 80.4 Wh. kg^{-1} and 20.4 kW kg^{-1} respectively.

3.2.3. EIS Study:

Fig.4 shows EIS study in terms of Nyquist plot of PPy/Co_3O_4 thin film within frequency range of 10 Hz to 1MHz at different potential such as 1V, 1.2V and 1.4V, respectively. The Nyquist plot PPy/Co_3O_4 thin film shows semicircle in high frequency region and straight line in low frequency region [9]. The intercept of the semicircle on Z' axis gives value of solution resistance (R_s) and diameter of semicircle gives value of charge transfer resistance (R_{CT}). The value R_s and R_{CT} calculated from Nyquist plot were found to be 0.62 Ω and 2.22 Ω, respectively for 1V; that of 0.74 Ω and 2.89 Ω, respectively for 1.2V; and that of 0.90 and 3.15 Ω, respectively for 1.4 potential of PPy/Co_3O_4 thin film. It was observed that as applied potential increases values of R_s and R_{CT} increases. The applied potential of 1V for PPy/Co_3O_4 thin film shows small values of R_s and R_{CT} than other potentials indicating superior rate capability of electrode due to porous and nanostructured PPy/Co_3O_4 thin film [4].

IV. CONCLUSION

Nanostructured layered heterostructures of PPy/Co_3O_4 thin film was successfully synthesized by electrochemical deposition method. Their structural and surface morphological behaviour were studied by using XRD and SEM techniques. The SEM study of PPy/Co_3O_4 thin film reveals that porous and nano-grains morphology which is favourable for electrochemical capacitor application it provide high surface area, easy transfer of electron for calation and decalation process. The layered PPy/Co_3O_4 thin film show better values of specific capacitance, specific energy and specific power due to synergistic effect of PPy and Co_3O_4 thin film. Thus, electrochemically deposited layered PPy/Co_3O_4 thin film is good electrode material for supercapacitor.

V. ACKNOWLEDGEMENT

Authors are grateful to Dr. S. B. Kulkarni, Institute of Science, Mumbai, for providing research facility and giving an inspiration during research work.

VI. REFERENCES

[1]. P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, Nat. Mater. 7(2008) 845-854.

[2]. D. Wei, M.R. Scherer, C. Bower, P. Andrew, T. Ryhanen, U. Steiner, A Nanostructured Elect rochromic Supercapacitor, Nano Lett. 12 (2012)1857-1862.

[3]. Z. Yu, B. Duong, D. Abbott, J. Thomas, Highly ordered MnO2 nanopillars for enhanced supercapacitor performance, Adv. Mater. 25(2013)3302-3306.

[4]. P.M. Kharade, S.B. Kulkarni, D.J. Salunkhe, Nanoflakes like hydrophilic Mn2O3 thin film as a supercapacitor electrode, Chinese J. Phy. 55 (2017)1684-1689.

[5]. P.M. Kharade, J.V. Thombare, A.R. Babar, R.N. Bulakhe, S.B. Kulkarni, D.J. Salunkhe, Electrodeposited nanoflakes like hydrophilic Co3O4 as a supercapacitor electrode, J Phys Chem Solids. 120 (2018)207–210.

[6]. L. Gu, Y. Wang, R. Lu, L. Guan, X, Peng, J. Sha, Anodic electrodeposition of a porous nickel oxide-hydroxide film on passivated nickel foam for supercapacitors, J. Mater. Chem. A. 2 (2014) 7161-1764. 7161-1764.

[7]. P. M. Kharade, S. M. Mane, S. B. Kulkarni, P. B. Joshi, D. J. Salunkhe, Ground nut seed like hydrophilic polypyrrole based thin film as a supercapacitor electrode, J. Mater. Sci. 27 (2016)3499–3505.

[8]. P. M. Kharade, J. V. Thombare, S. L. Kadam, S. B. Kulkarni, D. J. Salunkhe, Layered PPy/Cr2O3 as a supercapacitor electrode with improved electrochemical performance, J Mater Sci: Mater Electron (2017) 28:17908–17916.

[9]. J. Zhao, B. Tang, J. Cao, J. Feng, P. Liu, J. Zhao, Effect of hydrothermal temperature on the structure and electrochemical performance of manganese compound/ordered mesoporous carbon composites for supercapacitors, Mater. Manuf. Process. 27(2012)119-124.

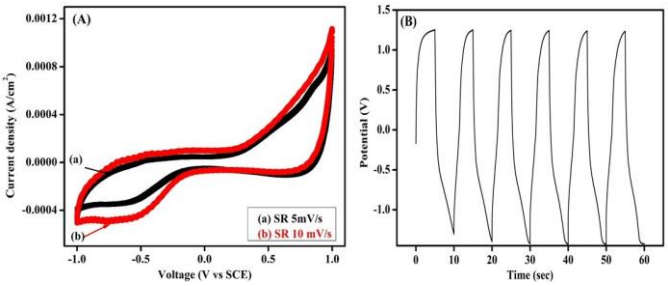

Figure 3 (A) CV study of PPy/Co_3O_4 thin film at scan rate of 5 and 10mV/s and **(B)** Charging-discharging study of PPy/Co_3O_4 thin film.

Figures:

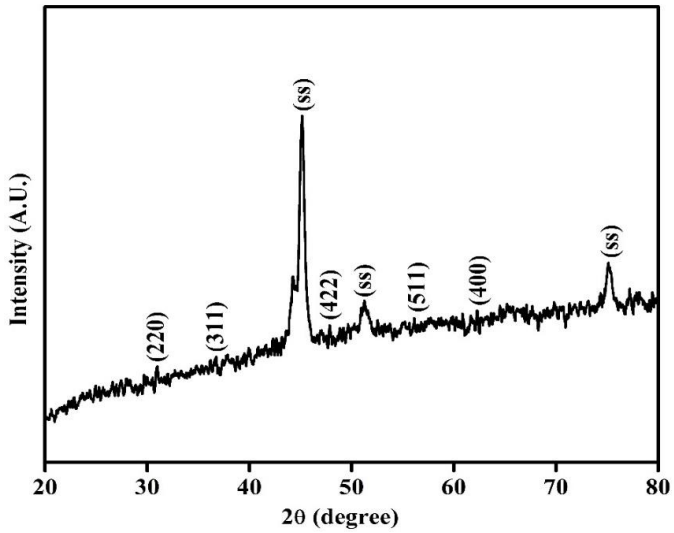

Figure 1. XRD spectra of PPy/Co_3O_4 thin film.

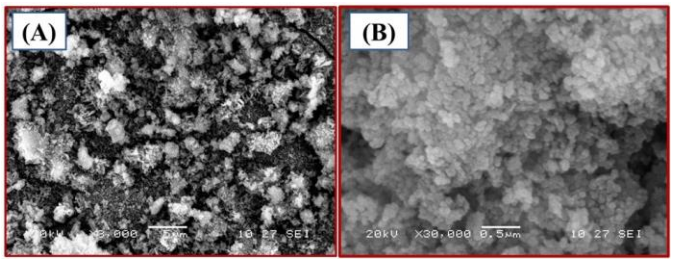

Figure 2. SEM images of PPy/Co_3O_4 thin film at **(A)** 3000kX and **(B)** 30000kX magnifications respectively

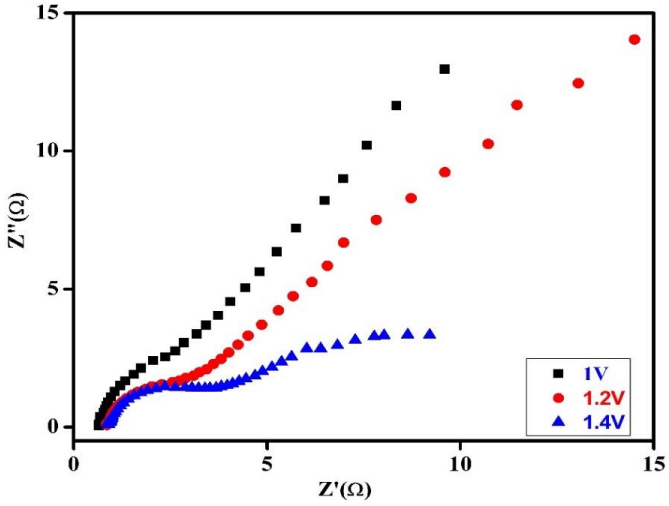

Figure 4. EIS study of PPy/Co_3O_4 thin film.