International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2022): 7.942

Synthesis of Polypyrrole / Mno_2 Composite and Characterization

Priti N. Jadhav[1], Dr. K. V. Sukhatankar[2]

[1, 2]Department of Physics, Gogate Jogalekar College Ratnagiri, 415612, Maharashtra, India
[1]*pnjadhav609[at]gmail.com*
[2]*ksukhatankar[at]gmail.com*

Abstract: ***This work is related with electrodeposition of composite form of MnO_2 and polypyrrole (PPY) using Potentiostatic electrodeposition Method, and study of super capacitive behaviour. Here supercapacitive behaviour is studied by Cyclic Voltammetry technique in 1M of Na_2SO_4, maximum specific capacitance for composite material is 128F/gm and maximum columbic efficiency is 99.97%.Similarly supercapacitive behaviour is also studied by charging-discharging, Nyquist Impedance spectroscopy. Surface morphology is observed by scanning electron microscope (SEM), x-ray diffraction (XRD), and Raman spectroscopy technique.***

Keywords: Composite, Surface Morphology, Columbic Efficiency, Potentiostatic

1. Introduction

Super capacitors are also known as electrochemical capacitor. They utilize high surface areas, electrode materials and thin electrolytic dielectric. Capacitance of super capacitors is larger than conventional capacitor [7-11]. Super capacitors have greatest energy density and power density. Super capacitors are generally used in electrochemical batteries and fuel cell, they are classified into two groups, one is electrochemical double-layer capacitor and other is pseudo capacitors .The electrochemical double layered capacitors are constructed from two carbon based electrode, electrolyte and separator, while pseudo capacitors store charge faradically through the transfer of charge between electrode and electrolyte. Pseudo capacitors are obtained from electrosorption, reduction-oxidation reaction and intercalation process [7,12]. Conducting polymer and metal oxides shows the pseudo capacitve behaviour.

There are many metal oxides available in nature .MnO_2 is one of most high electrochemical active material, environmental compatibility, low cost and abundantly available in earth. The electrochemical performance of MnO_2 nano particle is largely dependent on their microstructure and surface area. Similarly polypyr role is high conductive, easily synthesizable and low cost polymer. Polypyr role shows redox active properties hence, it is used in super capacitor and battery application.

Due to high super capacitor behaviour of polypyr role and MnO_2, most of the researchers studied their composite behavi our. Shalini Kulandaivalu, Nadhrah suhaimi and yusran Sulaiman [3] have reported specific capacitance of MnO_2/ppy as 786.6 F/g. Liang Zhang, Xiallei Peng [4] have reported specific capacitance in composite form as 239 F/g, R. K. Sharma, A. c. Rastogi [5] have reported specific capacitance as 620 F/gm, Jiaypu tao, Nishuang Liu [6] have reported specific capacitance for composite material as 69.3F/gm.

In this research paper, by using AR grade chemicals, we have Potentio statically deposited Polypyrrole and MnO_2 on stainless steel compositely. For confirmation of composite material, material was characterised by XRD, Raman spectra technique and its morphology was studied by using SEM technique. Electrochemical behaviour was studied by using Cyclic Voltammetry, galvonostatic charging-discharging and electrochemical impedance spectroscopy technique.

2. Experimental Method

For synthesis of Mno2/polypyr role, we have used AR grade $MnSO_4$. H_2O, KOH, Pyrrolemonomer (99%pure), dehydrated 5sulfosalycylic acid etc. Before electrode position of MnO_2/PPY, steel substrate was polished using zero grade polish paper, it was washed well with mild detergent, then rinse it with acetone and ethanol, etched substrate in HNO_3 for few secthen rinsed it ultrasonically with distilled water. For synthesis of MnO_2 ,we have used 0.1M of $MnSO_4.H_2O$, to adjust pH up to 6.5 we added(0.05M) KOH slowly and with the help of magnetic stirrer, kept the solvent for 1 hour to stir, after then using potentiostatic electrode position method 0.95V voltage was applied across reference and working electrode(Stainless steel) for 20 min. After deposition,MnO_2 electrode was rinsed with distilled water and annealed it at 200^0c for 1 hour, once MnO_2 was synthesized, for synthesis of polypyrrole 0.1M pyrrole monomer is used, to adjust pHUpto2.2,0.01M5sulfosalicylic acid is added slowly and solution was stirred for 1 hour. By using potentiostatic electrode position Method 0.7 V was applied across reference electrode and Mno2 electrode for 25 min, so polypyrrole deposited on MnO_2 electrode, this process is related with layer to layer electrodeposition process. After electrodeposition of polypyrrole, sample was rinsed with distilled water and was dried at room temparature,mno2/ppy sample was annealed at 70^0c for 3 hours. Electrodeposition Method was carried out by three electrode system, stainless steel was used as working electrode, graphite used as counter electrode and saturated calomel used as reference electrode.

For study of super capacitive behaviour of MnO2, in 0.1 $MnSO_4.H_2O$solution added 0.05M KOH for maintaining pH of solution equal to 6.5. $MnO_2$was deposited on Separate

Substrate Potentiostatically at 0.95V for 20 Min. similarly we have studied super capacitive behaviour of PolyPyrrole separately. For Polypyrrole bath contain 0.1 M Pyrrole and adjusted pH of Pyrrole solution equal to 2.2 by adding 5 sulphosalicylic acid. Polypyrrole was Potentiostatically deposited on steel substrate at 0.7 V for 25 min

The MnO_2/PPY, MnO_2, Poly Pyrrole samples were electrochemically characterized by cyclic voltammetry technique, charging-discharging technique, Nyquistimpedance spectroscopic technique using Metrohm autolab potentiostatic204, and is confirmed from the XRD and Raman spectroscopy technique.

3. Result and Analysis

3.1 XRD

Figure 1 shows that amorphous structure of MnO_2/polypyrrole, MnO_2, Polypyrrole. More intense peaks in XRD, which are indicated by square shows the peaks of stainless steel, Amorphous nature of XRD is more fissile for super capacitor. Because ion are easily penetrate inside the active material, all so from XRD it confirmed that amorphous phase of all material. from figure 1a peak at 23 - 35^0(indicated by triangle) indicating the diffraction peak of polypyrrole and suggest that Polypyrrole phase is amorphous and at 2thita =64.44^0(002), 37.35^0, 83.21^0(212), we have confirmed that peak of MnO_2(exactly match with Match3 software JCPD no.-96-151-4118), from fig 1b there is no diffraction peak other than substrate peak, substrate peak indicated by square. From figure 1b confirmed that amorphous phase Polypyrrole. And from fig 1c peak at 64.52^0 shows amorphous and slightly crystalline nature of gamma MnO_2 .

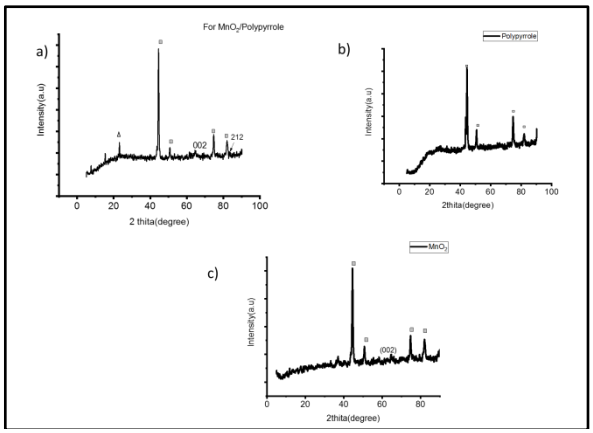

Figure 1: XRD of a) MnO_2/ polypyrrole composite b) for Polypyrrole c) For MnO_2

3.2. Raman spectra

Figure2 shows the Raman spectroscopy of MnO_2/ppy, PPY, MnO2. Peak at 921 cm-1,931 cm^{-1} attributes the polypyrrole ring, 975,972 cm^{-1}attributes C-H Bond, peak at 1045cm^{-1},1052 cm^{-1}shows C-H plane symmetry band, Peaks at 1323cm^{-1},1377 $cm^{-}$and 1416 cm^{-1} shows C-N asymmetry plane .Peaks at 1577 cm^{-1}, 1584 cm^{-1} are obtained because of the C=C backbone stretch of PPY, so the presence of polypyrrole is confirmed. Peaks at 645 $cm^{-1}$is main peak of MnO_2 .So from Raman spectra it is confirmed that MnO_2 and PPY are present. form fig a and b, shows composite Raman spectra almost same as polypyrrole Raman spectra because according to EDS Spectra the atomic weight of MnO_2 is small as compared to polypyrrole .

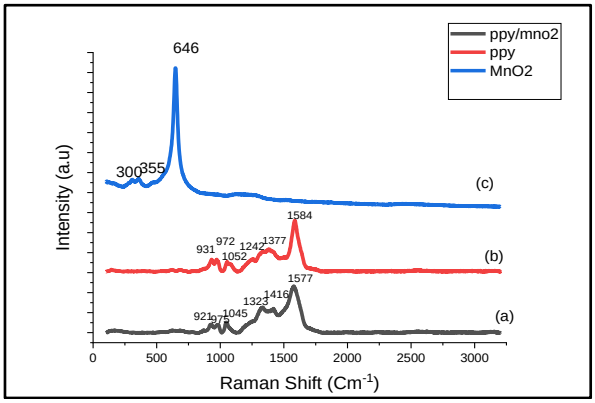

Figure 2: Raman spectroscopy for MnO_2/ PPY

3.3. Surface Morphology Material

Surface morphology of Materials was studied by Scanning of electron Microscope which is shown in figure. Figure3 shows MnO_2, PPY, MnO_2/PPY films grown with potentiostatic deposition on stainless steel substrate. Figure3c shows that the whole surface of film is covered with nano particles of $MnO_2$and its size is about 0.03 µm also particles of polypyrrole are deposited on it, in nodule like structure [14]. Film is slightly porous due to MnO_2.figure 3a shows that granular like structure of MnO_2 its size about0.1 µm. figure 3b shows that particles are uniformly distributed and shows cloud like cluster structure its size about 480 nm. so at composite deposition size of MnO_2 is less as MnO_2 thin film particle size.

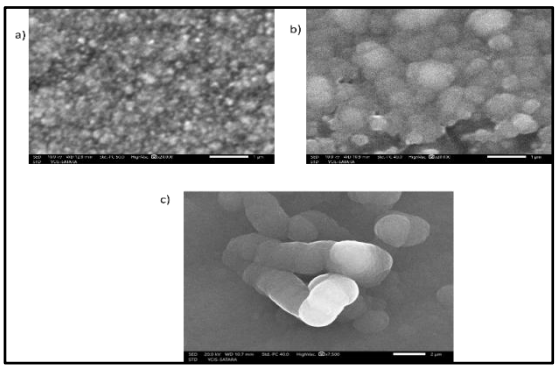

Figure 3: SEM Image of a) MnO_2 b)PPY c) MnO_2/PPY

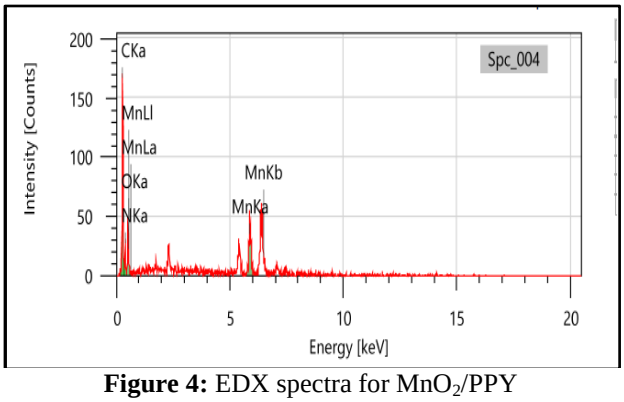

Figure 4: EDX spectra for MnO_2/PPY

Figure 4 shows EDX spectra of MnO_2/PPY. The coating of polypyrrole and MnO2 in composite form is further verified by energy-dispersive x- ray spectroscopy analysis (EDX). The significant amount of carbon, nitrogen, manganese, and oxygen signals are detected on MnO_2/PPY sample which is shown in the following table1

Table 1: EDAX data for MnO2/PPY

Element	Mass%	Atom%
C	42.85±0.78	54.13±0.99
N	21.04±1.62	22.79±1.76
O	19.49±1.35	18.49±1.28
Mn	16.61±0.93	4.59±0.26
Total	100	100

3.4. Electrochemical properties

3.4.1 *CyclicVoltammetry (CV)*

Super capacitive behaviour of MnO_2/PPY, MnO_2 were studied by cyclic voltammetry technique at voltage range from 0 to 1V for 20 mV/sec in 1 M of Na_2SO_4solution. Super capacitive behaviour of PPY was studied by cyclic Voltammetry technique at voltage range from -0.5 V to 0.4 V for 20 mV/sec in 0.5 M Na2SO4.The maximum capacitance Of MnO2/PPyY composite, MnO2 and polypyr role obtained at 20 mv/sec is 128 F/gm,145 F/gm,55.11 F/gm,figure5a,b,&c shows the pseudo capacitive behaviour of MnO_2/PPY film, MnO_2 film and PPY. Area of Cyclic Voltammetry curve For MnO2 is maximum as compared to MnO2/Ppy composite and ppy so it show maximum specific capacitance as compared to other films. The specific capacitance stability was studied by plotting graph of specific capacitance against number of cycle which is shown in figure 5d. After 1000 cycle for 100mV/sec in 1M of $Na_2So_4$the capacity retention for Mno2/PPy is 78.87% and coulomb efficiency is 99.97%.Andfor MnO_2 is 91.73% and coulomb efficiency is 99.99%. For Polypyrrole stability is very less due to Because of dissolution and oxidation of substrates in the electro polymerization process, adherence of film is a major challenge for electrodeposition of PPY on stainless steel. But MnO2 thin film is more stable than Mno2/ppy composite and PPy film.Mno2/ppy is also stable due to presence of MnO2.

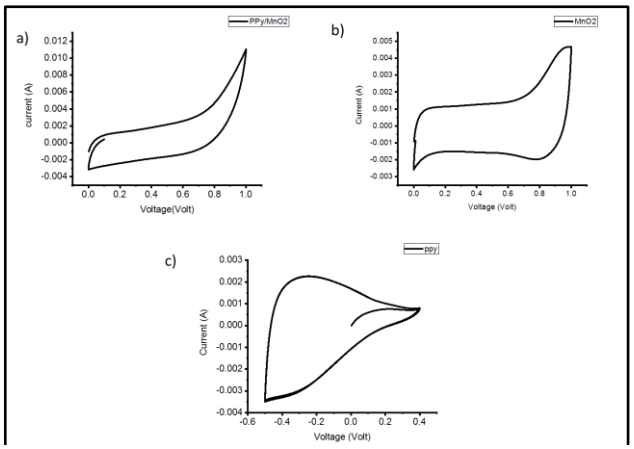

Figure 5(a): Cyclic Voltammetry for MnO_2/PPY in 1 M Na_2So_4 at 20 mV/sec

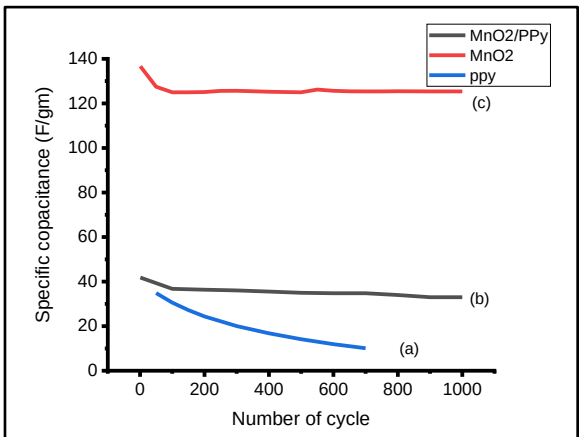

Figure 5(d): Plot of specific Capacitance Vs. Number of cycle for a) MnO_2b) MnO_2/PPY c) PPY for 100 mV/sec

3.4.2. Galvanostatic Charging-Discharging curve

Galvonostatic charging-discharging curve at currents 0.5 mA is shown in, at0.5 mA specific capacitance for MnO2/ppycomposite is50.86 F/gm,for PPY specific capacitance is 21.66 F/gm and for MnO2 specific capacitance is 203.92F/gm.so from Galvanostatic charging discharging curve MnO2 thin film shows maximum specific capacitance as compared to other material. Small voltage drop initially before discharging curve. The energy density for PPY,MnO_2/PPY composite and MnO2 is 10.57Wh/Kg,25.09Wh/Kg and 103.045 Wh/Kg.so MnO2 shows high current density as compaired to others film.

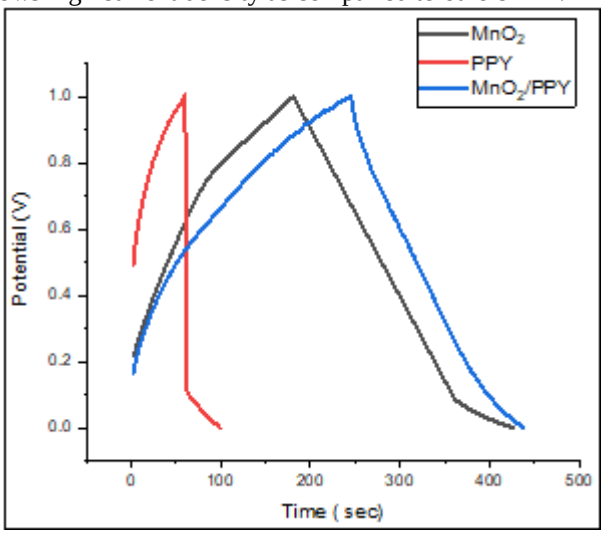

Figure 6 (a): galvonostatic charging-discharging curve for MnO_2/PPY in 1 M Na_2So_4

3.4.3 Electrochemical Impedance spectroscopy:-

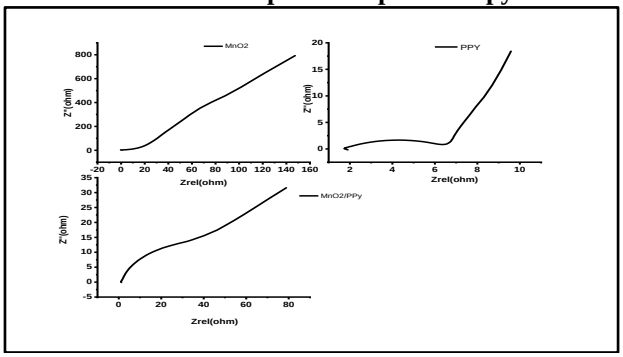

Figure 7: Nyquist plot for MnO_2/PPY composite in 1M Na2So4

In figure7, electrochemical performance of MnO_2, PPY and MnO_2/PPY were studied by electrochemical impedance spectroscopy technique, at frequency range from 0.1MHz to 0.1 Hz. The Electrochemical impedance Spectroscopy plots at high frequency region are collected and results show that, MnO_2/PPY, MnO_2, PPY gives lower equivalent series resistance (Rs) equal to 1.06, 4.54, 1.73ohm and semicircle is absent at high frequency side for MnO2/ppy and MnO2 film so it suggests that lower charge transfer resistance (Rct= 0 ohm),the charge transfer resistance for polypyr role is 4.7 ohm. At low frequency side, nature of the graph is linear. This result suggests that MnO_2/PPY, MnO_2 exhibits better capacitive performance with low charge transfer resistance and diffusion resistance.

4. Conclusion

XRD and Raman spectra confirmed that synthesis of MnO_2 /PPY in composite form, MnO2,PPy ,their nature is amorphous in nature, so maximum capacitance is obtained at 20mV/sec is 128 F/gm,145 f/gm,55.11 F/gm for MnO2/PPY,MnO2/PPY, using cyclic voltammetry, similarly in charging-discharging curve we observed super capacitive behaviour of MnO_2/PPY,MnO2,PPY Films. 78.87% and 99.97% retention and coulomb efficiency is obtained from stability curve of MnO_2/PPY and 91,73% and 99.99% retention and coulomb efficiency is obtained for MnO_2 so MnO2/PPY film is more stable than PPY but slightly less stable than MnO_2.

Acknowledgement
I would like to thanks Department of Physics, Chemistry Gogate Jogalekar college, Ratnagiri, Yashwant Roa Chavan institute of science Satara, Department of Physics Shivaji university for helping in research work, I would like to thanks my guides Dr. K. V. Sukhatankar and Dr. M. M. Belekar sir for their valuable guidance also lately i would like to thank my freelancer Miss. Manwa Sudesh Kamble for providing language help and proof reading.

References

[1] Sutar Rani Anand ,Murugrndrappa M.V,international journal of material Science ISSN0973-4589 volume 12 number 2(2017).
[2] Rashmi Saxena,Kananbala Sharma, N.S.Saxena, international Journal of applied Engineering research ISSN0973-4562 volume 13, number 8(2018) pp.40-43.
[3] Shalini Kulandaivalu,Nadhrah Slhaimi & yusran Sulaiman,Scientific reports 20 march 2019 https://doi.org/10.1038/s41598-019-41203-3.
[4] Liang Zhang,xiaolei Peng,Junning wan,Qiang cui,Xuefeng chu,World Scientific Publishing Nano Brief Rrports and Reviews Vol.15,NO.3 (2020)2050031, doi: 10.1142/S1793292020500319
[5] R.K Sharma, A.C.Rastogi,S.B.Desu,Electrochemica Acta 53(2008)7690-7695, doi:10.1016/j.electacta.2008.04.028.
[6] Jiaypu Tao,Nishuang Liu,Wenzhen Ma,Longwei Ding,luying Li,Jun Su &Yihua Gao,Scientific report 2013,DOI:10.1038/srep02286.
[7] Conway, B. E. (1999). Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications. New York, Kluwer-Plenum.
[8] Burke, A. (2000). "Ultracapacitors: why, how, and where is the technology." Journal of Power Sources 91(1): 37-50.
[9] Kotz, R. and M. Carlen (2000). "Principles and applications of electrochemical capacitors." Electrochimica Acta 45(15-16): 2483-2498.
[10] Aricò, A. S., P. Bruce, et al. (2005). "Nanostructured materials for advanced energy conversion and storage devices." Nature Materials (4): 366-377.
[11] Chu, A. and P. Braatz (2002). "Comparison of commercial supercapacitors and highpower lithium-ion batteries for power-assist applications in hybrid electric vehicles I.Initial characterization." Journal of Power Sources 112(1): 236-246.
[12] Supercapacitors: A Brief OverviewMarin S. Halper, James C. Ellenbogen, MITRE Nanosystems Group (2006).