RJC

RASĀYAN *J. Chem.*
Vol. 14 | No. 1 |359-367| January - March | 2021
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

ELECTRODEPOSITION OF Cu-PPY NANOCOMPOSITE AND ITS CORROSION RESISTANCE BEHAVIOUR

S. Ramalingam[1,2,✉], S.Raji[2] and A.Subramania[2,3]

[1]Department of Chemistry, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil-626 126, Tamil Nadu, India.
[2]Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003. India.
[3]Centre for Nanoscience and Technology, Pondicherry University, Puducherry 605 014, India.
✉Corresponding Author: rama.s.lingam@gmail.com

ABSTRACT

Polypyrrole (PPY) reinforced copper nanocomposites (Cu-PPY) are prepared by using a simple electrodeposition method and characterized by XRD, SEM, EIS and Tafel polarization techniques. Polypyrrole (PPY) nanoparticles are synthesized by surfactant assisted dilute polymerization method and characterized by UV-Vis, FTIR, and Cyclic voltammetry studies. As synthesized polypyrrole (PPY) nanoparticles are used to prepare Cu-PPY nanocomposites using acid copper sulphate bath by electrodeposition technique. The Debye-sherrer formula is used to measure the average crystallite size of the electrodeposited Cu and Cu-PPY nanocomposite coatings from their XRD data are found to be ~32 nm and ~23 nm, respectively. Its structure is crystalline fcc and the texture is (220). The surface morphology of Cu-PPY nanocomposite coatings on the copper matrix showed almost spherical shaped crystallites. The Cu-PPY nanocomposite coatings have increased microhardness compared to electrodeposited copper. This is due to the reduced grain size of Cu-PPY nanocomposite coatings. Electrochemical impedance and Tafel polarisation studies revealed that the Cu-PPY nanocomposite coating in 3.5 % NaCl solution has better corrosion resistance than the pure Cu coating.

Keywords: Polypyrrole (PPY), Cu-PPY Nanocomposite, Electrodeposited Copper, Corrosion Resistance, Electrochemical Impedance, Tafel Polarization Studies.

RASĀYAN *J. Chem.*, Vol. 14, No.1, 2021

INTRODUCTION

Electrodeposition technique has provided a path to synthesis number of newer nanostructured materials in the last decade, which include nanocrystalline electrodeposits, nanowires, nanotubes, nanomultilayers, and nanocomposites.[1-11] The metal-polymer composite coating can be done in two steps by depositing conducting polymer in the first step followed by deposition of metal in the second step over the polymer film. Metal nanoparticles suspension in solution tend to aggregate over time. To prevent this, nanoparticles are confined in to the conducting polymer matrix. The conductivity and the sensing behaviour of conductive polymers such as polyaniline and polypyrrole (PPY) were improved by embedding metal nanoparticles in to the polymer matrix to form a metal-polymer nanocomposite. These metal-polymer nanocomposites exhibits enhanced physical, chemical and electrochemical properties.[12-16]
Polypyrrole is one of the series of heterocyclic conductive polymers with conjugated double bonds that has been fascinated by its characteristic electrical and electronic properties.[17-20] Polypyrrole (PPY) can be used as gas sensors, biosensors, microactuators, wires, anti-electrostatic coatings, supercapacitors, electrochromic windows and screens, polymer batteries, electronic and packaging tools, etc. Polypyrrole (PPY) is a possible drug delivery vehicle; the polymer matrix acts as a protein container.[21-31] So far the polypyrrole (PPY) based electrodeposited metal–polymer nanocomposites such as Ni/PPY, Fe-PPY, Au-PPY etc.[12-16] and Cu-graphite, Cu-MoS_2, Cu-PTFE, Cu-PANI, Cu-PDPA , Cu-MWCNTs, Cu-Graphene etc[32-35] have been developed, but there is no report on Cu-PPY nanocomposite coatings. Hence, in the present investigation, the possibility of incorporation of polypyrrole nanoparticles in the copper matrix has been developed by acid copper sulphate bath using a direct current electrodeposition method. They were characterized by XRD, SEM ,Eectrochemical impedance and Tafel polarisation studies for the structural, morphological and corrosion resistance studies and compared with the pure Cu coating.

http://dx.doi.org/10.31788/ RJC.2021.1415939

EXPERIMENTAL

Materials and Methods

The chemicals $CuSO_4$. $5H_2O$, Sulphuric acid and Gelatin are used in this experimental study are of pure analytical grade and purchased from Merck. Polypyrrole (PPY) nanoparticles have been synthesized by using a surfactant-assisted dilute polymerization method and are used in the copper sulphate bath for the preparation of Cu-PPY nanocomposites. A simple and low-cost electrodeposition method is used for the preparation of Cu-PPY nanocomposites.

Synthesis of Polypyrrole

Polypyrrole (PPY) has been synthesized by surfactant-assisted dilute polymerization process using 0.1 M pyrrole monomer with 0.005 M CTAB (cetyltrimethylammonium bromide) surfactant in acidic medium. The oxidising agent, 0.5M ammonium persulphate was added to this reaction mixture drop by drop with continuous stirring for 24 hours. The polymerization was terminated with the addition of excess methanol. Thus, the polypyrrole (PPY) polymer formed was a block colour powder which was filtered and washed successively with distilled water, methanol and acetone and then dried.[17-21]

Electrodeposition of Cu-PPY Nanocomposites

Pure copper specimens (2 x 2 cm^2 size) have been polished using emery papers and degreased with acetone and then cleaned in alkaline solution and acid solution and washed with water to use as substrate for the deposition process. Chemically cleaned copper bar of the same size was used as anode. The $CuSO_4$ of 0.3M and 1.3M H_2SO_4 solutions at pH of ~1 was used as electrodeposition bath. Gelatin, 1.0 g/L was added as an additive for uniform, pore free and smooth surface electrodeposits. The polypyrrole (PPY) nanoparticles have been used to prepare Cu-PPY nanocomposites. Polypyrrole (PPY) concentrations of 1.0 g/L to 10 g/L were added in the electrodeposition bath with continuous stirring. Electrodeposition was carried out at 5.0 A/dm^2 for 30 minutes at 30°C. For the purpose of comparative study, the electrodeposited pure Cu coatings were also obtained from the acid copper sulphate bath under the same condition.

Charatcerization of Polypyrrole

The UV-Visible spectra for the synthesized polypyrrole were taken by Shimadzu-UVPC-2401 UV-Visible spectrophotometer. FT-IR spectrum was also taken by using a Perkin Elmer FT-IR spectrophotometer with KBr. The cyclic voltammetry studies were performed by BAS 100 A electrochemical analyzer using a three electrode cell assembly. The cyclic voltammograms were obtained by using the electrode coated with polypyrrole (PPY). The cycling potential was applied at a sweep rate of 50 mV / sec between 500 mV and 1100 mV in 1N HCl solution.

Characterization of Cu-PPY Nanocomposites

The crystallite size and structure of pure Cu and Cu-PPY electrodeposits were determined by XRD analysis (JEOL IDX 8030). The surface morphology of the electrodeposits was analyzed by SEM (Hitachi S3000H SEM model) studies. To evaluate the corrosion resistance behavior, a three electrode cell assembly was used. 1.0 cm^2 area of deposit was used as the working electrode. The Pt foil and SCE were used as the auxiliary and reference electrodes respectively. The electrodeposits were submerged for 5-10 minutes in 3.5 % NaCl solution to achieve a steady potential. Tafel polarization and AC impedance studies were carried out by Potentiostat/Galvanostat and Electrochemical impedance analyzer, respectively.

RESULTS AND DISCUSSION

Characterization of Polypyrrole

UV-Visible Spectral Studies

Figure-1 shows the polypyrrole UV-Vis spectrum. The absorption peak is observed at 337 nm is the analogous of π- π^* transition in the benzanoid ring.

FTIR Studies

The polypyrrole FTIR spectrum (Fig.-2) showed a peak at 1103 cm^{-1} suggesting C-N stretching of amines. The vibrations at 1347 cm^{-1} (N-O stretching) and 1516 cm^{-1} show the presence of pyrrole ring. The vibration at 2914 cm^{-1} suggests the C-H strong bond (sp^3 carbon).

Cyclic Voltammetry Studies

BAS-100A electrochemical analyzer was used to conduct cyclic voltammetry studies. Cyclic voltammograms were obtained using the polypyrrole coated electrode. The cycling potential between 500 mV to 1100 mV in 1N HCl solution at a sweep rate of 50 mV/sec was employed. Fig. 3 shows the cyclic voltammogram of polypyrrole (PPY) in 1N HCl solution. A cathodic peak around 1000 mV indicates the reduction behaviour of polypyrrole (PPY).

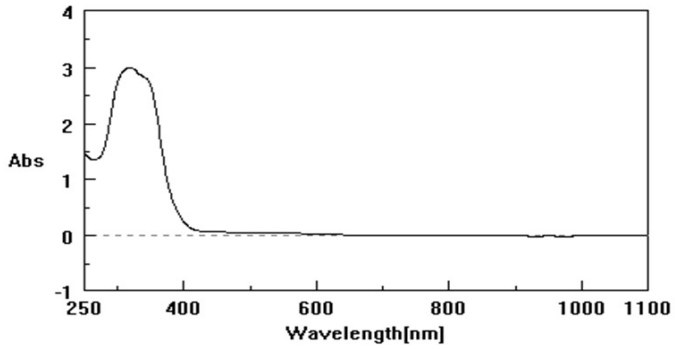


Fig.-1: UV-Visible Spectrum of Polypyrrole

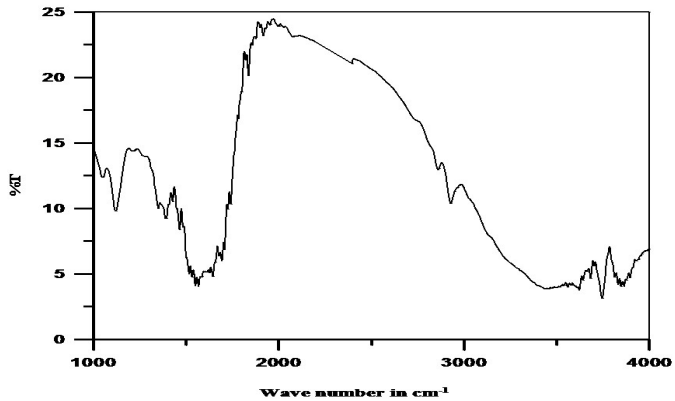


Fig.-2: FTIR Spectrum of Polypyrrole

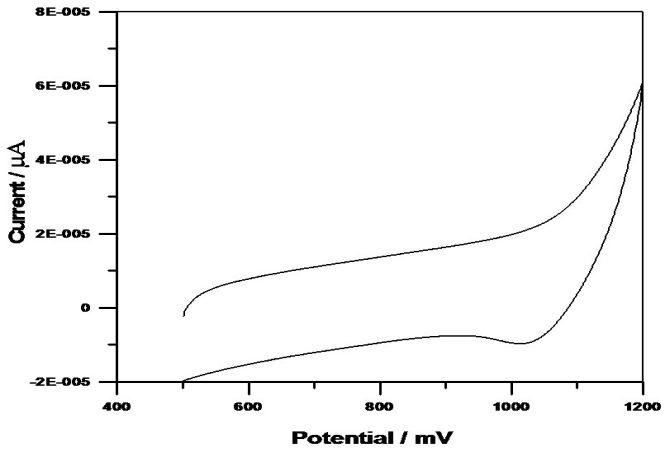


Fig.-3: Cyclicvoltammogram of Polypyrrole

Characterization of Cu-PPY Nanocomposites

The FT-IR spectrum (Fig.-4) confirming the inclusion of polypyrrole (PPY) in the copper matrix. Its corresponding spectral data are given in Table-1.

Table-1: FTIR Spectrum Data for Copper-PPY Nanocomposites

Peak cm^{-1}	Possible Assignment
2971 & 2866	Alkane C-H stretching
1530	Aromatic homocyclic C=C stretching
1499	Aromatic multiple bond C=C stretching
1295	Aromatic secondary (C-N-vib)
910	Monosubstituted alkanes C-H deformation
766	Five membered ring with 4 adjacent free H

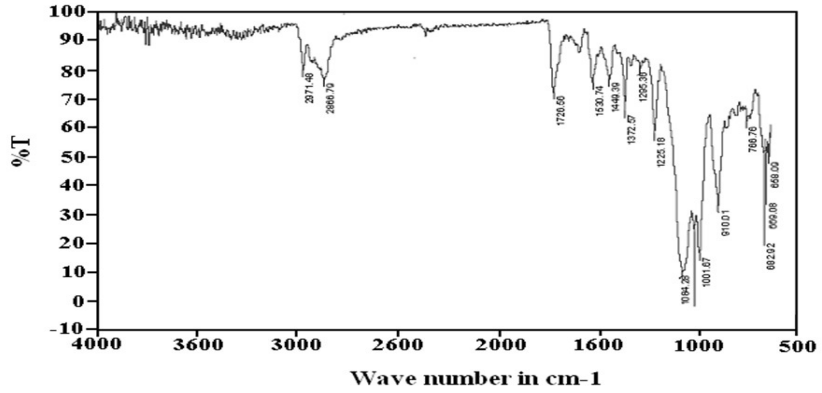


Fig.-4: FTIR Spectrum of Cu-PPY Nanocomposite Coating

The physical properties of electrodeposited Cu and Cu-PPY nanocomposite coatings were tested. The adhesion of pure Cu and Cu-PPY nanocomposite coatings are excellent. Qualitative examination of bending, scrubbing and heat / quench did not cause any separation of the coatings from the base materials. Vickers microhardness tester is used to determine the microhardness of the polished electrodeposited specimens. As compared to the electrodeposited pure copper, the microhardness of Cu-PPY nanocomposite coatings has higher value (Table-2).

Table-2: Microhardness of Electrodeposited Pure Cu and Cu-PPY Nanocomposites

S. No.	Electrodeposit	Vicker's hardness
1	Pure Cu	255
2	Cu-PPY(5 g/L) Nanocomposite coating	271

XRD Studies

The X-ray diffraction analysis (Fig.-5a and b)) determined the crystallite size and structure of the electrodeposited Cu and Cu-PPY nanocomposite coatings. Using the Debye-Scherrer formula the average crystallite size for pure Cu is calculated as ~32 nm and Cu-PPY nanocomposite coatings as ~23 nm (Table-3).

Table-3: Parameters derived from XRD Pattern for the electrodeposited pure Cu and Cu-PPY Nanocomposite

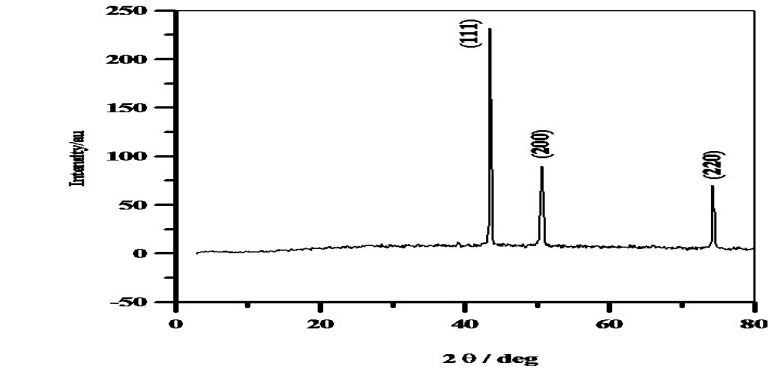
Electrod eposits	2θ	d-spacing (A°)		Miller Indices (h k l)	Lattice Parameter (a)		Str./ Phase	Avrge. Cryst. Size. (nm)
		Observed (A°)	Standard (A°)		Observed	Standard		
Pure Cu	43.486	2.0794	2.0883	(111)				

	50.615	1.8020	1.8082	(200)	3.605	3.615	fcc	~32
	74.247	1.2763	1.2780	(220)				
Cu-PPY (5 g/L) Nanocomposites	43.247	2.0903	-	(111)	3.620	3.615	fcc	~23
	50.377	1.8099	-	(200)				
	74.066	1.2790	-	(220)				

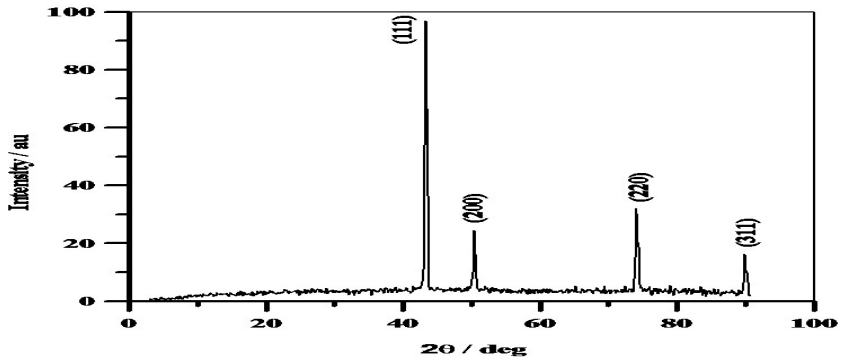
The structure of electrodeposited coatings (both Cu and Cu-PPY) is crystalline fcc which is matched with the JCPDS standard. The texture coefficient (TC) and relative texture coefficient (RTC) values for all the samples (Cu, Cu-PPY and reference Cu powder) are calculated and are given in Table-4. These results show that the electrodeposited Cu and Cu-PPY nanocomposite coatings have preferable orientations (220).

Table-4: Texture Parameters for Electrodeposited Pure Cu and Cu-PPY Nanocomposites

Electrodeposits	Plane	Intensity (%)		R_1 (%)	R_2 (%)	TC (hkl)	RTC (hkl)(%)
		Sample	Ref				
Pure Cu	(111)	100	100	59.2	60.2	0.98	30
	(200)	39	46	23.0	27.7	0.83	25
	(220)	30	20	17.8	12.0	1.48	45
Cu-PPY (5 g/L) Nanocomposite coating	(111)	95	100	59.4	60.2	0.99	28
	(200)	30	46	18.8	27.7	0.68	19
	(220)	35	20	22	12.0	1.83	52



(a)



(b)

Fig.-5. X-ray Diffraction Pattern of (a) Electrodeposited Cu and (b) Cu-PPY Nanocomposite Coatings

SEM Studies

SEM images of the electrodeposited Cu and Cu-PPY nanocomposite coatings are shown in Fig.-6(a and b). Compared to Cu-PPY nanocomposites, the electrodeposited pure Cu shows smooth and pore free surface. Polypyrrole inclusion has altered the surface morphology of Cu-PPY nanocomposite coatings. The Cu-PPY nanocomposite coating shows polypyrrole (PPY) particles of irregular size grown layer by layer.

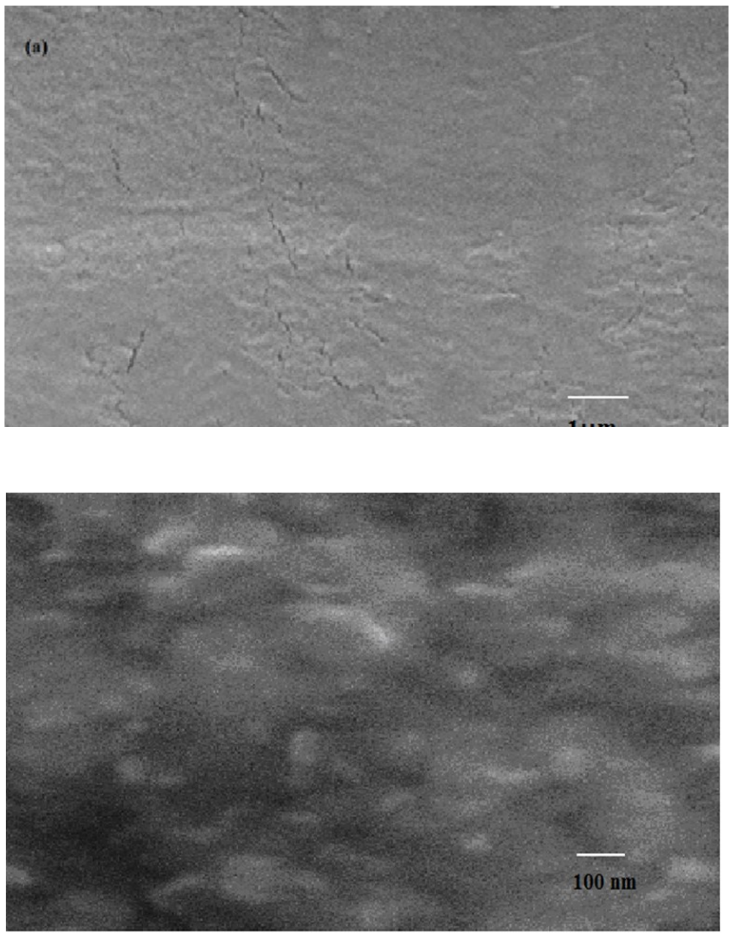


Fig.-6: SEM Images of (a) Electrodeposited Pure Cu and (b) Cu-PPY Nanocomposite Coatings.

Electrochemical Impedance Studies

The Electrochemical impedance study has been used to assess the corrosion resistance of the electrodeposited Cu and Cu-PPY nanocomposite coatings (Fig.-7). The 1.0 cm^2 coated specimen used as the working electrode, the saturated calomel electrode (SCE) was used as a reference electrode and the Pt foil was used as a counter electrode. These three electrodes were immersed in 3.5 % NaCl solution for 10 minutes to achieve a steady state open circuit potential, and then the impedance measurements were performed at the open circuit potential. The value of the charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}) are calculated from the Nyquist plots. For Cu-PPY nanocomposite coatings, the charge transfer resistance (R_{ct}) values are increased and the double layer capacitance (C_{dl}) values are decreased with increase in PPY content of the composite coatings (Table-5). It showed that Cu-PPY nanocomposite coating is found to be more corrosion resistance than the pure Cu coating.

Table-5: Impedance Parameters for the Electrodeposited Pure Cu and Cu-PPY Nanocomposites

Electrodeposit	R_{ct} (Ω/cm^2)	C_{dl}($\mu F/cm^2$)
Pure Cu	220	72.3
Cu-PPY nanocomposite (1 g/L)	550	31.2
Cu-PPY nanocomposite (3 g/L)	850	26.5
Cu-PPY nanocomposite (5 g/L)	900	12.2
Cu-PPY nanocomposite (10 g/L)	1150	9.9

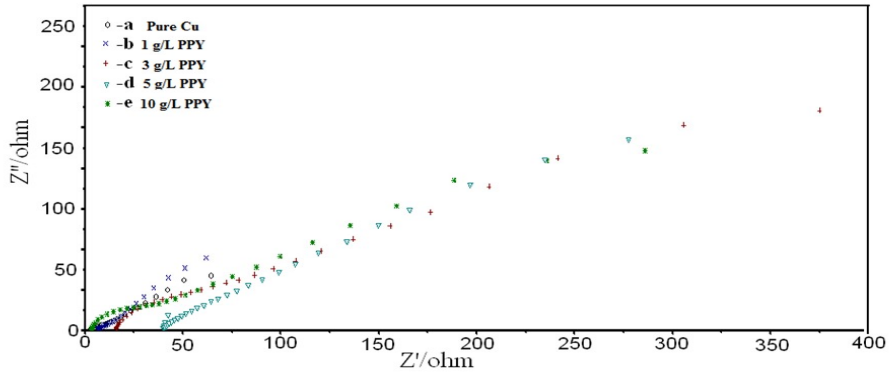


Fig.-7: Nyquist Plot of Electrodeposited Cu and Cu-PPY Nanocomposites.(a) Electrodeposited Cu and (b-d) Cu-PPY Nanocomposites

Tafel Polarization Studies

Tafel polarization studies were used to evaluate the corrosion resistance properties of electrodeposited Cu and Cu-PPY nanocomposite coatings. The cell design used for this analysis is the same as for electrochemical impedance studies. The coated 1.0 cm^2 sample was immersed in a 3.5 % NaCl solution to achieve a steady state potential. The electrode was then polarized cathodic to anodic direction from the OCP at a scan rate of 1 mV / sec in the potential range of $E_{corr} \pm 250$ mV. The corrosion current (i_{corr}) was findout by extrapolating the anodic and cathodic tafel curves (Fig.-8). For electrodeposited Cu and Cu-PPY nanocomposite coatings, the corrosion potential (E_{corr}), corrosion current (i_{corr}), corrosion rate and tafel slopes (b_a and b_c) were determined from the tafel polarization curves (Figure 8). For all Cu-PPY nanocomposite coatings, the corrosion current (i_{corr}) decreased than electrodeposited pure Cu (Table-6). The corrosion rate of the electrodeposited Cu and Cu-PPY nanocomposite coatings was measured and the corrosion rate dependency on the amount of PPY in Cu-PPY nanocomposite coatings is shown in Fig.-9. It shows that the Cu-PPY nanocomposite coating has more resistance than the electrodeposited pure Cu coating in 3.5 % NaCl solution.

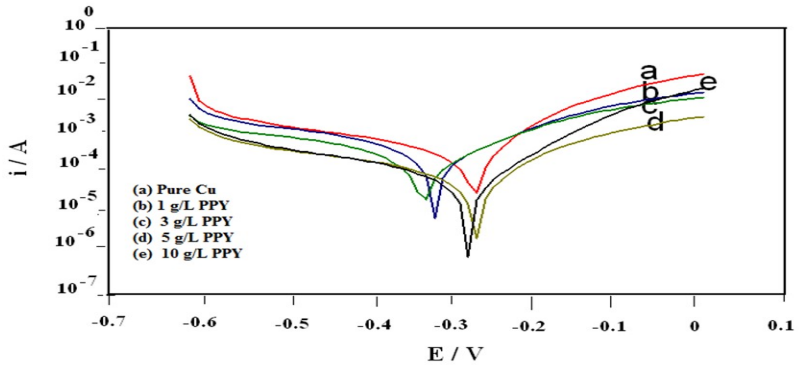


Fig.-8: Tafel Polarisation Plots of Electrodeposited Cu and Cu-PPY Nanocomposites.(a) Electrodeposited Cu, (b-d) Cu-PPY Nanocomposites.

Table-6: Tafel Polarization Parameters for the Electrodeposited Pure Cu and Cu-PPY Nanocomposites

Electrodeposit	E_{corr} (V) Vs SCE	i_{corr} ($\mu A/cm^2$)	Corrosion rate (mm/yr)
Pure Cu	-0.269	101.6	1.17
Cu-PPY nanocomposite (1g/L)	-0.318	88.6	1.00
Cu-PPY nanocomposite (3g/L)	-0.332	40.1	0.46
Cu-PPY nanocomposite (5g/L)	-0.300	8.5	0.10
Cu-PPY nanocomposite (10g/L)	-0.278	2.4	0.03

CONCLUSION

The polypyrrole (PPY) nanoparticles reinforced Cu-PPY nanocomposites were successfully prepared by electrodeposition method. The Debye-Sherrer formula is used to measure the average crystallite size of electrodeposited copper and Cu-PPY nanocomposite coatings and is found to be ~32 nm and ~23 nm, respectively. Its crystalline structure is fcc and its texture is (220). Surface morphology showed pore-free smooth surface with polypyrrole inclusion that altered the surface morphology of Cu-PPY nanocomposite coatings. In Cu-PPY nanocomposite coatings, polypyrrole (PPY) particles are grown layer by layer. Compared with the electrodeposited copper coating, the microhardness of Cu-PPY nanocomposite coating is much higher. The electrochemical impedance and Tafel polarization studies showed that the Cu-PPY nanocomposite coating in 3.5 % NaCl solution are found to be more corrosion resistant than the electrodeposited pure copper.

REFERENCES

1. S. Mosayebi, M. Rezaei and Z. Mahidashti, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **594,** 124654(2020), **DOI:**10.1016/j.colsurfa.2020.124654
2. S. Shanmugasamy, K. Balakrishnan, A. Subasri, S. Ramalingam and A. Subramania, *Journal of Rare Earths,* **36**, 1319(2018), **DOI:**10.1016/j.jre.2018.06.004
3. S. Ramalingam, K. Balakrishnan and A. Subramania, *Transactions of the IMF,* **93**, 262(2015), **DOI:**10.1080/00202967.2015.1114727
4. Toosinezhad, M. Alinezhadfar and S. Mahdavi, *Surface and Coatings Technology*, **385**, 125418 (2020), **DOI:**10.1016/j.surfcoat.2020.125418
5. S. Ramalingam, V.S. Muralidharan and A. Subramania, *Surface engineering*, **29,** 511(2013), **DOI:**10.1179/1743294413Y.0000000153
6. C.R. Raghavendra, S. Basavarajappa and I. Sogalad, *Indian Journal of Physics*, 1(2019), **DOI:**10.1007/s12648-019-01661-x
7. S. Ramalingam, V.S. Muralidharan and A. Subramania, *Journal of Solid State Electrochemistry,* **13**, 1777 (2009), **DOI:**10.1007/s10008-009-0870-x
8. P. Mandal and S.C. Mondal, *Surface Engineering,* **34**, 697(2018), **DOI:**10.1080/02670844.2017.1395981
9. S.Ramalingam, *Rasayan Journal of Chemistry,* **13**, 2143(2020), **DOI:**10.31788/ RJC.2020.1345893
10. R. Kannan, M. Selvambikai, I. Jeena Rajathy and S. Ananthi, *Rasayan Journal of chemistry,* **10,** 1213(2017), **DOI:**10.7324/RJC.2017.1041925
11. S. Ramalingam, *International Journal of Engineering and Advanced Technology*, **9,** 239(2019), **DOI:**10.35940/ijeat.A1153.1291S419
12. Y. Haseko, N.K. Shrestha, S. Teruyama and T. Saji, *Electrochimica Acta*, **51**, 3652(2006), **DOI:**10.1016/j.electacta.2005.10.032
13. S. Li, Y. Qiu and X. Guo, *Reactive and Functional Polymers*, **69,** 743(2009), **DOI:**10.1016/j.reactfunctpolym.2009.06.002
14. M.A. Dominguez-Crespo, A.M. Torres-Huerta, E. Onofre-Bustamante, A. Alanis-Valdelamar, M.L. Escudero-Rincón and S.B. Brachetti-Sibaja, *Journal of Solid State Electrochemistry,* **19,** 1073(2015), **DOI:**10.1007/s10008-014-2712-8
15. M. Chipara, R. Skomski and D.J. Sellmyer, *Materials Letters*, **61,** 2412(2007), **DOI:**10.1016/j.matlet.2006.09.024
16. T. Rapecki, M. Donten and Z. Stojek, *Electrochemistry Communications,* **12,** 624(2010), **DOI:**10.1016/j.elecom.2010.02.015

17. M. Chougule, S. Pawar, P. Godse, R. Mulik, S. Sen and V. Patil, *Soft Nanoscience Letters,* **1**, 6 (2011), **DOI:**10.4236/snl.2011.11002
18. A. Kausaite-Minkstimiene, V. Mazeiko, A. Ramanaviciene and A. Ramanavicius, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **483,** 224(2015), **DOI:**10.1016/j.colsurfa.2015.05.008
19. S. Rapi, V. Bocchi and G. Gardini, *Synthetic Metals*, **24,** 217(1988), **DOI:**10.1016/0379-6779(88)90259-7
20. L.X. Wang, X.G. Li, and Y.L. Yang, *Reactive and Functional Polymers*, **47,** 125 (2001), **DOI:**10.1016/S1381-5148(00)00079-1
21. J. C. Vidal, E. Garcia and J. R. Castillo, *Analytica Chimica Acta*, **385**, 213(1999), **DOI:**10.1016/S0003-2670(98)00838-1
22. H. J. Kharat, K. P. Kakade, P. A. Savale, K. Dutta, P. Ghosh and M. D. Shirsat, *Polymers for Advanced Technologies,* **18,** 397(2007), **DOI:**10.1002/pat.903
23. T. E. Campbell, A. J. Hodgson and G. G. Wallace, *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis,* **11,** 215(1999), **DOI:**10.1002/(SICI)1521-4109(199904)11
24. D. Kincal, A. Kumar, A. D. Child and J. R. Reynold, *Synthetic Metals*, **92,** 53(1998), **DOI:**10.1016/S0379-6779(98)80022-2
25. C. Jérôme, D. Labaye, I. Bodart and R. Jérôme, *Synthetic Metals*, **101,** 3(1999), **DOI:**10.1016/S0379-6779(98)00524-4
26. E. Smela, *Journal of Micromechanics and Microengineering,* **9**, 1(1999), **DOI:**10.1088/0960-1317/9/1/001
27. W. Su and J. O. Iroh, *Synthetic Metals,* **95**, 159(1998), **DOI:**10.1016/S0379-6779(97)04112-X
28. W. K. Lu and R. L. Elsenbaumer, The Corrosion Protection of Metals by Conductive Polymers. II. Pitting Corrosion. *Conductive Polymers and Plastics,*William Andrew Publishing, **195**, (1999), **DOI:**10.1016/B978-188420777-8.50028-X
29. S. Geetha, C.R.K. Rao, M. Vijayan and D.C. Trivedi, *Analytica Chimica Acta,* **568**, 119 (2006), **DOI:**10.1016/j.aca.2005.10.011
30. V. Bhalla, C. Ramasamy, N. Singh and M. Pushpavanam, *Plating and Surface Finishing,* **82,** 58(1995)
31. S. Ramalingam, A. Subramania, V.S. Muralidharan, *Journal of Electrochemical Society of India,* **57**, 1(2008)
32. S. Ramalingam, *International Journal of Recent Technology and Engineering (IJRTE*), **8**, 472(2019), **DOI:**10.35940/ijrte.D1156.1284S219
33. S. Ramalingam, K. Balakrishnan, S. Shanmugasamy and A. Subramania, *Surface Engineering,* **33**, 369(2017), **DOI:**10.1080/02670844.2016.1258164
34. C.L.P. Pavithra, B.V. Sarada, K.V. Rajulapati, T.N. Rao, and G. Sundararajan, *Scientific Reports*, **4,** 1(2014), **DOI:**10.1038/srep04049
35. A. Kamboj, Y. Raghupathy, M.Y. Rekha, and C. Srivastava, *JOM (The Journal of the Minerals, Metals & Materials Society)*, **69**, 1149(2017), **DOI:**10.1007/s11837-017-2364-0

[RJC-5939/2020]