International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Volume2, Issue 4 (December - February,2017) | Pages 181-194

ELECTRO SYNTHESIS OF POLY(ANILINE-co-2ETHYLANILINE) & POLY(ANILINE-co-O-ANISIDINE) FOR CORROSION PROTECTION OF STEEL

[1]KARTHIKA DURAISAMY, [2]KADAMBANATHAN K, [3]PREETHI L K
[1,2] ASSISTANT PROFESSOR, DEPARTMENT OF CHEMICAL ENGINEERING, AGNI COLLEGE OF TECHNOLOGY, THALAMBUR, CHENNAI.
[3] SCIENTIST, CENTRE FOR NANO SCIENCE AND TECHNOLOGY, SATHYABAMA UNIVERSITY, CHENNAI, CHENNAI.

ABSTRACT

Electro synthesis of poly(aniline-co-2-ethylaniline)(PANI-co-P2EA) and poly(aniline-co-o-anisidine) (PANI-co-POA) were performed by cyclic voltammetry technique on steel substrate in the presence of oxalic acid medium. The Steel sample was first passivated forming an iron(II)–iron(III) oxalate layer at potentials more negative than those used to polymerize aniline. The formation of this oxalate passivation layer is dependent upon the scan rate and only forms at low scan rate(4mV/s).With continued anodic polarization, the Fe(II)–Fe(III) oxalate coating forms an Fe(III) oxide layer followed by aniline polymerization at potentials greater than about 0.3 V Vs SCE. The effect of secondary monomer concentration and no. of cycles on corrosion properties were also investigated for these two copolymers. Corrosion protection properties of the copolymer film were determined by Impedance spectroscopy and potentiodynamic polarization method in the presence of 1M HCl. The copolymer film formed has also been characterized by Scanning Electron Microscopy, Fourier transform-Infrared spectroscopy and X-Ray Diffraction technique.

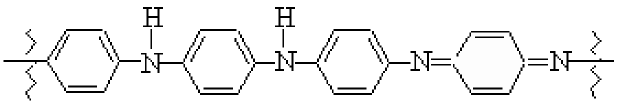
Key Words: *Cyclic voltammetry, passivation, copolymer, corrosion protection*

1.0 Introduction

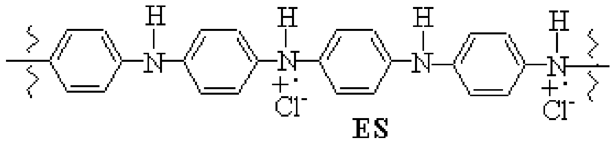
It is well known that the conventional methods used for protection of oxidizable metals against corrosion cause serious environmental effects. It has been shown that electroactive conducting polymers can be used as protective coatings to oxidizable metals. In particular, the electrodeposition of conducting polymers on common metals (Fe, Al, and Zn) has been a major subject of considerable interest in recent years. Conducting polymers do not only behave as barrier coatings on common metals in corrosive media, they also prevent easy reach of corrosive ions on metal surface due to its own redox electro activity for long exposure time in corrosive media. More stable passive oxide layer at the interface during electro polymerization occurs when compared to obtain in electrolysis solution containing only monomer free electrolyte.

Among the large number of electroconducting polymers, polypyrrole and polyaniline (PANI) are the most promising conducting polymers for corrosion protection. Nevertheless, the lower price of aniline monomer comparing to pyrrole makes PANI more challengeable[12].PANI emerged as one of the best candidates because of its ease of preparation, environmental stability, cheap raw material and wide applicability[9]. PANI is particularly interesting because of the presence of chemically flexible NH-group in the polymer back bone, which will not take part in protonation and de-protonation, but contributes to π-bond formation thus, ensuring greater environmental stability[27].PANI has a variety of oxidation states that are both pH and potential dependent. It is generally agreed [22,23]that PANI has four different fundamental forms: leucoemeraldine Base (LEB: fully reduced), Emeraldine base (EB:

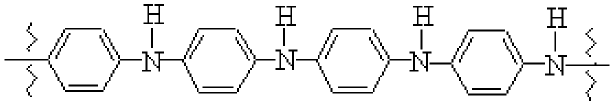
half oxidized), Emeraldine salt(ES) and pernigraniline (PN: fully oxidized). Among all these four oxidation states Emeraldine salt is the only conducting state.



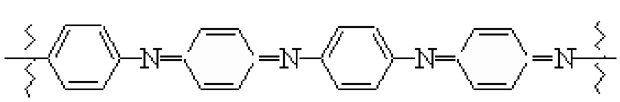
EB



ES



LEB



PN

One of the methods used to carry out changes in the properties of conducting polymers is copolymerization in which the precursor solution contains a mixture of monomers. In this case, it is expected that the properties of the copolymer will be intermediary to those of the homopolymers. Electro copolymerization is an effective way to obtain the properties of both monomers without adding any initiators as in chemical polymerization.

The aim of this project is to investigate optimum electro deposition condition for obtaining adherent coatings of Poly(aniline-co-2-ethyl aniline) (PANI-co-P2EA) & Poly(aniline-co-o-anisidine) (PANI-co-POA) on steel and to determine their protection efficiency against corrosion. Characterization of the structure of these electro active conducting polymer coatings and protective properties against corrosion were also elucidated.

2.0 Method and materials

2.1. BATH PREPARATION

The electrolytic baths were prepared by first adding 15.9g of oxalic acid (0.3M) in 250 ml beaker containing double distilled water. The oxalic acid gets dissolved in the double distilled water and forms oxalate ions. To this 4.65 ml of aniline(0.1M) was added. The aniline–oxalic acid solution formed white precipitate (anilinium oxalate), which re-dissolved after sonicating for about 10minutes. After that co monomer (2-ethyl aniline or o-anisidine) of different concentrations (0.01M, 0.05M, 0.1M) were added . By sonicating this, the dissolution of co monomer (2-ethyl aniline, o-anisidine) takes place. All studies were done at room temperature. For the synthesis of PANI-co-P2EA the following bath compositions were used.
BATH I: 0.3M aniline + 0.1M oxalic acid + 0.01M 2-ethyl aniline
BATH II: 0.3M aniline + 0.1M oxalic acid + 0.05M 2-ethyl aniline
BATH III: 0.3M aniline + 0.1M oxalic acid +0. 1M 2-ethyl aniline
For the synthesis of PANI-co-POA the following bath compositions were used.
BATH I: 0.3M aniline + 0.1M oxalic acid + 0.01M o-anisidine
BATH II: 0.3M aniline + 0.1M oxalic acid + 0.05M o-anisidine
BATH III: 0.3M aniline + 0.1M oxalic acid +0. 1M o-anisidine

2.2. SUBSTRATE PREPARATION

The working electrode was steel substrate embedded in a Teflon holder with an exposed area of $1cm^2$. Before each experiment, the working electrode was polished with different grades of emery paper.

After polishing, the steel electrode was washed with doubly distilled water, cleaned with acetone and dried at room temperature.

2.3. PROCEDURE

The measurements were carried out in a standard one-compartment three-electrode cell. The counter-electrode was Pt-foil, the reference electrode was saturated calomel electrode (SCE) and the working electrode was steel substrate mounted in a Teflon holder. Copolymer films were synthesized by means of cyclic voltammetry technique. The voltammetric experiments were carried out using SI 1280B Solatron (combined galvanostat & potentiostat) and a PC for storing and evaluating the results.

The experiments were carried out for different cycles in each bath. The coatings prepared electrochemically were immersed in distilled water to remove adsorbed electrolyte, monomer and the soluble oligomers formed during electro preparation of the coating and then dried at room temperature. Electrochemical impedance spectroscopy and Tafel polarization were used to investigate the corrosion performance of the coatings. Thickness of copolymer layer was estimated from the amount of charge Q_A necessary to switch from the LE, the reduced form of PANI, to the EM, the oxidised form of PANI. Polymer thickness was estimated according to the equation:

$$d = \frac{Q_A M_W}{zFA\rho}$$

Where Q_A is charge under the cyclovoltammetric peak
Mw - average molecular weight of monomers
z = 0.5 (number of electrons/monomer unit)
A - Area of the electrode
ρ - Specific density of aniline; F - Faraday's constant.

The method does not accommodate for the porosity factor and counter-ion volume, therefore the values calculated give only the estimated thickness for the sake of comparison[22].

2.4. IMPEDANCE SPECTROSCOPY

In this experiment, a.c. signals of 20 mV amplitude and various frequencies from 10 KHz to 0.1 Hz at open circuit potentials were impressed to the coated steel samples. The results were analyzed in the Nyquist format using the Z view software. The semicircular fit was made and the charge transfer resistance R_{ct} and the double layer capacitance values were obtained by analyzing the data. The impedance data were analysed by using simple Randel's circuit, since one semi circle is obtained in the Nyquist plot.Since copolymer coating is conducting in nature, the resistance of the coating is negligible and the impedance behaviour represents the charge transfer process of the steel dissolution. From the measured charge transfer resistance value the protection efficiency of the coating has been obtained from the below mentioned relationship,

$$\text{Protection Efficiency \%} = \frac{(R_{ct}^{1} - R_{ct}) * 100}{R_{ct}^{1}}$$

R_{ct}^{1}- charge transfer resistance of the coated sample
R_{ct} - charge transfer resistance of the blank steel

2.5. TAFEL POLARISATION

In potentiodynamic polarization, the potential of the working electrode is varied by –200mV to +200mV from the equilibrium potential through the potentiostat at a sweep rate of 1mV/sec. The potential Vs log current are plotted on the X-Y recorder and the corrosion potential(E_{corr}) are obtained by Tafel extrapolation method.

In this experiment, to determine the corrosion protection properties of the deposits obtained, the coated electrode were polarized between a potential range of -0.2v to +0.2V Vs OCP, at a scan rate of 1mv/s. Percent protection efficiency values were calculated by the equation below

$$\text{Protection efficiency\%} = \frac{(I^{1}_{corr} - I_{corr}) * 100}{}$$

$$I^{1}_{corr}$$

Where, I^{1}_{corr} – Corrosion current of uncoated substrate
I_{corr} – Corrosion current of coated substrate

3.0 Results and Discussion

3.1. PASSIVATION

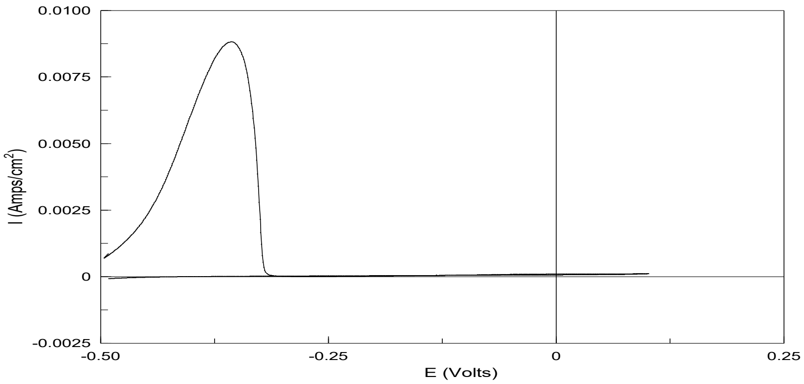


Fig 3.1.1 CV for initial passivation of steel

Fig 3.1 shows the CV recorded between the potential range of -0.5 to 0.3v, with a scan rate of 4mv/s for initial passivation. At these potentials only a passive layer is formed without polymerization of the monomers[16].During the forward scan an oxidation peak between -0.5 to -0.25V Vs SCE is attributed to the dissolution of steel electrode. The dissolved Fe^{2+} ions interact with the oxalate ions to form adherent Fe(II) oxalate film on the steel substrate [26].Beyond this potential the steel substrate is passivated. This passivated layer prevents the dissolution without affecting the electrocopolymerisation.

3.2. ELECTROSYNTHESIS OF COPOLYMER FILMS

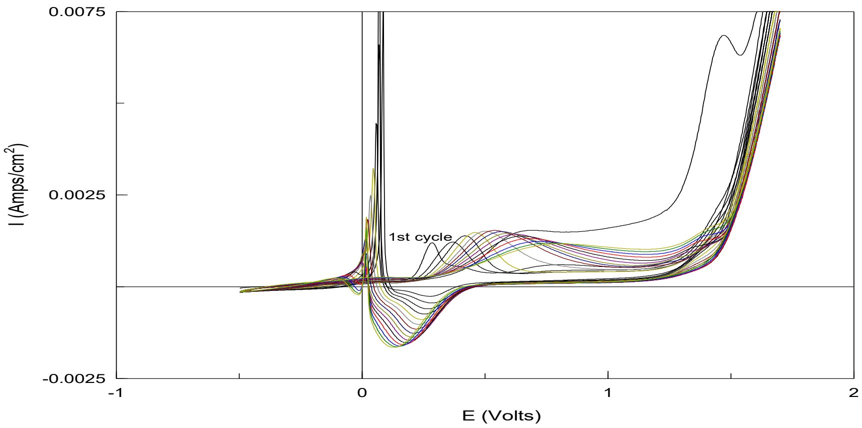


Fig 3.2.1 Cyclic Voltammogam of electrocopolymerisation of PANi-co-P2EA

Fig 3.2.1 shows the electrocopolymerisation of aniline & 2-ethyl aniline carried out at a scan rate of 20mv/s & potential range between -0.5 to 1.7V Vs SCE for different cycles(9,14,15,26).In electropolymerization solution, increase in the oxidation current is attributed to the formation of radical cation monomers and its oligomers during the first scan[2].More soluble iron(III)oxalate is formed during this initial positive scan which creates micropores on the surface. Oxidation of the underlying iron to iron(III)oxide occurs within these pores. At approximately +1.4V the current increases sharply and the emeraldine green form of PANi is observed on the steel substrate[26].During the first reverse scan, sharp oxidation peak at about 0.10V versus SCE is observed. This repassivation peak corresponds to the transition of the passive film from iron(III)oxide to iron(II)oxalate[31].This peak decreases gradually.

During subsequent scans new anodic and cathodic peaks appear which correspond to the oxidation and reduction of PANI -co- P2EA deposited on the steel electrode surface. These broad oxidation peak around +0.60V to +1.4Vand reduction peak around +0.25V versus SCE correspond to the transition of L to L•+, L to E and E to E•+ and vice versa[2].The film turns to a deep green color upon oxidation which proves the fact that the transition is only from leucoemeraldine to emeraldine The intensities of these peaks increase during following cycles which is the indication of the built up of an electroactive polymeric material on the steel surface[2]. The high separation of the oxidation and reduction peaks is apparently due to the much lower conductivity (i.e. higher resistivity) of the film.

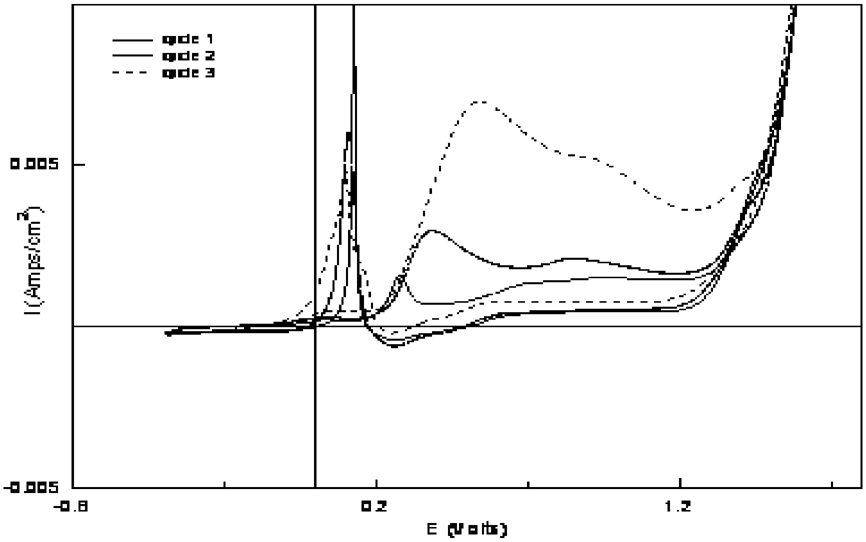


Fig 3.2.2 Cyclic Voltammogram of electrocopolymerisation of PANi-co-POA

The electrocopolymerisation was carried out at a scan rate of 10mv/s & potential range between -0.5 to 1.7V Vs SCE for different cycles(1 to 4cycles). Fig 3.2.2 shows the CV recorded for 3cycles. In electropolymerization solution, increase in the oxidation current is attributed to the formation of radical cations monomers and its oligomers during the first scan[2].During the first reverse scan, sharp oxidation peak at about 0.10V versus SCE is observed. This repassivation peak corresponds to the transition of the passive film from iron(III)oxide to iron(II)oxalate[15].This peak decreases gradually during subsequent scans. During subsequent scans new anodic and cathodic peaks appear which correspond to the oxidation and reduction of PANI -co- POA deposited on the steel electrode surface.

Anodic wave at approximately +0.25V & +0.75 V was attributed to the conversion of emeraldine (EM) to Leucoemeraldine (LE) structure of copolymer film. After the second cycle, current values corresponding to the monomer oxidation were found to increase regularly with increasing scanning numbers, due to increase in copolymer film thickness.

3.3 FILM THICKNESS MEASUREMENT

The thicknes of the copolymer films were determined by the amount of charge required for the conversion of Leucoemeraldine to Emeraldine.

Table 3.3.1 Charge & calculated thickness of PANI-co-P2EA

Number of Cycles	BATH I		BATH II		BATH III	
	Charge Q_A (c/cm^2)	Thickness (µm)	Charge Q_A (c/cm^2)	Thickness (µm)	Charge Q_A (c/cm^2)	Thickness (µm)
5	0.014579	0.2869	0.018408	0.3976	0.034991	0.801
10	0.22202	0.4369	0.10257	2.2151	0.28249	6.469
15	0.25191	4.957	0.25419	5.491	0.38304	8.772
20	0.5235	10.301	0.7535	16.275	0.8788	20.125

Table 3.3.1 shows the calculated charge and the estimated thickness of PANI-co-P2EA coated steel samples. The increase in number of cycles specifies the buildup of the copolymer film. After 15 cycles the increase in thickness is extremely high indicates the high rate of polymerization. It shows that the thickness obtained for Bath III is high compared to other Baths which implies that the deposition amount increases as the monomer concentration increases.

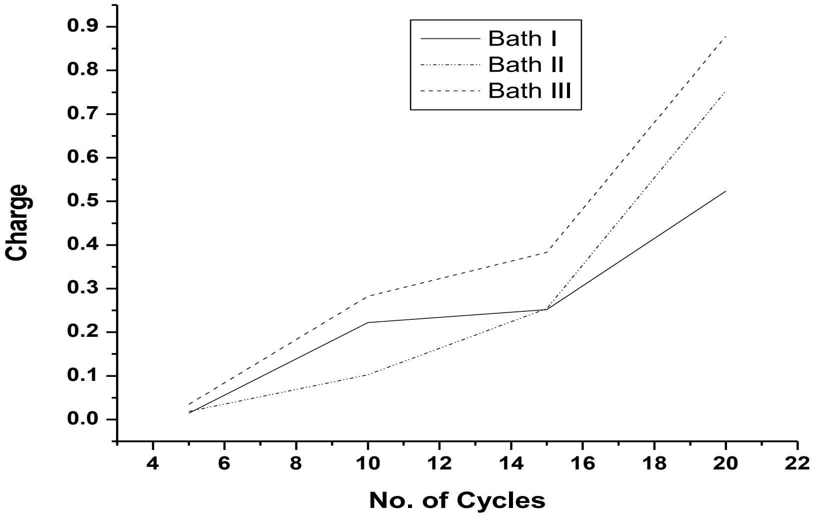


Fig 3.3.1 Charge Vs no.of cycles for the PANI-co-P2EA growth

The fig 3.3.1 shows the rate of PANI layer growth, i.e. the charge Q_A Vs number of cycles (N) during the electro copolymerization of PANI-co-P2EA for different bath concentration. It is apparent that synthesis is slower in the initial cycles and increases after certain number of cycles. The reason considered for slower synthesis on stainless steel, and for the shift of current peak to higher potentials, is an oxide film formed on a steel substrate, which, exhibiting a certain resistance, causes a potential drop at the interface. It also indicates that different rates of PANI layer growth can be distinguished during the synthesis.

Table 3.3.2 Charge & calculated thickness of PANI-co-POA

Number of Cycles	BATH I		BATH II		BATH III	
	Charge Q_A (c/cm^2)	Thickness (µm)	Charge Q_A (c/cm^2)	Thickness (µm)	Charge Q_A (c/cm^2)	Thickness (µm)
1	0.011322	0.215	0.034911	0.733	0.034911	0.733
2	0.84442	16.043	0.16961	3.561	0.16961	3.561
3	0.92339	17.544	0.99238	20.839	0.99238	20.839
4	1.3558	25.76	1.5917	33.425	1.5917	33.425

Table 3.3.2 shows the calculated charge and the thickness of PANI-co-POA coated steel samples . This table indicates that the amount of charge necessary to transfer from Leucoemeraldine to Emeraldine increases. There is also an increase in thickness as the number of cycles increases. The growth of copolymer film is initially small and the growth rate increases as the number of cycles increases. The slower rate at the beginning of synthesis follows from the difficulty of PANI-co-POA nucleus formation

on the oxide film. Once PANI-co-POA layer on steel is formed, the growth is easier and the rate of synthesis is also high.

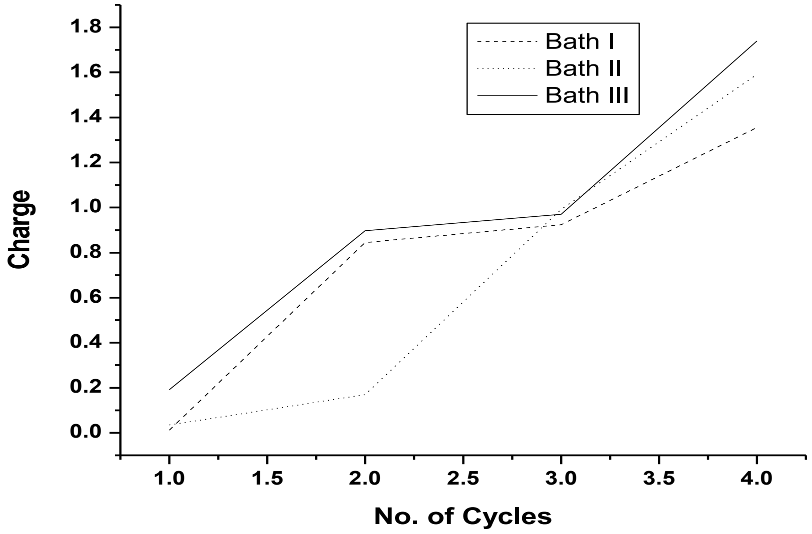


Fig 3.3.2 Charge Vs no.of cycles for the PANI-co-POA growth

The fig 3.3.2 shows the rate of PANI layer growth, i.e. the charge Q_A Vs number of cycles (N) during the electro copolymerisation of PANI-co-POA for different bath concentration. It is apparent that synthesis is slower in the initial cycles and increases after certain number of cycles. At the beginning, the rate of synthesis on steel is slow, but later on the rates increases. Slower rate at the beginning of synthesis is due to the difficulty in the formation of copolymer film. Once the film formation started the rate of synthesis also increases.

3.4. EVALUATION BY IMPEDANCE SPECTROSCOPY

The Nyquist plots were recorded by impressing Ac amplitude of 20mV over the steel sample over a frequency range of 0.1 to 20,000Hz in the presence of 1M HCl .The diagrams recorded for Blank steel electrode & the coated steel substrate are compared for all the baths and the protection efficiency was evaluated.

Table 3.4.1 Nyquist Impedance parameters for PANI-co-P2EA coated steel

No of Cycles	BATH I			BATH II			BATH III		
	R_{ct} ($\Omega.cm^2$)	(C_{dl}) ($\mu f/cm^2$)	ɳ (%)	R_{ct} ($\Omega.cm^2$)	(C_{dl}) ($\mu f/cm^2$)	ɳ (%)	R_{ct} ($\Omega.cm^2$)	(C_{dl}) ($\mu f/cm^2$)	ɳ (%)
Blank	28.495	185.9	_	28.495	185.9	_	28.495	185.90	_
5	44.284	140.75	36	145.08	277.26	80	109.08	125.78	74
10	54.009	137.18	47	145.97	103.48	81	121.22	137.10	77
15	123.16	113.79	77	170.37	101.97	83	80.24	147.06	65
20	19.395	323.77	_	112.94	106.01	75	26.053	629.74	_

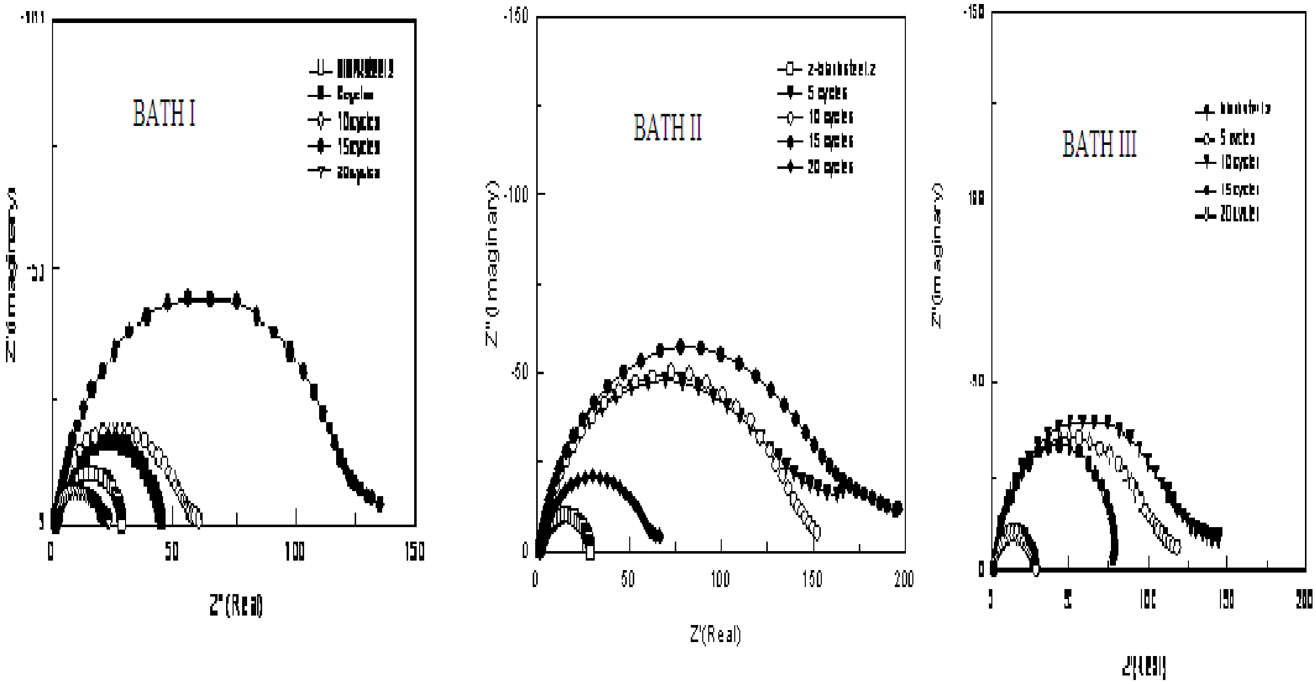


Fig 3.4.1. Impedance behavior of PANI-co-P2EA coated steel in 1M HCl

Fig 3.4.1 indicates the nyquist plots recorded for PANI-CO-POA coated steel in different baths. The EIS measurements on coated sample indicate the increased resistance value when compared to the blank steel. It indicates that the resistance value increases as the no of cycle increases. The rise in resistance value is due to the buildup of the film. The maximum resistance170.37Ω was obtained for 15 cycles with a protection efficiency of 83%.

Table 3.4.2 Nyquist Impedance parameters for PANI-co-POA coated steel

No of Cycles	BATH I			BATH II			BATH III		
	R_{ct} ($\Omega.cm^2$)	(C_{dl}) ($\mu f/cm^2$)	η (%)	R_{ct} ($\Omega.cm^2$)	(C_{dl}) ($\mu f/cm^2$)	η (%)	R_{ct} ($\Omega.cm^2$)	(C_{dl}) ($\mu f/cm^2$)	η (%)
Blank	28.495	185.9	_	28.295	185.9	_	28.495	185.9	_
1	72.35	137.82	61	77.282	160.08	63	135.19	187.83	66
2	103.46	138.24	73	127.59	160.08	78	172.14	195.71	84
3	56.023	187.98	50	96.647	143.04	71	167.43	142.67	83
4	43.942	208.81	35	75.288	187.52	62	94.005	126.52	70

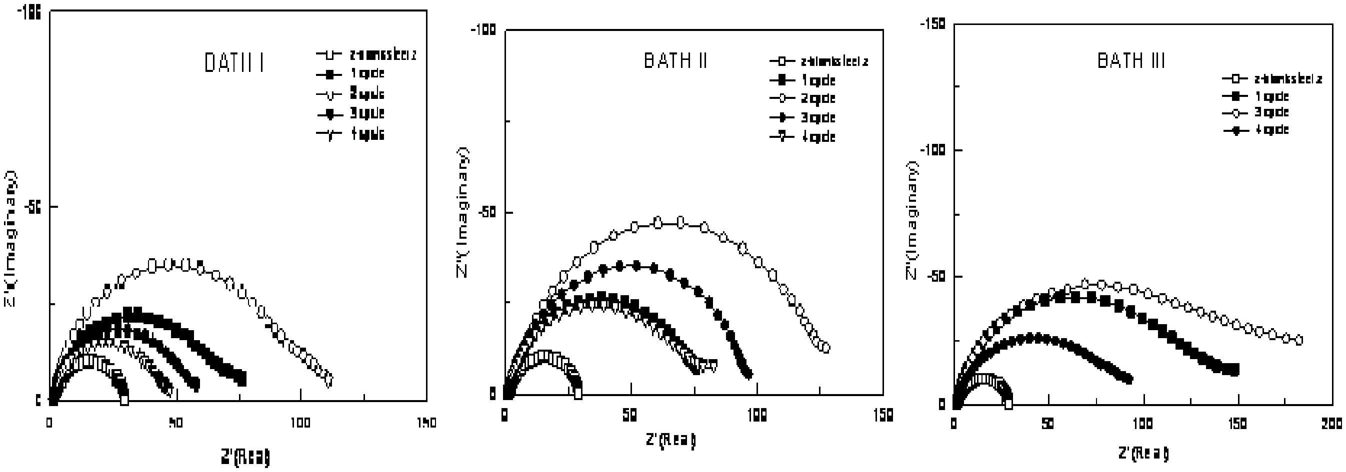


Fig 3.4.5 Nyquist plots obtained for blank & PANI-co-POA coated steel

The values of the impedance parameters obtained from fitting the experimental impedance plots for PANI-co-POA and uncoated steel are shown in fig3.4.4 and table 3.4.4. The R_{ct} value is found to be of the order of 195.71Ω. The higher value of the R_{ct} is attributed to the stable passive layer formed at the steel surface during the growth of PANI-co- POA coating and the effective barrier behavior. The lower values of C_{dl} for the coated steel provide further support the protection of mild steel by the PANI-co-POA coating. Thus, the higher values of R_{ct} and lower values of C_{dl} indicate the excellent corrosion performance of the PANI-co-POA coating.

3.5. EVALUATION BY POTENTIODYNAMIC POLARISATION METHOD

Fig 3.5.1 shows the comparison of polarization curves for the blank steel and PANI-co-P2EA coated sample and the related parameters are tabulated in Table 4.5.1. For blank steel the corrosion current was 382.71µA but for PANI-co-P2EA coated sample the corrosion current was significantly reduced. The maximum efficiency was obtained for 15 cycles with a current of 71.57µA& having a protection efficiency of 82%. These results were similar to that obtained in Impedance spectroscopy. The decreased corrosion current indicated that PANI-co-P2EA copolymer coating provide an adequate physical protection to metal between the corrosive environment and underlying metal.

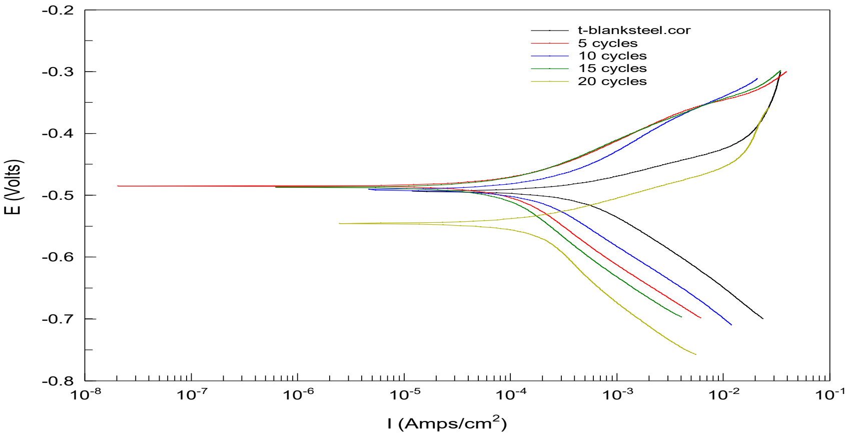


Fig 3.5.1 polarization curves for steel coated with PANI-co-P2EA(BATH II) in 1MHCl

Table 3.5.1 Polarisation parameter for steel coated with PANI-co-P2EA from Bath II.

No.of. cycles	b_a (mV/decade)	b_c (mV/decade)	I_{corr} (µA/cm^2)	E_{corr} V vs SCE	Protection Efficiency(%)
Blank	47.746	105.44	382.71	-0.49202	_
5	68.063	121.98	89.769	-0.4848	77
10	78.434	109.64	150.25	-0.49228	61
15	66.457	127.05	71.57	-0.48618	82
20	46.943	137.87	124.68	-0.547	68

Table 3.5.1 summarizes the corrosion current densities (I_{corr}) obtained by extrapolation of the linear portions of the Tafel plots. The calculated corrosion rate of uncoated and coated electrodes are also given in Table 3.5.1. Analysis of these data shows that I_{corr} and corrosion rate values decrease significantly for the copolymer coated sample

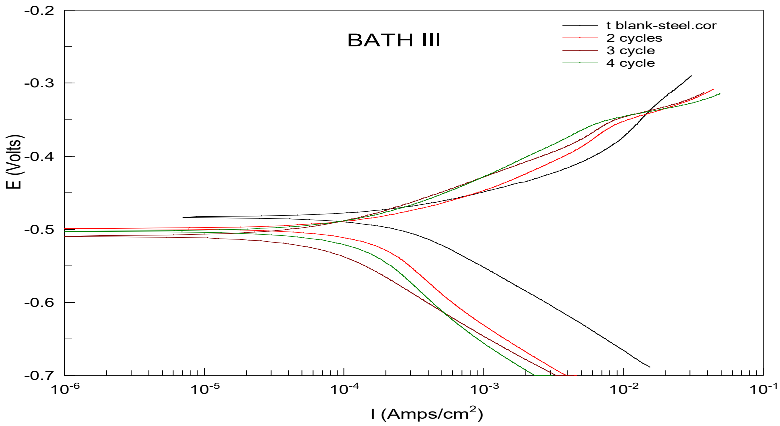


Fig 3.5.2 Polarization curves for steel coated with PANI-co-POA(BATH III) in 1M HCl

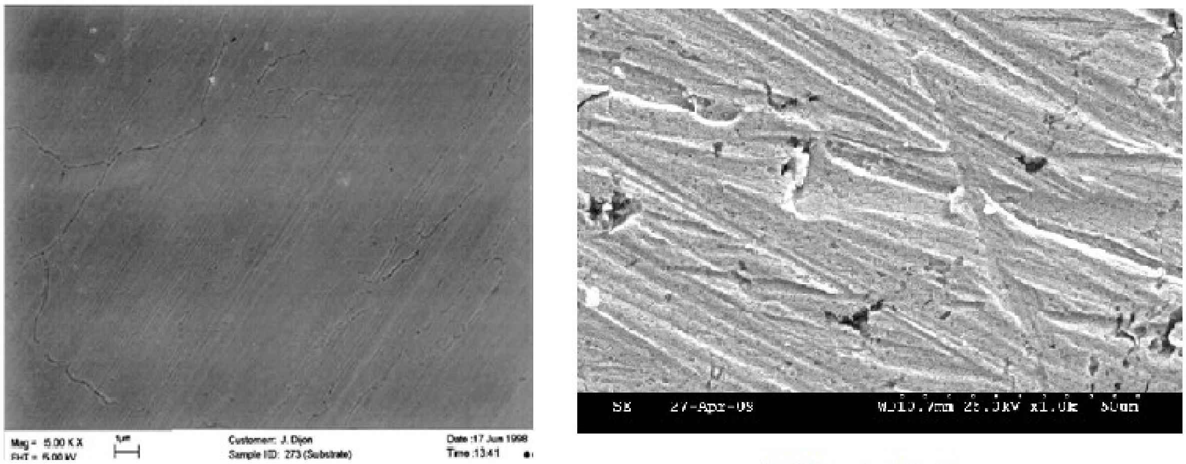
Fig 3.5.2 indicates the potentiodynamic polarization curves for uncoated & PANi-co-POA coated steel for BATH III obtained in 1M HCl and the related parameters are tabulated in fig 3.5.2. For blank steel the corrosion current was 382.71µA but for PANI-co-POA coated sample the corrosion current was significantly reduced to 63.234µA. under these optimum conditions PANI-co-POA coated sample provides Six times lesser corrosion rate compared to the bare steel. These results were similar to that obtained in Impedance spectroscopy.

Table 3.5.2 Polarisation parameter for steel and PANI-co-POA for Bath III

No.of. cycles	b_a (mV/decade)	b_c (mV/decade)	I_{corr} (µA/cm^2)	E_{corr} V vs SCE	Protection Efficiency(%)
Blank	47.746	105.44	382.71	-0.49202	_
1	57.031	163.36	126.2	-0.47686	67
2	75.174	131	130.14	-0.47686	66
3	67.551	114.39	63.234	-0.50924	84
4	77.775	163.2	109.55	-0.50222	72

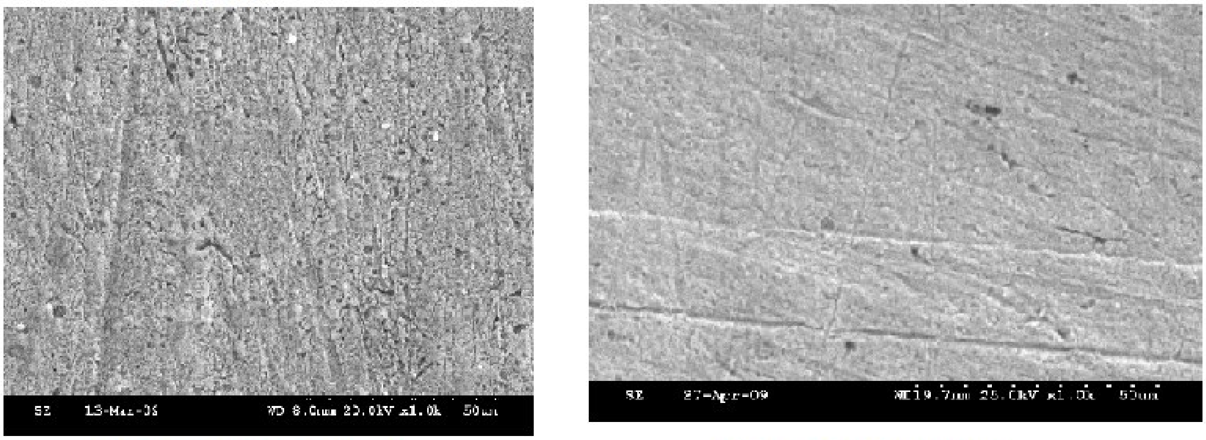
3.6 SURFACE MORPHOLOGY STUDIES

Fig 3.6. shows the SEM image of blank steel, PANI , PANI-co-P2EA and PANI-co-POA Coated Steel Samples .The steel substrate is smooth and small grain boundaries are seen transversing the surface [26]. The SEM image of PANI coated sample indicated that the steel substrate was coated with PANI when compared with the sample. The black spots in the sample specified the steel or uncoated area. The surface morphology of the PANI-co-P2EA and PANI-co-POA coated steel samples indicated that the deposits are uniform and of pore free in nature when compared with the image obtained for PANI coated steel.



Blank steel

PANI coated Steel



PANI-CO-P2EA Coated Steel

PANI-CO-POA Coated Steel

Fig 3.6: SEM images for blank, aniline and copolymer deposited steel samples

3.7 XRD CHARACTERISATION

Fig 3.7 shows the X-Ray diffraction patterns obtained for PANI-co-P2EA and PANI-co-POA coated on steel substrate. Fig 3.7 shows the peaks 2θ at 17.5699, 45.274, 82.7288 and 65.4953 values corresponding to the interface distance d=5.04785, 2.003, 1.16563 and 1.42518 respectively. XRD pattern for PANI-co-POA shows the peaks 2θ at 82.6945, 65.4459 and 45.2136 values corresponding to the interface distance d=1.16602, 1.42614 and 2.00553 respectively. The broad shoulder like peak between the 2θ value 20-25 corresponds to the polyaniline formation and the amorphous nature of the film

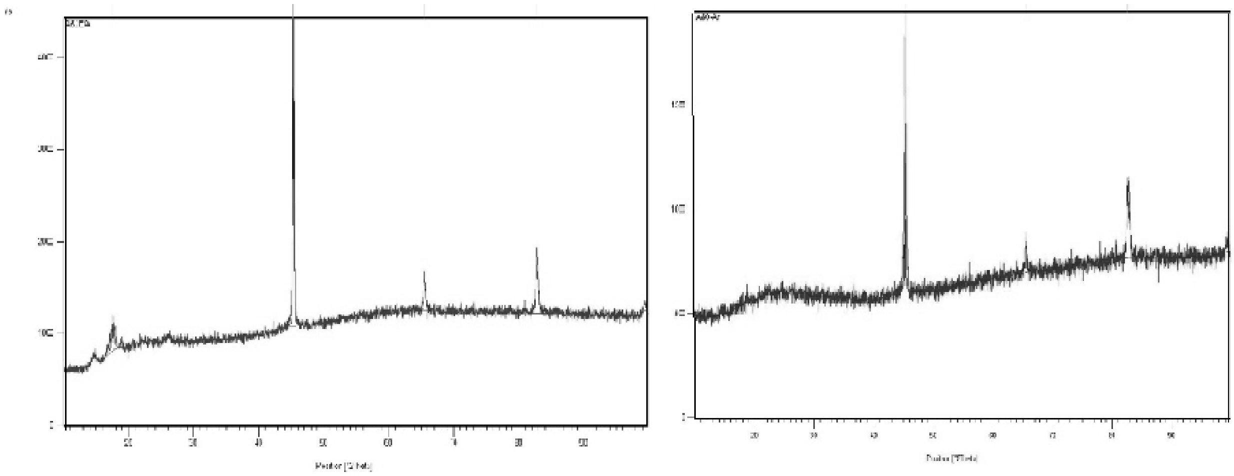


Fig 3.7 XRD pattern for PANI-co-P2EA coated steel and PANI-co-POA

.

3.8. FT-IR CHARACTERISATION

Infra red spectra of PANI-co-P2EA and PANI-POA coated steel samples are shown in figure 3.8.1 & 3.8.2. In fig 6.8.1 band at 3675.6 cm^{-1} was assigned to the N-H stretching vibration. The band at 2924cm^{-1} was due to the presence of methyl group in 2-ethyl aniline. The band at 1541 and 1398.3 cm^{-1} was attributed to the quinonoid and benzenoid ring. Similarly in the fig 3.8.2 the peak at 3645.1 cm^{-1} was assigned to N-H stretching vibration of the polyaniline. The band appeared at1687.2 was due to the C-O of the O-anisidine. The presence of bands at 1514.7 and 1454.7 cm^{-1} specified the presence of quinonoid and the benzenoid structure.

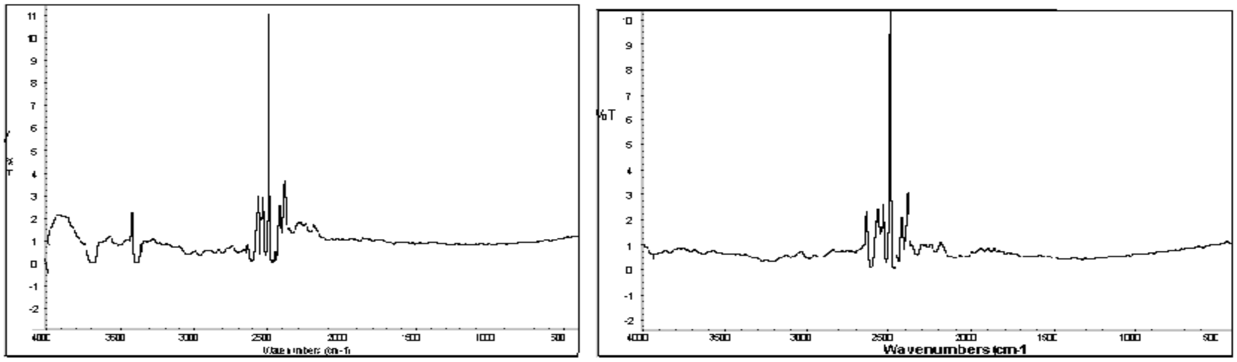


Fig 3.8 FT-IR spectras for PANI-co-P2EA & PANI-co-POA coated steel

4.0 Conclusion

Following conclusions have been drawn from the copolymerization process.

1. The cyclicvoltammetric investigation clearly indicates the formation of electroactive PANI-co-P2EA & PANI-co-POA copolymers in the oxalic acid medium which was confirmed by FT-IR.
2. It was observed that as the number of cycles increases the film thickness also increases.
3. It was observed that protection efficiency also increases as number of cycles increases but after certain number of cycles it starts decreasing.
4. From the tafel curves it was clear that the corrosion current was greatly reduced compared to the blank steel.
5. The protection efficiency is almost same(84%) for both the copolymer films

References:

[1] Ahmad.N, MacDiarmid, Synthetic metals 78 (1996) 103-110

[2] Aziz Yagan, Nuran O zc¸ic¸ek Pekmez, Attila Yıldız

[3] Beck, Barsch.U, Michaelis.R, Journal of Electrochemical Society 351(1993) 169-184

[4] Bergeron J.Y, Dao L.H., Polym. Commun. 32 (1991) 403.

[5] Bernard M.C, Hugot-Le Goff A, Joiret S, Dinh N.N, Toan N.N,J Electrochem. Soc146 (3) (1999) 995–998.

[7] Besner. S, Dao .L.H, Vijh.A.J, J. Electroanal. Chem. 381 (1995) 71

[8] Brusic .V, Angelopoulos. M, Graham.T, J. Electrochem. Soc. 144 (2) (1997) 436–442.

[9] Camalet.PJ.L, LacroixJ.C, Aeiyach.S, Chane-Ching.K, Lacaze, Synth.P.C. Met. 416 (1996) 179.

[10] Chaudhari, MandaleA.B, Patil.K.R, Sainkar.S.R, Patil.P.P, Surface Coating Technology. 200 (2006) 5557.

[11] Chauveau.E, P.-C. Journal of Electroanalytical Chemistry 481 (2000) 76–81

[12] Chevalier.J.W, Bergeron.J.Y, Dao.L.H, Macromolecules 25 (1992) 3325.

[13] DeBerry.D.W, J. Electrochem. Soc. 132 (5) (1985) 1022–1026.

[14] Dhawan.S.K, Trivedi.D.C, Synth. Met. 60 (1993) 63

[15] Diaz.A.F, Logan.J.A, J. Electroanal. Chem. 111 (1980) 111.

[16] Fahlman.M, Jasty.S, Epstein.A.J, Synth. Met. 85 (1997) 1323–1326

[17] Fenelon.A.M, Breslin.C.B, Surf. Coat. Technol. 190 (2005) 264

[18] Fernandes, E.G., coatings and corrosion-even the best fail. Ind. Eng. Chem. Prod 24 (1985) 353-357

[19] Frankel.G.S, Journal of Electrochemical society 145 (1998) 2186-2198

[20] Gospodinova.N, Terlemezyan.L, Prog. Polym. Sci. 23 (1998) 1443.

[21] Kinlen.P.J, Silverman.D.C and Jeffreys.C.R

[22] Kralji_c.M, Mandi_c.Z, Dui_c.L.J, Corrosion Science 45 (2003) 181–198

[23] Lacaze, Lacroix, Camalet.J.L, Aeiyach a.S, Chane-Ching a.K.I, Petitjean

[24] Lacroix.J.C, Camalet.J.L, Dung Nguyen.T, Aeiyach.S, Pham.M.C,

[25] MacDiarmid A.G, Short Course on Electrically Conductive Polymers, New Paltz, New York, 1985

[26] Martins.J.I, Reis.T.C, Bazzaoui.M, Bazzaoui.E.A, Martins.L, corrosion science 46 (2004) 2361-2381

[27] Nicholas M. Martyak, Page McAndrew, John E. McCaskie, Julien Dijon,Progress in Organic Coatings 45 (2002) 23–32

[28] Petitjean.J, Lacaze.P.C, J. Electroanal. Chem. 485 (2000) 13.

[29] Popovi.M.M, Grgur.B.N, Mikovi–Stankovi.V.B , Progress in Organic Coatings 52 (2005) 359–365
[30] Petitjean.J, Lacaze.P.C, J. Electroanal. Chem. 485 (2000) 13.
[31] Raja Kumar.P, Kalpana.D, Renganathan.N.G, Pitchumani.S synthetic Metals 157 (2007) 899–904
[32] Rajagopalan.R, Iroh.J.O, Appl. Surf. Science 218 (2003) 58-69
[33] Sazou.D, Georgolios.C, Synth. Met. 429 (1997) 81.
[34] Su.W, Iroh.J.O, Electrochemical Acta 44 (1999) 2173-2184
[35] Tang.H, Kitani.A, Ito.S, Electrochim. Acta 42 (1997) 3421.
[36] Tawde.S, Mukesh.D, Yakhmi.J.V, Synth. Met. 125 (2002) 401.
[37] Tuken.T, O zyılmaz.A.T, Yazıcı.B, Erbil.M Applied Surface Science 236 (2004) 292–305
[38] Wei.Y, Hariharan.R, Patel.S.A, Macromolecules 23 (1990) 764
[39] Wei.Y, Focke.W.W, Wrek.G.E, Ray.A, MacDiarmid,.A.G J. Phys. Chem. 93 (1989) 495.
[40] Wessling.B, Adv. Mater. 6 (3) (1994) 226–228.
[41]Zalewske.T,Lisowaska-Oleksiak.A,Biallozor.S,Jasulaitiene.V, Electrochemical Acta 45 (2000) 4031-4040
[42] Zarras.P, Andrson.N, Webber.C, Irvin.D.J, Irvin .J.A, Guenthner.A, Stenger-smith.J.D, Radiation physics and chemistry 68 (2003) 387-394