

Electrosynthesis of poly(aniline-co-m-amino benzoic acid) for corrosion protection of steel

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ABSTRACT

Conducting polymer (poly(aniline-co-m-amino benzoic acid)) has been deposited on steel surface by cyclic voltammetric technique. The copolymer film was characterized by FTIR, XPS and SEM techniques. The corrosion protection performance of copolymer film on steel was found out by impedance and tafel polarization methods in 1N HCl. The copolymer film was found to be highly corrosion resistant.

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1. Introduction

Conducting polymers are interesting materials both for fundamental research as well as technological applications. There has been an increasing interest in the use of these polymers for protection of oxidisable metals against corrosion. Due to the technological importance of iron and ferrous alloys there is a great deal of interest in finding new surface coatings to improve their corrosion protection. The conducting polymers which find more application in this regard are polypyrrole and polyaniline and they have certain advantages for this purpose [1]. A noticeable enhancement of protection of ferrous materials against corrosion using conducting polymers as coatings has been demonstrated [2–5]. It has been reported by many authors that electroactive polymer coatings can provide both anodic protection and barrier effect to prevent attack by a corrosive environment on steel [6–9]. Electrochemical synthesis of conducting polymers has many advantages, most important of that is, it permits the synthesis without oxidizing agent together with doping with different organic and inorganic ions and also by adjusting the conditions, both powders and films can be obtained [10]. The electropolymerisation is very difficult when a strong dissolution of the substrate initiates at potentials more negative than that corresponding to the oxidation of the monomer. Thus, it is absolutely necessary to establish the appropriate experimental conditions to overcome the dissolution of the metal without hindering the monomer oxidation and further polymerisation.

The formation of the electropolymerised coatings from aqueous solutions containing oxalate ions has been investigated by many researchers since this medium inhibits iron dissolution [11–13]. Other electrolytes such as nitrate [14], phosphate [15] and sulphate [16] have also been attempted for the electrosynthesis of conducting polymers over iron surface.

Economic aspects promote the usage of aniline monomer compared to pyrrole [10]. The use of polyaniline (PANI) in technological applications is hampered by its poor processability, related to low solubility in common solvents and poor miscibility with other polymers [17]. Both the properties are related to the strong interaction between polymer chains, either by columbic or hydrogen bonding effects. However, It has a low conductivity and little electrochemical property at pH > 4, which limits the practical application. So, it still requires the further improvement in practical and chemical properties of polyaniline.

This problem of non-processability of PANI can be tackled by three approaches viz (i) to synthesize new aniline based polymers from aniline derivatives as monomers [18,19], (ii) by changing polymerization condition of aniline or its derivatives [20,21], or post-treatment of aniline-based polymers [22,23] and (iii) by copolymerization of aniline with other polymers [24,25].

Copolymers of aniline and m-amino benzoic acid have been successfully synthesized by chemical [26] and electrochemical route [27]. Incorporation of the acidic groups like carboxylic [28], sulphonic [29] and phosphonic [30] acids as ring substituents influences the acidity constants of the amine groups and the polymerization of aniline may occur even in less acidic medium, and the conductivity does not fall off dramatically with increase in the pH as in the case of polyaniline.

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In order to elucidate further the effect of substituent on the resulting polymer in its corrosion protection ability, aniline with a carboxylic group substituent at *m*-position has been polymerized. The electropolymerisation and the electrochemical properties of the co-polymer film of aniline-co-*m*-amino benzoic acid has been found out by cyclic voltammetry. FTIR, XPS and SEM studies of the polymer film were made to characterize the film. The corrosion protection performance of copolymer film on steel has been evaluated by impedance and tafel polarization studies in 1N HCl.

2. Experimental

2.1. Reagents

Reagent grade aniline (Merck) was doubly distilled and resulting colorless liquid was kept under nitrogen in dark at 5 °C. The amino benzoic acid and oxalic acid of Sigma Aldrich were used as received.

2.2. Synthesis of poly(aniline-co-*m*-amino benzoic acid)

A simple three electrode cell was utilized with SCE electrode as reference and platinum as counter electrode. The working electrode was steel of area 1 cm². Before each experiment, the steel electrodes were polished in different grades of emery papers, degreased with acetone and washed with distilled water. A bath containing 0.1 mol dm⁻³ aniline, 0.01 mol dm⁻³ *m*-amino benzoic acid in 0.5 mol dm⁻³ oxalic acid was chosen for electropolymerisation. The deposition of copolymer on steel electrodes was carried out by cycling the potential between -0.5 and 2 V vs SCE for different cycles at a scan rate of 20 mV s⁻¹ using the electrochemical measuring unit (Solatron 1280B). The experiments were carried out at room temperature (28 ± 2 °C).

2.3. Characterization

2.3.1. FTIR spectroscopy

The electrocopolymerised poly(aniline-co-*m*-amino benzoic acid) (PACA) over steel was recorded using Nicolet 380 FTIR instrument having ATR attachment.

2.3.2. Morphology studies

The morphology of the electropolymerised PACA film was analyzed using Hitachi (Model S3000 H) scanning electron microscopy.

2.3.3. XPS studies

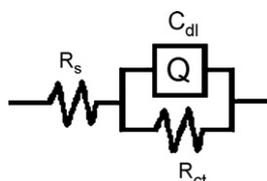
X-ray photoelectron spectra (XPS) of the steel sample with polymer film were recorded on MultiLab 2000 (ThermoFisher Scientific, UK) fitted with a twin anode x-ray source using MgK_α radiation (1253.6 eV). The sample was mounted on the SS sample stubs using conducting silver paint (Agar Scientific Ltd., UK). The stub was initially kept in the preparatory chamber overnight for desorbing any volatile species at 10⁻⁹ mbar and was then introduced into the analysis chamber having a base pressure of 9.8 × 10⁻¹⁰ mbar for recording the spectra. High-resolution spectra averaged over 5 scans with a dwell time of 100 ms in steps of 0.05 eV were obtained at pass energy of 20 eV in Constant Analyzer Energy Mode. The binding energy was referenced with C (1s) at 284.98 eV within accuracy of ±0.05 eV.

2.4. Corrosion resistance property evaluation

The poly(aniline-co-*m*-amino benzoic acid) film coated steel samples were evaluated for their corrosion resistance property in 1N HCl by tafel polarization and electrochemical impedance spectroscopy (EIS).

In the case of tafel polarization, the potential was scanned from -0.2 V vs open circuit potential (OCP) to +0.2 V vs OCP at a scan rate of 0.5 mV s⁻¹ using Corr Ware software. From this anodic and cathodic polarization curves, the tafel regions were identified and extrapolated to corrosion potential (*E*_{corr}) to get corrosion current (*i*_{corr}) using the Corr View software.

In the case of electrochemical impedance spectroscopy, a.c. signals of 20 mV amplitude and various frequencies from 10 kHz to 0.1 Hz were impressed to the coated steel at open circuit potential. The impedance values are reproducible by ±2 to 3%. From the impedance plots, the charge transfer resistance (*R*_{ct}) and the double layer capacitance (*C*_{dl}) values were calculated using ZsimpWin 3.21 software using the equivalent circuit



where *R*_s is the solution resistance, *R*_{ct} is the charge transfer resistance and *Q* is the constant phase element of the double layer capacitance.

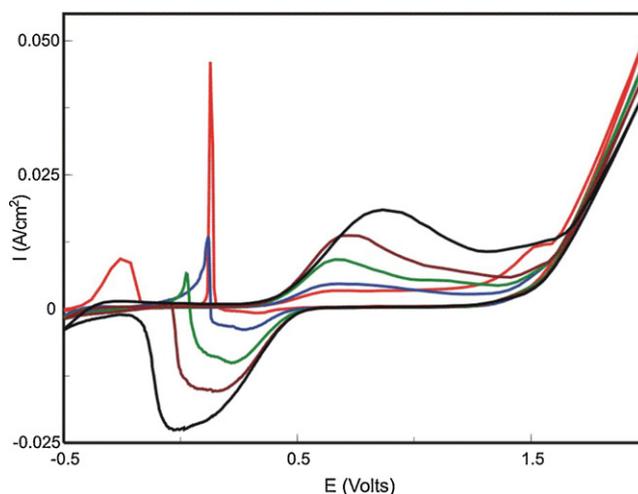


Fig. 1. CV of copolymerization of aniline and *m*-amino benzoic acid on steel electrode at the potential range of -0.5 to 2 V at the scan rate of 20 mV s⁻¹. (—) first cycle; (—) fifth cycle; (—) ninth cycle; (—) 12th cycle; (—) 16th cycle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

For the description of a frequency independent phase shift between an applied a.c. potential and its current response, a constant phase element (CPE) is used which is defined in impedance representation as

$$Z(Q) = Y_0^{-1} (j\omega)^{-n}$$

where *Y*₀ is the CPE constant, ω is the angular frequency (in rad s⁻¹), *j*² = -1 is the imaginary number and *n* is the CPE exponent (*n* > 0, for ideal capacitance *Z*(CPE) = *C*, *n* = 1). The following equation is used to convert *Y*₀ into *C*_{dl} [19]:

$$C_{dl} = Y_0 (\omega_m'')^{n-1}$$

where *C*_{dl} is the double layer capacitance and ω_m'' is the angular frequency at which *Z''* is maximum.

From the measured charge transfer resistance value the protection efficiency of the coating has been obtained from the relationship,

$$\text{protection efficiency (\%)} = \frac{R_{ct(C)} - R_{ct}}{R_{ct(C)}} \times 100$$

where *R*_{ct(C)} and *R*_{ct} are the charge transfer resistance values in the presence and absence of copolymer coating. From the tafel polarization studies, the protection efficiency of the coating has been evaluated using the equation:

$$\text{protection efficiency (\%)} = \frac{i_{corr} - i_{corr(C)}}{i_{corr}} \times 100$$

where *i*_{corr} and *i*_{corr(C)} are the corrosion current values in the absence and presence of the copolymer coating.

3. Results and discussion

3.1. Electrochemistry

Cyclic voltammetry (CV) results clearly show the deposition of copolymer when a mixture of aniline and *m*-amino benzoic acid are electropolymerized. There were three types of CVs are observed as shown in Fig. 1 During the first cycle, it shows three well defined peaks. The first peak at approximately -260 mV vs SCE with a peak current density of about 9.3 × 10⁻³ A cm⁻² is due to the dissolution of iron to ferrous ions [31]. With extended polarization, the deposition of copolymer is observed at a potential about 500 mV vs SCE on steel substrate. At fifth cycle, there is a broad oxidation peak at 500 mV vs SCE. There is also a sharp oxidation peak during reverse cycle. The oxidation peak in the positive scan of the film increases in intensity as the film grows and the oxidation peak at reverse scan decreases in intensity as number of cycles is increased. This confirms the growth of copolymer on surface with increasing cycles. The CV curves recorded at 12th & 16th cycles consists of

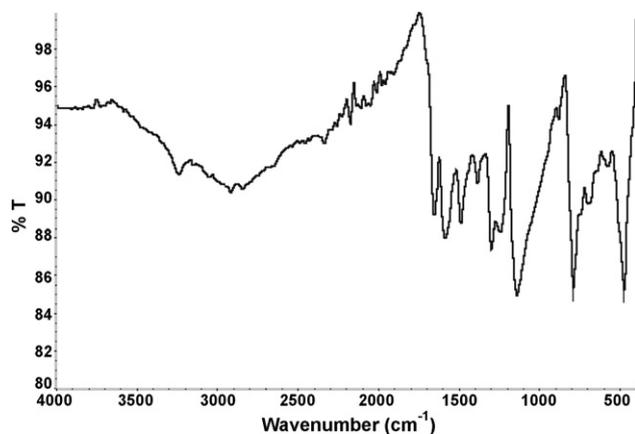


Fig. 2. FTIR spectrum for poly(aniline-co-m-amino benzoic acid).

broad oxidation and reduction peak indicates the redox property of copolymer. Increase in the current of peaks shows that the film thickness increases with cycles. The thickness of the electropolymerised poly(aniline-co-m-amino benzoic acid) coating on steel was measured using Elcometer thickness meter. After 16 cycles it was found to be 13 μm . In this stage, we could not find the sharp oxidation peak at reverse cycle due to coverage of polymer film over the passive layer of steel.

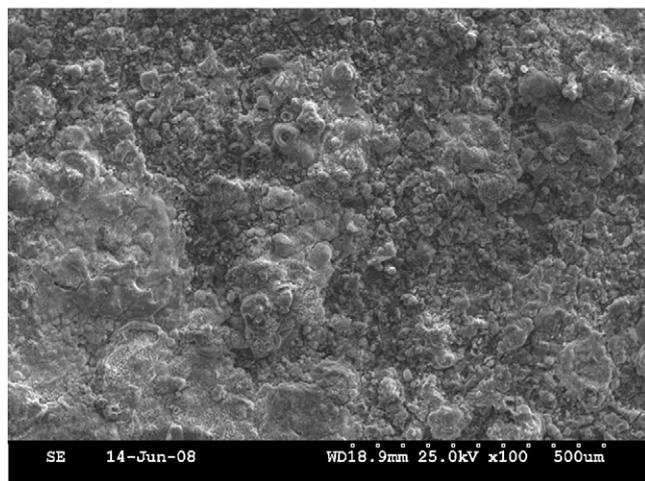
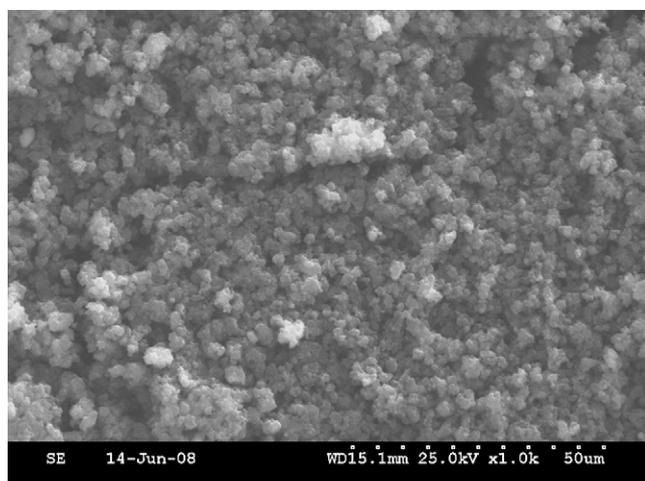


Fig. 3. SEM micrographs of poly(aniline-co-m-amino benzoic acid) on steel by electro copolymerization.

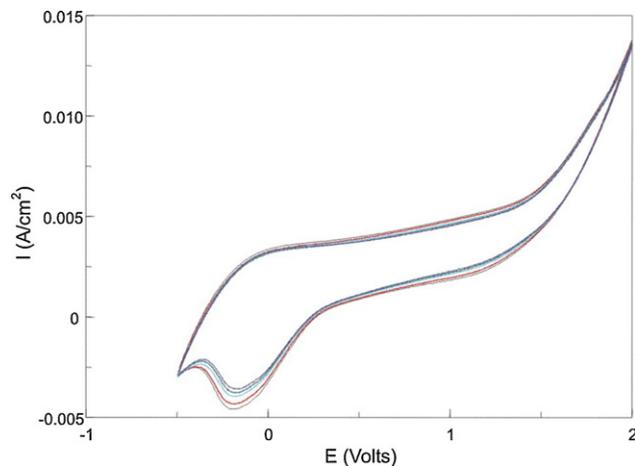


Fig. 4. Cyclic voltammogram of poly(aniline-co-m-amino benzoic acid) coated steel in monomer free 0.3 M oxalic acid solution (scan rate 20 mV s^{-1}). (—) 10 cycles; (---) 20 cycles; (···) 30 cycles; (----) 40 cycles; (-----) 50 cycles.

3.2. FTIR studies of poly(aniline-co-m-amino benzoic acid)

Fig. 2 shows the FTIR spectra of electropolymerised poly(aniline-co-m-amino benzoic acid) layer on steel. The FTIR spectra of poly(aniline-co-m-amino benzoic acid) copolymer display intense bands at 1580 cm^{-1} and 1480 cm^{-1} are due to quinoid and benzenoid rings. The peak around 800 cm^{-1} is due to 1,4 para substituted benzene ring. The peak at 1295 cm^{-1} corresponds to N–H bending. The medium intensity band near at 1245 cm^{-1} in the spectra corresponds to C–N stretching mode of the benzenoid ring. The peak around 1120 cm^{-1} is due to plane bending vibration of C–H which is formed during protonation. Besides the peak at 1700 cm^{-1} is due to C=O groups due to the presence of –COOH groups in the polymer [32–34].

3.3. Surface morphology studies of copolymer on steel

The morphology of copolymer formed after 16 cycles of cyclic voltammogram for $100\times$ and $1000\times$ magnification are shown in Fig. 3. The copolymer film exhibits granular structure and covers uniformly over the passive film covered steel electrode. It also depicts granular structure due to aggregation of copolymer on steel by continuous polymerization. It has been reported [33–35] that the use

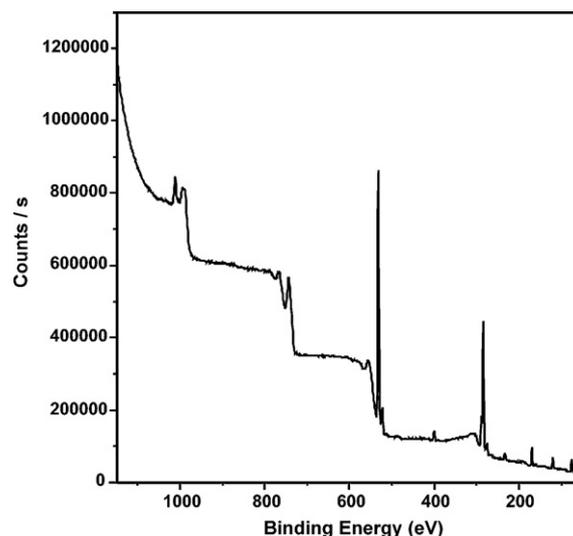


Fig. 5. XPS survey spectra of the poly(aniline-co-m-amino benzoic acid).

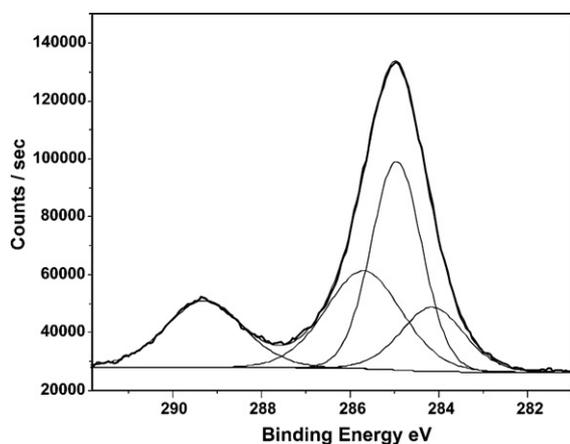


Fig. 6. C 1s core level spectra of the poly(m-amino benzoic acid-co-aniline).

of slower lower scan rate at 20 mV s^{-1} leads to the formation of more homogeneous film on steel substrate.

3.4. Stability of the poly(aniline-co-m-amino benzoic acid) on steel

In order to obtain further knowledge about electrochemical properties and stability of the copolymer, cyclic voltammetry was run in monomer free 0.3 M oxalic acid solutions (Fig. 4). The figure exhibits the redox property of copolymer through its oxidation and reduction peak. It is well known that PANI undergoes electrochemical degradation by application of sufficiently high anodic potential [36]. Though the current peaks in the cyclic voltammogram of copolymer diminish in height during prolonged potential cycling and it is found that the copolymer withstands up to 50 cycles which lead to the conclusion that the electrosynthesized poly(aniline-co-m-amino benzoic acid) exhibits more stable electro activity and lesser degree of degradation [37].

3.5. XPS analysis of copolymer on steel

Fig. 5 displays the XPS survey spectra of the copolymer film formed on steel. There are C, N and O atoms in the polymer. The presence of these three atoms has been observed in the polyaniline based polymer film [38,39].

The C 1s peak in the XPS of copolymer is shown in Fig. 6. The C 1s core level spectrum involved four peaks at 289.28, 285.7, 284.15 and 284.96 eV for copolymer, indicating that there are at least four different carbon atoms with different electronic states. It is obvious C 1s spectrum of copolymer obtained here is different from those of normal polyaniline since the later is split into three peaks in the binding energy between 284 and 289 eV [40,41]. As shown in figure, the peak 289.28 is referred to C=O bonds, since the carbon atom is attached to an electronegative oxygen atom via a double bond i.e., the chemical environment of C atom is differ from those of other C atoms. Thus, the effective attractive force of nucleus with regard to

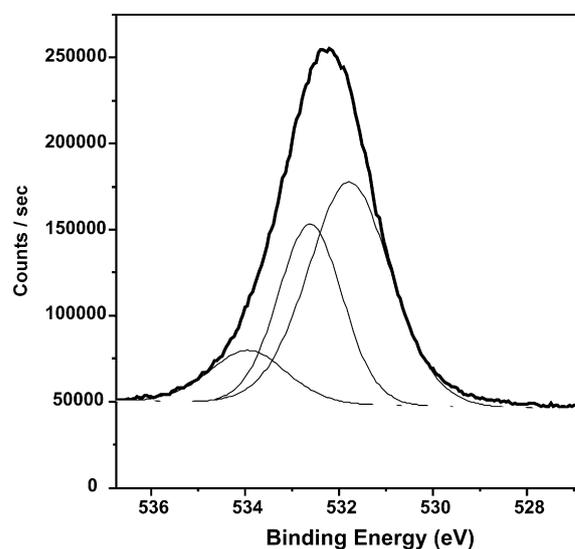


Fig. 7. O 1s core level spectra of the poly(aniline-co-m-amino benzoic acid).

the core electrons of C 1s is increased, i.e., the binding energy should be higher than those of carbon atoms in the polymer. The peak at 285.7 is assigned to C–OH bonds, the peak at 284.96 is attributing to C–N and C=N bonds, and the most intense peak at 284.15 is referred to C–C and C–H bonds [42]. The XPS spectrum of O 1s is shown in Fig. 7 indicated the involvement of three peaks at 533.94, 532.6 and 531.76 eV for the copolymer. The first peak at 533.94 might come from C–OH [42] group and/or adsorbed H_2O [43]. The second one at 532.6 eV should have originated from C=O group [42] and the third one at 531.7 eV, might be from oxalate ions. There is a single peak in N 1s core level XPS spectra with binding energy 400.1 eV as shown in Fig. 8 is attributed to the imine (–N=) and amine (–NH–) nitrogens [42–45].

3.6. Corrosion protection evaluation

The corrosion behavior of polyaniline and copolymer coated steel in 1N HCl has been found out by EIS and polarization methods. Fig. 9 shows the Nyquist representation of impedance behavior of polyaniline coated steel after 16 cycles in 1N HCl and the impedance parameters such as R_{ct} and C_{dl} are given in Table 1. It can be clearly seen from the figure and table that the electropolymerised polyaniline film formed on steel surface does not provide corrosion protection. The charge transfer resistance is decreased to $16.5 \Omega \text{ cm}^2$ from that $35.03 \Omega \text{ cm}^2$ corresponding to polyaniline free steel surface. Only after 16 potential cycles, the charge transfer resistance is increased marginally to $46.46 \Omega \text{ cm}^2$ resulting in 25% protection efficiency. Besides the C_{dl} values are found to be increased several folds due to the occurrence of iron dissolution up to 12 cycles. Similar results are found in the polarization studies of polyaniline coated steel as indicated by the tafel polarization curves shown in Fig. 10. The corrosion kinetic data obtained from

Table 1
Corrosion protection performance of electropolymerised polyaniline film on steel in 1N HCl.

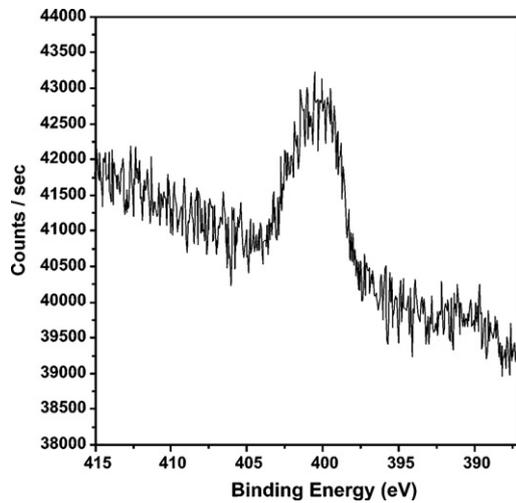
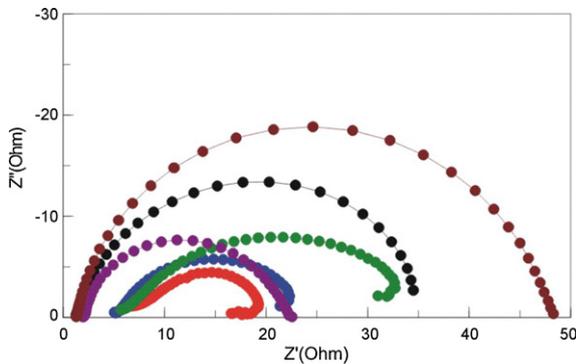
Number of cycles	Impedance			Tafel polarization		
	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	Protection efficiency (%)	E_{corr} mV vs SCE	I_{corr} ($\mu\text{A cm}^{-2}$)	Protection efficiency (%)
Blank	35.03	188.8	–	–495	248	–
1	16.5	200.6	–	–524	2677	–
5	19.38	495.2	–	–551	1305	–
9	31.7	588.8	–	–537	1160	–
12	20.11	457.5	–	–555	866	–
16	46.46	270.6	25.08	–496	171.4	30.9

Table 2

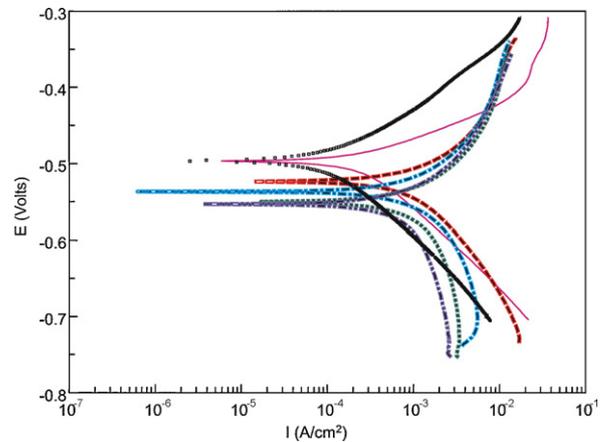
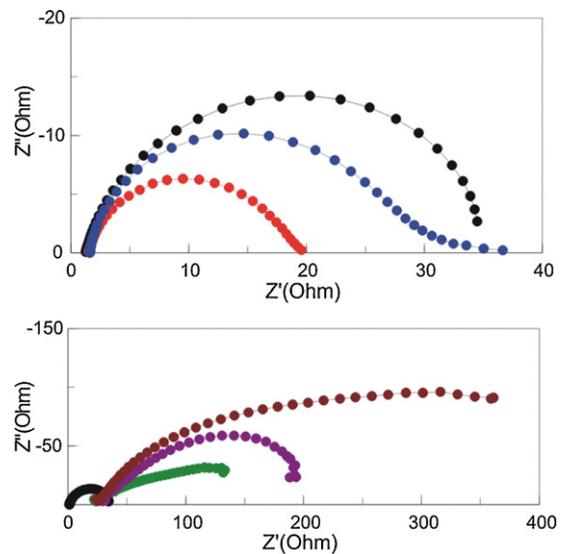
Corrosion protection performance of electrocopolymerised poly(aniline-m-amino benzoic acid) film on steel in 1N HCl.

Number of cycles	Impedance			Tafel polarization		
	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	Protection efficiency (%)	E_{corr} mV vs SCE	I_{corr} ($\mu\text{A cm}^{-2}$)	Protection efficiency (%)
Blank	35.03	188	–	–495	248	–
1	17.22	330.07	–	–483	415	–
5	28.94	465.81	–	–482	322	–
9	142.4	33.79	75.4	–496	109	56
12	207.6	39.04	83.1	–490	36	85.5
16	419	4.41	91.6	–480	12	95.1

these curves are also included in Table 1. The corrosion current density is increased to $2677 \mu\text{A cm}^{-2}$ for one cycle as compared to $248 \mu\text{A cm}^{-2}$ that of blank surface. With increase in potential cycling, the i_{corr} value is decreased and after 12 cycles, the film is found to offer marginal corrosion protection. The Impedance and polarization behavior of copolymer coated steel in 1N HCl are shown in Figs. 11 and 12 and results are given in Table 2. It can be seen from the impedance figure that the existence of copolymer film on steel resulted in one semi-circle corresponding to one time constant. In the case of lesser number of potential cyclings, the R_{ct} value is decreased and after 9 cycles it is increased largely and showed a protection efficiency greater than 80%. Besides the C_{dl} values are found to be decreased considerably which indicate the barrier effect of copolymer film. The i_{corr} values also reflect similar behavior with a large decrease in i_{corr} after 9 cycles.

**Fig. 8.** N 1s core level spectra of the poly(aniline-co-m-amino benzoic acid).**Fig. 9.** Impedance behavior of electrocopolymerised polyaniline on steel in 1N HCl. (●) Blank; (●) 1 cycle; (●) 5 cycles; (●) 9 cycles; (●) 12 cycles; (●) 16 cycles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Enhancement of corrosion protection of ferrous materials using conducting polymers as coatings have been reported [2–4] and anticorrosion properties of conductive polymers are due to the fact that such materials, when in their conductive states, might be capable of displacing the electro active interface from its usual location, i.e., the metal | solution interface [5]. It has been proposed that the film in its conductive state acts as an efficient oxidizer and offers anodic galvanic protection to maintain the metal in the pas-

**Fig. 10.** Polarisation behavior of electrocopolymerised polyaniline steel in 1N HCl. (—) Blank; (---) one cycle; (···) 5 cycles; (---) 9 cycles; (---) 12cycles; (□□□□□□) 16 cycles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)**Fig. 11.** Impedance behavior of electrocopolymerised poly(aniline-m-amino benzoic acid) on steel in 1N HCl. (●) Blank; (●) 1 cycle; (●) 5 cycles; (●) 9 cycles; (●) 12 cycles; (●) 16 cycles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

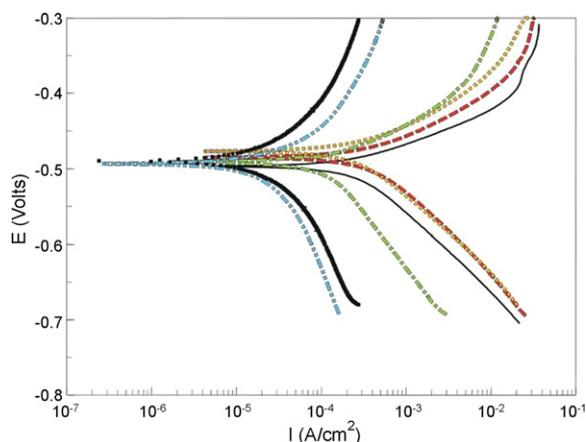


Fig. 12. Polarisation behavior of electrocopolymerised poly(aniline-m-amino benzoic acid) on steel in 1N HCl. (—) Blank; (■ ■ ■ ■ ■) one cycle; (■ ■ ■ ■ ■) 5 cycles; (■ ■ ■ ■ ■) 9 cycles; (■ ■ ■ ■ ■) 12 cycles; (■ ■ ■ ■ ■) 16 cycles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

sive state [7]. In yet another mechanism, it has also been proposed that the conducting polymer serves to mediate the anodic current between the passivated surface and oxygen reduction on the polymer film. The Fe^{2+} released during the initial corrosion reacts with the doped anion released as a consequence of polymer reduction to form insoluble iron-dopant salt and it passivates the pinhole [8,9].

In this case of co polymer formed between aniline and m-amino benzoic acid, the better corrosion protection may be attributed to the formation of compact film of cross linked individual polymers of aniline and m-amino benzoic acid and hence good barrier effect leading to the better isolation of steel surface from the corrosive electrolyte.

4. Conclusions

Electropolymerisation of poly(aniline-co-m-amino benzoic acid) on steel surface from oxalic acid bath yields uniform copolymer film. The copolymer film is formed on the iron oxalate layer. The nature of copolymer film was found out by FTIR and XPS studies. The copolymer film is found to be highly corrosion resistance in 1N HCl in comparison with that of polyaniline film due to the formation of compact copolymer film.

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