

# Corrosion protection of stainless steel by electropolymerised pani coating

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## Abstract

Polyaniline coatings have been obtained on stainless steel electrochemically from sulphuric acid medium under cyclic voltammetric, galvanostatic and potentiostatic conditions. The corrosion performance of the coating has been evaluated by EIS and polarization methods in 1 M H<sub>2</sub>SO<sub>4</sub>, 1 M HCl, and 1 M NaCl solutions. The polyaniline coating has been found to offer more than 90% protection in acid medium. However, the polyaniline coating is not protective in NaCl media. Besides, it is observed that polyaniline coating is much more stable in sulphuric acid than in hydrochloric acid.

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**Keywords:** Pani coating; Stainless steel; Corrosion protection; Sulphuric acid; Hydrochloric acid; EIS

## 1. Introduction

There has been profound interest on the possible use of conducting polymers for corrosion protection and the most promising candidates are known to be Polyaniline (pani) and Polypyrrole (Ppy)[1–5] owing to their usage in electronic application areas as well their practical use as anticorrosive coatings for almost two decades [6–9]. Nevertheless, the lower price of aniline monomer compared to pyrrole makes pani more challengeable [10]. 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]. It was reported that chemically synthesized pani (dispersed in a medium oil alkyd resin and applied to the surface by a brush) could provide a very good protection for steel [11]. It has been found out in several investigations that steel electrodes coated with thin layers of pani could keep its passivity in acidic solutions. It also shows that formation of a stable passive layer could be obtained by using organic acids [12,13]. Researchers have proved that pani film synthesized on electrode surfaces using inorganic acids have insufficient protective properties against corrosion in corrosive

medium [14]. Lu et al. proposed a mechanism where the passivation occurs with the formation of layers of Fe<sub>2</sub>O<sub>3</sub> on iron. The formation of specific oxide layers occurs when the polymer is formed on the surface during galvanostatic deposition [15]. The reaction sequences responsible for the passivation by oxide layer formation and the corrosion protection induced by pani layer are also studied [16]. Thompson et al. [17] obtained the corrosion inhibition of mild steel, coated with Polyaniline, that had been exposed to saline (3.5% NaCl) and acidic (0.1N HCl) solutions. It has been proved that the level of protection provided by doped pani is more significant for dilute acid conditions than that for neutral saline conditions [18]. Camalet et al. had observed the passivation of steel by oxalate during the deposition of pani in oxalate during the deposition of pani in oxalic acid solution [19,20]. Many other publications have reinforced the significance of pani for the corrosion protection of steels [21–24]. Over the years, numbers of important patents on the protection of steel by pani have appeared [25–27].

Studies have been conducted on the protective behaviour of conducting and insulating forms of polymers on stainless steel. While insulating coatings act actually only as a diffusion barrier, conductive coatings stabilize the metal within the potential range of the passive region. Measurement of open circuit potential as a function of time has proved this [28–30]. DeBerry [28] found that electrochemically deposited pani on SS provides a form of anodic protection that significantly reduces corrosion rates in sulfuric acid solution. Kraljic et al. [30] obtained different results for protection behaviour of pani on SS in two different acidic solutions, namely phosphoric and sulphuric acids. Some authors

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accepted Cyclic Voltammetry (CV) technique as the best method for the synthesis of pani [14,31]. Blackwood and co-authors reported that Ppy/pani could provide excellent protection for both localized and general corrosion of 304-stainless steel in artificial seawater [7]. It was observed that pani coated SS had different corrosion behaviour according to the potential range for the polymerisation and also that the permeability of pani film was affected by synthesis conditions [32]. Studies have shown that the most homogeneous and best adhering Polyaniline films are grown electrochemically by potential cycling during anodic scans in aniline solutions, and the prolonged cycling results in ageing and improves stability of the passive layer on SS [33,34].

In this paper, the corrosion protection performance of Polyaniline coating on stainless steel, which has been obtained by Cyclic Voltammetry (CV), potentiostatic and galvanostatic conditions, is reported.

## 2. Experimental

AR grade chemicals were used for this experimental study. Triple distilled water was used for the preparation of solutions. The electrode material used was stainless steel (chemical composition in wt.% C – 0.072; Mn – 9.17; P – 0.059; S – 0.0139; Cr – 14.08; Ni – 1.21; Fe – rest) of 1 cm<sup>2</sup>. Before each experiment, the SS electrodes were polished in 1/0 to 3/0 grade emery papers, degreased with acetone, etched for 1 h in 10% HNO<sub>3</sub> and 1% HF, and washed with distilled water. An electrolyte solution of 0.07 M aniline + 0.07 M H<sub>2</sub>SO<sub>4</sub> was used for polymerisation. The deposition of pani on SS electrodes was carried out (1) galvanostatically at a current density of 5 mA cm<sup>-2</sup>, (2) potentiostatically at 1.6 V versus SCE, and (3) using Cyclic Voltammetric technique for a potential range between –0.2 and 1.6 V versus SCE for 25 cycles with a scan rate of 10 mV/s. All the experiments were carried out using the electrochemical system solartron 1285. The corrosion performance of the obtained pani films was studied by Electrochemical Impedance Spectroscopy (EIS) and Polarization method, using Electrochemical measuring unit (Solartron 1280B). The experiments were carried out after the steady state attainment of corrosion potential, i.e., after 15 min immersion in either acidic (1 M sulphuric and 1 M hydrochloric acids) or 1 M NaCl solutions.

Impedance measurements were carried out at corrosion potential with the ac amplitude of 10 mV for the frequency range of 10 kHz–10 mHz. The real and imaginary parts of the impedance were plotted in Nyquist plots. From these diagrams, the charge transfer resistance ( $R_{ct}$ ) values and the double layer capacitance ( $C_{dl}$ ) values were calculated. For potentiodynamic polarization studies, the experiments were carried out over the potential range of –200 mV to +200 mV with respect to OCP at a scan rate of 1 mV/s. The corrosion current ( $I_{corr}$ ) values were obtained by extrapolating the linear portion of Tafel plots to corrosion potential. The protection efficiency of coating has been obtained from  $I_{corr}$  and  $R_{ct}$  values using the following relationship:

$$\text{protection efficiency (\%)} = \left\{ \frac{I_{corr} - I_{corr(c)}}{I_{corr}} \right\} \times 100 \quad (1)$$

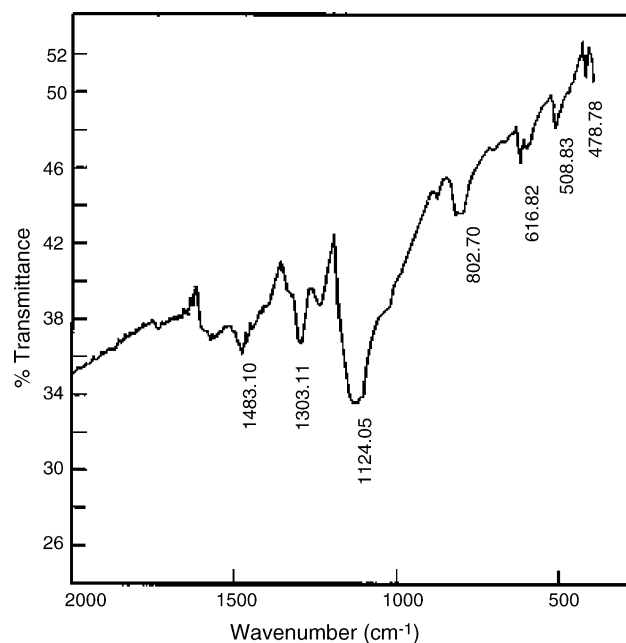


Fig. 1. FT-IR spectrum of pani deposited on SS.

$$\text{protection efficiency (\%)} = \left\{ \frac{1/R_{ct} - 1/R_{ct(c)}}{1/R_{ct}} \right\} \times 100 \quad (2)$$

where,

$I_{corr}$  and  $I_{corr(c)}$  are the corrosion current values for bare and coated stainless steel, and  $R_{ct}$  and  $R_{ct(c)}$  are the charge transfer resistance values for bare and coated stainless steel.

The double layer capacitance ( $C_{dl}$ ) values have been obtained by the following relationship:

$$C_{dl} = 1/[2\pi f_{max} R_{ct}]$$

where,  $f_{max}$  is the frequency at which  $z''$  is maximum.

FTIR experiments were performed with Thermo Nicolet Make (Nexus 670 model) for the wave numbers (2000–400) to characterize the coatings. The FTIR spectrum of Polyaniline coating synthesized on SS under CV conditions (25 cycles) is shown in Fig. 1. The special features exhibited by the spectrum are given in Table 1. From the table, it can be inferred that the electrochemical polymerisation of aniline has occurred, which

Table 1  
FT-IR parameters (absorption bands) for pani

Reference absorption bands (cm <sup>-1</sup> ) [35]	Vibrational assignments	Experimental absorption bands (cm <sup>-1</sup> )
1490	C–C aromatics	1483
1315	C–N str. In QB <sub>C</sub> Q, QBB, BBQ	1303
1115	C–H in-plane bending of 1,2,4rings	1124
850	C–H out-of-plane bending of 1,4 rings	803

str.: stretching; B: benzenoid unit; Q: quinonoid unit.

results in the deposition of Polyaniline coating on the SS electrode.

### 3. Results and discussion

#### 3.1. Synthesis of electropolymerised pani coating

Polyaniline coatings were synthesized by three electrochemical techniques, viz., CV, potentiostatic and galvanostatic methods. Cyclic Voltammogram recorded for stainless steel in 0.07 M  $H_2SO_4$  and 0.07 M aniline electrolyte is shown in Fig. 2a. As

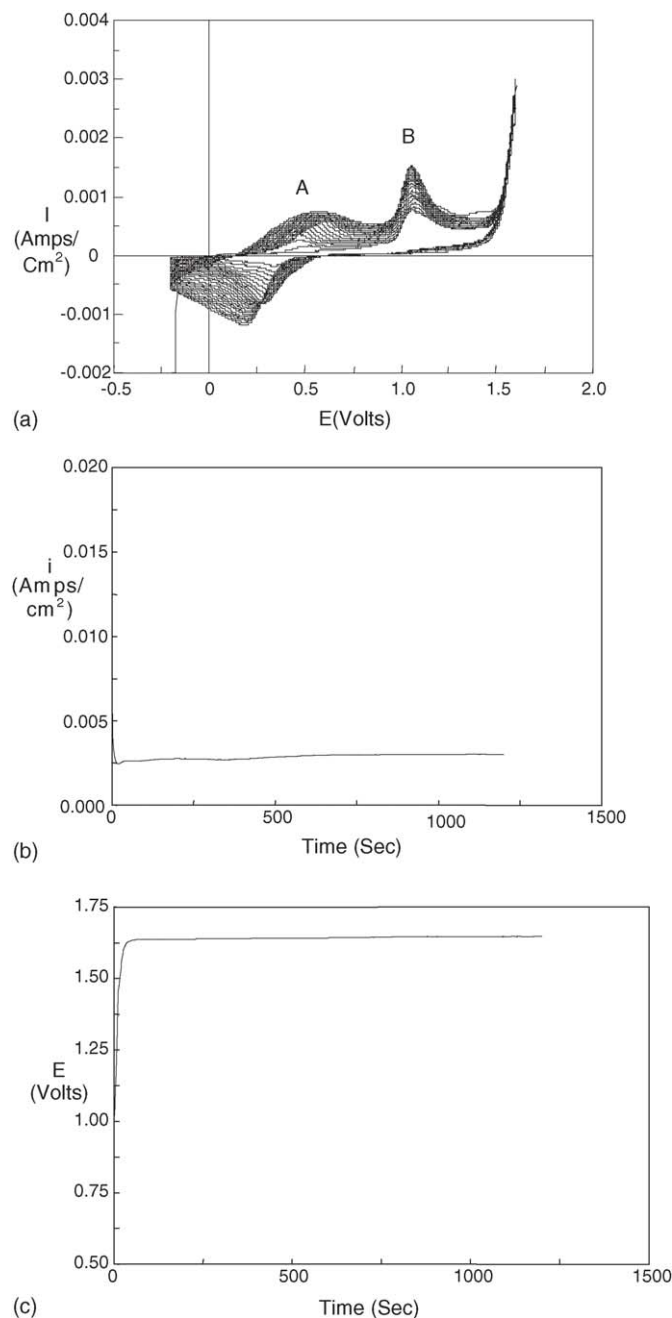


Fig. 2. (a) Cyclic Voltammogram obtained during deposition of pani on SS; (b)  $I-t$  transit during electropolymerisation at potential 1.6 V; (c)  $E-t$  transit during electropolymerisation at current 5 mA.

can be seen from Fig. 2a, the first positive cycle is characterized by the onset of an oxidation wave at  $\sim 0.89$  V followed by the oxidation peak at  $\sim 1.04$  V. The anodic current decays very sharply and a negligibly small current is observed till 0.5 V and the negative cycle terminates with reduction peak at  $\sim 0.32$  V, which shifts towards more negative value with increase in number of cycles. From second cycle, a new peak is observed around 0.5 V and the value is shifted to more positive potentials with increase in number of cycles. Increase in the current of peaks A and B shows that the deposition thickness increases with cycles. The peak A has been attributed to the transformation of pani from reduced leucoemeraldine (LE) state to the partially oxidized emeraldine (EM) state and the peak B has been explained due to the conversion of emeraldine to fully oxidized pernigraniline (PE) form. The reduction peak at +0.3 V is due to the transformation of Polyaniline from EM to LE state. Kraljic et al. [30] have observed LE/EM transition peak at  $\sim 0.4$  V and Andrade et al. [36] have reported that the transition of LE to EM takes place at  $\sim 0.1$  V. Fig. 2b and c show the deposition curves obtained for potentiostatic (+1.6 V) and galvanostatic ( $5 \text{ mA cm}^{-2}$ ) techniques, respectively. It can be seen that the time taken for formation of electropolymerised coating is very short.

#### 3.2. Evaluation of corrosion resistance property of pani coatings

The corrosion behaviour of the electropolymerised aniline on SS substrates was determined by polarization and electrochemical impedance spectroscopic techniques in 1 M  $H_2SO_4$ , 1 M HCl and 1 M NaCl solutions.

##### 3.2.1. $H_2SO_4$ medium

Fig. 3 and inset show the impedance behaviour of bare stainless steel and coated stainless steel in 1 M  $H_2SO_4$ . The impedance parameters are given in Table 2. It can be seen that the  $R_{ct}$  values of coated stainless steel are several times higher than that of bare stainless steel. Besides, the  $C_{dl}$  values are found to be

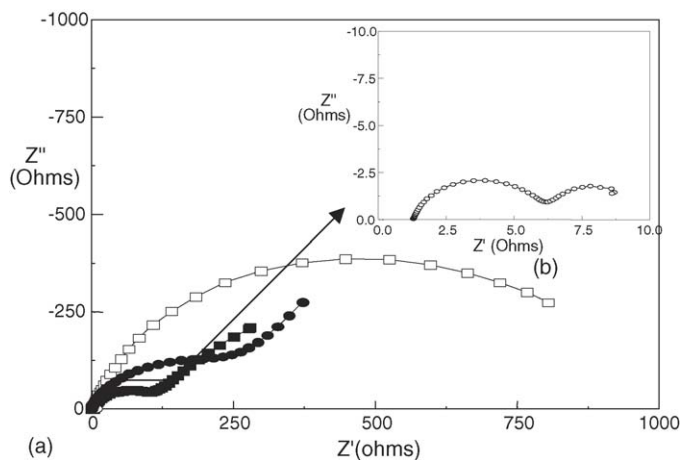


Fig. 3. Nyquist plot of pani coated SS and bare SS in 1 M  $H_2SO_4$ : (□) pani deposited using CV technique; (■) pani deposited using potentiostatic technique; (○) Bare SS; (●) pani deposited using galvanostatic technique.

Table 2  
Impedance and polarization parameters for pani coated and bare SS in 1 M H<sub>2</sub>SO<sub>4</sub>

Experimental condition	EIS		Protection efficiency (%)	Polarization		Protection efficiency (%)
	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> )	$C_{dl}$ (F cm <sup>-2</sup> )		$I_{corr}$ (A cm <sup>-2</sup> )	$E_{corr}$ (V vs. SCE)	
Bare	4.99	0.0012	–	$3.88 \times 10^{-4}$	–0.439	–
Potentiostatic	140.42	$1.02 \times 10^{-4}$	96.45	$1.73 \times 10^{-5}$	0.319	96.5
CV	955.55	$7.18 \times 10^{-5}$	99.48	$9.98 \times 10^{-6}$	0.298	97.4
Galvanostatic	432.17	$6.76 \times 10^{-5}$	98.85	$1.29 \times 10^{-5}$	0.383	96.7

Table 3  
Impedance and polarization parameters for pani coated and uncoated SS in 1 M HCl

Experimental condition	EIS		Protection efficiency (%)	Polarization		Protection efficiency (%)
	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> )	$C_{dl}$ (F cm <sup>-2</sup> )		$I_{corr}$ (A cm <sup>-2</sup> )	$E_{corr}$ (V vs. SCE)	
Bare	5.95	0.0026	–	0.170	–0.365	–
Potentiostatic	67	$2.29 \times 10^{-4}$	91.12	$6.59 \times 10^{-3}$	–0.440	96.12
CV	74.58	$2.08 \times 10^{-4}$	92.02	$1.87 \times 10^{-3}$	–0.441	98.9
Galvanostatic	90.99	$1.69 \times 10^{-4}$	93.46	$1.80 \times 10^{-3}$	–0.428	98.94

5–10 times less for coated stainless steel in comparison with that of bare stainless steel. Fig. 4 shows the polarization behaviour of bare and coated stainless steel in 1 M H<sub>2</sub>SO<sub>4</sub> and the polarization parameters are given in Table 2. It can be seen that the corrosion potentials of the coated stainless steel are nobler by 700–800 mV in comparison with that of bare stainless steel, indicating the strong passivating tendency of Polyaniline coating. The corrosion current values of the coated stainless steel are nearly 5–10 times less than that of bare stainless steel. It is further observed that the percentage of protection of the coating is more than 96%.

### 3.2.2. HCl medium

The impedance behaviour of bare and coated SS in 1 M HCl medium is shown in Fig. 5. The figure clearly shows that the charge transfer resistance offered by the pani coated stainless steel is very high in comparison to the bare SS. The impedance parameters are given in Table 3. However, the  $R_{ct}$  values of coated SS in HCl medium are not as high as that observed in H<sub>2</sub>SO<sub>4</sub> medium. Fig. 6 shows the polarization curves for bare and coated SS in 1 M HCl medium. The corrosion current values

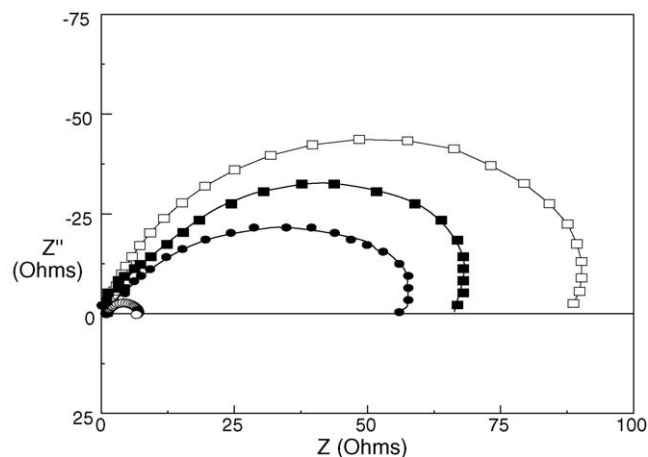


Fig. 5. Nyquist plots for pani coated and bare SS in 1 M HCl: (□) pani deposited using galvanostatic technique; (●) pani deposited using potentiostatic technique; (○) bare SS; (■) pani deposited using CV technique.

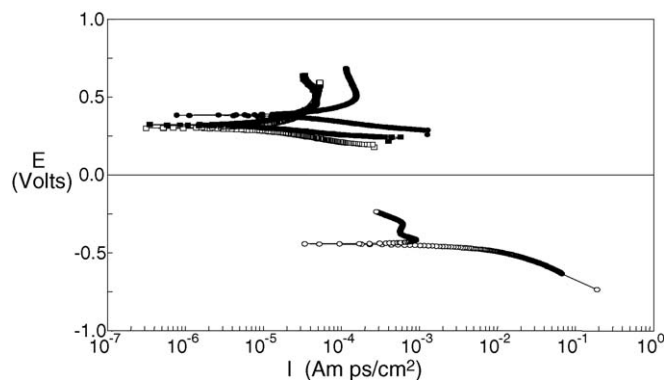


Fig. 4. Polarization curves for pani coated and bare SS in 1 M H<sub>2</sub>SO<sub>4</sub>: (□) pani deposited using CV technique; (■) pani deposited using potentiostatic technique; (○) bare SS; (●) pani deposited using galvanostatic technique.

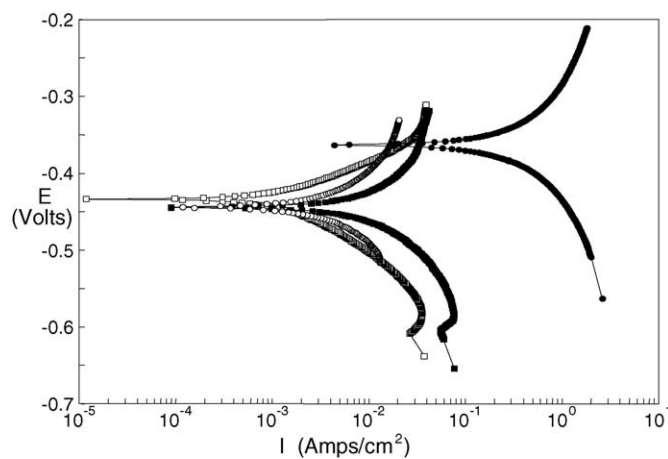


Fig. 6. Polarization curves for pani coated and bare SS in 1 M HCl: (□) pani deposited using galvanostatic technique; (■) pani deposited using potentiostatic technique; (●) bare SS; (○) pani deposited using CV technique.

Table 4  
Impedance and polarization parameters for pani coated and uncoated SS in 1 M NaCl

Experimental condition	EIS		Protection efficiency (%)	Polarization		Protection efficiency (%)
	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$C_{dl}$ ( $\text{F cm}^{-2}$ )		$I_{corr}$ ( $\text{A cm}^{-2}$ )	$E_{corr}$ (V vs. SCE)	
Bare	$5.23 \times 10^4$	$2.97 \times 10^{-5}$	–	$2.33 \times 10^{-7}$	–0.23	–
Potentiostatic	862.92	$1.86 \times 10^{-4}$	–	$1.87 \times 10^{-6}$	–0.02	–
CV	309.64	$1.52 \times 10^{-4}$	–	$2.11 \times 10^{-5}$	–0.11	–
Galvanostatic	468.09	$2.25 \times 10^{-4}$	–	$3.17 \times 10^{-5}$	–0.04	–

Table 5  
Variation of  $R_{ct}$  and  $E_{corr}$  values with time for pani coated and bare SS in 1 M  $\text{H}_2\text{SO}_4$  and 1 M HCl

Duration (days)	1 M $\text{H}_2\text{SO}_4$				1 M HCl			
	Bare SS		Pani coated SS		Bare SS		Pani coated SS	
	$E_{corr}$ (V vs. SCE)	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$E_{corr}$ (V vs. SCE)	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$E_{corr}$ (V vs. SCE)	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$E_{corr}$ (V vs. SCE)	$R_{ct}$ ( $\Omega \text{ cm}^2$ )
Initial	–0.439	4.99	0.383	432.17	–0.365	5.95	–0.428	90.99
4	–0.369	10.08	0.431	2683.88	–0.431	1.63	–0.437	1.28
6	–0.361	7.89	0.304	2493.94	–	–	–	–
12	–0.393	1.49	0.321	2679.73	–	–	–	–

are given in Table 3. From the curves, it can be observed that, the  $I_{corr}$  values of the coated SS are 20–25 times higher than that of the bare one. It is also found out that there is a shift in corrosion potentials of the pani coated SS, towards cathodic direction. The corrosion protection efficiency of the coating is more than 92%.

### 3.2.3. NaCl Medium

The Nyquist diagrams for pani coated SS and bare SS are shown in Fig. 7 and inset. Impedance parameters of pani coated SS are compared with that of the bare are given in Table 4. The  $R_{ct}$  values of the bare SS are far greater than that of the coated SS. Fig. 8 gives the Tafel curves of both coated and bare SS and the  $I_{corr}$  values are given in Table 4. These curves also have emphasized the same result. These results show that the pani coating on SS is not protective in NaCl medium.

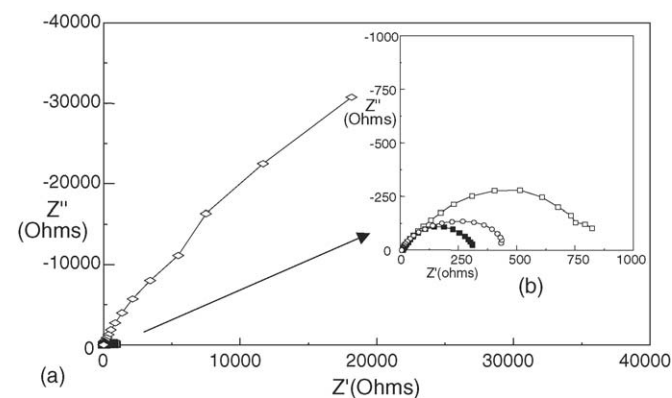


Fig. 7. Nyquist plots for pani coated and bare SS in 1 M NaCl: (□) pani deposited using potentiostatic technique; (■) pani deposited using CV technique; (◇) bare SS; (○) pani deposited using galvanostatic technique.

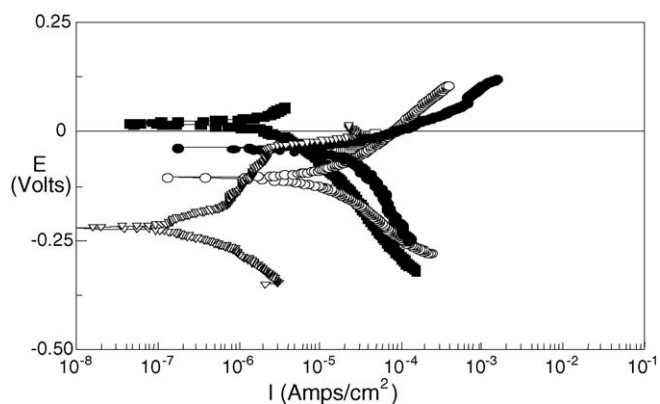


Fig. 8. Polarization curves for pani coated and bare SS in 1 M NaCl: (■) pani deposited using potentiostatic technique; (○) pani deposited using CV technique; (●) pani deposited using galvanostatic technique; (▽) bare SS.

### 3.3. Evaluation of corrosion protection performance of pani coated SS in acid medium for different exposure times

Using EIS method, the performance of the pani coating has been studied in 1 M  $\text{H}_2\text{SO}_4$  and 1 M HCl solutions for different immersion period. The results are summarized in Table 5. From the table, it can be seen that the pani coating is able to offer protection to stainless steel for the studied period in 1 M  $\text{H}_2\text{SO}_4$ , which is evident from the high  $R_{ct}$  values. However, the pani coating is not able to protect in HCl medium for longer period, even though it has offered protection initially.

## 4. Conclusion

Electropolymerised pani coatings on stainless steel are found to protect efficiently in acid medium. The pani coating is found to be highly protective in  $\text{H}_2\text{SO}_4$  medium. In HCl medium, the

pani coating is found to be moderately protective. In 3% NaCl, the pani coating is not protective. The pani coating is found to be more stable in H<sub>2</sub>SO<sub>4</sub> medium than in HCl medium.

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