

Electrosynthesis, Characterization and Corrosion Inhibition Study of DBSA-Doped Polyaniline Coating on 310 Stainless Steel

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ABSTRACT: The synthesis of polyaniline doped with dodecylbenzene sulphonic acid (Pani-DBSA) coatings on 310 stainless steel (310 SS) surfaces has been investigated by using the galvanostatic method. The synthesized coatings were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), UV-Visible absorption spectrometry and Scanning Electron Microscopy (SEM). The anticorrosion performances of Pani-DBSA coatings were investigated in 5% NaCl solution by the potentiodynamic polarization technique and Electrochemical Impedance Spectroscopy (EIS). The corrosion rate of Pani-DBSA coated 310 SS was found ~30 times lower than bare 310 SS and potential corrosion increased from -0.84 V versus Ag/AgCl for uncoated 310 SS to -0.71 V versus Ag/AgCl for Pani-DBSA coated 310 SS electrodes. Electrochemical measurements indicate that Pani-DBSA coated have good inhibiting properties with a mean efficiency of ~96% at 5 mA cm⁻² current density applied to 310 SS corrosion in chloride media. The results of this study clearly ascertain that the Pani-DBSA has an outstanding potential to protect 310 SS against corrosion in a chloride environment.

KEYWORDS: Electrosynthesis; 310 Stainless Steel; Corrosion; EIS; dodecylbenzene sulphonic acid.

INTRODUCTION

Organic coatings provide an adherent and homogenous layer on metal surfaces without any toxic residues, which can occur in conventional chromating and phosphating systems. Hence, polyaniline (Pani), polypyrrole, polythiophene and their copolymers have attracted considerable attention because of their anti-corrosion ability and less detrimental effects on the environment. Due to their low cost, easy preparation and excellent corrosion resistance, conducting polymers may play a significant role in automotive, processing and

appliance industries. Therefore, oxidizable metals such as mild steel, copper, and zinc have been recently coated by Pani in acidic or neutral solutions. Several reports have appeared on the synthesis and characterization of Pani the film in primary literature during the past decade [1-8]. However, being the first of this kind, the idea of the synthesis of conducting polymers coating onto the surface of metal alloys has not yet been reported in the primary literature, until our earlier work was released recently [9].

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Among these conducting polymers, polyaniline is considered to be one of the best anticorrosive materials [10-13] not only because of its unique redox tenability, environmental stability, and simple acid-base doping–dedoping process but also because passivation of the oxide layer between metal and coating is induced by Pani, which protects the metal from further corrosive attack [14]. Pani nanoparticles are of great interest to researchers because of their unique quantum size effect, small size effect and surface effect. They have demonstrated enhanced performance in applications such as corrosion protection, [15-17] electrochromic devices [18], sensors [19], biomimetic scaffolds [20], energy storage [21,22] and supercapacitors [23-25].

In the case of corrosion protection mechanism, it has been reported that Pani can function as inhibitor because of the presence of the functional group C=N which can be adsorbed on the metal surface. Soluble Pani can absorb on the metal surface and restrain the anodic and cathodic reaction [26]. *Yang et al.* studied the mechanism of corrosion protection of polyaniline electrochemically deposited on carbon steel substrates [27]. They proposed that the corrosion protection ability of Pani is mainly attributed to the passivating effect and oxidizing ability of its emeraldine state. They observed that the Open Circuit Potential (OCP) is more positive than the OCP value of bare Cu, Ni, Fe and Zn electrodes and the loss of emeraldine character of Pani due to a redox reaction with the metal surface. They concluded that the degree of redox conversion of Pani, from emeraldine to leucoemeraldine state, strongly depends on the reducing power of metals, showing a galvanic coupling between the substrate and Pani.

The conducting properties of the polymer films greatly depend on the method of synthesis and different parameters such as electrolytes, deposition time, solvent, etc. Thus, in order to improve conducting properties of polymer films suitable for a particular application, it is necessary to critically control and optimize the various synthesis parameters, the addition of functionalized protonic acid, such as Dodecyl Benzene Sulphonic Acid (DBSA) to the polymer. Several methods are available to improve the processing ability of Pani. *Radhakrishnan et al.* [28] have demonstrated that soluble Pani in the conducting emeraldine salt form can be synthesized by using protonic surfactants such as Dodecyl Benzene Sulphonic Acid (DBSA) and Camphor Sulphonic Acid (CSA). *Diniz et al.*

[29] recently reported the formation of strongly adherent Pani coatings on mild steel from an aqueous DBSA solution.

Iron and its alloys are widely used in many applications and diversity of these applications were intensified in the studies relating to enhancement of corrosion resistance of iron-based metals in various neutral or aggressive environments [30-33] Type 310 stainless steel (310 SS) belong to a class of metals and alloys that are protected by a passive film formed on their surface. However, these alloys are susceptible to localized attack; even high alloyed steels may corrode in strong chloride solutions. The localized corrosion of SS 310 is one of the most serious problems facing the use of these alloys. This localized attack is an especially important limitation of the material for biomedical applications. The release of metal ions such as iron, chromium, and nickel in the biological environment surrounding the alloy results in a decreased biocompatibility. Several strategies have been used to generate more protective interfaces on stainless steels, including the use of conducting polymers [34,35].

In the work reported in this paper, we have made an attempt to synthesize strongly adherent polyaniline (Pani) coatings on 310 SS substrates by electrochemical polymerization from aqueous DBSA solution and examined the ability of these coatings to serve as corrosion protective coatings on 310 SS. To the best of our knowledge, there are no reports in the literature dealing with the direct deposition of Pani coating on SS 310 from aqueous DBSA solution. The objectives of the present study are: (a) to find the best applied current density, low cost and easily available electrolyte for the electrochemical synthesis of strongly adherent Pani coating on 310 SS substrates; (b) to characterize these coatings by using spectroscopic techniques and (c) to examine the possibility of utilizing the Pani coatings for corrosion protection of 310 SS in aqueous 5% NaCl.

EXPERIMENTAL SECTION

The chemical composition of the steel employed in this study is given in Table 1. The metal sheet was cut into rectangular samples of 1 cm² area soldered with Cu-wire for an electrical connection. The metal sheet then mounted onto the epoxy resin to offer only one active flat surface exposed to the corrosive environment.

Table 1: Nominal chemical composition of the stainless steel 310.

Element	Si	C	Mn	Mo	Ti	Cr	Ni	Fe
Wt %	1.7	0.04	1.95	0.36	0.09	25	20.1	Rem.

Before each test, the steel surface was abraded with a 1200 grit emery paper then washed with bi-distilled water to remove excess reactant from the coated steel. Analytical reagents grade chemicals were used throughout the present study. The aniline monomer was double distilled prior to its use. The aqueous DBSA solution was used as the supporting electrolyte. The concentrations of DBSA and aniline were kept constant at 0.1 M and 0.05 M, respectively.

Electropolymerization of the Pani coating over 310 SS surface was also carried out by keeping a fixed current for certain duration of time. In this regard, three current densities were applied, and the corresponding potential transients were recorded for a period of 700 sec.

The FT-IR spectrum of electro synthesized Pani -DBSA over 310 SS was obtained using a Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electro synthesized Pani was dissolved in pure dimethyl sulfoxide (DMSO) and UV-Vis spectrum of this polymer solution was recorded on a Perkin Elmer Lambda2S UV-Vis spectrometer. The morphology of the electropolymerized PANi-DBSA coating on 310 SS was analyzed using a SERON model AIS-2100 SEM instrument operating at 10 kV.

For the characterization of electro synthesized Pani, the samples were mounted on a double-sided adhesive carbon disc and sputter coated with a thin layer of gold to prevent sample charging problems. XRD patterns were recorded by a Rigaku D-max CIII X-ray diffractometer using Ni-filtered Cu K α radiation.

The 310 SS sample with electro synthesized Pani coated was evaluated for their corrosion protection properties in 5% NaCl by Tafel polarization and Electrochemical Impedance Spectroscopy (EIS). The working electrode was first immersed in the test solution for 3 h to establish a steady state Open Circuit Potential (OCP).

In the case of Tafel polarization, the potential was scanned at ± 200 mV versus OCP at a scan rate of 0.001 V/s. From the anodic and cathodic polarization curves, the Tafel regions were identified and extrapolated

to the corrosion potential (E_{corr}) to obtain the corrosion current density (j_{corr}) using the NOVA 1.6 software. In the case of electrochemical impedance spectroscopy, a.c. signals of 10 mV amplitude and various frequencies from 100 kHz to 0.01 Hz at open circuit potentials were impressed to the coated 310 SS in the electrode surface (1 cm 2). A Pentium IV powered computer and NOVA 1.6 software was applied for analyzing impedance data.

RESULTS AND DISCUSSION

Electropolymerization

The experiments were performed under galvanostatic conditions. The E-t transient curves were obtained during the formation of Pani -DBSA coatings on 310 SS for three different applied constant current densities 0.5, 2.5, and 5.0 mAcm $^{-2}$ (Fig 1). Coatings of homogeneous appearance were obtained at all applied current densities. The time to reach the maximum potential value is different for the applied current densities that it is nominated as induction time. As it can be seen in Fig. 1, the polymerization potential values were the same for all applied current densities and homogeneous coatings were obtained at various applied current densities. The Pani -DBSA coating synthesized by a current density of 5 mA cm $^{-2}$ is adhesive. The galvanostatic procedure gave rise to the deposition of a green coating, characteristic of Pani -DBSA in the emeraldine oxidation state on the surface of 310 SS.

Spectroscopic characterization

The FTIR spectrum of the Pani -DBSA is shown in Fig. 2. The main characteristic bands of Pani -DBSA are assigned as follows [28, 29]:

The broadband at ~ 3200 cm $^{-1}$ is due to N-H stretching mode, C=N and C=C stretching mode for the quinoid (Q) and benzoid (B) rings occur at ~ 1600 and 1550 cm $^{-1}$, the band at ~ 1400 cm $^{-1}$ is due to C-N stretching vibrations in quinoid imine units, the band at ~ 1300 cm $^{-1}$ is assigned to the C-H stretching mode. It is a characteristic peak of emeraldine salt (ES) phase of Pani; the band at ~ 1025 cm $^{-1}$ is attributed to the 1-4 substitution

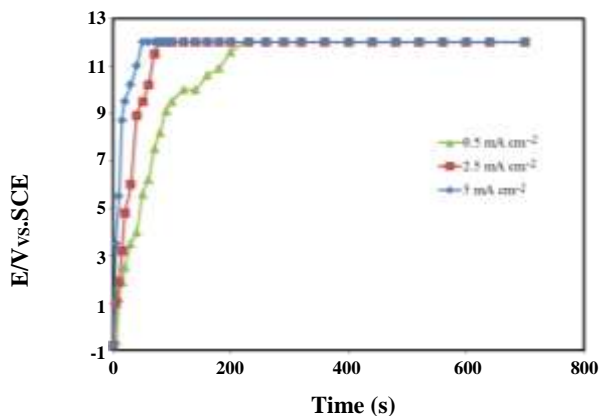


Fig. 1: E-t curves under galvanostatic polymerization conditions in 0.05 M DBSA solution containing 0.1 M aniline for 310 SS electrode at various current densities (mA/cm^2).

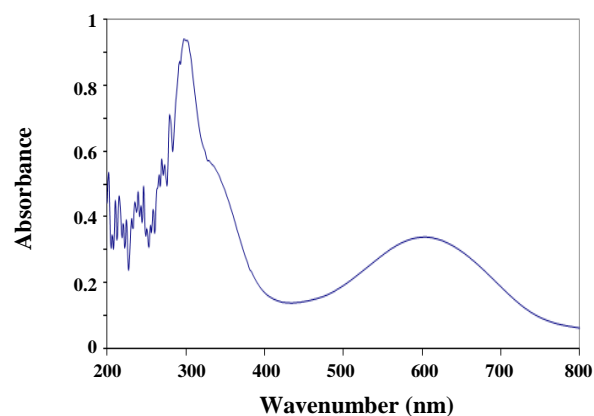


Fig. 3: UV-visible spectrum recorded for Pani-DBSA electro synthesized on the 310 SS.

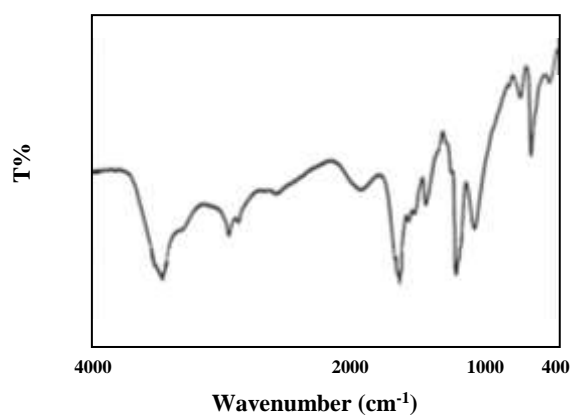


Fig. 2: FT-IR spectra of electropolymerized Pani-DBSA on the surface of 310 SS.

on the benzene ring; the strong band at $\sim 752 \text{ cm}^{-1}$ indicates ortho substituted. The peak at about 1115 cm^{-1} is related to the polaron band formed by doping. The R-SO₃ group of doped DBSA is seen at 1037 cm^{-1} . The C-H_{ar} stretching is observed at 2900 cm^{-1} [36]. Thus, the FTIR spectroscopic study reveals that the electrochemical polymerization of aniline has occurred and results in the formation of Pani-DBSA coating on the 310 SS surface.

Fig. 3 shows the UV-Vis absorption spectra for Pani-DBSA coatings in pure DMSO solvent obtained under galvanostatic conditions on the surface of SS 310. The broad peak appearing at about 320 nm in Fig. 3 can be attributed to the π^* transition in the benzenoid ring of the polymer. The broadband around 620 nm can be attributed to the intramolecular transition between the benzenoid and quinoid moieties in the polymer [37].

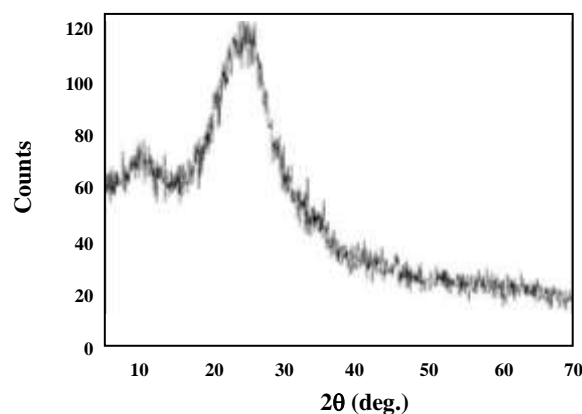


Fig. 4: X-ray diffraction patterns Pani-DBSA coated 310 SS for $5 \text{ mA}/\text{cm}^2$.

Fig. 4 shows the XRD patterns of Pani-DBSA coating in the emeraldine salt form. Pani has basically pseudo-orthorhombic crystal structure with chains parallel to the c-axis where the dopant ions are present at the centre of the cell. The XRD pattern of Pani shows a broad peak at around 25° . This reflection is indexed to the (110) hkl-plane and the ionomer decreases the order of the stacking formed by Pani chains and DBSA. The appearance of broad peaks in this diffraction pattern is attributed to the residual ordered DBSA after doping [38].

Scanning electron microscopy (SEM)

Fig. 5 shows SEM micrographs of the surface uncoated 310 SS (image a), Pani-DBSA coated SS 310 (image b) samples at current densities $5 \text{ mA}/\text{cm}^2$. By comparing images b with image a, it can be seen

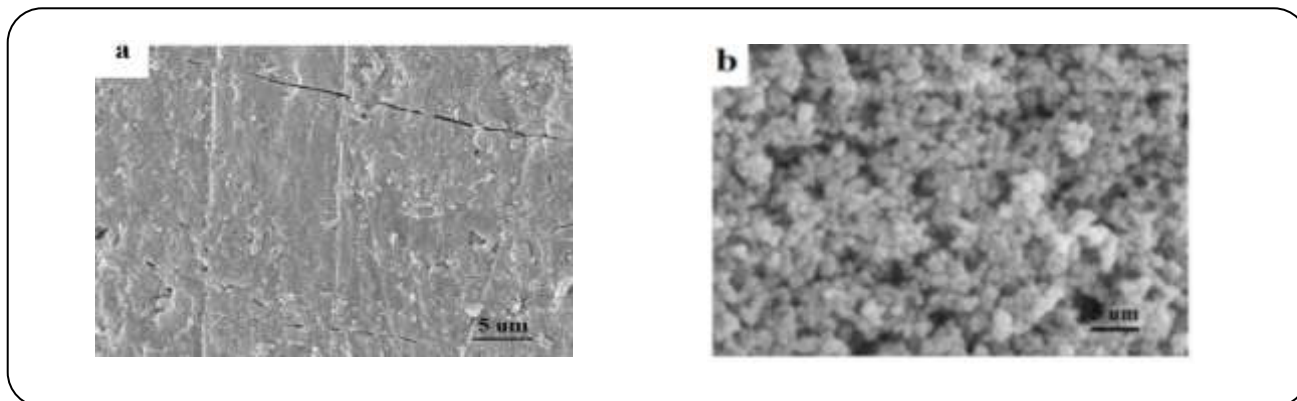


Fig. 5: SEM images of the (a) abraded 310 SS and electrosynthesized (b) Pani-DBSA coated 310 SS for 5 mA cm⁻².

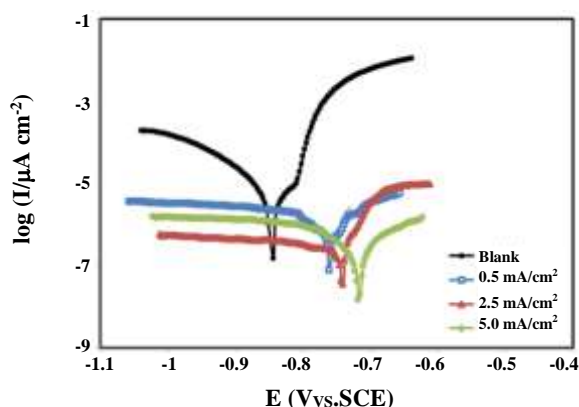


Fig. 6: Polarization behavior of electropolymerized Pani-DBSA coated on 310 SS at various current densities (mA/cm²) in 5% NaCl.

that the SS 310 surface is covered completely after applied current densities 5 mA/cm².

Corrosion protection evaluation of the coatings

The corrosion protection performance of Pani-DBSA coating synthesized under galvanostatic conditions were examined in an aqueous 5 wt% NaCl solution using potentiodynamic polarization and EIS studies.

Tafel polarization measurements

The corrosion current density (J_{corr}), corrosion potential (E_{corr}), polarization resistance (R_p), Corrosion Rate (CR) and Protection Efficiency (PE) were determined by extrapolation of the linear portions of the anodic and cathodic Tafel curves from Fig. 6. The electrochemical parameters of the electro synthesized Pani-DBSA on 310 SS in aqueous 5% NaCl solutions are summarized in Table 2. As shown in the curves, the E_{corr} for Pani-DBSA coated

310 SS has shifted to more positive potentials, about 130 mV vs. Ag/AgCl than the uncoated 310 SS (anodic protection). The electrochemical protection is caused by the increase of the E_{corr} and the formation of a protective passive layer on 310 SS surface.

From the measured J_{corr} values, the PE was obtained from the following equation [39]:

$$PE = \frac{J_{corr} - J_{corr(c)}}{J_{corr}} \times 100 \quad (1)$$

That J_{corr} and $J_{corr(c)}$ are the corrosion current density values in the absence and presence of the coating, respectively.

As it can be seen in Table 2, when the applied current density increases, the PE increases, too. On the other hand, J_{corr} decrease from 2.00 μA/cm² for uncoated 310 SS to 0.08 μA/cm² for Pani-DBSA coated 310 SS under optimal condition. From Table 2, it can be also found that the corrosion rate of 310 SS is significantly reduced as a result of the reduction in J_{corr} . The corrosion rate of the Pani-DBSA coated 310 SS is found to be 2.7 × 10⁻⁴ mm/year, which are about 30 times lower than that observed for bare 310 SS. Table 2 also shows that with increasing of applied current density, corrosion protection efficiency will increase.

The porosity of the coating strongly governs the anticorrosive behavior of the coatings; therefore, the determination of porosity in the coating is essential in order to estimate the overall corrosion resistance of the coated substrate. The porosity in Pani-DBSA coatings on 310 SS substrates was determined from potentiodynamic polarization measurements. The porosity of the polymer coatings was calculated using the following equation [40]:

Table 2: Electrochemical parameters of electropolymerized of Pani -DBSA coatings on 310 SS in aqueous 5% NaCl solution under the galvanostatic conditions at different current densities for 3 h.

sample	J_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (V vs. Ag/AgCl)	R_p ($\Omega \text{ cm}^2$)	C_R (mm/year)	PE%	porosity% ^a
Bare ^b	2.00	-0.84	22.1×10^4	8.3×10^{-3}	-	-
0.5 mA cm^{-2}	0.50	-0.76	13.0×10^5	3.3×10^{-3}	75.0	1.1
2.5 mA cm^{-2}	0.32	-0.74	47.5×10^5	9.2×10^{-4}	84.0	0.2
5.0 mA cm^{-2}	0.08	-0.71	21.2×10^6	2.7×10^{-4}	96.0	0.1

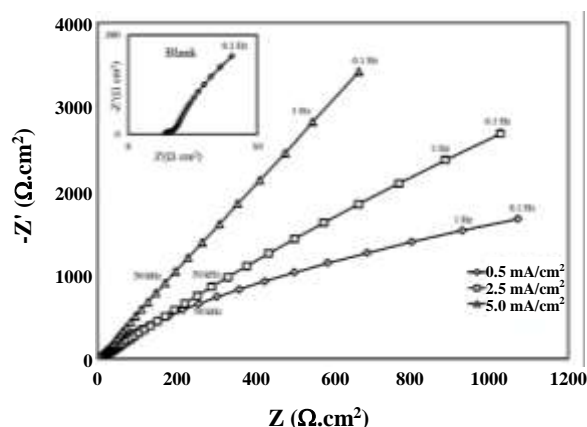


Fig. 7: Nyquist impedance plots for uncoated 310 SS Pani -DBSA coated 310 SS synthesized under galvanostatic conditions at various current densities (mA cm^{-2}) and the plots recorded at open circuit potential in the aqueous solution of 5% NaCl.

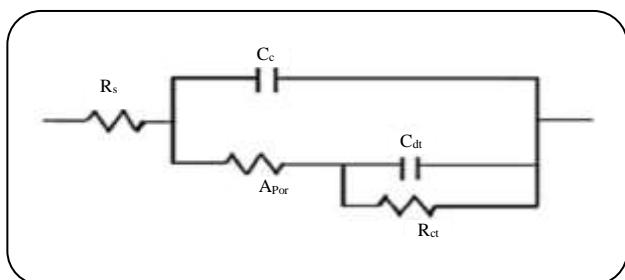


Fig. 8: Equivalent circuit model.

$$P = \frac{R_{\text{puc}}}{R_{\text{pc}}} \times 10^{-\left(\frac{\Delta E}{b_a}\right)} \quad (2)$$

Where P is the total porosity, R_{puc} and R_{pc} are the polarization resistance of the uncoated and coated 310 SS, respectively. ΔE_{corr} is the difference between the corrosion potentials and b_a is the anodic Tafel slope for the uncoated 310 SS substrate. The calculated porosity value of the Pani -DBSA coating is also given in Table 2. As

seen in the tables, the P value of the coating decreases with an increase in the applied current densities. As a result, there is a decrease in the accessibility of the aggressive species to the 310 SS surface and therefore a decrease occurs in the corrosion rate and corrosion current values. The lower values of the porosity in the Pani -DBSA coatings permit an improvement of the corrosion resistance by hindering the access of the electrolyte to the 310 SS substrates.

Electrochemical impedance measurements

In this study, electrochemical impedance spectroscopy was also used to evaluate the corrosion activity variation for 310 SS coated with the Pani -DBSA. The Nyquist impedance plots of uncoated 310 SS and Pani -DBSA coated 310 SS recorded in an aqueous 5% NaCl solution and are shown in Fig. 7. These impedance plots were modeled by the equivalent circuit depicted in Fig. 8. The equivalent circuit consists of the electrolyte resistance (R_s), pore resistance (R_{por}), coating capacitance (C_c), charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) [41].

The impedance parameter values of the electro synthesized Pani -DBSA on SS 310 at various deposition applied current density in aqueous 5wt% NaCl solution that are shown in Fig. 7 are summarized in Table 3.

From the measured charge transfer resistance values, the protection efficiency of the coating was obtained from the following equation [41]:

$$\text{PE} = \frac{R_{\text{ct}(c)} - R_{\text{ct}}}{R_{\text{ct}(c)}} \times 100 \quad (3)$$

That $R_{\text{ct}(c)}$ and R_{ct} are the charge transfer resistance values in the presence and absence of polymer coating, respectively. The R_{ct} value is approximately $57.2 \text{ k}\Omega \text{ cm}^2$ for Pani -DBSA coated, which is about 12 times higher than that of uncoated 310 SS. The higher value of R_{ct}

Table 3: Impedance parameter values of the electrosynthesized Pani -DBSA extracted from the fit to the equivalent circuit for the impedance spectra recorded in aqueous 5% NaCl solution.

sample	R_s (Ω cm ²)	C_c (F cm ⁻²)	R_p (Ω cm ²)	R_{ct} (k Ω cm ²)	C_{dl} (F/cm ²)	d^* (μ m)	PE%
Bare	3.8	3.3×10^{-6}	7.0	5.0	6.3×10^{-5}	-	-
0.5 mA cm ⁻²	30.4	4.2×10^{-7}	127.0	13.3	1.8×10^{-6}	1.2	62.4
2.5 mA cm ⁻²	26.1	9.9×10^{-8}	243.0	46.4	7.9×10^{-7}	5.2	89.2
5.0 mA cm ⁻²	13.9	6.5×10^{-8}	533.0	57.2	1.2×10^{-7}	8.0	91.2

* ($\epsilon_0 = 8.85 \times 10^{-12}$ F cm⁻¹, $\epsilon = 5.9$, $A = 1$ cm²)

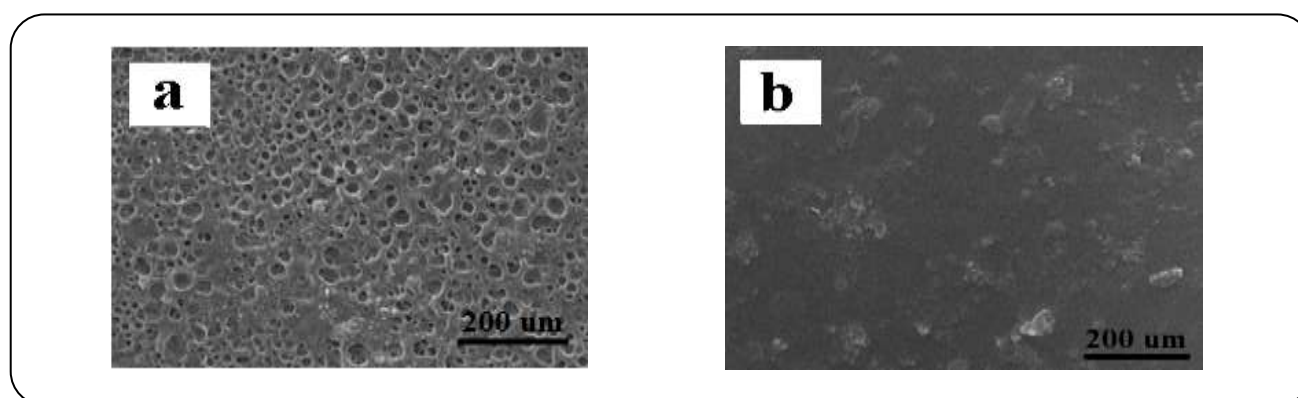


Fig. 9: SEM images of pre-treated 310 SS after corrosion (image a), Pani -DBSA coating after corrosion coatings have grown by an applied current density of 5 mA/cm² after corrosion (image b).

is attributed to the effective barrier behavior of the Pani -DBSA coating. The values of C_c and C_{dl} for the Pani -DBSA are lower than the uncoated 310 SS, therefore, these results provide further support for the protection of 310 SS by the Pani -DBSA coating. On the other hand, the higher values of R_{ct} and R_{por} and lower values of C_c and C_{dl} indicate the excellent corrosion performance of the Pani -DBSA coating 60. The PE% calculated from EIS data are found to be 91.2% for Pani -DBSA coated 310 SS, which are in agreement with the potentiodynamic polarization results. The polymer coating thickness on the surface 310 SS of the C_c can be achieved according to the following equation [40]:

$$C_c = \epsilon_0 \epsilon A d^{-1} \quad (4)$$

Where ϵ is the dielectric constant of the environment, ϵ_0 is the vacuum permittivity, A is the electrode area and d is the thickness of the protective layer. As can be seen in Table 3, the thickness of the uncoated electrode is aluminum oxide and also with increasing applied current density increased thickness and reduced coating capacitance. The thickness is for Pani -DBSA coated 310 SS synthesized

under galvanostatic conditions at 5 mA cm⁻² current densities to the 8.0 μ m.

SEM characterization

The SEM images of pre-treated 310 SS after corrosion (image a), Pani -DBSA coating after corrosion grown by an applied current density of 5 mA cm⁻² after corrosion (image b) are shown in Fig. 9. Image a show that numerous large pits and inequalities were formed after corrosion, which reveals severe damage on the surface due to metal dissolution. Image b shows that the Pani -DBSA coating was electrodeposited on the surface and protected it from the corrosion the 310 SS, which does not change dramatically. It clearly reveals that the formed coatings on 310 SS surface are uniform and dense. The quality of the coatings is so excellent that no crack or detachment of the coatings is observed.

CONCLUSIONS

The electrochemical polymerization of aniline from aqueous dodecylbenzene sulfonic acid medium generates adhesive Pani -DBSA coatings on the 310 stainless steel. The result of the optical absorption spectroscopy reveals

the formation of the emeraldine salt forms of Pani -DBSA. The potentiodynamic polarization and electrochemical impedance spectroscopy study reveal that the Pani -DBSA acts as a protective layer on 310 SS against corrosion in 5% NaCl solution. The corrosion rate of Pani -DBSA coated SS310 is found to be ~30 times lower than that observed for uncoated stainless steel. The protection efficiency is found to be ~96%. The EIS results are in good agreement with the potentiodynamic polarization measurements. This study reveals that the Pani -DBSA coating has excellent corrosion protection properties and it can be considered as a potential coating material to protect stainless steel against both localized and general corrosion in aqueous 5% NaCl.

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