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# Inhibition of nickel coated mild steel corrosion by electrosynthesized polyaniline coatings

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#### ABSTRACT

Polyaniline (PANI) coatings were electrochemically synthesized on nickel (Ni) coated mild steel (MS) and their corrosion protection properties were investigated. In this work, the Ni layer ( $\sim 1 \mu m$  thick) was electrodeposited on MS under galvanostatic condition. Thereafter, the PANI coating was deposited over the Ni layer from aqueous salicylate medium by using cyclic voltammetry. These bi-layered composite coatings were characterized by cyclic voltammetry, UV-vis absorption spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The corrosion protection properties of Ni coated MS (Ni/MS) and PANI coated Ni/MS (PANI/Ni/MS) were investigated in aqueous 3% NaCl by using open circuit potential (OCP) measurements, potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). It was shown that the top layer of PANI exhibits a lower porosity behavior with respect to Ni coating and reduces the corrosion rate of Ni/MS almost by a factor of 3500 and increases the lifetime of Ni coating.

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#### 1. Introduction

During the last decade, several research groups studied the electrochemical synthesis of conducting polymer coatings on oxidizable metals for corrosion protection purposes [1–19]. The common feature of these studies is that the electrochemical synthesis of conducting polymer coatings on oxidizable metals is preceded by the dissolution of the base metal at a potential lower than the oxidation potential of monomer. Hence, a successful electrochemical synthesis of conducting polymer coatings on oxidizable metal demands a careful choice of the solvent and/or supporting electrolyte and the establishment of electrochemical parameters, which will strongly passivate the metal without impeding the electropolymerization process.

Only few electrolytes such as oxalate [9,19], salicylate [17], tartrate [20], malate [21] and sulphate [10] suitable for the electrochemical synthesis of conducting polymers have been reported. However, the extent of using the conducting polymers is limited due to the exclusivity of the monomers that are essential for their synthesis. To overcome this limitation, different synthesis

approaches such as synthesis of substituted conducting polymers, copolymers and bilayers have been attempted.

Our group has developed appropriate electrochemical polymerization procedures to synthesize strongly adherent poly(o-anisidine) (POA) [15,17,22], poly(o-toluidine) (POT) [16,23] and poly(2,5-dimethylaniline) (PDMA) [24,25] coatings on MS and copper (Cu). It was shown that these coatings have remarkable capability to protect MS and Cu against corrosion. Pawar et al. [26] reported recently, the synthesis of poly(aniline-co-o-toluidine) coatings on MS from aqueous salicylate solution using cyclic voltammetry and investigated the corrosion properties of these copolymer coatings in aqueous 3% NaCl. It was found that the poly(aniline-coo-toluidine) coatings provide better protection for MS against corrosion than the corresponding homopolymer coatings. The corrosion rates of PANI, POT and poly(aniline-co-o-toluidine) (with feed ratio of o-toluidine as 0.5) coated MS are found to be  $\sim$  3, 20 and 50 times, respectively, lower than that observed for uncoated MS.

Bilayer coating consists of either a top coat of conducting polymer on the layer of the other conducting polymer or a top layer of conducting polymer on the metallic coating such as nickel. Recently, we electrochemically synthesized the bi-layered composites of poly(o-anisidine) (POA) and PANI on MS from aqueous salicylate medium and investigated the corrosion protection performance of these bi-layered composites in aqueous 3% NaCl solution [27]. It was shown that the combinations of the bi-layered composite coatings provide better protection to MS than single

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layered PANI or POA coatings. However, the corrosion protection offered to MS depends on the deposition order of polymer layers in the composite. Tuken and his research group [28] studied the electrochemical synthesis of PANI and PPY coatings on nickel plated MS and Cu substrates from aqueous media.

The objectives of the present study are: (i) to develop an appropriate electrochemical polymerization recipe to synthesize PANI layer on Ni coated MS from aqueous media; (ii) to find potentially good, low cost and easily available supporting electrolyte for the electropolymerization of aniline on Ni coated MS; (iii) to synthesize uniform, compact and strongly adherent PANI layer on Ni coated MS and (iv) to examine the corrosion protection performance of PANI coated Ni/MS in aqueous 3% NaCl solution.

Pawar et al. [29] have investigated the electrochemical polymerization of aniline on MS from the aqueous salicylate solution by cyclic voltammetry. It was shown that the aqueous salicylate solution is a suitable medium for the electropolymerization of aniline and it results in the deposition of uniform and strongly adherent PANI coatings on MS. Therefore, in the present work an aqueous solution of sodium salicylate was chosen as the supporting electrolyte for the electrochemical synthesis of PANI on Ni coated MS. To the best of our knowledge, there are no reports in the literature dealing with the electrochemical synthesis of corrosion protective PANI coatings on Ni coated MS from aqueous salicylate medium by using cyclic voltammetry.

#### 2. Experimental

#### 2.1. Materials

All chemicals were of analytical grade. The monomer aniline was procured from Fluka and was doubly distilled prior to being used for the synthesis. Sodium salicylate ( $NaC_7H_5O_3$ ), nickel sulphate ( $NiSO_4$ ), nickel chloride ( $NiCl_2$ ) and boric acid ( $H_3BO_3$ ) were procured from Merck and used as received without further purification. Bi-distilled water was used to prepare all the solutions.

#### 2.2. Substrate preparation

The MS substrates (size  $\sim 10 \text{ mm} \times 15 \text{ mm}$  and 0.5 mm thick) were polished with a series of emery papers of different grit sizes (180, 400, 600, 800 and 1200). After polishing, the substrates were cleaned with acetone and double distilled water and dried in air. Prior to any experiment, the substrates were treated as described and freshly used with no further storage. The chemical composition (by wt%) of the MS used in this study was: 0.03% C, 0.026% S, 0.01% P, 0.002% Si, 0.04% Ni, 0.002% Mo, 0.16% Mn, 0.093% Cu and 99.64% Fe.

#### 2.3. Synthesis of bi-layered structure of PANI and Ni on MS

The bi-layered PANI/Ni coating was synthesized on MS using the following procedures.

#### 2.3.1. Electrodeposition of Ni layer on MS

The Ni layer was first deposited on MS substrate from an aqueous bath containing NiSO<sub>4</sub> (30 wt%), NiCl<sub>2</sub> (1 wt%) and H<sub>3</sub>BO<sub>3</sub> (1.25 wt%) [28]. The pH of the electrolyte bath was found to be ~5.6–6.2. The thickness of Ni layer was controlled by monitoring the amount of charge passing for the deposition under constant applied cathodic current of 10 mA. The deposition process was carried out in open atmosphere and under stirring conditions using Ni electrode (99.9% purity, 3 cm<sup>2</sup> surface area) as anode.

#### 2.3.2. Electrodeposition of PANI on Ni/MS

The PANI was deposited over the Ni layer from 0.1 M aqueous salicylate solution containing 0.3 M aniline to prepare a PANI/Ni/MS bi-layered structure. The electrochemical synthesis was carried out under cyclic voltammetric conditions in a single compartment three electrode cell with MS as a working electrode (150 mm<sup>2</sup>), platinum as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The cyclic voltammetric conditions were maintained using the electrochemical measurement System (SI 1280B, Solartron, U.K.) controlled by corrosion software (CorrWare, Electrochemistry/Corrosion Software, Scribner Associates Inc. supplied by Solartron, U.K.) [30]. The synthesis of PANI was carried out by cycling the electrode potential between -1.0V and 1.8V with the scan rate of 0.02V/s. After deposition, the working electrode was removed from the electrolyte and rinsed with double distilled water and dried in air.

#### 2.4. Characterization of the coatings

The FTIR transmission spectrum was recorded with a Perkin Elmer spectrometer (1600 Series II, U.S.A.) in horizontally attenuated total reflectance (HATR) mode in the spectral range of 4000–400 cm<sup>-1</sup>. The UV–vis absorption study was carried out *ex situ* at room temperature in the wavelength range of 300–1100 nm using a microprocessor controlled double beam UV–vis spectrophotometer (Model U 2000, Hitachi, Japan). The thickness of the PANI was measured by a conventional magnetic induction based microprocessor controlled coating thickness gauge (Minitest 600, ElectroPhysik, Germany). The error in the thickness measurements was less than 5%.

#### 2.5. Evaluation of corrosion protection performance

The corrosion protection properties of the Ni/MS and bi-layered structure PANI/Ni/MS were evaluated in 3% NaCl solution by using OCP measurements, potentiodynamic polarization technique and EIS using an electrochemical measurement system (SI 1280B, Solartron, U.K.). For these measurements, a Teflon holder was used to encase the substrates so as to leave an area of ~ $0.4 \,\mathrm{cm^2}$  exposed to the solution. All the measurements were repeated at least four times and good reproducibility of the results was observed.

The potentiodynamic polarization measurements were performed by sweeping the potential between -0.25 V and 0.25 V from OCP with the scan rate of 0.002 V/s. Before polarization the substrates were immersed into the solution and the OCP was monitored until a constant value was reached. The potentiodynamic polarization curves were analyzed by using Corr-view software from Scribner Associates which performs the Tafel fitting and calculates the values of the corrosion potential ( $E_{corr}$ ), corrosion current density ( $j_{corr}$ ) and corrosion rate (CR) in mm per year [30].

The EIS measurements were carried out at the OCP in the frequency range from 0.1 Hz to 20 kHz with amplitude of superimposed AC signal of 0.010 V. The spectra were also recorded after different immersion times in aqueous 3% NaCl solution. The analysis of the impedance spectra was done by fitting the experimental results to equivalent circuits using Z-view software from Scribner Associates [31]. The quality of fitting to equivalent circuit was judged firstly by the Chi-square value ( $\chi^2$ , i.e. the sum of the square of the differences between theoretical and experimental points) and secondly by limiting the relative error in the value of each element in the equivalent circuit to 5%.



**Fig. 1.** Cyclic voltammograms of (a) first, (b) second and (c) third scans recorded during the polarization of MS electrode in 0.1 M aqueous salicylate solution. Inset depicts the cyclic voltammogram of first scan recorded during the polarization of Pt electrode under identical experimental conditions.

#### 3. Results and discussion

#### 3.1. Synthesis of PANI coatings on Ni/MS

The MS electrodes were first polarized in 0.1 M aqueous salicylate solution (without aniline) by cycling continuously the electrode potential between -1.0 and 1.8 V versus SCE at a potential scan rate of 0.02 V/s in order to understand the different processes occurring at the electrode surface. The first scan of the voltammetric response of the MS electrode in 0.1 M aqueous salicylate solution is shown in Fig. 1(a). The first positive cycle is characterized by (i) an anodic peak (A) at -0.498 V versus SCE; (ii) a small oxidation peak (B) at  $\sim 1.05$  V versus SCE and beyond this potential high anodic current flows. The anodic current decays very sharply and a negligibly small current is observed till 0.043 V versus SCE. The negative cycle terminates with the reduction peak C at  $\sim -0.838$  V versus SCE.

To discriminate between the origin of the different peaks, the platinum (Pt) electrode was polarized under identical experimental conditions and the corresponding first scan of the cyclic voltammogram is presented in the inset of Fig. 1. When the Pt electrode was used, the first positive cycle is characterized by the reversible oxidation peak B at  $\sim$ 1.04V versus SCE which is attributed to the oxidation of the salicylate electrolyte. The absence of peak A in the voltammogram corresponding to the Pt electrode polarized under the same electrolytic conditions proves that in the case of MS this peak comes from the oxidation of the MS electrode.

Hence, the anodic peak A is attributed to the dissolution of the MS electrode surface which produces  $Fe^{2+}$  ions in its vicinity. These ions interact with salicylate, corresponding to complexation of the  $Fe^{2+}$  cation by salicylate counter-ions which inhibit the dissolution of the electrode surface [32]. As a result, just after the peak A, the current density decreases and attains a negligibly small value. The soluble colored products of the reaction diffuse into the electrolyte. Indeed, the color of the electrolyte gradually changes to brownish-pink during the polarization process. It seems that the major portion of the reaction products is soluble which may be due to the presence of carboxylic acid groups on the oligomers produced during the polarization peak B is assigned to the oxidation of the salicylate electrolyte.

On repetitive cycling, the voltammograms identical to that of first scan are obtained. However, the position of the peak A is shifted in the positive direction and the current density corresponding to it increases with an increase in the number of scans. This may



**Fig. 2.** XRD pattern of (a) as received MS and (b) polarized MS substrates. Inset shows the XRD pattern of polarized Pt electrode. (**X** indicates the diffraction peaks corresponding to iron salicylate.)

be attributed to the partial stabilization of the MS electrode surface due to the formation of the complexation of  $Fe^{2+}$  cations by salicylate counter-ions.

In order to understand the observed cyclic voltammetry results, we have performed the XRD measurements of the MS electrode polarized in 0.1 M aqueous salicylate solution. The XRD patterns of the uncoated MS and the polarized MS electrode are shown in Fig. 2. Apart from the characteristic peak of MS, the XRD pattern of the MS electrode polarized in 0.1 M sodium salicylate solution [Fig. 2(b)] indicates the presence of diffraction peaks at  $2\theta$  values of 11.90°, 18.10°, 28.80° and 38.10° due to iron salicylate (JCPDS # 01-055). Thus, the XRD result clearly reveals the formation of iron salicylate on the MS electrode surface. The XRD pattern of the polarized Pt electrode is shown in the inset of Fig. 2. It exhibits the presence of diffraction peaks at  $2\theta$  values of 40.10° and 46.60° corresponding to the Pt (JCPDS # 04-0802). We do not observe the presence of any other peak due to salicylate complex, which confirmed that the polarization of the MS electrode in 0.1 M sodium salicylate solution results in the passivation of the electrode surface via the formation of iron salicylate phase.

The cyclic voltammogram of the first scan recorded during the synthesis of PANI coating on the MS is shown in Fig. 3(a).



**Fig. 3.** Cyclic voltammograms of the first scan recorded during the synthesis of PANI coating on (a) uncoated MS and (b) Ni/MS.



**Fig. 4.** Cyclic voltammogram of the (a) first, (b) second and (c) tenth scans recorded during the synthesis of PANI coating on Ni/MS.

This voltammogram is significantly different from that recorded in aqueous salicylate solution without aniline (cf. Fig. 1(a)). Indeed, the anodic peak A corresponding to the dissolution of the MS substrate was not observed and the first potential sweep indicates the anodic peak A1 at 1.36 V versus SCE. During reverse cycle, the anodic current density decreases rapidly and a negligibly small current density is observed until the end of the cycle. The non-observance of the anodic peak A corresponding to the dissolution of the MS when aniline is in the solution indicates that aniline is involved in the passivation process and the electrochemical polymerization takes place without dissolution of the electrode surface. The anodic peak A<sub>1</sub> corresponds to the oxidation of aniline and formation of radical cations, which is considered to be the first step in the polymerization of the conducting polymers [33]. The non-observance of the reduction peaks implies the occurrence of the irreversible oxidation of aniline on the uncoated MS.

The cyclic voltammogram of the first scan recorded during the synthesis of PANI coating on the Ni/MS is shown in Fig. 3(b). This cyclic voltammogram exhibits good resemblance with the first potential sweep [*cf*. Fig. 3(a)] recorded during the synthesis of PANI layer on uncoated MS. In the first potential sweep, a well-defined anodic peak at  $\sim$ 1.42 (peak A<sub>1</sub>) versus SCE is observed, which obviously attributed to the oxidation of aniline. The non-observance of the reduction peak implies the occurrence of the irreversible oxidation of aniline on the Ni/MS.

The cyclic voltammograms of the first, second and tenth scans recorded during the synthesis of PANI coating on Ni/MS are shown in Fig. 4. The cyclic voltammogram of the first scan is also presented in Fig. 4(a) for comparison. The cyclic voltammogram of the second scan [Fig. 4(b)] is identical to that of first scan. However, the current density corresponding to the oxidation peak decreases gradually with the number of scans. The cyclic voltammogram of the tenth scan [Fig. 4(c)] does not show well-defined redox peaks.

The thickness of PANI layer was estimated by using the equation [34]:

$$d = \frac{QM}{2F\rho} \tag{1}$$

assuming a two electron mechanism based on the monomer involved in the polymerization process and a current efficiency of 100%. In this equation, Q is the specific overall charge for the electrochemical polymerization,  $\rho$  is the density of the PANI, Mis the molar mass and F is the Faraday constant (96,500 C). The thickness of PANI layer (20 sweeps) calculated by using this equa-



Fig. 5. FTIR spectrum of the PANI coating synthesized on Ni/MS.

tion was found to be  $\sim$ 12.7  $\mu$ m, which is fairly in agreement with that measured by using a conventional magnetic induction based microprocessor controlled coating thickness gauge.

The FTIR spectrum of PANI coating synthesized on Ni/MS recorded in HATR mode is shown in Fig. 5. Main characteristic bands of PANI are assigned as follows [35–38]: a broad band at  $\sim$ 3360 cm<sup>-1</sup> is due to the N–H stretching mode, the C=N and C=C stretching modes for the quinoid (Q) and benzoid (B) rings occur at 1594 and 1491 cm<sup>-1</sup>, respectively, a band at  $\sim$ 1380 cm<sup>-1</sup> is assigned to the C–N stretching, a band at  $\sim$ 1299 cm<sup>-1</sup> is assigned to the presence of carboxylic groups of sodium salicylate, the bands at 1177 and 1023 cm<sup>-1</sup> are attributed to the 1–4 substitution on the benzene ring and the bands between 800 and 700 cm<sup>-1</sup> reveal the occurrence of the 1–3 substitutions.

The UV–vis absorption spectrum of PANI coating synthesized on uncoated MS is shown in Fig. 6(a). It exhibits a shoulder peak at  $\sim$ 540 nm, which is attributed to the formation of pernigraniline base (PB) form of PANI. The PB is the fully oxidized form of PANI and is insulating in nature [39]. The UV–vis absorption spectrum of the PANI coating on Ni/MS [Fig. 6(b)] does not exhibit major changes as compared to the spectrum shown in Fig. 6(a), except the decrease in the overall absorbance level.



Fig. 6. UV-vis absorption spectra of the PANI coated (a) MS and (b) Ni/MS.



**Fig. 7.** Open circuit potential-time curves recorded for (a) PANI/MS and (b) PANI/Ni/MS.

#### 3.2. Evaluation of corrosion protection performance

The corrosion protection performance of PANI coating on Ni/MS was evaluated in 3% NaCl solution by using OCP measurements, potentiodynamic polarization technique and EIS.

#### 3.2.1. OCP measurements

The evolution of OCP for PANI/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl was studied. The corresponding OCP-time curves are shown in Fig. 7. The OCP of PANI/MS [Fig. 7(a)] was measured to be ~-0.483 V versus SCE, which is more positive than that of the uncoated MS by up to ~0.227 V versus SCE. The initial decrease in the potential is associated with the initiation of the water uptake process in the coating. After 8 h of immersion the potential decreases sharply and it remains fairly constant at ~-0.608 V versus SCE, which is close to the corrosion potential of MS. The protection time of the coating is determined by measuring the elapsed time until the OCP of the polymer coated MS drops to

#### Table 1

Result of potentiodynamic polarization measurements.

		CURRENT DENSITY /A/m <sup>-2</sup>
	-1.0	1x10 <sup>-5</sup> 1x10 <sup>-2</sup> 1x10 <sup>1</sup> 1x10 <sup>4</sup>
POTENTIAL vs SCE/V	<b>-0.6</b> –	
	-	(a)
	-0.2 -	(b) (c)
	-	(d)
	0.2	

**Fig. 8.** Potentiodynamic polarization curves recorded in aqueous 3% NaCl solution for (a) uncoated MS, (b) Ni/MS, (c) PANI/MS and (d) PANI/Ni/MS.

that of the uncoated electrode. Thus, the PANI protects the MS in 3% NaCl for almost 8 h.

In case of PANI coated Ni/MS [Fig. 7(b)], initially the OCP of PANI coated Ni/MS was measured to be  $\sim$ -0.555 V versus SCE, which is more positive than that of the uncoated MS by up to  $\sim$ 0.155 V versus SCE. In the early stages of the immersion, the potential decreases sharply and it attains a plateau wherein the potential remains fairly constant at  $\sim$ -0.586 V versus SCE during the first 5 h of immersion. This plateau is observed for 77 h during which the PANI coating exhibits barrier behavior by limiting the diffusion of the corrosive species towards the underlying steel substrate. After 77 h of immersion the OCP decreases sharply and a second plateau is  $\sim$ 122 h and finally the potential decreases sharply to -0.615 V versus SCE, which is close to the corrosion potential of the MS. Thus, the PANI/Ni protects the MS in 3% NaCl for almost 199 h.

#### 3.2.2. Potentiodynamic polarization measurements

The behavior of the uncoated MS, Ni/MS and PANI coated MS and PANI coated Ni/MS (12.7  $\mu$ m thick) in aqueous 3% NaCl under the potentiodynamic polarization conditions is presented in Fig. 8. The values of the  $E_{\text{corr}}$ ,  $j_{\text{corr}}$ , Tafel constants ( $\beta_a$  and  $\beta_c$ ), polarization resistance ( $R_{\text{pol}}$ ) and CR obtained from these curves are given in Table 1.

The potentiodynamic polarization curve for Ni/MS is shown in Fig. 8(b). It is observed that the  $j_{corr}$  decreases from  $3.07 \times 10^{-5}$  A/cm<sup>2</sup> for uncoated MS to  $1.74 \times 10^{-5}$  A/cm<sup>2</sup> for Ni/MS. The  $E_{corr}$  increases from -0.710 V versus SCE for uncoated MS to -0.389 V versus SCE for Ni/MS. The positive shift of 0.321 V in  $E_{corr}$ indicates the protection of the MS surface by the Ni plating. The CR of Ni/MS is found to be  $\sim 0.20$  mm/year which is  $\sim 1.75$  times lower than that observed for uncoated MS.

The potentiodynamic polarization curve for PANI coated MS recorded in aqueous 3% NaCl solution is shown in Fig. 8(c). The

Sample	$E_{\rm corr}$ (V <sup>a</sup> )	$j_{\rm corr}~({\rm A/cm^2})$	$\beta_{\rm a}$ (V dec <sup>-1</sup> )	$\beta_{ m c}$ (V dec $^{-1}$ )	$R_{\rm p}\left(\Omega ight)$	CR (mm year <sup>-1</sup> )	% P
Uncoated MS Ni/MS (~1 µm)	-0.710 -0.389	$\begin{array}{c} 3.07 \times 10^{-5} \\ 1.74 \times 10^{-5} \end{array}$	0.084 0.197	0.185 0.659	$\begin{array}{c} 8.17\times10^2\\ 3.78\times10^3\end{array}$	0.35 0.20	-
PANI/MS (~2.90 μm) PANI/Ni/MS (~12.7 μm)	-0.502 -0.143	$\begin{array}{c} 9.60 \times 10^{-7} \\ 1.49 \times 10^{-8} \end{array}$	0.225 0.130	0.399 0.156	$\begin{array}{c} 6.51\times10^{4}\\ 2.07\times10^{6}\end{array}$	0.01 0.0001	$\begin{array}{c} 4.19 \times 10^{-3} \\ 7.10 \times 10^{-9} \end{array}$

<sup>a</sup> Potentials versus SCE.

 $E_{\rm corr}$  value increases from -0.710 V versus SCE for uncoated MS to -0.502 V versus SCE for PANI coated MS. The  $j_{\rm corr}$  decreases from  $3.07 \times 10^{-5}$  A/cm<sup>2</sup> for uncoated MS to  $9.6 \times 10^{-7}$  A/cm<sup>2</sup> for PANI coated MS. The CR of PANI coated MS is found to be ~0.01 mm/year which is ~35 times lower than that observed for uncoated MS.

The potentiodynamic polarization curve for PANI coated Ni/MS recorded in aqueous 3% NaCl solution is shown in Fig. 8(d). The  $E_{\rm corr}$  value increases from -0.710 V versus SCE for uncoated MS to -0.143 V versus SCE for PANI coated Ni/MS. Further, the  $j_{\rm corr}$  value for PANI coated Ni/MS is observed to be far lower than the corresponding values for uncoated MS as well as for Ni/MS indicating the corrosion resistant feature of the PANI coating. The  $j_{\rm corr}$  decreases from  $3.07 \times 10^{-5}$  A/cm<sup>2</sup> for uncoated MS to  $1.49 \times 10^{-8}$  A/cm<sup>2</sup> for PANI coated Ni/MS. The CR of PANI coated Ni/MS is found to be  $\sim 0.0001$  mm/year which is  $\sim 3500$  times lower than that observed for uncoated MS. The protection efficiency (PE) of the coating was calculated by using the expression:

$$PE\% = \left[\frac{R_{\text{pol}}(\text{coated}) - R_{\text{pol}}(\text{uncoated})}{R_{\text{pol}}(\text{coated})}\right] \times 100$$
(2)

where  $R_{pol}$  (uncoated) is the polarization resistance of uncoated MS and  $R_{pol}$  (coated) is the measured polarization resistance for coated MS. The PEs of Ni/MS, PANI/MS and PANI/Ni/MS calculated from potentiodynamic polarization data are found to be ~78%, 98% and 99%, respectively.

The porosity in the coating is a very important parameter to determine whether a coating is suitable or not to protect the substrate against corrosion. In order to calculate the porosity of these deposits we have used the relationship [40]:

$$P = \frac{R_{\text{pol}}(\text{uncoated})}{R_{\text{pol}}(\text{coated})} \times 10^{-(|\Delta E_{\text{corr}}|/\beta_a)}$$
(3)

where *P* is the total porosity,  $\Delta E_{\rm corr}$  is the difference between corrosion potentials and  $\beta_{\rm a}$  is the anodic Tafel slope for uncoated MS substrate. Table 1 also gives the porosity values in the polymer deposits. The porosity in PANI coating synthesized on MS and Ni/MS calculated from potentiodynamic polarization data is found to be  $\sim 4.19 \times 10^{-3}\%$  and 7.01  $\times 10^{-9}\%$ , respectively. Thus, PANI coating synthesized on Ni/MS is more compact and the porosity in this coating is almost  $5.9 \times 10^5$  times lower than the porosity in PANI synthesized on uncoated MS.

#### 3.2.3. EIS studies

The Nyquist impedance plot of uncoated MS recorded in 3% NaCl is shown in Fig. 9(a) and is modeled by an electrical equivalent circuit [41–43] model A depicted in Fig. 10(a), where  $R_s$  represents the electrolyte resistance,  $CPE_p$  the phase element that represents all the frequency dependent electrochemical phenomena, namely double layer capacitance ( $C_{dl}$ ) and diffusion processes and  $R_{ct}$  the charge transfer resistance connected with corrosion processes. The constant phase element, CPE, is introduced in the circuit instead of a pure capacitor to give a more accurate fit. Thus, the impedance plot of the uncoated MS can be fitted with a semicircle, which is attributed to the processes occurring at the MS surface.

The Nyquist impedance plot of Ni/MS recorded in aqueous 3% NaCl solution is shown in Fig. 9(b). The electrical equivalent circuit model B depicted in Fig. 10(b) is used to model this impedance plot. It consists of the electrolyte resistance ( $R_s$ ), pore resistance ( $R_p$ ), coating capacitance ( $C_c$ ),  $R_{ct}$  and  $C_{dl}$ . The constant phase element (CPE) was used instead of capacitance. The CPE represents the deviation from the true capacitance behavior. Thus, the impedance plot of Ni/MS was fitted with two semicircles, a smaller one at high frequency range followed by a larger one at lower frequencies. The first semicircle is attributed to the characteristics of the Ni/electrolyte interface and it is characterized by the  $R_p$  and CPE<sub>c</sub>. The second



**Fig. 9.** Nyquist impedance plots for (a) uncoated MS and (b) Ni/MS recorded in aqueous 3% NaCl solution.

semicircle in the low frequency region is attributed to the Ni/MS interface and it is characterized by the  $R_{ct}$  for the charge transfer reactions occurring at the bottom of the pores in the coating and the CPE<sub>dl</sub>.

The Nyquist impedance plot and phase angle–frequency Bode curve of PANI/Ni/MS recorded in aqueous 3% NaCl solution are shown in Fig. 11(a) and (b), respectively. This impedance plot was modeled by the electrical equivalent circuit, model B, shown in Fig. 10(b). The first semicircle is attributed to the characteristics of the PANI/electrolyte interface and it is characterized by the  $R_p$  and CPE<sub>c</sub>. The second semicircle in the low frequency region is attributed to the PANI/Ni interface and it is characterized by the bottom of the pores in the coating and the CPE<sub>dl</sub>. The values of the impedance plots for uncoated MS, Ni/MS and PANI/Ni/MS are given in Table 2.

The values of  $R_{ct}$  for Ni/MS, and PANI/Ni/MS are found to be ~3.379 and 97.457 k $\Omega$ , respectively, which are about ~5 and 149 times higher than that observed for uncoated MS. The protective effect of Ni and PANI/Ni is obvious as the  $R_{ct}$  values are significantly higher as compared to the uncoated MS. However, PANI/Ni bi-layered composite provides effective protection to MS against corrosion than Ni coating, which is in agreement with the potentiodynamic polarization results. The lower values of CPE<sub>c</sub> and CPE<sub>dl</sub> for the PANI/Ni/MS provide further support for the protection of MS by the PANI/Ni coating. Thus, the higher values of  $R_{ct}$  and  $R_p$ 



**Fig. 10.** Electrical equivalent circuit models: (a) model A, (b) model B and (c) model C used for the fitting of impedance plots.

and lower values of  $C_c$  and  $C_{dl}$  indicate the excellent corrosion performance of the PANI/Ni coating. The PE was also calculated by using the expression (2) from the EIS data with the  $R_{pol} = R_p + R_{ct}$ . The PEs calculated from EIS data for Ni/MS and PANI/Ni/MS were found to be ~85 and 99%, which is fairly in agreement with the potentiodynamic polarization results.

#### 3.2.4. Immersion tests

In order to gain further insight into corrosion protection properties, the impedance plots of Ni/MS and PANI/Ni/MS were recorded as a function of immersion time in 3% NaCl solution.

The Nyquist impedance plots of PANI/Ni/MS recorded after 4, 48, 72, 96 and 240 h of immersion times in aqueous 3% NaCl are shown in Fig. 11(a) (curves 2–6). These impedance plots exhibit systematic variations in terms of the values of the impedance parameters, which are the result of the changes in the dielectric characteristics of the coating due to electrolyte penetration through the pores in



**Fig. 11.** Nyquist impedance (a) and Bode plots (b) for PANI/Ni/MS recorded after 0 h (curve 1), 4 h (curve 2), 48 h (curve 3), 72 h (curve 4), 96 h (curve 5) and 240 h (curve 6) of immersion in aqueous 3% NaCl solution.

the coating and consequently, the onset of corrosive processes at the surface of the Ni coated MS.

3.2.4.1. Immersion time: from 4 to 48 h. The Nyquist impedance plot recorded at 4 h of exposure time during the immersion in aqueous 3% NaCl solution is shown in Fig. 11(a) (curve 2). This plot is analyzed in terms of the same equivalent circuit model B, as shown in Fig. 10(b). It is fitted with two semicircles with diameters  $R_p$  (at higher frequency range) and  $R_{ct}$  (at lower frequencies). The  $R_p$  is related to the penetration of the electrolyte into the micropores

Table 2

Impedance parameter values extracted from the fit to the equivalent circuit for the impedance spectra recorded in aqueous 3% NaCl solution.

1 1			1 1	•		
Immersion time	$R_{\rm p}\left(\Omega\right)$	$C_{\rm c}$ (F)	$R_{\rm ct}\left(\Omega\right)$	$C_{\rm dl}$ (F)	$R_{ m diff}\left(\Omega ight)$	$C_{\rm diff}$ (F)
Uncoated MS						
As it is	-	-	$6.54 \times 10^{2}$	$7.99  imes 10^{-4}$	-	-
Ni/MS						
As it is	1087	$1.95  imes 10^{-5}$	$3.379 \times 10^3$	$9.1  imes 10^{-5}$	-	-
PANI/Ni/MS						
As it is	5408	$1.03 imes10^{-6}$	$97.46 \times 10^{3}$	$4.53 \times 10^{-7}$	-	-
4 h	4576	$1.30 imes10^{-6}$	$20.06  imes 10^4$	$1.21  imes 10^{-6}$	-	-
16 h	4021	$1.46 imes10^{-6}$	$20.30  imes 10^4$	$1.65  imes 10^{-6}$	-	-
48 h	3891	$2.88\times10^{-6}$	$24.07  imes 10^4$	$2.44  imes 10^{-6}$	-	-
72 h	3497	$4.47 imes10^{-6}$	$15.90 \times 10^{3}$	$1.57 \times 10^{-5}$	$21.38\times10^3$	$2.44  imes 10^{-5}$
96 h	2589	$5.02 imes10^{-6}$	$60.55 \times 10^{2}$	$2.03  imes 10^{-5}$	$23.23\times10^3$	$3.22  imes 10^{-5}$
144 h	1790	$1.38  imes 10^{-5}$	$45.44 \times 10^{2}$	$2.53 \times 10^{-5}$	$27.03\times10^3$	$2.94  imes 10^{-6}$
240 h	845	$1.55\times10^{-5}$	$33.34  imes 10^2$	$2.91  imes 10^{-5}$	$32.48\times 10^3$	$2.69\times10^{-5}$

of the coating. The  $R_p$  value decreases slightly during this immersion time. The slight decrease in the value of the  $R_p$  is attributed to the entry of the electrolyte into the micropores in the coating [41]. The  $R_{ct}$  is related to the charge transfer process occurring at the metal substrate beneath the coating [41]. In the present study, the charge transfer process is attributed to anodic oxidation of Ni to its oxide rather than the underlying MS, under accelerating effect of top PANI layer. The  $R_{ct}$  value is observed to increase during this immersion period with respect to Ni/MS. This observation reveals an efficient barrier property of the PANI layer against corrosion and it is attributed to the oxidation of the Ni by the PANI, which results in the formation of Ni oxide compounds at the PANI/Ni interface and also to partial reduction of the polymer film.

It is known that the phase angle is more sensitive to the state change of both coating and metal surface. The phase angle–frequency Bode curve recorded for PANI/Ni/MS at 4 h exposure time during immersion in aqueous 3% NaCl solution is shown in Fig. 11(b) (curve 2). It is seen that the value of the phase angle is maximum ( $\sim 60^\circ$ ) at the middle frequencies and then it decreases sharply to  $\sim 13^\circ$  at the lowest frequency. This observation provides the evidence for a limited diffusability through the PANI/Ni composite coating.

The Nyquist impedance plot recorded for PANI/Ni/MS after 48 h of exposure time during the immersion in aqueous 3% NaCl solution is shown in Fig. 11(a) (curve 3). This plot is also fitted satisfactorily to the equivalent circuit model B, as shown in Fig. 10(b). The  $R_{ct}$ value is observed to increase further, whereas the R<sub>p</sub> decreases further during this immersion time. Further decrease in the  $R_p$  value during this immersion time indicates the increase in the amount of the electrolyte solution held within the pores of polymer coating. When Ni layer comes into contact with sufficient amount of electrolyte solution, dissolution of Ni starts. In the mean time the polymer film is reduced at the PANI/Ni interface. As a result of these events, the thickness of the Ni oxide layer increases and the polymer film reduces, consequently the increase in the R<sub>ct</sub> value is observed. The R<sub>ct</sub> value after this immersion time was found to be 240.74 k $\Omega$ . The E<sub>corr</sub> value at this immersion time is measured to be -0.557 V versus SCE, which is more positive than that of the corrosion potential for the uncoated MS by up to 0.153 V. Therefore, it can be said that even after 48 h of exposure time, the detectable corrosion processes were not started at the MS surface under the coating.

The phase angle–frequency Bode curve recorded for PANI/Ni/MS at 48 h exposure time [Fig. 11(b) (curve 3)] is similar to that observed at 4 h of exposure time. This suggests that the PANI/Ni/MS composite has a limited diffusability for corrosive species even after 48 h of immersion.

3.2.4.2. Immersion time: from 72 to 240 h. Further increasing the exposure time does not result in obvious variation in the shape of the Nyquist impedance plots. The Nyquist impedance plot for the PANI/Ni/MS at 72 h of exposure time during the immersion in the aqueous 3% NaCl solution is shown in Fig. 11(a) (curve 4). As seen earlier, the Nyquist impedance plots before 72 h of immersion are fitted satisfactorily to the equivalent circuit model B. However, the experimental Nyquist impedance plot after 72 h of immersion cannot be well fitted to model B. During immersion, the electrolyte penetrates via the pores in the coating and develops the electrolyte pathways with time through coating. The corrosive species along with the water diffuse through these paths towards the Ni surface. When the sufficient amount of electrolyte reaches the Ni surface, the corrosion processes are initiated at the PANI/Ni interface and as a consequence the  $E_{\rm corr}$  value shifts to less noble value. The measured open circuit potential value at this moment is found to be  $\sim$ -0.515 V versus SCE. Therefore, it can be said that after 72 h of immersion the anodic dissolution of the passive oxide layer begins

at the bottom of the pores which interacts with the electrolyte solution and results in the formation of corrosion products which diffuse towards the coating surface through the pores in the coating.

More recently, we investigated the corrosion protection performance of POA coatings on MS in 3% NaCl through immersion tests by EIS. It was observed that a single equivalent circuit was inadequate to explain the various physical and electrochemical processes occurring at different immersion times. It was shown that a diffusion combination, which consists of the diffusion resistance  $(R_{\text{diff}})$  and the diffusion capacitance  $(C_{\text{diff}})$  related to the diffusion of corrosion products from steel surface towards coating must be considered in the equivalent circuit after a certain immersion time [41]. The same equivalent circuit, model C, depicted in Fig. 10(c) was used to fit the impedance plot of PANI/Ni/MS recorded after 72 h of immersion. The model C consists of three time constants in which the first time constant is a representative of the characteristics of the PANI coating, while the second and third capacitive loops are attributed to the complex reactions occurring at the surface of the Ni coated MS. The second loop is characterized by charge transfer resistance  $(R_{ct})$  and double layer capacitance  $(C_{dl})$  and the third loop is correlated to diffusion processes ( $R_{diff}$  and  $C_{diff}$ ) caused by the presence of corrosion products. It is found that the fitting curve gives a good fit to the experimental impedance plot after 72 h of immersion when the equivalent circuit model C is used.

After 72 h of immersion, the  $R_{ct}$  value is observed to decrease and its value is found to be ~15.896 k $\Omega$ . However, it is higher than that of the uncoated MS. The decrease in the value of  $R_{ct}$  may be due to the dissolution of the passive oxide layer on the MS surface. The diffusion resistance is the resistance against the diffusion of the corrosion products from MS surface towards coating and its value is observed to be ~21.376 k $\Omega$ .

The phase angle–frequency Bode curve recorded for PANI/Ni/MS at 72 h exposure time during immersion in aqueous 3% NaCl solution is shown in Fig. 11(b) (curve 4). It is clearly observed that the value of the phase angle exhibits two maxima and then it decreases sharply. Therefore, it is expected to observe two separate semicircles in the Nyquist impedance plot; however these semicircles cannot be resolved well.

The Nyquist impedance plot recorded at 96 h of exposure time during the immersion in aqueous 3% NaCl solution is shown in Fig. 11(a) (curve 5). The equivalent circuit model C [as shown in Fig. 10(c)] is used to fit the experimental data. After 96 h of immersion time, the  $R_{ct}$  value is observed to decrease further to  $6.055 \,\mathrm{k\Omega}$ . However, it is higher than that of the uncoated MS. It is important to note that the  $R_{diff}$  value is observed to increase during this immersion time and it is found to be ~23.230 k $\Omega$ . The corrosion products are partially deposited into the pores in the coating and as a result, further diffusion of the corrosion products towards the coating surface is hindered. Consequently, the increase in the  $R_{diff}$  is observed during this immersion time.

The Nyquist impedance plot recorded at 240 h of exposure time during the immersion in aqueous 3% NaCl solution is shown in Fig. 11(b) (curve 6). After 240 h of immersion time, the significant decrease in the  $R_{ct}$  value is observed and its value is found to be  $\sim$ 3.334 k $\Omega$ , which is still higher than that of the uncoated MS. As expected the  $R_{diff}$  value increases significantly and its value is found to be  $\sim$ 32.483 k $\Omega$ . During this immersion time, the diffusion of the corrosion products is hindered and they are accumulated at the bottom of the coating, resulting in the formation of a loose corrosion product layer. However, the detachment of the coating was not observed even after 240 h of immersion.

#### 3.2.5. Evolution of impedance parameters with immersion time

The variation of  $R_p$  for Ni/MS and PANI/Ni/MS as a function of immersion time is shown in Fig. 12(a). It is seen that the value of  $R_p$  decreases rapidly and continuously for Ni/MS thereby indicating



**Fig. 12.** (a) Variation of pore resistance  $R_p$  for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (b) variation of coating capacitance  $C_c$  for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (c) volume fraction of the electrolyte in Ni/MS and PANI/Ni/MS coating as a function of immersion time in 3% NaCl solution; (d) variation of charge transfer resistance  $R_c$  for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (e) variation of double layer capacitance  $C_d$  for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; (f) delamination area for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; for Ni/MS and PANI/Ni/MS as a function of immersion time in 3% NaCl solution; for Ni/MS and PANI/Ni/MS as a function of immersion timmersion

the least corrosion protection offered by Ni plating to MS. In the case of PANI/Ni/MS composite, almost constant value of  $R_p$  was observed up to 96 h of immersion and thereafter a slow decrease in the value of  $R_p$  was seen to occur. This observation reveals that development of electrolyte pathways through the composite reached steady state since the first measurements [42,43]. Moreover, even after 240 h of immersion, the values of  $R_p$  for PANI/Ni/MS composite were found to be higher than those observed for Ni/MS. The coating capacitance  $C_c$  is the capacitance of the intact coating layer or the capacitance of the areas where rapid solution uptake does not occur [41]. The evolution of the  $C_c$  with the immersion time is shown in Fig. 12(b). The square root of time,  $t^{1/2}$ , is used in the figure to improve the resolution of the time axis. The increase in the values of  $C_c$  for Ni/MS and PANI/Ni/MS can be interpreted as consequence of continuous water uptake. The values of  $C_c$  for the bi-layered PANI/Ni/MS composite are significantly lower than

those observed for Ni/MS even after 240 h of immersion. Thus, in the case of PANI/Ni/MS composite the water permeation is very small up to 240 h of immersion.

The volume fraction of the water in the polymer coating when in contact with 3% NaCl solution as a function of time is determined using Brasher–Kingsbury equation [44]:

$$\phi = \frac{\log C_t / C_0}{\log 80} \tag{4}$$

where  $C_t$  is the coating capacitance at an instant t and  $C_0$  is the capacitance at time t=0; the value 80 is the dielectric constant of water at 25 °C. The volume fraction of water in the coating as a function of immersion time is shown in Fig. 12(c). It is seen that water permeation in the bi-layered PANI/Ni/MS composite is very small up to 144 h of immersion, which shows that this composite resists water uptake and it is corrosion resistant.

The variation of  $R_{ct}$  as a function of the immersion time is shown in Fig. 12(d). In the case of Ni/MS, the value of  $R_{ct}$ decreased rapidly with the immersion time up to 96 h and thereafter it remained fairly constant with the immersion time. It is observed that for PANI/Ni/MS, the  $R_{ct}$  value increased up to 72 h of immersion and after 72 h of immersion, it decreased abruptly to 15.896 k $\Omega$ . Thereafter, the value of  $R_{ct}$  for PANI/Ni/MS remained almost constant with the immersion time and after 240 h, it was found to be ~3.334 k $\Omega$  which is about ~5.1 times higher than that observed for uncoated MS. Thus, the PANI/Ni/MS composite provides better protection to MS against corrosion than Ni plating.

The double layer capacitance  $C_{dl}$  represents the wet area under the coating, which is the area in contact with the electrolyte. The value of  $C_{dl}$  for Ni/MS (Fig. 12(e)) increases sharply after 96 h of immersion which indicates an increase in the area at which delamination and/or corrosion occurred under the coating. It is observed that for PANI/Ni/MS composite the  $C_{dl}$  values are the lowest and they remain almost constant up to immersion time of 240 h indicating that this bi-layered composite provides better protection to MS than PANI/Ni/MS composite.

The delamination area is evaluated by comparing the values of the measured  $C_{dl}$  with a specific capacitance  $C_{dl}$  (measured on uncoated substrate) [45]. The determined delamination area values as a function of immersion time [Fig. 12(f)] clearly indicate negligible delamination up to 240 h as evident from the lowest values of the order of 0.0003–0.008 cm<sup>2</sup>. This confirms the stability of PANI/Ni composite coating on MS when exposed to 3% NaCl solution.

Thus, the experimental results of the present study reveal that the PANI acts as a corrosion protective layer on Ni coated MS in 3% NaCl solution. The top layer of PANI exhibits a lower porosity behavior with respect to Ni coating and reduces the corrosion rate of Ni coated MS almost by factors of 3500 (relative to uncoated MS).

As mentioned earlier, Tuken et al. [28] studied the electrochemical synthesis of PANI and PPY coatings on Ni plated MS from aqueous oxalic acid medium. Corrosion tests, including EIS, anodic polarization curves and OCP-time curves, in 3.5% NaCl, all indicated that the PANI top coated Ni/MS provide better protection for longer periods than the single PPY film. Although the potentiodynamic polarization measurements indicate the positive shift of 0.398 V in  $E_{\rm corr}$  of the PANI coated Ni/MS after 24 h of immersion in 3.5% NaCl, the I<sub>corr</sub> value (0.017 mA) is higher than that of Ni/MS. These results emphasized that the PANI layer synthesized from aqueous oxalic acid solution on Ni/MS is not protective in NaCl medium. These authors also performed the long term immersion experiments and found that after 120h of exposure, the PANI layer saturates with the electrolyte and consequently its efficiency diminished significantly. In the case of PPY top coat on Ni/MS, the potentiodynamic polarization measurements indicate the positive shift of 0.471 V in  $E_{\rm corr}$  of the PPY coated Ni/MS after 24 h of immersion in 3.5% NaCl and the  $I_{\rm corr}$  value is not reported.

In the present study, it is observed that the OCP of the PANI/Ni/MS remains fairly constant at ~0.592 V for a longer period of time (more than 120 h) under the given experimental conditions. This observation indicates barrier behavior of the PANI top coat on Ni/MS, which limits the diffusion of the corrosive species towards the underlying substrate. The most important result of the corrosion protection of Ni/MS by PANI top coat is the positive potential shift (0.567 V versus SCE) in the  $E_{corr}$  to noble value in comparison to the uncoated Ni/MS. This potential shift to more noble values is regarded as the anodic protection. Moreover, the  $j_{corr}$  values are  $\sim$ 2060 times lower than that of the uncoated MS. The EIS study indicates that the R<sub>ct</sub> value of PANI/Ni/MS is higher (~149 times) than that of the uncoated MS. Moreover, it is seen that water permeation is negligibly small up to 144 h of immersion, which shows that the coating resists water uptake and it is corrosion resistant. Thus, it is possible to deposit strongly adherent PANI top coat on Ni/MS using sodium salicylate as a supporting electrolyte and it can be considered as a potential coating material to protect Ni/MS against corrosion in aqueous 3% NaCl.

It is now apparent that the conducting polymer accepts electrons from the metal and gives them to oxygen. This reaction generates the formation of a passive oxide layer at the polymer/metal interface which lowers the corrosion rate and shifts the  $E_{\rm corr}$  to more positive values. The result of the potentiodynamic polarization measurements for the PANI coated MS shows a shift in the  $E_{\rm corr}$  to more positive value (0.208 V) and reduces the corrosion rate of MS almost by a factor of 35. The positive shift of 0.208 V versus SCE in Ecorr indicates the protection of the MS surface by the PANI layer. Thus, the protection effect of PANI layer seems to be related to its passivation effect as well as its barrier behavior. The potentiodynamic polarization measurement of PANI/Ni/MS exhibits a shift in the  $E_{corr}$  to more positive value (0.567 V) and reduces the corrosion rate of MS almost by a factor of 3500. In this case, the Ni (and its oxide) acts as the additional barrier as they are more stable and corrosion protective in neutral or near alkaline conditions [46]. Besides, the PANI top coat on Ni/MS itself constituted an effective barrier with low permeability on the surface. Thus, corrosion protection performances of Ni/MS and PANI/Ni/MS indicate that the bi-layered PANI/Ni coating provides much better protection to MS for longer period.

#### 4. Conclusions

Corrosion protective PANI coatings were successfully synthesized on Ni coated MS by electrochemical polymerization of aniline from aqueous salicylate solution. The electrochemical polymerization process occurs without noticeable dissolution of MS. It was shown that the sodium salicylate is a suitable supporting electrolyte for the electrochemical polymerization of aniline on Ni coated MS. The UV-vis absorption spectroscopy study of PANI reveals the formation of the pernigraniline base (PB) form of PANI. The potentiodynamic polarization and electrochemical impedance spectroscopy studies reveal that the PANI acts as a corrosion protective layer on Ni coated MS in 3% NaCl solution. The top layer of PANI exhibits a lower porosity behavior with respect to Ni coating and reduces the corrosion rate of Ni coated MS almost by factors of 3500 (relative to uncoated MS) and increases the lifetime of Ni coating.

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