Electrochemical synthesis of corrosion protective polyaniline coatings on mild steel from aqueous salicylate medium

Pritee Pawara, A.B. Gaikawadb, P.P. Patila*

*Department of Physics, North Maharashtra University, Jalgaon 425 001, Maharashtra, India
bCentre for Materials Characterization, National Chemical Laboratory, Pashan Road, Pune 411 008, India

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Abstract

Strongly adherent polyaniline coatings were electrochemically synthesized on mild steel from an aqueous salicylate medium. These coatings were characterized by cyclic voltammetry, UV-visible absorption spectroscopy, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy. The extent of the corrosion protection offered by polyaniline coatings to mild steel was investigated in aqueous 3% NaCl solution, 0.01 M Na2SO4 solution and in aqueous solutions of NaCl+N2SO4 with different concentrations by potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The results of these studies reveal that the corrosion resistance of the polyaniline-coated mild steel is significantly higher and the corrosion rate is considerably lower than that of uncoated steel.

Keywords: Corrosion protective coatings; Conducting polymer coatings; Polyaniline coatings; Mild steel; Electrochemical polymerization; Cyclic voltammetry

1. Introduction

In recent years, conducting polymers have received great attention as advanced materials due to their remarkable physical attributes [1–3]. One of the most important applications of these materials, which is attracting considerable attention is in corrosion protection of metals [4,5]. The electrochemical polymerization is a simple, relatively inexpensive and most convenient route for the synthesis of conducting polymers on metallic surfaces [1,2]. Although, the conducting polymers are found to be most promising materials for corrosion protection, the electrochemical polymerization of conducting polymers is not easy on oxidizable metals. A number of reports on the synthesis and characterization of conducting polymer coatings on oxidizable metals such as iron [6,7], aluminum [8,9], zinc [10], etc. have appeared in the literature during the last couple of years. The common feature of these studies is that the 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. Thus, the oxidation of the metal appears as a simultaneous and competitive oxidation process at the potentials adequate for the formation of polymer. A successful electrochemical polymerization of conducting polymer on oxidizable metals demands a careful choice of the solvent, supporting electrolyte and the establishment of electrochemical parameters, which will strongly passivate the metal without impeding the electropolymerization process.

Among the conducting polymers, polyaniline [11,12] and polypyrrole [13,14] are the most promising conducting polymers for corrosion protection of metals. Nevertheless, the polyaniline is more challengeable due to the low cost of aniline monomer as compared to pyrrole. The possibility of using polyaniline coating for corrosion protection of metals was first reported by DeBerry and Viehback [11]. It was further proved that the polyaniline has ability to serve as a corrosion protective coating on metals in both acidic and neutral solutions.
It was shown that the electrochemically synthesized polyaniline films on mild steel can be used as corrosion protective coatings. However, the protection performance of the coatings depends on the choice of the supporting electrolyte used for their synthesis. Camlet et al. [15–17] investigated three different supporting electrolytes for the electrochemical polymerization of aniline on mild steel. They used aqueous solutions of oxalic acid, tosylic acid and neutral solution of LiClO₄ to synthesize the adherent polyaniline films on mild steel under galvanostatic conditions. It was shown that these polyaniline films exhibit good protection to mild steel in acidic solution.

Fenelon and Breslin [18] electrodeposited polyaniline coatings from aqueous oxalic acid solution onto iron and investigated the corrosion protection properties of these coatings as a function of electrolyte pH. It was found that these polyaniline coatings exhibit a limited effect on the corrosion protection of iron in acidic solutions containing acetate and borate anions. However, in an alkaline borate solution, these coatings show a clear beneficial effect on the local breakdown of the iron by chloride anions.

Popovic and Grgur [6] electrochemically synthesized thin, adherent polyaniline coatings from aqueous sodium-benzoate solution on mild steel. They investigated the corrosion behavior of mild steel coated with polyaniline in 0.1 M H₂SO₄ and 0.5 M NaCl (pH = 3) solutions using spectrophotometric method and EIS. It was shown that the electrochemically synthesized polyaniline films from benzoate solution on mild steel are potentially good corrosion protective coatings.

Recently, Petitjean et al. [19] have discovered a general one-step process for ultra-fast electropolymerization of pyrrole on oxidizable metals. The process is based on the use of the aqueous sodium salicylate solution and pyrrole. They observed that the salicylate salt passivates the substrate without preventing the electropolymerization of pyrrole and uniform and strongly adherent polypyrrole films were obtained.

More recently [20], we have investigated the electrochemical polymerization of o-anisidine on copper (Cu) in the aqueous salicylate solution by cyclic voltammetry. It was shown that the aqueous salicylate solution is a suitable medium for the electrochemical polymerization of o-anisidine and it results into the deposition of uniform and strongly adherent poly(o-anisidine) coatings on Cu substrates. These coatings exhibit excellent corrosion protection properties and the poly(o-anisidine) is found to be most promising coating material for corrosion protection of Cu in aqueous 3% NaCl.

The objectives of the present study are—(a) to find potentially good, low cost and easily available supporting electrolyte for the electrochemical polymerization of aniline on mild steel substrates; (b) to synthesize uniform, compact and strongly adherent polyaniline coatings on mild steel substrates; and (c) to study the corrosion behavior of a polyaniline coating deposited on mild steel in different corrosive environments by potentiodynamic polarization technique and EIS.

In this work, cyclic voltammetry is used to synthesize the polyaniline coatings on mild steel substrates from aqueous salicylate solution. The sodium salicylate was chosen as the supporting electrolyte for the electrochemical polymerization of aniline due to its ability to form a non-conducting passive layer on mild steel surface without preventing the monomer oxidation. These coatings were characterized by cyclic voltammetry, Fourier transform infrared spectroscopy (FTIR), UV-visible absorption spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction measurements (XRD). The extent of corrosion protection offered by these coatings to mild steel in aqueous 3% NaCl solution, 0.01 M Na₂SO₄ solution and in aqueous solutions of NaCl + Na₂SO₄ with different concentrations was examined by the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS).

2. Experimental

Analytical reagents (AR) grade chemicals were used throughout the present study. The aniline monomer was double distilled prior to its use. The aqueous sodium salicylate (NaC₆H₄O₃) solution was used as the supporting electrolyte. The concentrations of sodium salicylate and aniline were kept constant at 0.1 and 0.3 M, respectively.

The chemical composition (by wt%) of the mild steel 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. The mild steel substrates (size ~10 × 15 and 0.5 mm thick) were polished with a series of emery papers, followed by thorough rinsing in 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 polyaniline coatings were synthesized by electrochemical polymerization of aniline on mild steel substrates from aqueous salicylate solution under cyclic voltammetric conditions. The electrochemical polymerization was carried out in a single compartment three electrode cell with steel as working electrode (150 mm²), platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The cyclic voltammetric conditions were maintained using a Electrochemical Measurement System (SI 1280B Solartron, UK) controlled by corrosion software (CorrWare, Electrochemistry/Corrosion Software, Scribner Associates Inc. supplied by Solartron, UK). The synthesis was carried out by cycling continuously the electrode potential between −1.0 and 1.8 V at a potential scan rate of 0.02 V/s. After deposition the working electrode was removed from the electrolyte and rinsed with double-distilled water and dried in air. The thickness of the coatings was determined 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%.

The FTIR transmission spectrum of polyaniline coating was recorded in horizontally attenuated total reflectance (HATR) mode in the spectral range 4000–400 cm⁻¹ using a Perkin-Elmer spectrometer (1600 Series II, Perkin-Elmer, USA). The optical absorption studies of these coatings were carried out ex situ at room temperature in the wavelength range 300–1100 nm using microprocessor controlled double beam UV-visible spectrophotometer (Model U2000, Hitachi, Japan). The structural properties were investigated using XRD technique. The XRD patterns were recorded with a Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having Cu Kα (λ = 0.1542 nm). SEM was employed to characterize the surface morphology with a Leica Cambridge 440 Microscope (UK).

The corrosion protection performance of these coatings was investigated in aqueous 3% NaCl solution, 0.01 M Na₂SO₄ solution and in aqueous solutions of NaCl + Na₂SO₄ with different concentrations by using potentiodynamic polarization technique and EIS. For these measurements, a teflon holder was used to encase the polymer-coated mild steel substrates so as to leave an area of ~40 mm² exposed to the solution. The potentiodynamic polarization measurements were performed by sweeping the potential between −0.25 and 0.25 V from open circuit potential at the scan rate of 0.002 V/s. The substrates were allowed to stabilize in the electrolyte for 30 min prior to the potentiodynamic polarization measurements. The Tafel slopes of the anodic (βₐ) and cathodic (βᵦ) parts of the polarization curve were obtained. The corrosion current density (Icorr) in A/m² was calculated by using Stern–Geary equation [21] and it is converted into the corrosion rate (CR) in mm/year by using the expression [22]:

$$ CR = \frac{3.268 \times 10^{-3} I_{corr} MW}{\rho z}, $$

where MW is molecular weight of mild steel (g), ρ is the density of mild steel (kg/m³) and z is the number of electrons transferred in the corrosion reaction; z = 2 in the case of mild steel reaction. All the measurements were repeated at least four times and good reproducibility of the results was observed.

The cyclic potentiodynamic polarization measurements were performed by sweeping the potential between −0.25 and 0.25 V at the scan rate of 0.002 V/s in aqueous 3% NaCl solution. When a user-programmed threshold anodic current density value (10 A/m²) and/or the anodic limit was reached, the substrate was scanned in the cathodic direction. In the subsequent analysis of the recorded cyclic potentiodynamic polarization curves, the pitting potential (Eₚᵣᵦ) is defined as the potential at which the sustained anodic current density is ~3 mA/cm². The protection potential (Eₚᵦₒᵦ) is defined as the potential at which the reverse scan crossed the forward scan.

The EIS measurements of the polyaniline-coated mild steel were carried out at the open circuit potential in aqueous solution of 3% NaCl solution, 0.01 M Na₂SO₄ solution and in aqueous solutions of NaCl + Na₂SO₄ with different concentrations. The frequency was varied from 0.1 Hz to 20 kHz using an ac excitation potential of 10 mV. The analysis of the impedance spectra was done by fitting the experimental results to equivalent circuits using the non-linear least-square fitting procedure. The quality of fitting to equivalent circuit was judged firstly by the χ²-value (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%.

3. Results and discussion

3.1. Electrochemical behavior of mild steel in an aqueous salicylate solution

In order to understand the different processes occurring at the electrode surface, the mild steel electrodes were first polarized in 0.1 M aqueous sodium salicylate solution (without monomer) by cycling continuously the electrode potential between −1.0 and 1.8 V at a potential scan rate of 0.02 V/s. The first scan of the voltammetric response of the mild steel electrode in 0.1 M aqueous sodium salicylate medium is shown in Fig. 1(a). This cyclic voltammogram exhibits good resemblance with that reported by Shinde et al. [23] and have some common features such as: (i) In the first positive cycle the anodic peak at −0.489 V versus SCE (peak A) and 1.14 V versus SCE (peak B) are observed. The oxygen evolution process is observed at ~1.799 V versus SCE. During the negative cycle, the anodic current decays very sharply and the anodic peak C is observed at −0.461 V versus SCE.

![Fig. 1. Cyclic voltammogram (a) first and (b) tenth scans recorded during the polarization of mild steel electrode in 0.1 M sodium salicylate solution. Scan rate: 0.02 V/s.](image-url)
The anodic peak A is attributed to the dissolution of the mild steel electrode surface which produces Fe^{2+} ions in its vicinity. These ions interact with the salicylate counter-ions of the electrolyte to form a thin insoluble passive layer at the electrode surface, corresponding to complexation of the Fe^{2+} cation by salicylate counter-ions which inhibits the dissolution of the electrode surface. 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. In fact, during the polarization process, the color of the electrolyte gradually changes to brownish-pink. 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 process. The anodic peak B is assigned to the oxidation of the salicylate electrolyte.

The anodic peak C observed at $\sim 0.461$ V versus SCE during the reverse cycle is attributed to the reactivation of the mild steel electrode surface during the negative cycle. It corresponds to the transition of the iron (Fe^{3+}) oxide to complexation of the Fe^{2+} cation with salicylate counter-ions which occurs by a simultaneous and instantaneous reactivation of the mild steel. It may be argued that during the anodic cycle, complexation of the Fe^{2+} cation with salicylate counter-ions is converted into iron (III) complex. The iron (III) complex, being more soluble, does not remain on the electrode surface and is released into the electrolyte. Its dissolution generates micropores in the passive layer. These micropores are then filled up by iron oxide Fe$_2$O$_3$, which is formed simultaneously with the dissolution of iron (III) complex. During reverse scan, iron oxide is slowly destroyed and a sharp oxidation process occurs in the potential range $\sim 0.388$ to $\sim 0.625$ V versus SCE resulting into precipitation of new iron (II) salicylate on the mild steel electrode surface.

On repetitive cycling, the anodic peaks at $\sim 0.330$ V versus SCE (peak A) and 1.113 V versus SCE (peak B) are observed. The anodic peak C is disappeared and the position of the peak A is shifted in the positive direction. The current density corresponding to anodic peaks A and B increases with the increase in the number of scans. The non-observance of the peak C may be attributed to the stabilization of the mild steel electrode surface due to formation of the complexation of the Fe^{2+} cation by salicylate counter-ions. The redox potentials and current densities corresponding to the redox peaks are given in Table 1(a).

In order to understand the observed cyclic voltammetry results, we have performed the XRD measurements of the mild steel electrode polarized (with 10 cycles) in 0.1 M aqueous salicylate solution. The XRD patterns of the uncoated mild steel and the mild steel electrode polarized in 0.1 M sodium salicylate solution are shown in Fig. 2. The XRD pattern of uncoated mild steel substrate (Fig. 2(a)) shows a characteristic diffraction peak at an angle of 45°, indicating its polycrystalline nature. Apart from the

![Fig. 2. XRD pattern of (a) uncoated mild steel and (b) mild steel substrate polarized in 0.1 M sodium salicylate solution. (●) indicates the peaks for iron salicylate.](image-url)

| Sample | Scan number | Redox potential (V) | Current density (A/m^2) |
|--------|-------------|---------------------|------------------------|
|        |             | A       | B       | C       | A       | B       | C       |
| Polarized mild steel | 1 | 0.489  | 1.140  | $-0.461$ | 5.62  | 85.0  | 2.46  |
|         | 2 | 0.330  | 1.800  | $-0.811$ | 19.8  | 85.3  | 10.0  |
|         | 10 | 0.248 | 1.798  | $-0.792$ | 29.8  | 71.0  | 6.80  |
| Synthesis of polyaniline coating on mild steel under cyclic voltammetric conditions | | | | | | | |
| Polyaniline-coated mild steel | 1 | — | 1.473 | $-0.620$ | — | 60.0 | 4.47 |
|          | 2 | 0.353 | 1.798 | $-0.601$ | 10.0 | 52.5 | 4.78 |
|          | 10 | 0.529 | 1.798 | $-0.527$ | 4.19 | 32.2 | 6.05 |

### Table 1

Redox potentials and current densities at the redox peaks

(a) Polarization of the mild steel in 0.1 M aqueous salicylate solution under cyclic voltammetric conditions

(b) Synthesis of polyaniline coating on mild steel under cyclic voltammetric conditions
characteristic peak of mild steel, the XRD pattern of the mild steel electrode polarized in 0.1 M sodium salicylate solution (Fig. 2(b)) indicates the presence of diffraction peaks at angles of 11.20°, 18.60°, 38.00° and 44.20° due to the iron salicylate. Thus, the XRD result clearly reveals the formation of the iron salicylate on the mild steel electrode surface. Thus, the polarization of the mild steel electrode in 0.1 M sodium salicylate solution results into the passivation of the electrode surface via the formation of iron salicylate phase.

The SEM image of the mild steel electrode polarized (with 10 cycles) in a 0.1 M aqueous salicylate solution is shown in Fig. 3. It does not indicate the formation of crystalline phases on the mild steel electrode surface. Nevertheless, it reveals the deposition of a thin film on the electrode surface, which may be due to the formation of iron salicylate phase.

3.2. Electrochemical synthesis of polyaniline coatings on mild steel from an aqueous salicylate solution

The cyclic voltammogram of the first scan recorded during the synthesis of polyaniline coating on the mild steel electrode from aqueous solution containing 0.3 M aniline and 0.1 M sodium salicylate are shown in Fig. 4(a). This cyclic voltammogram is significantly different from that recorded in aqueous salicylate solution without aniline. Indeed, the anodic peak A corresponding to the dissolution of mild steel is not observed. During the first positive cycle, there is little oxidation till the potential is greater than 0.517 V versus SCE, beyond this potential a sharp increase in the anodic current density is observed (peak A1). This increase in the anodic current density is attributed to the oxidation of the monomer, the generation of radical cations and the onset of the polymerization process [24]. During the reverse cycle, the anodic current density decreases rapidly and a negligibly small current is seen till −0.342 V. The negative cycle terminates with a broad reduction peak (C) at −0.620 V. This reduction peak is due to reduction of an anodically formed species. The absence of the anodic peak A corresponding to the dissolution of the mild steel substrate when aniline is in the solution, indicates that the aniline is involved in the passivation process and the electrochemical polymerization takes place without dissolution of the electrode surface.

During the next scan (Fig. 4(b)), a broad anodic peak A2 at ~0.353 V versus SCE is observed and rest of the features are similar to that of the first scan. The anodic peak A2 is assigned to the oxidation of polyaniline deposited at the mild steel surface. On repetitive cycling, the voltammograms identical to that of second scan are obtained. However, the current density corresponding to the anodic peaks decrease gradually with the increase in the number of scans. The redox potentials and current densities corresponding to the redox peaks are also given in Table 1(b).

Thus, the electrochemical polymerization of aniline on mild steel substrate occurs in a single step from aqueous salicylate solution. The visual inspection of the mild steel electrode after 10th scan reveals the formation of a black colored polyaniline coating. The coating is uniform, crack free and strongly adherent to the mild steel substrate.

The FTIR spectrum of polyaniline coating (~6 μm thick) synthesized on mild steel under cyclic voltammetric conditions (with 10 cycles) recorded in HATR mode is shown in Fig. 5. This spectrum exhibits the following spectral features: (i) a band at ~3370 cm⁻¹ due to the characteristic N–H stretching vibration suggests the presence of −NH− groups in aniline units [25,26]. (ii) The band at ~3040 cm⁻¹ is associated with C–H stretching in methylene group. (iii) The band at ~1592 cm⁻¹ is an indicative of stretching vibrations in quinoid (Q) rings [25–28]. (iv) The band ~1491 cm⁻¹ represents the
The stretching vibrations of the benzoic (B) rings [25–28].

(v) The presence of Q and B bands clearly show that the polyaniline coating is composed of imine and amine units.

(vi) The band at 1247 cm\(^{-1}\) are attributed to the presence of carboxylic groups of sodium salicylate in the polyaniline coating. (vii) The presence of the C–N stretching band at \(\sim 1380\) cm\(^{-1}\) is consistent with the results reported by Tang et al. [25]. This band is assigned to the C–N stretching in QBtQ environment, where Bt represents a trans-benzoic unit.

(viii) The bands at 1177 and 1023 cm\(^{-1}\) are attributed to the 1–4 substitution on the benzene ring. (ix) The observation of the bands between 800 and 700 cm\(^{-1}\) reveals the occurrence of the 1–3 substitutions. Thus, the FTIR spectroscopic study indicates that the electrochemical polymerization of aniline has occurred and results into the formation of oxidized form of polyaniline on the electrode surface.

The optical absorption spectrum of polyaniline coating synthesized on mild steel recorded ex situ in DMSO solution is shown in Fig. 6. It exhibits high value of the absorbance between 600 and 800 nm with a shoulder at \(\sim 740\) nm. This shoulder peak at 740 nm is attributed to the formation of emeraldine salt (ES) form of polyaniline in the coating [29]. The higher value of the absorbance between 600 and 740 nm may be due to the formation of some species with other oxidation states. Thus, the optical absorption spectroscopy reveals the formation of ES form along with the some other oxidation state species.

The SEM image of the polyaniline (\(\sim 6\) \(\mu\)m thick) coating on mild steel is shown in Fig. 7. The SEM image clearly reveals that the coating is uniform, crack free and featureless.

3.3. Corrosion protection properties of the polyaniline coating

In order to evaluate the corrosion protection performance of the polyaniline coatings, the potentiodynamic polarization and EIS studies of uncoated mild steel and polyaniline-coated mild steel were carried out in aqueous 3% NaCl solution, 0.01 M Na\(_2\)SO\(_4\) solution and aqueous solutions of NaCl + Na\(_2\)SO\(_4\) with different concentrations.
3.3.1. Electrolyte: 3% NaCl

The potentiodynamic polarization curves for uncoated mild steel and polyaniline-coated mild steel (≈6 μm thick) recorded in aqueous 3% NaCl solution are shown in Fig. 8. The Tafel extrapolations show that the polyaniline caused a remarkable potential shift ≈0.352 V versus SCE in the corrosion potential \(E_{corr}\), relative to the value of the uncoated mild steel (≈0.710 V). The positive shift in \(E_{corr}\) confirms the best protection of the mild steel when its surface is covered by the polyaniline. Also, the Tafel measurements clearly show that a substantial reduction in corrosion current density \(I_{corr}\) occurs for the polyaniline-coated mild steel with respect to the uncoated mild steel. The values of the \(E_{corr}\), \(I_{corr}\) and corrosion rates obtained from these curves are given in Table 2. The corrosion rate of mild steel is significantly reduced as a result of the reduction in the \(I_{corr}\). It is important to note that the cathodic current density of the polyaniline-coated mild steel is significantly lower than that of the uncoated mild steel. This observation suggests that the polyaniline coating is strongly adherent and it provides nearly perfect coverage of the mild steel surface. The measured cathodic current density may be due to the reduction of the polyaniline and thus, it is contributed by the polyaniline itself.

The corrosion rate of polyaniline-coated mild steel is found to be ≈0.0005 mm/year which is ≈400 times lower than that observed for uncoated mild steel. The protection efficiency (PE) was calculated by using the expression:

\[
\text{PE}\% = \left[\frac{R_{pc} - R_p}{R_{pc}}\right] \times 100,
\]

where \(R_p\) and \(R_{pc}\) denote the polarization resistance of uncoated mild steel and polyaniline-coated steel, respectively. The PE calculated from potentiodynamic polarization data is found to be ≈98.85%. Thus, these results reveal the capability of polyaniline to act as a corrosion protective layer on mild steel.

Further, it is found that the corrosion rate depends on the thickness of the polyaniline (cf. Table 2) and it is lowest for the 6 μm thick coating. Thus, it seems that the thickness of the coating affects the corrosion protection properties of the polyaniline coating.

We have also performed the potentiodynamic polarization measurements by using the polyaniline-coated mild steel substrates after storing them in air at 25 °C for 30 days and the corresponding polarization curve is shown in Fig. 9(b). The potentiodynamic polarization curve for freshly prepared polyaniline-coated mild steel is also presented in Fig. 9(a). These curves clearly reveal that there is no indication of any substantial loss in corrosion protection properties of the polyaniline coatings. Thus, the polyaniline coating shows high chemical as well as physical stability because the coating keeps its adherence to mild steel substrate even after the storage.

The cyclic polarization measurements were performed to determine susceptibility of the polyaniline-coated mild steel to pit in aqueous 3% NaCl solution. The cyclic potentiodynamic polarisation curves recorded in aqueous 3% NaCl solution for uncoated mild steel and polyaniline-coated steel are shown in Fig. 10. These curves clearly reveal the distinct differences in the behavior between uncoated mild steel and polyaniline-coated steel. The cyclic potentiodynamic polarization curve for uncoated mild steel substrates after storing them in air at 25 °C for 30 days and the corresponding polarization curve is shown in Fig. 11(b). The potentiodynamic polarization curve for freshly prepared polyaniline-coated mild steel is also presented in Fig. 11(a). These curves clearly reveal that there is no indication of any substantial loss in corrosion protection properties of the polyaniline coatings. Thus, the polyaniline coating shows high chemical as well as physical stability because the coating keeps its adherence to mild steel substrate even after the storage.

![Fig. 8. Potentiodynamic polarization curves for (a) uncoated mild steel and (b) polyaniline coated (~6 μm thick) on mild steel in aqueous 3% NaCl solution.](image)

**Table 2**

| Sample                      | \(E_{corr}\) (V) | \(I_{corr}\) (A/m²) | \(\beta_a\) (V/dec) | \(\beta_c\) (V/dec) | \(R_p\) (Ω/m²) | CR (mm/yr) |
|-----------------------------|------------------|---------------------|---------------------|---------------------|----------------|-------------|
| 3% NaCl                     |                  |                     |                     |                     |                |             |
| Uncoated steel              | −0.710           | 0.1779              | 0.0912              | 0.2704              | 1.6645 × 10⁷   | 0.20        |
| Polyaniline-coated mild steel (3 μm) | −0.436           | 0.0034              | 0.253               | 0.2105              | 1.45034 × 10⁷  | 0.0039      |
| Polyaniline-coated mild steel (6 μm) | −0.358           | 0.0005              | 0.0423              | 0.288               | 3.20793 × 10⁷  | 0.0005      |
| Polyaniline-coated mild steel (12 μm) | −0.342          | 0.0010              | 0.0136              | 0.215               | 5.3404 × 10⁸   | 0.0012      |
| Polyaniline-coated mild steel (16 μm) | −0.417           | 0.0016              | 0.0491              | 0.379               | 1.16510 × 10⁸  | 0.0018      |
| 0.01 M Na₂SO₄              |                  |                     |                     |                     |                |             |
| Uncoated steel              | −0.487           | 0.15                | 0.1062              | 0.5550              | 2.5839 × 10⁷   | 0.173       |
| Polyaniline-coated mild steel (6 μm) | −0.343           | 0.0006              | 0.0545              | 0.1550              | 3.13035 × 10⁷  | 0.0006      |
(Fig. 10(a)) exhibits a positive hysteresis loop as the reverse scan current density is one order of magnitude higher than the forward current density. The pitting potential ($E_{\text{pit}}$) and protection potential ($E_{\text{pro}}$) values are found to be $-0.499$ and $-0.642$ V versus SCE, respectively, which indicates that the pitting occurs in the aqueous 3% NaCl solution.

The cyclic potentiodynamic polarization curve recorded in aqueous 3% NaCl for polyaniline-coated mild steel is shown in Fig. 10(b). Interestingly, a positive hysteresis loop is observed and the final value of the $E_{\text{corr}}$ ($-0.607$ V) is much more negative than the starting values of the $E_{\text{corr}}$ ($-0.499$ V). Tait [30] has shown that the positive hysteresis occurs when the damage in the passive film is not repaired and/or pits are initiated. Thus, it seems that the polyaniline coating deteriorates and it does not contribute to the localized corrosion protection in 3% NaCl.

The Nyquist impedance plot of uncoated mild steel is shown in Fig. 11(a). It is important to note that there was not any coating on the steel surface and therefore, the passivation of the steel surface cannot be expected. Hence, the diameter of the impedance plot must be equal to the charge transfer resistance value of the mild steel. This impedance plot was modeled by the equivalent circuit depicted in Fig. 12(a). The equivalent circuit consists of the electrolyte resistance ($R_s$), charge-transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$). The impedance plot of the uncoated mild steel can be fitted with a semicircle, which is attributed to the processes occurring at the steel surface.

The Nyquist impedance plot of polyaniline-coated mild steel is shown in Fig. 11(b). This impedance plot is modeled by using the equivalent circuit depicted in Fig. 12(b), which consists of the electrolyte resistance ($R_s$), pore resistance...
(Rs), coating capacitance (Cc), charge-transfer resistance (Rct) and double layer capacitance (Cdl). In both cases the constant phase element (CPE) was used instead of capacitance. The CPE represents the deviation from the true capacitance behavior. Table 3 gives the values of the representative parameters of the best fit to the experimental data using equivalent circuits shown in Figs. 12(a) and (b) for uncoated mild steel and polyaniline-coated mild steel, respectively. The impedance plot of polyaniline-coated mild steel (Fig. 11(b)) can be 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 polyaniline coating itself and the second one to processes occurring underneath the coating.

The values of the impedance parameters obtained from the fitting of the experimental impedance plots for uncoated mild steel and polyaniline-coated mild steel using equivalent circuits shown in Fig. 12 are given in Table 3. The PE calculated from EIS data is found to be \(~98.07\%\) which is in agreement with the potentiodynamic polarization result.

3.3.2. Electrolyte: 0.01 M Na2SO4

The potentiodynamic polarization curves for uncoated mild steel and polyaniline-coated mild steel (\(~6\mu m\) thick) recorded in aqueous 0.01 M Na2SO4 solution are shown in Fig. 13. The positive potential shift \(~0.144\) V versus SCE in the corrosion potential \((E_{corr})\), relative to the value of the uncoated mild steel \((-0.487\) V) indicates the protection of the mild steel by the polyaniline coating. Also, the corrosion current density \((I_{corr})\) decreases from 0.15 to 0.0006 A/m² which significantly reduces the corrosion rate by an amount of \(~288\) times lower than the uncoated mild steel. The PE calculated from this data is found to be \(~99.17\%\). Thus the polyaniline coating provides the good corrosion protection to the mild steel in aqueous sulfate medium.

The Nyquist impedance plots of the uncoated mild steel and polyaniline-coated mild steel recorded in aqueous 0.01 M Na2SO4 solution are shown in Fig. 14. The values of the impedance parameters obtained by modeling these impedance plots using the equivalent circuits depicted in Fig. 12 are given in Table 3. The PE calculated from EIS data is found to be \(~99.76\%\) which is in agreement with the polarization result.

![Fig. 13. Potentiodynamic polarization curves for (a) uncoated mild steel and (b) polyaniline coated (~6 \(\mu m\) thick) on mild steel in aqueous 0.01 M Na2SO4 solution.](image-url)

![Fig. 12. Equivalent circuit models.](image-url)

Table 3

| Parameter | Uncoated mild steel | Polyaniline-coated mild steel |
|-----------|---------------------|-------------------------------|
| R_s (\(\Omega\)) | 5.76 | 47.00 |
| R_p (\(\Omega\)) | — | 190.40 |
| C_c (F/m) | — | \(3.4972 \times 10^{-7}\) |
| R_ct (\(\Omega\)) | 654.30 | 33911 |
| C_dl (F/m) | 7.9987 \(\times 10^{-4}\) | 8.2912 \(\times 10^{-4}\) |

\(0.01 \text{ M Na}_2\text{SO}_4\)

| Parameter | Uncoated mild steel | Polyaniline-coated mild steel |
|-----------|---------------------|-------------------------------|
| R_s (\(\Omega\)) | 109.90 | 3.7349 \(\times 10^{-5}\) |
| R_p (\(\Omega\)) | — | 12542 |
| C_c (F/m) | — | \(2.6909 \times 10^{-9}\) |
| R_ct (\(\Omega\)) | 1057 | \(4.4772 \times 10^{5}\) |
| C_dl (F/m) | 9.5950 \(\times 10^{-4}\) | \(2.4925 \times 10^{-7}\) |

\(\text{PE} = \frac{R_{ctp} - R_{ct}}{R_{ctp}} \times 100\),

where \(R_{ctp}\) and \(R_{ct}\) denote the charge-transfer resistance of mild steel without and with coating, The PE calculated from EIS data is found to be \(~98.07\%\) which is in agreement with the potentiodynamic polarization result.
3.3.3. Mixed electrolyte: NaCl+Na₂SO₄

We have also examined the ability of the polyaniline coatings to protect the mild steel against corrosion in aqueous solutions of NaCl+Na₂SO₄ with different concentrations. The potentiodynamic polarization curves for uncoated mild steel and polyaniline-coated mild steel (~6μm thick) recorded in 0.001, 0.01 and 0.1 M mixed electrolyte are shown in Figs. 15–17. The values of the $E_{\text{corr}}$, $I_{\text{corr}}$ and corrosion rates obtained from these curves are given in Table 4. The potentiodynamic polarization curves for uncoated mild steel and polyaniline-coated mild steel (~6μm thick) recorded in 0.001 M aqueous solution of NaCl+Na₂SO₄ is shown in Fig. 15. The analysis of these polarization curves reveals that the polyaniline coating causes a positive potential shift ~0.085 V versus SCE in the $E_{\text{corr}}$, relative to the value of the uncoated mild steel (~0.392 V) and reduces the corrosion rate by a factor of approximately 300.

The potentiodynamic polarization curves for uncoated mild steel and polyaniline-coated mild steel (~6μm thick) recorded in 0.1 M mixed electrolyte is shown in Fig. 17. The polyaniline coating results into a positive potential shift ~0.085 V versus SCE in the $E_{\text{corr}}$, relative to the value of the uncoated mild steel (~0.392 V) and reduces the corrosion rate by a factor of approximately 300.
shift \( \sim 0.115 \) V versus SCE in the \( E_{\text{corr}} \) of the uncoated mild steel relative to the value of the uncoated mild steel (\( -0.451 \) V) and decreases the corrosion rate by a factor of approximately 127. The inhibition efficiencies calculated from the potentiodynamic polarization data for 0.001, 0.01 and 0.1 M mixed electrolyte are found to be \( \sim 99.47\% \), 99.10\% and 99.53\%, respectively.

The Nyquist impedance plots of uncoated mild steel and polyaniline-coated mild steel recorded in 0.001, 0.01 and 0.1 M mixed electrolyte are shown in Figs. 18–20. These plots are modeled by using the equivalent circuits depicted in Fig. 12. The values of the impedance parameters obtained by modeling these impedance plots are given in Table 5. The protection efficiencies calculated from the EIS data for 0.001, 0.01 and 0.1 M mixed electrolyte are found to be \( \sim 99.80\% \), 99.87\% and 99.86\%, respectively. Thus the polyaniline coating has the ability to protect the mild steel in binary mixture consisting of NaCl and Na\(_2\)SO\(_4\).

The results of this work reveal that the aqueous salicylate solution is a suitable medium for the electrochemical polymerization of aniline on the mild steel substrate. The salicylate-ions play the dual role: (a) they acts as a passivating agent of the steel surface as the electrochemical polymerization proceeds and (b) they are incorporated into
the polyaniline coating as dopants. Uniform and strongly adherent polyaniline coatings were obtained on mild steel from aqueous salicylate medium as compared with those synthesized from aqueous oxalic acid and sodium benzoate solutions. The potentiodynamic polarization and EIS study reveals that the polyaniline acts as a protective layer on mild steel against corrosion in 3% NaCl, 0.01 M Na2SO4 and mixed NaCl + Na2SO4 solution. The polyaniline coatings reduce the corrosion rate of mild steel in 3% NaCl and 0.01 M Na2SO4 almost by a factor of 400 and 288, respectively.

Thus, the polyaniline coatings synthesized from aqueous salicylate solution exhibit the outstanding corrosion protection properties. The outstanding corrosion protection offered by polyaniline coating to the mild steel may be attributed to the fact that the deposited polymer is strongly adherent and uniformly covers the entire electrode surface as evident by the SEM. Sathiyanarayanan et al. [31] studied the interaction of the metallic surface with monolayers of adsorbed monomers and polymers. They showed that the co-existence of delocalized \( \pi \)-electrons and the quaternary ammonium nitrogen in the polymer facilitates its strong adsorption on the iron surface, which result in the effective corrosion inhibition. Therefore, the delocalized \( \pi \)-electrons in polyaniline facilitate its strong adsorption on the mild steel surface leading to the outstanding corrosion inhibition.

4. Conclusions

Uniform and strongly adherent polyaniline coatings were synthesized on mild steel by electrochemical polymerization of \textit{aniline} from aqueous salicylate medium. It is observed that the electrochemical polymerization process occurs in a single step without dissolution of mild steel. The result of the optical absorption spectroscopy reveals the formation of the ES form of polyaniline. The potentiodynamic polarization and EIS study reveal that the polyaniline acts as a corrosion...
Table 5

| Parameter | Uncoated mild steel | Polyaniline-coated mild steel |
|-----------|---------------------|------------------------------|
| $0.01 M \text{NaCl}+\text{Na}_2\text{SO}_4$ | | |
| $R_i (\Omega)$ | 469.5 | $2.5488 \times 10^{-4}$ |
| $R_p (\Omega)$ | 30292 | |
| $C_e (\text{F/m})$ | — | $5.7856 \times 10^{-10}$ |
| $R_e (\Omega)$ | 2092 | $1.086 \times 10^6$ |
| $C_{dl} (\text{F/m})$ | $1.0736 \times 10^{-3}$ | $3.8836 \times 10^{-7}$ |
| $0.01 M \text{NaCl}+\text{Na}_2\text{SO}_4$ | | |
| $R_i (\Omega)$ | 59.20 | $2.5415 \times 10^{-5}$ |
| $R_p (\Omega)$ | 38078 | |
| $C_e (\text{F/m})$ | — | $1.9542 \times 10^{-9}$ |
| $R_e (\Omega)$ | 810.30 | $6.1198 \times 10^{-1}$ |
| $C_{dl} (\text{F/m})$ | $1.3675 \times 10^{-3}$ | $5.0808 \times 10^{-7}$ |
| $0.1 M \text{NaCl}+\text{Na}_2\text{SO}_4$ | | |
| $R_i (\Omega)$ | 12.26 | $2.2887 \times 10^{-3}$ |
| $R_p (\Omega)$ | 9262 | |
| $C_e (\text{F/m})$ | — | $2.7117 \times 10^{-9}$ |
| $R_e (\Omega)$ | 695.20 | $5.1094 \times 10^{-1}$ |
| $C_{dl} (\text{F/m})$ | $1.0692 \times 10^{-3}$ | $7.50368 \times 10^{-7}$ |

The protective layer on mild steel in 3% NaCl, 0.01 M Na$_2$SO$_4$ and mixed NaCl + Na$_2$SO$_4$ solution. The corrosion protection properties of these coatings are retained even after storing them in air at 25 °C for 30 days. This study clearly reveals that the polyaniline coating has excellent corrosion protection properties and it can be considered as a potential coating material for corrosion protection of the mild steel in different corrosive environments.

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