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CORROSION PROTECTION PERFORMANCE OF LOW CARBON STEEL BY USING POLY (O-ANISIDINE) COATINGS AT DIFFERENT PH CONDITION

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ABSTRACT

The possibility of using the electrochemically synthesized poly(o-anisidine) (POA) coatings on low carbon steel (LCS) for corrosion protection purposes was examined under different pH condition. The POA coatings were synthesized from an aqueous solution of oxalic acid under cyclic voltammetry. The extent of the corrosion protection offered by these coatings to LCS in aqueous 3% NaCl was examined by potentiodynamic polarization technique. The potentiodynamic polarization measurements demonstrate that the POA acts as a protective layer on LCS against corrosion in chloride solution. The porosity in the coating was estimated by using the potentiodynamic polarization data and it is observed that the porosity depends on the pH condition used for the synthesis of the POA coatings. The protection of low carbon steel against corrosion in 3% NaCl by the POA coatings can be achieved more effectively when the synthesis was carried out in electropolymerization solution of pH 7.0. This study shows that a POA coating can be considered as a potential coating material to protect LCS against corrosion in a chloride environment

Keywords : *Corrosion protective coatings, Conducting polymer coatings, Poly(o-anisidine) coatings, Electrochemical polymerization, Cyclic voltammetry*

1. INTRODUCTION

The use of conducting polymers as advanced coating materials for corrosion protection of oxidizable metals has become one of the most exciting new research fields in most recent times [1-3]. Although the conducting polymers are found to be most promising material for corrosion protection, the electrochemical polymerization of conducting polymers is not easy on oxidizable metals. The electrochemical polymerization of conducting polymers 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. Hence, a successful electrochemical polymerization of conducting polymer on oxidizable metals 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 electrochemical polymerization process.

Among the conducting polymers, polyaniline [4] and polypyrrole [1] are the most promising conducting polymers for corrosion protection of metals. The main advantage of this polymer is the possibility of controlling the thickness of the protective layer by fixing the charge of electrosynthesis. The main difficulty to overcome in this technique is the classical problem of metal dissolution which competes with the first step of polymerization. Some authors propose the use of passivating agents, such as sodium oxalate [5,6] or

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sodium tartrate [7] as the electrolyte; others suggest sodium salicylate [8,9], which besides has been shown to be successful for most oxidizable metals. More recently, Bereket et al.[10] reported the electrochemical synthesis of poly(aniline-co-2-anisidine) films on stainless steel in tetrabutylammonium perchlorate/acetonitrile solution containing perchloric acid. They found that the anti-corrosion behaviour of the poly(aniline-co-2-anisidine) films was slightly poorer than that of polyaniline. Since then, several research groups have systematically investigated the electrochemical synthesis of various conducting polymers on oxidizable metals for corrosion protection purposes.

In the present work the attention is mainly focused on the development of poly(o-anisidine) coatings on LCS from an aqueous solution of oxalic acid at different pH condition and consequently the corrosion protection performance of the coatings with different pH conditions. The results of the investigation of the corrosion protection offered by the POA coatings to LCS in aqueous 3% NaCl solution are presented. The extent of the corrosion protection offered by the POA coatings to LCS in aqueous 3% NaCl was examined by potentiodynamic polarization technique and cyclic voltammetry.

2. EXPERIMENTAL

Analytical reagents (AR) grade chemicals were used throughout the present study. The *o-anisidine* monomer was double distilled prior to its use. The aqueous oxalic acid solution was used as the supporting electrolyte. The concentrations of oxalic acid and monomer o-anisidine was kept constant at 0.3 M and 0.1 M, respectively. The LCS substrates (size ~ 10 x 15 mm 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 POA coatings were synthesized by electrochemical polymerization of *o-anisidine* on LCS substrates from an aqueous oxalic acid solution under cyclic voltammetric conditions. The electrochemical polymerization was carried out in a single compartment three electrode cell with steel as working electrode (150 mm^2), platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The cyclic voltammetric conditions were maintained using a SI 1280B Solartron Electrochemical Measurement System (U.K.) controlled by corrosion software (CorrWare, Electrochemistry/Corrosion Software, Scribner Associates Inc. supplied by Solartron, U.K.). The electrochemical polymerization procedures developed by our group, were used to synthesize the POA coatings on LCS. After the completion of the pre-defined number of cycles, the working electrode was removed from the electrolyte and rinsed with double distilled water and dried in air. Scanning electron microscopy (SEM) was employed to characterize the surface morphology with a Leica Cambridge 440 Microscope (U.K.).

The synthesized POA coatings were abbreviated by taking into consideration the supporting electrolytes and pH of the solution used for the synthesis. For example, the POA coating synthesized with an aqueous oxalic acid solution with pH 1.12 was abbreviated as POA (oxalate-1.12). The electropolymerization solution of different pH 2.5, pH 5.0 and pH 7.0 was adjusted by using sodium hydroxide (NaOH) pelletes.

The corrosion protection performance of these coatings was investigated in aqueous 3% NaCl solution by using potentiodynamic polarization measurements and cyclic voltammetry. For these measurements, a teflon holder was used to encased the polymer coated LCS substrates so as to leave an area of ~ 40 mm^2 exposed to the solution. The polarization resistance measurements were performed by sweeping the potential between – 0.25V and 0.25 V from open circuit potential at the scan rate of 0.002 V/sec. Before polarization the substrates were immersed into the solution and the open circuit potential was monitored until a constant value was reached. The Tafel slopes of the anodic (b_a) and cathodic (b_b) parts of the polarization curve were obtained. The corrosion current density (I_{corr}) in A/m^2 was calculated by using Stern-Geary equation [11] and it is converted into the corrosion rate (CR) in mm per year by using the expression [12]–

$$CR(mm/year) = 3.268x10^3 \frac{I_{corr}}{\rho} \frac{M\,W}{z}$$

where MW is molecular weight of LCS (g), r is the density of LCS (kg/m^3) and z is the number of electrons transferred in the corrosion reaction; z =2 in the case of LCS reaction. All the measurements were repeated at least four times and good reproducibility of the results was observed.

3. RESULTS AND DISCUSSIONS

3.1 Synthesis of poly(o-anisidine) coatings on low carbon steel.

The POA coatings were synthesized on LCS substrates by electrochemical polymerization of *o-anisidine* from an aqueous solution of oxalic acid under cyclic voltammetric conditions. The electrochemical polymerization procedures reported for the synthesis of POA coatings on LCS from an aqueous solution of oxalic acid was used for this study [13-15]. The resulting coatings were uniform and strongly adherent to the substrate. The coatings were characterized by cyclic voltammetry, UV-visible absorbance spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction measurements and Scanning electron microscopy. It has been observed that the formation of POA coatings on LCS occurs after the passivation of its surface via the formation of passive interphase [13-15].

3.2 Corrosion protection performance by POA(oxalate) coatings

In this section, the results of the investigation of the corrosion protection offered by the POA (oxalate) coatings to LCS in aqueous 3% NaCl solution are presented. The POA(oxalate) coatings were synthesized on LCS substrates by electrochemical polymerization of *o-anisidine* in the aqueous oxalic acid solution under cyclic voltammetry conditions.[14]. The pH of the electropolymerization solution (i.e. aqueous solution containing 0.1 M o-anisidine + 0.3 M oxalic acid) was found to be ~ 1.12. The coating porosity is one of the important parameters, which strongly governs the anticorrosive behavior of the coatings. The porosity in POA(oxalate) coatings on LCS substrates was determined from potentiodynamic polarization measurements. The potentiodynamic polarization curves were recorded for uncoated LCS and POA (oxalate) coated LCS in aqueous 3 % NaCl. The values of the corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel constants $\hat{a}_a$ and $\hat{a}_c$, polarization resistance R_p and corrosion rate obtained from these curves are given in Table. The porosity in POA (oxalate) coating was calculated using the relation[16]

$$P = (Rps/Rp)10^{-(|\Delta Ecorr|/\beta a)}$$

Sample	Ecorr (V)	Icorr (A/m^2)	Ba (V/dec)	Bc (V/dec)	Rp (Ω/cm^2)	CR (mm/year)	% E	% P
Uncoated LCS	-0.710	0.3072	0.0697	0.1842	715.44	0.30	—-	—-
LCS/POA/Oxalate pH=1.12	-0.683	0.1872	0.0642	0.2057	1134.94	0.21	36.96	25.83
LCS/POA/Oxalate pH=2.5	-0.702	0.1672	0.0625	0.1588	1166.72	0.19	38.68	47.07
LCS/POA/ oxalate pH=5.0	-0.641	0.0892	0.0892	0.1336	2373.26	0.10	69.85	3.08
LCS/POA/ oxalate pH=7.0	-0.540	0.0675	0.0835	0.2657	4092.53	0.078	82.5	0.063

where P is the total porosity, R$_{ps}$ is the polarization resistance of the uncoated LCS, R$_p$ the measured polarization resistance of coated LCS, DE$_{corr}$ is the difference between corrosion potentials and b$_a$ the anodic Tafel slope for uncoated LCS substrate.

The protection efficiency (PE) was calculated by using the expression –

$$PE\% = \left[\frac{R_{pc} - R_p}{R_{pc}} \right] x100$$

where R$_p$ and R$_{pc}$ denote the polarization resistance of uncoated LCS and POA (oxalate) coated LCS, respectively.

The potentiodynamic polarization curves for uncoated LCS and POA (oxalate-1.12) coated LCS in aqueous 3 % NaCl are shown in Figure1. The values of the E$_{corr}$, I$_{corr}$, Tafel constants â$_a$ and â$_c$, polarization resistance R$_p$ and corrosion rate obtained from these curves are given in Table. The porosity in the POA (oxalate-1.12) coating was found to be ~ 25.83 % which indicates that the coating is porous.

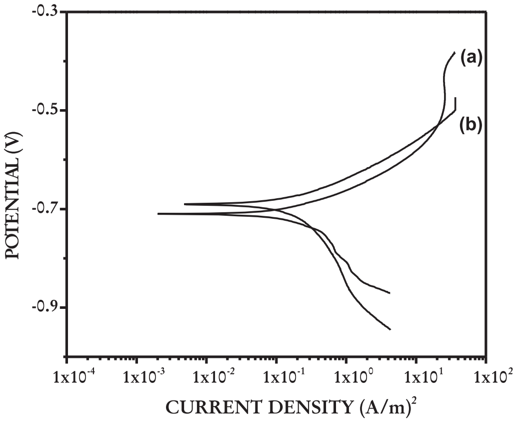

Figure 1 : Potentiodynamic polarization curves for (a) uncoated LCS and (b) POA (oxalate-1.12) coated on LCS in aqueous 3% NaCl solution.

The I$_{corr}$ value decreases from 0.3072 A/m^2 for uncoated steel to 0.1872 A/m^2 for the POA (oxalate-1.12) coated LCS. The E$_{corr}$ increases from -0.710 V for the uncoated LCS to -0.683 V for the POA (oxalate-1.12) coated LCS. This positive shift of 0.027 V in E$_{corr}$ indicates very poor protection of the steel surface by the POA (oxalate-1.12) coating. The corrosion rate of the LCS is found to be 0.21 mm/year which is ~ 1.43 times lower than that observed for the uncoated LCS. The protection efficiency calculated from potentiodynamic polarization data is found to be ~ 36.96%.

The SEM micrograph of the POA (oxalate-1.12) coated LCS is shown in Figure 2. It is observed that the surface is porous and granular surface morphology**.**

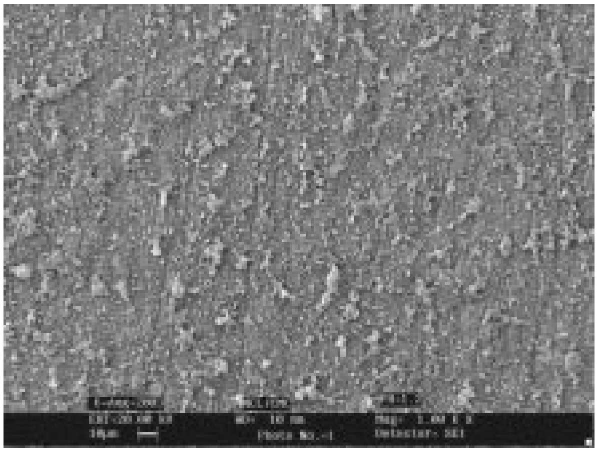

Figure 2 : SEM micrograph of the POA (oxalate-1.12) coated LCS substrate under cyclic voltammetric condition

In order to improve the corrosion protection performance of the POA (oxalate) coatings, the synthesis was carried out in electropolymerization solutions (i.e. aqueous solution containing 0.1 M o-anisidine + 0.3 M oxalic acid) of different pH. The electropolymerization solution of different pH 2.5, 5.0 and 7.0 was adjusted by using sodium hydroxide (NaOH) pelletes.

The SEM micrographs of the POA(oxalate-2.5) coatings are shown in Figure3(a). It is observed that the surface is more porous than POA (oxalate-1.12) and granular surface morphology. The SEM micrograph of the POA (oxalate-5.0) coated LCS and POA (oxalate-7.0) coated LCS is shown in Figure3(b) and Figure 3(c) respectively. It is observed that the surface is uniformly covered with POA coatings. It clearly confirms that the surface morphology drastically changed with the pH of the electrochemical solution.

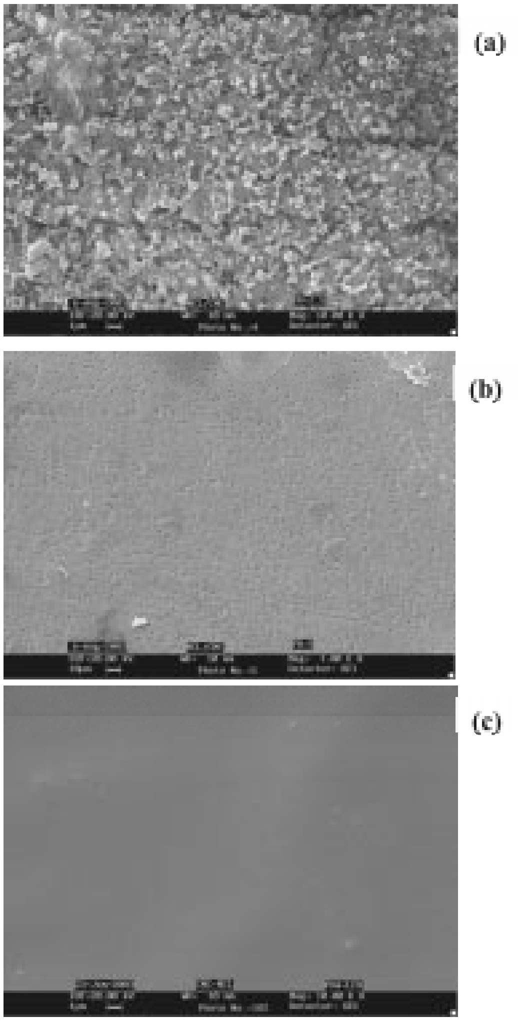

Figure 3 : SEM micrograph of the (a) POA (oxalate-2.5) (b) POA (oxalate-5.0) (c) POA (oxalate-7.0) coated LCS substrate under cyclic voltammetric condition.

The potentiodynamic polarization curves for POA(oxalate) coated LCS synthesized in electropolymerization solutions of different pH in aqueous 3 % NaCl are shown in Figure 4. The porosity in POA(oxalate-2.5), POA(oxalate-5.0) and POA (oxalate-7.0) coatings was found to be and 47.07 %, 3.08 %, 0.063 %, respectively. This suggests that the porosity in the coating depends on the pH of the electropolymerization solution and it decreases with the increase in the pH. The analysis of the potentiodynamic polarization curves [Figure 4] shows that the shift in the E_{corr} depends on the pH of the electropolymerization solution and it is increases with the increase in the pH. It is observed that the I_{corr} decreases due to the POA(oxalate-2.5), POA(oxalate-5.0) and POA (oxalate-7.0) coatings. The corrosion rates of POA(oxalate-2.5), POA(oxalate-5.0) and POA(oxalate-7.0) coated LCS are found to be ~ 0.19, 0.10 and 0.078 mm/year which are ~ 1.58, 3 and 4 times lower than that observed for uncoated LCS. This implies that the POA(oxalate-7.0) coating provides protection to LCS against corrosion in aqueous 3% NaCl. The protection efficiencies for POA(oxalate-2.5), POA(oxalate-5.0) and POA (oxalate-7.0) calculated from potentiodynamic polarization data are found to be ~ 38.68, 69.85 and 82.5 %. These results reveal that the pH of the electropolymerization solution affects the corrosion protection efficiency of the POA coatings.

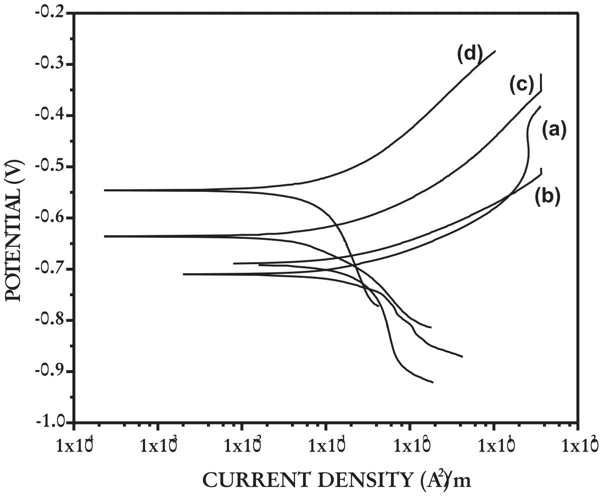

Figure 4 : Potentiodynamic polarization curves for (a) uncoated LCS (b) POA(oxalate-2.5) (c) POA(oxalate-5.0) and (d) POA (oxalate-7.0) coating on LCS in aqueous 3% NaCl solution.

The corrosion protection offered by POA coating to the LCS 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. Based on the corrosion protection mechanism putforth by several researchers [17,18]; 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 corrosion potential to more positive values. The result of the potentiodynamic polarization measurements for the POA coated LCS shows a shift in the corrosion potential to more positive value and reduce the corrosion rate of LCS. However, the corrosion potential remains within the active range of LCS dissolution and hence the passivation of the LCS does not take place. Thus, the POA coating has a direct effect on the corrosion protection of LCS, however, it is not based on the passivation mechanism. According to the alternative mechanism [19,20], it may be thought that the POA layer serves as a mediator between two processes viz, metal dissolution and the oxygen reduction. As a result, the increase in the local pH at the metal surface will be prevented and subsequently the cathodic disbondment.

4. CONCLUSIONS

The possibility of using the electrochemically synthesized poly(o-anisidine) (POA) coatings for corrosion protection of low carbon steel (LCS) in aqueous 3% NaCl solution was investigated by the potentiodynamic polarization technique. The following main findings resulted from the present investigation –

- The potentiodynamic polarization studies reveal that the poly (o-anisidine) acts as a corrosion protective coating on low carbon steel.
- The porosity in the coating was estimated by using the potentiodynamic polarization measurements and it is observed that the porosity in the coating depends on the pH of the electropolymerization solution.
- The protection of low carbon steel against corrosion in 3% NaCl by the poly(o-anisidine) coatings synthesized in oxalic acid solution can be achieved more effectively when the synthesis was carried out in electropolymerization solution of pH 7.0.
- This study clearly shows that the poly (o-anisidine) coating can be considered as a potential coating material to protect steel against corrosion in aqueous 3% NaCl

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