Published by :
https://www.ijert.org/
An International Peer-Reviewed Journal

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 15 Issue 04 , April - 2026

Measurement of Porosity in Poly(O-Anisidine) Coatings on Low Carbon Steel

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Abstract - The coating porosity is one of the important parameters, which strongly governs the anticorrosive behaviour of the coatings. Therefore, measurement of the coating porosity is essential in order to estimate the overall corrosion resistance of the coated substrate. In this work, the porosity in poly(O-anisidine) (POA) coatings on low carbon steel substrates was measured by polarization resistance measurements. The poly(O-anisidine) coatings have been synthesized electrochemically on low carbon steel (LCS) substrates under cyclic voltametric conditions from an aqueous solution of oxalic acid. It has been found that the porosity in POA coatings depends on the coating thickness.

Keyword- Conducting polymer, Porosity Corrosion protection,

INTRODUCTION

Conducting Polymer have received a great attention as advanced materials due to their outstanding properties and new application areas. The use of conducting polymers as an alternative to the traditional anticorrosive coatings for metals/alloys.[1-4] has become one of the most exciting research field. For synthesizing uniform and continuous conducting polymer coatings directly on a variety of substrates, the electrochemical polymerization (ECP) is an inexpensive, environment friendly and effective technique.[4] In this technique, the properties of the polymer coatings can be controlled effectively by proper choice of the process parameters such as supporting electrolyte, synthesis temperature, pH of electrolyte, monomer concentration and synthesis time etc.

The electrochemical synthesis of conducting polymer coating is not easy on reactive metals because of their preferred dissolution at a potential lower than the oxidation potential of monomer. More recently, few studies have been reported on the synthesis of conducting polymer coatings on LCS inspite of its use in wide range of industrial applications.[5-10] Recently our group has investigated the electrochemical polymerization of o-anisidine on low carbon steel substrate under cyclic voltammetric condition from aqueous oxalic acid medium.[14] POA coatings were synthesized on LCS by using different aqueous solution shows better corrosion protection performance.[15-16]

Notter and Gabe[10] clearly described the nature and effect of porosity on corrosion resistance of electrodeposited coatings. He points out different methods developed for detecting porosity of metallic coatings. The major problem in using protective coatings in aggressive environment is the possible presence of open porosity in the coatings. The performance of such coatings against corrosion depends on the porosity and the adhesion of the coating[11]. Owing to the generation of corrosion resulting from the direct path between the corrosive environment and the substrate, porosity is the primary focus of the investigation of corrosion behaviour. However, hardly any attempts have been made to measure the porosity in conducting polymer coating.

In this article, we have reported the results of our studies on the measurement of porosity in POA coating on LCS substrate through the use of potentiodynamic polarization resistance measurements. The POA coatings on LCS substrates were synthesized by ECP of O-anisidine under cyclic voltammetric conditions.

EXPERIMENTAL

A. Synthesis of poly(O-anisidine (POA) coatings on LCS substrates

The POA coatings were synthesized by ECP of O-anisidine on LCS substrates under cyclic voltammetric conditions. In the present studies, aqueous solution of oxalic acid was used as the supporting electrolyte. The O-anisidine monomer was double distilled prior to use. The concentrations of oxalic acid and O-anisidine were kept constant at 0.3 M and 0.1 M, respectively. The synthesis was carried out by sweeping the potential between –500 mV and 1800 mV at a potential scan rate of 20 mV/sec. After deposition the working electrode was removed from the electrolyte and washed with the supporting electrolyte solution.

B. Measurement of porosity in POA coatings

The porosity in POA coatings on LCS substrates was determined from potentiodynamic polarization resistance measurements. Prior to measurement, the POA coated LCS electrode was firstly immersed in the electrolyte solution for 1 hour. The 0.1 M aqueous solution of oxalic acid was used as the electrolyte. After an initial potential stabilization of 1 hour, the polarization resistance measurements were performed by sweeping the potential between –600 mV and 200 mV at a potential scan rate of 20 mV/sec.

The electrochemical measurements were carried out in a single compartment three electrode cell with LCS as working electrode (1.5 cm^2), platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The potentials were measured with respect to a SCE. The cyclic voltammetry (CV) and potentiodynamic polarization measurements were performed using a SI 1280B Solartron Electrochemical Measurement System (U.K.) interfaced with a personal computer. A dedicated computer was used to control the applied potentials and to plot the resulting CV and polarization curves.

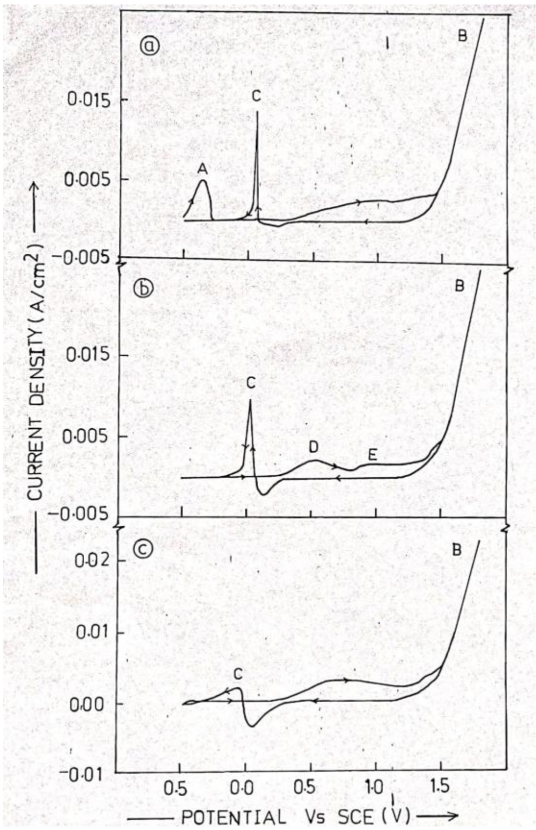


Fig.1 : Cyclic voltammogram scans (a) first, (b) second and (c) twenty fifth recorded during the synthesis of POA coating on LCS substrate under cyclic voltammetric conditions. Scan rate : 20 mV/sec.

RESULTS AND DISCUSSIONS

The first, second and twenty-fifth scans of the CV recorded during the ECP of O-anisidine on the LCS electrode from 0.3 M oxalic acid solution are shown in Fig.1. Most of the features of these CVs exhibit good resemblance with those reported by Camalet et al.[7] In the previous investigation[13] we have shown that the oxalic acid is a suitable medium for the ECP of o-anisidine (OA). The POA coatings on LCS substrate is characterized by UV visible spectroscopy, FTIR spectroscopy, X-ray diffraction, Scanning Electron Spectroscopy which confirms the strongly adherent POA coatings on LCS. The corrosion protection performance was also reported for strongly adherent POA coatings on LCS

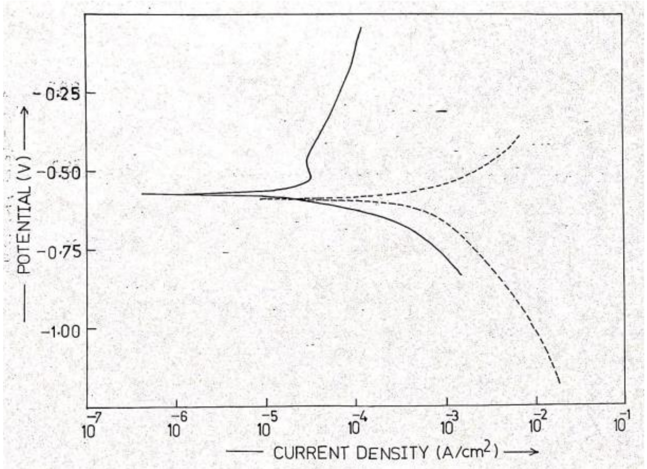
The first positive cycle [Fig.1(a)] shows – (i) an anodic peak (A) at – 360 mV; (ii) small oxidation current between 200 mV and 1300 mV and (iii) onset of an oxidation wave (B) at ~1300 mV and beyond this potential high anodic current flows due to the oxidation of oxalic acid. In the reverse scan, the anodic current decays very sharply and a negligibly small current is seen till 200 mV. The negative cycle terminates with a sharp oxidation peak (C) in the potential range 200 to –100 mV.

The anodic peak A is attributed to passivation process of the LCS electrode surface in the oxalic acid medium[6-7]. In the potential range -497 mV to –268 mV, the LCS electrode is active and undergoes anodic dissolution which produces Fe^{2+} ions in its vicinity. These ions interact with the electrolyte to form insoluble iron(II) oxalate (FeC_2O_4, $2H_2O$) which adheres to the electrode surface thereby forming an iron oxalate film. Once the LCS electrode surface is completely covered by an iron oxalate layer it is said to be ‘passivated’. The iron oxalate film isolates the electrode surface from the electrolyte and inhibits its further dissolution without affecting other electrochemical processes. Therefore, it can be argued that once the passivation has occurred during the first scan, the electrode surface behaves like an inert metal.

The peak C is attributed to the reactivation of the LCS electrode surface during the negative cycle[8-9]. Mengoli and Musiani[12] argued that during the anodic cycle, iron (II) oxalate is converted into iron (III) oxalate. The iron (III) oxalate, being more soluble, does not remain on the electrode surface and is released into the electrolyte. Its dissolution generates micro pores in the passive layer. These micro pores are then filled up by iron oxide Fe_2O_3, which is formed simultaneously with the dissolution of iron (III) oxalate. During reverse scan, iron oxide is slowly destroyed and a sharp oxidation process occurs in the potential range 118 mV to - 28 mV resulting into precipitation of new iron (II) oxalate on the LCS electrode surface. Finally, it can be concluded that passivation of LCS electrode in oxalic acid medium is due to formation of an inorganic interphase comprised of iron (II) oxalate and iron oxide on the electrode surface.

During the second scan [Fig.1(b)], the anodic peak A is not observed, however, rest of the features are similar to that of the first scan. On repetitive cycling, the voltammograms identical to that of second scan are obtained. A typical twenty-fifth scan is shown in Fig.1(c). A careful observation indicates a regular increase in the oxidation current in the potential range 450 to 1400 mV, which reveals oxidation of O-anisidine monomer and thus its actual polymerization [15-16] On repetitive cycling, the oxidation wave B and peak C are still observed. However, it is clearly seen that the current density corresponding to the peak C decreases gradually with the number of cycles. This may be attributed to the stabilization of the LCS electrode surface due to formation of an adherent POA coating. In addition to this, new peaks D and E are seen, which are assigned to conversion of amine units into radical cations indicating oxidation of POA deposited at the LCS electrode surface. The visualization of the LCS electrode after twenty fifth scan reveals the formation of a dark green colored POA coating.

The potentiodynamic polarization curves of virgin LCS and POA coated LCS are shown in Fig.2.



The thickness of the POA coating is about ~ 0.25 µm. The electrochemical parameters determined from these polarization curves are given in Table-1.

The porosity in POA coating was calculated using the relation[11]

$$P = (R_{ps}/R_p)\ 10^{(-|\Delta E_{corr}|/\beta a)}$$

where P is the total coating porosity rate, R_{ps} is the polarization resistance of the virgin LCS, R_p the measured polarization resistance of coated LCS , ΔE_{corr} is the difference potential between free corrosion potentials of the coated steel and bare substrate and β_a the anodic Tafel slope for virgin LCS substrate.

Table-1 Electrochemical parameters of POA coated LCS after 1 Hr immersion in 0.1M oxalic acid solution and porosity calculation from potentiodynamic polarization resistance measurements

Samples	R_p (Ωcm^2)	E_{corr} (mV)	I_{corr} (mA/cm^2)	β_a (mV/dec)	β_c (mV/dec)	P(%)
Virgin LCS	58	-588	1.27	226	694	0.99
POA coated LCS	4482	-562	5.80	154	69	

The porosity in POA coating (~ 0.25 µm thick) on low carbon steel was found to be ~ 0.99 %.

We have investigated the effect of the POA coating thickness on the porosity. The variation of porosity with thickness of POA coating is shown in Fig.3. It is observed that the porosity in POA coating increases with the thickness upto ~ 0.5 μm. and beyond which it saturates.

CONCLUSIONS

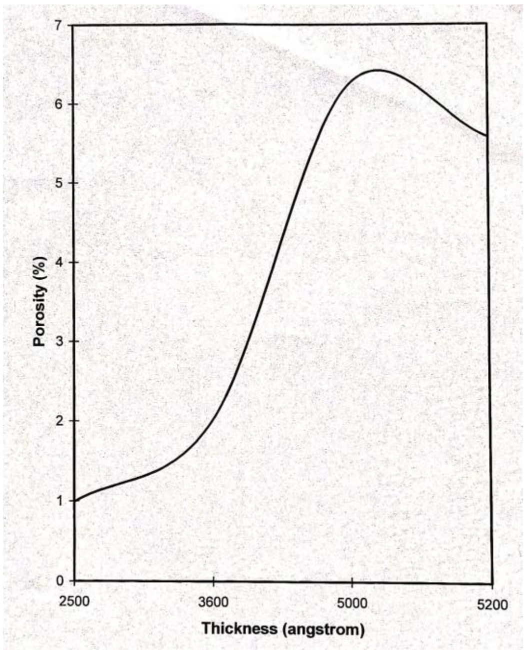


Fig.3 : Variation of porosity with thickness of POA coating

We have estimated the porosity in POA coatings on LCS substrates through the use of

potentiodynamic polarization resistance measurement. It is observed that the porosity in coating increases with the coating thickness upto ~ 0.5 μm.

ACKNOWLWDGEMENT

The author is thankful to Principal Government Polytechnic Ambad for support and carry research activity at the institute.

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