



Comparison of polyaniline electrodeposition on carbon steel from oxalic acid and salicylate medium



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ABSTRACT

Polyaniline (PANI) coatings on carbon steel (CS) substrate were electrodeposited from two different mediums such as oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) and sodium salicylate ($\text{C}_7\text{H}_5\text{NaO}_3$). In oxalic acid, the importance of the passivation of the carbon steel surface prior to PANI electrodeposition was investigated by linear potentiodynamic test. It showed below 0.3 M oxalic acid concentration PANI film formation was not complete. The extent of passivation of the carbon steel was found to depend on the strength of the oxalic acid, which determined the formation and the nature of the PANI film. Whereas, deposition from the sodium salicylate solution did not show any passivation peak, but resulted in the formation of a transparent, uniform, compact and adherent PANI coating. The formation, morphology and characteristics of the coatings were compared by cyclic voltammetry, scanning electron microscopy (SEM) and Raman spectroscopy.

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1. Introduction

Conducting polymers are an important class of materials used for various applications. Application areas include sensors [1,2], energy storage [3], catalyst [4], membrane filters [5] and giant magnetoresistance [6,7], etc. Another important application of conducting polymer coatings is corrosion protection of metals and alloys. Various types of conducting polymer coatings have been developed for different substrates and their corrosion protection performance have been evaluated [8–12]. Among several conducting polymers, formation and performance of polyaniline (PANI) coating are most studied because of its long-term environmental stability and easy of synthesis [13–15]. Electropolymerization of PANI, its derivatives, and its composite coatings are widely studied on several active and noble metal substrates [16–22].

The most efficient way to synthesize conducting polymers is by electrochemical polymerization. Electrochemical polymerization method has minimum processability issues and offers good control on the thickness and morphology of the coatings by controlling potential and current density. Besides, electropolymerization is a very economical process. However, electrodeposition of conducting polymer on an active metal surface (such as carbon steel) is challenging. The oxidation potential of active metals are more negative than the oxidation potential of the monomer, leading

to metal dissolution before the formation of polymer coating [8]. Therefore, it is necessary to passivate the metal before the electropolymerization process. Active metal surfaces can be passivated by air-formed passive oxide films naturally formed on the surface of the metals in contact with air [23,24], and by passivating the surface in the aqueous inorganic acid solution (such as nitric acid). However, most metals do not form a protective surface passivation film in the air, and in inorganic acids, the formation of a passive layer on the surface and electropolymerization becomes a two-step process. Therefore, PANI deposition on iron or steel surface is mostly carried out from the oxalic acid solution, where a film of the oxalate salt of iron passivate the surface before polymerization [18,25,26]. While there are several reports on the electrodeposition of PANI from oxalic acid, reports on its electrodeposition from salicylate medium is very limited [17].

When deposited from organic acids, the formation of a PANI layer on active metals depends on several parameters. Such factors as the composition of the solution, the concentration of the monomer, pH, and applied potentials can affect the nature of the PANI film. Choice and application of various electrochemical methods for polymerization have a strong influence on the nature of the film. The simplest means of inducing the polymerization process is to apply a sufficiently positive constant potential. The potential chosen will influence the rate of oxidation and, therefore, polymerization. If the rate of polymerization is too slow, oxidation of the monomer may occur without deposition of a continuous film because the critical chain length, necessary for nucleation, growth and propagation, may not be reached.

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Surface passivation of active metal would depend on the oxidizing power of the oxalic acid, which can influence the degree and the continuity of the PANI film. Also, the nature of the doping ion (oxalate or salicylate) can influence the nature of the film formed. Therefore, a comparison of the quality of coating generated from these solutions is necessary. In this report, polyaniline (PANI) coatings on carbon steel (CS) substrate were deposited by electropolymerization (by cyclic voltammetry) from two different solutions such as oxalic acid and sodium salicylate. The influence of the oxalic acid concentration on the passive film formation on the CS and its influence on the PANI film formation was investigated. The nature of the PANI films formed from the two different solutions was characterized by cyclic voltammetry, scanning electron microscopy (SEM) and Raman spectroscopy.

2. Experimental details

2.1. Materials

All the chemicals were obtained from Sigma–Aldrich. The monomer, aniline and electrolytes, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) and sodium salicylate ($\text{C}_7\text{H}_5\text{NaO}_3$) were analytical grade and were used as received without further purification. Deionized water (DI) of $18.2 \Omega \text{ cm}$ resistivity was used to prepare all the solution.

2.2. Sample preparation

The chemical composition of the steel used was: 0.07% C, 0.3% Mn, 0.03% Si, 0.03% S, 0.009% P, 0.02% Al, 0.003% N, and rest Fe. The sample of $1 \text{ cm} \times 1.5 \text{ cm}$ were cut from a 1 mm thick plate and embedded into the acrylic resin so that only one surface was exposed. The embedded sample was then polished by emery papers of different grit size starting from 800, 1000, and 1200 followed by ultrasonic cleaning in deionized water (DI).

2.3. Electrochemical synthesis

The electrochemical synthesis was carried out by cyclic voltammetry (CV) on SP300 (BioLogic SAS) potentiostat/galvanostat using EC Lab v10.2x analysis software. The three-electrode configuration was used for all the electrochemical experiments. CS ($1 \text{ cm} \times 1.5 \text{ cm}$) was used as a working electrode, a 0.25 mm thick platinum foil ($1.5 \text{ cm} \times 1.5 \text{ cm}$) is used as a counter electrode and Mercury/Mercury sulfate/ K_2SO_4 (saturated) (MSE) ($E^0 = +650 \text{ mV}$ vs. NHE) was used as a reference electrode. All the potentials are reported w.r.t. MSE unless otherwise mentioned. Electropolymerization was carried out in 0.1 M aniline solutions in various concentrations of oxalic acid (0.3 M and 0.1 M) and sodium salicylate solution (0.3 and 0.5 M). Passivation experiments of CS in oxalic acid were studied by linear potentiodynamic method in different concentrations, and the passivation potentials were calculated from the polarization curve.

2.4. Characterization

The Raman spectra were recorded with Ramnor H-2S Spectrometer, Jobin-Yvon, France by using 514.5 nm wavelength laser having a power of 1 mW within the spectral range of $200\text{--}1800 \text{ cm}^{-1}$. Scanning electron microscopy (SEM) images were recorded using Hitachi, S-3400N at 15 keV and 10 mm working distance.

3. Results and discussion

3.1. Passivation behavior of CS in oxalic acid

The electrodeposition of polymer on a steel surface takes place in three stages [27]: (1) initiation of passive film formation along with

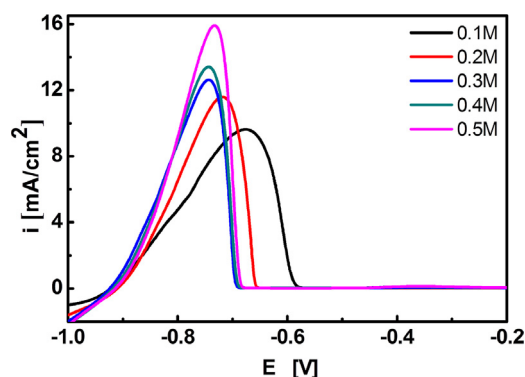


Fig. 1. Linear potentiodynamic scan (at 10 mV/s) of carbon steel in different concentration of oxalic acid.

adsorption of monomer on the steel surface; (2) growth of passive film; (3) formation of polymer onto the surface. That implies surface passivation before electropolymerization is an essential step for an active metal like carbon steel, as monomer oxidation takes place at a potential more positive than the corrosion potential of the CS. In the literature, various concentrations of oxalic acid have been used for electrodeposition of polyaniline. Correspondingly, polymer films of different nature and degree of corrosion protectiveness were reported. This indicates the passivation potential of CS depends on oxalic acid concentration. To verify the effect of the concentration, the linear potentiodynamic scan was carried out in different concentrations of oxalic acid. Fig. 1 represents the linear potential scan in various concentrations of the oxalic acid, which shows features typical of an active–passive metal such as CS. A clear passivation peak is observed, indicating the formation of Fe (II) oxalate on the surface [28]. From the figure, the primary passivation potential and the passivation potential gradually shift to negative potential with the increase in the concentration of the oxalic acid. From 0.1 M to 0.3 M oxalic acid, the passivation potential shifts negatively by ca. 100 mV. Beyond 0.3 M concentration, the change in the passivation potential is insignificant for further increase in concentration.

The formation of the passive film becomes easier for concentrations above 0.3 M oxalic acid due to the lowering of the passivation potential. Below 0.3 M passive film formation can be incomplete, which would affect polyaniline film formation. Our study indicates that oxalic acid concentrations from 0.3 M and higher are suitable for the formation of a complete oxalate passivation layer which is required for the PANI film formation by electropolymerization. This is corroborated by several works in the literature where 0.3 M oxalic acid was used for PANI deposition on CS [29–33]. Therefore, 0.3 M of oxalic acid was used in all subsequent studies.

3.2. Electrochemical synthesis of polyaniline

3.2.1. PANI coating from oxalic acid

Accordingly, electrodeposition of polyaniline carried from 0.3 M has different characteristics than any concentration lower. A comparison of cyclic voltammetry in 0.1 and 0.3 M oxalic acid containing 0.1 M aniline is presented in Fig. 2. In 0.1 M oxalic acid (Fig. 2A) the characteristic passivation peak of CS is absent, and only a clear reactivation peak [28] is observed. The anodic aniline oxidation peak appears suppressed, indicating rudimentary growth of polymer film on the surface. This is due to incomplete passivation of the substrate. This observation is also reflected in the SEM image of the coating (Fig. 2C), where the PANI film does not completely cover the substrate and oxalate crystals are still visible.

However, the CV deposition curve in 0.3 M oxalic acid exhibits all prominent features of PANI deposition [8,9,34,18]. In the first cycle

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