ELECTRODEPOSITION OF POLYANILINE ON STAINLESS STEEL AND ITS ROLE ON CORROSION PREVENTION

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ABSTRACT

The conducting polymer polyaniline (PANI) was prepared by electrochemical polymerization method. Electrochemical deposition of polyaniline coatings on stainless steel was carried out by the constant potential technique. This study will provide a better understanding of the corrosion protection mechanism of the PANI coating. The structure of the coating was determined by using Reflection Absorption Infrared spectroscopy (RAIR). The RAIR peaks ratios of the characteristic peaks (1590 and 1500) were used to monitor the changes in the structure of polymer with respect to the process parameters. The change in corrosion current with process parameters was correlated with the extent of oxidation of the polymer. The mean roughness, rms roughness and the 3-D morphology of the coatings obtained from atomic force microscopy (AFM) were used to correlate the surface energy changes of the coatings.

Key words: polyaniline, conducting polymer, corrosion, Reflection Absorption Infrared spectroscopy (RAIR), Atomic Force Microscopy (AFM)

I. INTRODUCTION

Corrosion of metals is a major problem in the aerospace and automobile industry. The current methods of corrosion protection such as chromate conversion coatings are under increased scrutiny from the Environmental Protection Agency (EPA) due to their carcinogenic nature. Intrinsically conducting polymers (ICPs) like polyaniline and polypyrrole have been considered as a potential replacement for chromate conversion coatings and have been under investigation since past decade. Conducting polymers such as polyaniline, polypyrrole and polythiophene have been paid much attention as key materials for developing electronic devices, e.g., Li batteries [Osaka et al., 1989, Yonezawa et al., 1993], capacitors, and other electrochromic devices [Jelle et al., 1993]. Among these conductive polymers, polyaniline appears to be promising because of its good stability in air and of the ease in preparing a thin film via electrochemical polymerization [Genies et al., 1990].

The organic coatings containing intrinsically conducting polymers like polyaniline have been found to be useful to replace toxic inhibiting pigments like zinc chromate [Lu et al., 1990, DeBerry, 1985]. Polyaniline is a macromolecular substance formed by constitutional aniline units. A PANI chain can contain hundreds to thousands of these units, thus being a polymeric material. Polyaniline is synthesized by the polymerization of aniline and creates a structure that connects oxidized and

reduced structural units. Polyaniline can exist in several fundamental forms mutually differentiated by the degree of oxidation or protonation. Each form has a characteristic chemical structure, stability, color, and electric properties. The most important is the conducting green protonated emeraldine form of PANI and the corresponding non-conducting blue PANI base. The anion in the PANI structure is derived from an acid used for the protonation of imine nitrogens. Inorganic acids are most frequently employed [Abdiryim et al., 2005], e.g., hydrochloric, sulfuric, or phosphoric acid. The protonated emeraldine form of PANI is stable and, except concentrated sulfuric acid, is insoluble in any solvent. The acids used during polymerization can be replaced with organic acids [Ahmed, 2002]. Polyaniline prepared in this way becomes soluble in some organic solvents. In an alkaline environment, emeraldine salt is transformed into the deprotonated form of emeraldine base.

Based on the corrosion resistant properties of polyaniline, in this work, a polyaniline film is electrochemically synthesized on stainless steel electrode in aqueous oxalic acid solution by constant potential technique and then the corrosion behavior were measured by RAIR and the mean roughness, rms roughness and the 3-D morphology of the coatings obtained from Atomic Force Microscopy (AFM) were used to correlate the surface energy changes of the coatings. Subathira et al : Electrodeposition of Polyaniline on Stainless...

Polyaniline preparation

The most frequently employed method of synthesizing electroactive polymers is, in addition to electrochemical polymerization, chemical oxidative polymerization. The possibilities of oxidative polymerization are affected by the solubility of the monomer in the aqueous solutions of acids and by their ability to create salts in an acidic environment [Zhang et al., 2004]. The oxidation of aniline is an exothermic reaction. The released heat can thus be subsequently used to monitor the course of the reaction. The efficient polymerization of aniline with oxidation agents is achieved only in an acidic environment in which aniline exists as an aniline cation. The aniline cation radical is considered to be the first product of the oxidation reaction of aniline [Stejskal et al., 1996]. A doping component used in PANI synthesis can be selected from a broad variety of various concentrations of inorganic and organic acids that predetermine the properties of PANI. Depending on the acid used, the final protonated PANI is characterized by specific solubility, electric conductivity and stability.

II. MATERIALS AND METHODS

The monomers used in electrochemical deposition were aniline (99.5%). This chemical was bought from Aldrich chemicals. Two stainless steel electrodes $(0.9 \times 25 \times 76 \text{ rromanmm})$ were used as the counter electrodes. The reference electrode used in the experiment is the saturated calomel electrode (SCE), which was purchased from Fischer Scientific Company. Stainless steel coupon $(0.9 \times 70 \times 70 \text{ mm})$ was the working electrode for all the experiments. Oxalic acid was used as the electrolyte. It was purchased Fluka chemical company. The electrolyte concentration was kept constant at 0.2 M. All aqueous solutions used in the experiment were prepared by using double distilled water.



Fig. 1. Sketch of Electrodeposition setup

Electrochemical reaction was performed in a glass beaker. Fig 1 shows a schematic representation of an electrochemical cell. An EG&G Princeton Applied Research Potentiostat/Galvanostat Model 363 was used for electrochemical polymerization. The stainless steel samples were rinsed thoroughly with double distilled water, hexane and dried by using kim wipes. About 300 ml of electrolyte was used for each experiment. The initial monomer concentration was varied from 0.1 M to 0.3 M. Concentration higher than 0.3 M did not dissolve in the solution. Oxalic acid was used as the electrolyte. The concentration of oxalic acid was also systematically varied between 0.1-0.3 The Μ. concentration of oxalic acid used was such that the PH of solution is maintained around 1.5-1.7. The deposition of polyaniline coating on stainless steel alloy SS-304 takes place at this lower PH (range 1 to 2). The ferrous oxide layer is not stable in the PH range 1 to 2 and allows the deposition of conducting polymer layer onto the substrate. Oxalic acid was also used to in-situ clean the SS-304 substrate. Oxalic acid and N ethyl aniline were dissolved in deionised water. Galvanostatic polymerization (constant current technique) was used to electrodeposit the conducting polymer coating onto SS-304 coupon. The applied current was varied between $\frac{2}{6}$ mA/cm². The deposition time was varied between 30seconds to 3 minutes. Thus by varying the electrochemical deposition parameters like monomer concentration, electrolyte concentration, applied current density and deposition time the primer properties were optimized. After electro deposition the SS-304 coupons were rinsed with deionised water and heated to 100 \$C for 1 hr. The thickness of the primer coating was controlled by changing the deposition time and the applied current density. The thickness of the primer coat varied between 0.5-2 microns.

III. RESULTS AND DISCUSSIONS

Electrochemical deposition

Constant potential method was employed for electrochemical deposition of polyaniline. As soon as the experiment started, coating was visible on the stainless steel substrate within few seconds. It was only from 30 seconds deposition that the stainless steel substrate was fully covered by polyaniline coatings. The polyaniline coating has a very good adhesion onto stainless steel substrate. If the coating is too thick, coating may act as a physical barrier instead of chemical or electronic diffusion barrier. It was interesting to see change in color of the coating with change in the deposition time and concentration of the monomer. Polyaniline coatings showed light blue, blue and light brown colors with change in concentration and deposition time.

Reflection Absorption Infrared Spectroscopy

The chemical structure and composition of the resulting coatings were determined by using RAIR spectroscopy at a resolution of 8 cm^{-1} . A total of 256 scans were carried out over a scan range of 4000 400 cm⁻¹. A background spectrum of bare stainless steel was subtracted from the sample spectrum.



Fig. 2. Infrared spectra of polyaniline formed on stainless steel, 0.3 M aniline at 1 minute deposition time.



Fig. 3. Infrared spectra of polyaniline formed on stainless steel, 0.1 M aniline at 30 seconds deposition time.



Fig. 4 Infrared spectra of polyaniline formed on stainless steel, 0.1 M aniline at 1 minute deposition

Infrared spectroscopic analysis was performed to study the structure of the electro polymerized polymer coatings on stainless steel substrate. Polyaniline was deposited on stainless steel by electrochemical deposition. Fig 2 shows the Infrared spectra of polyaniline formed on stainless steel, 0.3 M aniline at 1 minute deposition time. Fig 3 and Fig 4 shows the IR spectra of polyaniline at different deposition times. The IR peaks at 1590, 1500, 1300 and 830 cm⁻¹ confirm the structure of polyaniline in agreement with the literature [Davidson et al., 1995]. The peaks at 1590 and 1500 are due to the quinoid (C = N) and benzoid (C - N) groups respectively. The ratio of the quinoid to benzoid absorption peaks was used to estimate the extent of oxidation of the polymer, which is the ratio of quinoid peak to the sum of quinoid and benzoid peaks. As discussed earlier, polyaniline exists in three different oxidation states. The oxidation state of polyaniline coating can be predicted from extent of oxidation values (Table 2). The polyaniline is in emeraldine state, which is partially oxidized form. Table 2 shows change in extent of oxidation with change in process parameters for polyaniline coating. The extent of oxidation increases with deposition time and it decreases with increase in concentration. The IR peak at 1300 cm⁻¹ is characteristic of the aromatic N-H group. The peak at 830 cm⁻¹ is due to the para substitution of benzene ring, which is expected for linear polyaniline structure. The peak at 1175 cm^{-1} is due to sulfonic group of the toluene-4sulfonic acid sodium salt (dopant). Table 1 shows all the characteristic peaks of polyaniline coating.

Atomic Force Microscopy

The morphology and the roughness of the coatings were determined by using AFM at a scan size of 20 μ m. The approximate thickness of the coatings can also be obtained from AFM. The roughness and rms values are noted for each coating that was tested.



Fig. 5. AFM picture of bare stainless steel

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Fig. 6. AFM picture of polyaniline coating on stainless steel at 0.1 M aniline, 30 seconds deposition.



Fig. 7. AFM picture of polyaniline coating on stainless steel at 0.2 M aniline, 30 seconds deposition.



Fig. 8. AFM picture of polyaniline coatings on stainless steel at 0.3 M aniline, 30 seconds deposition



Fig. 9. AFM picture of polyaniline coatings on stainless steel at 30 seconds deposition, 0.1 M aniline.

Atomic Force Microscopy was used to study the change in morphology of the coatings with process parameters and compare the surface roughness of the coatings. Fig 5 shows the morphology of bare stainless steel. The three-dimensional morphology of polyaniline coated on stainless steel at different concentrations of aniline is shown in Fig 6,7 and 8. The change in mean roughness and the rms roughness of polyaniline coatings with concentration of the monomer is shown in Table 3. The change in morphology with deposition time of polyaniline coating on stainless steel is shown in Fig 9 and 10. The change in mean roughness and the rms roughness of polyaniline coatings with deposition time is shown in Table 4. The roughness values of polyaniline coatings increased with increase in aniline concentration and deposition time.



Fig. 10. AFM picture of polyaniline coatings on stainless at 1 minute deposition, 0.1 M aniline.

Peaks (cm ⁻¹)	Functional groups
1590	Quinoid
1500	Benzoid
1175	Sulfonic group (dopant)
830	Secondary amine

 Table 1. Characteristic peaks of polyaniline coating

Table 2. Extent of oxidation for polyaniline

Polyaniline	1590/1500	Extent of oxidation
0.1 M, 30 sec	1.014	50.35 %
0.1 M, 1 min	1.194	54.42 %
0.2 M, 1 min	0.614	38.04 %
0.3 M, 1 min	0.426	29.87 %
0.3 M, 3 min	0.918	47.86 %

Table 3. Roughness of polyaniline coatings onstainless steel with change in concentration of
the monomer

Polyaniline coatings	Mean roughness (nm)	RMS roughness (nm)
0.1 M Aniline at 30 sec	62	81
0.2 M Aniline at 30 sec	175	208
0.3 M Aniline at 30 sec	301	365

Table 4. Roughness of polyaniline coatings on stainless steel with change in deposition time

Polyaniline coatings	Mean roughness (nm)	RMS roughness (nm)
0.1 M Aniline at 30 sec	62	81
0.1 M Aniline at 1 min	151	195

IV. CONCLUSION

The formation of polyaniline coatings on stainless steel was successfully achieved by the constant potential method. Electrochemical deposition was carried out at different deposition times and concentrations of monomers. The effect of these parameters was studied by using RAIR and AFM. Infrared spectroscopy was used to understand the structure of the coatings. Atomic force microscopy was used to study the morphology of the coating formed on stainless steel.IR spectra showed that extent of oxidation, which is determined by ratio of quinoid to benzoid peaks, changes systematically with change in process parameters. As the concentration of the monomer increases, the extent of oxidation was shown to decrease. As the deposition time increases, the extent of oxidation was shown to increase. Since the oxidizing form is the conducting form of these polymers, extent of oxidation might affect the corrosion current of the coating. Atomic force microscopy showed the three dimensional morphology of the Polyaniline coatings. The roughness values were also obtained from AFM. In polyaniline coatings showed a decrease in roughness with increase in concentration of monomer.

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