Studies on the Effects of the Potential Sweep Rates and pH on the Corrosion Rate of Polyaniline Coated Steel

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Abstract. Polyaniline (PAni) film was successfully electrodeposited on the surface of steel substrates in oxalic acid electrolyte by cyclic voltammetry at different potential sweep rates (dE/dt) (10, 20 and 30 mVs⁻¹) and different pH values (1.55, 2.55 and 3.55). The coated steel with PAni was characterized by Field Emission Scanning Electron Microscopy (FESEM) and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The corrosion resistance of the electrodeposited layers was evaluated by potentiodynamic polarization in 0.1 M NaCl aqueous solution. The results showed that with increasing pH and sweep rate the amount of corrosion rate decreased and increased respectively. Moreover, the correlation between variation of anodic charge (Qₘ) with pH and sweep rate has been evaluated. The variation of anodic charge confirmed that the growing rate of polymer decreased with increasing sweep rate and pH. The result of potentiodynamic polarization showed that the coated steel with synthesized PAni in pH 3.5 and sweep rate 0.01Vs⁻¹ had better protective properties against corrosion.

Introduction

Iron is widely used in the form of steel in industrial applications, and because of its importance, the protection of iron against corrosion is one of the main areas in research. Polyaniline (PAni) is one of the conducting polymers that due to its high electrical conductivity, has been suggested to be used as protective coatings on oxidizable metals [1-4].

The electrochemical synthesis of PAni on active metals has been introduced by Deberry [5]. He found that the corrosion rate of stainless steel is significantly reduced when PAni is electrochemically deposited on the surface of it. PAni exists in three well defined oxidation states of leucoemeraldine (LE), emeraldine (EM) and pernigraniline (PE). LE is fully reduced form (all amine nitrogens), while PE is fully oxidized form (all imine nitrogens). The EM form has an amine/imine ratio of about 0.5 [6, 7]. Starting from the electronically insulated LE, electronically conducting EM can be obtained by standard chemical or electrochemical oxidation similar to other conjugated polymers. Upon further oxidation a fully oxidized PE can be produced. In addition, these various oxidation pH sensitive states, except LE, can also be readily switched between doped salt and undoped base forms [8]. Only the emeraldine salt form is conducting among all the five forms of PAni.

In this work, PAni was synthesized in different potential sweep rates and pH on the surface of steel in oxalic acid electrolyte by cyclic voltammetric method. The corrosion behavior of coated steel with PAni coated was studied by Tafel polarization method in 0.1 M NaCl solution. The corrosion protection ability of the coated steel in different condition was compared with each other.

Experimental procedure

The elemental composition analysis of the steel plate substrate of 1 cm² was: (weight%: 2.71% C, 0.49% Si, 94.79% Fe). Graphite counter electrode of 2 cm² area facilitated the conductivity of the steel plates during deposition process. A saturated calomel electrode (SCE) was used as a
reference electrode. The working electrodes of steel plates were degreased in ethanol and dried at 45°C after mechanically polishing with fine emery paper of 320-1200 grades. The pure aniline used in the experiment was always stored in darkness. Then PANi coating were synthesized on the steel plates by cyclic voltammetric method. The potential range applied was: -0.6 to 1.5 V. The samples were prepared from baths containing aniline concentration of 0.1 M and oxalic acid concentration of 0.2 M. At the first step PANi was polymerized on the surface of steel in pH 1.55 and different sweep rates (dE/dt) 0.01, 0.02 and 0.03 Vs\(^{-1}\) in a one compartment cell separately. In the second step, while keeping the sweep rate fixed at 0.01Vs\(^{-1}\), three samples were prepared with pH 1.55, 2.53 and 3.5. The electropolimerized PANi on the steel were scratched and mixed with KBr separately to make cylindrical pellet for FTIR analysis. Nicolet 380 FTIR instrument was used for the experiment. The micrographs of the coated steel were taken from the surface to observe the details of coated layers. The experiment was performed employing a field emission scanning electron microscope (FESEM-Jeol JSM-840A). The corrosion resistances of uncoated steel and coated with PANi were studied using the potentiodynamic polarization technique. Each surface was exposed to a 0.1 mol L\(^{-1}\) NaCl aqueous solution (pH 5.68). The polarization curves were obtained starting from the open circuit potential (OCP) and varying the potential up to 3500 mV in a set of experiments (anodic branch of the Tafel plot) and down to -3500 mV in another set of experiments (cathodic branch of the Tafel plot). The potential sweep rate was 5mVs\(^{-1}\).

Synthesis of PANi on stainless steel by cyclic voltammetric method in pH1.55 and sweep rate 0.01Vs\(^{-1}\) is illustrated in Fig. 1A. Current peaks (a), representing LE to EM transformation, develops at 0.5 V, and current peak (b), representing EM to PE transformation, develops at 1.5 V [9]. In the first cycle a current peak of -0.5 V represented an active to passive state transformation while on the repeated scanning through the same potential region that current peak was not observed. The sharp peak at -0.1 V indicated the reactivation of the steel during the reverse negative scan, but it decreased gradually in the consequence cycles. This sharp peak was related to reduction of Fe\(^{3+}\) to Fe\(^{2+}\) oxalate, which occurs by simultaneous and instantaneous reactivation of the Fe electrode [10].

In Figure 1-B, the current peak (a) in pH 3.5 is lower than pH 1.55. The pH has an influence on the conductivity of polymer formed at the electrode [11]. With decreasing pH emeraldine salt convert to emeraldine base, while conductivity of PANi correlates to percentage of emeraldine salt.

Figure 1(C) shows the voltammograms of PANi in different sweep rate in pH 1.55. After eight cycles the current peak at -0.25V (peak “a”) indicates a passive film transition form Fe\(^{3+}\) to Fe\(^{2+}\). As can be seen, this peak at 0.03Vs\(^{-1}\) is bigger than of 0.02 and 0.01Vs\(^{-1}\). This result is an evidence that shows synthesized PANi at 0.03Vs\(^{-1}\) could not cover all the surface of steel. Moreover, increasing the sweep rate resulted in a shift to higher potential conversion of LE to EM. This can be explained by the size of the diffusion layer formation and the record time taken for scan. Clearly, the linear sweep voltammogram will take longer record time at lower sweep rates. Therefore, the size of the diffusion layer above the electrode surface will vary depending upon the voltage sweep rate. In a slow voltage...
scan the diffusion layer will be thicker and its front of growing layer is further from the electrode surface in comparison with fast scan [12].

The peak corresponding to the electrodissolution of Fe in different pH is shown in Figure 2. As can be seen, increasing pH resulted in a shift of the peak to higher potential and lower current. This result is according to potential-pH diagram for iron [13].

Figure (3-A) shows the variation of the anodic ($Q_a$) charges with the cycle number during electropolymerization of PANi in 0.2 M oxalic acid solution in different pH. In pH 1.55 and 2.55, the $Q_a$ was increased with increasing the cycle number. But in pH 3.55 the $Q_a$ was decreased by increasing the cycle number. One of the reasons of this phenomenon is PANi conductivity decreasing with increase of pH. This result proved the role of pH variation in polymerization of PANi.

During the electropolymerization of PANi in different sweep rates, the $Q_a$ was increased with increasing the cycle number (Fig. 3-B). The amount of $Q_a$ at 0.01Vs$^{-1}$ was higher than at 0.02 and 0.03 Vs$^{-1}$. This result illustrated the highest growing of PANi at 0.01 Vs$^{-1}$ compared with 0.02 and 0.03 Vs$^{-1}$. It confirms that the biggest size of the diffusion layer was achieved at 0.01 Vs$^{-1}$.

The FTIR spectrum of PANi coatings are shown in Figure 4. A large descending baseline appears in the spectral region of 1700 to 2800 cm$^{-1}$ indicating the free-electron conduction in conducting polymers In the FTIR spectrum of PANi a special peak in 1400.42cm$^{-1}$ was observed (head-to-head coupling). This peak is related to an oxidized benzidine and it is due to over oxidation as mentioned before. The peaks at 1650.99 and 1314.64 cm$^{-1}$ indicate that the polymerization occurs through the formation of C-N=C and C-NH-C bonds which result from head-to-tail coupling during the polymerization of aniline [10].

The FESEM was used to investigate the morphology of electrodeposited PANi. It is reported by various authors that the nature of the anions affects the PANi structure [10, 14]. Two different types of PANi morphology in oxalic acid electrolyte were mainly observed; the fibre and the nodular structures. Figure 5 shows various morphologies of PANi in different pH. As can be seen, the morphology of PANi in pH 1.55 is fibre form, while the nodular structures were observed in pH 2.53, 3.5. The FESEM of PANi in pH 1.55 indicates a rather porous polymer, but in pH 3.5 with variation type of morphology, number of porous is lower than pH 1.55.
Fig. 5 FTIR spectra of steel coated with synthesized PAni in oxalic acid 0.2 molL$^{-1}$ in pH 1.55

![FTIR spectra](image)

Fig. 6 FESEM of steel coated with synthesized PAni films (A: pH 1.55, B: pH 2.5, C: pH 3.5) in oxalic acid 0.2 mol L$^{-1}$ and sweep rate 0.01 Vs$^{-1}$

The morphology of PAni in different sweep rate in pH1.55 is shown in Figure 6. The morphology of synthesized PAni at 0.03Vs$^{-1}$ is between the fibre and the nodular structures. The process of gradual changes in the structure formation can be seen with variation of sweep rate from 0.01to 0.03Vs$^{-1}$.

Fig. 6 FESEM of steel coated with synthesized PAni films (A: 0.01, B: 0.02, C: 0.03 Vs$^{-1}$) in oxalic acid 0.2 mol L$^{-1}$ and pH 1.55

Figure 7 represents the potentiodynamic polarization curves after 7 h immersion time in 0.1 mol L$^{-1}$ NaCl aqueous solutions for uncoated steel surface and coated steel with PAni films. Table 1 shows the corrosion kinetic parameters derived form these curves presented in figure (7-A). The value of $E_{ocp}$ of steel coated with PAni at 0.03 Vs$^{-1}$ is -0.675 that is near to $E_{ocp}$ of uncoated steel. This result indicates that with increasing the sweep rate the barrier property of PAni coating decreases. This is an evidence of the porous polymer formation on the top of the steel. The coated PAni at 0.03Vs$^{-1}$ does not act as a barrier and then dose not prevent oxygen and chloride diffusion due to its permeability. Furthermore the incorporation of the chloride ions into the polymer could cause depassivation of the substrate and consequently the corrosion attack. This property results in slops observed of Tafel test which are very close to that of the uncoated steel (Table 1).
Coated steel with synthesized PANi in pH 3.55 exhibits significantly lower $j_{corr}$ and corrosion potential ($E_{corr}$) values (Fig. 7B) (Table 1). This result is in agreement with the theory proposed by Wessling et al [15] who predict that PANi helps in stabilizing a thin layer of iron oxide on the surface, which helps in preventing corrosion. On the other hand, these results indicated that type of morphology influenced on level of PANi films protection as barrier. While amount of growth rate of PANi in pH 3.5 is lower than pH 1.55, but increasing of pH decreased the porosity in the morphology of PANi. In pH 3.55 the concentration of $H^+$ is lower than pH 1.55 therefore amount of hydrogen evolution that creates channels for electrolyte penetration would be decreased. These results confirmed with polarization resistance ($R_p$) evaluation. The $R_p$ of PANi coated steel in pH 3.55 is about three times bigger than pH 1.55. The corrosion resistance of PANi in pH 3.5 was better than pH 1.55 with variation of morphology. Moreover, the percent protection efficiency ($E_\%$) of PANi in pH 3.5 and 1.55 is 79.3% and 27% respectively. This result confirms that using pH 3.5 can improve the percent protection efficiency.

**Conclusion**

PANi was successfully synthesized on the surface of steel by cyclic voltammetric method in different pH values and sweep rates. The result indicated that with increasing the sweep rate the corrosion rate increased. The porous polymer formation on the surface of the steel was the evidence of this phenomenon. The results showed that the barrier properties of synthesized PANi increased with the increase of pH, while the variation of the anodic charge versus cycle number confirmed that the amount of growth rate of PANi in pH 3.5 was lower than pH 1.55. With increasing pH the porosity in synthesized PANi decreased. Therefore the anticorrosion behavior of the coated steel with synthesized PANi in pH 3.5 and sweep rate 0.01Vs$^{-1}$ was better than other conditions that were investigated in this work.
Reference


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