Synthesis of Poly (Aniline-Co-O-Anisidine) Film in Electrolyte Mixture and Its Anticorrosion Behavior

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Abstract

Poly (aniline-co-o-anisidine) of copolymer coating was synthesized on copper surface (Cu) in an aqueous solution containing 90 ml of 0.20 M NaOX + 10 ml of 0.20 M oxalic acid. The copper substrate in NaOX solution containing oxalic acid had a fairly reliable passive surface mainly due to the formation of copper (II) oxalate layer. The addition of oxalic acid to working electrolyte contributed to both the amount of copolymer deposition (growth) and that of copolymer coated per unit time of electropolymerization (growth rate). The corrosion performances of copolymer coatings were investigated in 3.5 % NaCl solution with anodic polarization curves and electrochemical impedance spectroscopy. The results showed that oxalic acid led to the diminishing of the permeability of copolymer film. The copolymer coating exhibited an effective barrier property on copper electrode and provided a remarkable anodic protection to substrate for longer exposure time.

Introduction

Copper is one of the most important commodity metal from technological point of view; however, it must be protected against corrosion under normal environmental conditions (Goncalves et al., 2002). The protection of copper substrate against corrosion has been investigated by many researchers using various methods including inhibitors, organic coatings and metallic (Guenbour et al., 2000; Ozyilmaz, 2006; Kilinççeker et al., 2008; Kilinççeker et al., 2013). Morphological and electrical properties of conducting polymers like polyaniline, polypyrrole and polythiophene have opened a large field for specific applications such as batteries, sensors and corrosion. Consequently, conducting polymers have been an interesting subject of research. Some of their important

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properties include electrical conductivity, electroactivity, electrochromism, environmental stability, chemical stability and corrosion inhibitive property (Kim et al., 2000; Shah et al., 2002; Ozyilmaz et al., 2018). Polyaniline (PANI) and its derivatives have been successfully synthesized by electrochemical applications for many years for the protection of mild and stainless steel and copper against corrosion (Ozyilmaz et al., 2013; Ozyilmaz et al., 2014; Bagherzadeh et al., 2016). However, especially PANI is not easily electropolymerized on oxidizable metals. A number of reports on the synthesis of PANI have appeared in the literature during the recent years. The common feature of these studies is that they demand a careful choice of electrochemical parameters such as electropolymerization conditions, applied technique, electrolyte solution and its pH value, potential range and scan rate. PANI has been able to serve as anticorrosion protective coating on metals in both acidic and neutral solutions because it has been found out that passivation of oxidizable metals prior to electropolymerization is very important to synthesize of a homogenous and adherent polyaniline film (Presa et al., 1999; Sazou 2001; Borole et al., 2002; Martyak et al., 2002; Kraljic et al., 2003; Özyılmaz 2005; Ozyilmaz et al., 2011).

The aim of the present study was to synthesize electrochemically PANI-co-POA films on Cu in a novel medium including sodium oxalate (NaOX) and oxalic acid (OX). The synthesis of PANI-co-POA film was achieved by using a NaOX medium including OX as an organic acid the amount of which would only be enough to enable the passivation of the electrode surface. Electrochemical synthesis of PANI-co-POA was carried out through monomers containing NaOX and OX solution. The corrosion performance of copolymer film synthesized on copper substrate was investigated in 3.5 % NaCl and compared with the AC impedance diagrams and anodic polarization curves.

Materials and Method

All chemicals were purchased from Merck. Aniline and o-anisidine were freshly distilled and stored in the dark. The solutions were prepared using distilled water and all the experiments were carried out at room temperature open to the atmosphere. In this study, all the electrochemical experiments were performed in a single compartment cell with three electrode configurations. The reference electrode was an Ag/AgCl (sat, KCl) electrode and the counter electrode was a platinum sheet with a surface area of 2 cm^2. A CHI 660B model digital controlled electrochemical analyzer (serial number: A1420) was used in electrochemical experiments. All of the potential values were referred to the Ag/AgCl (sat, KCl) electrode. The copper (99.89%) electrode was cylindrical rods with a diameter of 0.40 cm. Copper electrodes were embedded in a thick polyester block. In order to remove any existing passive film, the surface of working electrodes was polished with the help of up to 1200 grade emery paper prior to each experiment and, before electropolymerization, rinsed in 1:1 ethanol acetone mixture, washed with bi-distilled water and dried.

The PANI-co-POA coatings were synthesized by means of cyclic voltammetry technique. Synthesis of copolymer film was carried out in presence of 0.075 M monomers and in an aqueous solution containing 90 ml of 0.20 M NaOX+10 ml of 0.20 M oxalic acid. Electrochemical impedance spectroscopy and anodic polarization curves were used to investigate the corrosion performance of the coatings. The Nyquist plots were recorded at instantaneous open circuit potentials for various exposure times and in the frequency range from 10^5 to 10^{-3} Hz using amplitude of 7 mV.

Results

Figure 1(a) shows the first scan of the cyclic voltammograms recorded for Cu electrode from aqueous solution containing 100 ml 0.20 M sodium oxalate (1) 90 ml of 0.20 M sodium oxalate + 10 ml of 0.20 M oxalic acid (1) and 90 ml of 0.20 M sodium oxalate + 10 ml of 0.20 M oxalic acid + 0.075 M monomers (2) which are referred to here as Cu1 and Cu2, respectively. All measurements were taken at scan rate of 20 mV s^{-1}. In presence of 0.075 M aniline + 0.075 M o-anisidine Figure 1(b), the monomer oxidation process could be identified at around + 0.84 and + 0.90V.
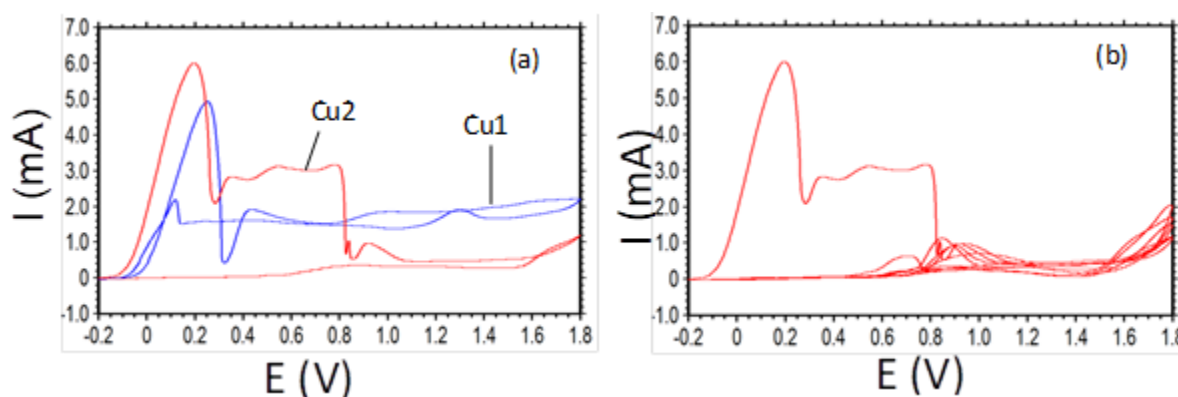

Figure 1. Cyclic voltammograms recorded for Cu electrode in 100 ml 0.20 M sodium oxalate (1) 90 ml of 0.20 M sodium oxalate + 10 ml of 0.20 M oxalic acid (Cu1) and 90 ml of 0.20 M sodium oxalate + 10 ml of 0.20 M oxalic acid + 0.075 M monomers (Cu2) Scan rate: 20 mV/s.

The open circuit potential values (E_{ocp}) of bare Cu and Cu/PANI-co-POA electrodes were monitored with time and plotted against immersion time in hours (Figure 2). The initial E_{ocp} value of the bare Cu electrode was – 223 mV. This value then decreased down to around -279 mV, after 4 h. Then the E_{ocp} value remained almost unchanged for the rest of the immersion time. The E_{ocp} value of bare copper electrode was - 235 mV in the same solution, after 192 h. In the case of the Cu/PANI-co-POA electrode, the initial E_{ocp} value was -90 mV. The E_{ocp} value was observed to decrease to - 218 mV, after 4 h exposure time. The E_{ocp} value of Cu/PANI-co-POA electrode was - 140 mV in 3.5 % NaCl solution, after 192 h.
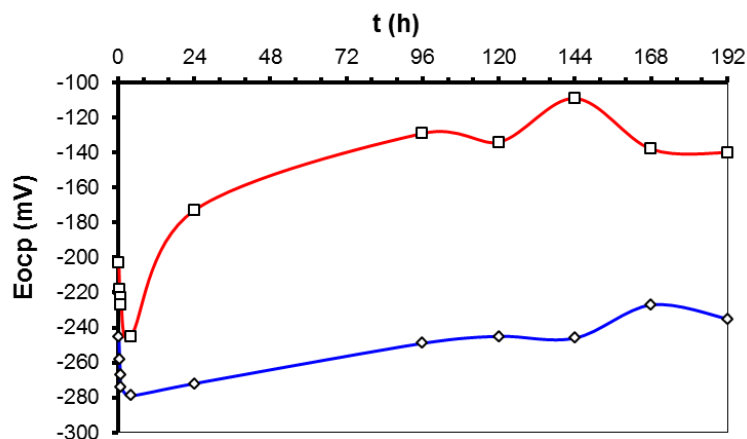

Figure 2. E_{ocp}-time diagrams in various immersion periods obtained for Cu (◊) and Cu/PANI-co-POA (□) electrodes, in 3.5 % NaCl solution.

Anodic polarization curves obtained for uncoated copper and PANI-co-POA copolymer film coated copper samples after 240 h exposure time in 3.5 % NaCl solution are given in Figure 3.
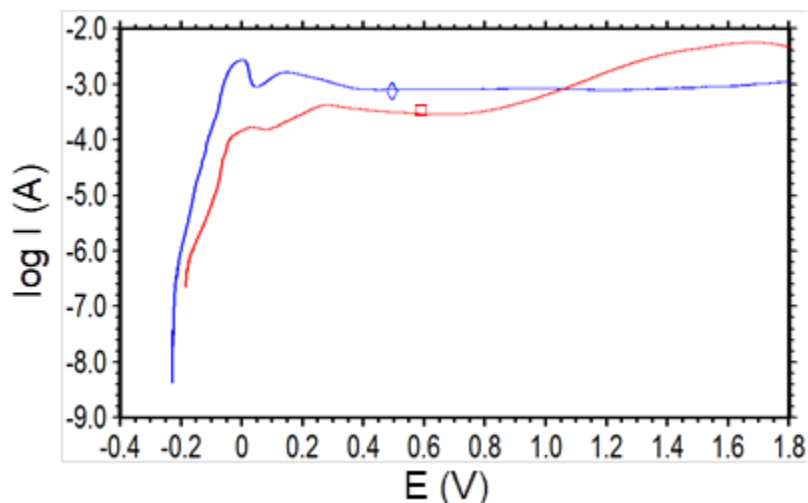

Figure 3. Anodic polarization curves obtained for Cu (□) and Cu/PANI-co-POA (□) electrodes, after 240 h of exposure in 3.5 % NaCl solution.

The Nyquist diagrams recorded for uncoated copper electrode are given in Figure 4, for various immersion times in 3.5% NaCl solution. There was a depressed semicircle at high and mid frequencies and a linear part at lower frequencies, initially. The R_p value of Cu/PANI-co-POA electrode was found to be approximately 26.6 kohm, after 4 h of immersion time (this value was 26.0 kohm for bare Cu). After 168 h of exposure time, the R_p and E_{corr} values of bare Cu electrode were found to be approx. 72.0 kohm and - 219 mV. However, the R_p and E_{corr} value decreased as 41.3 kohm and – 241 mV, after 240 h of immersion.
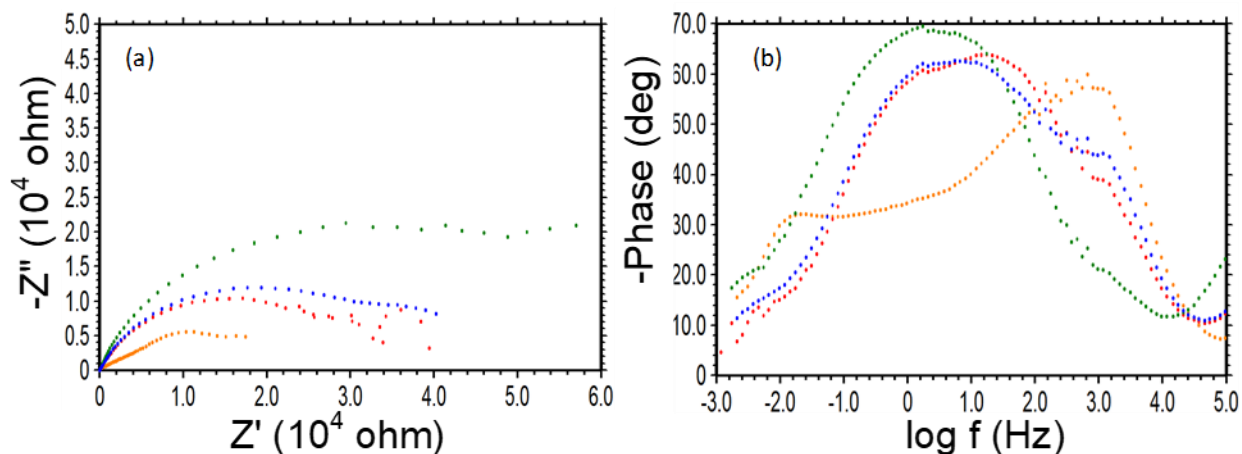

Figure 4. Nyquist (a) and Bode (b) curves obtained for Cu electrode, after 4 h, 72 h, 168 h and 240 h of exposure in 3.5 % NaCl solution.

The Nyquist diagrams and log frequency (f)-phase angle (θ) curves of Cu/PANI-co-POA electrode are given in Figure 5, for various exposure times, in 3.5% NaCl solution. There were two depressed semicircles, which could not be well resolved from each other, in Nyquist diagrams. These depressed semicircles were attributed to charge transfer resistance (Rct) at high frequency and to total oxide film (Ro) and copolymer film resistance (Rf) of the depressed semicircle at low frequency region, the sum of which was equal to polarization resistance (Rp) (Walter, 1986; Özyılmaz et al., 2005; Ozyilmaz et al., 2006). This Rp value of Cu/PANI-co-POA electrode was found to be approximately 26.6 kohm, after 4 h of immersion time. After 240 h of exposure time, Nyquist diagrams, the first and second depressed semicircles at high and mid-frequencies consisted of Rct corresponding to dissolution of substrate at the bottom of the pores and the resistances of Ro and Rf. The linear part extending to low frequency region was attributed to the Warburg impedance.
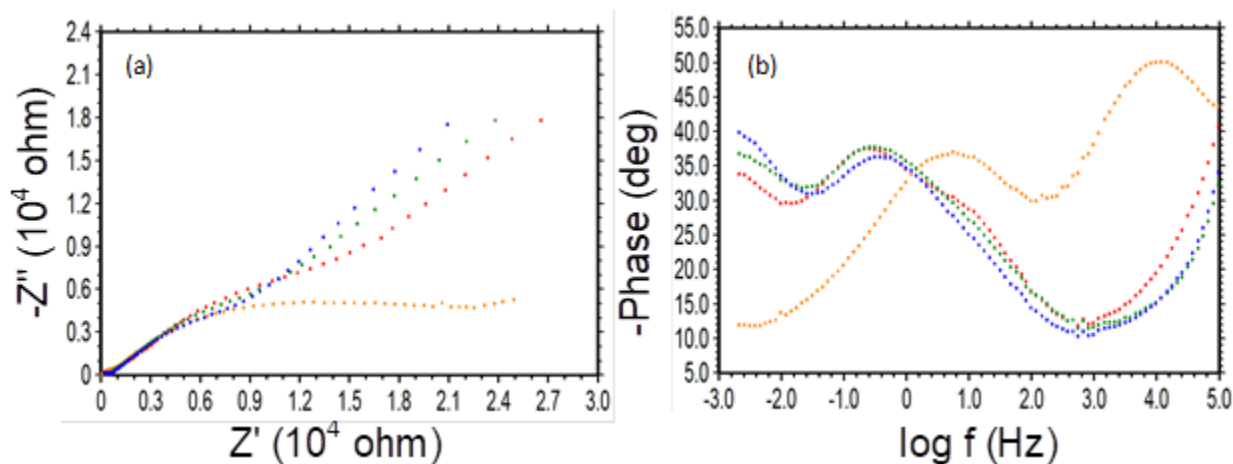

Figure 5. Nyquist (a) and Bode (b) curves recorded for Cu/PANI-co-POA electrode, after 4 h, 72 h, 168 h and 240 h of exposure in 3.5 % NaCl solution.

Discussion

Synthesis

Figure 1(a) shows the first scan of the cyclic voltammograms recorded for Cu electrode from aqueous solution containing 100 ml 0.20 M sodium oxalate (1) 90 ml of 0.20 M sodium oxalate + 10 ml of 0.20 M oxalic acid (1) and 90 ml of 0.20 M sodium oxalate + 10 ml of 0.20 M oxalic acid + 0.075 M monomers (2) which are referred to here as Cu1 and Cu2, respectively. All measurements were taken at scan rate of 20 mV s^{-1}. During the first positive cycle for Cu1 electrode, the current value started to increase around- 0.15 V due to copper dissolution. This dissolution process continued in a wide potential range and passivation of the surface could be completed at around + 0.80 V. Then, it started to increase again slightly due to further dissolution through the porous passive layer. This passive layer must consist of copper oxides (CuO and Cu$_2$O) and copper oxalate (CuC$_2$O$_4$), which are insoluble in water (Özyılmaz et al., 2005).

In presence of 0.075 M aniline + 0.075 M o-anisidine (Figure 1(b)), the monomer oxidation process could be identified at around + 0.84 and + 0.90V. These peaks were found to the shift of the monomer oxidation potential toward cathodic region. It was concluded that the poly(aniline-co-o-anisidine) (PANI-co-POA) film growth was happening very slowly on passivated copper surface. The voltammograms recorded during the film growth showed that the oxidation-passivation behavior of copper indicated to disappear after the second cycle, due to the coating of copper electrode. This case was a sign for PANI-co-POA copolymer film synthesis on copper substrate surface where the disappeared oxidation/passivation peak and well defined monomer oxidation peaks during the film growth.

As the film thickness increases the surface becomes more protected and the oxidation-passivation peak disappeared or smaller than the previous one. On the other hand, the transitions between the oxidation states of PANI-co-POA film were observed as a current increase at different potentials.

As the film thickness increases with increasing cycle number, the current changes corresponding to these transitions also changed regularly. In this study, 10 cycles were applied to obtain PANI-co-POA coated copper (Cu/PANI-co-POA). The synthesized film showed to be very homogeneous. Also, the adherence of synthesized coating was tested by a simple sello tape test and satisfactory results were obtained.

Corrosion Protection Performances

The open circuit potential values (E_{ocp}) of bare Cu and Cu/PANI-co-POA electrodes were monitored with time and plotted against immersion time in hours (Figure 2). The initial E_{ocp} value of the bare Cu electrode was – 223 mV. At the beginning, the Cu surface became passive with insoluble copper oxalate and copper oxides. These passive layers exhibited a physical barrier behavior and provided some protection to copper. But their efficiency could not resist against the attack of the chloride containing corrosive medium. This value then decreased down to around - 279 mV, after 4 h. Then the E$_{ocp}$ value remained almost unchanged for the rest of the immersion time. The E$_{ocp}$ value of bare copper electrode was - 235 mV in the same solution, after 192 h. In the case of the Cu/PANI-co-POA electrode, the initial E$_{ocp}$ value was -90 mV, this value was

significantly noble when compared with that of uncoated Cu electrode. This was giving evidence for barrier behavior of the PANI-co-POA film. The porosity of the polymer film is an important characteristic for initiation and continuation of corrosion under the coating. The sponge like polymer film takes electrolyte solution up within its pores, as soon as it is placed in the corrosive environment. This leads to an increase in mobility of the corrosive species through the coating. The E_{ocp} value was observed to decrease to - 218 mV, after 4 h exposure time. It was concluded that the synthesized PANI-co-POA film had a less porous structure and was able only to provide important barrier efficiency, which increased quickly. The E_{ocp} value exhibited a tendency to decrease with time. This case was result from the catalytic effect of PANI-co-POA film on the passivation of copper with a protective oxide layer. It is already known that electroactive polymers behave like oxidizing inhibitors, when the electrolyte solution comes into contact with the underlying metal, at the bottom of the pores. As the metal oxidizes, the polymer film is reduced at the metal/polymer interface even though the main cathodic reaction is usually hydrogen evolution or dissolved oxygen reduction. This behavior limits metal dissolution and also stabilizes the oxide formation with its electron rich structure. The E_{ocp} value of Cu/PANI-co-POA electrode was - 140 mV in 3.5 % NaCl solution, after 192 h. A similar behavior exhibited the PANI-co-POA film.

Anodic polarization curves obtained for uncoated copper and PANI-co-POA copolymer film coated copper samples after 240 h exposure time in 3.5 % NaCl solution are given in Figure 3. In the case of uncoated Cu sample, corrosion potential (Ecorr) value was observed to be - 227 mV. The current values of Cu electrode increased rapidly that there was not any possibility for passivation of the copper electrode surface under aggressive chloride ions condition. In the case of PANI-co-POA film coated Cu electrode, the Ecorr value was moved to nobler region than that of uncoated Cu electrode and was found to be – 184 mV. Positive shift of the Ecorr value recorded for PANI-co-POA film coated electrode simply indicated that copolymer coating provided an adequate physical protection to Cu metal between the corrosive environment and underlying metal. This occasion supported that the current values of PANI-co-POA coated electrode were significantly lower when compared with uncoated Cu electrode. These current values obtained for Cu/PANI-co-POA electrode were indicated an effective barrier property of PANI-co-POA coating on copper electrode. This showed that copolymer film synthesized in NaOX + OX solution mixture had lower permeability and higher barrier property. On the other hand, this event suggested that the anodic wave at approx. 0.78 V attributed to the conversion of emeraldine (EM) to fully oxidized pernigraniline (PE) structure, during synthesis of copolymer film on the electrode (Martyak et al., 2002).

The Nyquist diagrams recorded for uncoated copper electrode are given in Figure 4, for various immersion times in 3.5% NaCl solution. There was a depressed semicircle at high and mid frequencies and a linear part at lower frequencies, initially. The depressed semicircle was known as the charge transfer resistance (Rct) for processes occurring at the bottom of the pores of the oxide layers and the oxide layer resistance (Ro). The sum of these resistances was equal to polarization resistance (Rp) (Walter, 1986; Özyılmaz et al., 2005; Ozyilmaz et al., 2006). The linear part consisting of copper corrosion products was observed as a resistance against the diffusion species within pores. The diffusion resistance (Rd) increased the total resistance either by adsorbing on metal surface as a protective layer or plugging the pores. The Rp values increased during 168 h of immersion due to an increase in the amount of electrolyte solution within the pores of oxide layers. The relevant log f – θ diagrams showed that the θ values exhibited a tendency to increase

at mid frequency region. This could be explained by freshly produced oxide layers building up upon dissolution of copper at metal/solution interface. Consequently, these copper oxide layers contributed to the total Rp value. After 168 h of exposure time, the Rp and Ecorr values of bare Cu electrode were found to be approx. 72.0 kohm and - 219 mV. However, the Rp and Ecorr value decreased as 41.3 kohm and – 241 mV, after 240 h of immersion. This case was observed as a decrease in maximal phase angle value at mid frequency region, in the relevant log f - □ curves. It was clear that bare copper did not resist to corrosion products due to very high permeability structure on the surface.

The Nyquist diagrams and log frequency (f)-phase angle (θ) curves of Cu/PANI-co-POA electrode are given in Figure 5, for various exposure times, in 3.5% NaCl solution. There were two depressed semicircles, which could not be well resolved from each other, in Nyquist diagrams. These depressed semicircles were attributed to charge transfer resistance (R_{ct}) at high frequency and to total oxide film (R_o) and copolymer film resistance (R_f) of the depressed semicircle at low frequency region, the sum of which was equal to polarization resistance (R_p) (Walter, 1986; Özyılmaz et al., 2005; Ozyilmaz et al., 2006). This R_p value of Cu/PANI-co-POA electrode was found to be approximately 26.6 kohm, after 4 h of immersion time (this value was 26.0 kohm for bare Cu). This indicated that the copolymer film exhibited a small physical barrier property on copper electrode, after 4 h of immersion time. After 72 h the R_p value was found to increase further due to further oxide film growth and polymer film reduction. It showed that there was an increase in the amount of electrolyte solution within copolymer coating. Thus, this case was indicating a conversion of copper from anodic oxidation to its oxides (CuO and Cu_2O) under catalyzing effect of copolymer film (Pourbaix, 1966). The catalytic behavior of copolymer film could be explained by electrochemical processes taking place at metal/polymer interface. Metal at the bottom pores of copolymer coating was oxidized thereby yielding its oxides as soon as the electrolyte solution was placed on the metal surface. Consequently, the copolymer film was reduced at the metal/coating interface due to ion exchange providing charge compensation at the metal/coating/solution interface. Therefore, the formation of oxide layers and reduction of copolymer film provided an increase in polarization resistance, after 72 h of exposure time. After 168 h, the R_p value increased further and the curve feature at low frequencies was almost linear. In relevant phase angle-log frequency diagram, it is observed that the θ value increased. This was giving evidence for enhancement in barrier efficiency. The barrier property of the polymer film must have increased with time due to water ingren. Therefore, the observed increasing is explained by the production of many protective and compact copper oxides on the surface. The oxides film with very low permeability increased the barrier efficiency against the attack of corrosive environment. It was apparent that this efficiency reached its highest value at the end of 240 h of exposure time. After 240 h of exposure time, Nyquist diagrams, the first and second depressed semicircles at high and mid-frequencies consisted of R_{ct} corresponding to dissolution of substrate at the bottom of the pores and the resistances of R_o and R_f. The linear part extending to low frequency region was attributed to the Warburg impedance. The R_p was equal to the sum of these resistance values ($R_{ct}+R_o+R_f$) (Walter, 1986; Özyılmaz et al., 2005; Ozyilmaz et al., 2006). The R_p values for the Cu/ PANI-co-POA electrode were found to decrease in small amounts in parallel with extended immersion time. This decrease suggested that the catalytic behavior of PANI-co-POA film contributed to the formation of oxide layers and the reduction in PANI-co-POA coating. So, it was observed in the low frequency region that a linear part indicated effective barrier behavior of PANI-co-POA coating. Consequently, this linear part showed a typical charge transfer process occurring under

diffusion control (Ozyilmaz et al., 2010). This behavior recorded for the PANI-co-POA film coated Cu electrode showed the Warburg diffusion region attributable to the semi-infinite diffusion of ions at the polymer/electrolyte interface (Ozyilmaz et al., 2010). During this response, the corrosion process was under diffusion control as PANI-co-POA coating prevented significantly corrosive solution from moving to the Cu electrode surface, after 240 h of exposure time.

In this study, poly (aniline-co-o-anisidine) coating was successfully synthesized on copper substrate applying cyclic voltammetry technique. Homogenous and adherent copolymer film was synthesized from 0.075 M aniline + 0.075 M o-anisidine containing NaOX solution with and without oxalic acid. The passivation of copper surface reached prior to monomer oxidation and film growth. It was found out on MS electrode that OX in NaOX solution mixture led to the formation of oxidation/passivation process on the copper surface. It must be noted that the transition between oxidation structures of copolymer film during synthesis also gave evidence for presence of oxalic acid. The corrosion performance of PANI-co-POA coated Cu electrode was evaluated by means of EIS technique and anodic polarization curves, in 3.5 % NaCl solution. The results of the present investigation clearly pointed out that PANI-co-POA coating synthesized in mixture solution exhibited significant barrier behavior against the attack of corrosion products such as aggressive chloride ions to copper electrode. As a result, PANI-co-POA coating showed high stability and low permeability, under aggressive condition and provided significant anodic protection behavior on copper, in longer periods.

Author Contributions

Ali Tuncay Ozyilmaz contributed to the experimentation of the study and the writing of the article.

Conflict of Interest

The author declares that he has no competing interests.

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