



Conducting Polymer Films on Zn Deposited Carbon Electrode

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Abstract

Zn plating on carbon steel (CS) was achieved applying current of 4 mA with galvanostatic technique in acidic medium. Zn particles had homogenous, smooth with spherical structure. It was shown that the Zn particles exhibited active behavior on CS substrate. Poly(aniline), poly(pyrrole), poly(N-methylpyrrole) and poly(o-anisidine) homopolymer films were obtained on CS/Zn electrode. Evaluation of anticorrosion performance of these homopolymer coatings in 3.5 % NaCl solution was investigated by using AC impedance spectroscopy (EIS) technique, anodic polarization and the E_{ocp} -time curves. Homopolymer films exhibited significant physical barrier behavior on Zn plated carbon steel, in longer exposure time.

Keywords:

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Introduction

In industry, iron-based metals such as mild and stainless steel have been widely used in numerous applications for many years. The corrosion of the oxidizable metals has become one of the most important problems in the world. Therefore, protective coatings such as organics, silicones, inorganic compounds and metallic coatings have been used widely for metal corrosion control (Guenbour et al., 2000; Kiliñçeker et al., 2008; Ozyilmaz, 2011; Kiliñçeker et al., 2013). Zinc coatings via electrodeposition technique are considered as one of the many ways of corrosion protection of steel. The use of zinc and zinc-based alloys for improving the corrosion resistance of carbon steel has been growing worldwide and as a coating for high-cost cadmium coating and toxic. Generally metallic zinc based thin film layers provide cathodic protection as sacrificial anode on

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the base metal (Bajat et al., 2001; Martins et al., 2004). In industrial area, metallic surfaces are still coated with thin chromate or phosphate layers, thus improving the corrosion resistance of these metals (Sohi & Jalali, 2003). However, considering that these coatings occur to be applied in parts such as bolts and nuts or in automotive industry, they appear not to last for longer periods. Therefore, when the coatings corrode or scale off, they will leave the base metal vulnerable to corrosion. On the other hand, chromatings and phosphate coatings are not only costly, but they also cause pollution. Thus, scientific studies tend to aim other coating techniques which provide longer protection at lower expense as an alternative to chromatings and phosphate coatings. Therefore, recently conducting polymers are used to enhance corrosion resistance of metallic deposition, which is used in several areas such as automotive accessories, industrial pipes and household items. Today, recent techniques curtain practices such as thin film coatings have a considerable role. Polymeric coatings as monolayer and bilayer offer good protection against oxidizable metal and alloy corrosion. The protection of iron and iron-based metal against corrosion via the use of metallic and polymeric coatings have been the subject of considerable research in many years. The polymeric coatings have some advantages as the ease of their deposition, low toxicity, and low impact on the environment and human health. Several studies related to the use of conducting polymer coatings on metals and alloys for corrosion protection have been reported in recent years. Polyaniline (PANI) and its derivatives are one of the most interesting conducting polymers because of ease in production, environmental stability, antitoxic property and adjustable conductivity. These coatings, which provide a barrier property to oxidizable metals such as copper and mild steel, have already found numerous applications in various industrial sectors including the automotive industry, biosensors, electric and electronic industry (Kim et al., 2000; Shah et al., 2002; Ozyilmaz et al., 2006; Ozyilmaz et al., 2013; Bagherzadeh et al., 2016; Ozyilmaz et al., 2018; Yalçinkaya et al., 2021). Camalet et al. clearly state that the synthesis of polyaniline films on zinc and zinc-nickel alloy in acidic solution such as oxalic acid was unsuccessful (Camalet et al., 1998). However, in our earlier work (Özyilmaz et al., 2005) we reported that polyaniline film which was synthesized in acidic solution such as oxalic acid on nickel (1 μm) plated mild steel electrode was successfully used against to corrosion. It was also reported that zinc-cobalt alloy deposited carbon steel (CS/ZnCo) electrode was modified with PANI film in neutral solution as sodium tartrate, in our previous work (Ozyilmaz et al., 2013). It was found that this coating was considerably suitable for the protection of carbon steel.

This study aims to electrochemically synthesize poly(aniline), poly(pyrrole), poly(N-methylpyrrole) and poly(o-anisidine) homopolymer films on thin zinc (Zn) plated carbon steel in sodium oxalate (NaOX) medium, which would enable the passivation of the Zn plated carbon steel surface. The corrosion performances of Zn plated carbon steel substrates with and without homopolymer coating were investigated in 3.5 % NaCl and compared using the AC impedance diagrams, anodic polarization curves, time-open circuit potential curves and linear sweep voltammograms.

Materials and Methods

All the chemicals were purchased from Merck. All electrochemical experiments were carried out in a standard one-compartment, three-electrode cell. The reference electrode was Ag/AgCl (3 M, KCl) and the counter electrode was a platinum sheet with surface area of 0.36 cm². In this study, all electrode potential values were referred to this reference electrode. In this study, the working electrode obtained from Metal At company was carbon steel with the composition: 0.0561 % C, 0.4498 % Mn, 0.0103 % P, 0.0036 % S, 0.14085 Si and 99.3394 % Fe. The surface of this electrode was carefully polished with abrasive paper (1200 grid), degreased with 1/1 acetone/ethanol mixture, washed with distilled water and dried. CHI 606C and CHI 660B model digital electrochemical analyzers were used for all electrochemical measurements. Zn plating was obtained using a bath based on 18.25 zinc chloride (ZnCl₂), 65.70 ammonium chloride (NH₄Cl), 14.59 carrier (surtec-758-1) and 1.46 polisher (surtec-758-2) by weight % and pH was approx. 5.5. The thickness of Zn plating was determined as 5.93 μm by estimation of the passing charge amount applying 4 mA constant current.

Poly(aniline) (PANI), poly(pyrrole)(PPy), poly(o-anisidine)(POA) and poly(N-methylpyrrole)(PNMP) homopolymer films were synthesized electrochemically using cyclic voltammetry technique. After 48 h and 168 h of exposure time, electrochemical impedance measurements were obtained at measured open circuit potential values applying 7 mV of amplitude in frequency range from 105 to 10⁻³ Hz. The anodic polarization curves were recorded after 168 h of immersion time in corrosive test solution. The scan rate was 4 mV/s and the measured open circuit potential value was the initial potential for the scan. Scanning electron microscopy (SEM) was employed to characterize the surface structure with a JEOL JSM-5500LV scanning electron microscope.

Results and Discussions

Zn plating on carbon steel (CS) was carried out applying 1, 2, 3, 4 and 5 mA constant current values in acidic chloride solution medium. Pt anode used for the plating was taken as 0.36 cm² surface area and coatings were obtained with stirring the solution open to atmosphere. It was observed that Zn plating obtained by applying 4 mA constant current value exhibited the better corrosion performance against the attack of corrosion products such as aggressive chloride ions to carbon steel electrode. In this study, Zn particles were successfully deposited on CS applying current of 4 mA with chronopotentiometry technique in which a constant current. As seen in Figure 1, while the bare CS electrode indicated the evidence of emery, average grain sizes of Zn particles, which has more homogeneous and smooth structure plated on carbon steel were observed using SEM images as similar measurement.

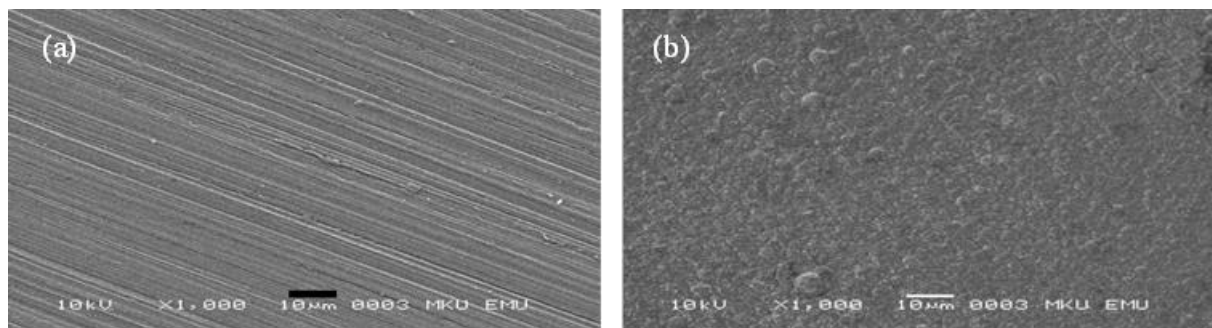


Figure 1. SEM images of CS (a) and CS/Zn (b) electrodes.

In order to improve the corrosion resistance of zinc (Zn) plating, four conducting homopolymer films were electrochemically synthesized on Zn plating surface by using cyclic voltammetric technique in a two-step process. So, polyaniline (PANI), polypyrrole (PPy), poly(N-methylpyrrole) (PNMP) and poly(o-anisidine) (POA) homopolymer films were electropolymerized on Zn deposited carbon steel (CS/Zn) electrode from sodium oxalate (NaOX) medium, which would enable the passivation of the CS/Zn surface using 10 mV/s scan rate in the potential range from -1.10 to + 0.40 V. In the second step, the film growth curves, which had seventy-five segments, were obtained using 150 mV/s scan rate in the potential range between 0.00 and 1.80 V (Figure 2). Although variation of potential range and scan rate was applied to obtain homogenous and smooth coating on zinc plated carbon steel, the highest anticorrosive coating was synthesized in condition given in this study.

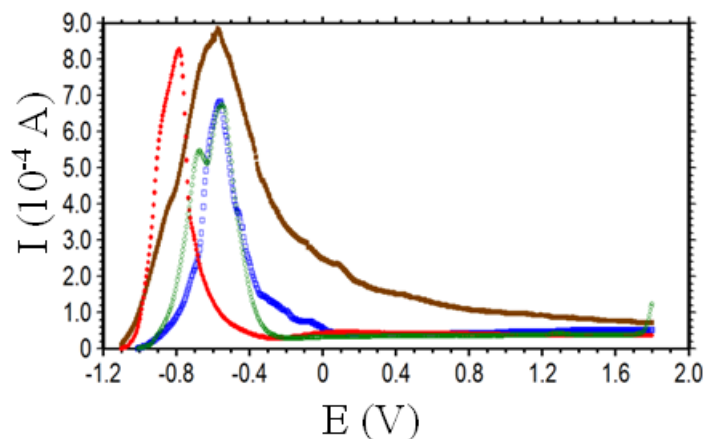


Figure 2. First CVs recorded for CS/Zn electrode in aniline (●), pyrrole (□), o-anisidine (○) and N-methylpyrrole (■) containing 0.20 M NaOX solution, scan rate: 10 mVs⁻¹.

In Fig. 3 given are the SEM images of CS/Zn/PANI, CS/Zn/PPy, CS/Zn/POA and CS/Zn/PNMP electrodes. SEM images clearly show that zinc plated carbon electrode was covered with a different homopolymer film of strongly adherent homogeneous crystalline structure.

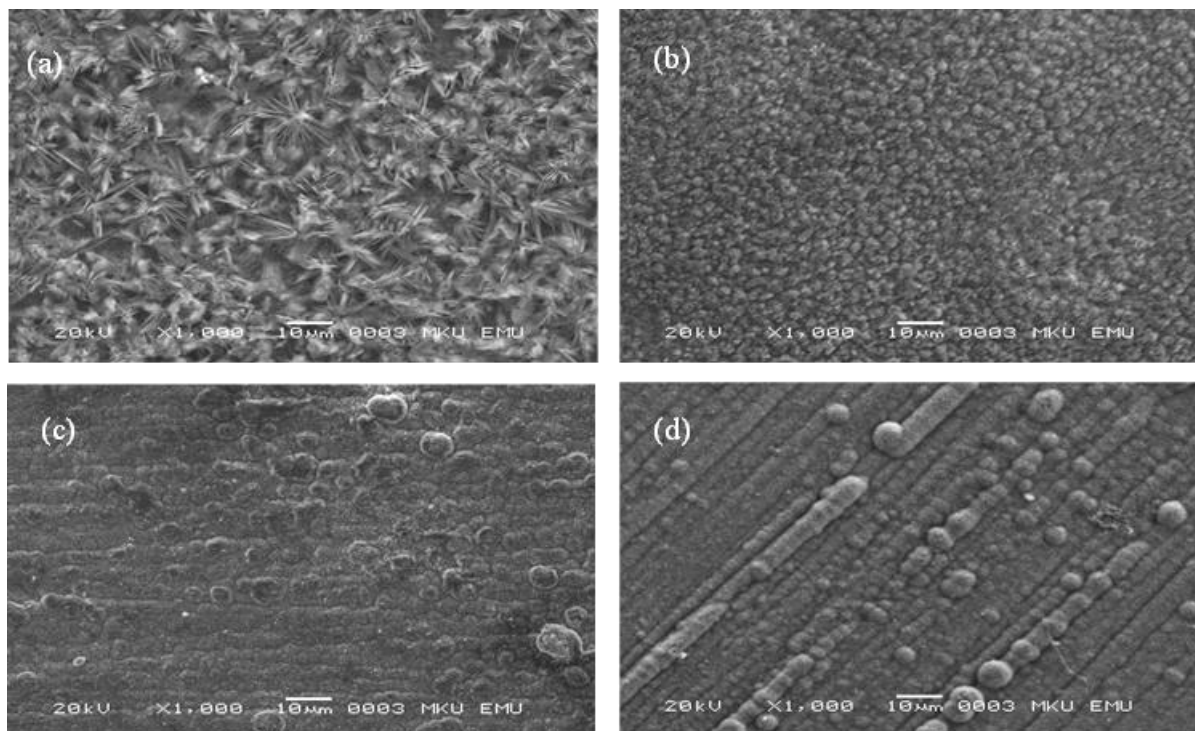


Figure 3. SEM images of CS/Zn/PANI (a), CS/Zn/PPy (b), CS/Zn/POA (c) and CS/Zn/PNMP (d) electrodes.

Linear sweep voltammograms for CS, CS/Zn, CS/Zn/PANI, CS/Zn/PPy, CS/Zn/POA and CS/Zn/PNMP electrodes in 0.05 M EDTA containing 0.50 M sodium sulphate solution are given in Figure 4. All measurements were taken at scan rate of 5 mV/s. While only single anodic peak for bare CS electrode was observed for the dissolution of iron and formation of iron complex with EDTA, there were two anodic dissolution peaks of zinc and iron at approx. -0.86 and 0.42 V, respectively, in presence of CS/Zn. The peak at the negative potential recorded was not seen for CS electrode. All of CS/Zn/PANI, CS/Zn/PPy, CS/Zn/POA and CS/Zn/PNMP electrodes exhibited two anodic dissolution peaks due to formation of zinc and iron complex with EDTA. It must be noted that the peak corresponding to the negative anodic dissolution in Fig. 4 was evidence for presence of zinc plating under polymer film coating. However, the dissolution peaks of homopolymer film coated CS/Zn electrodes had low intensity, corresponding to its significant barrier behavior against dissolution, while bare CS and CS/Zn electrodes exhibited high dissolution peak at the positive potential region. This event indicated that the top coated homopolymer films did not allow significant dissolution of CS and Zn plating on CS electrode surface. The lowest peak intensity was observed for CS/Zn/POA electrode, due to the effective barrier behavior of the POA film.

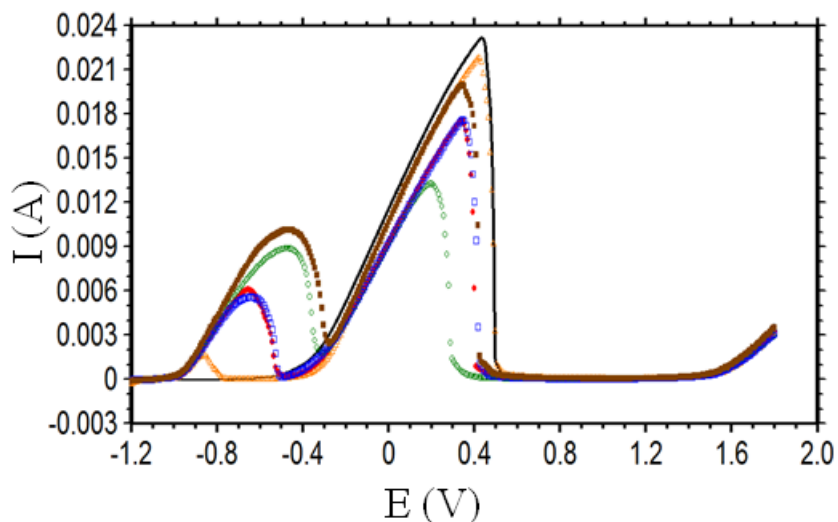


Figure 4. The linear sweep voltammograms recorded for CS (-), CS/Zn (Δ), CS/Zn/PANI (\bullet), CS/Zn/PPy (\square), CS/Zn/POA (\circ) and CS/Zn/PNMP (\blacksquare) electrodes in 0.05 M EDTA containing 0.50 M sodium sulphate solution. Scan rate : 5 mV/s.

Immediately after the immersion time, the E_{ocp} -time curves obtained for CS, CS/Zn, CS/Zn/PANI, CS/Zn/PPy, CS/Zn/POA and CS/Zn/PNMP electrodes in 3.5 % NaCl solution are given in Figure 5. To determine the property of the Zn metal coated on the CS electrode, it was clearly seen that the E_{ocp} value of the Zn-coated CS electrode was negative compared to the uncoated CS electrode. This behavior of Zn plated electrode showed the presence of a layer on CS electrode. In case of homopolymer film coated electrodes, the E_{ocp} values of homopolymer film coated CS/Zn electrodes appeared to be at positive potential when compared with value of CS/Zn sample, immediately after the immersion time. The positive shift in the E_{ocp} values obtained for PANI, PPy, POA and PNMP film coated CS/Zn electrodes simply indicated that Zn plating and these homopolymer films provided an adequate physical protection to metal between the corrosive environment and base metal. The E_{ocp} values of CS/Zn/PANI, CS/Zn/PPy, CS/Zn/POA and CS/Zn/PNMP electrodes were cathodic direction due to their conductive structure and the presence of zinc in the polymer film pore base when compared with uncoated CS electrode.

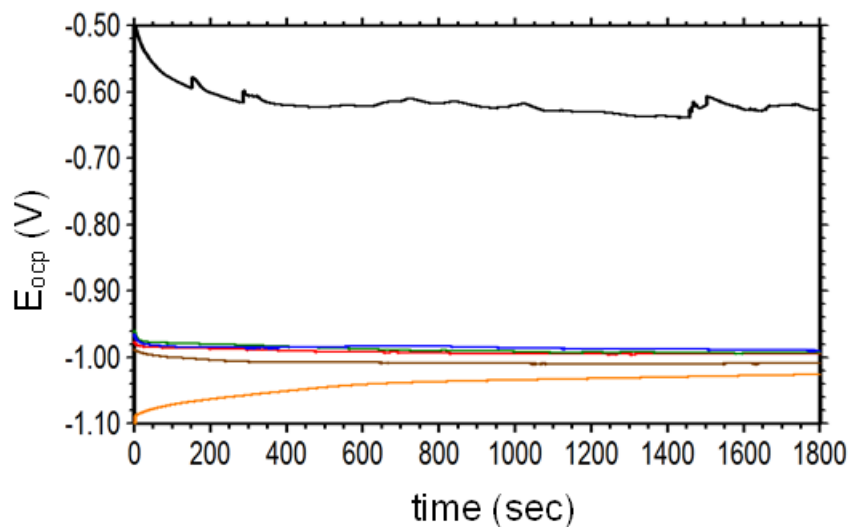


Figure 5. E_{ocp} -time curves recorded for CS (-), CS/Zn (Δ), CS/Zn/PANI (\bullet), CS/Zn/PPy (\square), CS/Zn/POA (\circ) and CS/Zn/PNMP (\blacksquare) electrodes after exposure time in 3.5 % NaCl solution.

Anodic polarization curves obtained for CS, CS/Zn, CS/Zn/PANI, CS/Zn/PPy, CS/Zn/POA and CS/Zn/PNMP electrodes after 168 h exposure time in 3.5 % NaCl solution are given in Figure 6. In the case of uncoated CS sample, corrosion potential value (E_{corr}) was obtained to be -0.665 V. Current values increased so rapidly that there was not any possibility for passivation of the CS electrode surface under the aggressive chloride ions condition. The E_{corr} value of CS/Zn electrode (-0.895 V) shifted in the active region due to zinc dissolution than that of uncoated CS electrode. It is clearly seen that CS/Zn electrode exhibited significantly highest current values. On the other hand, the E_{corr} value of CS/Zn/PANI, CS/Zn/PPy, CS/Zn/POA and CS/Zn/PNMP electrodes were measured as -0.916, -0.893, -0.592 and -0.903 V, respectively. The positive shift in the E_{corr} value for CS/Zn/POA electrode simply indicated that POA homopolymer film had less conductivity when compared with PANI, PPy and PNMP on CS electrode surface. The current values of CS/Zn/PANI electrode were significantly lower when compared with other homopolymer film coated Zn plated carbon electrode as well as Zn plated carbon steel and bare carbon steel electrode. This study revealed that PANI homopolymer film provided important corrosion protection to CS electrode.

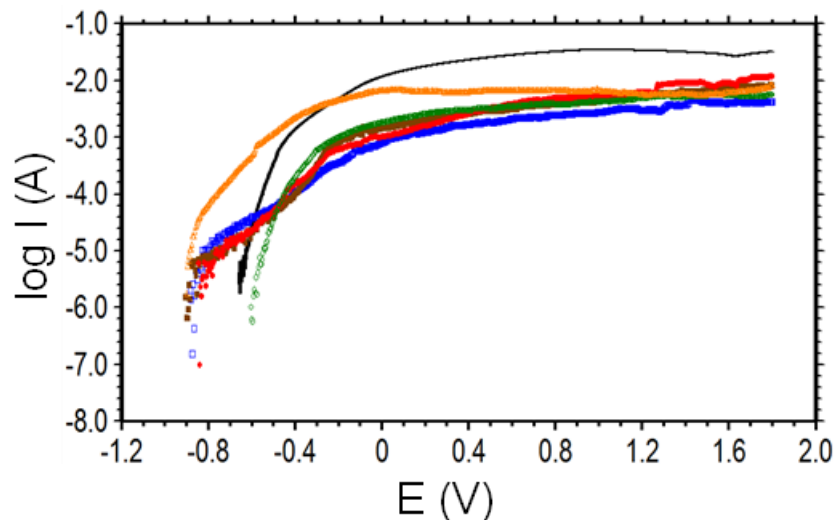


Figure 6. Anodic polarization curves recorded for CS (-), CS/Zn (Δ), CS/Zn/PANI (\bullet), CS/Zn/PPy (\square), CS/Zn/POA (\circ) and CS/Zn/PNMP (\blacksquare) electrodes after 168 h of exposure time in 3.5 % NaCl solution, scan rate: 4 mV/s.

The Nyquist diagrams recorded for CS, CS/Zn, CS/Zn/PANI, CS/Zn/PPy, CS/Zn/POA and CS/Zn/PNMP electrodes obtained in 3.5 % NaCl solution are given in Figure 7, after 48 h and 168 h of exposure time. In Figure 7(a), Nyquist plots obtained for CS and CS/Zn electrodes consisted of one depressed semicircle ranging from high frequency to low frequency for both electrodes, after 48 h of immersion time. The diameters of these depressed semicircles were equal to polarization resistance (R_p). The depressed semicircle for bare CS electrode was equal to R_p including the total of the charge transfer resistance (R_{ct}) that is responsible for the anodic dissolution of bare metal and diffusion resistance (R_d) (Walter, 1986; Mansfield 1995; Ozyilmaz, 2011). At this time, the E_{ocp} value of bare CS electrode was found to be approx. -0.669 V, while that of CS/Zn electrode was -0.990 V. The E_{ocp} value of CS/Zn electrode was cathodic direction when compared with CS electrode. The more negative E_{ocp} value for the CS/Zn electrode indicated the presence of active zinc metal coating on the CS metal. On the other hand, indicated prominent differences between dissolution behavior of Zn plated layer and the corrosion reactions at the CS and CS/Zn surfaces. It has been observed that the Zn alloy coating exhibits a significant active layer appearance on the carbon steel against corrosive products. Consequently, this behavior observed for CS/Zn electrode within 48 h were an indication that the highest R_p value which was equal to the R_{ct} and film resistance (R_f), was attributed to the total of Zn plating resistance (R_{Zn}) and oxide layer resistance (R_o) formed on the surface was observed for CS/Zn electrode (Walter, 1986; Mansfield 1995; Ozyilmaz, 2011). On the other hand, there was one depressed semicircle for PANI, PPy, POA and PNMP homopolymer film coated CS/Zn electrodes, after 48 h of exposure time. In the Nyquist diagram, the depressed semicircle which was equal to the R_p value consisted of polymer film resistance (R_{pf}), R_{Zn} , R_o and R_{ct} corresponding to dissolution of substrate at the bottom of the coating pores. This R_p value of CS/Zn/PANI electrode was higher when compared

with those of other coated CS electrodes and as well as CS/Zn. Moreover, the R_p value of CS/Zn/PNMP electrode was lowest due to high permeability and conducting property of homopolymer film, when compared with that of other homopolymer film coated CS/Zn electrodes, during this period. After 168 h of immersion time, decreasing in R_p values obtained for CS/Zn and bare CS electrodes were an indication that there was an increase in the amount of electrolyte solution within Zn plating and CS surface. Yet, the R_p value recorded for CS/Zn electrode also was found to be lower than that of uncoated CS metal, after 168 h of exposure time. As seen from Figure 7(b), there was one depressed semicircle for CS/Zn/PANI, CS/Zn/PPy, CS/Zn/POA and CS/Zn/PNMP electrodes, after 168 h of exposure time. In the Nyquist diagram, the depressed semicircle which was equal to the R_p value consisted of R_{pf} , R_{Zn} , R_o and R_{ct} corresponding to dissolution of substrate at the bottom of the pores. This R_p value of CS/Zn/PANI electrode was higher when compared with those of other coated CS electrodes. Moreover, the R_p value of CS/Zn/PPy electrode was lowest due to high permeability and conducting property of homopolymer film, when compared with that of other homopolymer film coated CS/Zn electrodes, during this period.

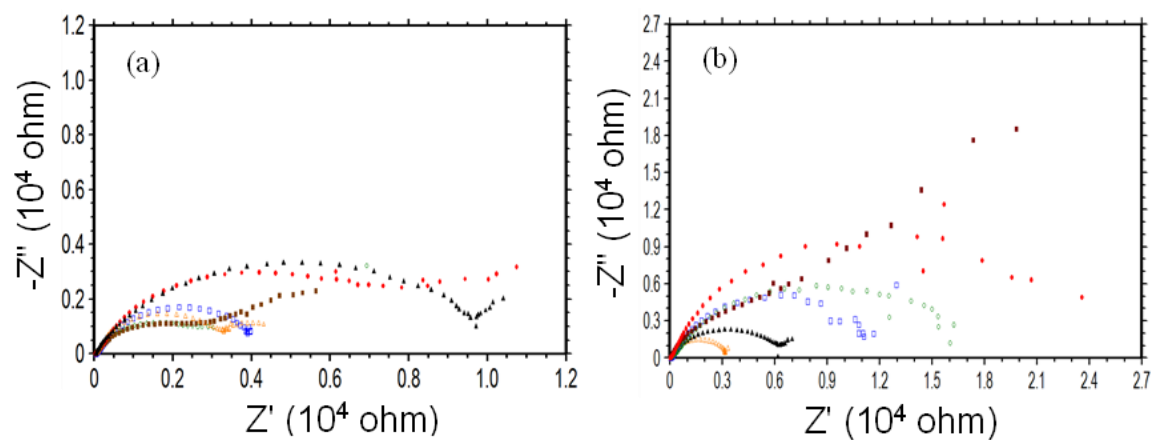


Figure 7. The Nyquist plots recorded for CS (\blacktriangle), CS/Zn (\triangle), CS/Zn/PANI (\bullet), CS/Zn/PPy (\square), CS/Zn/POA (\circ) and CS/Zn/PNMP (\blacksquare) electrodes after 48 (a) and 168 h (b) of exposure time in 3.5 % NaCl solution.

In conclusions, according to results of SEM analysis, PANI, PPy, POA and PNMP coatings were successfully synthesized on CS/Zn electrode, applying cyclic voltammetry technique. Homogenous and adherent homopolymer films were produced using 0.10 M monomer solution containing 0.20 M sodium oxalate as electrolyte. It was found that the passivation of CS/Zn surface was necessary for homogenous homopolymer film synthesis prior to monomer oxidation and film growth. The corrosion performances of bare CS and CS/Zn electrodes were lower when compared with homopolymer film coated CS/Zn electrodes. PANI homopolymer film exhibited significant highest physical barrier behavior on Zn plated carbon steel, in longer exposure time.

Acknowledgments

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Conflict of Interest

The author declared that they have no competing interests.

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