

# Different copolymer films on ZnFeCo particles: Synthesis and anticorrosion properties



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## ABSTRACT

Zinc–iron–cobalt (ZnFeCo) particles were electrochemically deposited on carbon steel (CS) electrode applying current of 3 mA with chronopotentiometry technique. ZnFeCo particles had homogenous, smooth with prismatic structure. It was shown that the ZnFeCo particles exhibited important barrier effect on CS substrate. Poly(aniline-*co*-*o*-anisidine), poly(aniline-*co*-pyrrole), poly(aniline-*co*-*N*-methylpyrrole) and poly(*o*-anisidine-*co*-pyrrole) copolymer films were obtained on CS/ZnFeCo electrode. Evaluation of anticorrosion performance of copolymer coatings in 3.5% NaCl solution was investigated by using AC impedance spectroscopy (EIS) technique, anodic polarization and the  $E_{ocp}$ –time curves. Copolymer films exhibited significant physical barrier behavior on ZnFeCo plated carbon steel, in longer exposure time.

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## 1. Introduction

Oxidizable materials have been widely used in numerous applications for many years. Therefore, great attention has been paid to studies on the corrosion of oxidizable metals. In industry, metallic platings have been widely used to protect oxidizable metals against corrosion [1–10]. On the other hand chromate and phosphate conversion coatings as a later improve protection for metallic surfaces against aggressive environments. These conversion coatings which are generally applied for long periods convert the metal surface from an active to a passive state [11–15]. In recent years, the organic or polymeric electroactive compounds have been studied to protect oxidizable products from corrosion. 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 [16–24]. Camalet et al. clearly describe that the synthesise of polyaniline films on zinc and zinc–nickel alloy in acidic solution such as oxalic acid was unsuccessful [25]. However, in our earlier work [26], we reported that polyaniline film which was synthesized in acidic solution such as oxalic acid on nickel (1  $\mu$ m) 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 [27]. It was found that this coating was considerably suitable for the protection of carbon steel.

This study aims to electrochemically synthesize poly(aniline-*co*-*o*-anisidine), poly(aniline-*co*-pyrrole), poly(aniline-*co*-*N*-methylpyrrole) and poly(*o*-anisidine-*co*-pyrrole) copolymer films on thin zinc–iron–cobalt (ZnFeCo) alloy plated carbon steel in sodium oxalate (NaOx) medium, which would enable the passivation of the ZnFeCo plated carbon steel surface. The corrosion performance of ZnFeCo plated carbon steel substrate with and without copolymer coating was investigated in 3.5% NaCl and compared using the AC impedance diagrams, anodic polarization curves, time–open circuit potential curves and linear sweep voltammograms.

## 2. Experimental

All the chemicals were purchased from Merck. All electrochemical experiments were performed 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 cm<sup>2</sup>. 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

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carefully polished with abrasive paper (1200 grid), degreased with 1/1 ethanol/acetone mixture, washed with distilled water and dried. CHI 606C and CHI 660B model digital electrochemical analyzers were used for all electrochemical measurements. ZnFeCo particles were obtained using a bath based on 40.90 zinc sulphate ( $\text{ZnSO}_4$ ), 7.87 cobalt sulphate ( $\text{CoSO}_4$ ), 2.78 iron(II) sulphate ( $\text{FeSO}_4$ ), 12.68 sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ), 12.68 boric acid ( $\text{H}_3\text{BO}_3$ ), 22.84 ammonium chloride ( $\text{NH}_4\text{Cl}$ ), 0.25 sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) by weight% and pH was approx. 5.0 [3–6]. The thickness of ZnFeCo alloy plating was determined between 3.43 and 4.65  $\mu\text{m}$  by estimation of the passing charge amount applying 3 mA constant current. The ZnFeCo coating composition was determined as 78.14 Zn, 0.86 Fe and 21.00 Co by weight% via an energy dispersive X-ray spectrometer (EDX).

Poly(aniline-co-o-anisidine) (PANI-co-POA), poly(aniline-co-pyrrole)(PANI-co-PPy), poly(aniline-co-N-methylpyrrole)(PANI-co-PNMP) and poly(o-anisidine-co-pyrrole)(POA-co-PPy) copolymer films were synthesized electrochemically using cyclic voltammetry technique. Electrochemical impedance measurements were obtained at measured open circuit potential values applying 7 mV of amplitude in frequency range from  $10^5$  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 JEOL JSM-5500LV scanning electron microscope. The preferable orientation of the ZnFeCo deposit was determined by X-ray diffraction (XRD) analysis, with a Philips PANalytical X'Pert Pro X-ray diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The  $2\theta$  range of  $20$ – $60^\circ$  was recorded at the rate of  $0.02^\circ 2\theta/0.5 \text{ s}$ . The crystal phases were identified comparing the  $2\theta$  values and intensities.

### 3. Results and discussions

In order to improve the corrosion resistance of zinc–iron–cobalt alloy plating (ZnFeCo) alloy plating, four different copolymer films were electrochemically synthesized on alloy surface. So, ZnFeCo alloy plating was successfully deposited on carbon steel (CS) applying current of 3 mA with galvanostatic technique. Then, PANI-co-POA, PANI-co-PPy, PANI-co-PNMP and POA-co-PPy copolymer films were electropolymerized on ZnFeCo alloy deposited carbon steel (CS/ZnFeCo) electrode from sodium oxalate (NaOx) medium, which would enable the passivation of the CS/ZnFeCo surface using proper scan rate in cyclic voltammetric technique. The corrosion performance of ZnFeCo alloy plated carbon steel substrate with and without copolymer coating was investigated in 3.5% NaCl and compared using the AC impedance diagrams, anodic polarization curves, time–open circuit potential curves and linear sweep voltammograms.

ZnFeCo alloy plating was achieved on carbon steel applying 1, 2, 3, 4 and 5 mA constant current values in acidic solution medium. Pt anode using for the plating was taken as  $0.36 \text{ cm}^2$  surface area and platings were obtained with stirring the solution open to atmosphere. It was observed that ZnFeCo particles obtained by applying 3 mA constant current value exhibited the highest corrosion performance against the attack of corrosion products such as aggressive chloride ions to carbon steel electrode. In this study, ZnFeCo particles were successfully deposited on CS applying current of 3 mA with chronopotentiometry technique in which a constant current. As seen in Fig. 1, while the bare CS electrode showed the evidence of emery, average grain sizes of ZnFeCo prism particles, which had more homogenous and smooth structure plated on carbon steel were measured using SEM images as  $4.73 \mu\text{m}$  for length and  $1.20 \mu\text{m}$  for width. The XRD patterns of the electrodeposited

ZnFeCo films are given in Fig. 1(c). Adding Fe and Co atoms in the zinc matrix caused to similar reflection peaks angles of Zn reflection. It was clearly seen that ZnFeCo alloys had only the  $\eta(101)$  and  $\eta(102)$  reflections. The presence of more than one phase on a coating surface could also influence the measured corrosion values. XRD patterns were indicated highly crystalline structures. As these local microstructural variations adopt different equilibrium potentials in aqueous solutions, these are susceptible to local galvanic corrosion. On this basis it is expected that the corrosion rates of the single phase alloys is lower than the binary or multiphase alloys. These XRD results were in agreement with the results observed in the literature [1]. From SEM images, it was observed that the deposit structure was fine grained. For zinc-rich ZnFeCo alloy, distorted hexagonal structure was noted.

Electropolymerization of PANI-co-POA, PANI-co-PPy, PANI-co-PNMP and POA-co-PPy copolymer films were carried out onto the surface of ZnFeCo particle plated CS in NaOx medium. Copolymer films were synthesized using totally 0.20 M monomer mixture solution with (1:1) molar ratio in 0.20 M NaOx solution. In order to obtain the best corrosion performance, a lot of the electrochemical parameters such as scan rate, potential range and segment number were applied for synthesis of copolymer films. As a result, copolymer films were synthesized by using cyclic voltammetry technique in two steps. Firstly, the passivation of ZnFeCo alloy plated carbon steel electrode and formation of thin copolymer films were provided by using anodic and cathodic scans from  $-1.10$  to  $1.80 \text{ V}$  with scan rate of  $100 \text{ mV/s}$  for PPy-co-POA film and  $50 \text{ mV/s}$  for other copolymer films. In the second stage, film growth cycles were taken at potential range from  $0.00$  to  $1.80 \text{ V}$  with same scan rate corresponding to first step. Fifty segments for PPy-co-POA film, 26 segments for PANI-co-PNMP, and 46 segments for PANI-co-POA and PANI-co-PPy films were applied to synthesis of the copolymer films.

Fig. 2 shows first cyclic voltammograms recorded for CS/ZnFeCo electrode in 0.20 M NaOx solution without and with proper monomers and for CS in NaOx solution. The cyclic voltammograms recorded during the first potential sweep on bare CS and CS/ZnFeCo electrodes in NaOx solution are given in Fig. 2(a). Measurements for bare CS and CS/ZnFeCo electrodes in NaOx solution were taken at the scan rate of  $50 \text{ mV/s}$ . The oxidation/passivation processes of CS and CS/ZnFeCo electrodes were observed as well as the defined peak. The dissolution of CS and CS/ZnFeCo electrodes began at approx.  $-0.580 \text{ V}$  and  $-0.998 \text{ V}$ , respectively. The passivation of the CS electrode was observed to cease at approx.  $+0.05 \text{ V}$ , while the passivation of CS/ZnFeCo electrode was completed at approx.  $1.24 \text{ V}$ . The passivation mechanism was based on the formation of insoluble iron(II) oxalate for the CS and insoluble zinc oxalate, iron oxalate and cobalt oxalate for the CS/ZnFeCo electrode. At continued anodic scan, there was not any change on the CS electrode in the potential range of  $0.40$  and  $1.24 \text{ V}$ . Oxygen gas evolution recorded for the CS and CS/ZnFeCo electrodes was observed as an increase in current value after approx.  $1.24 \text{ V}$ , whereas this event could not be seen on CS electrode up to  $1.24 \text{ V}$  potential. At the reverse scan, the sharp peak appearing at approx.  $-0.35 \text{ V}$  came about as the repassivation peak corresponding to CS electrode. This peak was attributed to the reduction from ferric compounds back to ferrous compound on the surface. It was clear that the repassivation peak disappeared in a wide cathodic potential region applied for CS/ZnFeCo electrode. This could be explained by the very thin ZnFeCo alloy plating produced on CS surface. The first voltammograms obtained for the CS/ZnFeCo electrode in 0.20 M proper monomer mixture containing NaOx solution are shown in Fig. 2(b). First cyclic voltammograms recorded for CS/ZnFeCo electrode in 0.20 M NaOx solution without and with monomer exhibited completely different behavior from each other. In presence of monomers, the oxidation/passivation peak could be well

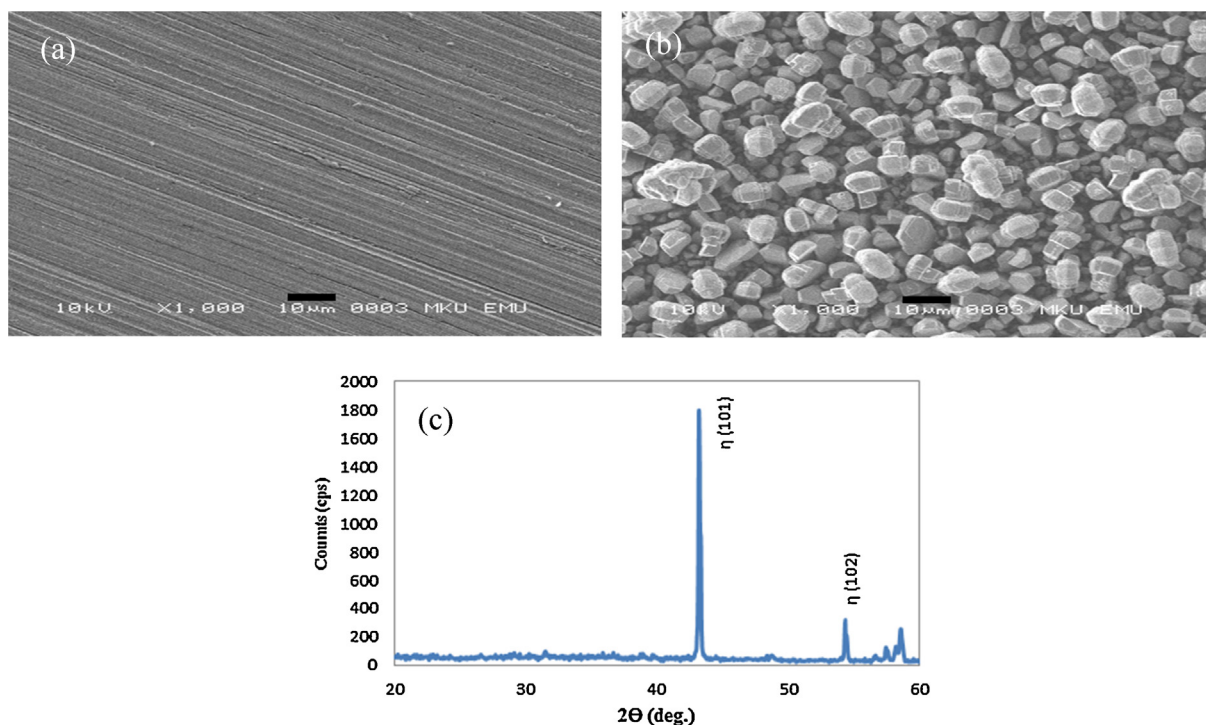


Fig. 1. SEM images of CS (a) and CS/ZnFeCo (b) electrodes and X-ray diffractogram of ZnFeCo alloy plating (c).

identified during each solution mixture. Passivation of CS/ZnFeCo electrode was required to generate a suitable surface prior to the electropolymerization process [23]. The monomer oxidation process recorded for all solution on the ZnFeCo alloy surface were observed as broad current increase above approx. 1.00 V. Besides the current values recorded for monomer oxidation process was lowest in presence of aniline + pyrrole monomer containing NaOx solution.

Film growth cycles (not shown here) showed that current values corresponding to the monomer oxidation for all of monomers were found to decrease regularly with increasing scanning numbers. Characterizations of copolymer coatings were carried out by SEM technique. The surface of CS/ZnFeCo electrode was covered with copolymer films of different granular structure (Fig. 3).

Linear sweep voltammograms for CS, CS/Zn, CS/ZnFeCo, CS/ZnFeCo/PANI-co-POA, CS/ZnFeCo/PANI-co-PPy, CS/ZnFeCo/PANI-co-PNMP and CS/ZnFeCo/PPy-co-POA electrodes in 0.05 M EDTA containing 0.50 M sodium sulphate solution are given in Fig. 4. All measurements were taken at scan rate of 5 mV/s. In order to indicate the presence of different metal layers, linear sweep

voltammogram of Zn plating was given here. Consequently, the thickness of Zn plating which was plated applying 4 mA constant current was estimated to be approx. 5.93  $\mu\text{m}$ . There were one, two and three anodic dissolution peaks for bare CS, CS/Zn and ZnFeCo electrodes, respectively. The peak at approx.  $-0.87$  V for CS/Zn electrode and the peaks which could not be well resolved from each other at  $-0.534$  V and  $-0.396$  V for CS/ZnFeCo electrode were due to dissolution of zinc, iron and cobalt and formation of zinc and cobalt complex with EDTA, while these peaks for CS electrode were not seen in this potential. The single peak corresponding to the anodic dissolution of iron substrate was observed at approx.  $+0.43$  V [28]. On the other hand, there was a difference between the heights of CS/Zn or ZnFeCo alloy dissolution peaks and bare CS metallic dissolution, which could be attributed to the presence of ZnFeCo alloy plating on CS electrode. The dissolution current peak recorded for iron dissolution of the underlying ZnFeCo alloy plating had low intensity while bare CS electrode exhibited the highest dissolution peak. This event indicated that the ZnFeCo layer substantially prevented the dissolution of CS electrode. Consequently, the formation of complex  $\text{ZnO}\cdot\text{H}_2\text{O}$  and zinc and cobalt oxide layers on

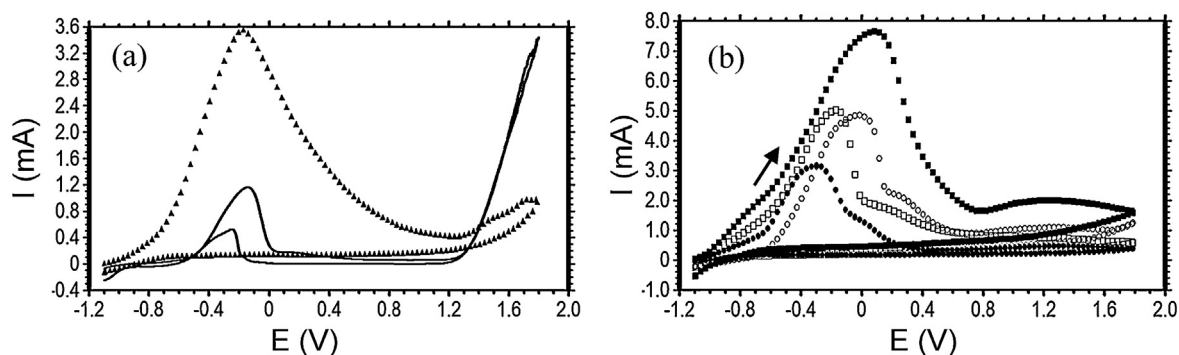
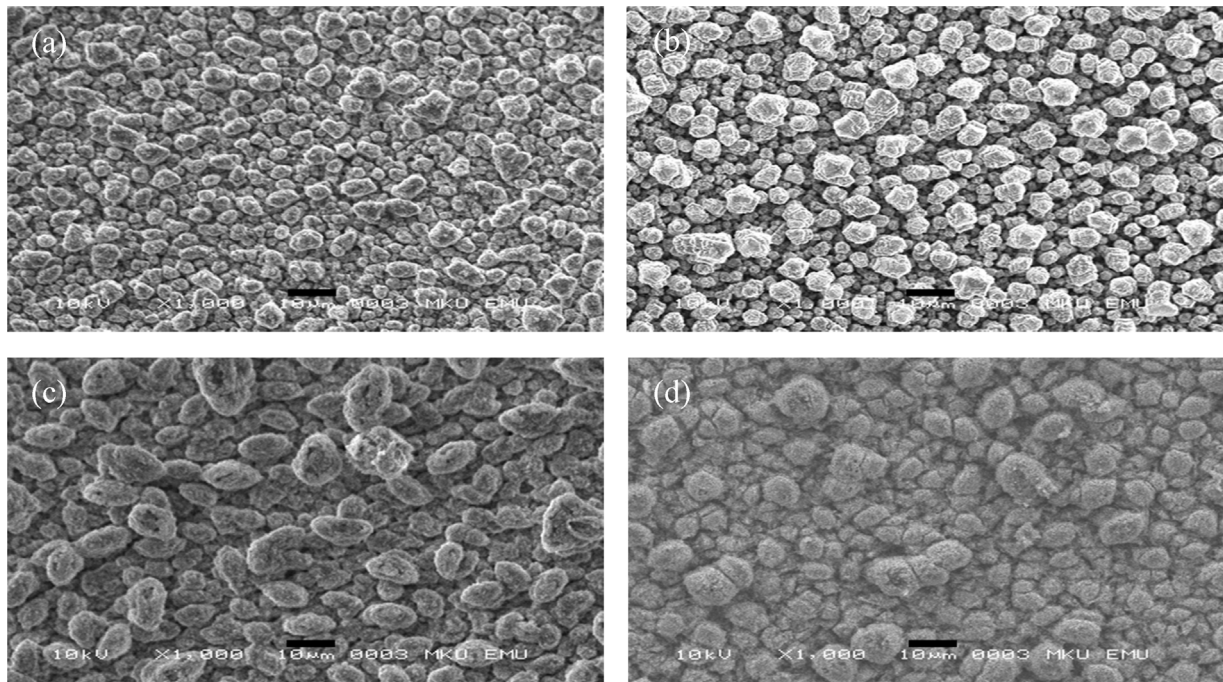


Fig. 2. First CVs recorded for CS (—) and CS/ZnFeCo ( $\blacktriangle$ ) electrodes in monomer free (a) and CS/ZnFeCo in aniline + *o*-anisidine ( $\circ$ ), aniline + pyrrole ( $\bullet$ ), aniline + *N*-methylpyrrole ( $\square$ ) and pyrrole + *o*-anisidine ( $\blacksquare$ ) containing 0.20 M NaOx solution (b), scan rate: 50 mV/s.





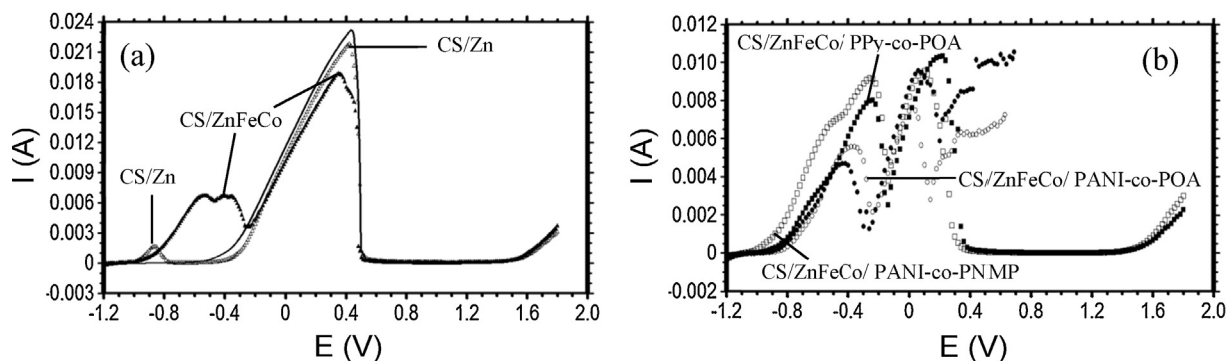
**Fig. 3.** SEM images of CS/ZnFeCo/PANI-co-POA (a), CS/ZnFeCo/PANI-co-PPy (b), CS/ZnFeCo/PANI-co-PNMP (c) and CS/ZnFeCo/PPy-co-POA (d) electrodes.

CS/ZnFeCo electrode exhibited an efficient barrier property against the corrosive products. In Fig. 4(b), there were three anodic dissolution peaks for CS/ZnFeCo/PANI-co-POA, CS/ZnFeCo/PANI-co-PPy, CS/ZnFeCo/PANI-co-PNMP and CS/ZnFeCo/PPy-co-POA electrodes. The current values recorded for dissolution peak of iron were the lowest in presence of copolymer films. It was clear that copolymer coatings on CS/ZnFeCo electrode provided an adequate physical protection to metal between the corrosive environment and ZnFeCo alloy plating. When CS/ZnFeCo electrodes coated with different copolymer films were compared, zinc dissolution peak of CS/ZnFeCo/PANI-co-PPy electrode had the lowest intensity, while CS/ZnFeCo/PANI-co-PNMP electrode exhibited the highest dissolution peak. This event indicated that the CS/ZnFeCo/PANI-co-PPy layer did not allow significant dissolution of ZnFeCo plating.

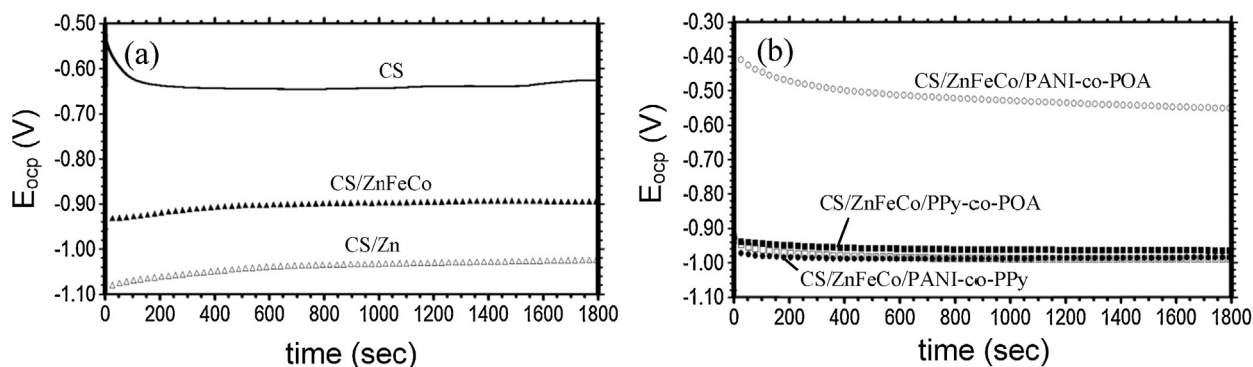
Immediately after the immersion time, the  $E_{ocp}$ -time curves obtained for CS, CS/Zn, CS/ZnFeCo, CS/ZnFeCo/PANI-co-POA, CS/ZnFeCo/PANI-co-PPy, CS/ZnFeCo/PANI-co-PNMP and CS/ZnFeCo/PPy-co-POA electrodes in 3.5% NaCl solution are given in Fig. 5. In order to compare the properties of alloy plating layer obtained on CS electrode, the  $E_{ocp}$  curve of Zn plating was given in

Fig. 5(a). It was clearly seen that the  $E_{ocp}$  values of Zn and ZnFeCo plated CS electrodes were the negative direction when compared with uncoated CS electrode. This behavior of metal or metal alloy plated electrodes showed the presence of a layer on CS electrode. The positive shift in the  $E_{ocp}$  value obtained for ZnFeCo plated electrode simply indicated that alloy plating which was different from Zn metal took place on the CS electrode. In case of copolymer film coated electrodes, the  $E_{ocp}$  values of CS/ZnFeCo/PANI-co-POA electrodes appeared to be at positive potential when compared with values of all uncoated and coated samples, immediately after the immersion time. The positive shift in the  $E_{ocp}$  values obtained for PANI-co-POA film coated CS/ZnFeCo electrode simply indicated that alloy plating and this copolymer film provided an adequate physical protection to metal between the corrosive environment and base metal. The  $E_{ocp}$  values of CS/ZnFeCo/PANI-co-PPy, CS/ZnFeCo/PANI-co-PNMP and CS/ZnFeCo/PPy-co-POA electrodes were cathodic direction due to their conductive structure when compared with ZnFeCo alloy plating.

Anodic polarization curves obtained for CS, CS/Zn, CS/ZnFeCo, CS/ZnFeCo/PANI-co-POA, CS/ZnFeCo/PANI-co-PPy, CS/ZnFeCo/PANI-co-PNMP and CS/ZnFeCo/PPy-co-POA electrodes



**Fig. 4.** The linear sweep voltammograms for CS (-), CS/Zn ( $\Delta$ ), CS/ZnFeCo ( $\blacktriangle$ ) (a) and CS/ZnFeCo/PANI-co-POA ( $\circ$ ), CS/ZnFeCo/PANI-co-PPy ( $\bullet$ ), CS/ZnFeCo/PANI-co-PNMP ( $\square$ ) and CS/ZnFeCo/PPy-co-POA ( $\blacksquare$ ) electrodes in 0.05 M EDTA containing 0.50 M sodium sulphate solution. Scan rate: 5 mV/s.

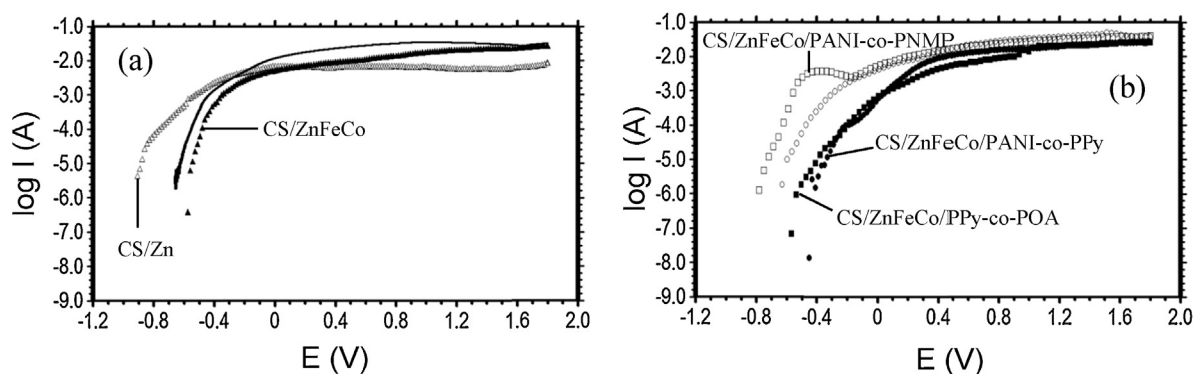


**Fig. 5.**  $E_{ocp}$ -time curves obtained for CS (—), CS/Zn ( $\Delta$ ), CS/ZnFeCo ( $\blacktriangle$ ) (a) and CS/ZnFeCo/PANI-co-POA (o), CS/ZnFeCo/PANI-co-PPy ( $\bullet$ ), CS/ZnFeCo/PANI-co-PNMP ( $\square$ ) and CS/ZnFeCo/PPy-co-POA ( $\blacksquare$ ) electrodes after 168 h of exposure time in 3.5% NaCl solution.

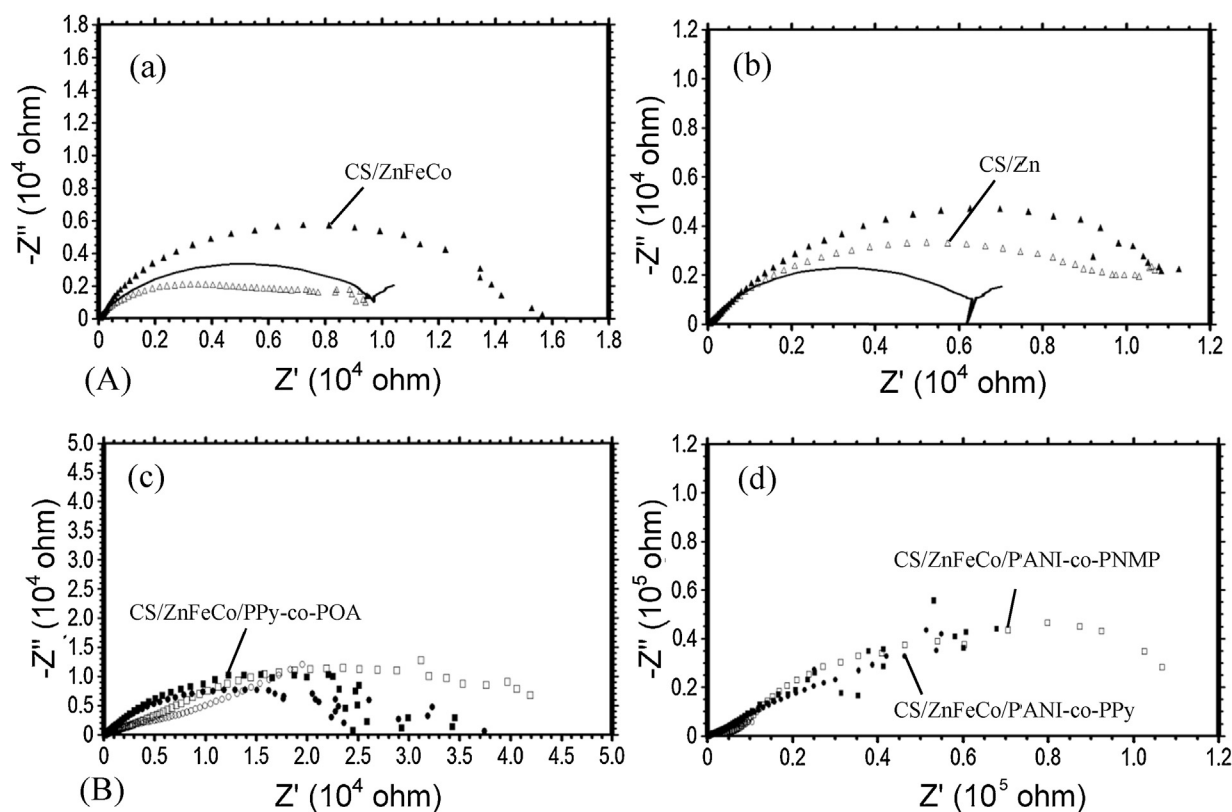
after 168 h exposure time in 3.5% NaCl solution are given in Fig. 6. In the case of uncoated CS sample, corrosion potential value ( $E_{corr}$ ) was observed to be  $-0.665$  V. Current values increased so rapidly that there was not any possibility for passivation of the CS electrode surface under the 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 electrode. In the case of CS/ZnFeCo electrode, the  $E_{corr}$  was observed to be  $-0.575$  V. The  $E_{corr}$  value shifted toward nobler potential region with respect to bare CS electrode as well as CS/Zn electrode. It is clearly seen that CS/ZnFeCo electrode exhibited significantly lowest current values. Therefore, ZnFeCo alloy plating provided an adequate physical protection to metal between the corrosive environment and base metal. On the other hand, the  $E_{corr}$  of CS/ZnFeCo/PANI-co-POA, CS/ZnFeCo/PANI-co-PPy, CS/ZnFeCo/PANI-co-PNMP and CS/ZnFeCo/PPy-co-POA electrodes were measured as  $-0.629$ ,  $-0.451$ ,  $-0.774$  and  $-0.569$  V, respectively. The positive shift in the  $E_{corr}$  values for CS/ZnFeCo/PANI-co-PPy and CS/ZnFeCo/PPy-co-POA electrodes simply indicated that these copolymer films provided an adequate physical protection to ZnFeCo plated carbon steel between the corrosive environment and the underlying metal. This occasion supported the idea that current values of CS/ZnFeCo/PANI-co-PPy and CS/ZnFeCo/PPy-co-POA electrodes were significantly lower when compared with other copolymer film coated ZnFeCo plated carbon electrode as well as Zn, ZnFeCo plated carbon steel and bare carbon steel electrode. This study revealed that PANI-co-PPy and PPy-co-POA copolymer films provided important corrosion protection to CS electrode.

The Nyquist diagrams recorded for CS, CS/Zn, CS/ZnFeCo, CS/ZnFeCo/PANI-co-POA, CS/ZnFeCo/PANI-co-PPy, CS/ZnFeCo/PANI-co-PNMP and CS/ZnFeCo/PPy-co-POA electrodes

obtained in 3.5% NaCl solution are given in Fig. 7, after 48 h and 168 h of immersion time. In Fig. 7(a), Nyquist plots recorded for CS, CS/Zn and CS/ZnFeCo electrodes consisted of one depressed semicircle ranging from high frequency to low frequency for all 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 ( $R_d$ ) [27–30]. At this time, the  $E_{ocp}$  value of bare CS electrode was found to be approx.  $-0.669$  V, while that of CS/Zn and CS/ZnFeCo electrode was  $-0.633$  and  $-0.754$  V, respectively. This value for CS/Zn electrode was partly cathodic direction when compared with CS electrode, while the  $E_{ocp}$  value recorded for CS/Zn electrode was  $-1.02$  V after 1800 s in Fig. 5(a). This case was related to the dissolution of active zinc metal which had porous structure. On the other hand, appearance of more negative  $E_{ocp}$  value for CS/ZnFeCo electrode indicated prominent differences between dissolution behavior of Zn and ZnFeCo plated layers and the corrosion reactions at the CS/Zn and CS/ZnFeCo surfaces. This showed that ZnFeCo alloy plating exhibited an important passive layer against to corrosive products on carbon steel electrode. Consequently, this behavior observed for CS/ZnFeCo 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 alloy plating resistance ( $R_{ZnFeCo}$ ) and oxide layer resistance ( $R_o$ ) formed on the surface was observed for CS/ZnFeCo electrode [27–30]. After 168 h of exposure time, decreasing in  $R_p$  values for CS/ZnFeCo and bare CS electrodes were an indication that there was an increase in the amount of electrolyte solution within alloy platings and CS surface. Yet, the  $R_p$  value obtained



**Fig. 6.** Anodic polarization curves obtained for CS (—), CS/Zn ( $\Delta$ ), CS/ZnFeCo ( $\blacktriangle$ ) (a) and CS/ZnFeCo/PANI-co-POA (o), CS/ZnFeCo/PANI-co-PPy ( $\bullet$ ), CS/ZnFeCo/PANI-co-PNMP ( $\square$ ) and CS/ZnFeCo/PPy-co-POA ( $\blacksquare$ ) (b) electrodes after 168 h of exposure time in 3.5% NaCl solution, scan rate: 4 mV/s.



**Fig. 7.** The Nyquist plots recorded for CS (–), CS/Zn ( $\Delta$ ), CS/ZnFeCo ( $\blacktriangle$ ) (A) and CS/ZnFeCo/PANI-co-POA ( $\circ$ ), CS/ZnFeCo/PANI-co-PPy ( $\bullet$ ), CS/ZnFeCo/PANI-co-PNMP ( $\square$ ) and CS/ZnFeCo/PPy-co-POA ( $\blacksquare$ ) (B) electrodes after 48 (a–c) and 168 h (b–d) of exposure time in 3.5% NaCl solution.

for CS/Zn electrode increased due to the formation of stable complex  $\text{ZnO} \cdot \text{H}_2\text{O}$  on Zn plating surface. Nevertheless, the  $R_p$  values recorded for CS/Zn and CS/ZnFeCo electrodes were found to be higher than that of uncoated metal, after 168 h of exposure time, while the highest  $R_p$  value was obtained for CS/ZnFeCo electrode. As seen from Fig. 7(c), there were double layer capacitance at high frequency region and low frequency pseudocapacitance at low frequency region, in presence of CS/ZnFeCo/PANI-co-PNMP and CS/ZnFeCo/PPy-co-POA electrodes, after 48 h of immersion time. The double layer capacitance at high frequency region was related to the  $R_{ct}$  for electrochemical reaction processes occurring at metal/electrolyte interface within the pores of copolymer film and alloy plating. The second one, which was equal to the  $R_f$ , was attributed to the total of  $R_{\text{ZnFeCo}}$  and  $R_o$  and the polymer film resistance ( $R_{pf}$ ) on the surface. On the other hand, there was one depressed semicircle for CS/ZnFeCo/PANI-co-POA and CS/ZnFeCo/PANI-co-PPy electrodes, after 48 h of exposure time. In the Nyquist diagram, the depressed semicircle which was equal to the  $R_p$  value consisted of  $R_{pf}$ ,  $R_{\text{ZnFeCo}}$ ,  $R_o$  and  $R_{ct}$  corresponding to dissolution of substrate at the bottom of the pores. This  $R_p$  value of CS/ZnFeCo/PANI-co-PNMP electrode was fairly higher when compared with those of other coated CS electrodes. Moreover the  $R_p$  value of CS/ZnFeCo/PANI-co-POA electrode was lowest due to high permeability and conducting property of copolymer film, when compared with that of other copolymer film coated CS/ZnFeCo electrodes, during this period. In Fig. 7(d), the total diameters of two depressed semicircles which were equal to  $R_p$  value were found to increase for copolymer film coated CS/ZnFeCo electrodes, in longer immersion time. After 168 h of exposure time, the  $R_p$  value obtained for CS/ZnFeCo/PANI-co-PNMP electrode was highest when compared with that of other copolymer film coated CS/ZnFeCo electrodes.

#### 4. Conclusions

Copolymer coatings were successfully synthesized on CS/ZnFeCo electrode, applying cyclic voltammetry technique. Homogenous and adherent copolymer films were produced using totally 0.20 M monomer solution at (1:1) molar ratio containing 0.20 M sodium oxalate as electrolyte. It was found that the passivation of CS/ZnFeCo surface was necessary for homogenous copolymer film synthesis prior to monomer oxidation and film growth. The corrosion performances of bare CS and CS/ZnFeCo electrodes were fairly lower when compared with copolymer film coated CS/ZnFeCo electrodes. Copolymer films exhibited significant physical barrier behavior on ZnFeCo alloy plated carbon steel, in longer exposure time.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2014.04.177>.

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