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**THE INFLUENCE OF POLYPYRROLE COATING ON CORROSION BEHAVIOR OF ZnNi  
DEPOSITED COPPER ELECTRODE**

**ABSTRACT**

Bilayer and monolayer coatings offer good protection against metal and alloy corrosion. The protection of copper against corrosion via the use of metallic and polymeric coatings has been the subject of considerable research in the last decade. In this study, ZnNi plating was successfully deposited on the Cu electrode applying current of 7 mA with chronopotentiometry technique in the acidic solution. The PPy film was synthesized on thin ZnNi plating which deposited electrochemically on the copper surface. Homopolymer film was achieved using cyclic voltammetry technique in sodium oxalate solution containing pyrrole monomer. PPy coating provided a significant barrier property due to its lower permeability as well as the improvement the barrier behavior in time.

**Keywords:** Corrosion, Polypyrrole, Alloy, Copper, EIS

**ZnNi KAPLANMIŞ BAKIR ELEKTRODUN KOROZYON DAVRANIŞI ÜZERİNE POLİPİROL  
KAPLAMANIN ETKİSİ**

**ÖZ**

Tek ve iki katlı kaplamalar metal ve alaşım korozyonuna karşı iyi koruma tercihidir. Korozyona karşı bakırın korunmasına yönelik metal ve polimer kaplamaların kullanımı son yıllarda birçok araştırmaya konu olmuştur. Bu çalışmada ZnNi kaplama bakır yüzeyine asidik ortamda 7 mA akım uygulanarak kronopotansiyometrik teknik ile kaplanmıştır. PPy film ise ZnNi kaplanmış bakır yüzeyine elektrokimyasal olarak sentezlenmiştir. Homopolimer film monomer içeren sodyum oksalat çözeltisinde dönüşümlü voltammetrik teknik ile kazandırılmıştır. PPy kaplama zamanla gelişen bariyer davranışın yanı sıra düşük geçirgenliğinden dolayı önemli bir bariyer özellik sağlamıştır.

**Anahtar Kelimeler:** Korozyon, Polipirol, Alaşım, Bakır, EIS

**How to Cite:**

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## 1. INTRODUCTION

Among well-known metallic coatings, zinc (Zn) and zinc alloys (ZnFe, ZnCo, ZnNi) are widely used to improve the corrosion resistance of oxidizable metals such as steel and copper. Zinc alloys can create improved corrosion resistance compared to pure zinc in the protection of copper. This is easily achieved by alloying Zn with more noble metals such as Fe, Ni and Co. Among zinc alloy coatings, zinc-nickel (ZnNi) alloy coating has attracted considerable attention due to their excellent corrosion resistance, good paintability, formability, and weldability. Single layer ZnNi plating for anticorrosive purpose is insufficient to protect the oxidizable metals. Therefore, an additional application such as conducting polymer top coatings on single metal layer increases the total thickness of coatings and contributes to the corrosion resistance of electrodeposited metals [1 and 10].

Recently, electropolymerization has also been investigated as a technique for the forming of conducting polymeric coatings on oxidizable metals. In view of the emerging technological applications of electrically conducting polymer films in various fields like rechargeable batteries, molecular electronics, sensors, Schottky diodes, electrochromic display devices, non-linear optics, etc., there is a growing interest in recent years particularly to synthesize good quality conducting polymer films on a variety of substrates. The use of conducting polymers on mild steel and copper as a protection against corrosion has been reported. Numerous studies have been reported on the possible use of polypyrrole coatings (PPy) against corrosion, under various conditions. Amongst the family of conducting polymers, polypyrrole was chosen for the reasons; (a) The monomer of pyrrole is commercially cheap, (b) It has quite good solubility in water c) the electropolymerization of pyrrole may provide an alternative for reducing the use of hazardous chemicals. To form polypyrrole film, it is necessary to build up electrochemical conditions, which will affect the passivation of the metallic surface [11 and 19].

We introduced on the copper the zinc-nickel electroplating layer on which the PPy layer was subsequently formed. In this paper, we report successful preparation of the top PPy coating in sodium oxalate aqueous solution containing pyrrole monomer on the ZnNi electroplating on the copper. We examined the corrosion protection properties of the coatings on the copper in 3.5% sodium chloride aqueous solution.

## 2. RESEARCH SIGNIFICANCE

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## 3. EXPERIMENTAL

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 a surface area of 0.36 cm<sup>2</sup>. In this study, all electrode potential values were referred to this reference electrode. The working electrode used in this study was copper with a surface area of 0.268 cm<sup>2</sup>. The surface of this electrode was 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. Zinc-nickel plating (ZnNi) was carried out in a bath including by concentration 0.20 M zinc sulfate ( $\text{ZnSO}_4$ ), 0.20 M nickel sulfate ( $\text{NiSO}_4$ ), 0.20 M sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ), 0.15 M boric acid ( $\text{H}_3\text{BO}_3$ ) and 0.40 M sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). Meanwhile pH was approximately 3.0. ZnNi plating was accomplished under atmospheric condition without stirring the solution. Polypyrrole film was synthesized electrochemically using the cyclic voltammetry technique. Electrochemical impedance measurements were obtained at measured open circuit potential values applying 7 mV of amplitude in the frequency range from  $10^5$  to  $10^{-3}$  Hz. The anodic polarization curves were recorded after 236 h of immersion time in corrosive test solution. The scan rate was 5 mV/s and the measured the open circuit potential value was the initial potential for the scan.

#### 4. RESULTS AND DISCUSSIONS

##### 4.1. Synthesis

##### 4.1.1. Zinc-Nikel Plating

ZnNi alloy plating was achieved on the copper electrode applying different constant current values in the acidic solution medium. It was observed that ZnNi alloy plating obtained by applying 7 mA constant current value exhibited the highest corrosion performance against the attack of corrosion products such as aggressive chloride ions to the copper electrode. Therefore, ZnNi plating was successfully deposited on the copper by applying this current amount with this current amount with chronopotentiometry technique. The thickness of ZnNi alloy plating was determined by estimation of the passing charge amount applying 7 mA constant current and was estimated to be between approx. 3.00 and 4.17  $\mu\text{m}$ .

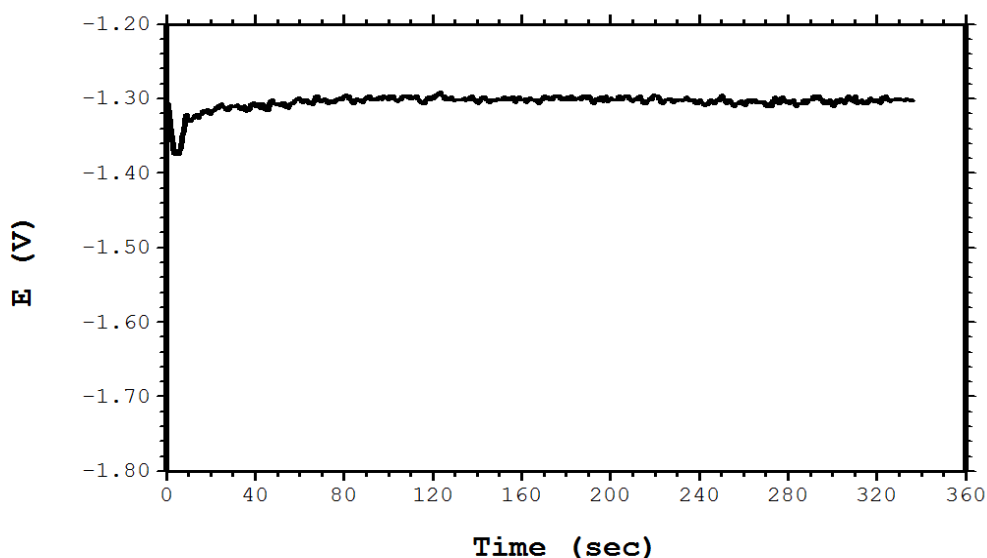


Figure 1. The chronopotentiometric diagram of ZnNi alloy plating deposited on copper electrode applying current of 7 mA in chloride condition

##### 4.1.2. Electropolymerization

Cyclic voltammograms recorded for copper and zinc nickel plated copper (Cu/ZnNi) electrodes in 0.20 M sodium oxalate ( $\text{NaOx}$ ) solution in the absence and in the presence of pyrrole monomer are given in

Figure 2. All measurements were taken at a scan rate of 50 mV/s. For Cu electrode, the anodic waves at approximately -0.40 V were related to oxidation/passivation behavior. The passivation mechanism was based on the formation of insoluble zinc and nickel oxalate for Cu/ZnNi. Cycles showed that, current values corresponding to the oxidation/passivation behavior were found to decrease regularly with increasing scanning numbers due to passivation of Cu/ZnNi electrode surface. The voltammograms obtained from the Cu/ZnNi electrode in 0.10 M monomer containing NaOx solution are shown in Figure 2(b). Cyclic voltammograms recorded for Cu/ZnNi electrode in 0.20 M NaOx solution in the absence and in the presence of monomer exhibited completely different behavior from each other. In the presence of monomer, the oxidation/passivation peak could be well identified during each scan prior to third segment. The low current values of this peak recorded for monomer containing NaOx solution were attributed to the inhibitor like behavior of pyrrole monomer. Passivation of Cu/ZnNi electrode was required to generate a suitable surface prior to the electropolymerization process. In monomer containing medium, the monomer oxidation process recorded for pyrrole on the ZnNi alloy surface was observed as a broad current increase above approx. 1.00 V. Film growth cycles showed that current values corresponding to the monomer oxidation were found to decrease regularly with increasing scanning numbers. The current values corresponding to these oxidation and reduction peaks decreased proportional to the number of cycles, which accounts for a decrease in conductivity of the PPy film. The other anodic and cathodic peaks were determined as the characteristic oxidation and reduction peaks of PPy due to transitions between its oxidation states.

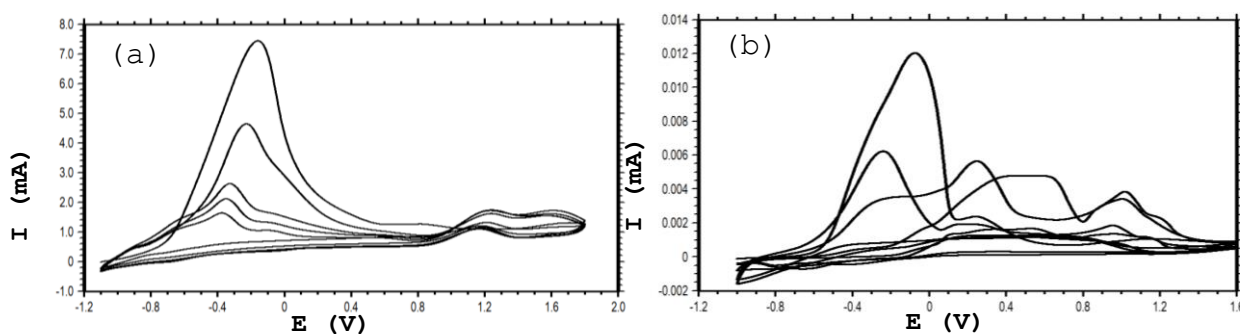


Figure 2. The Cyclic voltammogram recorded for Cu/ZnNi electrode a) in monomer free b) 0.10 M pyrrole monomer containing 0.20 M NaOx solution. Scan rate: 50 mV/s

#### 4.2. Characterization

Linear sweep voltammograms for Cu, Cu/ZnNi and Cu/ZnNi/PPy electrodes in 0.05 M EDTA containing 0.50 M sodium sulfate solution are given in Fig. 3. All measurements were taken at a scan rate of 5 mV/s. In order to indicate the presence of alloy layers on Cu electrode, linear sweep voltammograms of Cu, Cu/ZnNi and Cu/ZnNi/PPy electrodes were given here. There were three anodic dissolution peaks for Cu/ZnNi and Cu/ZnNi/PPy electrodes. The peaks which could not be well resolved from each other at -0.43 V and -0.29 V recorded for Cu/ZnNi and Cu/ZnNi/PPy electrodes were due to dissolution of zinc and nickel and formation of zinc and nickel complex with EDTA, while these cathodic peaks for Cu electrode were not seen in this potential. The single peak corresponding to the anodic dissolution of copper substrate was observed at approx. +0.260 V for Cu and 0.087 V for

Cu/ZnNi and Cu/ZnNi/PPy electrodes. On the other hand, there was a difference between the heights of Cu/ZnNi dissolution peaks and bare Cu metallic dissolution, which could be attributed to the presence of ZnNi alloy plating on Cu electrode. The dissolution current peak recorded for copper dissolution of the underlying ZnNi alloy plating had a low intensity while bare Cu electrode exhibited the highest dissolution peak. This event indicated that the ZnNi layer substantially prevented the dissolution of Cu electrode. Consequently, the formation of complex  $ZnO \cdot H_2O$  and zinc and nickel oxide layers on Cu/ZnNi electrode exhibited an efficient barrier property against the corrosive products. In Figure 3, there were three anodic dissolution peaks for Cu/ZnNi/PPy electrode. The current values recorded for the dissolution peak of copper were the lowest in the presence of the PPy homopolymer film. It was clear that PPy coating on the Cu/ZnNi electrode provided an adequate physical protection to the metal between the corrosive environment and ZnNi alloy plating.

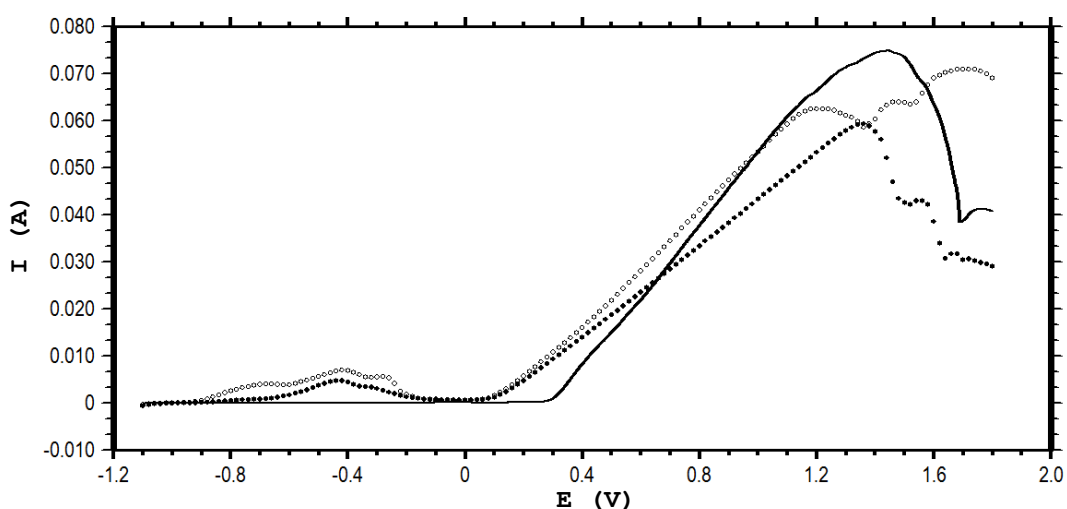


Figure 3. The linear sweep voltammograms for bare Cu (-), Cu/ZnNi (o) and Cu/ZnNi/PPy (•) electrodes in 0.05 M EDTA containing 0.50 M sodium sulfate solution. Scan rate: 5 mV/s

### 4.3. Corrosion Tests

#### 4.3.1. Anodic Polarization Measurements

Anodic polarization curves obtained for uncoated and coated electrodes after 236 h exposure time in 3.5% NaCl solution are given in Figure 4. At this moment, the corrosion potential ( $E_{corr}$ ) values recorded for Cu, Cu/ZnNi and Cu/ZnNi/PPy electrodes were measured as -0.155 V, -0.209 V and -0.108 V, respectively. In the near  $E_{corr}$  region, current values increased so rapidly that there was not any possibility for passivation of the Cu electrode surface under aggressive chloride ions condition. The  $E_{corr}$  value of Cu/ZnNi electrode shifted in the active region due to zinc dissolution than those of Cu and Cu/ZnNi/PPy electrodes. The positive shift in the  $E_{corr}$  value obtained for Cu/ZnNi/PPy electrode simply indicated that PPy film provided an adequate anodic protection to the metal between the corrosive environment and ZnNi alloy plating. This occasion supported that the current values of Cu/ZnNi/PPy electrode were significantly lower when compared with uncoated Cu and Cu/ZnNi electrodes. It indicated that PPy film provided a significant physical property against corrosion products on the Cu/ZnNi electrode. This showed that PPy film synthesized on ZnNi plated Cu electrode had lower permeability and

higher barrier property against the attack of corrosive products like dissolved oxygen and chloride ions.

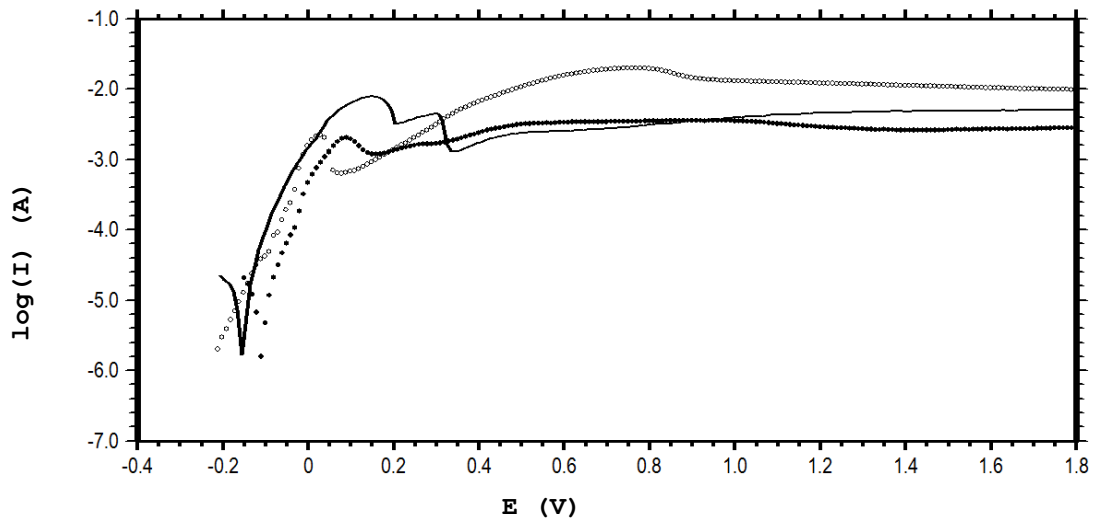


Figure 4. The anodic polarization curves recorded for bare Cu (-), Cu/ZnNi (o) and Cu/ZnNi/PPy (•) electrodes, after 236 h of exposure time in 3.5% NaCl solution, scan rate: 5 mV/s

#### 4.3.2. AC Impedance Technique

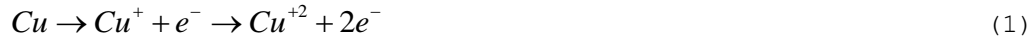
The Nyquist and Bode diagrams of Cu and Cu/ZnNi electrodes are given in Figure 1(b), 168 hours immersion times in 3.5% NaCl solution. There were two depressed semicircles for all of electrodes ranging from high frequency to low frequency. The sum of diameters of these depressed semicircles was equal to the polarization resistance ( $R_p$ ) [5]. The depressed semicircles obtained from the Cu electrode were equal to  $R_p$  including the total of the charge transfer resistance ( $R_{ct}$ ) that is responsible for the anodic dissolution of bare Cu metal and diffusion resistance ( $R_d$ ) for the high frequency region and oxide layers ( $R_o$ ) for the low frequency region ( $R_p=R_{ct}+R_d+R_o$ ). At the same time, the  $E_{ocp}$  value of bare Cu electrode was found to be approx. -0.199 V, while that of the Cu/ZnNi electrode was -0.141 V. This showed that ZnNi alloy plating exhibited an important physical property against corrosive products on copper electrode.

This result suggested that, the  $R_p$  value corresponding to the depressed semicircles for Cu/ZnNi electrode was relatively higher when compared with that of the bare Cu electrode. This  $R_p$  value obtained for Cu/ZnNi electrode was the sum total of the  $R_{ct} + R_d$  for high frequency and the sum of the resistances of alloy coating ( $R_{alloy}$ ) +  $R_o$ . The  $R_{ct}$  was responsible for the anodic dissolution of copper surface, while oxide layers were produced by zinc and cobalt metals. These plots for Cu/ZnNi/PPy electrode consisting of two depressed semicircles included the  $R_{ct}$  resistance in the high frequency region and the  $R_o+R_{alloy}+R_{pf}$  (polymer film resistance) for the low frequency region that was equal to  $R_p$  resistance. After 22 h of immersion times, the  $R_p$  value obtained for Cu/ZnNi/PPy electrode was relatively higher when compared with those of Cu and Cu/ZnNi electrodes. It is clear that PPy coating exhibited an efficient barrier property against the corrosion products, whereby providing a decrease in diffusion rate of ions. Consequently, corrosion resistance was highest in the presence of Cu/ZnNi/PPy electrode. At the same time, this case could be explained by the decrease in porosity properties of coating on the surface. The



$R_p$  value of Cu electrode increased due to the formation of stable oxide layers, while the depressed semicircles corresponding to Cu/ZnNi and Cu/ZnNi/PPy electrodes in the low frequency region turned into linear part, after 236 h of exposure time. The linear part for Cu/ZnNi and Cu/ZnNi/PPy electrodes indicated the effective barrier behavior of coatings. This linear part showed a typical charge transfer process occurring under diffusion control. This established that, Cu/ZnNi and Cu/ZnNi/PPy electrodes exhibited efficient barrier behavior and prevented corrosion products from attacking the base metal.

In the Nyquist and Bode curves of Cu/ZnNi electrode, the transformation from the capacitive semicircle to linear part could be ascribed to the significant phenomena revealing a change to passive the ZnNi at the metal/solution interface. This case indicated prominent differences by the formation of passive oxide layers on the Cu/ZnNi surface. In the presence of Cu/ZnNi/PPy electrode, the formation of protective oxide layers and the improvement of the barrier property of the coating were provided by the reduction in polymer coating at the alloy/polymer interface. Consequently, the electrochemical processes enhanced the resistance of a coating on the surface while the permeability of polymer film decreased. Thus, these electrochemical processes occurring at the metal/polymer interface led to the formation of protective zinc and nickel oxides on metal surface and improved the barrier behavior of PPy coating. Anodic and cathodic reactions which occurred at alloy/polymer/solution interface are given below.



P: Polymer film A: Anion in electrolyte solution

These reactions seem to be possible with ion diffusion processes taking place through the pores of the PPy coating on ZnNi alloy plating surface. Because of its barrier behavior, the PPy coated electrode exhibited highest corrosion resistance by high  $\theta$  value at the low frequency region, in relevant  $\theta$ -log (f) diagram.

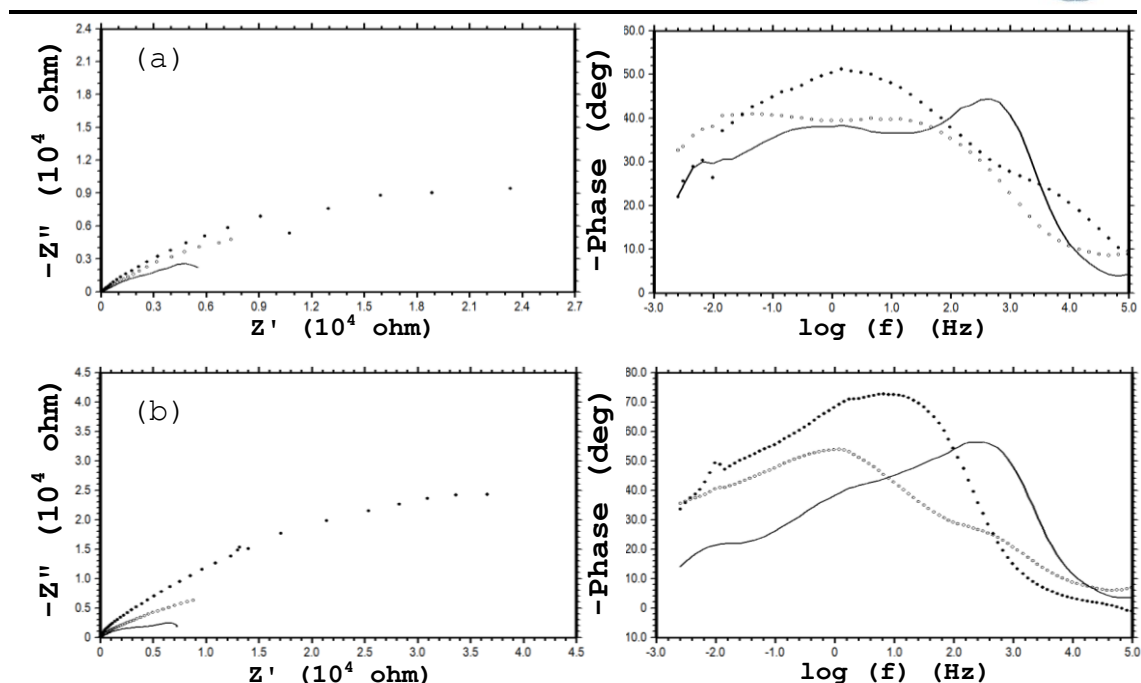


Figure 5. The Nyquist and Bode plots recorded for bare Cu (-), Cu/ZnNi (o) and Cu/ZnNi/PPy (•) electrodes after 22 and 236 h of exposure time in 3.5% NaCl solution

## 5. CONCLUSIONS

In this study, zinc-nickel alloy plating was electrochemically deposited on copper applying current of 7 mA with chronopotentiometry technique and had more homogenous and smooth structure. PPy coating was successfully synthesized on Cu/ZnNi electrode applying cyclic voltammetry technique. Homogenous and adherent PPy film was produced from 0.10 M pyrrole containing 0.20 M NaOx solution. It was found that, the passivation of ZnNi alloy surface was necessary for the homogenous polymer film synthesis prior to monomer oxidation and film growth. The corrosion performance of the bare Cu electrode was compared with PPy coated Cu/ZnNi and Cu/ZnNi electrodes. The single ZnNi alloy plating exhibited significant physical barrier behavior on copper. PPy coating provided an increase in corrosion resistance of Cu/ZnNi electrode. The corrosion performance of Cu/ZnNi/PPy electrode improved the formation of ZnNi oxide layers and the reduction of PPy coating, by the electrocatalytic behavior of PPy film, in time.

## NOTICE

This work was presented at the 14<sup>th</sup> International Corrosion Symposium held in Bayburt between 5-7 October 2016.

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