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The corrosion performance of polyaniline film modified on nickel plated copper in aqueous *p*-toluenesulfonic acid solution

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Abstract

Polyaniline (PANI) coatings were synthesised on 1 μm Ni plated on copper (Cu/Ni). Polyaniline films were achieved under cyclic voltammetric conditions in 0.1 M aniline containing *p*-toluenesulfonic acid solution. Polyaniline coatings which indicated that the *p*-toluenesulfonic acid solution was a suitable medium for the formation and deposition of polyaniline on a Cu/Ni substrate. Electrochemical polymerization of polyaniline resulted in the deposition of uniform, compact and strongly adherent PANI coatings on Cu/Ni . Their corrosion protection performance in 3.5% NaCl was investigated by using the AC impedance spectroscopy (EIS) technique and anodic polarization curves, which showed that polyaniline coating exhibited a significant physical barrier property against the attack of corrosive products on nickel plated copper, for longer periods and drastically reduced the corrosion rate of copper. It was found out that the barrier properties of the polyaniline coating was improved by its catalytic behaviour on formation of freshly produced nickel oxide layers and the reduction of polymer film at metal/polymer interface.

Keywords: Impedance spectroscopy; Plating; Copper; Multilayer

1. Introduction

In industry, metallic coatings such as nickel and zinc have been widely used for many years, in numerous applications. These substances are used to improve the corrosion resistance of oxidizable metals [1–4]. Among well-known metallic coatings are nickel plating and its alloys, which have drawn particular interest of many investigators on account of their decorative feature as well as their practical use as anticorrosive coatings. The nickel plating and its alloying components are widely used for many applications such as the improvement of corrosion resistance of the components used as mechanical parts in particularly automotive industry. Rossi et al. [5] clearly describe the behaviour of some industrial coatings on carbon steel, utilised to improve tribological behaviour. However, single layer nickel plating for anticorrosive purpose is insufficient to protect the oxidizable metals. On the other hand, an additional application such as chromate conversion coatings, phosphate coatings and conducting polymer top coatings on nickel layer increases the total thickness of coatings and contributes to the corrosion resistance of electrodepositing metals [6–10].

Recently, the use of conducting polymers on mild steel and copper as a protection against corrosion has been reported [11–15]. Numerous studies have been reported on the possible use of polyaniline coatings against corrosion, under various conditions. To form polyaniline film, it is necessary to build up electrochemical conditions, which will affect the passivation of the metallic surface. To this end, electrosynthesis of polyaniline film on mild steel in oxalic acid solution has been reported to be suitable for use in protection of components. As yet, rather slow coating rate of polyaniline restricts it to be of any industrial interest [16–22].

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There are no reports devoted to the corrosion protection properties of polyaniline coatings when applied to copper based alloys and nickel plated copper used successfully in many different industries including automotive and electronic industries due to their desirable physical and mechanical properties.

The purpose of this study was to synthesise adherent PANI film on 1 μm thick Ni plated Cu and electrochemical synthesis of polyaniline was carried out in 0.1 M monomer containing *p*-toluenesulfonic acid (PTSA) solution. Afterwards, the corrosion performances of Ni plated electrodes with and without a top coat were investigated in 3.5% NaCl solution.

2. Experimental

All electrochemical experiments were performed in a single compartment cell with three electrode configurations. The reference electrode was Ag/AgCl (sat., KCl) electrode and the counter electrode was a platinum sheet with a surface area of 2 cm^2. In this study, A CHI 604 model electrochemical analyzer (serial number: 6A721A) under computer control was used in electrochemical experiments. All electrode potentials were referred to the Ag/AgCl electrode. The working electrode had a copper surface (Cu) measuring 0.50 cm in diameter with a composition of 99.89%. Copper electrodes were embedded in a thick polyester block. In order to remove any existing passive film, the surface of working electrodes was polished using 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.

Nickel plating (Cu/Ni) was carried out using a bath based on 30 $NiSO_4$, 1.0 $NiCl_2$ and 1.25 H_3BO_3 by weight % and pH was between 5.6 and 6.2. The thickness of plating was determined by the estimation of the passing charge amount applying 3 mA constant current. The thickness of Ni plating obtained was estimated to be about 1 μm. Ni anode used for plating was estimated to have a surface area of 0.64 cm^2 (99.9% purity) and all nickel plating was obtained by stirring the solution under atmospheric condition.

Aniline was freshly distilled and stored in the dark. All the chemicals were analytical grade from Merck. PANI coats were electrochemically synthesised using cyclic voltammetry in the 0.1 M aniline containing 0.2 M *p*-toluenesulfonic acid on Cu/Ni.

The corrosion performances of these coating were examined in 3.5% NaCl solution by electrochemical impedance spectroscopy (EIS) and anodic polarization measurements. The EIS measurements were recorded in the frequency range from 10^5 to 10^{-3} Hz using the amplitude of 7 mV.

3. Results and discussion

3.1. Synthesis

Fig. 1 shows the cyclic voltammograms recorded for Pt electrode in monomer free and 0.1 M aniline containing 0.2 M *p*-toluenesulfonic acid solutions. All measurements were taken at scan rate of 50 mV s^{-1}. In the first scan of monomer free solution, the anodic peak at approx. −0.20 V was related to oxidation of Pt itself to its oxides. At continued anodic scan, the current value remained almost constant at approx. 0.10 V up to +0.90 V. A small current increase at approx. 0.90 V was evaluated as the oxidation of Pt itself to its oxides, in cavity region of platinum. Then, the oxygen gas evolution was observed as a current increase at approx. 1.40 V, continuously. At the reverse scan, the reduction of previously produced oxides was observed as a cathodic reduction peak at approx. +0.30 V. In presence of 0.10 M aniline, the current value remained almost constant at approx. −0.20 V up to +0.75 V. The anodic peak formed at approx. 0.80 V was attributed to oxidation of Pt itself to its oxides and its charge value was relatively lower with respect to that total of monomer free medium. The monomer oxidation process was observed at approx. 1.15 V. At the reverse scan of first cycles, the reduction of PANI film was observed as a current increase at approx. 0.40 V. It is significant that the oxygen evolution did not appear up to the potential value of 1.65 V, in presence of aniline.

The first cyclic voltammograms recorded for 1 μm nickel plated copper electrode (Cu/Ni) in *p*-toluenesulfonic acid with and without aniline medium are given in Fig. 2. In monomer free medium, the current remained constant in potential domain between −0.50 V and 0.10 V. The oxidation/passivation peak of Cu/Ni was observed at approx. +0.48 V, in *p*-toluenesulfonic acid solution. The charge amount was found to be about 10.7 C. Then, the current increase at approx. 0.92 V was attributed to another oxidation of the component due to partial destruction of the passive layer. Afterwards, it started to

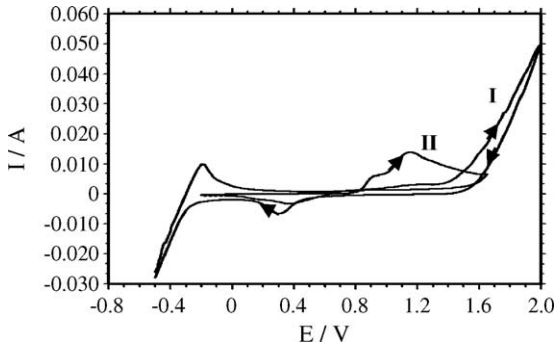

Fig. 1. The first cyclic voltammograms recorded for Pt electrode in monomer free (I) 0.2 M *p*-toluenesulfonic acid solution and in presence of 0.10 M aniline(II), scan rate: 50 mV/s.

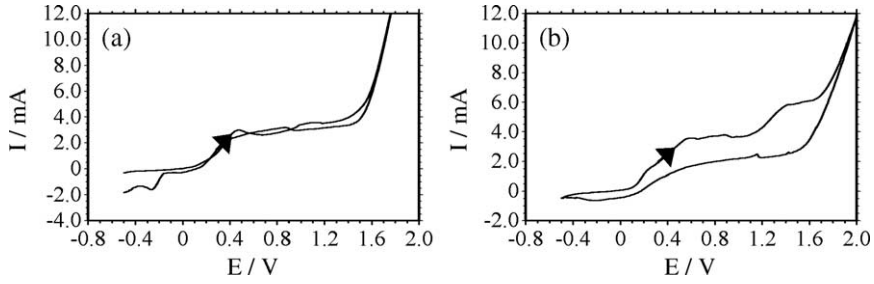

Fig. 2. The voltammograms recorded for Cu/Ni electrode in 0.2 M *p*-toluenesulfonic acid (a) and 0.2 M *p*-toluenesulfonic acid+0.10 M aniline solutions (b), scan rate: 50 mV/s.

increase due to oxygen gas evolution. In the presence of monomer condition, the oxidation/passivation peak and the partial destruction peak of the passive layer shifted to the relatively negative region when compared with monomer free medium and the electrode passivation peak was found as 0.22 V. The potential shift could be explained by inhibitor effect of aniline on electrode surface. The monomer oxidation peak was found to be at approx. 1.41 V. The reduction of freshly produced thin polyaniline film on surface was observed as a current increase at approximately 0.20 V, in reverse scan.

In this study, 30 whole cycles were applied to synthesis of the polyaniline film on 1 μm nickel plated copper electrode (Fig. 3). The thickness of PANI coating was calculated to be approx. 1.38 μm by using the charge amount (Q) involved in emeraldine–leucoemeraldine transition [18,22]. At the anodic scan of first cycle, the monomer oxidation peak was observed at approx. 1.53 V and its charge amount was found to be 1.5×10^{-2} C, as seen in Fig. 3. At the further scanning of second and subsequent cycles, the monomer oxidation peak shifted to upper potential value and the current values decreased regularly with increasing cycle numbers. The anodic peak at approx. +0.42 V was attributed to the conversion of the non-conducting leucoemeraldine form to the conducting emeraldine form and this peak contributed to the formation of redox couple polymer with cathodic peak at almost same potential. The current values of these peaks increased according to film growth on surface. This could be explained by better film growth on freshly thin polyaniline coated surface when compared with that on nickel compound. It was noted that the current increase of redox couple peaks by scan numbers and the observing of the monomer oxidation peak during each cyclic scan at the high potential showed that it was necessary to observe upper potential limit during the film growth [15,21]. It could be seen that the film growth curve recorded for polymer coating produced in *p*-toluenesulfonic acid solution was different from those of oxalic acid solution [7]. It was clearly seen that the upper potential limit of film growth curves in *p*-toluenesulfonic acid solution was relatively higher than the degradation potential value for polyaniline, which was given as +0.75 V. However, the upper potential limit was suitable for homogenous and smooth polyaniline coating, in this medium. This was attributed to the large sulphonate anion because no polyaniline coating was obtained on copper, in p-toluenesulfonic acid solution. On the other hand, the anodic peak at approx. +0.55 V was determined as a degradation products of polyaniline and its current values decreased regularly with continued cycling.

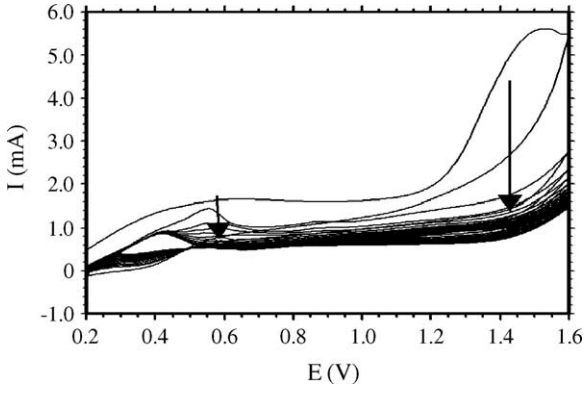

Fig. 3. The voltammograms recorded during the film growth on 1μ nickel coated copper electrode in 0.2 M *p*-toluenesulfonic acid+0.10 M aniline solutions, scan rate: 50 mV/s.

3.2. Corrosion performances

The corrosion performance of PANI coated nickel plating on copper (Cu/Ni/PANI) was investigated in 3.5% NaCl solution, by using AC impedance spectroscopy and the anodic polarization curves. The anodic polarization curves recorded for Cu, Cu/Ni and Cu/Ni/PANI are given in Fig. 4. The current values of bare copper electrode were observed to increase with continued potential values and its corrosion potential (E_{corr}) value was measured as −0.184 V. It should be noted that the uncoated electrode exhibited no passivation behaviour under this corrosive medium. Single nickel plating on copper had relatively nobler potential value corresponding to bare copper and the E_{corr} value was −0.104 V. The current values for Cu/Ni lowered relatively when compared to bare electrode up to potential value of 0.30 V. This was indicating that the nickel metal and its oxide layers exhibited an important physical property against corrosive products on copper electrode. The current increase beyond potential value of 0.30 V increased due to dissolution of nickel oxides. The similar behaviour was also

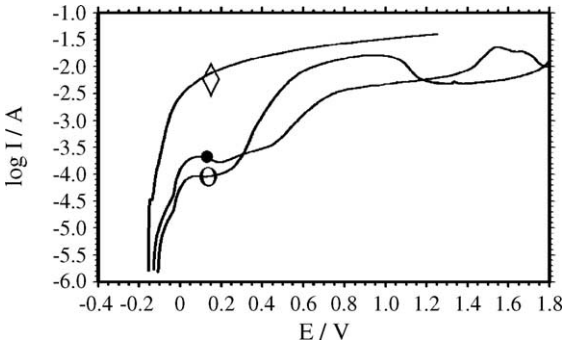

Fig. 4. The polarization curves recorded for Cu (◇) and Cu/Ni (○) after 4 h and Cu/Ni/PANI (●) after 168 h of exposure time in 3.5% NaCl, the scan rate: 4 mV/s.

observed for polyaniline coated nickel plating on copper. However, the current change in potential region between 0.20 and 0.50 V was attributed to transition between oxidation structures of polyaniline and the current values were relatively lower according to single nickel coating electrode. The oxidation of polyaniline film and dissolution of a little amount nickel oxides brought about a current increase for Cu/Ni/PANI, beyond potential value of 0.73 V. The current values of Cu/Ni/PANI were still lower than the single nickel coating electrode as well as uncoated copper electrode, at higher potential region (Fig. 4). The current increase beyond potential value of 1.40 V was evaluated as degradation of polyaniline film.

The Nyquist diagram and phase angle (θ)–log frequency (f) curve of bare copper electrode is given in Fig. 5, for various immersion times in 3.5% NaCl solution. There was a depressed semicircle at high frequency and a linear part at lower frequencies in Nyquist diagrams. The diameter of this depressed semicircle consisted of charge transfer resistance (R_{ct}) and the oxide film resistance (R_o). The total of these resistances must be equal to polarization resistance value (R_p). The linear part was evaluated as diffusion resistance (R_d), which consisted of corrosion products of copper due to being at around 28 of phase angle, in θ–log f curves [12,22–24].

In Fig. 6, the Nyquist plots recorded in 3.5% NaCl solution for 1 μm Ni plated copper electrode are given for various exposure times. There were two depressed semicircles, which cannot be well resolved from each other, in Nyquist plots. The first semicircle at high frequency and the second one at low frequencies consisted of charge transfer

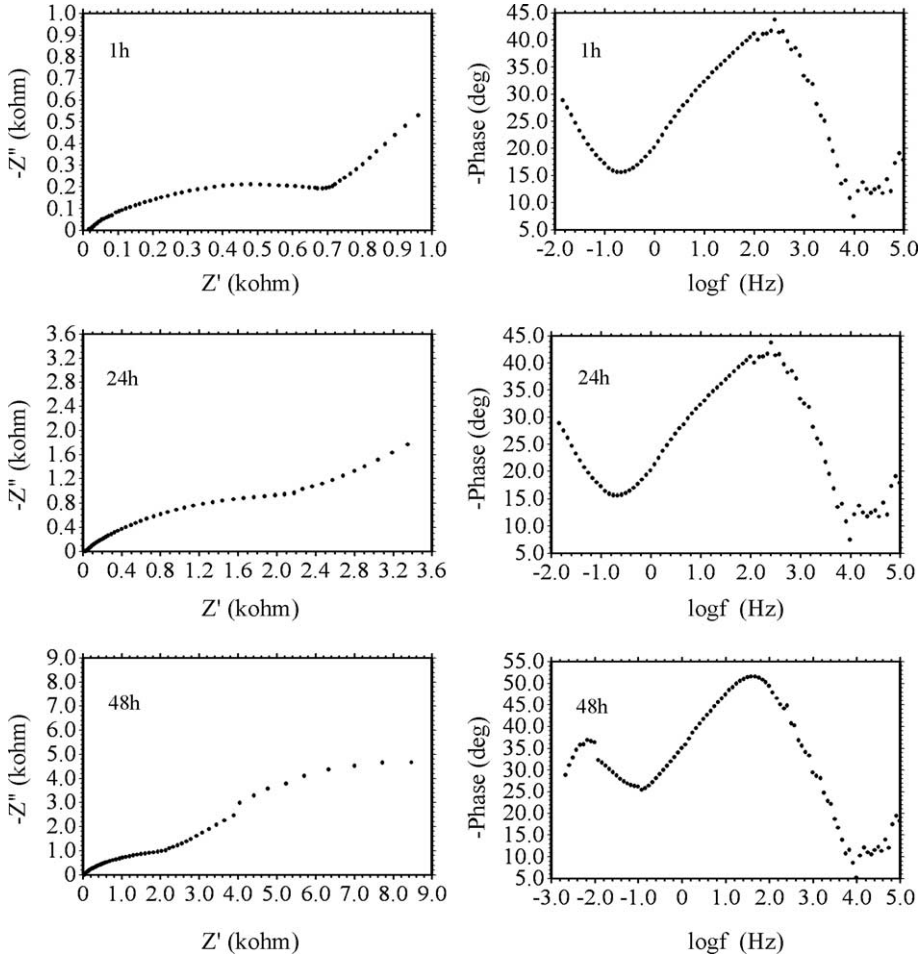

Fig. 5. The Nyquist plot and θ–log(f) curves recorded for uncoated Cu electrode, after 4 h of exposure time in 3.5% NaCl.

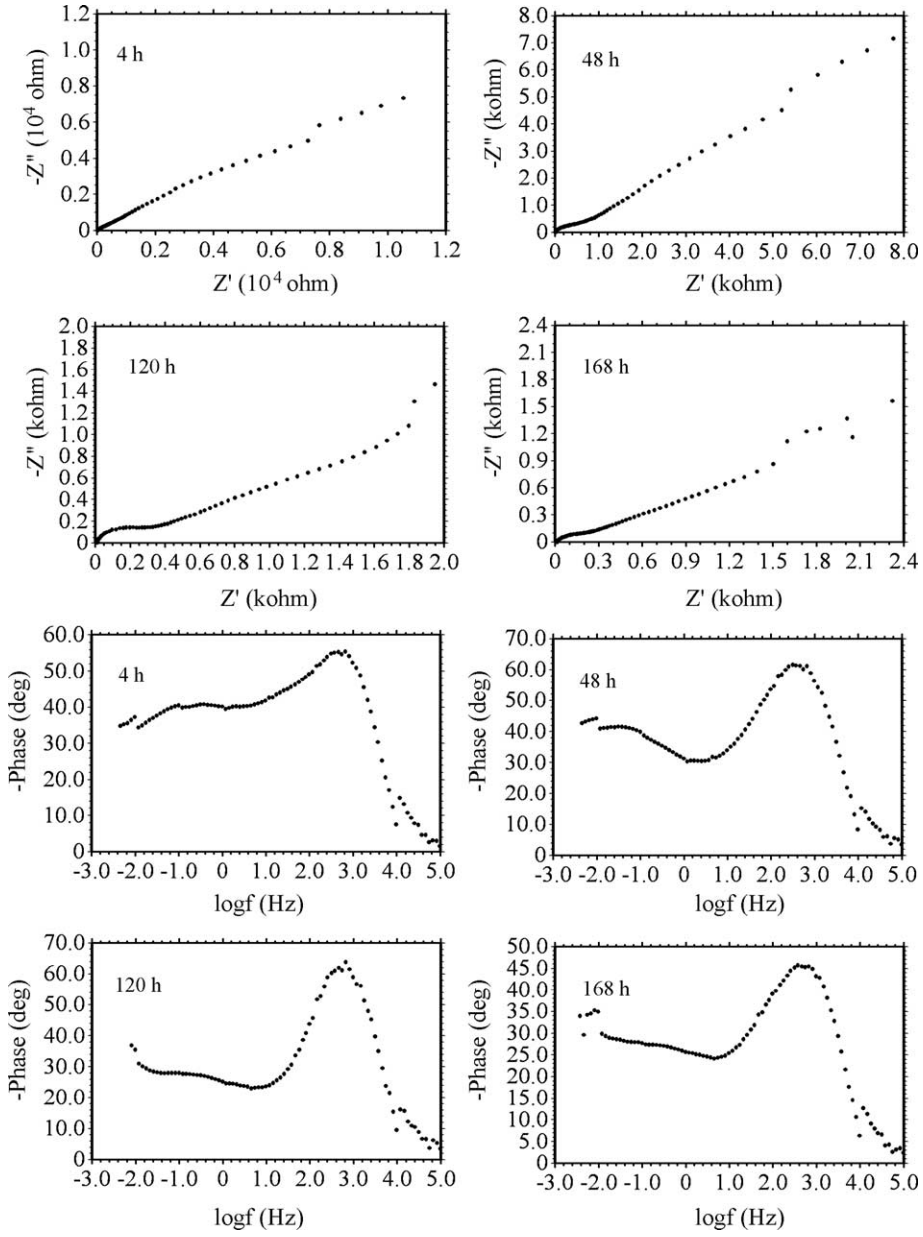

Fig. 6. The Nyquist plots and θ–log(f) curves recorded for Cu/Ni electrode at various exposure times in 3.5% NaCl.

resistance corresponding to oxidation of Ni layer to its oxides and dissolution of copper at the bottom of the pores and film resistance (R_f), respectively [7,22–24]. The sum of these two semicircles was equal to polarizatiom resistance (R_p) and its value was relatively higher with respect to bare copper electrode. This showed the physical barrier property of the nickel metal and its oxide compounds on copper surface. Even though the θ value started to increase at 0.5 Hz, its value had the lower phase angle than 45 at continued low frequency values. Therefore, the linear part could not be regarded as Warburg impedance. After 48 h of immersion time, the R_p value decreased due to an increase in amount of electrolyte solution within the pores of the nickel plating. However, it increased again, 96 h later. This could be explained by quite nobler characteristic of copper when compared with the nickel metal. The nickel oxide layers formed on dissolution of nickel instead of copper. Consequently, these nickel oxide layers contributed to the total R_p value.

Fig. 7 shows the Nyquist results recorded for polyaniline modified nickel coating on copper electrodes (Cu/Ni/PANI), after various exposure times in 3.5% NaCl solution. The feature of Nyquist plot consisted of a well resolved depressed semicircle at high frequencies and a linear region at lower frequencies, after 4 h of exposure time. This depressed semicircle was included to the charge transfer resistance (R_{ct}), oxide film resistance (R_o) and polymer film resistance (R_f) [7,15,22–24]. The polarization resistance (R_p) must be equal to total of these resistances which the diameter of semicircular region. The straight line

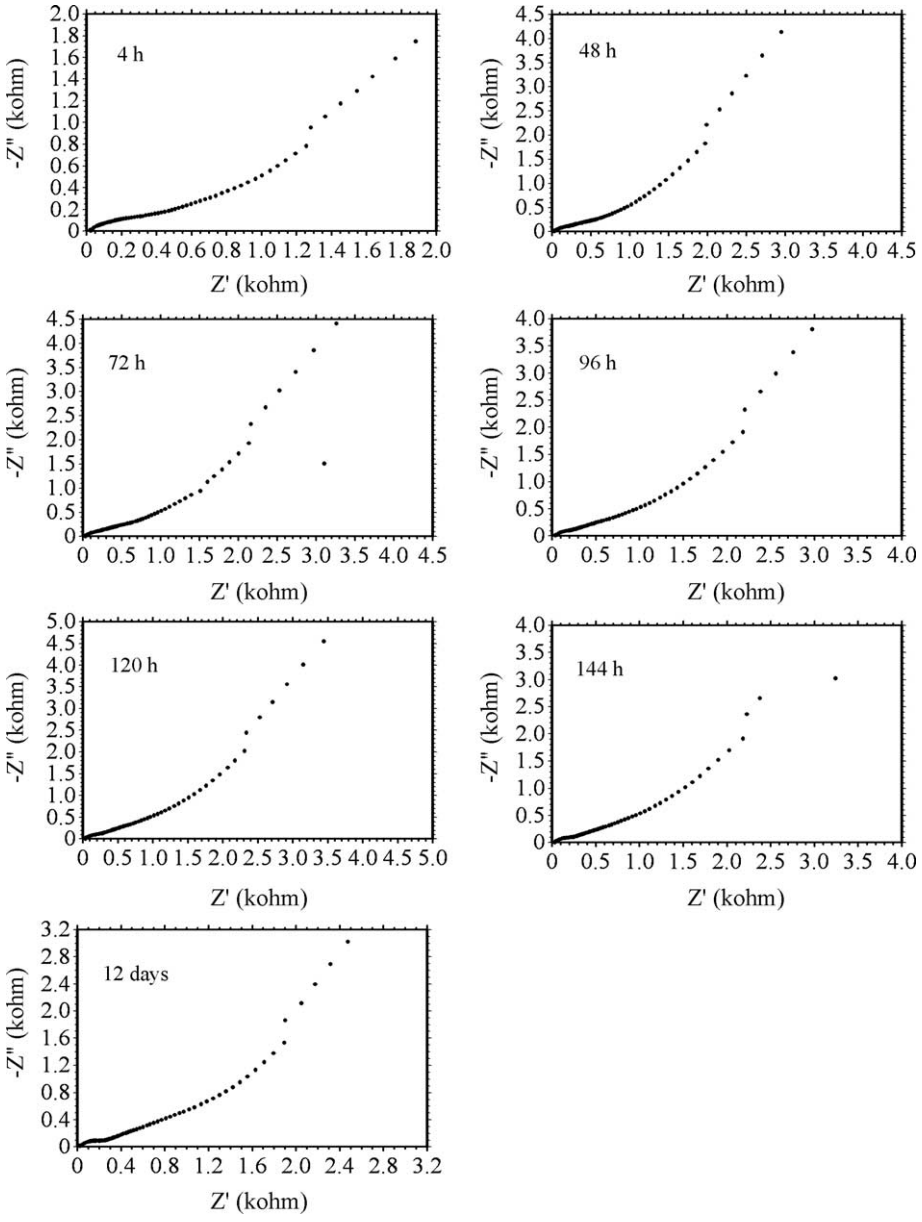

Fig. 7. The Nyquist plots recorded for Cu/Ni/PANI electrode at various exposure times in 3.5% NaCl.

expanding to mid and low frequency region was determined as Warburg impedance indicating the very effective barrier property of coating. In relevant θ–log f diagram (Fig. 8), θ value was found as approx. 45. This value increased constantly, towards the extremely low frequency values, 48 h later. At this moment, this linear part was evaluated as a typical charge transfer process occurring under diffusion control. The charge transfer process was attributed to Ni(II) oxides produced by anodic oxidation of nickel rather than the underlying copper, under accelerating catalytic effect of polyaniline top coat. The catalytic behaviour of polymer film could be explained with the increase in the amount of electrolyte solution at the bottom of the pores. Consequently, while nickel oxide layer was provided on dissolution of nickel which relatively nobler according to copper and the reduction of polymer film was observed at the metal/polymer interface. The reduction of polymer film and the efficiency of freshly produced oxide layer enhanced the polarization resistance, 48 h of immersion time. This case was also observed as an increase in θ value, at low frequency region of relevant θ–log f diagram. The EIS results recorded for 72, 96 and 120 h immersion times were almost identical. The coating system behaved like an almost perfect coating and exhibited the excellent barrier property, during these periods. This was also supported by the relevant θ–log f diagram that the θ value kept its value approx. 55 at minimal frequency region of about 0.003 Hz (Fig. 8). After 144 h, even though the linear part was observed as Warburg impedance, its θ value decreased at minimal frequencies region in the relevant θ–log f diagram. It could be explained by partial break down of passive nickel oxide

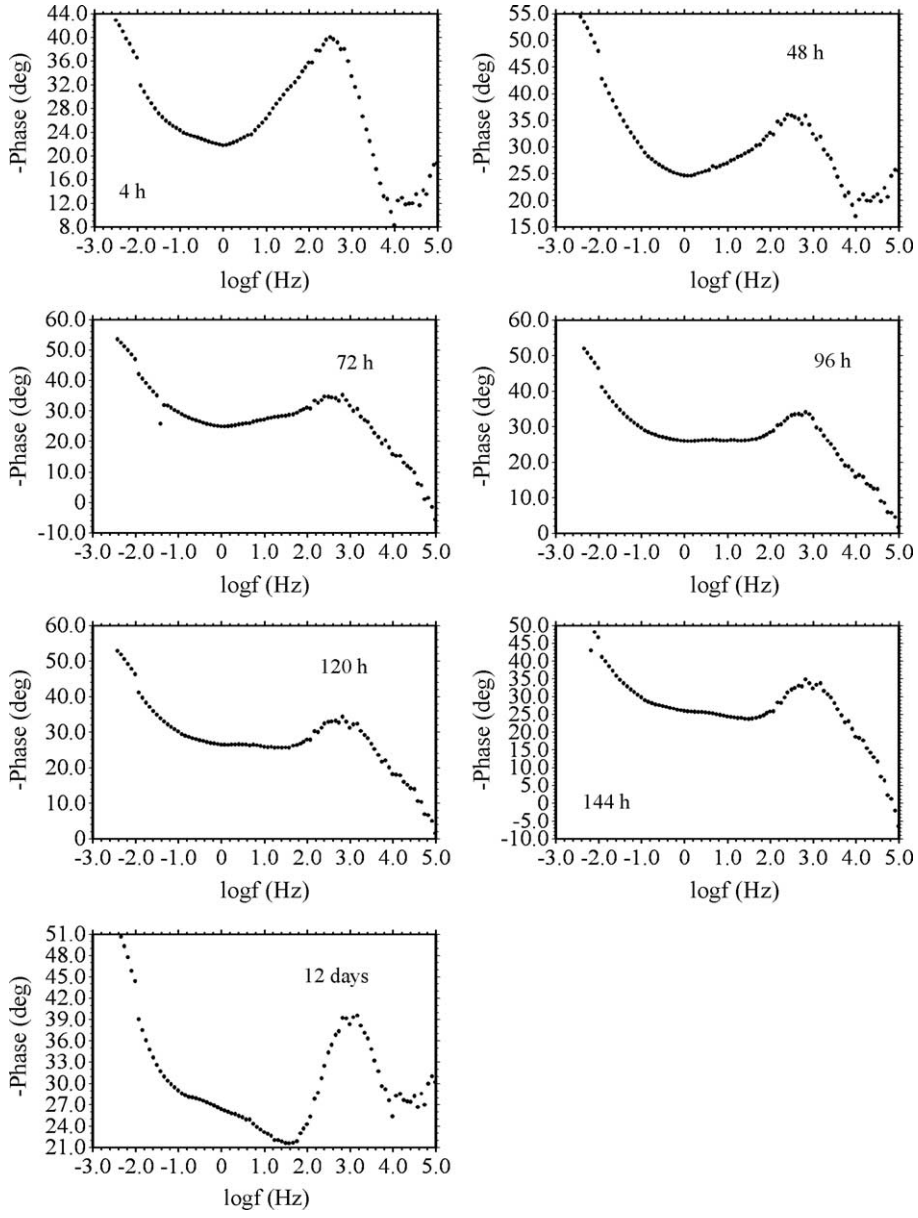

Fig. 8. The θ–log(f) curves recorded for Cu/Ni/PANI electrode at various exposure times in 3.5% NaCl.

layer on electrode surface. Consequently, this event was regarded as the increase in amount of electrolyte solution held within polymer film. After 12 days of exposure time, the clarity of charge transfer resistance was related to anodic oxidation of nickel to its oxides, under catalysis behaviour of polymer coating as discussed above. The Warburg impedance was observed even during these longer periods. Therefore, it was indicating that the polymer film and the formation of protective nickel oxides on surface exhibited an efficient barrier property against the corrosion products and hindered an increase in diffusion rate of ions, in aggressive medium such as chloride ion. It could be easily said that PANI film had much better corrosion performance as a top coat on nickel according to nickel plating.

4. Conclusions

Electrochemical synthesis of PANI coating was carried out successfully on Ni coated copper electrode, by using cycling voltammetry technique. The upper potential limit for PANI film growth in *p*-TSA solution was necessary. Indeed, in the presence of lower potential limit, it was not possible to form an adherent polyaniline coating at the Cu/Ni electrode. The polymer film synthesised in *p*-toluenesulfonic acid solution was uniform, compact and strongly adherent PANI coatings on Cu/Ni and this top coating exhibited much better corrosion performance when compared with single nickel plating, in chloride ions medium. The EIS results showed that the catalytic effect of polymer film played important role on physical barrier property of

nickel and its oxide layers. The accelerating effect of chloride ions contributed to reduce of polymer film at metal/polymer interface on formation of nickel oxides, under catalysis behaviour of polymer coating. In this way, polyaniline coating provided to a significantly protect against attack of corrosive products, in longer periods.

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