Corrosion performances of polyaniline and poly(N-methylaniline) coated stainless steel by impedance spectroscopy

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Electrochemical depositions of polyaniline (PAni) and poly(N-methylaniline) (PNMA) coatings on 304 stainless steel (SS) electrodes were carried out potentiodynamically between −0.2 V and 1.1 V vs SCE with a scan rate of 20 mV/s by using cyclic voltammetry technique from aqueous oxalic acid electrolyte solution. Properties of adhesive and electroactive PNMA coatings were successfully investigated using cyclic voltammetry tecnique. On the other hand, electrochemical impedance spectroscopy (EIS) was used to investigate long-term corrosion performance of PAni and PNMA coated electrodes separately in 0.5 M NaCl and 0.5 M HCl solutions. EIS measurement results showed that PAni and PNMA coatings improved the protection for SS in neutral and acidic corrosive solutions. Also, PAni and PNMA coatings were able to offer the protection to SS electrodes for longer immersion period in NaCl solution when compared to HCl. While PAni coating on steel was insufficient to prevent corrosion after 168 hours of immersion in NaCl, PNMA coating lost its protective properties after 240 hours.

1. INTRODUCTION

Conductive polymers like polyaniline and its derivatives are extensively studied as protective coatings against corrosion of SS electrode [1-4]. More recently, it has shown that the electrochemical synthesis, electrochemistry and structural properties of poly(N-methylaniline) (PNMA) coatings on SS and Pt electrodes were investigated in detail [4]. It was reported that electroactive and conducting PNMA films on 304 SS have been successfully electrodeposited potentiodynamically from an aqueous solution of N-methylaniline (NMA) and oxalic acid by using cyclic voltammetry. Also, linear

voltammetry, Tafel test, chronoamperometry and electrochemical impedance spectroscopy (EIS) techniques were used to investigate the corrosion behavior of PNMA coated stainless steel electrodes in 0.5 M aqueous HCl solutions. The results showed that the PNMA decreased the corrosion rate of stainless steel since it can exhibit effective protective behavior in highly corrosive media containing acidic chloride anions.

On the other hand, recently several papers published about bilayer coatings on oxidable metals by electrosynthesis from aqueous electrolyte solution containing monomers [5-7]. They reported the homopolymers, copolymers and bilayers of PAni and PNMA films electrochemically on mild steel electrodes in an oxalic acid solution [5]. They concluded that when compared to the homopolymer coatings, copolymers and their composite-bilayer coatings exhibited better corrosion protection in a 3.5% NaCl solution. Also, the protection and stability of the PAni/PNMA composite layer are better than those of the PNMA/PAni composite layer [6]. Based on these findings, it was concluded metal–PAni–PNMA showed higher stability and better performance than metal–PNMA–PAni composite-bilayer coatings [5].

The impedance behaviour of bare and conducting polymer coated on SS electrode in neutral and acidic corrosive media provides important information for protective properties and long term protection time of coatings**.** To the best of my knowledge, there is no report on corrosion performance of PNMA coatings on stainless steel electrodes and for investigation of their corrosion performance. In this study, PAni and PNMA coatings were tried to synthesize electrochemically on 304 SS substrates in aqueous media by using cyclic voltammetry, PAni coatings was used to compare to PNMA. Against the corrosion of SS electrode, the protective performance of PAni and PNMA coatings was investigated in aqueous 0.5 M NaCl and 0.5 M HCl solutions via EIS measurements.

2. EXPERİMENTAL

Doubly distilled monomers, aniline (Ani) and N-methylaniline (NMA) were storage under inert atmosphere before using. The cross-section of a stainless steel (AISI 304) wire with a 3mm diameter (surface area = 0.07 cm^2) embedded in a 1 cm diameter Teflon cylinder was used as a working electrode. Before each experiment, the SS electrode was polished by a series of wet sandings using different grit size (180, 320, 600, 800, 1000 and 1200). After mechanical polishing, SS electrodes were rinsed with twice-distilled water. A volume of 100 mL was maintained in a three-electrode electrochemical cell. A Pt plate and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. A CHI 660B electrochemical analyzer was used for all electrochemical studies.

The polymerization was carried out in an aqueous 0.3 M oxalic acid electrolyte solution containing 0.1 M monomer (Ani or NMA) prepared by using twice-distilled water. The PAni films were deposited electrochemically by sweeping the potential between -0.2 V and 1.1 V with a scan rate of 20 mV/s. The electroactivity of coatings obtained on SS discs was tested between -0.2 V and 1.1 V with a scan rate of 20 mV/s in a monomer free electrolyte solution containing 0.3 M oxalic acid. Electrochemical impedance measurements were performed in the frequency range of 10^5 to 10^{-2} or 10^{-3}

Hz with amplitude of 7 mV at the corrosion potential of uncoated electrodes (surface area = 0.542 cm^2) and the coated electrodes with PAni and PNMA films in 0.5 M HCl and 0.5 M NaCl solutions.

3. RESULT AND DISCUSSION

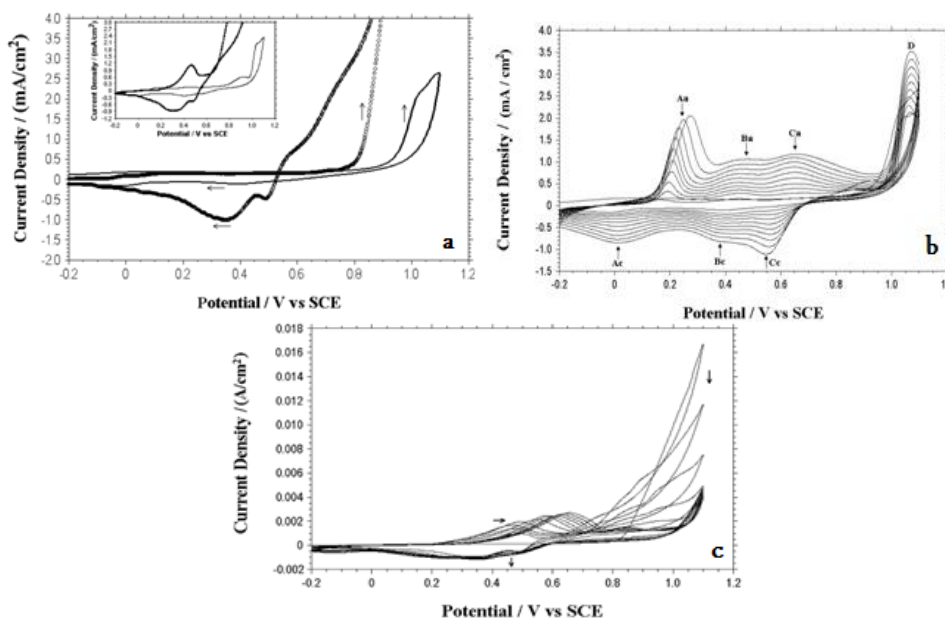*3.1. Electrochemical synthesis of PAni and PNMA coatings on SS surfaces*

Figure 1. Potentiodynamic polarization curves of SS electrode in 0.3 M oxalic acid solution containing 0.1 M Ani and 0.1 M NMA (dot line) in the potential region between -0.20 V and 1.10V vs. SCE at a scan rate of 20 mV/s; a) first scans (inset: tenth scans), b) full scan in Ani and c) full scan in NMA monomer.

As shown in Figure 1(a), electropolymerization of 0.1 M Ani was carried out successfully after each successive scan recorded during in 0.3 M oxalic acid solution between -0.20 V and 1.10 V at a scan rate of 20 mV/s. It can be easily seen that the electrode surface remains in a passive state in a potential window from -0.2 V to 0.92 V vs. SCE. At this stage, a passive oxide layer deposited on the SS surfaces which behavior was a barrier to corrosive ions [8]. This Ni and Cr oxide compounds are stable against the corrosive ions [9]. As seen in Fig 1a (line), an irreversible peak attributed to the oxidation of Ani was start to appear about 0.92 V vs. SCE. First of all, this irreversible peak, which is responsible from the polymerization, resulted in the formation of nucleation on the SS substrate. As a result of nucleation, oligomers and then the growth of polymer chain occured after nine successive potential cycles (see inset of Fig.1(a)). Also, after first cycle, the characteristic peaks for PAni started to appear [4, 10, 11]. Intensified current peak values after each successive scan confirmed an increase in the tickness of the deposited polymer film on the electrode surface (Figure 1(b)). The electropolymerization of NMA exhibits several stages like PAni [11]. In the first scan, an oxidation wave at about 0.82 V vs. SCE can be attributed to the oxidation of NMA monomer. It can be proposed

that the oxidation of NMA shifted to lower potentials (0.82 V) compared to that of PAni (0.92 V) because of the electron donating effect of the methyl group on NMA [4]. Well-defined oxidation and reduction peaks of PNMA indicated the formation and growth of the polymer film (inset in Fig. 1a) when the polymerization was performed between 0.3 and 0.7 V vs. SCE.

As can be seen from the second cycle in the cyclic voltammogram depicted in Figure 1(b), a new peak started to appear at around 0.20 V due to the formation of cation-radicals, which is responsible from the first redox couple of Pani [8]. It is well-known that the first redox couple of Pani exhibited the transformation of PAni from reduced leucoemeraldine (LE) form to the partially oxidized emeraldine (EM) form, and the potential of this redox couple peak is shifted to somewhat positive potentials as a function of increasing number of cycles.

In addition, an increase in cathodic charge density after each successive scan can be thought as the growth of the PAni and PNMA film on the electrode surface (see Figure 2). Furthermore, it can be easily seen than the growth rate of PNMA is higher than that of PAni at the beginning of electrosynthesis. The growth of polymers received almost the same rate after eight cycles. It is concluded that the growth processes of PNMA and PAni are absolutely different from each other.
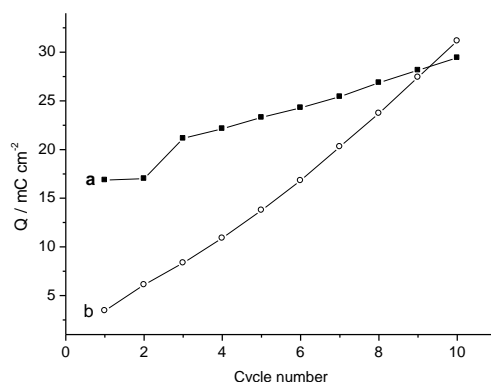

Figure 2. Variation of the cathodic charge density (Q) as a function of cycle number during electropolymerization of (a) PNMA and (b) PAni on the SS surface.

3.2. Electrochemical properties of PAni and PNMA coated SS surfaces

After PAni and PNMA coatings are grown by potential cycling between -0.20 V and 1.10 V, the coated SS electrodes were placed in a monomer free electrolyte solution to perform cyclic voltammetry characterization. Figure 3 exhibited the typical doping-undoping process of the PAni within a potental range from 0.20 V to 0.80 V [8]. LE oxidation to EM at approximately 0.5 V and EM reduction to LE approximately at 0.42 V can be seen in Figure 3 [12]. The results indicated the formation of PAni films on SS surface. Also, as depicted in Figure 3, PAni coated SS electrode lost its electroactivity slowly during successive cycles. However, the electrochemical properties of the PNMA coating on the SS substrates are different than those of PAni coating, which can be inferred from their voltammetric profiles. .
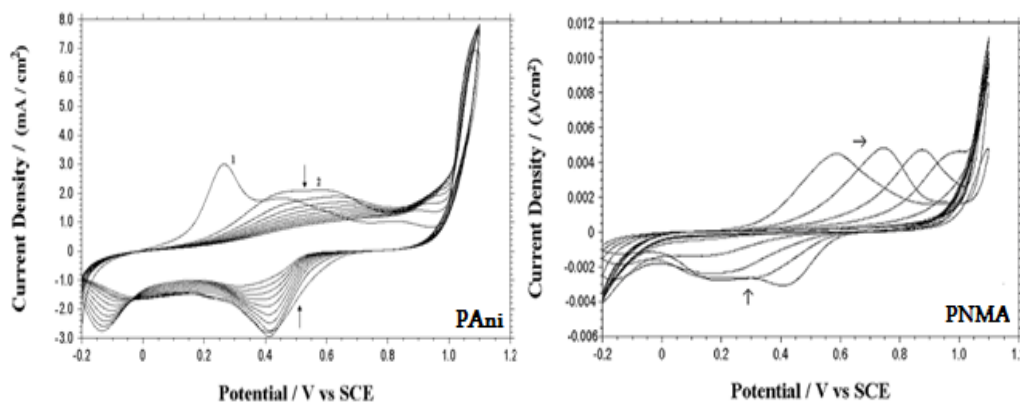
Figure 3. Cyclic voltammograms of PAni and PNMA coated steel electrodes in a monomer-free electrolyte solution of 0.3 M oxalic acid in the potential region between -0.20 V and 1.10 V at a scan rate of 20 mV/s.

During repetitive cycles of PNMA, its oxidation peak continuously shifted to more anodic potentials and the cathodic peak density is decreased gradually, which confirmed that unfortunately, its electroactivity degrades significantly (see Figure 3). Also, the overoxidation of the polymer film was observed as a decrease in electroactivity of the film during the positive potential scanning in the monomer-free oxalic acid medium.

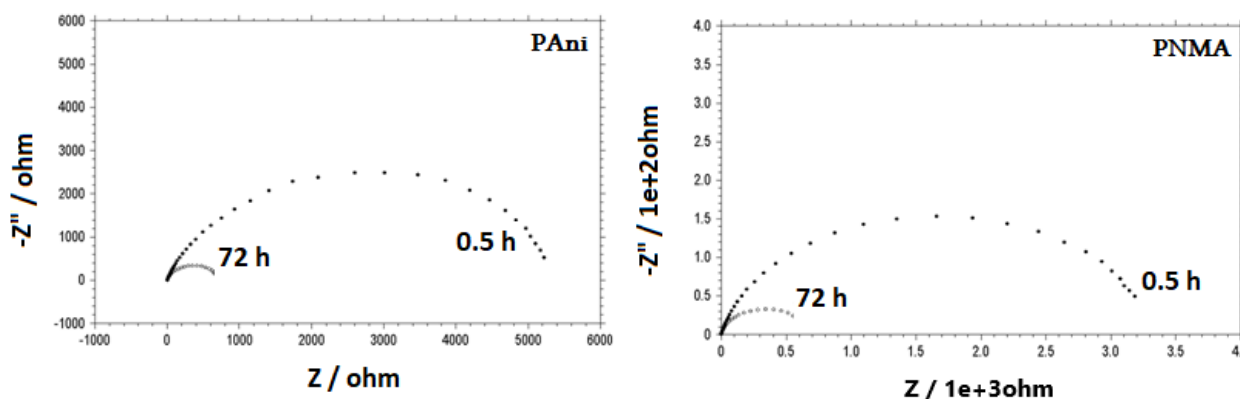*3.3. Long-term corrosion performance of PAni and PNMA coated SS surfaces*

Figure 4. Impedance spectra recorded after immersion time of 0.5 and 72 h of PAni and PNMA coated SS electrodes in 0.5 M HCl solution at open circuit potentials.

Figure 4 showed the Nyquist plot recorded for various immersion times of the SS/PAni and the SS/PNMA electrodes in HCl solutions. The presence of the semicircle loop in the studied frequency region can be attributed to the blocking properties of a rough electrode [13]. This observation confirmed extremely the slow faradaic process of the ionic exchange at the polymer/electrolyte interface. The ohmic resistance (R_s) can be found from the high-frequency intercept of the semicircle on the real axis and the diameter of this semicircle provides the charge transfer resistance (R_{ct}) of the substrate|/electrolyte interface [13, 14]. As represented in Figure 4, the SS|PAni exhibited a high impedance value confirming the protective effect of coating deposited at the beginning of immersion

in corrosive medium due to inhibition of electron transfer [10,15]. R_{ct} is continuously decreased after immersion during 72 h. It can be due to the penetration of corrosive chloride ions on electrode surface without any hindrance [13].

The shape of Nyquist plots for SS|PNMA electrode is also similar to that for PAni. R_{ct} value of the SS|PNMA is higher than that of the SS|PAni, which can be thought as the most protective properties than the SS|PAni. While R_{ct} value of the SS|PNMA is high in the beginning of immersion, it decreases during immersion. It can be concluded that the PNMA coating for protection of SS electrode against the penetration of corrosive acidic chloride anions during exposure time is mostly effective. The results presented in Figure 4 showed that the PNMA coating provides a more effective inhibition of the corrosion of SS in HCl solutions than the PAni coating.
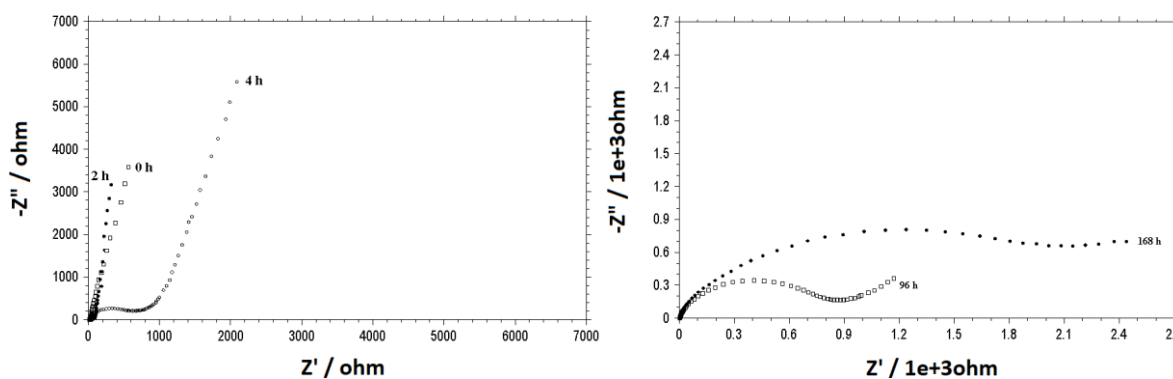

Figure 5. Impedance spectra of PAni coated SS electrode in 0.5 M NaCl solution at open circuit potential after various immersion time.
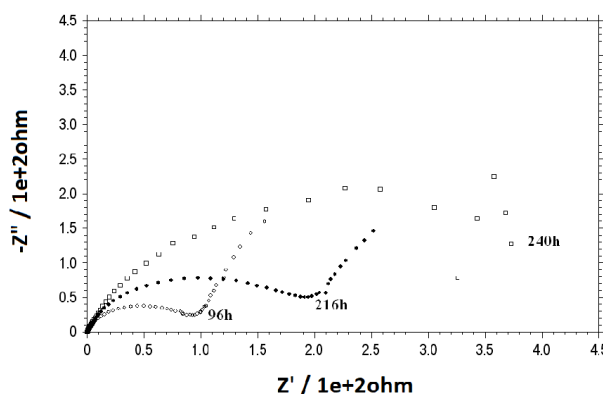

Figure 6. Impedance spectra of PNMA coated SS electrode in 0.5 M NaCl solution at open circuit potential after various immersion time.

Figure 5 and Figure 6 were given for the impedance spectra of the SS|PAni and SS|PNMA electrodes, respectively. Under the light of these spectra, several features have to be described. The impedance curves of all the electrodes showed a depressed semicircle in the high-frequency region and a vertically linear spike in the low-frequency region which is due to the charge diffusion within the conductive PAni layer [16]. It can be seen from Figure 5 that there is only a relatively small variation in the impedance distribution in the low-frequency capacitance during 2 h. It is known that the conductivity and electroactivity of PAni is maximum between the emeraldine and pernigraniline states

[17]. The conductivity of the polymer will be inversely proportional to the R_{ct} value due to redox process between polymer|electrolyte interface: the higher the conductivity, the lower the R_{ct} value [18]. The high-frequency resistance (R_{ct1}) significantly increased after immersion time of 4 h, and doping and undoping of anions occured via diffusion-controlled process, which confirmed Warburg behavior (W). W values are increased during long immersion time, which can be attributed to slightly increased resistive of coating PAni on the electrode against the diffusion of corrosive ions in NaCl solution. As a result, the insertion and the transport rate of anions will be difficult in aqueous neutral chloride solutions from PAni to metal interface.

On the other hand, the SS|PNMA electrodes reflects the similar behavior to Nyquist plots recorded for SS|PAni in NaCl media (see Figure 6). At the beginning of immersion of the PNMA coated electrode in NaCl medium, R_{ct1} value slightly increases during the exposure time of 6 h, and then decreased till 12 h. This decrease can be due to a decrease in the electronic and ionic resistance of PNMA and also the replacement of counter ions in the polymer with oxalate ions in solution.

An increase in W value indicated significantly an increase in the resistive of coating against the diffusion of corrosive ions in the PNMA coated electrode in NaCl solution during long immersion period of 240 hours. This behavior confirmed the presence of a protection mechanism in which the formation of a high-resistance oxide film is induced by electroactive polymer coating [2,4,8-11]. This increase is related to the lowering of the charge transfer rate between the metal and the solution. The charge transfer reactions are known to take place at the metal/polymer interfaces. Consequently, the higher Rct values of all coated electrodes can be explained by the build up of protective passive layers and the effective barrier behaviour of polymer film [4, 5, 7, 12, 18-20].

These results suggested that the conducting polymer coated SS is in its passive state and the passivation remained stable for a long term immersion [9,21]. In conclusion, the insertion and the transport rate of anions will be difficult on the interface of SS|PNMA system in aqueous neutral chloride solution. The electroactive PNMA coating showed effectively the protective properties and the performance in NaCl compared to HCl solution. The foregoing corrosion results obtained from impedance measurements are in full agreement with two different highly corrosive media.

4. CONCLUSIONS

In summary, electroactive PAni and PNMA coatings on 304 SS have been successfully electrodeposited from aqueous solutions of Ani and NMA in oxalic acid by using cyclic voltammetry technique. Corrosion performance of PNMA and PAni coated SS electrodes elucidated by EIS during long immersion time in corrosive HCl and NaCl solutions. Based on the results obtained from EIS measurements, it was confirmed that the PNMA coatings provides a protection against the corrosion of SS in highly aggressive neutral and acidic chloride solutions. When compared to PAni, the PNMA coatings inhibited the penetration of aggressive ions onto the metal surface during long term immersion and induced the pitting corrosion in solutions containing chloride ions. As a result, the PNMA film can be considered as a potential coating material for the corrosion protection of SS in aqueous corrosive solutions for various lengths of time.

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