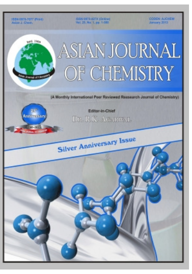
Asian Journal of Chemistry; Vol. 25, No. 5 (2013), 2533-2536

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13443



Ion Exchange and Corrosion Behaviour of Polyaniline Coated Mild Steel Electrode

FATI KARCI[1,*] and MELIKE KABASAKALOGLU[2]

[1]Chemical Programme, Higher Vocational School of Denizli, Pamukkale University, Denizli, Turkey
[2]Department of Chemistry, Faculty of Arts and Science, Gazi University, 06500 Ankara, Turkey

*Corresponding author: Fax: +90 258 2118065; Tel: +90 258 2123788; E-mail: fati@pau.edu.tr

(*Received*: 14 January 2012; *Accepted*: 12 November 2012) AJC-12395

The corrosion behaviour of mild steel and mild steel covered by the electrodeposited polyaniline films was investigated by electrochemical impedance spectroscopy. The electrodeposition of polyaniline coatings on mild steel was carried out by cyclic voltammetry using oxalic acid as the electrolyte. Protective properties of polyaniline coatings were investigated by monitoring the open-circuit potential and by applying electrochemical impedance spectroscopy. Nyquist plots explained as assuming underfilm oxidation at high frequency region and ion exchange process between polyaniline and electrolyte interface performed by oxygen reduction at low frequency region. Polyaniline layer provides corrosion protection due to having high ion exchange polarization resistance between the film and the electrolyte solution.

Key Words: Corrosion, Impedance, Polyaniline, Electropolymerization, Ion exchange.

INTRODUCTION

In recent years there has been increased interest in conducting polymers and the application of these materials in various fields, such as rechargeable batteries[1,2], electrochemical sensors[3], electrochemical capasitors[4] and corrosion resistant coatings[5-8]. Over the last 10 years a great variety of conductive polymers have been tested as corrosion inhibitors or anticorrosive coatings namely polyaniline, polyaniline derivatives and polypyrrole. Polyaniline is one of the important conducting polymers, because of its specific properties, has a highly stable, has synthesized easily and has highly conducting. Polyaniline has different oxidation states namely leucoemeraldine, emeraldine, pernigraniline and emeraldine is the most stable one. The emeraldine base form of polyaniline has been used as a corrosion protecting undercoat on steel and iron samples[9].

Polyaniline has been synthesized on various substrates like iron[10,11], steel[12] and aluminum[13]. It has also been copolymerized extensively with polypyrrole[14,15]. De Berry reported reducing the corrosion rate of stainless steel with an electroactive polyaniline coating in perchloric acid solution[16]. Polyaniline coatings provided a form of anodic protection that significantly reduced the corrosion rate due to the polyaniline redox states capable of maintaining the native passive film on the metal. On the other hand, other authors[17,18] have found that electrochemically deposited polyaniline provided very little corrosion protection to mild steel surfaces.

In the present study, the corrosion behaviour of mild steel in 0.1 M NaCl solution covered by electrodeposited polyaniline film in oxalic acid solution was investigated by ac impedance technique.

EXPERIMENTAL

Mild steel samples were provided in rod form. Suitable lengths of the rods were embedded in Teflon to give a surface area of 1 cm^2.

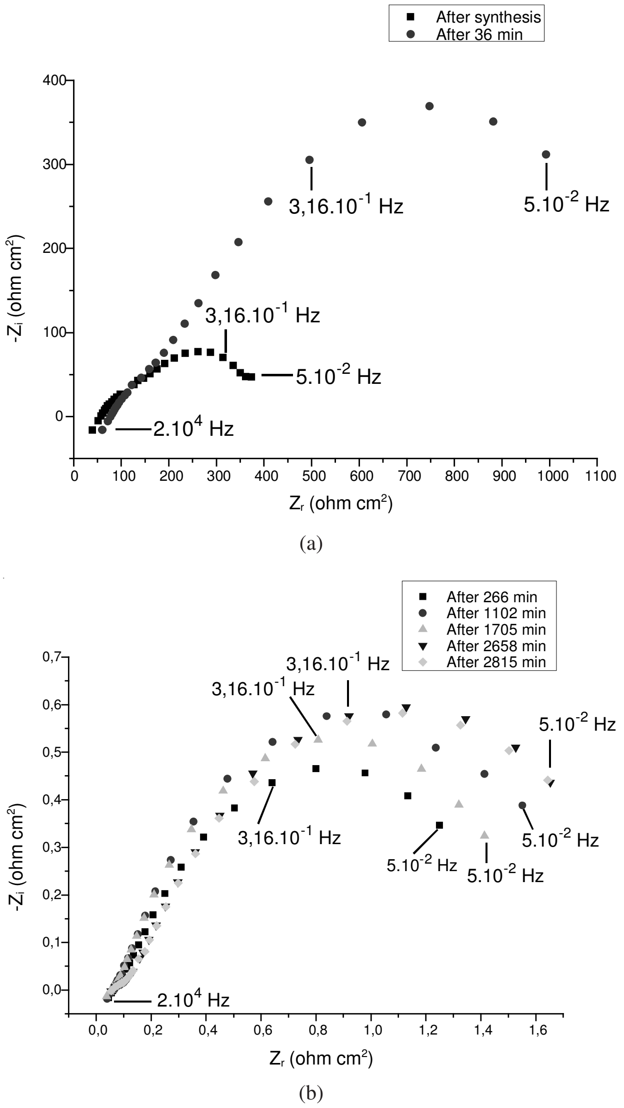
Prior to electropolymerization the samples were polished to a smooth surface finish, using successively finer grades of SiC paper, washed with distilled water and dried under an air stream. The synthesis of polyaniline film was carried out in a standard one compartment three electrode cell with Pt foil (1 cm^2) as counter electrode and mild steel electrode as working electrode. Saturated calomel electrode (SCE) served as a reference electrode.

An aqueous solution of polyaniline and oxalic acid was prepared in deionized water. Aniline and oxalic acid were purchased from Merck chemicals. The concentrations of aniline and oxalic acid were kept constant at 0.1 and 0.3 M, respectively. A Volta Lab 40 (PGZ 301 Dynamic-EIS Voltammetry) potentiostat was used in all studies. Polyaniline film was deposited by means of cyclic voltammetry. Thirty successive scans were applied between -600 to 1500 mV *versus* SCE at 20 mVs^{-1} scan rate. The polymer coated electrodes were washed bidistilled water and then the corrosion behaviour of mild steel covered by the electrodeposited polyaniline films was investigated by the ac impedance technique.

The ac impedance measurements were also carried out at open circuit potentials with a Volta Lab 40 potentiostat. The superimposed sinusoidal voltage signal of 10 mV amplitude was applied. The impedance measurements were carried out in the frequency region of 50 mHz to 20 kHz, taking five points per decade. The real (Z') and imaginary (Z") components of the impedance spectra in the complex plane were analyzed using the Circular Regression programmer in the Volta Lab 40 potentiostat. Soif XJP-6A model metal microscope was used to investigate the changes on polymer covered surfaces after corrosion experiments.

RESULTS AND DISCUSSION

Nyquist plots for the corrosion of polyaniline covered steel electrodes in 0.1 M NaCl solution measured after various exposure times at corrosion potential are shown in Fig. 1. Variation of open circuit potentials of bare and polyaniline covered electrodes with time are given in Fig. 2. Steady-state corrosion potentials were reached after 5 min later.



(a)

(b)

Fig. 1. (a-b) Nyquist plots for the corrosion of polyaniline covered mild steel in 0.1 M NaCl solution measured after various exposure times

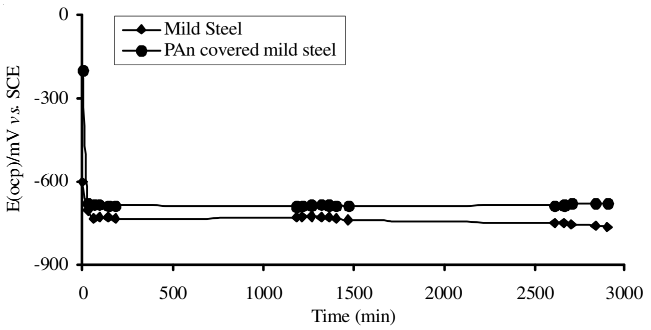


Fig. 2. Open circuit potential-time curve for mild steel (◆) and POLYANILINE covered mild steel (●) in 0.1 M NaCl solution

Nyquist plots show the two capacitive loops, a smaller one at high frequency range followed by a larger one at lower frequencies (Fig. 1a). After 4.5 h one semicircle was obtained in increasing exposure time (Fig. 1b). Impedance data were analyzed by the equivalent circuit given in Fig. 3. R_s is the electrolyte resistance, $C_{m/p}$ is taken as the equivalence to the capacitance of double layer between metal/polymer interface, Z_{Fe} is taken equivalent to pore and the anodic metal dissolution resistance in the pores, $Z_{p/e}$ and $C_{p/e}$ are taken as the polymer/electrolyte ion exchange resistance and capacitance.

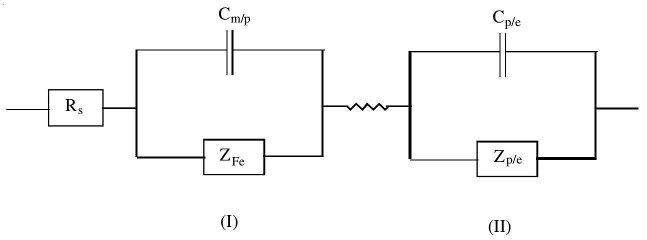


Fig. 3. Equivalent circuit considered for the corrosion of polyaniline coated mild steel in 0.1 M NaCl solution

When the outer surface of covered of polyaniline electrode in contact with the electrolyte water uptake and ionexchange process begin at the same time.

In the present study the first capacitive loop at high frequency region was considered to the processes between metal and polymer film and the second one to the ion exchange processes of polyaniline with the electrolyte. At high frequency region for the analysis of Nyquist plots, equivalent circuit of part (I) was attributed to the dissolution as Fe^{2+} and then passivity of metal with Fe(II) oxalate and Fe(II) hydroxide formation after the pores between metal and polyaniline interface filled with water uptake. For this reason $C_{m/p}$ and Z_{Fe} values were found from the first loop, since the process has shorter time constant, $\tau = RC$ and diminishes with time. Z_{Fe} is taken as the polarization resistance of the corrosion reaction takes place at the interface between metal and polyaniline layer. According to this analysis corrosion rate is high in the pores of the film, but does not proceed further since cathodic reaction in this region is the reduction of emeraldine form of polyaniline accompanied by the concurrent ion undoping processes.

Corrosion process in the pores can be explained as

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1\ a)$$

$$Fe^{2+} + H_2O \rightarrow Fe(OH)_2 + 2H^+ \quad (1\ b)$$

$$Fe + H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^- \quad (2)$$

$$\text{EM(doped with } C_2O_4^{2-}) + 2H^+ + 2e^- \rightarrow \text{LE} + C_2O_4^{2-} \quad (3)$$

In the reduced state polyaniline (LE) has lower conductance then the oxidized states[19]. Moreover precipitation of Fe(II) oxalate and hydroxide filled the pores and hinders further dissolution. After one week immersion time in 0.1 M NaCl solution polyaniline shows good barrier protection and its adhesion to the metal was good. After the experiment, it is scraped hardly from the surface. One can see different colours of polyaniline film and bright steel surface as spots are seen on the scrapped surface of the electrode in Fig. 5(a-f).

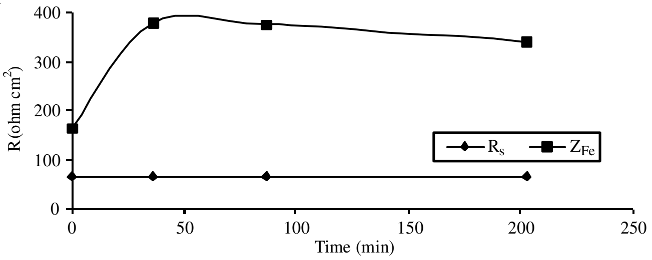


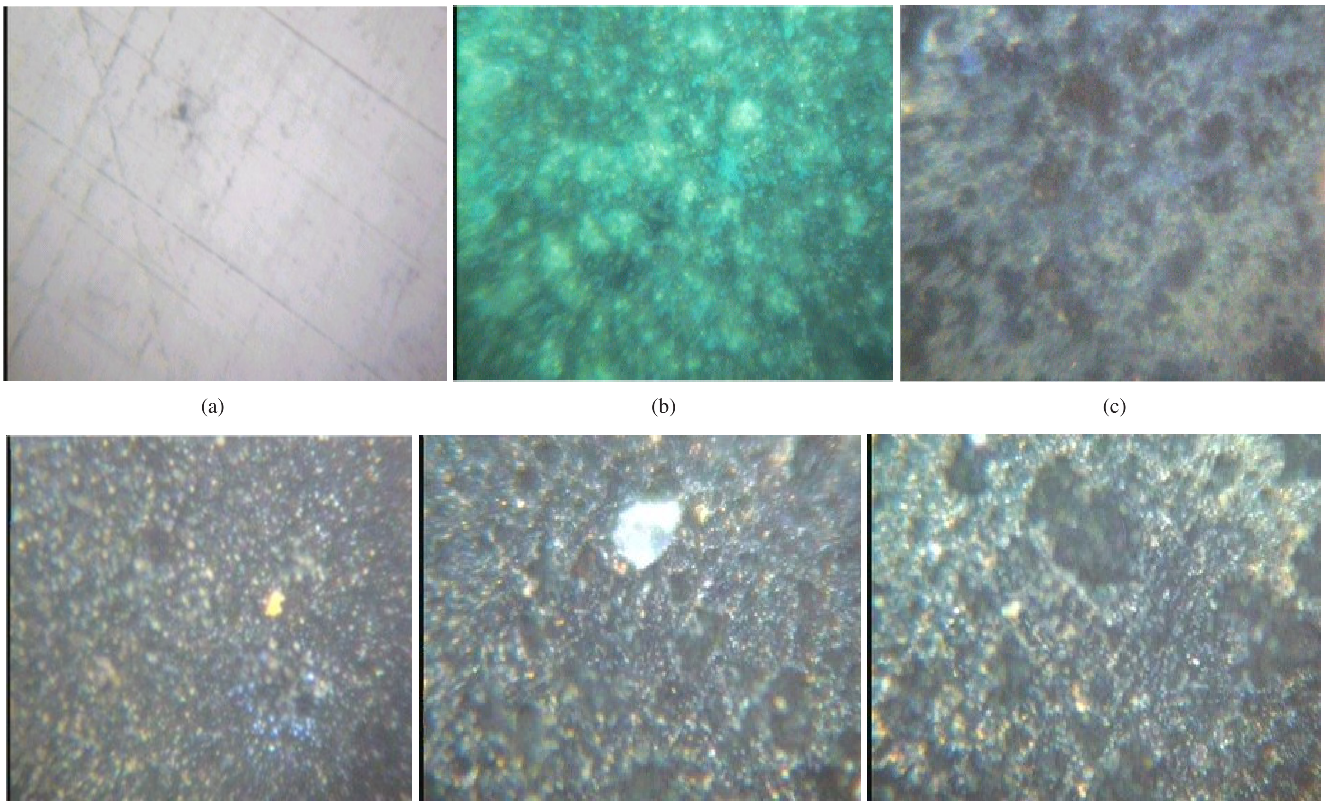
Fig. 4. Resistance for POLYANILINE coated steel during immersion in 0.1 M NaCl solution. R values were found from the first loop of Nyquist plots according to equivalent circuit in Fig. 3

Before the experiments electrode surface covered with polyaniline film by 30 potential cycling between -600 and +1500 mV, green emeraldine structure was seen by naked eyes on the surface. The optic microscopic films of polyaniline covered surface and after exposure time to corrosion in 0.1 M NaCl are given in Fig. 5. Green, black and blue form of polyaniline structures are seen (Fig. 5b-c).

After one week immersion time the steel surface was coated with different colours indicate different polyaniline structures, a semi-oxidized emeraldine green, dark greenish bluish colour of higher oxidation state of polyaniline and black colour of pernigraniline. If we use the resistance value obtained for coated electrode at the high frequency region, corrosion rate of coated steel must be very high. During a short period open circuit potential of coated electrode also shifted toward to more negative values and reaches to corrosion potential of bare steel electrode which indicates corrosion reaction takes place (Fig. 2).

However, there is unimportant corrosion damage underneath of the polyaniline film with respect to bare electrode surface (Fig. 5d-e). This is due to the hindrance of corrosion reaction at metal/polymer interface by leucoemaraldine formation. Reaction (3) converts adjacent polyaniline film to leucoemaraldine structure, less conductive state of polyaniline. In addition, inorganic Fe(II) oxalate and oxide/hydroxide also act as insulating filling materials for pores of the polyaniline film. After the blockage of the pores with iron insoluble salts, ion exchange process became considerable.

Thirty successive scan forms rather thick film on the surface and dielectric constant of polyaniline film is rather high. For this reason, processes between metal/polyaniline and polyaniline/electrolyte take place independently from each other. Wetted polyaniline film oxidized in air and gets black colour of pernigraniline. One can expect the outer surface of polyaniline in contact with electrolyte react with dissolved oxygen. Ion exchange with chloride ions helps emeraldine


(a) (b) (c)

(d) (e) (f)

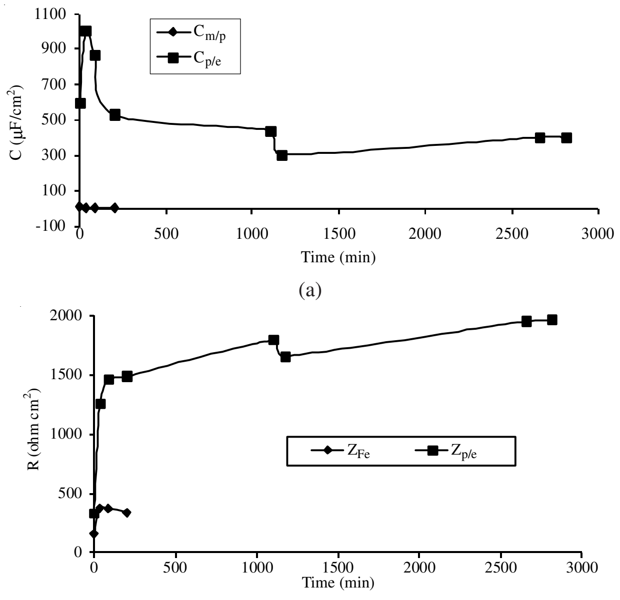
Fig. 5. Optic microscopic films, (a) bare steel surface, (b) after polyaniline covered, (c), (d) after immersion 0.1 M NaCl solution, (e), (f) after polyaniline scraped from mild steel surface (one week immersed 0.1 M NaCl solution)

oxidation. In prolonged exposure time reduction of oxygen and oxidation of polyaniline with ion exchange reaction are the main processes at polyaniline/electrolyte interface.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (4)$$

$$((EMH^+)_2(C_2O_4^{2-}))_y + 2yCl^- \rightarrow 2ye^- + 2yH^+ + yC_2O_4^{2-} + PER(2Cl^-) \quad (5)$$

where $((EMH^+)_2(C_2O_4^{2-}))_y$ shows ($C_2O_4^{2-}$) doped emeraldine form and PER ($2Cl^-$) shows pernigraniline form of polyaniline film. $C_{p/e}$ and $Z_{p/e}$ values were obtained from the circular regression analysis of Nyguist plots in Fig. 1b and shown in Fig. 6. During the open circuit measurements pH of the 0.1 M NaCl solution was also measured (Fig. 7). Before the experiment pH of the solution was 6. After the experiment, it decreased to value 4 in a short time. This is the verification of ion exchange reaction between oxalate and the chloride ions performed with oxidation of emeraldine (Reaction 5).



(a)

(b)

Fig. 6. Capacitance (a), Resistance (b) for polyaniline coated steel after various immersion times in 0.1 M NaCl solution. Circular regression analysis was applied to Nyquist plots in Fig. 1b and part II in equivalent circuit in Fig. 4 is considered

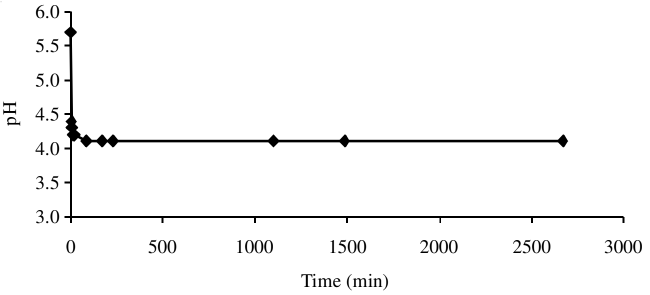


Fig. 7. pH as a function of time for polyaniline coated mild steel immersed in 0.1 M NaCl solution

According to this explanation LE is dominant at metal/polymer interface and pernigraniline form is dominant at the polyaniline/electrolyte interface. There are separated charge regions between two sides of the polyaniline coating. After four hour metal/polymer/electrolyte system reach equilibrium of high capacitance value about 500 μF/cm² and resistance of *ca.* 2000 ohm cm² (Fig. 6).

Conclusion

According to this study polyaniline film contact with the electrolyte has permanently charged positive sites and possess the property of anion exchange in chloride solution. Because of the anion exchange property of polyaniline film, covered steel electrode has a resistance to corrosion process. In addition the films which are deposited on the electrode surface during electrolysis bind strongly to the electrode surface in used solutions. Polyaniline film is also stable in the air.

REFERENCES

1. P.J. Nigrey, D. Maclnnes Jr., A.G. MacDiarmid and A.J. Heeger, *J. Electrochem. Soc.*, **128**, 1651 (1981).
2. A.G. MacDiarmid, S.L. Mu, N.L.D. Somasiri and W. Wu, *Mol. Cryst. Liq. Cryst.*, **121**, 187 (1985).
3. N.C. Foulds and C.R. Lowe, *Anal. Chem.*, **60**, 2473 (1988).
4. A. Rudge, A. Raistrick, S. Gottesfeld and J.P. Ferraris, *Electrochim. Acta*, **39**, 273 (1994).
5. P.J. Kinlen, D.C. Silverman and C.R. Jeffreys, *Synth. Met.*, **85**, 1327 (1997).
6. V. Brusic, M. Angelopoulos and T. Graham, *J. Electrochem Soc.*, **144**, 436 (1997).
7. N. Ahmad and A.G. MacDiarmid, *Synth. Met.*, **78**, 103 (1996).
8. P. Li, T.C. Tan and J.Y. Lee, *Synth. Met.*, **88**, 237 (1997).
9. M. Fahlman, S. Jasty and A.J. Epstein, *Synth. Met.*, **85**, 1323 (1997).
10. S. Jasty and A.J. Epstein, *Polym. Mater. Sci. Eng.*, **72**, 565 (1995).
11. A. Mirmohseni and A. Oladegaragoze, *Synth. Met.*, **114**, 105 (2000).
12. W.S. Araujo, I.C.P. Margarit, M. Ferreira, O.R. Mattos and P. Lima Neto, *Electrochim. Acta*, **46**, 1307 (2001).
13. K.G. Conroy and C.B. Breslin, *Electrochim. Acta*, **48**, 721 (2003).
14. B. Sari and M. Talu, *Synth. Met.*, **94**, 221 (1998).
15. C.K. Tan and D.J. Blackwood, *Corros. Sci.*, **45**, 545 (2003).
16. D.W. DeBerry, *J. Electrochem. Soc.*, **132**, 1022 (1985).
17. F. Troch-Nagels, R. Winand, A. Weymeersch and L. Renard, *J. Appl. Electrochem.*, **22**, 756 (1992).
18. I. Sekine, K. Kohara, T. Sugiyama and M. Yuasa, *J. Electrochem. Soc.*, **139**, 3090 (1992).
19. N.M. Martyak, P. McAndrew, J.E. McCaskie and J. Dijon, *Sci. Technol. Adv. Mater.*, **3**, 345 (2002).