Influence of PANI Layer Protonation Degree on Corrosion Protection of Steel

M. Kraljić Roković, M. Kalić, and Lj. Duić
Faculty of Chemical Engineering and Technology, University of Zagreb,
P.O. Box 177, Zagreb, Croatia

The aim of this work was to study the protective properties of polyaniline (PANI) layers of different degrees of protonation on stainless steel immersed in $c = 0.1$ mol dm^{-3} NaCl solution. Methods of testing were open circuit potential monitoring, and electrochemical impedance spectroscopy. Different degrees of PANI protonation were obtained by keeping stainless steel covered with PANI layer during one day time in solutions of different pH values. The testing solutions were $c = 3$ mol dm^{-3} phosphoric acid solution (pH 0.4), and buffer solutions of pH 4.3 and pH 7.8. Although all PANI layers were tested in the same solution of $c = 0.1$ mol dm^{-3} NaCl, depending on a degree of previously achieved protonation, different protection time of steel samples was obtained. The best protective properties were obtained for steel covered with the PANI layer kept one day in the buffer solution of pH 7.8, before testing, where a complete deprotonation was achieved. The results obtained point out that PANI, under those conditions, presents a physical barrier to the ingress of chloride ions into the passive film, and the electrochemical mechanism of protection is not significantly involved.

Key words:
Polyaniline, electrochemical synthesis, stainless steel, chlorides, corrosion protection

Introduction

It has been shown in a number of papers that emeraldine (EM) state of polyaniline (PANI) can be effective in the corrosion protection of steel,[1–7] and of some other metals like copper[8] and aluminium.[9] Although different states of PANI were tested for corrosion protection of steel, it was mostly protonated emeraldine.[1–5] PANI has the ability to maintain steel in the passivation potential region. The reason for such behaviour is the fact that the potential range of EM overlaps with the passive region of steel, and therefore PANI layer enables stabilisation of the oxide film in an acidic environment. When protonated emeraldine is used, the proposed mechanism is described as an interaction between EM and steel, where EM is reduced to leucoemeraldine (LE) and metal is oxidised. The protection will last as long as EM is present on the metal surface.[1,2,4,5]

However, good protective properties with PANI base, i.e. with deprotonated polymer, were also referred in some papers,[8,10] while in other[11] it was reported that PANI base does not offer corrosion protection. The protection mechanism with PANI base is not clear since PANI base is not a conductive form of PANI.

Some contradictions are also found about PANI protection in chloride medium. There are reports that electrochemically synthesised PANI[1,4] is not suitable for corrosion protection in chloride medium, but there are also reports that electrochemically synthesised PANI can offer an effective corrosion protection in a chloride medium.[12–14]

Deslouis et al. studied polypyrrole layer on mild steel in NaCl solutions.[15,16] They found that the improvement of corrosion protection with polypyrrole in NaCl solutions is achieved by choosing a suitable type of anion. Thus, when oxalate anions are replaced with dodecyl sulfate anions, a permselectivity of the layer changes from anion selective to cation selective layer and better protection is obtained.[16]

Good protective properties of Nafion/PANI composite film in chloride medium were obtained by *Sazou* et al.,[7] and the effects are ascribed mainly to the cation permselectivity of a composite film, but also PANI corrosion inhibiting properties were not neglected.

The aim of this paper was to test electrochemically synthesised PANI layers of a different degree of protonation for corrosion protection of stainless steel in NaCl solution.

Experimental

PANI layers were deposited by cyclic voltammetry from the solutions of $c = 0.5$ mol dm^{-3} aniline using 3 mol dm^{-3} H$_3$PO$_4$ as supporting electrolyte solutions. The potential range of synthesis

*Corresponding author. Tel: +385 1 4597112, Fax: +385 1 4597139,
E-mail address: mkralj@marie.fkit.hr

was from –400 mV to 1000 mV at the potential scan rate ν = 50 mV s^{-1}. Polymer layers of the same amount of charge (Q_A = 16 mC cm^{-2}), i.e. of the same thickness (0.32 μm) were synthesised. The charge, Q_A, necessary to switch PANI from leuco-emeraldine (LE), the reduced form of PANI, to emeraldine (EM), the oxidised form of PANI, was calculated by integrating the area under the current peak A (Fig. 1).[1] The working electrode was stainless steel-disc (A = 0.95 cm^2). Pt-foil served as the counter electrode and Ag/AgCl (3 mol dm^{-3} KCl) as the reference electrode. The stainles steel sample was AISI 420 (χ = 13 % Cr, max.: 1 % Si, 0.03 % S, 0.04 % P, 1 % Mn; C > 15 %). All the potentials are referred to Ag/AgCl reference electrode. Stainless steel samples were polished using 600 grit emery paper, washed with bi-distilled water and, finally, with ethanol.
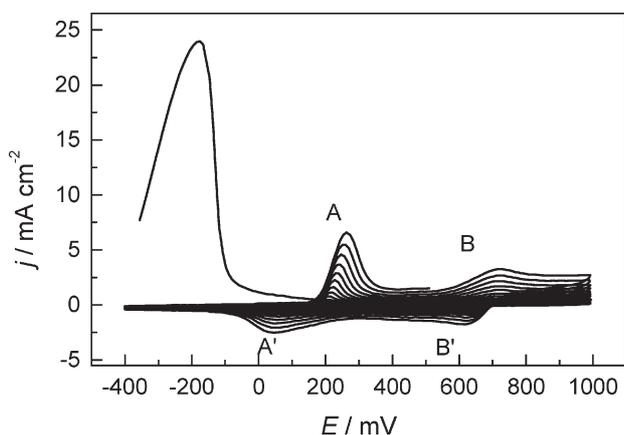
F i g . 1 – *Cyclic voltammograms of PANI layer growth. c_{an} = 0.5 mol dm^{-3}, c_{el} = 3 mol dm^{-3}, ν = 50 mV s^{-1}*

Solutions of different pH values were prepared as follows: c = 3 mol dm^{-3} H$_3$PO$_4$ (pH 0.4) and Sorensen's phosphate mixtures of Na$_2$HPO$_4$ × 2H$_2$O and KH$_2$PO$_4$ of different ratio to obtain pH 4.3 and pH 7.8. The pH value of NaCl solution amounted to 5.6. All the solutions were prepared using bi-distilled water. All the chemicals used were of analytical grade.

The voltammetric experiments were carried out using a potentiostat (Wenking, LB75L), a function generator (Wenking, VSG 83), and a PC for storing and evaluating the results. EIS measurements were carried out using a potentiostat (EG &G PAR Model 263), and a frequency response detector (EG&G PAR Model 1025). The superimposed sinusoidal voltage signal of 5 mV amplitude was applied. Data were collected within the frequency range of f = 10^5 – 10^{-2} Hz, taking five points per decade.

Results and discussion

Cyclic voltammogram showing synthesis of polyaniline (PANI) on stainless steel is illustrated in Fig. 1. In the first cycle a current peak, representing an active to passive state transformation, is obtained at –150 mV, but on the repeated scanning through the same potential region that current peak is no longer observed. Current peaks, characteristic for PANI, are also registered. Current peak A, representing leucoemeraldine (LE) to emeraldine (EM) transformation, develops at 250 mV, and current peak B, representing EM to pernigraniline transformation, develops at 750 mV.

The electrode coated with PANI layer, after the synthesis is immersed in the supporting electrolyte solution, and poised at 500 mV to convert the layer from LE form in EM form. After that the electrode is transferred to 3 mol dm^{-3} phosphoric acid solution (pH 0.4), or in buffer solutions (pH 4.3, pH 7.8), and the open circuit potential (E_{oc}) is monitored (Fig. 2). The obtained difference in E_{oc} is a consequence of a different degree of PANI protonation. The electrochemical impedance measurements where done at E_{oc} in order to characterise each stainless steel-PANI electrode investigated. Bode diagrams for PANI layers, maintained at different pH values during one day, are represented in Fig. 3. It is evident that at pH 0.4 and 4.3 the capacitive behaviour, a characteristic of protonated EM, is obtained within the range of medium to low frequencies, while in the solution of pH 7.8 a high resistance of the order of magnitude ca 10^5 Ω cm^2 is obtained at the lowest frequencies, indicating that the PANI layer is deprotonated.

The corrosion protection of stainless steel covered with polymer layers was tested in c = 0.1 mol dm^{-3} NaCl solutions (Fig. 4). The longest protection period is achieved with the sample maintained
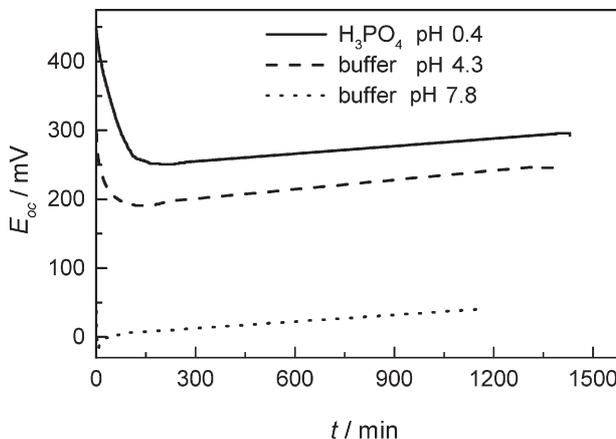
F i g . 2 – *The open circuit potential (E_{oc}) vs. time dependences for stainless steel electrode coated with PANI in different solutions*
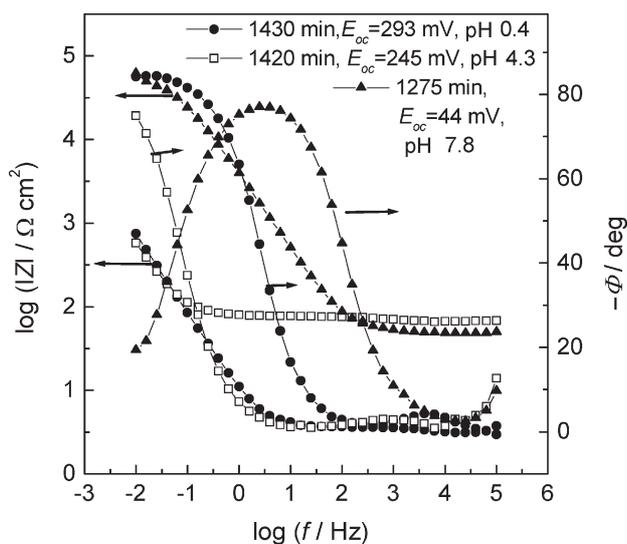
Fig. 3 – *Bode diagrams for stainless steel electrodes coated with PANI layer and maintained during one day in different solutions*
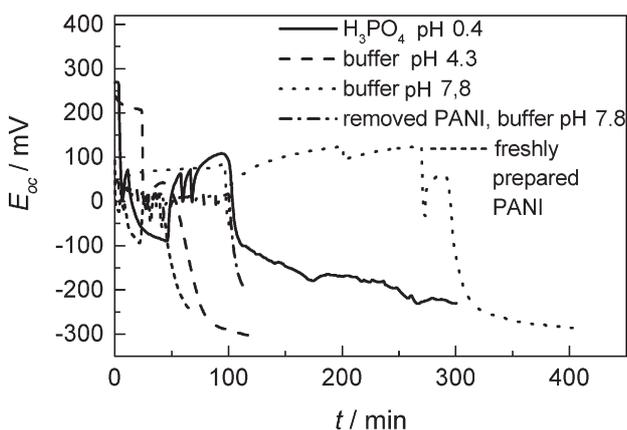
Fig. 4 – *The open circuit potential (E_{oc}) vs. time dependences for stainless steel electrodes coated with PANI tested in c = 0.1 mol dm^{-3} NaCl solution*

Fig. 5 – *PANI SEM micrographs of the PANI layer maintained during one day at a) pH 0.4 and b) pH 7.8*

in a buffer solution of pH 7.8. At that pH PANI layer is completely deprotonated, while at two other pH values the layers are not deprotonated, which was shown by electrochemical impedance spectroscopy (EIS) measurements. Although all the investigated layers are, for the sake of testing, immersed in the same solution of $c = 0.1$ mol dm^{-3} NaCl, the effect of the pretreatment in solutions of different pH values is evident. The deprotonation induces a change in layer structure due to the expulsion of counter-ions causing the "free volume" within the polymer layer to decrease,[17] and thus a more compact layer is obtained. The evidence for more compact structure of PANI layer kept in pH 7.8, compared to PANI layer maintained in pH 0.4, is evident from SEM images shown in Fig. 5 a-b. The ingress of Cl$^-$ ions through such a compact layer is slowed down, compared to layers where no depro-

tonation was attained. In that way better corrosion protection of the underlying steel is achieved.

These results are in accordance with the results obtained for PANI layers modified with *ortho*-phenylenediamine additions. Namely, layers modified with *ortho*-phenylenediamine additions are more compact, thus providing better corrosion protection even in a chloride medium.[18]

However, beside the ingress of chloride ions through the pores, there is also a possibility of ion exchange effects.[15, 16] Thus, chloride ions in the solution can exchange counter-ions present in the layer ($H_2PO_4^-$ or HPO_4^{2-}) which is an alternative way for chloride ions to reach the metal surface and to trigger the corrosion process.

The behaviour of bare stainless steel was tested in solutions of different pH values, as it is shown by monitoring E_{oc}, in Fig. 6, and by recording polarisation curves of stainless steel given in Fig 7 a-c.
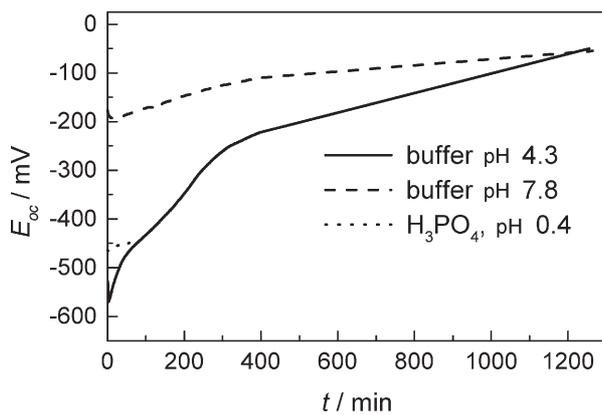
F i g . 6 – *The open circuit potential (E_{oc}) vs. time dependences for stainless steel electrode in different solutions*
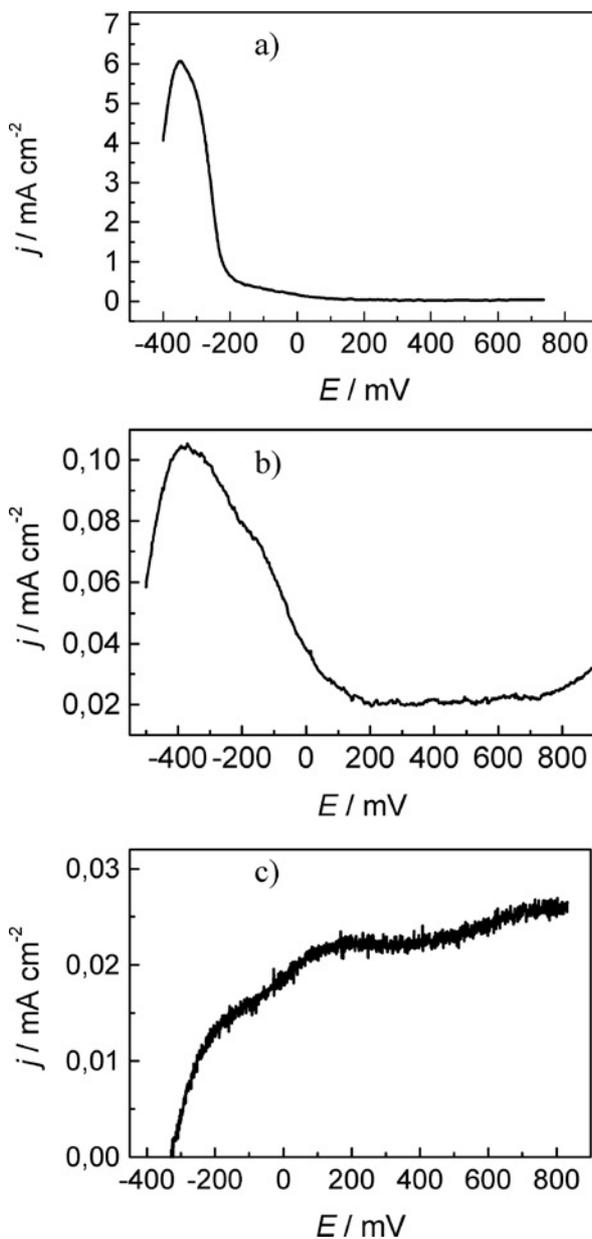
F i g . 7 – *Cyclic voltammograms of stainless steel electrode in solutions of different pH values. a) pH 0.4; b) pH 4.3; c) pH 7.8; v = 2 mV s⁻¹*

When the electrode was maintained in the solution of pH 0.4, during the time of the measurement E_{oc} remained in the active region and the electrode was considerably damaged. Therefore, the measurement was interrupted after one hour. However, bare stainless steel electrodes kept in the solutions of pH 4.3 and 7.8 during one-day period, became passive spontaneously. The spontaneously passivated steel samples were tested in $c = 0.1$ mol dm⁻³ NaCl solution and, as it is shown in Fig. 8, the oxide film breakdown appears ca 100 to 110 min after the exposure to corrosive environment. The protection by a spontaneously formed passive film appears to be similar to the case where stainless steel was protected with protonated PANI layer. However, when the sample with the PANI layer was kept in the solution of pH 7.8, the protection period was three times longer than at pH 4.3. These results indicate that the deprotonated PANI layer can act as an effective corrosion protection in chloride medium. To confirm that the better protection is not a consequence of the improved oxide quality due to one day aging, a fresh stainless steel-PANI sample was prepared and kept in the solutions of pH 7.8 during one-day period. After that period the PANI film was removed according to the procedure described elsewhere,[19] and the underlying oxide layer was tested in a chloride solution. As shown in Fig. 4, the time of protection was significantly shorter after the PANI layer was removed. These measurements are strong evidence that the improved protection is the consequence of the deprotonated polymer layer, and not of the improved quality of the oxide film.

In a number of papers dealing with the corrosion protection by PANI, protonated emeraldine is fundamental for the proposed corrosion protection mechanism.[1] However, in this case, the time of the protection with protonated emeraldine is similar to the time of the protection with spontaneously passivated film. Better protection effects are obtained
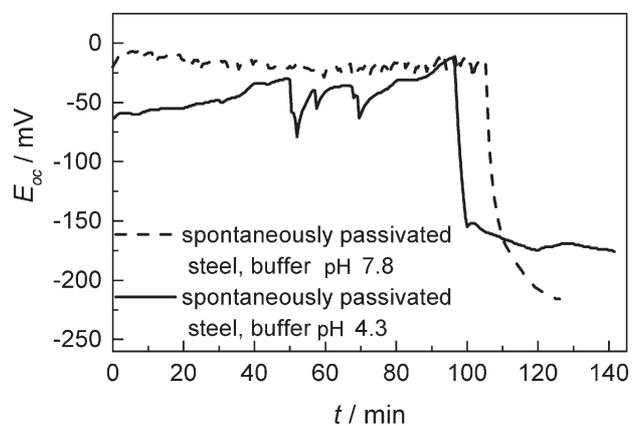
F i g . 8 – *The open circuit potential (E_{oc}) vs. time dependences for spontaneously passivated steel samples tested in $c = 0.1$ mol dm⁻³ NaCl solution*

with a deprotonated PANI. Since the worst effects of protection are obtained with protonated EM, it seems reasonable to conclude that in solutions containing chloride ions, the protection cannot be explained by the previously proposed electrochemical mechanism. It seems plausible to suggest that in a chloride medium PANI imposes only a physical barrier to the ingress of chloride ions through the layer. But when chloride ions reach the oxide film, PANI layer is no longer an adequate protection. The electrochemical mechanism of the corrosion protection is therefore negligible, if any at all.

It is interesting to note that the time of the protection is different with freshly prepared PANI layer compared to PANI layer maintained during one day in the solution of pH 0.4 (Fig. 4), and in the last case a better protection is achieved. That effect can be a consequence of a changed polymer structure or of a changed oxide structure. Comparing EIS measurements of these two layers, it was found that responses, characteristic of polymer layers, are similar. This indicates that the better protection, achieved with the layer maintained during one day in pH 0.4, is a consequence of the improved oxide quality. It is fair to assume that the amount of chromium oxide in the oxide layer is increased,[19] and because of that a better protection is obtained.

The most important factor in obtaining the stable passive film on stainless steel is the amount of chromium[20] that should be $\geq$ 12 %. Chromium atoms must be close enough in the lattice structure so that the adsorbed oxygen anions can bridge oxidised chromium. An oxidised chromium network will enhance stability of the passive film in an aggressive environment. As it was shown before[19, 21] the amount of chromium oxide will increases with time and protective properties are improved. The enrichment of chromium in the passive films appears due to the preferential dissolution of iron into the solution, and due to lower mobility of chromium in the film. It is also possible that the improved passive film is a consequence of some other transformations that occur in time, like stoichiometric changes, dehydration, recrystallisation, or depletion of defects.[22] There are some other parametars important for passive film properties like anion present in the solution during the formation of the film and during the testing, as well as pH value of the solution. It was shown that anions present could be incorporated within passive film.[23–26] Thus, it was found for sulphate-ion in alkaline chloride solution to influence the pitting potential,[23] and for phosphate-ion in a neutral chloride solution to influence the repassivation potential but not the passivation potential.[24] It was found that a phosphoric acid solution is suitable for a conductive polymer formation on either iron[27] or stainless steel.[1]

Compared to some other inorganic acids, in phosphoric acid solutions a oxide film with enhanced corrosion resistance is obtained. With the increase of pH value a lower metal dissolution rate will be obtained that leads to a thicker oxide film and a larger fraction of iron within the film.[28] This shows that many parameters influence the stability of the passive film. It is, however, important to point out, that in the case of the sample kept in buffer solution of pH 7.8, there is a possibility that the passive film is improved, but the main factor that increases the protection time is a deprotonated PANI layer. The test with the underlying passive film, resulting in a much shorter protection time (Fig. 4), supports that assumption.

Conclusion

Corrosion protection of stainless steel with PANI layer, in solutions containing chloride ions, is not significantly influenced by the electrochemical mechanism of corrosion protection proposed previously. In the solutions of higher pH values, PANI results in a more compact layer and thus imposes a physical barrier to the ingress of chloride ions through the layer. The best protective properties in a chloride medium were obtained with the PANI layer kept during one day before testing in a buffer solution of pH 7.8, where a complete deprotonation was achieved. It was shown that better corrosion protection is not a consequence of the improved oxide quality but of the deprotonation that is followed by a change of PANI structure, i.e. it is a consequence of a decreased polymer "free volume" resulting in a more compact PANI layer structure.

List of symbols

A – area, cm^2

j – current density, $A\ cm^{-2}$

c – concentration, $mol\ dm^{-3}$

I – current, A

E – potential, V

E_{oc} – open circuit potential, V

f – frequency, Hz

t – time, s

Z – impedance, $\Omega\ cm^2$

Q – surface charge density, mC cm^{-2}

χ – mole fraction, %

ν – potential scan rate, mV s^{-1}

φ – deg – phase angle

A c r o n y m s

EM   – emeraldine form of polyaniline

LE   – leucoemeraldine form of polyaniline

PANI– polyaniline

SEM – scanning electron microscopy

EIS   – electrochemical impedance spectroscopy

R e f e r e n c e s

1. *Kraljić, M.; Mandić, Z.; Duić, Lj.*, Corr. Sci. **45** (2003) 181.

2. *DeBerry, D. W.*, J. Electrochem. Soc. **132** (1985) 1022.

3. *Gašparac, R., Martin, C. R.,* J. Electrochem. Soc. **148** (2001) B138.

4. *Bernard, M. C., Hugot-Le Goff, A., Joiret, S., Dinh, N. N., Toan, N. N.*, J. Electrochem. Soc. **146** (1999) 995.

5. *Bernard, M. C., Joiret, S., Hugot-Le Goff, A., Phong, P. V.,* J. Electrochem. Soc. **148** (2001) B12.

6. *Kinlen, P. J., Menon, V., Ding, Y.*, J. Electrochem. Soc. **146** (1999) 3690.

7. *Sazou, D., Kosseoglou, D.,* Electrochim. Acta **51** (2006) 2503.

8. *Brusic, V., Angelopoulos, M., Graham, T.,* J. Electrochem. Soc. **144** (1997) 436.

9. *R. Racicot, R.,. Brown, R., Yang, S. C.*, Synth. Met. **85** (1997) 1263.

10. *Fenelon, A. M., Breslin, C. B.,* Surf. Coat. Technol. **190** (2005) 264.

11. *Araujo, W. S., Margarit, I. C. P., Ferreira, M., Mattoso, O.R., Lima Neto, P.,* Electrochim. Acta. **46** (2001) 1307.

12. *Özyilmaz, A. T., Erbil, M., Yazici, B.,* Prog. Org. Coat. **51** (2004) 47.

13. *Tuken, T., Özyilmaz, A. T., Yazici, B., Kardas, G., Erbil, M.,* Prog. Org. Coat. **51** (2004) 27.

14. *Huh, J. H., Oh, E. J., Cho, J. H.*, Synth. Met. **153** (2005) 13.

15. *Nguyen Thi Le, H., Garcia, B., Desluis, C., Le Xuan, Q.,* Electrochim. Acta **46** (2001) 4259.

16. *Hien, N. T. L., Garcia, B., Pailleret, A., Deslouis, C.,* Electrochim. Acta **50** (2005) 1747.

17. *Kumins, K., Kwei, T. K.*, Free volume and other theories in Diffusion in polymers, Chapter 4, pp 107 - 140. in Crank J. and Park, G. S., (Ed.), Academic Press, London, 1968

18. *Jurišić, A., Žic, M., Kraljić Roković M., Duić, Lj., Schauperl, Z.,* to be published.

19. *Hermas, A. A., Nakayama, M., Ogura, K.,* Electrochim. Acta **50** (2005) 2001.

20. *Sieradzki, K., Newman, R. C.,*J. Electrochemical. Soc. **133** (1986) 1979

21. *Ferreira M. G. S., Hakiki, N. E., Goodlet, G., Faty, S., Simões, A. M. P., Da Cunha Belo, M.*: Electrochim. Acta **46** (2001) 3767.

22. *Schultze, J. W., Lohrengel, M. M.,* Electrochim. Acta 45 (2000) 2499.

23. *El-Egamy, S. S., Badaway, W. A.,* J. Appl. Electrochem. **34** (2004) 1153

24. *Lakatos-Varsényi, M., Falkenberg, F., Olefjord, I.,* Electrochim. Acta **43** (1998) 187.

25. *Varga K., Baradlai, P., Barnard, W. O., Myburg, G., Halmos, P., Potgieter, J.H.*, Electrochim. Acta **42** (1997) 25.

26. *Keddam, M., Pallotta, C.,* J. Electrochem. Soc. **132** (1985) 781

27. *Bernard, M.-C., Hougot-LeGoff, A., Joiret, S.,* Synth. Met. **102** (1999) 1383

28. *Olsson, C.-O. A., Landolt, D.,* Electrochim. Acta **48** (2003) 1093.