Undoped polyaniline anticorrosive properties

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Abstract

The anticorrosive properties of undoped polyaniline (PAni) casted onto mild- and galvanised steels were studied by a classical methodology used for organic coatings. Pure PAni, as well as, PAni plus an epoxy topcoat were tested in total immersion conditions monitored by electrochemical impedance. The influence of the substrate and the electrolyte composition were discussed. PAni performance was evaluated in terms of underfilm corrosion and adhesion loss in comparison with other coating systems. It was shown that undoped PAni did not have good barrier properties and adhesion to the substrates was very poor. Even with an epoxy topcoat, PAni coated samples had the worst performance in comparison with the other coating systems herein used as reference. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The use of conductive polymers as anticorrosive coatings is based on the formation of an active electronic barrier on a metallic surface [1]. Over the last years, a great variety of conductive polymers have been tested as corrosion inhibitors and/or anticorrosive coatings namely polyaniline (PAni), polyaniline derivatives and polypyrrole. It is curious to note that anticorrosive properties are ascribed both for doped and undoped PAni, where a similar protective mechanism based on substrate passivation is attributed independent of conductive properties [2–7]. The mechanism of passivation has been proposed based on positive potential shifts measured for PAni coated samples [2–4] and/or PAni/

Fe complexes identified by spectroscopic surface analysis techniques [5–7].

A survey of the literature reveals contradictory results about the efficiency of PAni-based coatings which can be partially associated with differences in experimental procedures. For instance, PAni film deposition can be carried out via electrochemical synthesis [8–11] or casting [2–4]. Regarding the utilisation form, PAni can be used as a single coating [2–4], a primer [5,6,12,13] or blended [7,14]. Thickness of the PAni layers can vary from 14 [2] to 200 μm [7]. The working electrolytes can be neutral or acid, with or without chloride [2–7,13] in different contents. Therefore, it is very difficult to compare reported results. Nevertheless, even when experimental conditions are similar, contradicting results can be found. For example, Santos et al [4] reported excellent adhesion properties for undoped PAni tested in NaCl 3%. While Wei-Kang et al. [6] found poor adhesion in NaCl 3.5%. The main restric-

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tions attributed to PAni by the ones who did not find good performance are, lack of adhesion and porosity [3,15]. Another feature to be taken into account is the consensus that to evaluate organic coatings, it is necessary to work with areas representing the whole coating performance. In general, areas in the range of 0.1–5 cm^2 normally used for kinetic studies are not appropriate for coated samples. This is not commonly considered in papers dealing with PAni [2–4,7].

In order to be considered as a good corrosion protective material, a coating must fulfil some basic requirements. Adhesion is essential and this is known to strongly depend on the compatibility between coating and substrate as well as on surface pre-treatment. The material itself must present intrinsic properties that make it a good barrier or an active inhibitor. Therefore, the study of a new coating as PAni claims for precise material description and tests in comparison with reference coatings of well-known performance. Characterisation of underfilm corrosion and adhesion loss is particularly important for the ranking of a new coating. Potential shifts and polarisation curves, which are currently employed on the studies of PAni anticorrosive properties, have very restrict application on organic coatings evaluation [2–4,6,7]. In the present work, the main purpose is to study casted undoped PAni as an eventual protective coating for mild- and galvanised steels in comparison to some reference systems.

2. Experimental

Mild- and galvanised steel plates were used as substrates. Mild steel was degreased with toluene, blasted and degreased again. Blasting was done with glass microspheres resulting in a 10 μm roughness profile,

which was measured by a Dektak IIA Profilometer. Some samples of mild steel were also polished with 600 emery paper. Galvanised steel was only degreased with toluene. Undoped PAni was obtained following the procedure described by Santos et al. [4]. Weight-average molecular weight (M_w) was 52 500 as estimated by GPC (Gel Permeation Chromatograph) with N-methyl-pirrolidone(NMP) + 0.1% acetic acid as eluent at 0.6 cm^3 min^{-1} flow rate. Polymer casting solution was prepared by dissolving 2% wt vol^{-1} of the polymer powder in NMP. The powder was slowly added to the solvent and the resulting solution was kept stirring overnight. The solution was then paper filtered and deposited onto the substrates, which dried at 60°C during 14 h [16]. Dry thicknesses of about 15 μm were measured with a Fischerscope Multi Measuring System calibrated for the different substrates. This thickness was obtained by depositing 8 cm^3 of the filtered solution onto 56 cm^2 substrate area, from where, 19.4 cm^2 was chosen as working area. It was very difficult to obtain homogeneous PAni coatings in such conditions. Therefore, a great number of samples had to be prepared in order to choose the best ones. PAni free-standing films were obtained by casting the solution onto glass and then removing the dried film by immersion in water. Free films thicknesses varied in the range 15–25 μm. Before testing, the films were kept in dissicator during at least 1 week.

The effect of a topcoat on PAni performance was also evaluated. A commercial epoxy topcoat was air-sprayed on a group of samples already coated with PAni. The performance of PAni coated samples was compared with some reference systems. Basic features of all kinds of samples employed are described in Table 1.

All tests were conducted with replicate samples. Loss of adhesion, blistering and underfilm corrosion was evaluated on scribed and unscribed samples. The adhesion was characterised by an adaptation of the ASTM D3359 because the objective was to measure the adhesion on the sample total area. Tests were conducted in total immersion conditions monitored by EIS. Classical three-electrode and four-electrode cells were employed for metal samples and free-standing films, respectively. The working electrolyte was 0.01 M Na$_2$SO$_4$ pH 6.5. This solution has medium aggressiveness and it was chosen based on results discussed elsewhere [17]. In order to investigate the pH dependence of the results, the electrolyte was pH adjusted with sulphuric acid to pH 4. The EIS measurements were made at the open circuit potential with 10 mV signal perturbation. The experimental set-up as well as procedure for EIS measurements are described elsewhere [17].

Table 1
Basic description of tested samples

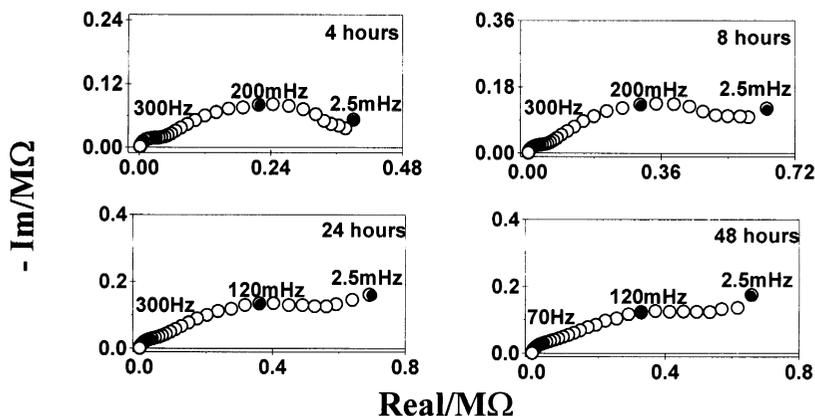| Mild steel	Galvanised steel
Blasted mild steel (CS) without any coating	Galvanised steel (GS) 20 gZn m^{-2} without any coating
CS + PAni-15μm; polished steel + PAni-15μm	GS + PAni-15μm
CS + PAni + epoxy topcoat (one layer)-85μm	GS + PAni + epoxy topcoat (one layer)-85μm
CS + epoxy topcoat (one layer)-70μm	GS + epoxy topcoat (one layer)-70μm
CS + phosphate layer (4g m^{-2}) + epoxy topcoat (one layer)-75μm	

Fig. 1. Nyquist plots for PAni coated steel at different immersion times in Na_2SO_4 0.01 M.

3. Results and discussion

Fig. 1 shows Nyquist plots representative of PAni coated steel samples at different immersion times. The diagrams show at least two capacitive loops, a smaller one at high frequency range followed by a larger one at lower frequencies. Such electrochemical behaviour suggests interaction between metal/PAni interface and the electrolyte. The first capacitive loop was attributed to the coating itself and the second one to processes occurring underneath the film [17].

The capacitances and resistances associated to the first capacitive loop are shown for replicate samples on Fig. 2. The almost constant resistances denote that development of electrolyte pathways through the PAni coating reached steady state since the first measurements. Meanwhile, increase of capacitance values can be interpreted as consequence of continuous water uptake [18,19].

Free-standing film impedance measurements corroborate that PAni permeation occurs rapidly. Indeed, for only 30 min immersion time the Nyquist plots are characterised by a high frequency capacitive loop followed by a linear behaviour. Film resistances of 0.8 $M\Omega$ cm^2 were found and this value does not change as time elapses.

Fig. 3 shows the EIS diagrams for PAni coated galvanised steel for various immersion times. The first measurement was obtained only 1 h after immersion, as previous observations indicated fast changes in the system. Indeed, the splitting of the initial capacitive loop into two others can be better followed within the immersion time although the total impedance remained constant.

On Fig. 4 resistances and capacitances obtained for the high frequency loop are shown. Comparing Figs. 2 and 4, similar electrochemical properties can be attributed to PAni independent of the substrate. Indeed,

resistances and capacitances are varying in the same order of magnitude for both mild- and galvanised steels.

Fig. 5(a) shows an impedance diagram obtained for bare steel after 4 h immersion time. Approximate values of resistance and capacitance obtained by extrapolation of the high frequency loop to the real axis are shown on Fig. 5(b) and (c) for replicate samples. Comparing data on Figs. 2 and 5 it is possible to attribute barrier properties to the PAni coating. Indeed, for PAni coated samples the resistive component of impedances increased three orders of magnitude and capacitances decreased six orders of magnitude as compared to bare steel. Nevertheless, after only 2 days, PAni samples were severe blistered, with underfilm corrosion and adhesion was completely lost. The same performance was observed for the polished samples where the ratio PAni dry thickness/roughness profile was higher.

Actually, PAni adhesion to both substrates is not good even in as prepared (non-tested) samples. The visual aspect of a sample after initial adhesion measurement by tape test is shown on Fig. 6(a). Still on Fig. 6, there are pictures of mild- and galvanised steels showing the underfilm corrosion after only 2 days immersion
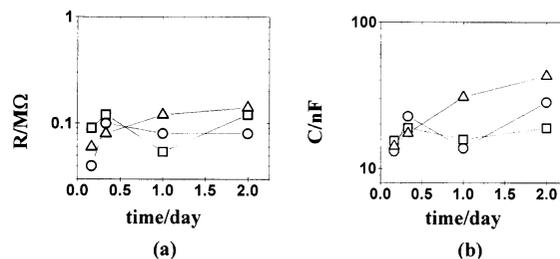

Fig. 2. Resistances (a) and capacitances (b) for PAni coated steel during immersion in 0.01 Na_2SO_4. Replicate samples (□) AP1; (○) AP2 and (Δ) AP3.
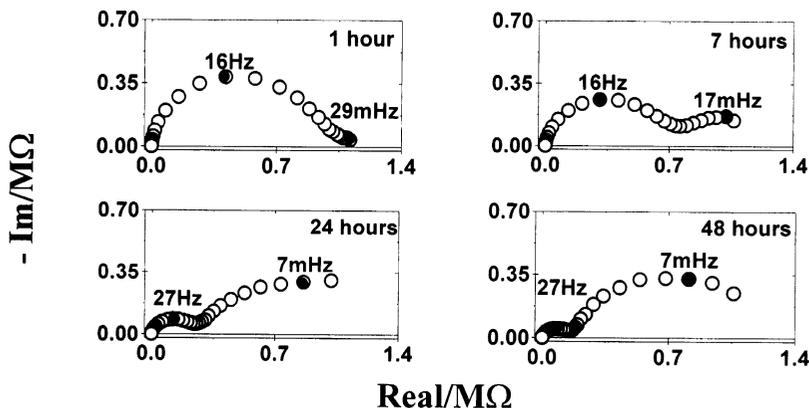
Fig. 3. Nyquist plots for PAni coated galvanised steel at different immersion times in Na_2SO_4 0.01 M.

time. On Fig. 6(b) many corrosion spots are observed and although positive potential shifts were measured as shown on Table 2, underfilm corrosion was so severe, that passivation effect can not be proposed for undoped PAni as reported by others [4]. On Fig. 6(c), the stains are due to white corrosion of the galvanised steel.

Potentials measured for epoxy coated samples are characterised by higher values than for PAni coated samples, as can be observed on Table 2. Indeed, high potentials are commonly observed for barrier coatings and are explained by ohmic heterogeneity within the coatings [20], or by increase on the ratio of cathodic/anodic area at the coating/metal interface [21]. There is no reason to give different interpretation for undoped PAni. So, high potentials can not be used as an argument to attribute good performance to PAni.

The bad performance of PAni coated samples has two main reasons. One reason is the porosity that has been already pointed out by Ahmad and MacDiarmid [3]. In this work, such porosity is confirmed by the results shown on Fig. 2 and by the behaviour described for free-standing films. On Fig. 7, resistance and capacitance values measured for PAni coated samples plus an epoxy topcoat suggests that this problem would be solved by the use of a topcoat or, perhaps increasing the PAni coating thickness. Indeed, resistances increase two orders of magnitude and lower capacitances with more constant values were measured for longer periods of immersion. However, even in this condition the corrosion protection offered by the PAni-epoxy system was not satisfactory and the reason is discussed in Fig. 8.

The second main reason for undoped PAni bad performance is the lack of adhesion. This deficiency can be better evaluated by comparison with other coating systems using scribed samples. Fig. 8 shows the visual aspect of samples with the epoxy topcoated systems described on Table 1. These samples were immersed during 15 days. Their adhesion loss was measured by a

cross-tape test. When PAni was tested as a primer, the loss of adhesion was complete and important underfilm corrosion was detected in spite of the epoxy topcoat, Fig. 8(a) and (b). As a reference, Fig. 8(c) shows the visual aspect of a phosphatised steel sample topcoated
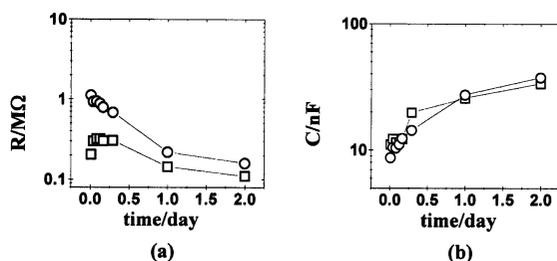

Fig. 4. Resistances (a) and capacitances (b) for PAni coated galvanised steel during immersion in 0.01 Na_2SO_4. Replicate samples ($\square$) ZP1 and ($\bigcirc$) ZP2.
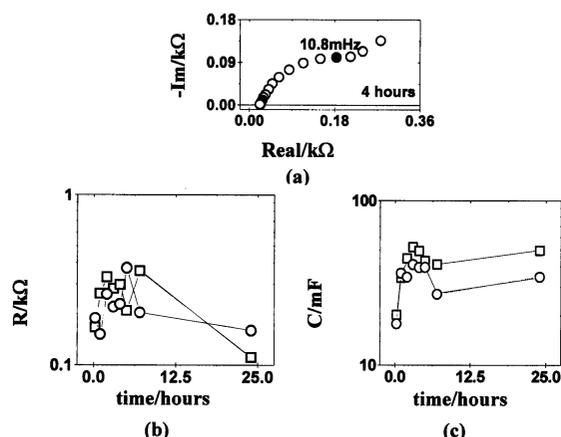

Fig. 5. EIS for bare steel in 0.01 Na_2SO_4 (a) Nyquist plot after 4 h immersion time; (b) resistances and (c) capacitances obtained for the high frequency loop. Replicate samples ($\square$) A1 and ($\bigcirc$) A2.
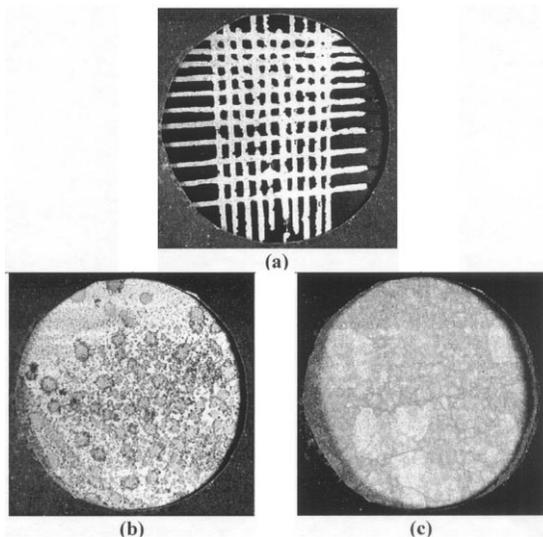
Fig. 6. Visual aspect of (a) PAni coated steel after initial adhesion measurement; underfilm corrosion of steel (b) and galvanised steel (c) after removing the PAni coating.

with the same epoxy paint. After 15 days of immersion the sample did not show any adhesion loss. Similar results were observed for steel painted with only the epoxy topcoat. The galvanised samples, where the epoxy topcoat was directly sprayed on, Fig. 8(d), also exhibited better adhesion than the PAni containing systems. It is important to emphasise that an epoxy topcoat directly applied on galvanised steel is a painting system well-known by its poor adhesion. Even such system showed better behaviour than the ones containing PAni. Results shown in Figs. 3 and 8 lead to the conclusion that undoped PAni peeling-off does not depend on the presence of chlorides in solution as reported by Ahmad and MacDiarmid [3].

PAni coated steel was also tested at lower pH, using the same Na_2SO_4 solution adjusted to pH 4. At this pH some doping effect can be expected. Nyquist plot obtained after 8 h immersion time is shown in Fig. 9(a). Two capacitive loops were again observed. Values of resistance and capacitance related to the high frequency loop do not differ significantly from the ones discussed
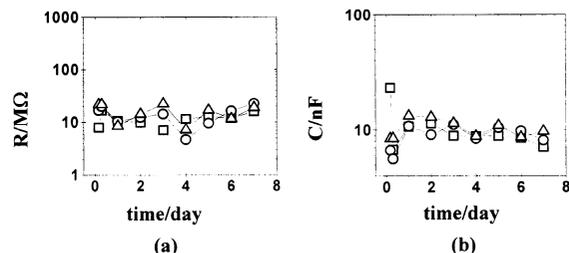

Fig. 7. Resistances (a) and capacitances (b) for steel coated with PAni plus an epoxy topcoat during immersion in Na_2SO_4 0.01 M. Replicate samples ($\square$) APE1; ($\bigcirc$) APE2 and (Δ) APE3.

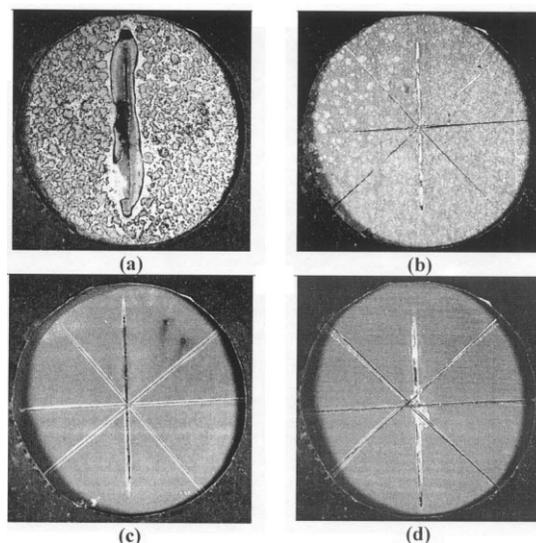
Fig. 8. Visual aspect after adhesion measurements of samples immersed during 15 days in 0.01 M Na_2SO_4. (a) PAni + epoxy topcoated steel; (b) PAni + epoxy topcoated galvanised steel; (c) Phosphatisation + epoxy topcoated steel; (d) epoxy topcoated galvanised steel.

on Fig. 2. Otherwise, the total resistances are lower. After 2 days immersion time underfilm corrosion was present as shown on Fig. 9(b). Eventhough the whole surface has been attacked, the corrosion was not as

Table 2
Typical open circuit potentials measured for bare and coated steel in 0.01 M Na_2SO_4

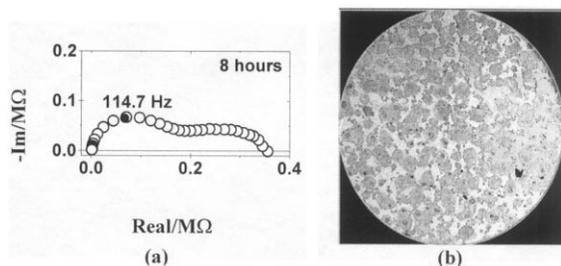| Immersion time (h)	Open circuit potential (mV vs. SSE)		
	Bare steel	PAni coated steel	Epoxy coated Steel
4	−1156	−942	−558
8	−1157	−948	−583
24	−1162	−893	−584
48	−1170	−861	−639

Fig. 9. Bare steel in 0.01 Na$_2$SO$_4$; pH 4. (a) Nyquist plot after 8 h immersion time; (b) Visual aspect of PAni coated steel after 2 days immersion time.

deep as on the samples tested in the neutral electrolyte (Fig. 3(b)). This suggests that doped PAni can really play an active role in the substrate corrosion protection. Study of doped PAni is out of the scope of the present paper. A systematic study here presented for undoped PAni does not exist in the literature for doped PAni, but it should be emphasised that although the visual aspect of sample in Fig. 9 indicates that doped PAni could be more efficient, adhesion still remained a problem. Indeed, after only 2 days immersion time adhesion was also completely lost. Therefore, neither in neutral nor in acid solution, PAni can be pointed out as an anticorrosive coating. Troch-Nogels et al. [9] and Sekine et al. [10] reached the same conclusions for PAni electrochemically deposited.

The present results are relative to pure PAni and so-called commercial PAni-based products were not tested. Whether these products work, surely they have additives to improve adhesion and diminish porosity. In any case, based on results discussed above, it is not possible to continue attributing to undoped PAni itself anticorrosive properties.

4. Conclusions

EIS results and visual inspection of PAni coated samples indicate that in undoped state PAni does not present essential properties to be proposed as an anticorrosive coating. Thin PAni films are porous and the adhesion onto mild- and galvanised steels is very poor. The lack of adhesion leads to bad performance even when PAni is topcoated with a high-performance paint as an epoxy one. Such behaviour does not depend on the composition of the solution employed for the im-

mersion tests. These conclusions are based on comparison of PAni performance with other coating reference systems following experimental procedures currently applied to the study of anticorrosive organic coatings.

References

[1] F.C. Jain, J.J. Rosato, K.S. Kalonia, V.S. Agarwala, Corrosion 42 (1986) 700.
[2] Y. Wei, J. Wang, X. Jia, J.M. Yeh, P. Spellane, Polymer 36 (1995) 4535.
[3] N. Ahmad, A.G. MacDiarmid, Synth. Met. 78 (1996) 103.
[4] J.R. Santos, Jr., L.H.C. Mattoso, A.J. Motheo, Electrochim. Acta 43 (1998) 309.
[5] P.J. Kinlen, D.C. Silverman, C.R. Jeffreys, Synth. Met. 85 (1997) 1327.
[6] W.K. Lu, R.L. Elsenbaumer, B. Wessling, Synth. Met. 71 (1995) 2163.
[7] A. Talo, P. Passiniemi, O. Forsen, S. Ylasaari, Synth. Met. 85 (1997) 1333.
[8] D.W. DeBerry, J. Electrochem. Soc. 132 (1985) 1022.
[9] G. Troch-Nagels, R. Winand, A. Weymeersch, L. Renard, J. Appl. Electrochem. 22 (1992) 756.
[10] I. Sekine, K. Kohana, T. Sugyama, M. Yuasa, J. Electrochem. Soc. 139 (1992) 3090.
[11] J.L. Camalet, J.C. Lacroix, S. Aeiyach, K. Chane-Ching, P.C. Lacaze, Synth. Met. 93 (1998) 133.
[12] B. Wessling, J. Posdorfer, Electrochim. Acta 44 (1999) 2139.
[13] D.E. Tallman, Y. Pae, G.P. Bierwagen, Corrosion 55 (1999) 779.
[14] S.P. Sitaram, J.O. Stoffer, T.J. O'Keefe, J. Coat. Technol. 69 (1997) 65.
[15] C. Deslouis, T. El Moustafid, M.M. Musiani, A. Nicoara, B. Tribollet, Abstracts of the 50th ISE, (1999) 984.
[16] Y. Wei, G.W. Jang, K.F. Hsuen, E.M. Scherr, A.G. MacDiarmid, A.J. Epstein, Polymer 33 (1992) 314.
[17] A.A.O. Magalhães, I.C.P. Margarit, O.R. Mattos, Electrochim. Acta 44 (24) (1999) 4281.
[18] I.C.P. Margarit, O.R Mattos, Electrochim. Acta 44 (2-3) (1998) 363.
[19] G.G. Nascimento, J.L.C. dos Santos, I.C.P. Margarit, O.R. Mattos, J. Appl. Electrochem. 29 (1999) 383.
[20] J. Wolstenholme, Corrosion Sci. 13 (1973) 521.
[21] M.W. Kendig, H. Leidheiser, J. Electrochem. Soc. 123 (1976) 982.