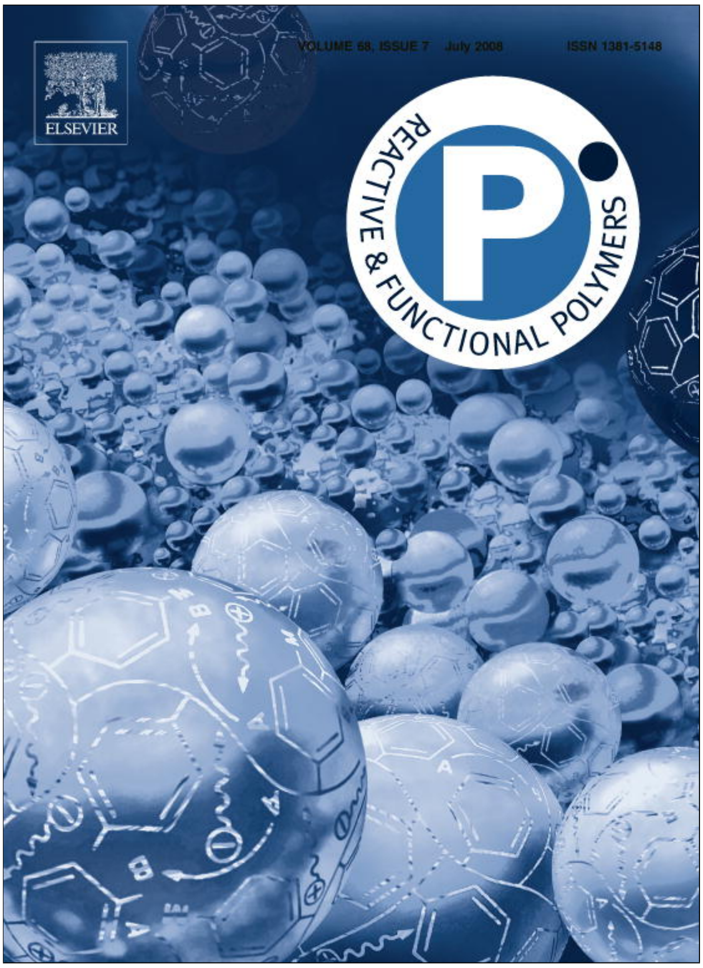
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Electrochemical impedance study of iron electrodes covered by polypyrrole films electrosynthesized in the presence of AOT

I.L. Lehr, S.B. Saidman *

Instituto de Ingeniería Electroquímica y Corrosión (INIEC), Departamento de Ingeniería Química, Universidad Nacional del Sur, Av. Alem 1253,
8000 Bahía Blanca, Argentina

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ABSTRACT

The electrosynthesis of polypyrrole (PPy) onto iron electrodes in the presence of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) solutions is characterized by the formation of a gelatinous material in parallel to the growth of the polymer. The electrochemical behaviour of this system under different experimental conditions was investigated using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry. The study was focused in understanding the effects of various parameters, such as nature of the electrolyte and film thickness, on the dissolution process of iron. The response at low frequencies is related with the activity of the substrate. It was found that the electrode impedance for thick films is governed by diffusion of iron ions across the polymer and gel-like layers. Mass transfer contribution is prominent at the early stages of corrosion in chloride solution.

1. Introduction

In recent years there has been much interest in the electrodeposition of conducting polymers onto active metals due principally to the corrosion protection properties of these coatings. We have previously found that PPy films electrosynthesized in the presence of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) onto Al [1] and onto Fe [2] have good protecting properties in chloride solutions. Because AOT has two bulky hydrocarbon tails it acts as an immobilized dopant, contributing to hinder chlorides penetration into the polymer matrix. While studying this electropolymerization process onto iron electrodes it was observed the unusual formation of a gel-like product surrounding the polymer (Fig. 1a). To the best of our knowledge, the simultaneous formation of the polymer and a gel-like material during electrosynthesis was observed for the first time. To obtain more information about the phenomena involved in this system the electrochemical behaviour of iron in pure aqueous AOT solutions was studied [3]. It was found that a gelatinous material was formed onto the bare electrode as a result of iron dissolution (Fig. 1b). It was postulated that this material is a mixed NaAOT-Fe$(AOT)_3$ lamellar mesophase where the iron ion is surrounded by three AOT molecules and this structure is covered by NaAOT.

EIS has been applied to characterize active metals covered by conducting polymers because the technique allows the separation of the different phenomena that occur at the interfaces [4–11]. A large variety of impedance responses exist because the great diversity of preparation methods for conducting polymers as well as the different electrochemical behaviour of the active substrate. Interpretation of the measurements is usually done by fitting the data to an equivalent circuit and all results obtained by other techniques should be taken into account in the construction of the appropriate circuit.

To better understand the peculiar behaviour described above, we present a study on the impedance behaviour of PPy coatings formed in the presence of AOT onto iron substrate. The effects of the nature of the electrolyte, film thickness and applied potential upon impedance measurements have been considered. For comparative purposes,

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* Corresponding author. Tel./fax: +54 291 4595182.
E-mail address: ssaidman@criba.edu.ar (S.B. Saidman).

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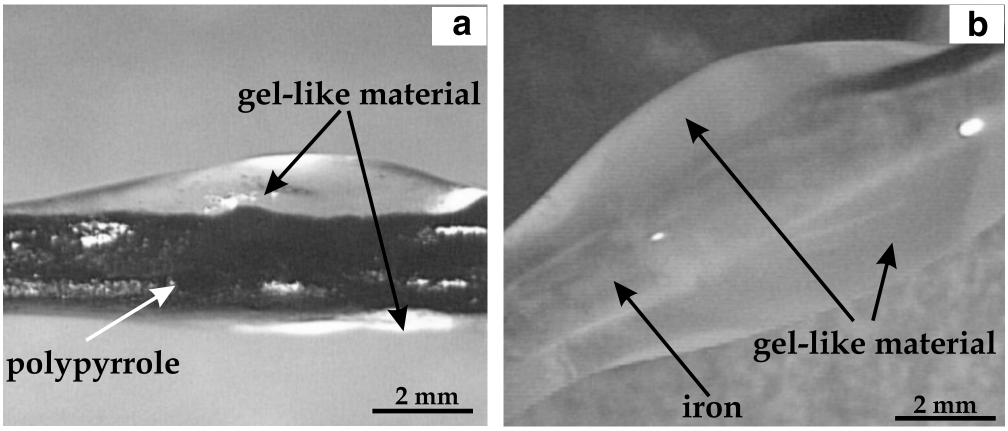

Fig. 1. Photographs of an iron wire (1 mm in diameter) covered by (a) PPy and the gel-like film. The iron wire was polarized at 0.9 V for 60 min in 0.05 M AOT, pH 7 with 0.25 M Py; (b) the gel-like material. The uncovered iron wire was polarized at 0.9 V for 60 min in 0.05 M AOT, pH 7.

EIS analysis was also performed for PPy films electrosynthesized onto vitreous carbon.

2. Experimental

Pure iron rods embedded in a Teflon holder with an exposed area of 0.070 cm^2 were used as working electrodes. Before each experiment, the exposed surfaces were polished to a 1000 grit finish using SiC, then degreased with acetone and washed with triply distilled water. All the potentials were measured against a saturated calomel electrode (SCE) and a platinum sheet was used as a counter electrode. The cell was a 20 cm^3 Metrohm measuring cell.

Electrochemical measurements were done using a VoltaLab 40 Potentiostat PGZ301. The frequency used for the impedance measurements was changed from 100 kHz to 100 mHz, and the signal amplitude was 10 mV. The electrodes were allowed to equilibrate at the fixed voltage before the ac measurements.

Electrosynthesis of the PPy films for impedance measurements was always performed at 0.9 V from a 0.25 M Py + 0.05 M AOT, pH 7 solution in a purified gas saturated atmosphere at 25 °C. Assuming a film thickness of 1 μm for 0.4 C cm^2 charge [12], polypyrrole films of about 4 and 30 μm were electrodeposited during 5 and 30 min, respectively. In order to avoid the slow hydrolysis of AOT all the measurements were done with freshly prepared samples. All chemicals were reagent grade and solutions were made in twice distilled water. Pyrrole was purchased from Across Organics and it was freshly distilled under reduced pressure before use.

3. Results and discussion

The stabilized cyclic voltammogram of the PPy-coated iron electrode at 0.05 V s^{-1} in 0.05 M AOT, pH 7 solution is shown in Fig. 2, curve a. The film was electrogenerated at 0.9 V for 20 s. The polymer can be reversibly switched between the oxidized and neutral form. The reduction peak was attributed to the compensation of the polymer charge by Na^+ insertion [13]. When PPy was electrodeposited for 5 min the *I–E* curve indicates an increased polymer resistance (Fig. 2, curve b).

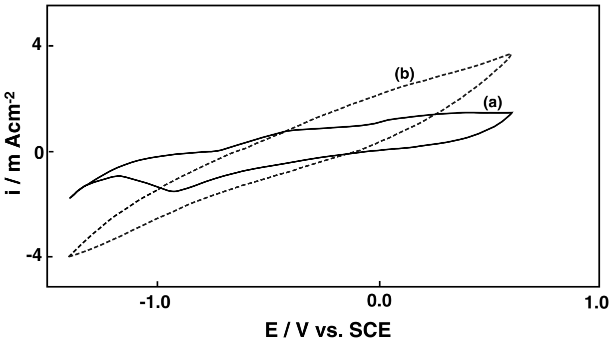

Fig. 2. Cyclic voltammograms of a polypyrrole-coated Fe electrode at 0.05 V s^{-1} in 0.05 M AOT, pH 7 solution. The polymer films were electrosynthesized in the same solution containing 0.25 M Py at 0.9 V for (a) 20 s and (b) 5 min.

Polypyrrole films were deposited at different electropolymerization times in 0.05 M AOT solution containing the monomer and then impedance measurements were performed in the same solution. Figs. 3 and 4 display the Nyquist and Bode plots of the impedance spectra at 0.0 V, a potential at which the polymer is oxidized. As observed in the figures, both Nyquist spectra show a high-frequency partial semicircle. The response at lower frequencies depends on the electropolymerization time. While for a thinner film the impedance response at low frequencies is an incomplete semicircle (Fig. 3), the Nyquist diagram presents a straight-line with a slope lower than 1 for a higher electropolymerization time (30 min) (Fig. 4). Thus, diffusional phenomena are visible only in the spectra of the thicker films. The linear part in the low-frequency region of Bode plot can be associated with the diffusion-like step. The phase angle values were low but they display tendency to increase. A thick gel-like product layer covering the polymer was visible after the EIS analysis, although in a smaller amount for the lower electropolymerisation time. The formation of the gel material on top of the polymer implies that some porous structure may have developed in the polymer.

The behaviour of the electrode covered with PPy electrosynthesized during 30 min can be described adequately

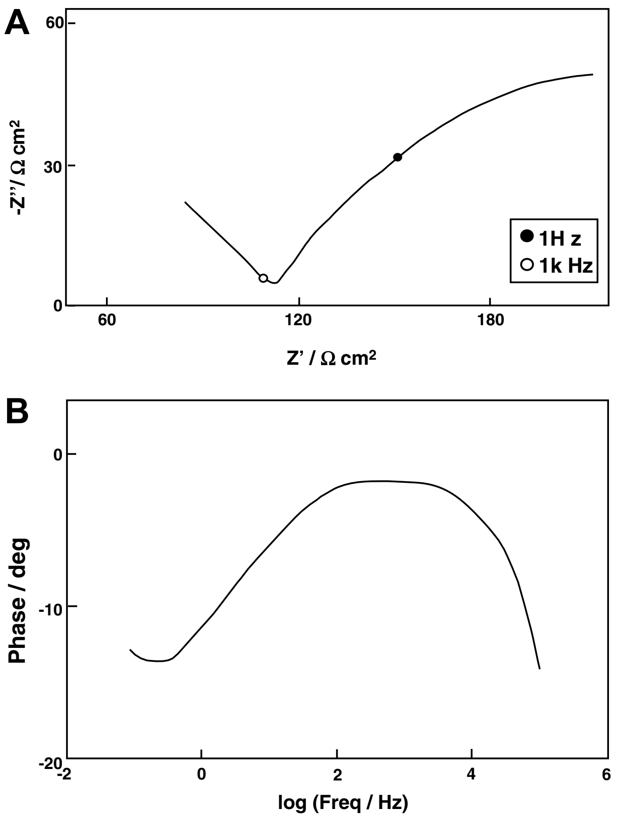

Fig. 3. (A) Nyquist and (B) Bode plots of the impedance spectra for PPy-coated iron electrode at 0.0 V in 0.05 M AOT, pH 7 with 0.25 M Py. The polymer was synthesized potentiostatically at 0.90 V in the same solution for 5 min.

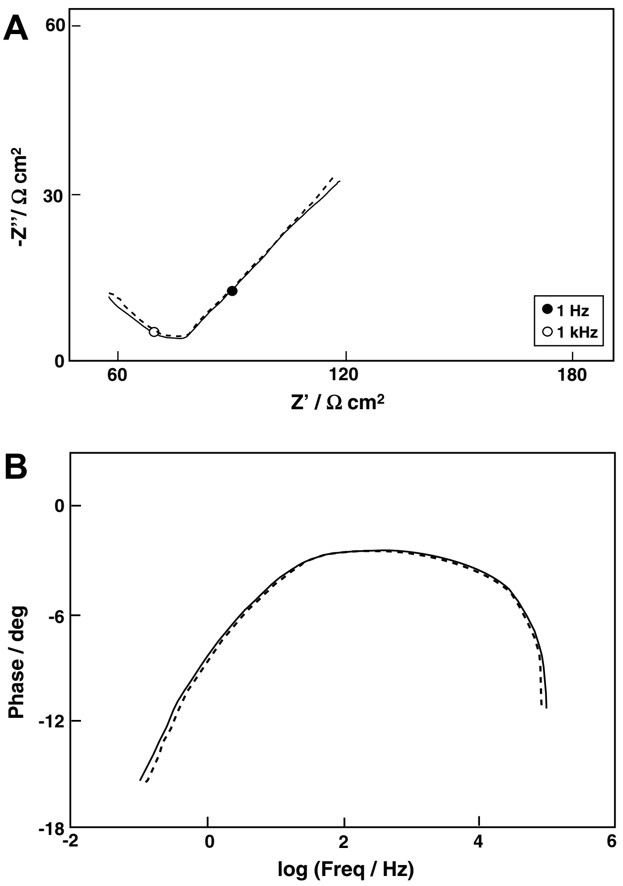

Fig. 4. (A) Nyquist and (B) Bode plots of the impedance spectra for PPy-coated iron electrode at 0.0 V in 0.05 M AOT, pH 7 with 0.25 M Py. The polymer was synthesized potentiostatically at 0.90 V in the same solution for 30 min.

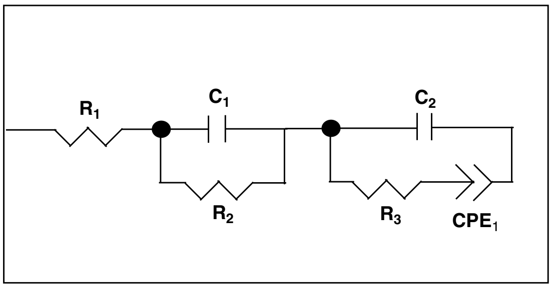

Fig. 5. Equivalent circuit proposed to simulate the impedance behaviour of an iron electrode covered by a PPy film synthesized potentiostatically at 0.9 V during 30 min (Fig. 3, curve b). The significance of the parameters is given in the text.

by the equivalent circuit depicted in Fig. 5. The results of fitting are presented in Table 1. The errors of fitting are lower than 3% for all the parameters. R_1 represents the solution resistance having a value of $47\,\Omega\,\mathrm{cm}^2$, and R_2 and C_1 can be ascribed to the resistance and capacitance of the polymer and gel films, with values of $6\,\Omega\,\mathrm{cm}^2$ and $10\,\mu\mathrm{F\,cm}^{-2}$, respectively. The response at low frequencies is related with the activity of the iron substrate, in accordance with that proposed to represent the polyaniline-coated iron [8]. It consists of a charge transfer resistance against iron dissolution, R_3, of $19\,\Omega\,\mathrm{cm}^2$, a capacitance, C_2, of $0.08\,\mu\mathrm{F\,cm}^{-2}$, and a constant phase element, CPE_1 [14]. The impedance of the CPE is defined as $Z_{\mathrm{CPE}} = [Q(\mathrm{j}\omega)^n]^{-1}$ where the exponent n gives information about the degree of non-ideality in the impedance behaviour. In the present case we obtain $n = 0.41$. C_2 can be ascribed to the capacity of the metal/solution interface at the bottom of the pores. Its low value is associated with the smaller area between the metal and the electrolyte solution [4]. CPE_1 represents a non-ideal diffusion process.

Fig. 6 shows the Nyquist and Bode representations obtained under similar conditions to those of Figs. 3 and 4 except that after electropolymerization, the PPy-covered electrodes were thoroughly washed with water and, thus, the gel was rinsed away [3]. The impedance spectra also show in these cases an incomplete semicircle at high frequencies (Fig. 6, curves a and b). Decreasing the frequency, two overlapped semicircles are obtained for the thinner film while a straight-line that overlaps with a less evident semicircle was observed for the thicker one. The line has a slope lower than 1. Visual observation of the samples after the EIS analysis showed that the gel-like layer was formed, although it was thinner than that generated during measurement presented in Figs. 3 and 4. In the same figure it is included the response of the covered electrode under rotation (Fig. 6, curve c), which is qualitatively very similar to that obtained for the stationary electrode. No gel layer was visually noted after measurement and in this case

Table 1
Values of the elements corresponding to the equivalent circuit of Fig. 5

	R_1 (Ω cm^2)	R_2 (Ω cm^2)	C_1 (F cm^{-2})	R_3 (Ω cm^2)	C_2 (F cm^{-2})	CPE$_1$	
						Q/mF cm^{-2}	n
Fe/PPy	47	6	10	19	0.08	22	0.41

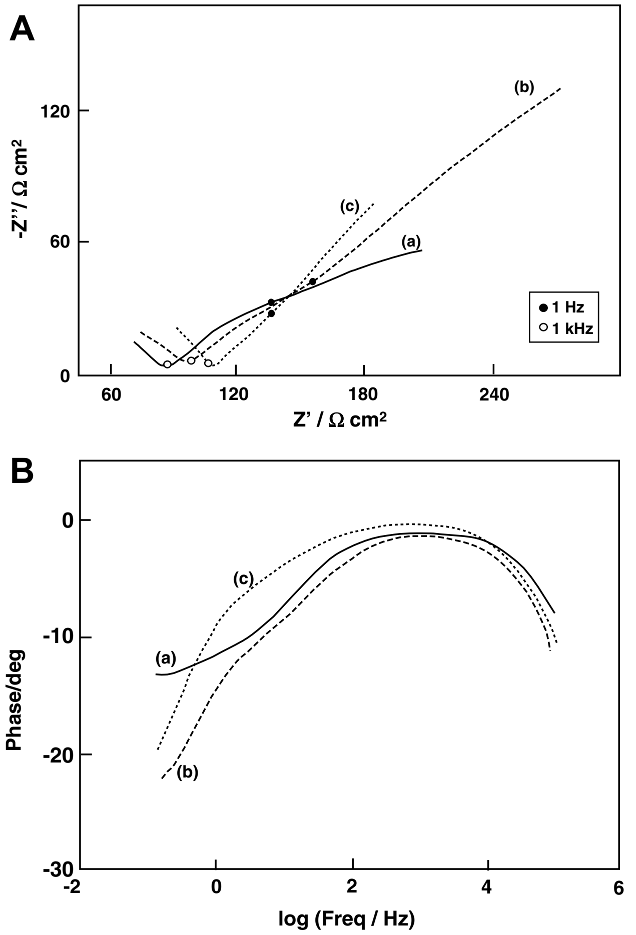

Fig. 6. (A) Nyquist and (B) Bode plots of the impedance spectra for PPy-coated iron electrode at 0.0 V in 0.05 M AOT, pH 7. The polymer was synthesized potentiostatically at 0.90 V in the same solution containing 0.5 M Py for (a) 5 min and (b) 30 min. (c) The polymer was synthesized at 0.90 V for 30 min and EIS measurement was carried out at a rotation rate of 600 rpm. After electrosynthesis and prior to EIS measurements the gel-like film was removed by washing.

the classical Warburg line can be observed in the impedance diagram.

The diffusion process observed could take place in the electrolyte solution, in the polymer film or in the gel layer. The dependence of the impedance behaviour at low frequencies on the thickness of the films indicates that the rate controlling step is not diffusion in the solution. On the other hand, since the gel-like film cannot be developed under electrode rotation, the straight-line in Fig. 6, curve c, can be interpreted in terms of the diffusion of ferrous/ferric ions through the pores of the polymer. Under stagnant conditions (Fig. 6, curve b) the impedance increases in size because the resistance not only contains the diffusion through the pores but also the resistance for the transport of Fe ions across the gel-like film developed between the polymer and the electrolyte. This film might have some internal porosity or inhomogeneity in the structure, considering the slopes lower than 1 [15]. It is expected that the main contributions to the restriction of ions motion in the gel are the decrease of the liquid volume fraction which is the conductive phase in the gel and the high viscosity of the material.

Comparing the responses for static electrodes presented in Figs. 4 and 6, it can be observed that although the straight-lines have not very different slopes, there is a considerable difference between impedance values. The reason for this difference can be understand from the fact that the gelatinous layer was formed under different conditions. While for the diagram in Fig. 4 the gel was developed principally during the electropolymerization process at 0.9 V, the growth of the gel over those films presented in Fig. 6 took place principally at 0.0 V. On the other hand, the n value in the CPE related to the diffusion process deviates more from the ideal behaviour in the first case ($n = 0.41$) than in the second one ($n = 0.44$). Moreover, the ratio between amounts of gel and electrolyte in the ionically conducting paths of the polymer should be different in the two experiments.

Impedance measurements were also made at −1.0 V where it is expected that only the reduced polymer exists. Likewise iron dissolution does not occur at this potential. It can be observed that the impedance increases and it is probably dominated by the conducting properties of the polymer (Fig. 7). Because the neutral PPy is less conductive the charge transfer resistance is high and it can control the impedance response. The absence of a diffusion contribution provides evidence that the diffusion process described above is related to dissolution of the iron substrate.

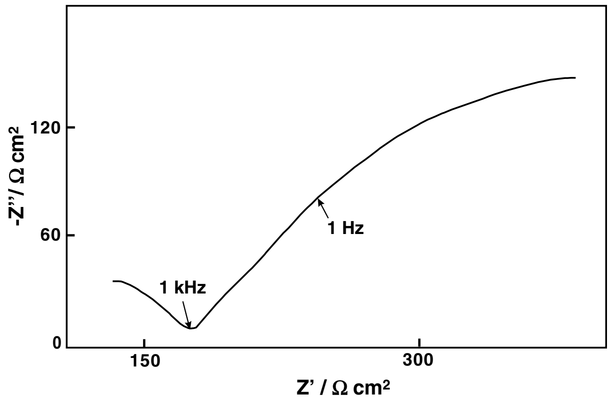

Fig. 7. Nyquist plot of the impedance spectrum for PPy-coated iron electrode at −1.0 V in 0.05 M AOT, pH 7 with 0.25 M Py. The polymer was synthesized potentiostatically at 0.90 V in the same solution for 30 min.

One way to obtain a better comprehension of the phenomena involved in the simultaneous formation of PPy and the gel-like material is to perform the impedance measurements with an inert substrate. A comparison with the polymer formed onto vitreous carbon was made. The impedance spectrum of a vitreous carbon electrode coated with PPy exhibits a high-frequency semicircle followed by another very large arc (Fig. 8). This type of diagram for conducting polymer has been interpreted considering that one time constant is related to the properties of the polymer/electrolyte interface, namely a charge transfer resistance and a double layer capacitance, whereas the other time constant corresponds to the resistance and capacitance of the polymer [16,17]. The absence of a diffusion line indicates that the oxidation-reduction process is not limited by diffusion of ions in the bulk of the polymer film.

The impedance response was also examined in the presence of sodium dodecylbenzene sulfonate (SDBS), a bulky surfactant which promotes iron dissolution but not lead to the formation of a gel product. For the sake of comparison the potentiodynamic polarization curves of uncovered iron in AOT and SDBS solutions obtained at the same conditions are shown in Fig. 9. The shape of the anodic curves indicates an active dissolution of the substrate in both media.

After washing, the electrode covered by the PPy film electrosynthesized in presence of AOT was exposed to a SDBS solution. Again, it can be observed that the diffusion impedance disappears and that the diagram presents a large semicircle, indicating a high resistive interface (Fig. 10). In spite iron ions transport would continue through the pores of the PPy exposed to the DBS, the impedance response is very similar to that obtained for PPy-covered vitreous carbon electrode. This can be interpreted in the same manner as was explained the anticorrosion properties of the PPy formed onto iron in AOT solution [2]. Namely, the gel material inside the polymer should have some kind of stabilization and in this way it contributes to hinder iron dissolution even in an aggressive medium. On the contrary, the presence of AOT in the electrolyte solution stimulates iron dissolution.

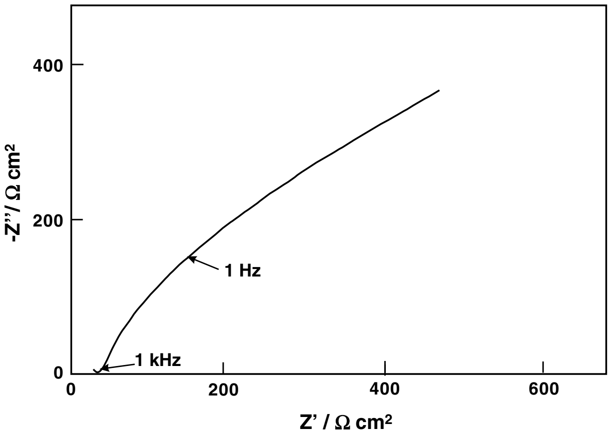

Fig. 8. Nyquist plot of the impedance spectrum for PPy-coated vitreous carbon electrode at 0.0 V in 0.05 M AOT, pH 7 with 0.25 M Py. The polymer was synthesized potentiostatically at 0.90 V in the same solution for 60 min.

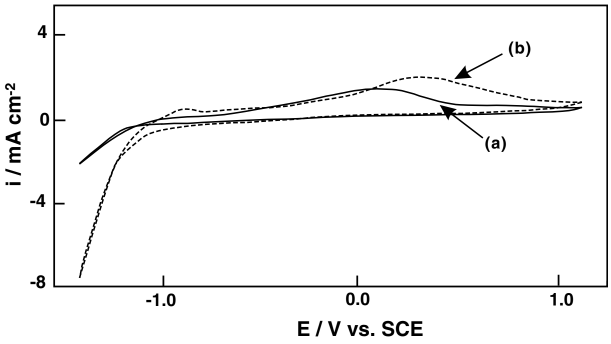

Fig. 9. Stabilized cyclic voltammograms at 0.05 V s^{-1} of bare iron in (a) 0.05 M NaAOT and (b) 0.05 M SDBS.

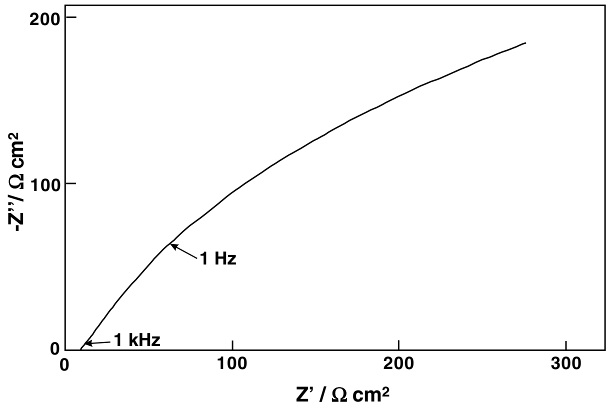

Fig. 10. Nyquist plot of the impedance spectrum for PPy-coated iron electrode at 0.0 V in 0.05 M SDBS, pH 7. The polymer was synthesized potentiostatically at 0.90 V in 0.05 M AOT, pH 7 with 0.25 M Py for 30 min.

In order to obtain more information the impedance behaviour of the bare iron electrode was analyzed in AOT solution without the monomer at open circuit potential (Fig. 11). Under these conditions, dissolution of iron produces the gel material. The response at high frequencies was generally considered to be the sum of the charge resistance against metal dissolution in parallel with electrical double layer capacitance of the metal–solution interface [8,9]. At lower frequencies a linear part is observed and

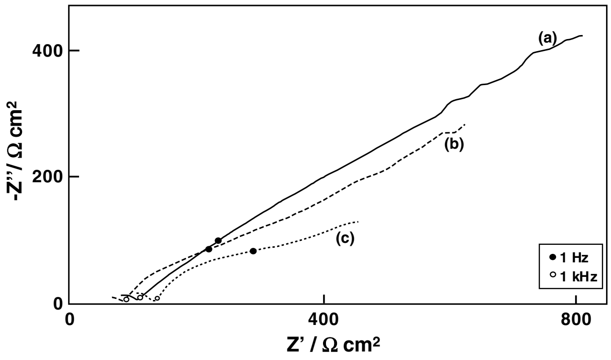

Fig. 11. Nyquist plots of the impedance spectra for uncoated iron electrode at the open circuit potential (−0.50 V) in 0.05 M AOT, pH 7 after different immersion times: (a) 0 min, (b) 300 min and (c) 1500 min.

the most likely explanation to this branch of the circuit is that it originates from diffusion of iron ions through the gel layer whose thickness increases with time. These results allow confirming some of the conclusions reached previously. On one hand, the impedance response is a consequence of a decrease in the ionic mobility of the diffusion species in a medium with increased viscosity. On the other hand, the mass transport in the gel layer is a complex phenomena as indicate the slope lower than 1. Contrary to that it is expected, the diffusion impedance decreases, even disappears as the film thickness increases, which can be explained considering that the gel material is an inhomogeneous structure that changes with exposure time.

Because the PPy synthesized in AOT solution has good protecting properties in chloride solution, electrochemical impedance data were also recorded under open circuit conditions in chloride solution. According to the results presented in Fig. 12A, three stages can be distinguished as the immersion time increases. At the beginning of immersion a diffusion impedance dominates the response of the electrode exposed to the chloride solution. The gel material inside the pores of the coating may hinder the diffusion of species such as chloride, dissolved oxygen or iron ions. Then, mass transport limitations should also be considered to explain the inhibition of chloride corrosion.

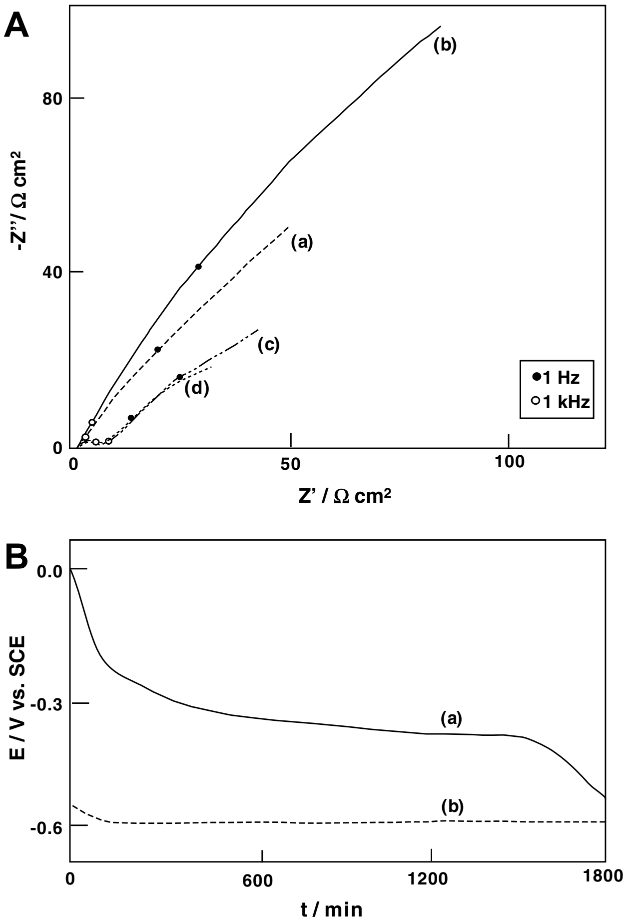

Fig. 12. (A) Nyquist plots of the impedance spectra for PPy-coated iron electrode at the open circuit potential in 0.5 M NaCl after different immersion times: (a) 0 min, (b) 120 min, (c) 1500 min and (d) 1800 min. (B) Time dependence of the corrosion potential in 0.5 M NaCl of: (a) PPy-coated iron electrode; (b) uncoated iron. The polymer was synthesized potentiostatically at 0.90 V in 0.05 M AOT, pH 7 with 0.25 M Py for 30 min.

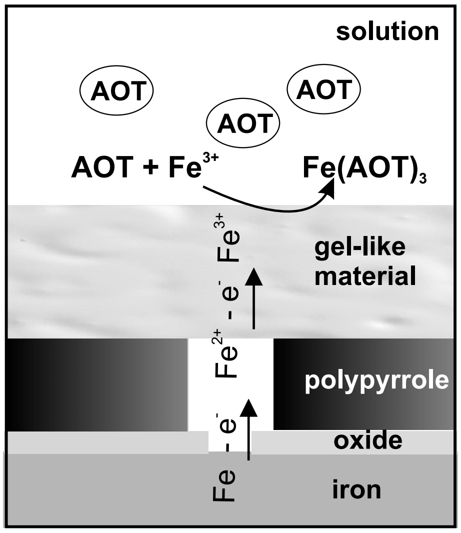

Fig. 13. Schematic representation of iron ions diffusion through the pores of the polymer and the gel layer.

After 2 h the diagram is characterized by a loop with a straight-line portion at high frequencies that could also correspond to a diffusion process. At this stage, the potential remains more positive than that corresponding to uncoated iron, whose surface is already pitted (Fig. 12B). After 24 h of exhibition to the corrosive medium, the potential is near to that of the bare electrode. A semicircle can be observed at the higher frequencies and this response can be explained by considering the charge transfer resistance against iron dissolution in parallel with electrical double layer capacitance. This charge transfer resistance does not vary in size with increasing exposure time, indicating a constant iron dissolution rate. Thus, the effect of mass transport in the system has progressively a lower influence in the corrosion process until the electrode kinetics is controlled by accelerated dissolution of the substrate in the presence of chloride.

4. Conclusions

The electrochemical behaviour of PPy films electrosynthesised onto iron electrodes in the presence of AOT has been investigated by EIS. The impedance results analized in terms of the diffusion resistance show that the response of the thicker films is mainly governed by diffusion of ferrous/ferric ions through the pores of the polymer and through the gel-like film developed between the polymer and the electrolyte. When diffusion occurs exclusively in the polymer film, which is the case of the rotated electrode, the impedance of the electrode follows the Warburg behaviour. The diffusion process gradually deviates from the ideal behaviour as the gel film thickness increases. An schematic representation of the formed films can be proposed (Fig. 13). The scheme includes the oxidation of iron at the bottom of the pores and the diffusion of ions through the pores of the polymer and the gel layer. When the ions reach the gel/solution interface they react with AOT, thickening the gel film.

Whereas iron oxidation continues when the polymer is in contact with AOT solutions, the dissolution of the substrate is inhibited in the presence of other aggressive anions. Mass transfer has a great influence in the corrosion reactions in chloride media which contributes to increase the film protective character.

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