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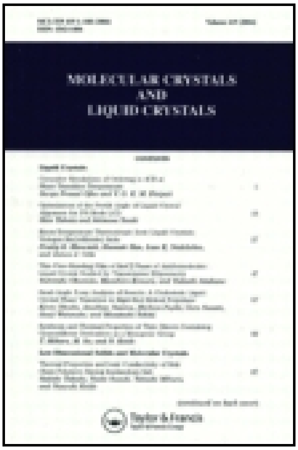

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Electrochemical Activity and Corrosion Protection Properties of Doped Polypyrrole Electrodeposited at Pure Aluminium Electrode

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Polypyrrole films were electrodeposited at pure aluminium from aqueous solution of sodium sulphate containing pyrrole and organic compounds as dopants. Substrate-adherent polypyrrole films were obtained by electrochemical oxidation of pyrrole using the potentiodynamic method and cycling the electrode potential from 50 up to 100 cycles on the potential range of $0 \div 800\,mV$.

Since the conducting polymers, such as polypyrrole, are electrosynthesized easily at inert electrodes such as gold and platinum, but much more difficult at aluminium electrodes, the surface protective oxide, Al_2O_3, *was removed, as it acts as a barrier inhibiting electron transfer and the polymerization process.*

The electrochemical properties of polypyrrole films electrosynthesized from aqueous solutions containing sodium dodecylsulphate (SDS) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as doping electrolytes were studied by cyclic voltammetry and electrochemical impedance spectroscopy. The results indicate that the mechanism of the redox process is complex and may be governed by the diffusion of the electrolyte. The cyclic voltammograms of polypyrrole film synthesized in solutions having different concentrations of SDS and AOT indicate that the dopant concentration plays a very relevant role in the electrochemical response of the doped polypyrrole films like as: PPY/SDS/aluminium oxide and PPY/AOT/aluminium oxide. The results indicate that the SDS and AOT anions

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favor redox processes which are faster and more reversible than those associated to usual polypyrrole electrodes.

However, the aluminium substrate had a considerable effect on the electrochemical activity of the polypyrrole films and that, because in the presence of pyrrole, anodization of these electrolytes resulted in formation of Al_2O_3 and PPY layers simultaneously. This is consistent with a galvanic interaction between the polymer and the aluminium substrate, giving rise to oxidation of the aluminium and reduction of the polymer.

The corrosion performance of polypyrrole coated aluminium was evaluated by DC polarization and Electrochemical Impedance Spectroscopy. Our results show that the presence of polypyrrole coatings significantly increases the corrosion potential and drastically reduces the corrosion current and corrosion rate of pure aluminium. The corrosion resistance of polypyrrole coated aluminium was higher than of uncoated aluminium.

Keywords: barrier oxide film; electroactive polymers; oxidation state; polymer backbone; protective coating

INTRODUCTION

Organic coatings have long been used to protect metals against corrosion. The primary effect of an organic coating is to act as a physical barrier against aggressive species. However, for all organic coatings, pathways will be created for the corrosive species to reach substrate, and localized corrosion will occur. Recently, there have been attempts to use electroactive polymers to control pitting corrosion resulting from the permeation and breakdown of the protective coating. It is well known that the conducting polymers are an extremely important class of materials because they present a combination of properties of classical metals, semiconductors and polymers. Generally, electropolymerization of heterocycles like pyrrole, thiophene and their derivatives is performed anodically on chemically inert electrodes (Au, Pt, graphite, glassy carbon). Films, which are electrosynthesised at metal surfaces, using these monomers, constitute promising new materials because of their interesting mechanical and electronic properties. Indeed, these electrochemically prepared polymer films form often homogenous and adhesive coatings at metal substrates, when in the oxidized state, they present a relative high electrical conductivity and their thickness can be electrochemically controlled, as needed. These coatings can be also reduced to insulating material, allowing their possible use as corrosion inhibitors for different metals. Consequently, much of the recent research has focused on formulating new and more environmentally acceptable polymeric-type

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coatings. For example, Guenbour *et al.* [1] have studied the corrosion protection of copper by polyaminophenol films obtained through the electropolymerization of the monomer in special conditions. There have also been reports [2–6] on the formation of polymeric films through the electrochemical oxidation and also, about insulating polymers fabricated by oxidizing 2-mercaptobenzimidazole in alkaline water-methanol solutions [7]. Although there is an extensive literature on the corrosion protection properties of conducting polymers, such as polyaniline and polypyrrole on iron or iron-based alloys [8–10] there are very few reports devoted to the corrosion protection properties of these polymers when applied to aluminium or aluminium-based alloys. It was found that these polymers could either enhance the corrosion rate or produce significant corrosion protection properties depending on the chemical nature of the polymer backbone and on the oxidation state and extent and nature of polymer doping.

In this paper, the polypyrrole films electrodeposited on pure aluminium substrate using potentiodynamic method and cycling the electrode potential were studied related to the electrochemical properties and protective corrosion properties.

EXPERIMENTAL

The electrochemical measurements were performed with a conventional three-electrode system and a potentiostat/galvanostat type Princeton Applied Research Model 173 provided with a computer interface for the data acquisition. A platinum electrode and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. The reference electrode was placed in a separated cell and was connected to the electrolytic cell via a salt bridge, which ends as a Luggin capillary in the electrolytic cell. This arrangement was used to reduce chloride ion contamination of the electrochemical system from the reference electrode. All electrode potentials were measured *versus* this reference electrode. Substrate-adherent polypyrrole films were obtained by electrochemical oxidation of pyrrole using the potentiodynamic method and cycling the electrode potential from 50 up to 100 cycles on the potential range of $0 \div +800\,\text{mV}$. Polypyrrole films were electrodeposited on pure aluminium from an aqueous solution which contained 0.1 M pyrrol and 0.1 M SDS (sodium dodecylsulphate) and from another solution with 0.1 M pyrrol and 0.02 M AOT (sodium bis(2-ethylhexyl) sulphosuccinate). The electrochemical properties of polypyrrole films electrosynthesized from aqueous solutions containing SDS and AOT as doping electrolytes were studied by cyclic voltammetry using 0.1 M Na_2SO_4 aqueous solutions as cycling solution. The cyclic voltammograms were obtained by potential sweep rate of $5\,mVs^{-1}$.

Impedance spectroscopy measurements were carried out using a Frequency Analyzer (Solartron 1260) coupled to a potentiostat type Solartron 1287. The impedance diagrams were interpreted based on the equivalent circuits using the Z.View software (version 2.4a Scribner Associates inc. Southern Pines, USA).

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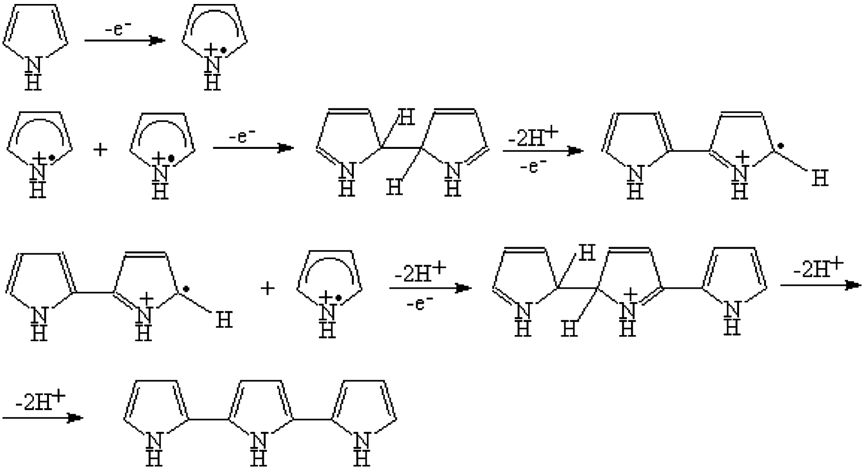
RESULTS AND DISCUSSION

Aluminium is a valve metal and its excellent corrosion resistance is due to the formation of very stable, continuous, highly adherent and protective oxide films on metal surface. Since aluminium is highly reactive and has an extremely high affinity for oxygen, these beneficial surface oxide films form spontaneously and instantly when fresh metal surfaces are exposed to air and/or moisture.

In fact, a damaged oxide film can generally reheal itself instantaneously if at least traces of oxygen or water (moisture) are present in the environment. Hence, aluminium electrodes are easily oxidized, giving a non-conducting dielectric (Al_2O_3) film on the electrode. The Al_2O_3 film acts as an excellent barrier, inhibiting an electron transfer and this inhibiting the electrochemical formation of polypyrrole (PPY). The electrodeposition of PPY on aluminium substrate is difficult, but it is not impossible. The electrodeposited PPY film on aluminium has been obtained by removing the barrier oxide film (Al_2O_3) from the aluminium surface. For that, prior to anodic polarization the electrode surface was etched in 0.1 M KOH for a period of 10 minutes. The aluminium electrode was then rinsed with distilled water and immersed in synthesis solution from the electrolytic cell. The following aqueous solutions have been used: 0.1 M pyrrole + 0.1 M SDS and 0.1 M pyrrole +0.02 M AOT.

The polymeric film was electrodeposited using potentiodynamic method, the electrode potential was scanned on the range of $(0 \div 800\,mV)$ with a sweep rate of $5\,mV \cdot s^{-1}$ for a period of 50 cycles. After this anodic polarization, a successful formation of both films have taken place, the porous Al_2O_3 film and the polymeric PPY film in their pores at the same time.

The formation process of PPY film can be illustrated by the following mechanism:



The electropolymerization reaction appears to involve two electrons per molecule of Py monomer and it proceeds through a radical coupling mechanism [11]. During the film formation, a stoichiometric amount of anions provided by the supporting electrolyte is incorporated into the polymer layer to neutralize the positive charge of the PPY chains. Therefore, the nature of the anions plays an important role in conferring the properties of the PPY films [12].

As it was shown above, during anodic polarization the formation of Al_2O_3 and PPY films proceeds simultaneously. For Al_2O_3 the formation process can be explained as follows: the primary process in the electrochemical corrosion of aluminium is the formation of hexahydrated aluminium ion $[Al(H_2O)_6]^{3+}$. In aqueous solutions of pH (4–10), hexacoordinated aluminium ion forms different hidroxo complexes. Polynuclear complexes can be also formed depending on pH and aluminium ion concentration, consequently $Al[O_x(OH)_y(H_2O)_z]$ is the idealized formula for the solid gel – like hidroxo complexes of undefined structure assigned to gelatinous alumina [13–15].

Gelatinous alumina tends to form fibers due to its crystal structure. The fibrous structure was observed by using a microscope in a study of the aluminium electrode during electrochemical polarization experiments. This gelatinous alumina transforms into pseudoboehmite, boehmite and finally bayerite in aqueous media [14,15] according to the following equations:

$$\begin{aligned} Al[O_x(OH)_y(H_2O)_z] &\rightarrow (AlOOH)_4\ xH_2O \quad &&\text{pseudoboehmite} \\ (AlOOH)_4\ xH_2O &\rightarrow AlOOH &&\text{boehmite} \\ AlOOH + H_2O &\rightarrow Al(OH)_3 &&\text{bayerite} \end{aligned}$$

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Finally one can obtain:

$$Al(OH)_3 \rightarrow 1/2\,Al_2O_3 + 3/2\,H_2O$$

The two films interact with each other and one can consider that the bilayer – film was obtained consisting in a barrier – type Al_2O_3 and an electronically – conducting PPY film. The formation of Al_2O_3 proceeds at two interfaces, namely at the aluminium/Al_2O_3 and at the Al_2O_3/PPY. It is assumed that, the species are continuously generated at metal/oxide interface. Then they migrate through growing Al_2O_3 layer toward the solution under high electric field, while oxide ions (O^{2-}) migrate toward the aluminium electrode [16]. At the interface of Al_2O_3/PPY, the Al^{3+}encounter water species to form Al_2O_3 film. In the case of simultaneous formation, surfactant electrolytes are considered to play three important roles:

(i) as supporting electrolytes for forming Al_2O_3 film;
(ii) dopants incorporated into electropolymerized PPY film [17];
(iii) micelle assemblies at the electrode interface to enable the PPY formation simultaneously with the formation of the insulating oxide under-layer film.

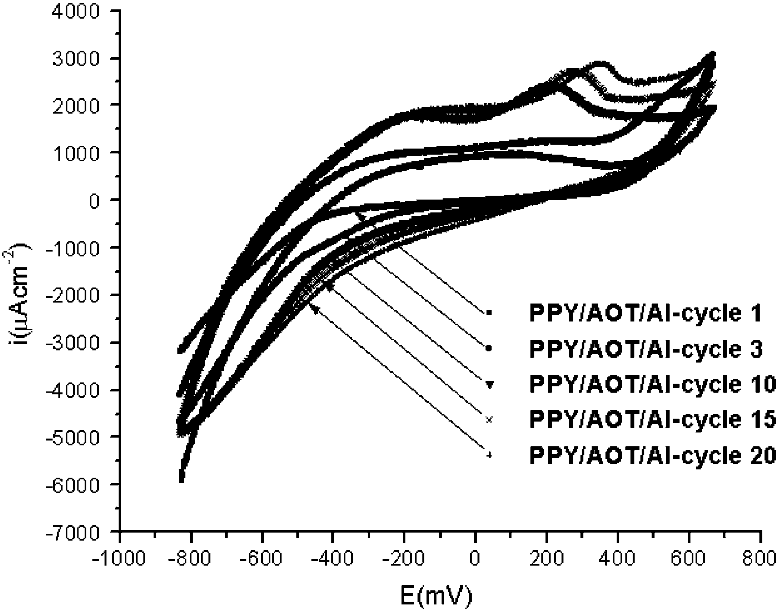

FIGURE 1 Cyclic voltammograms of PPY(AOT)/Al modified electrodes at different cycles in 0.1 M Na_2SO_4 at a scan rate of 10 mVs^{-1}and 25°C.

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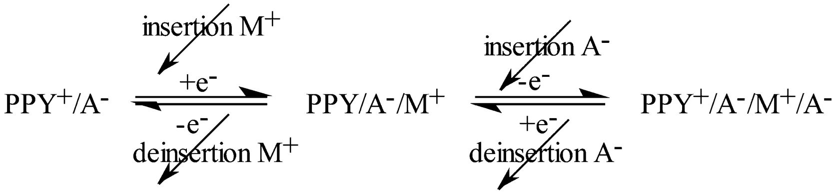
Aluminium ions generated by the electrochemical oxidation of the aluminium electrode undergo one of two types of reactions, a film – formation process resulting in Al_2O_3, or a dissolution process resulting in soluble species which migrate into the bulk of the solution. The pK_a of the electrolyte anions determines which of these reactions occurs. Regarding the role of dopants, sulfonate anions are often used as dopants for PPY to support the polymerization process and the electrical/electrochemical properties of the resulting PPY.

Therefore the polarization behaviour of the PPY(DS)/Al and PPY(AOT)/Al modified electrodes has been studied by cyclic voltammetry in 0.1 M N_2SO_4 aqueous solutions. In Figure 1 the cyclic voltammograms of PPY(DS)/Al modified electrode are shown at the different cycles in 0.1 M N_2SO_4.

From the analysis of Figure 1, one can see that, at the anodic potential scan two anodic current peaks (oxidation peaks) are obtained, while at the reverse potential scan, two cathodic current peaks (reduction peaks) are noticed. We presume the following reactions:



where A^- represents an anion dopant and M^+ a cation from supporting electrolyte. One or the other steps may be favored depending on the diffusion coefficient of the ionic species in the PPY films. The shape of the voltammetric curve also confirms this redox mechanism. The same behaviour is obtained for the PPY(AOT)/Al modified electrode. Figure 2 shows the cyclic voltammograms of this modified electrode in 0.1 M Na_2SO_4 aqueous solutions at different cycles. Comparative analysis of two figures led to the following conclusions: increasing the number of cycles results in all the cases to increasing the height of anodic and cathodic peaks and hence, to increasing the anodic and cathodic current peaks respectively; the PPY (DS)/Al modified electrode shows much sharper peaks and lower peak separation than the PPY (AOT)/Al modified electrode, this indicating that the former is characterized by faster and more reversible electrochemical redox processes.

This is confirmed by Table 1, where the voltammetric data of the two electrodes are compared and summarized.

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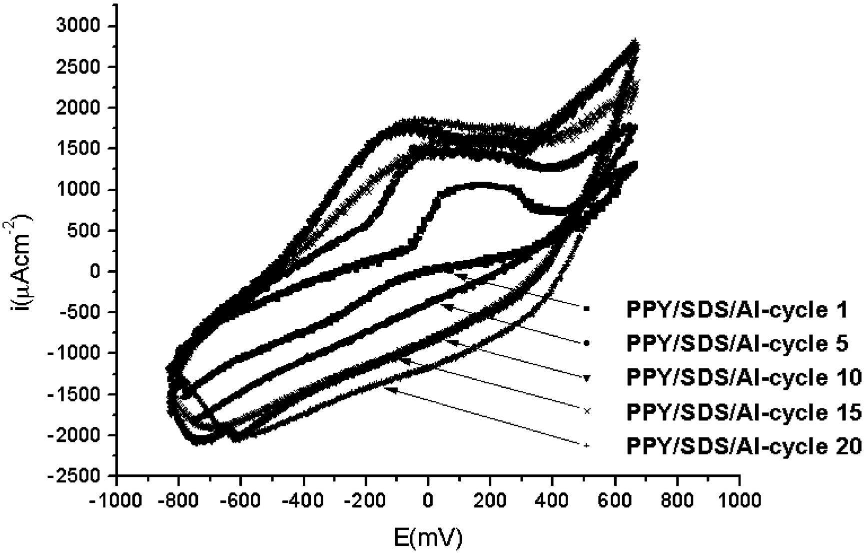

FIGURE 2 Cyclic voltammograms of PPY(SDS)/Al modified electrodes at different cycles in 0.1 M Na_2SO_4 at a scan rate of 10 mVs^{-1} and 25°C.

One of the most important applications of electrochemical impedance spectroscopy is the evaluation of corrosion protection by polymer coatings. In Figures 3–6 the impedance diagrams for

TABLE 1 The Kinetic Parameters of PPY(AOT)/Al and PPY(SDS)/Al Modified Electrodes for Different Cycles in Aqueous Solution of 0.1 M Na_2SO_4 (The Cycling Electrolyte)

Doping anion	Cycle number	ipa_1 (mA·cm^{-2})	Epa_1 (mV)	ipa_2 (mA·cm^{-2})	Epa_2 (mV)	ipc_1 (mA·cm^{-2})	Epc_1 (mV)
AOT	1	4.87	170	–	–	–	–
AOT	5	7.54	−50	–	–	–	–
AOT	10	7.81	−20	–	–	9.66	−690
AOT	15	8.80	−125	–	–	10.03	−730
AOT	20	9.18	−100	–	–	10.1	−600
SDS	10	8.73	−190	12.30	200	–	–
SDS	15	9.16	−156	13.45	270	–	–
SDS	20	9.22	−120	14.73	340	–	–

ipa, ipc: the anodic and cathodic peaks current densities.
Epa, Epc: the potentials corresponding to anodic and cathodic peaks.

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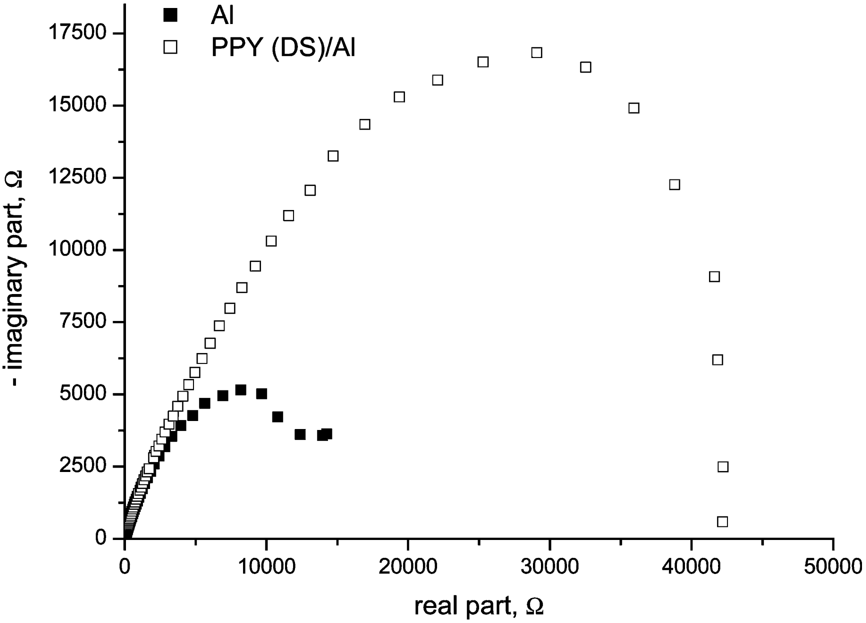

FIGURE 3 Nyquist diagrams for Al and PPY(SDS)/Al electrodes in 0.1 M Na_2SO_4 at the rest potential.

PPY(DS)/Al modified electrode are presented at the potential of +100 mV and at the open circuit potential.

All diagrams were characterizated by depressed capacitive loops in the high frequency range. In the Nyquist diagram for the PPY(DS)/Al modified electrode at +100 mV two capacitive loops appear, one small at high frequencies and another (well defined) at the medium frequency. Also, one can see an inductive loop at the low frequencies. Bode diagrams have been confirmed these results from Nyquist diagrams.

These experimental impedance spectra for polymer – coated aluminium electrode are in agreement with equivalent circuit presented in Figures 7 and 8.

In this case the general interfacial impedance (Z_1), which is the parallel combination of the polarization resistance (R_p) and the capacitance (C), consists in the corrosion elements.

All impedance data were obtained by fitting the equivalent circuits from the Figures 7 and 8 and were summarized in the Tables 2 and 3.

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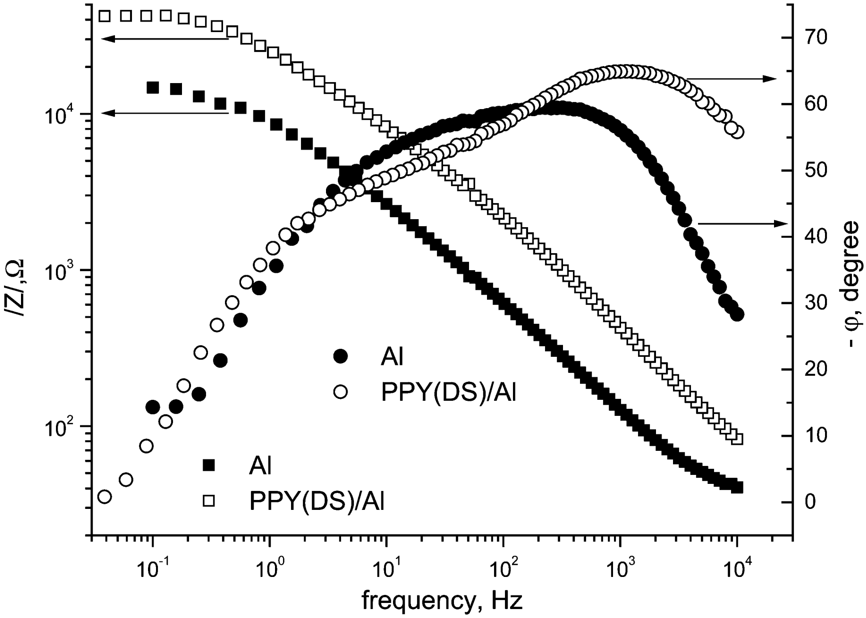

FIGURE 4 Bode diagrams for Al and PPY(SDS)/Al electrodes in 0.1 M Na_2SO_4 at the rest potential.

Comparative analysis of the data from Tables 2 and 3 shows that the corrosion resistance increases with increase of the electrode potential in anodic direction.

Also, the PPY(DS)/Al electrode has a higher polarization resistance then aluminium electrode uncoated. At noble potential appear two capacitive loops which represent the two interfaces from the electrode surface, which are Al_2O_3 film/Al substrate and PPY(DS) film/Al substrate.

CONCLUSIONS

The obtaining of PPY film by electropolymerization on aluminium substrate is possible after removing the oxide barrier film (Al_2O_3) from the electrode surface.

The formation processes of PPY film and the porous film of Al_2O_3 proceeds at the electrode surface simultaneously.

The two films interact with each other and form a composite material at the electrode surface.

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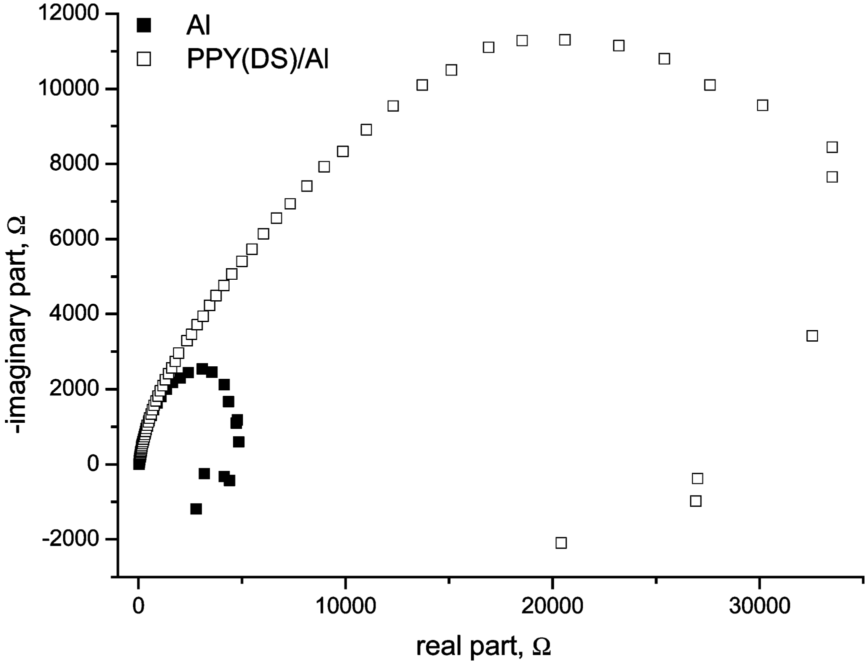

FIGURE 5 Nyquist diagrams for Al and PPY(SDS)/Al electrodes in 0.1 M Na_2SO_4 at the potential of 100 mV.

The stability of this composite material increases with the number of cycles and anodic polarization.

By increasing the cycles number results in all the cases to increase of the height of the anodic and cathodic peaks, respectively, of the anodic and cathodic current peaks.

The electrochemical impedance spectra of polypyrrole films in aqueous media respond to the changes occurring during the insulator-conductor transition. These include charge carrier generation, conformational changes, a higher porosity and increased ionic transport capabilities.

The uncoated aluminium electrode shows a single capacitive semicircle on Nyquist diagrams reflecting the influence of Al_2O_3 film/pure aluminium interface.

The appearance of the second loop on the Nyquist diagram of the coated aluminium electrode [PPY(DS)/Al] suggests that there is an additional electrochemical process other then the interfacial charge transfer reaction. This fact suggests that a new interface was formed.

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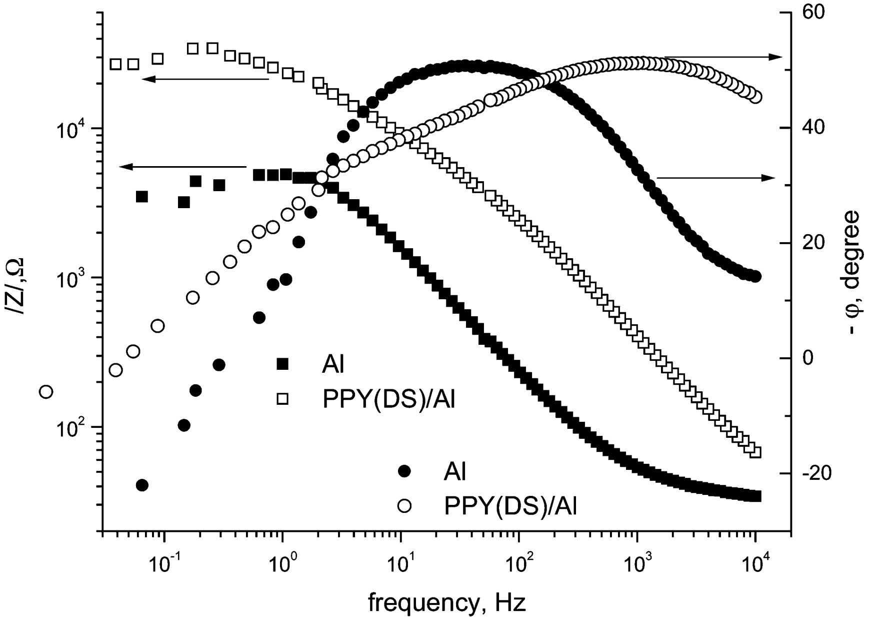

FIGURE 6 Bode diagrams for Al and PPY(SDS)/Al electrodes in 0.1 M Na_2SO_4 at the potential of 100 mV.

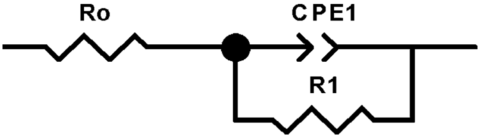

FIGURE 7 Equivalent circuit used to simulate the impedance spectra for Al electrode.

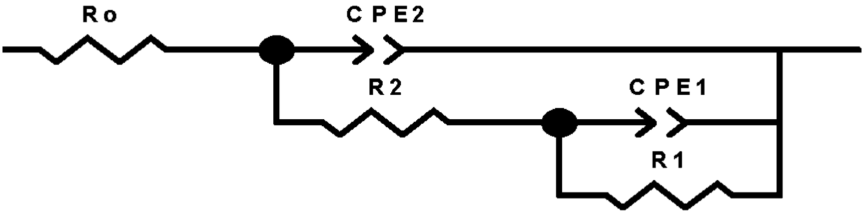

FIGURE 8 Equivalent circuit used to simulate the impedance spectra for PPY(SDS)/Al modified electrode.

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TABLE 2 Values of Circuit Elements Obtained by Fitting the Experimental Data to the Proposed Equivalent Circuit for Al Electrode in Aqueous Solution of 0.1 M Na_2SO_4 at Different Potentials

Circuit element E, mV	R0, Ω	R1, Ω	CPE1, $\Omega^{-1}s^{\varphi}$
Rest potential	30	15364	$1.8 \cdot 10^{-5}$, respectively $\varphi = 0.7$
100 mV	35	5658	$1.6 \cdot 10^{-5}$, respectively $\varphi = 0.87$

*CPE is a constant phase element with impedance given by: $Z_{CPE} = (1/\sigma)(j\omega)^{-\varphi}$, where σ and φ are positive constants. A CPE describes a capacitor when $\varphi = 1$, in which case $\sigma = C$ and tends to a resistor as $\varphi \to 0$.

TABLE 3 Values of Circuit Elements Obtained by Fitting the Experimental Data to the Proposed Equivalent Circuit for PPY(SDS)/Al Electrode in Aqueous Solution of 0.1 M Na_2SO_4 at Different Potentials

Circuit element E, mV	R0, Ω	R1, Ω	CPE1, $\Omega^{-1}s^{\varphi}$	R2, Ω	CPE2, $\Omega^{-1}s^{\varphi}$
Rest potential	30	47063	$6.9 \cdot 10^{-6}$, respectively $\varphi = 0.64$	4822	$1.9 \cdot 10^{-6}$, respectively $\varphi = 0.81$
100 mV	30	40695	$8.9 \cdot 10^{-6}$, respectively $\varphi = 0.56$	3905	$1.0 \cdot 10^{-6}$, respectively $\varphi = 0.89$

At high frequency, two charge transfer semicircles appear traducing the interface effects, the double layer capacity in parallel with the charge transfer resistance for the substrate/polymer interface and the double layer capacitance in parallel with the charge transfer resistance for the polymer/solution interface.

REFERENCES

[1] Guenbour, A., Kacemi, A., & Benbachir, A. (2000). *Prog. Org. Coat.*, *39*, 151.

[2] Trachli, B., Keddam, M., Takenouti, H., & Srhiri, A. (2002). *Corros. Sci.*, *44*, 997.

[3] Kerit, S., Aride, J., Srhiri, A., BenBachir, A., Elkacemi, K., & Etman, M. (1993). *J. Appl. Electrochem.*, *23*, 835.

[4] Taneichi, D., Haneda, R., & Aramaki, K. (2001). *Corros. Sci.*, *43*, 1589.

[5] Haneda, R. & Aramaki, K. (1998). *J. Electrochem. Soc.*, *145*, 1856.

[6] Haneda, R. & Aramaki, K. (1998). *J. Electrochem. Soc.*, *145*, 2786.

[7] Perrin, F. X. & Pagetti, J. (1998). *Corros. Sci.*, *40*, 1647.

[8] Camalet, J. L., Lacroix, J. C., Aeiyach, S., & Lacaze, P. C. (1998). *J. Electroanal. Chem.*, *445*, 117.

[9] Sazou, B. D. & Georgolios, C. (1997). *J. Electroanal. Chem.*, *429*, 81.

[10] He, J., Gelling, V. J., Tallman, D. E., Bierwagen, G. P., & Wallace, C. G. (2000). *J. Electrochem. Soc.*, 147, 3667.

[11] Genies, E. M., Bidan, G., & Diaz, A. F. (1983). *J. Electroanal. Chem.*, *49*, 101.

[12] Diaz, A. F. & Kanazawa, K. K. (1983). Polypyrrole: An electrochemical approach to conducting polymers, In: *Extended Linear Chain Compounds*, Miller, J. (Ed.), Plenum Press: New York, Vol. 3, 41–441.

[13] Lowson, R. T. (1974). *Aust. J. Chem.*, *27*, 105.

[14] Baes, C. F. & Mesmer, R. E. (1976). *The Hydrolysis of Cation*, Wiley: New York, 122.

[15] Wefers, K. & Bell, G. M. (1972). *Oxides and Hydroxides of Aluminium*, Alcoa, Techinical Paper, 191.

[16] Lohrenged, M. M. (1993). *Mater. Sci. Eng.*, *R11*, 243.

[17] Naoi, K. (2000). *Electrochim. Acta*, *45*, 3413.

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