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ORIGINAL PAPER

Polypyrrole electropolymerized on aluminum alloy 1100 doped with oxalate and tungstate anions

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Abstract Polypyrrole films doped with oxalic acid and tungstate were potentiostatically electropolymerized on aluminum alloy 1100. Two statistical factorial designs (fractional and complete) were used to study the influence of the synthesis variables on the film performance against corrosion. Corrosion protection of the polypyrrole films doped with oxalate and tungstate anions (PPy/OXA/W) on the aluminum alloy was evaluated by potentiometric and electrochemical impedance spectroscopy (EIS) measurements in a 0.05 mol L^{-1} NaCl solution. The results obtained showed that the best performance against corrosion was detected with the PPy/OXA/W film synthesized at 1.0 V, 1.5 C in 0.2 mol L^{-1} pyrrole, 0.1 mol L^{-1} oxalic acid and 0.05 mol L^{-1} sodium tungstate solutions provide a protective effect against corrosion.

Keywords Polypyrrole · Aluminum · Tungstate · Corrosion

1 Introduction

Intrinsically conducting organic polymers, such as polyaniline and polypyrrole, have been studied intensively during the last two decades due to their high conductivity, good thermal and environmental stability and their varied technological applications in batteries, supercapacitors, sensors, anhydrous electrorheological fluids and corrosion protection.

The use of conducting polymers (CPs) as barrier coatings on metal substrates in corrosion control is pointed out as a replacement for Cr(VI)-based coatings. However, the mechanism of corrosion protection in CPs has not yet been fully understood. Most of the proposed mechanisms support the idea of an anodic protection mechanism to valve metals with a passivity domain (Fe, carbon steels, Al, etc.) or a simple barrier effect for those metals which do not present such behavior (Zn, Cu, etc.). Effective corrosion protection is achieved by conducting polymer systems when they are in the doped and oxidized state or conducting form, and loss of protection corresponds to the reduced form of the film [1, 2].

Polypyrrole (PPy) is the most promising conducting polymers because of its high conductivity, stability and easy synthesis in aqueous solutions [3–5]. However, the electropolymerization of pyrrole on active metals has proved to be a difficult task [6–8], since the potential required to oxidize the monomer is higher than the corrosion potential of such metals. Cheung et al. [6] have demonstrated that the oxidation potential of the monomer and the anodic current intensity values vary from one substrate to another, the highest oxidation potential and lowest current intensity being obtained for aluminum, owing to the formation of a fine layer of nonconductive oxide on the metal surface at −1.35 V versus SHE. It is well known that the presence of Al_2O_3 on aluminum inhibits the electron transfer process hindering PPy deposition and, hence, the polymer formation and growth.

Recently several researchers studied the electrosynthesis of CPs by anodic oxidation of monomer in the presence of

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anions with corrosion-inhibiting properties [9, 10]. Rammelt et al. [9] studied the corrosion protection for mild steel obtained by films of PPy doped with molybdate. The results demonstrated that once the corrosion reaction starts at a film defect, PPy is partially reduced thereby releasing the dopant anion molybdate, which then stops the corrosion within the defect. Lehr and Saidman [10] electrosynthesized PPy onto aluminum electrodes in an alkaline solution in the presence of molybdate and nitrate anions. Corrosion resistance was improved in chloride media and an increased pitting potential was detected on the coated aluminum. They observed that molybdate remains entrapped in the polymer matrix during the oxidation/reduction of the film.

Similarly to chromate and molybdate anions, tungstate has been used as a corrosion inhibitor for aluminum and aluminum alloys in chloride solutions [11, 12]. According to Zein El Abedin [11] the main inhibiting factor observed when tungstate is added is attributed to the adsorption of WO_4^{2-} anion in flawed areas. However, little attention has been given to the use of tungsten compounds as corrosion inhibitors in aqueous medium [13].

The quality of PPy films is affected by many experimental factors, such as: concentration of monomer and dopants, polymerization potential, polymerization time and others. Choosing the best synthesis condition may be complicated if we consider the great number of experiments involved. This difficulty has been overcome largely by the use of the statistical design of experiments, which allows optimizing the synthesis conditions through a smaller number of experiments. The statistical design of experiments has been widely employed in the optimization of industrial processes [14, 15], in analytical work [16] and in electrochemical processes [17–20].

The aim of this work is to investigate the electrochemical deposition of PPy doped with tungstate and oxalic acid on AA 1100 alloy to obtain a protective film against corrosion. A fractional 2^{4-1} factorial design was carried out in order to achieve the best synthesis conditions. The films obtained were analyzed by using electrochemical techniques.

2 Experimental methods

Prior to use, Pyrrole (Aldrich, 99%) was vacuum-distilled and stocked at 4 °C.

The experiments were performed in the presence of dissolved oxygen and at room temperature (24 °C). A 1.0 × 1.0 cm Al-1100 sheet, a Pt gauze and saturated calomel electrode (SCE) were employed as the working, counter and reference electrodes, respectively.

The working electrode was pretreated by galvanostatic activation for 120 s at 27 mA cm^{-2} in a mixture of 0.1 mol L^{-1} HNO_3 and 0.1 mol L^{-1} Py. This procedure was carried out based on the work of Hülser and Beck [21] who reported that this method provides a cohesive and adherent layer of deposited PPy.

Following this pretreatment, the electrode was washed with deionized water and transferred to the electrochemical cell.

As a typical procedure, sodium tungstate (Na_2WO_4) and oxalic acid ($H_2C_2O_4$) were dissolved under magnetic stirring and pyrrole was added afterwards. Then, the electropolymerization was performed potentiostatically. The electrochemical measurements were performed using an AUTOLAB PGSTAT 30/FRA 2 system open to the air at room temperature (24 °C). Electrolytic solutions of Na_2WO_4, $H_2C_2O_4$ and NaCl were used. The potentiodynamic polarization tests were carried out at 0.020 V s^{-1}. The EIS tests were performed at the open-circuit potential in the 100 kHz to 10 mHz frequency range and the amplitude of the sinusoidal voltage was 10 mV.

3 Results and discussion

3.1 Influence of dopant

The influence of the dopant on the electrosynthesis of polypyrrole was investigated through cyclic voltammetry on a glassy carbon electrode at 0.020 V s^{-1} in 0.2 mol L^{-1} pyrrole and 0.05 mol L^{-1} Na_2WO_4 and, alternatively, in a 0.1 mol L^{-1} $H_2C_2O_4$ + 0.05 mol L^{-1} Na_2WO_4 medium (Fig. 1).

As shown in Fig. 1, in 0.1 mol L^{-1} $H_2C_2O_4$ + 0.05 mol L^{-1} Na_2WO_4 (curve a) there is a current increase starting at about 0.5 V indicating the onset of PPy electropolymerization. On the reverse scan a cathodic peak is observed, at −0.61 V relating to the reduction of the film from the cationic to the neutral form. The films obtained

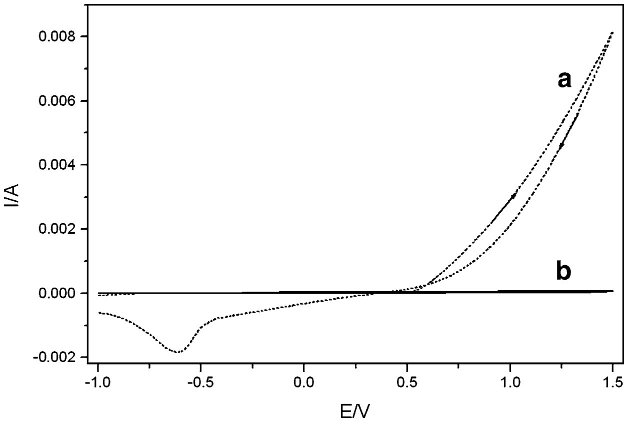

Fig. 1 Cyclic voltammogram on GC electrode at 0.020 V s^{-1} in: (a) 0.2 mol L^{-1} pyrrole + 0.1 mol L^{-1} $H_2C_2O_4$ + 0.05 mol L^{-1} Na_2WO_4; (b) 0.2 mol L^{-1} pyrrole + 0.05 mol L^{-1} Na_2WO_4 solution

with the combination of these dopants are uniforms. Oxalic acid has been mentioned as an electrolyte to obtain well-adhering homogeneous PPy films [21]. When the dopant is only tungstate anion (curve b), a marked current rise, like curve a, could not be detected meaning that no electropolymerization occurs. Just as the other oxi-anions of group VI, tungstate anion (WO_4^{-2}) is nucleophilic and can attack the radical cations hindering the electropolymerization process and, consequently, film formation and growth.

Although neutral or slightly alkaline aqueous solutions are the conditions of thermodynamic stability for WO_4^{-2} at 25 °C [22], the electropolymerization of PPy on aluminum in alkaline media carried out in the presence of 0.1 mol L^{-1} $K_2C_2O_4$ + 0.05 mol L^{-1} Na_2WO_4 (data not shown here) did not produce uniform films on the substrate.

3.2 Electrosynthesis

Potentiostatic electrodeposition was chosen as the electrosynthesis method due to easy potential control [22]. The films obtained by this method are homogeneous and easily reproduced. Figure 2 shows the *I–t* transients obtained for the electrosynthesis of PPy on AA 1100 at 1.0 V in 0.2 mol L^{-1} pyrrole and 0.05 mol L^{-1} Na_2WO_4 in the (a) presence and (b) absence of 0.1 mol L^{-1} $H_2C_2O_4$.

As can be seen in Fig. 2 (curve a) there is an initial current decay, followed by a period in which the anodic current increases called induction period [23], which corresponds to the onset of the PPy electropolymerization. After this induction period, the current decays. By using the theory model of conducting polymer growth several works have attributed this behavior to a diffusion-controlled process [24, 25]. The *I–t* transients obtained for this condition presented an induction time of 350 s and an anodic current of 1.48 × 10^{-3} A cm^{-2}. Potentiostatic polymerization was carried out during 1,600 s until 1.5 C of total charge. When the dopant is only WO_4^{-2} (curve b), the PPy electrosynthesis fails, since after 3,400 s the current density is 0.33 × 10^{-6} A cm^{-2} and the total charge is 0.107 C. These results agree with the CV measurements, indicating that the PPy electropolymerization is hindered in the WO_4^{-2} solutions.

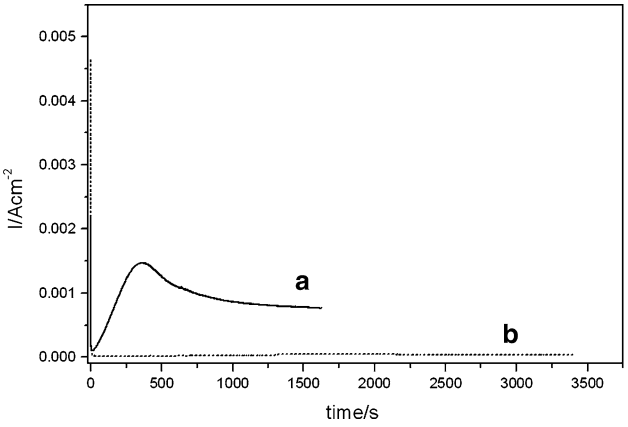

Fig. 2 *I–t* transients obtained for the electrosynthesis of PPy on aluminum alloy at 1.0 V in: (a) 0.2 mol L^{-1} pyrrole + 0.1 mol L^{-1} $H_2C_2O_4$ + 0.05 mol L^{-1} Na_2WO_4; (b) 0.2 mol L^{-1} pyrrole + 0.05 mol L^{-1} Na_2WO_4 solution

In order to investigate the redox behavior of polypyrrole film doped with oxalate and tungstate anions (PPy/OXA/W) films were electrosynthetized on a GC electrode and cyclic voltammetric curves were made in a monomer-free solution. The film was electropolymerized at 1.0 V in 0.2 mol L^{-1} pyrrole, 0.1 mol L^{-1} $H_2C_2O_4$ and 0.05 mol L^{-1} Na_2WO_4 until a charge value of 1.5 C. The GC coated electrode was subjected to potential cycling between 0.75 and −1.25 V at 0.010 V s^{-1} in 0.1 mol L^{-1} $H_2C_2O_4$ + 0.05 mol L^{-1} Na_2WO_4 (Fig. 3a) and 0.05 mol L^{-1} NaCl (Fig. 3b) solutions.

Figure 3a shows a reduction peak at −0.5 V and oxidation peak at 0.0 V at the first scan. These peaks are

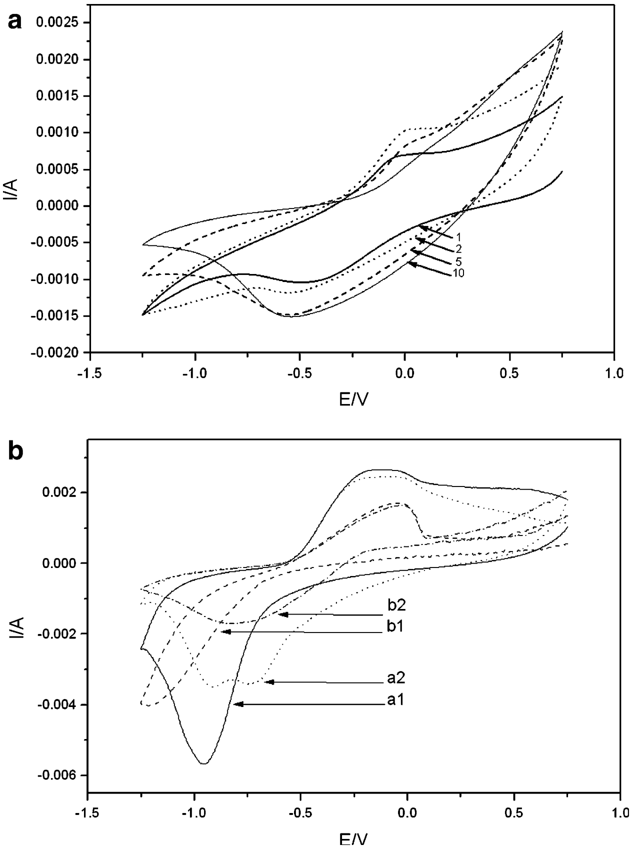

Fig. 3 (**a**) Cyclic voltammogram for GC/PPy/OXA/W electrode immersed in 0.1 mol L^{-1} $H_2C_2O_4$ + 0.05 mol L^{-1} Na_2WO_4 solutions between 0.75 and −1.25 V at 0.010 V s^{-1}. (**b**) Cyclic voltammogram for GC/PPy/OXA/W electrode between 0.75 and −1.25 V at 0.010 V s^{-1} immersed in 0.05 mol L^{-1} NaCl solution (curves a1, a2) and 0.1 mol L^{-1} $K_2C_2O_4$ (curves b1, b2)

associated with the exchange of oxalate anion, since these peaks also appear when the polymer is formed in oxalic acid solution only. By increasing the number of scans, the current of the cathodic and anodic peaks increases, indicating that the film electroneutrality is reached by oxalate anion exchange. This feature suggests that there is no exchange of tungstate during the cycling, and this anion remains in the polymer matrix. Similar results were reported by Shimidzu et al. [26] using electrogenerated PPy-phosphotungstate films and by Cheng and Otero [27] with electrogenerated PPy-polyoxometalate films. According to these authors, the amount of polyoxometalate anions released decreases in acidic solution. Thus, the polyoxometalate anions can remain in the PPy matrix when the hybrid film is in acidic solution irrespective of the polyoxometalate anions used.

In order to evaluate the ability of tungstate anions to release from the PPy/OXA/W film in neutral media, CVs were performed in 0.05 mol L^{-1} NaCl solution and in 0.1 mol L^{-1} $K_2C_2O_4$ (Fig. 3b) using a GC/PPy/OXA/W electrode. In NaCl solution the CV shows a reduction peak at −0.95 V and an oxidation peak at −0.125 V at the first scan. In the second cycle, two cathodic peaks at −0.95 and −0.70 V are observed followed by a decrease of the reduction charge, which is generally observed in CV for redox reaction of conducting polymers. Similar behavior was detected in the voltammograms obtained in free chloride oxalate solution. The first cycle shows a cathodic peak shifted to more negative potential values and at the second scan a broad peak is detected around −0.85 V. The decrease of the reduction charge in the second cycle, observed at the CVs obtained in the presence and absence of chloride, suggests that the dopant anions released from the PPy matrix are not completely incorporated into the PPy, on subsequent oxidation being substituted by the electrolyte ions. Previous data [26] have demonstrated that the amount of PPy-phosphotungstate released in NaCl solution pH 7 can be three times higher than that released in HCl pH 3. Rammelt et al. [9] also detected the release of molybdate anion during the reduction of polypyrrole films containing molybdate as dopant.

3.3 Fractional factorial design

In order to evaluate the influence of the synthesis variables in the film performance against corrosion, a fractional 2^{4-1} factorial design was performed using four variables, with two levels for each variable: 0.4 and 0.2 mol L^{-1} Py concentration; 0.05 and 0.025 mol L^{-1} tungstate concentration; 1.5 and 1.0 C electropolymerization charge (Q_{pol}); 1.0 and 0.8 V polymerization potential (E_{pol}). These values for the two levels of the factors were chosen after a systematic study carried out in our laboratory involving the following parameters: potential and polymerization charge, tungstate and pyrrole concentration.

Table 1 Matrix design with the corresponding responses, E_{CORR} and R_{P}, used to evaluate the corrosion protection of the film PPy/OXA/W

[WO_4^{-2}] (mol L^{-1})	[Py] (mol L^{-1})	Q (C)	E_{pol} (V)	E_{CORR} (V)	R_{P} (Ω cm^2)
+	+	+	+	−0.543	1494
+	+	−	−	−0.618	607
+	−	+	−	−0.569	473
+	−	−	+	−0.615	878
−	+	+	−	−0.540	107
−	+	−	+	−0.597	1273
−	−	+	+	−0.546	2110
−	−	−	−	−0.657	248

As response variables, to evaluate the corrosion protection of the PPy/OXA/W film, the corrosion potential (E_{CORR}) and the polarization resistance (R_{P}) were chosen. The R_{P} was obtained from EIS measurements of the PPy/OXA/W films electropolymerized in different conditions. The E_{CORR} and the R_{p} of the PPy/OXA/W films were measured after 1-h immersion of these electrodes in a 0.05 mol L^{-1} NaCl solution. The matrix design with the corresponding responses is given in Table 1.

The statistical significance of the results concerning the influence of changing the level of one variable (main effects) and the interactions between two variables (second-order effects) related to the E_{CORR} and R_{P} show that high values of potential and electropolymerization charge allows obtaining PPy/OXA/W films with good corrosion performance. Thus, it only appears possible to optimize the response at high levels of potential and charge of electropolymerization.

In order to elucidate the effect of the Py and tungstate concentration at high potential and charge a complete factorial design of those variables was carried out. In addition to the two previous runs performed at 1.0 V and 1.5 C, two new experiments were performed to complement the study (Table 2).

The analysis of the statistical significance of the effects, related to the complete factorial design, show that a positive effect on the E_{CORR} and R_{P} can be obtained when

Table 2 Complete matrix design for 1.0 V and 1.5 C with the corresponding response, E_{CORR} and R_{P}, of corrosion protection of the film PPy/OXA/W

[Py] (mol L^{-1})	[WO_4^{-2}] (mol L^{-1})	E_{CORR} (V)	R_{P} (Ω cm^2)
+	+	−0.543	1494
+	−	−0.669	673
−	+	−0.530	1756
−	−	−0.546	2110

increasing the tungstate concentration and decreasing the pyrrole concentration.

3.4 Influence of the tungstate concentration

Aiming to validate the statistical analysis which predicts the influence of the tungstate concentration on the corrosion performance of the PPy/OXA/W film, an additional set of experiments was carried out utilizing an increased concentration of tungstate anion.

Figure 4 shows the *I–t* transients obtained for the electrosynthesis of PPy on aluminium alloy at 1.0 V in: (a) 0.2 mol L^{-1} pyrrole + 0.1 mol L^{-1} $H_2C_2O_4$ + 0.05 mol L^{-1} Na_2WO_4; (b) 0.2 mol L^{-1} pyrrole + 0.1 mol L^{-1} $H_2C_2O_4$ + 0.1 mol L^{-1} Na_2WO_4 solution.

As can be seen, in the presence of 0.05 mol L^{-1} Na_2WO_4 (curve a) a total charge of 1.5 C is reached after 1,600 s of electropolymerization. On increasing the tungstate concentration to 0.1 mol L^{-1} Na_2WO_4 (curve b) the electropolymerization is apparently difficult, since the current densities are very low. In this condition, the total charge of 1.5 C is reached only at 3,800 s with 0.375×10^{-3} A cm^{-2} anodic current.

It is well known that polymeric anions are formed in tungstate solutions under acidic conditions. At pH 2.0 the metatungstate anion $H_2W_{12}O_{40}{}^{-6}$ is one of the most probable species of polytungstate anion [28]. Previous data show that the polytungstate anion acts as a catalyst for the electrochemical polymerization of pyrrole [29]. However, under the experimental conditions employed in this work, it was detected that, on increasing the $WO_4{}^{-2}$ concentration the electropolymerization of PPy is hindered. These findings are in agreement with those reported in the potentiostatically polymerization of pyrrole in polyoxometalate solutions [30], where an increased $WO_4{}^{-2}$ concentration does works against electropolymerization due to the nucleophilic character of tungstate anion. Besides, the films synthesized in 0.1 mol L^{-1} Na_2WO_4 solution, when tested in a 0.05 mol L^{-1} NaCl medium, did not provide good protection of the AA 1100 alloy against corrosion.

3.5 Influence of the polymerization charge

The results obtained by statistical fractional design show that it is possible to obtain a PPy/OXA/W film with good corrosion performance when increasing the polymerization charge. Thus, PPy/OXA/W films were electrosynthesized on AA 1100 at 1.0 V in 0.2 mol L^{-1} pyrrole, 0.1 mol L^{-1} $H_2C_2O_4$ and 0.05 mol L^{-1} Na_2WO_4 solutions at 1.5 and 5.0 C of polymerization charge. The performance of these films in the protection of the alloy against corrosion was evaluated in 0.05 mol L^{-1} NaCl solution.

The variation of the E_{CORR} of the AA 1100 coated with the PPy/OXA/W films with the immersion time is given in Fig. 5. The E_{CORR} of the bare alloy remains in the active region [31] and for the Al/PPy/OXA and Al/PPy/OXA/W films the potential shifts to more positive values. This effect is more pronounced at PPy/OXA/W film with a higher polymerization charge. After 1,500 s exposure, the profile of the E_{CORR} versus time curve of the PPy/OXA/W film formed with 5.0 C shows potential oscillations tending to a slight decrease. This trend can be related to the inhibition action of tungstate. For longer immersion time the E_{CORR} values for the coated alloy remain in the passive region as given in Table 3.

The anticorrosion performance of the PPy/OXA/W films on the aluminum alloy was investigated by EIS measurements during different immersion times in a 0.05 mol L^{-1}

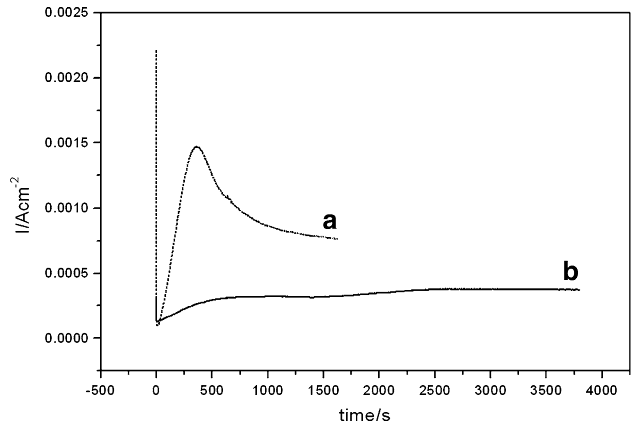

Fig. 4 *I–t* transients obtained for the electrosynthesis of PPy on aluminum at 1.0 V in: (a) 0.2 mol L^{-1} pyrrole + 0.1 mol L^{-1} $H_2C_2O_4$ + 0.05 mol L^{-1} Na_2WO_4 solution; (b) 0.2 mol L^{-1} pyrrole + 0.1 mol L^{-1} $H_2C_2O_4$ + 0.1 mol L^{-1} Na_2WO_4 solution

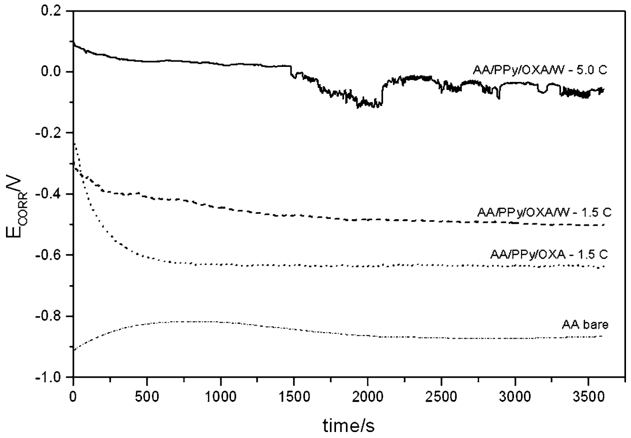

Fig. 5 The corrosion potential (E_{CORR}) as a function of the immersion time in 0.05 mol L^{-1} NaCl solution of the AA 1100 coated with PPy/OXA/W film with 1.5 and 5.0 C, AA 1100 coated with PPy/OXA film with 1.5 C and bare alloy

Table 3 Equivalent circuit elements obtained from fitting experimental data to the equivalent circuit proposed in Fig. 8

Film	Stored charge (C)	Time (h)	E_{CORR} (V)	R_S (Ω cm^2)	Q (μF cm^{-2})	n	R_P (Ω cm^2)	W (Ω cm^{-2})
PPy/OXA	1.5	24	−0.62	70.4	3.4	0.81	9.27	–
PPy/OXA	1.5	48	−0.64	81.6	4.7	0.86	1.47	162
PPy/OXA/W	1.5	24	−0.66	86.6	1.3	0.80	2129	167
PPy/OXA/W	1.5	48	−0.69	74.8	1.2	0.78	2530	230
PPy/OXA/W	5	24	−0.66	62.4	2.1	0.59	759	108
PPy/OXA/W	5	48	−0.67	89.3	3.9	0.69	1218	167

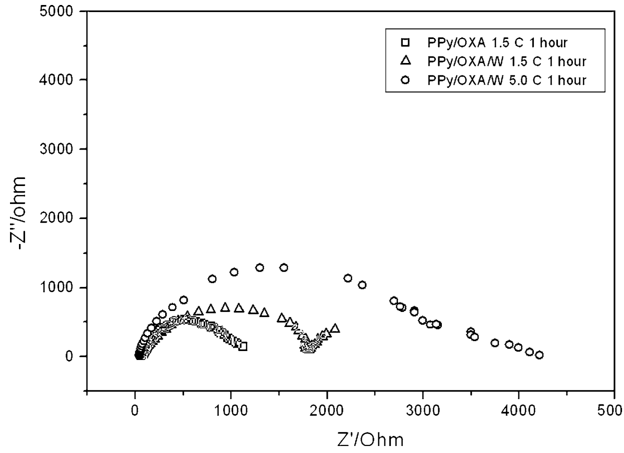

Fig. 6 Nyquist plots of the Al electrode coated with PPy/OXA and PPy/OXA/W films, with 1.5 and 5.0 C after 1 h immersion time

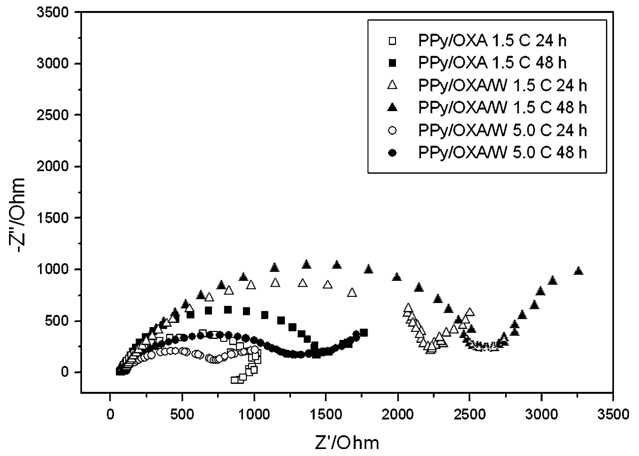

Fig. 7 Nyquist plots of the Al electrode coated with PPy/OXA films, with 1.5 C, and PPy/OXA/W films, with 1.5 and 5.0 C after 24 and 48 h immersion time

NaCl solution at ocp. Figure 6 shows the Nyquist plots of the AA 1100 electrode coated with PPy/OXA and PPy/OXA/W films, with 1.5 and 5.0 C after 1-h immersion. All diagrams show a depressed capacitive loop at a broad frequency range, the diameter of the semicircles being increased in the PPy films containing tungstate, which agrees with the potentiometric measurements. The polarization resistance value Rp derived from these EIS spectra corresponds to the overall resistance, including resistance due to the processes of substrate dissolution, charge transfer resistance during PPy reduction, pore electrolyte resistance and mass transport process resistance.

The evolution of the EIS spectra (Fig. 7) with the immersion time is characterized by a semicircle at high frequency range and a Warburg impedance at lower frequencies for the AA 1100 coated with PPy/OXA/W films. A decrease of the overall impedance is observed from 1 to 48 h, for the PPy/OXA/W film with 5.0 C charge meaning that a less protective coating was produced, allowing a faster surface attack by the electrolyte. For the AA 1100 coated with PPy/OXA/W film with 1.5 C charge the diameter of the capacitive loop increases after 24 and 48 h of immersion time. The diagrams obtained for the AA 1100 coated with PPy/OXA with 1.5 C after 24 h of immersion shows a distinct behavior, which is partially masked by the scatter of the data points at frequencies below 0.064 Hz. Thus, a change of the phase angle sign from negative to positive is detected accompanied by a decrease of the polarization resistance when compared to the PPy/OXA/W film with 1.5 C. Increasing the immersion up to 48 h the Al/PPy/OXA and Al/PPy/OXA/W spectra are similar. A comparison with the data obtained for AA 1100 coated with PPy/OXA/W film with 5 C evidence that besides the role of tungstate, the charge of polymerization is determinant on the corrosion protection.

The EIS diagrams were analyzed using the equivalent electric circuit (EC) given in Fig. 8. The EC proposed to fit the experimental data of the coated electrodes was $R_s(Q[R_P W])$, which has been already used in similar systems [21, 32, 33]. In this EC, R_s represents the ohmic resistance between the reference and the working electrode, evaluated at the high frequency limit, R_P is the polarization resistance, Q is the impedance related to a constant phase element (CPE) expressed as $Z_{CPE} = [Q\ (j\omega)^n]^{-1}$ where Q is a frequency-independent constant, ω the angular frequency and n values are the correlation coefficients for the CPE [34]. The CPE impedance replaces the system

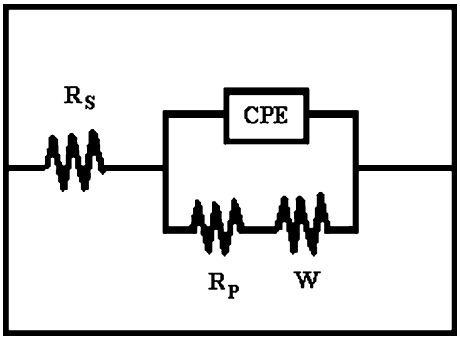

Fig. 8 Equivalent circuit obtained from fitting and simulation of Fig. 7 Nyquist plots

capacitance, taking into account the non-homogeneities of the surface ($n = 1$ for an ideal capacitor). A finite Warburg element, in serial connection with the polarization resistance, was included in this EC, taking into account the effect of mass transport within the pores and coating defects [21, 32, 35]. The fitting quality was judged based on the error percentage associated with each component. The fitted data in Table 3 show errors smaller than 5%.

Higher polarization resistance values were obtained for the Al coated with PPy/OXA/W films with 1.5 C polymerization charge when compared to those with 5.0 C. After 24 h the Rp values for the Al/PPy/OXA/W 1.5 and 5.0 C are 2.1×10^3 and $7.6 \times 10^2\ \Omega\ \text{cm}^2$, respectively. The n exponent related to the CPE element are 0.8 and 0.6 for the Al/PPy/OXA/W 1.5 and 5.0 C, respectively, indicating an important contribution of the diffusive phenomena for the film with 5.0 C. At the PPy/OXA/W films with 1.5 C decreased CPE and higher n exponent values were detected. The CPE includes the contribution of the capacitance of each interface and that of the film, being influenced by the morphology and composition of the electrodeposited PPy films. An effective corrosion protection of polymer coatings is usually associated with high resistance and low capacitance values [35–37].

A comparison between the corrosion behavior of AA 1100 coated with the PPy/OXA/W and PPy/OXA films with increasing immersion time in NaCl solution can be attributed to a partial reduction of PPy film, during which the tungstate anions are released from the bulk of the polymer layer. Based upon the results given in Fig. 3b and the EIS data, the release of tungstate anions during the immersion can inhibit the corrosion of the AA 1100 by increasing blockage of the metallic substrate exposed at defects in the coating, making diffusion more difficult and improving the corrosion resistance. Thus, the access of the aggressive electrolyte to the metal surface is hindered and the dissolution rate decreases. Similar impedance variation with time was obtained for the mild steel coated with PPy film doped with oxalate [38]. This behavior was explained by assuming that the dedoping of oxalate anions from the bulk of the polymer decreases the polymer conductivity which provokes the decrease of the corrosion rate. Improved corrosion protection has been reported with PPy films doped with molybdate [9]. This protection mechanism was explained by the release of the molybdate anion, which then stops the corrosion within the defects.

The data obtained in this work reveal that the electropolymerization of pyrrole on AA 1100 carried out in oxalic acid solution with sodium tungstate is advantageous. The tungstate ions act as an inhibitor of the alloy during the electropolymerization process and also as a dopant, being incorporated into the polypyrrole film. Hence, it can be postulated that a synergistic effect was obtained with the presence of tungstate in the PPy matrix, improving the corrosion resistance of aluminum alloy.

4 Conclusions

The results reported here demonstrate that the electropolymerization of pyrrole on AA 1100 alloy carried out using tungstate and oxalate as dopants (PPy/OXA/W) produces a protective film against corrosion. The data obtained revealed that the corrosion resistance of PPy/OXA/W coatings depends on the synthesis variables. A previous investigation using a two statistical factorial design (fractional and complete) was performed in order to evaluate the influence of the pyrrole and tungstate concentration, electropolymerization potential and polymerization charge on the corrosion performance of the coated alloy. The electrochemical measurements carried out in a 0.05 mol L^{-1} NaCl solution demonstrated that the PPy/OXA/W film synthesized at 1.0 V, 1.5 C in 0.2 mol L^{-1} pyrrole containing 0.1 mol L^{-1} $H_2C_2O_4$ and 0.05 mol L^{-1} Na_2WO_4 solutions presents higher polarization resistance.

The improved corrosion resistance in chloride solution detected at the AA 1100 coated with PPy/OXA/W films can be ascribed to the partial reduction of polypyrrole film thereby releasing the tungstate anions from the polymer matrix. This behavior can be attributed to the adsorbed $WO_4{}^{-2}$ at the defects of the metallic substrate and within the pit, by repairing both of them and leading to a more stable passivating oxide layer. Thus, under these conditions, the tungstate anion acts as a dopant and inhibitor.

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