Advances in Engineering Science
Sect. A (1), Sept. - Dec. 2007, PP 37-44

CORROSION INHIBITION OF ALUMINIUM BY DEPOSITION OF POLYPYRROLE AND SILANE COMPOUNDS

E. Mazarío, L. Cabrera and P. Herrasti*

Universidad Autónoma de Madrid, Facultad de Ciencias, Departamento de Química Física Aplicada. Cantoblanco s/n 28049 Madrid.

ABSTRACT

In this work it has been studied the electrodeposition of polypyrrole over 2024-T3 aluminum electrodes and deposition of silanes of short and long chain, either at the aluminum surface as over the deposited polypyrrole. It has been analyzed the inhibition that these deposits present towards corrosion in aggressive media, such as a 3 % NaCl solution. Results show that deposits composed by polypyrrole and long chain silanes conduct to a better protection as a result of their low porosity. This characteristic neither allows the insertion of chloride ions nor permits oxygen diffusion to the substrate's surface.

Key words: *Polypyrrole and silone compound Aluminium.*

INTRODUCTION

In the last years, corrosion has been the main subject of study for many researchers. Furthermore, there is a great interest in developing new techniques for the control of corrosion. These techniques are focused in eliminating some current processes, such as chromatized and phosphatized, where the use for example of Cr^{6+} generates waste waters that have a deep environmental impact [1].

One method that has been proved to be useful is the use of polymeric layers over the substrate to be protected. The deposition of these layers can be done by different techniques, as it is spin-coating or electrodeposition. The latter one presents a series of advantages over other techniques, for instance the coating of irregular surfaces. Overall, the deposition of conducting polymers by this procedure provides more homogenous and adherent deposits.

Within the conducting polymers, polyaniline (Pani) and polypyrrole (Ppy) have been broadly employed [2-5]. The electrodepositon of these polymers over materials that do not easily oxidize (for example, Pt, Au, graphite, etc.) is very simple [6,7]. However, the situation becomes complicated when the deposition is pretended to be done over oxidizing metals, such as Zn, Cu, mild steel, etc. [8,9]. The oxidation potentials of aniline and pyrrol are at the transpasivation zone of the metal, and the electropolymerization is inhibited by the metal's massive oxidation. The procedure followed in these cases is to use electrolytes that form a passive layer, which avoids the metal's oxidation and allows the oxidation of the monomer over the substrate. Aluminum (Al) is a metal easily oxidized to form a coat of Al_2O_3. This coat presents a very low electronic conductivity, and when an oxidation potential is applied, an increase in the thickness of this coat is generated. The observed result is the inhibition of the electropolymerization process.

Even when electropolimerization is a difficult process to perform over this substrate, different authors have developed a procedure to obtain polymeric deposits over this metal [10,11]. The first report where pretreatments of Al were determined to obtain the electrodeposition of Ppy was published by Hülser and Beck [12]. They state that for a proper electrodeposition it is essential to polish

*pilar.herrasti@uam.es

the surface in order to eliminate the relative inactive Al_2O_3 coat, and to perform activation at the pitting region in an acid solution. If the pretreatment of the metal only involves etching or degreasing, the Al_2O_3 coat regenerates, *i.e.* a repasivation is produced. Consequently, the polymeric deposits, if obtained, are very thin and poorly adherent.

The homogeneity and adherence of Ppy electrodeposits obtained over Al in different acidic media, like sulfuric acid, oxalic acid, and nitric acid will depend of the synthetic reaction conditions. However, in every case, due to the nature of the polymer the deposit is porous. With the purpose to improve the porosity of these films, and therefore its behavior towards corrosion, different silanes were adsorbed over the deposits. Some studies have been performed using silane coupling agents [13,14]. In the literature, it has been reported that Al substrates have to be pretreated before being covered with a silane layer [15-17]. The interaction of silane films with the metal is done by formation of M—OSi bonds, by reaction of silanol groups (SiOH) with the surface metal hydroxyls. Quinton *et al.* [18] have studied the interaction of organosilanes with the Al surface. They have concluded that the adsorption over the substrate is very complex, and the interaction mechanism that takes place depends on the exposure time of de substrate with the silane solution. They proposed a mechanism were a chemisorption is preceded by reversible physisorption. This mechanism is observed for what they call adsorption in intermedium time, or low organosilane concentrations. Cosgrove and co-workers monitored coating as a function of time [19,20], and reported a time scale over which the transition from physisorption to chimisorption was of the order of 10 h.

The purpose of this work is to study the behavior of Ppy, organosilanes and Ppy-organosilane layers deposited over Al towards corrosion in highly corrosive media containing chloride ions. Porosity values were measured from the generated films, and linear polarization data were obtained. Open circuit potential values were registered, in order to compare their properties, and determined which film presented the best adhesion, and most importantly, which one was a better barrier towards the attack of external agents that promote corrosion.

EXPERIMENTAL

The substrates were in all cases Aluminium 2024-T3. Before each experiment, the electrode was polished with emery paper degreased with acetone, and washed with triply distilled water. All potentials were measured against an Ag/AgCl reference electrode and a graphite rod was used as a counter electrode. Nitric acid was used as received and pyrrol was distilled under reduced pressure and stored under low temperature. Polarization curves were performed using 3% NaCl solutions without bubbling nitrogen to it. All the other chemical substances employed were reagent grade and solutions were freshly made with millipore milli Q triple distiller water. Electrochemical measurements were done using a potenciostat-galvanostat VerStat EG&G. Different techniques were used: cyclic voltammetry, chronoamperometry and chronopotentiometry. Porosity measurements were done by calculating the polarization resistance of Al and coated Al.

The silane solutions were prepared by mixing the corresponding silane in distiller water:methanol (1:5). pH of the solution was adjusted to 5 or 8 by adding acetic acid or sodium hydroxide, depending of the silane solution. The solution was previously hydrolysed for 24 h before depositing the film. The silane films were formed by dipping the pretreated Al substrates or Al/Ppy into the hydrolysed silane solutions for 100 s, and dried with hot air to remove any excess of humidity.

The morphology of the deposits was examined by scanning electron microscopy (SEM) with a Phillips XL30-EDAX PV 9900 microscope.

RESULTS AND DISCUSION

The current-time responses during deposition of Ppy from 0.5 M pyrrole and 0.1 M nitric acid solution at 0.9 V are presented in figure 1. It can be observed that current increases during the beginning of the polymer's growth due to Ppy nucleation over the pores in the Al oxide layer that is being generated simultaneously. This was previously observed by other groups (21,22). Ppy electrosynthesized on Al in aqueous medium is actually a bilayer-film composed by a layer of Al_2O_3, an electron barrier, and a Ppy film, a conducting layer. It is at the cracks or pores present in the Al_2O_3 coating were the polymerization of pyrrole takes place. Ppy is electropolymerized to form electronically conducting paths of Ppy, which extend from the Al electrode to the Al_2O_3 surface. This is showed by transient, due to a constant current decrease, which is an indication that a new less conducting surface is being formed.

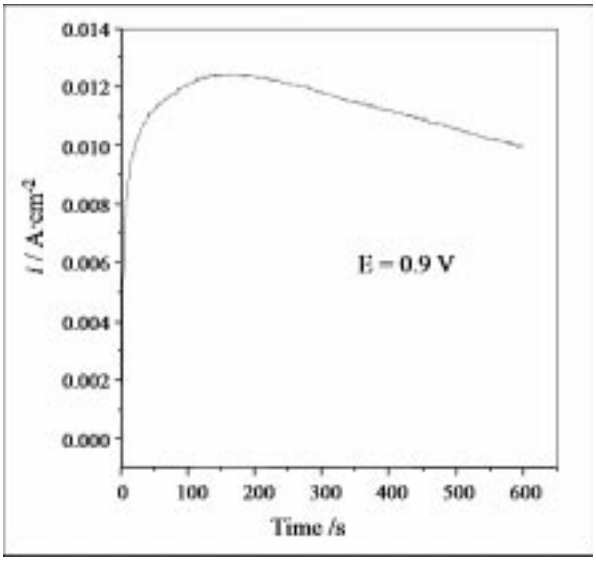

Figure 1 : Chronopotentiometry performed at E = 0.9 V for the deposition of Ppy from 0.5 M pyrrole in 0.1 M HNO_3.

Figure 2 presents the potential-current curve obtained for a current density of 10 mA·cm^{-2} using the same pyrrole solution. Once more, it can be noticed that potential first increases to reach *ca.* 1.4 V, to then decrease until it stays constant at 0.8 V during the rest of the deposition reaction time. In other words, once the polymerization process has begun with the simultaneous formation of Al oxide coat, the process stabilizes at a constant potential.

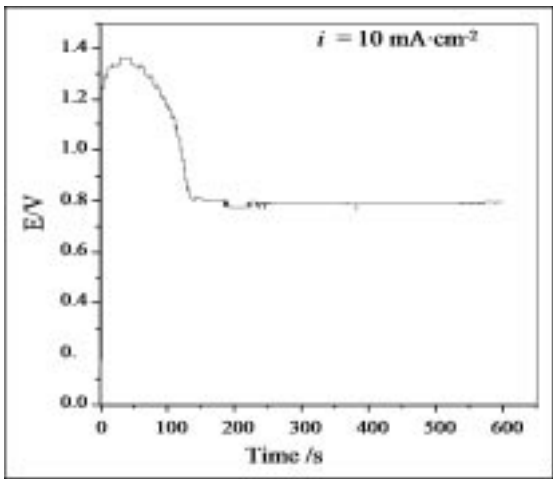

Figure 2 : Voltammogram obtained for *i* = 10 mA·cm^{-2} using a 0.5 M pyrrole solution in 0.1 M HNO_3.

Figure 3 shows the first and last voltammograms for the generation of Ppy on Al. In the first curve, current maintains very low, until it reaches 0.6 V, where it starts to increase. The reason for this behavior is explained with the formation of the first Ppy growing nuclei. This is confirmed by the loop that appears in the forward sweep. As the number of cycles increase, so does the current, to finally obtain a voltammetric profile similar to the ones generated for the growth of Ppy over a non-oxidizing substrate, like platinum.

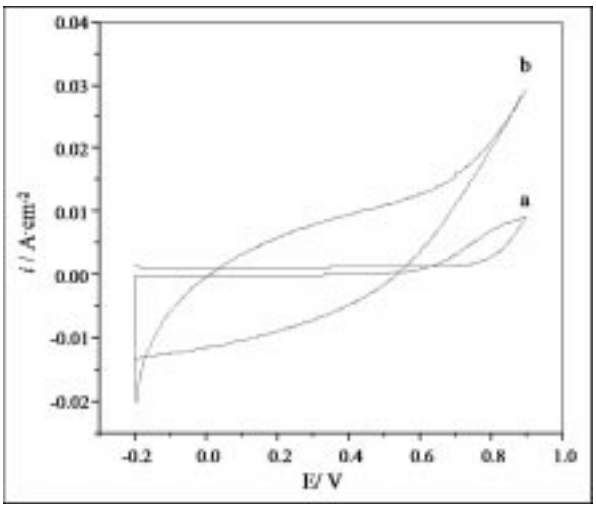

Figure 3 : First (a) and last (b) voltammograms for the generation of Ppy on Al using a 0.5 M pyrrole solution in 0.1 M HNO_3.

Ppy deposited over Al by any of the employed techniques shows good adherence to the substrate. A SEM photograph of Ppy films formed on Al with 0.5 M pyrrol in 0.1 M HNO_3, obtained at constant potential, is showed in figure. The morphology of the polymer was characterized by the formation of aggregates. The average of grains was 2-3 ìm, where size is a function of the electrosynthesis reaction conditions. The morphology remains unchanged when the oxidation potential is not very high, *i.e.* less then 0.6 V.

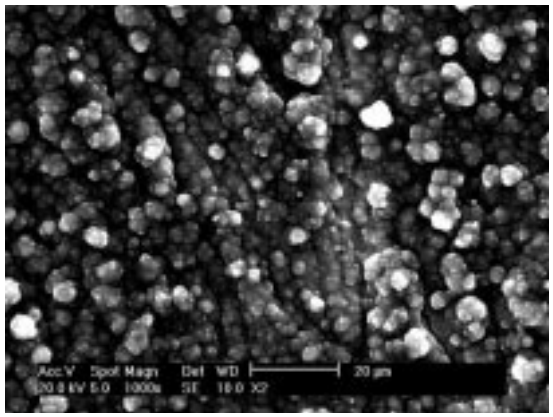

Figure 4 : SEM micrograph of Ppy deposited over Al from a 0.5 M pyrrol solution in 0.1 M HNO_3.

In contrast, if the potential value is increased, two important features take place. The first one is the overoxidation of the polymer; and the second, is water decomposition. The consequence of both factors is the formation of bubbles at the surface. At the spots where bubbles are present, the electrodeposition of Ppy does not occur. Figure 5 shows a micrograph corresponding to Ppy deposit at a high potential (E = 1.1 V). It can be observed there are zones that are not coated with the polymer. At these areas, oxygen bubbles were formed, and Ppy was electrodeposited around them.

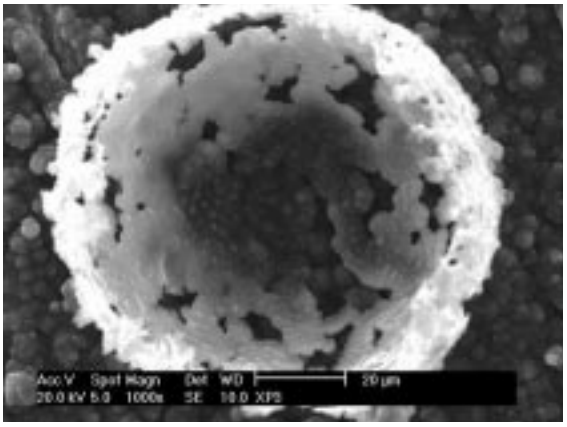

Figure 5 : SEM micrograph of a Ppy deposit obtained at E = 1.1 V.

As it was previously mentioned, it is possible to adsorb over the Al surface organosilane films. Following the procedure cited in the experimental section, layers of octadecyltrimethoxysilane (C_{18}) and propyltrimethoxysilane (C_3) were adsorbed over Al substrates pretreated and over Al substrates coated with Ppy. The corrosion protection properties of the Ppy coating, silane coating and Ppy-silane coating were studied using polarization curves in 3% NaCl solutions. Polarization plots recorded for bare Al, and Ppy coated Al are shown in figure 6. The plot depicted for bare Al electrode (figure 6a) is characteristic of a cathodic and anodic polarization behavior; at high potentials a passive region with an average current of 10^{-4} A·cm^{-2} is obtained. Breakdown and pitting of the Al electrode occurs at -0.45 V. A different behavior is

observed when a Ppy film covers Al. Figure 6b shows the polarization curve for this deposit, where corrosion potential is shifted towards more positive values, going from -0.8 V to -0.5 V. On the other hand, current increases at a higher rate, mainly due to the overlapping of the Red-Ox processes of the polymer with the Red-Ox processes of the substrate, an indication of the polymer's porous nature. Hence, chloride ions reach the Al surface, and oxygen diffusion takes place, provoking the metal's corrosion.

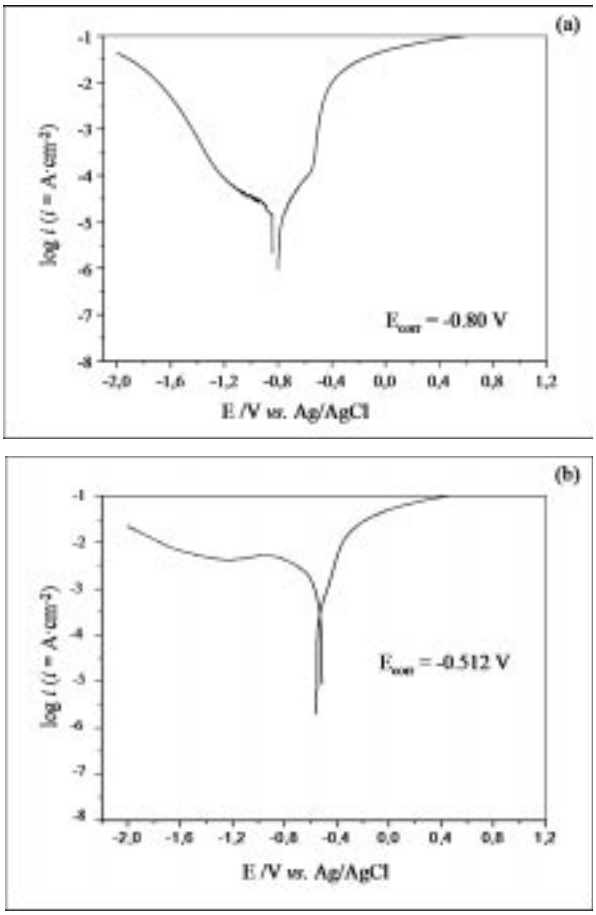

Figure 6 : Polarization plots for bare Al (a), and Al-Ppy (b).

Figure 7 shows polarization curves for substrates coated with silanes and the curve corresponding to bare Al. It can be noticed that only Al coated with C_{18} a decreases in current in the order of 100 times in magnitude, even when the corrosion potential is not modified.

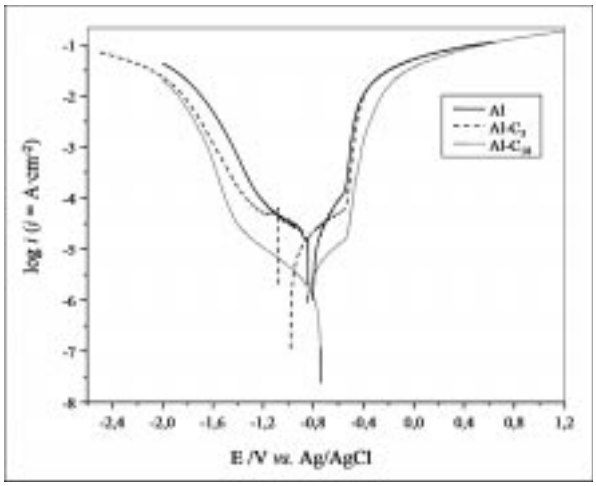

Figure 7 : Polarization curves for Al, Al-C_3, and Al-C_{18}.

The polarization curve for Ppy-silane coating is shown in figure 8. In this case we can observe two responses, the potential shifts from 400 mV to more positive values, and a decrease in current occurs with respect to the Al substrates that were only coated with Ppy and not with silane.

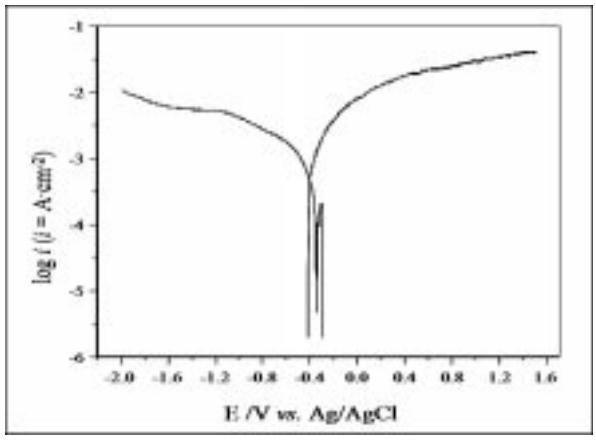

Figure 8 : Polarization curve for Al-Ppy-C_{18}.

In order to corroborate if the barrier layer effect was consistent with a less porous deposit, porosity measurements were performed using equation (1). [23]

$$P = \left(\frac{R_{ps}}{R_p} \right) x10^{-(\Delta E_{corr} / b_a)} \qquad (1)$$

Where P is the total coating porosity rate, R_{ps} is the polarization resistance of the substrate, R is the polarization resistance of the coated Al, $\triangle E_{corr}$ is the difference potential between the free corrosion potentials of the coated Al and the bare substrate, and b_a is the anodic Tafel slope for the substrate. Measurements of polarization resistance were done between ± 20mV around the free corrosion potential.

The porosity values found for the deposits are shown in table I. A decrease in the porosity of the deposits is noticeable, from the surface of the substrate to Ppy coated with silane. These data indicate a decrease in the order of magnitude of 100, the same magnitude that was observed for the current in the presence of silane over the substrate. Decrease in porosity indicates a better protection against corrosion because of the barrier effect that these deposits have towards the diffusion of species present in the electrolytic medium.

Substrate	P%
A1	
A1-Ppy	3.78
A1-Silane (c_{18})	1.102
A1-Ppy-Silane (C_{18})	0.03

Table I : Porosity values found for the deposits on Al.

With the purpose to corroborate that these deposits were good anti-corrosive layers, they were exposed to the same conditions in a saline chamber for 1 h. Figure 9 shows the anodic polarization curves for each one of the deposits. In every case, it can be observed that the anodic current is lower than with the bare substrate, and a decrease in current is shown for substrates coated with Ppy and silane C_{18}, as

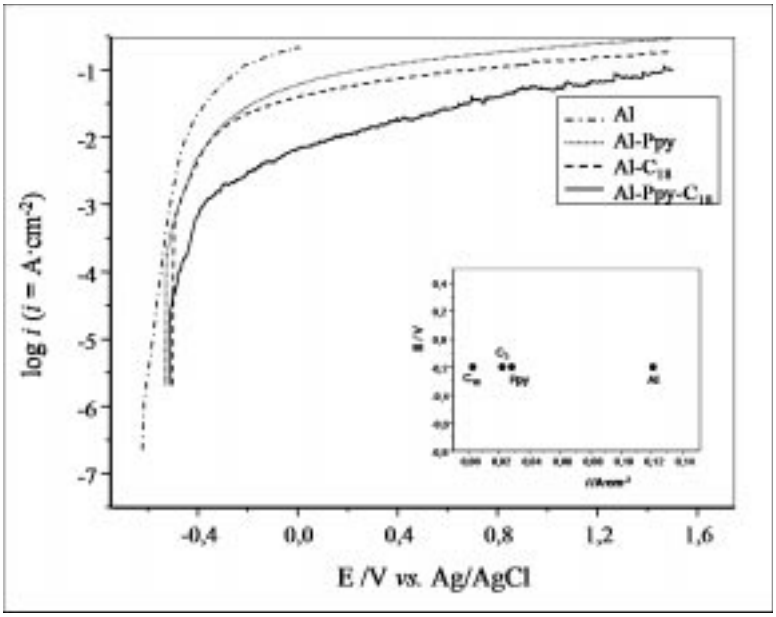

Figure 9 : Anodic polarization curves all the deposits on Al. Inserted graph shows the current density for E = -0.2 V.

expected, due to the lower porosity that such deposits present. The curve inserted within figure 9 shows the current density values for each of the electrodes at a potential 200 mV greater than the corrosion potential. It can be observed that these values are lower than the aluminium substrate which indicates that the corrosion rate is lower, decreasing in the same order as the porosity is decreasing.

CONCLUSIONS

Ppy adherent deposits have been obtained over aluminum substrates by different electrochemical techniques. In the same manner, it has been adsorbed over bare aluminum and aluminum-Ppy films of different silanes. Polarization curves generated in aggressive NaCl medium indicate that coatings with Ppy and long chain silanes (C_{18}) are good protectors. The reason for the decrease in rate corrosion is related with the difference in porosity of each deposit. A significant reduction in these values is observed when the aluminum substrate has been coated with Ppy and silane layers, where obtained layer is 100 times less porous than when only Ppy is deposited. When these coated substrates are exposed to a more aggressive environment in a saline fog chamber, its behavior remains unchanged, keeping its anti-corrosive capacity under those working conditions.

AKNOWLEDGMENTS

The authors acknowledge the Spanish M.E.C. (CTQ2005-04469/BQU) for financial support.

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