INHERENTLY CONDUCTING POLYMERS ON ALUMINIUM ALLOY 6061-T6
BY ELECTROPOLYMERIZATION

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ABSTRACT

Among ICP’s investigated for corrosion protection, polypyrrole (PPy) and polyaniline (PANI) are the most studied and have been prepared by electropolymerization of pyrrole or aniline on inert electrodes such as gold and platinum and also on stainless steel or copper. However, it is much more difficult to generate these polymers on valve metals such as aluminum and aluminum alloys. This could be related with the formation, on the metal surface, of a thin, but highly stable protective oxide-hydroxide layer that blocks electron transfer and impedes polymer formation and deposition. Furthermore, this oxide usually grows at positive potentials in the acidic conditions normally required for the electrosynthesis of conducting polymers.

In this work, some results concerning electrodeposition of polypyrrole and polyaniline on 6061-T6 aluminum alloy by two different processes (cyclic voltammetry and a potentiostatic method) will be presented. The coatings have been assessed through SEM observation and voltammetry and their anticorrosive properties were studied by polarization curves and electrochemical impedance spectroscopy.
INTRODUCTION

Through the second half of the twentieth century, aluminum and its alloys have become preferred materials in a large number of applications, such as in the case of automobile and aeronautical industries. This was mainly due to the significant improvements in the mechanical properties of aluminum, which have been achieved by alloying elements such as copper, zinc or magnesium that show a very low solubility in aluminum, leading to the formation of second-phase precipitates. Besides the positive effect of these precipitates in the mechanical properties, they are normally deleterious to the corrosion resistance of the materials, leading to the formation of galvanic couples that act as starting points for the onset of localized corrosion. Therefore, the use of such alloys is only possible if associated to effective corrosion protection systems and, in particular, with the use of adequate coatings.

In the above mentioned industries, the use of painted aluminum alloys has become very common and many parts of planes and cars are joined together by the use of adhesive bonding. Before the application of paint or the use of adhesives, adequate pre-treatments need to be used which, in the past, normally involved the use of chromates. However, these chemicals have been classified as hazardous to environment and human health. Thus, much effort has been undergoing to develop environmentally friendly alternatives to these treatments.

Inherently conducting polymers (ICP) are attracting attention as adhesion promoters and corrosion protection coatings in alternative to chromate-based treatments [1-3] Among ICP’s investigated for corrosion protection, polypyrrole (PPy) and polyaniline are the most studied and have been prepared by electropolymerization of pyrrole or aniline onto a variety of substrates with promising results [4-8].

Conducting polymers are electrosynthesized easily on inert electrodes such as gold and platinum, but it is much more difficult to generate these polymers on aluminium and aluminium alloys. This could be related with the formation, on the metal surface, of a thin, but highly stable protective oxide-hydroxide layer that blocks electron transfer and impedes polymer formation and deposition. Furthermore, this oxide usually grows at positive potentials in the acidic conditions normally required for the electrosynthesis of conducting polymers [9].

Up to now, the majority of the studies concerning the production and investigation of the properties of conducting polymers on aluminium substrates were focused mainly on pure aluminium and on the 2024-T3 alloy. So far, there are no reports in the literature relative to electrochemical deposition of polypyrrole on the aluminium alloy 6061-T6. This alloy is becoming more widely used in automotive industry and there is an interest in finding coating systems that could confer better corrosion resistance and enhanced adhesion between the metal and paint or adhesives.

The present work reports the production of films of polypyrrole and polyaniline on AA 6061-T6 through the electropolymerization of the respective monomers (0.5 M) in a supporting electrolyte of 0.5M H₂SO₄ and the characterization of their electrochemical behaviour.

EXPERIMENTAL PROCEDURE

Aluminium alloy 6061-T6 (wt.% composition: 0.15-0.40 Cu, 0.80-1.20 Mg, 0.40-0.80 Si, 0.00-0.70 Fe, 0.04-0.35 Cr, 0.00-0.15 Ti, 0.00-0.25 Zn, 0.00-0.15 Mn), with thickness 1 mm, from Future Metals and pure aluminium panels (99.999 %) from Goodfellow were used.
The aluminium substrates were degreased with acetone in an ultrasonic bath during five minutes, washed with distilled water and dried under nitrogen flow. The samples of aluminium were then masked with a mixture of bee wax and colophony resin (3:1) in order to isolate the cut edges, defining a small rectangular section of the working electrode.

Pyrrole and aniline were distilled under reduced pressure before use and the solutions of the monomers were freshly prepared for each experiment using Millipore® water.

The synthesis of polyaniline, polypyrrole and mixed polyaniline/polypyrrole films was carried out according to conditions previously defined through an optimization step.

Polyaniline (PANI) films were synthesized electrochemically on the surface of AA 6061-T6 in a solution of 0.5 M aniline and 0.5 M H₂SO₄ using two methods: potential cycling between -0.2 V and 1.25 V at a scan rate of 50 mV s⁻¹ (20 cycles) and at a constant potential of 1.25 V, during 20 min.

The polypyrrole (PPy) films were synthesized electrochemically from a 0.5 M H₂SO₄ solution containing pyrrole (0.5 M), also using two methods: potential cycling between -0.6 V and 1.0 V at a scan rate of 50 mV s⁻¹ (6 cycles) and at a constant potential of 1.0 V, during 5 min.

Finally, films of polyaniline and polypyrrole (PANI-PPy) films were synthesized electrochemically from a 0.5 M H₂SO₄ solution containing pyrrole (0.5 M), also using two methods: potential cycling between -0.2 V and 0.8 V at a scan rate of 50 mV s⁻¹ (40 cycles) and at a constant potential of 0.8 V.

In order to assess the anticorrosive properties of the coatings, electrochemical impedance spectroscopy (EIS) experiments were carried out in 0.05 M NaCl using an electrochemical interface FAS1™ Femtostat, from Gamry Instruments, at a potential of -0.02 V vs OCP (to avoid lack of linearity [10]), using a sinusoidal perturbation with 10 mV of amplitude (RMS) and a frequency ranging between $5 \times 10^{-4}$ Hz and $5 \times 10^{-3}$ Hz.

All the other electrochemical methods were performed using a VoltaLab PGZ100 potentiostat from Radiometer, in a three electrode cell, where a saturated calomel electrode (SCE) was used as reference and a platinum wire as the auxiliary electrode. All the values of potential are referred to the SCE electrode.

**RESULTS**

**Production of Polypyrrole Films**

The cyclic voltammograms obtained during the electropolymerization of pyrrole in 0.5 M H₂SO₄ + 0.5 M pyrrole solution are presented in Figure 1A. Oxidation of pyrrole is observed above 0.6 V, where the formation of a black film of polypyrrole may be noticed. Moreover, after the first cycle, two new peaks may be identified: an anodic peak at ca. 0.3 V, corresponding to the oxidation (doping) of polypyrrole, and the corresponding cathodic peak, at ca. -0.15 V. The intensities of these waves increase with the number of cycles till a maximum current is reached.

Polypyrrole films were also successfully electrosynthesized on AA 6061-T6 at constant potential, from 0.5 M H₂SO₄ solutions containing pyrrole (0.5 M). The current versus time curves obtained for the potentiostatic synthesis of polypyrrole is shown in Figure 1B. For comparative purposes, the curve recorded for AA6061-T6 in pyrrole-free sulphuric acid solution is also included.
FIGURE 1 - Electropolymerization of pyrrole in 0.5 M H$_2$SO$_4$ + 0.5 M pyrrole: (A) by potential cycling between -0.6 V and 1.0 V at a scan rate of 50 mV s$^{-1}$ (6 cycles); (B) at a constant potential of 1.0 V, during 5 min.

The potentiostatic curve obtained in the absence of the monomer is characterized by an initial rapid decrease in the anodic current followed by a slower decay to reach a near steady-state condition. This behavior is consistent with the formation of the aluminum oxide layer. In the presence of pyrrole, the current initially shows a fast drop similar to that observed in the absence of the monomer, but then, after a short period of time (that can be considered as an induction time), the anodic current shows an exponential increase, due to the nucleation and growth of the polymer, reaching a maximum ($i_{\text{max}}$) and then a decay, attaining a near steady-state value. Previous experiments have indicated that the value of $i_{\text{max}}$ and the time needed to reach it ($t_{\text{max}}$) depend on the applied potential. Increasing the potential from 0.9 V to 1.0 V leads to higher $i_{\text{max}}$ and lower $t_{\text{max}}$, attributed to an increase in the rate of polymerization. However, when the applied potential is increased above 1.0 V, the opposite trend is observed, with $i_{\text{max}}$ decreasing and $t_{\text{max}}$ increasing. This fact can be attributed to degradation by overoxidation of the PPy at these potentials [11,12] and is in accordance with the cyclic voltammetry data where for upper potential limits higher than 1.0 V a loss of electrochemical activity with increasing the number of cycles was observed.

The morphology of the PPy films was analysed by SEM. The micrographs obtained for films formed by potential cycling between -0.6 V and 1.0 V (after 6 potential cycles) for films obtained potentiostatically at E =1.0 V are presented in Figure 2. A cross-section of the same samples is shown in Figure 3, allowing for the determination of the film thickness in both cases. As shown in Figure 2, both polypyrrole films are homogeneous, presenting a globular structure that is not affected by the formation procedure. However, the size of the globules is apparently larger for the films produced by cyclic voltammetry, although the charge density consumed in their production is lower than for those potentiostatically formed [13]. From Figure 2, where the cross-section of the films is depicted, the thickness of the films is found to depend on the method of preparation, as films produced by cyclic voltammetry are thicker than those produced potentiostatically.

An estimate of the efficiency of the electropolymerization processes was obtained from a thickness/charge ratio defined as the thickness of the film divided by the charge density consumed during its production, calculated from the area under the peak associated to the polymerization process (in the case of the films formed by cyclic voltammetry, the charge accumulated in the 6 cycles was taken). It was possible to conclude that the production of polypyrrole via cyclic voltammetry is more efficient, as the thickness/charge ratio obtained in that case was 3.0 µmC$^{-1}$cm$^{-2}$ whereas in the case of the
potentiostatic formation a ratio of 1.1 µmC⁻¹cm² was obtained [13]. It seems therefore possible to conclude that the optimum conditions for the production of PPy films are obtained through cyclic voltammetry with E₀=1.0 V.

![SEM micrographs of PPy films deposited on AA 6061-T6: (A) by potential cycling between -0.6 V and 1.0 V at a scan rate of 50 mV s⁻¹ (6 cycles); (B) at a constant potential of 1.0 V, during 5 min.](image1)

The adherence of the polypyrrole films was assessed through a bending test. Both the films produced by cyclic voltammetry and those obtained by the potentiostatic method showed good adherence, only suffering some fractures upon bending.

![SEM cross-sections of PPy films deposited on AA 6061-T6: (A) by potential cycling between -0.6 V and 1.0 V at a scan rate of 50 mV s⁻¹ (6 cycles); (B) at a constant potential of 1.0 V, during 5 min.](image2)
Production of Polyaniline Films

Figure 4 illustrates the cyclic voltammograms obtained during the potentiodynamic electrodeposition of PANI on the aluminium alloy 6061-T6, from a 0.5 M H₂SO₄ solution containing aniline (0.5 M). In the first two cycles of potential (Figure 4A), the electrochemical behaviour of the aluminium alloy is similar to that obtain in the absence of aniline. The voltammogram recorded for the first cycle reveals a broad anodic wave attributed to the oxidation of the metal with formation of aluminium oxides. In the second cycle the current density decreases drastically due to the passivating nature of the aluminium oxide layer produced in the first cycle of potential. During the following cycles (Figure 4B) there is a gradual increase of the current but the electrodeposition at the electrode, only occurs after a few cycles, with the number of cycles needed (Nmin) depending on the value of the upper limit (Eₜₐ) of the scan. For example, when the upper limit is 0.8 V the electrodeposition begins by the 29th cycle whereas using 1.4 V as the upper limit it begins after 5 cycles. This is consistent with the first step of the electropolymerization being the generation of radical cations, which is favoured by higher anodic potentials.

The voltammograms obtained after the beginning of the electrodeposition process present two pairs of redox couples, (I/I’) and (II/II’), corresponding respectively to the interconversion between leucoemeraldine and emeraldine conducting form and between the emeraldine conducting form and pernigraniline. Successive scans result in gradual increase of the current intensity of the redox waves, reflecting the growth of the polymer (Figure 4B).

By increasing the upper limit of the scan, a shift of the oxidation peaks to positive values can be observed and the second peak of oxidation tends to disappear for Eₜₐ values higher than 1.0 V. Similar behaviour was also reported by other authors and was attributed to degradation of the polymer [14,15]. Aoki et al. [14] showed that at potentials higher than 0.7 V, the polymerization of polyaniline is always accompanied with degradation (overoxidation) because the polymerization potential is close to the degradation potential. The competition between the polymerization and the degradation is controlled by the concentration of aniline in solution and the potential applied, the latter being favoured for low concentrations of aniline and higher potentials. However, in the present results it was not possible to
observe the typical “middle peak” for the oxidation/reduction of soluble electrochemical degradation products, situated between (I/I’) and (II/II’), as reported by others [16-18].

Based on the minimum number of cycles needed for the formation of the polyaniline and on the results relative to the degradation of the deposit, values of the upper limit in the range of 1.2 V to 1.4 V were considered as appropriate, as in these conditions the number of cycles needed for the beginning of PANI production is low and overoxidation is still taking place at low rates.

Dark green PANI films were also successfully electrosynthesized on AA 6061-T6 at constant potential, from 0.5 M H$_2$SO$_4$ solutions containing aniline (0.5 M). Based on the competition between the polymerization process and the degradation by overoxidation, as referred above, an optimum value for the potential was defined as 800 mV.

With the goal of comparing the two processes used for the electropolymerization, the structure of the PANI films was analysed by SEM. The micrographs obtained for films formed by potential cycling between – 200 mV and 1250 mV are presented in Figure 5 and those obtained for films formed potentiostatically, during 10 minutes, at 800 mV are presented in Figure 6. As can be seen, the PANI films present a cauliflower structure which is independent of the formation procedure.

![FIGURE 5. SEM micrographs of a AA 6061-T6 surface covered with PANI produced by 20 potential cycles between -200 mV and 1250 mV in a 0.5 M H$_2$SO$_4$ solution containing 0.5 M aniline.](image1)

![FIGURE 6. SEM micrographs of a AA 6061-T6 surface covered with PANI produced by potentiostatic polarization at 800 mV during 10 minutes.](image2)

Adherence of the polymers to the substrate was tested by a simple adherence test that consisted in applying tape on the samples and then pulling back the tape. Using this test it was possible to
conclude both the films produced by cyclic voltammetry and potentiostatically present a satisfactory adherence, as the outer layer of the polymer could be removed, but an underlying layer remained adherent.

Production of PANI-PPy Films

The formation of PANI-PPy films through potential cycling between -0.2 V and 0.8 V at a scan rate of 50 mV s\(^{-1}\) in an equimolar solution of aniline and pyrrole (0.5 M), using 0.5 M H\(_2\)SO\(_4\) as supporting electrolyte, only begins after 25 cycles and a continuous film is only obtained after 40 cycles. Figure 7A depicts some typical cycles of the voltammogram obtained. Two peaks may be observed, one at ca. 190 mV and the other ca. -15 mV, corresponding respectively to the oxidation and to the reduction of the co-polymer obtained. The current associated to both peaks is found to increase with the number of cycles, which is consistent with the thickening of the polymer layer.

Films of PANI-PPy were also obtained after 20 minutes of constant polarization at 800 mV in the same solution. From the current vs time record (Figure 7B) it is possible to note an initial drop of the current (in accordance to what was observed in the case of polypyrrole or polyaniline formation) followed by a marked increase up to a maximum. By visual examination of the electrode it was possible to observe that the formation of the first black grains of polymer occurred simultaneously with the rise of the anodic current. It is worth to notice that a continuous film of polymer was already formed after 800 s of electropolymerization, corresponding to the maximum of the current vs time plot, and longer times did not increase the quality of the deposit.

![Electropolymerization of PANI-PPy in 0.5 M H\(_2\)SO\(_4\) + 0.5 M pyrrole + 0.5 M aniline: (A) by potential cycling; (B) at constant potential of 0.8 V, during 20 min](image)

Although the characteristics of the copolymer are similar to those of polypyrrole, the electropolymerization efficiency for the PANI-PPy films is much lower than for the PPy but slightly higher than for PANI. Moreover, the number of cycles needed for the onset of electrodeposition is consistent with the efficiency results, as indicated in Figure 8.
The structure of the PANI-PPy films was analysed by SEM, being shown in Figure 9. Contrarily to what was observed in the case of homopolymers, in this case the structure of the films seems to be dependent on the preparation procedure. However, some similarities may be found with the structure obtained for the PPy coatings.

The adherence of the PANI-PPy films was found to be higher than that of the PANI or PPy coatings.

Response of polymer coated electrodes in chloride media

In order to assess their anticorrosive properties, films of the different polymers were submitted to a series of electrochemical tests in aggressive chloride media. In particular, electrochemical impedance spectroscopy (EIS) was used to assess the evolution with time of the corrosion behaviour of the coated
alloy in 0.05 M NaCl solution. The spectra corresponding to the different polymer-coated specimens (and bare alloy, as reference) after 22h immersion in the test solution are presented in Figure 10. In all cases the spectra are characteristic of a metal undergoing pitting corrosion, assigned to the time constant observed in the low frequency domain [19,20]. Moreover, the impedance values are considerably lower for the coated specimens than those observed for the bare metal. In accordance with the traditional interpretation, that associates higher values of impedance to a higher resistance to corrosion, the data obtained would indicate that the coated AA6061-T6 presents lower corrosion resistance than the bare metal. However, the analysis of these spectra is not straightforward, because of the conductive nature of the polymer and also because the real surface area of the electrode is unknown. Bazzaoui et al. [12] also observed this type of behaviour for a polypyrrole coated aluminium sample, obtained from electropolymerization in an aqueous solution of saccharin sodium salt and pyrrole. No significant differences are found in the EIS results obtained for the films produced both potentiostatically and by cyclic voltammetry.

![EIS spectra](image)

**FIGURE 10** – EIS spectra obtained for the bare AA 6061 and for the specimens coated with PANI, PPy and PANI-PPy, after 22 h immersion in 0.05M NaCl.

**Conclusions**

Films of polypyrrole, polyaniline and polyaniline-polypyrrole were successfully electrodeposited by voltammetric and potentiostatic methods in acidic solution on ultrasonic acetone-cleaned aluminium alloy AA 6061-T6.

The choice of the upper potential limits for potential cycling and of the fixed potential for potentiostatic production should take in consideration the balance between their effect on the minimum number of cycles (or time) need to produce the film and on the rate of overoxidation.

The films formed are in all cases continuous and adherent to the substrate.

Electrochemical impedance spectroscopy results are, in all the specimens, typical of a system undergoing pitting corrosion. Thus, the corrosion resistance of the coated materials, as assessed from this technique, is not found to be higher than the one for the bare alloy. Due to the conductive character of the polymer, these tests were not conclusive and continue under investigation.
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References