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Electrodeposition of Polypyrrole Films: Influence of Fe₃O₄ Nanoparticles and Platinum Co-Deposition

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1. Introduction

Inorganic particles/conductive polymers composites in bulk or films have been subject of intense study during the last decade. This type of materials offer the potential to being used in batteries, electro-chemical display devices, molecular electronics, electromagnetic shields, opto-electronic applications, microwave-absorbing materials, and even for corrosion protection (Garcia et al., 2002; McNally et al., 2005). Conducting polymers have some specific problems that make difficult its use in the above applications. Instability under oxygen and UV exposure, easily doping and over-oxidation are the most common among others. A novel strategy have been reported to improve its properties and extend the application range of these materials, this is the incorporation of inorganic particles of metallic oxides such as MnO₂, V₂O₅, TiO₂, Fe₂O₃, Fe₃O₄ and WO₃ or metallic particles of Zn, Cu, Au, Pt into the conductive polymer (Demets et al., 2000; Ferreira et al., 2001; Kawai et al., 1990; Kuwabata et al., 2000; Lenz et al., 2003; Montoya et al., 2010; Vishnuvardhan et al., 2006). For example we have recently demonstrated that the incorporation of magnetite into polypyrrole (PPy) decreases the electric resistance of the polymeric film and not only stabilize the polaronic form of the polypyrrole, but also preserve the polymer from further oxidation (Montoya et al., 2010).

Polypyrrole (PPy) exhibits interesting properties such as high conductivity, relatively good environmental stability, and wide technological applications. PPy can be obtained either by chemical and electrochemical polymerization. The electropolymerization is considered a controlled synthesis method that provides better control of thickness and morphology of films (by controlling parameters as current, voltage, and time), efficient (high material-transfer efficiency with nearly 100% material utilization and recovery), and environmentally safe (usually a water-based process). The aim of this chapter is to show in detail, two particular cases concerning the development of PPy/inorganic particles composite coatings deposited on stainless steel. First of all, a brief introduction is presented discussing the electrochemical polymerization methods. Then, as a first case, the effect of magnetite (Fe₃O₄) nanoparticles on the polymer matrix is presented. The second case is the co-deposition of platinum/PPy. Both studies show the effect of the addition of the inorganic phase on the

electrical, morphological, structural and conductive properties of the polymer matrix. Finally we show the synergistic effect of PPy/Fe₃O₄/Pt composites on the final properties of the coating.

2. Electrochemical polymerization of pyrrole

Polypyrrole can be obtained by the oxidation of pyrrole monomer. Such oxidation can be accomplished by the following methods: 1) chemical polymerization in aqueous or organic media by oxidizing agents. 2) by electropolymerization on a metallic or conductive substrate by applying a potential or external current. 3) by photochemical or enzymatic catalysis polymerization. In general by chemical oxidation a final powder is obtained. Thin films are obtained by electrochemical deposition and from colloidal dispersions by enzymatic polymerization (Wallace, 2003).

Electropolymerization is a method in which a pyrrole monomer dissolved in an electrolyte solution, normally aqueous, is oxidized to form a conductive film over a work anodic electrode. Reported conductivities for electrochemically obtained PPy are between 10^{-10} – 10^3 S/cm, due mainly to variables as deposition time, concentration of the monomer, substrate and deposition method. Figure 1 shows a simplified mechanism of oxidation of PPy, where n can be 3-4 and m is related with the chain length and determining the molecular weight. A^- is a counter ion from the electrolyte to balance the charge over the polymer.

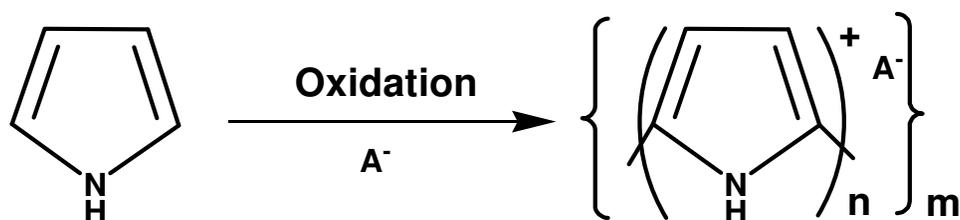


Fig. 1. Simplified mechanism of the polymerization of polypyrrole.

2.1 Steady state methods

These methods consist in applying a constant potential or current to an electrode giving place to a constant response upon time in current or potential, respectively. Between two, potentiostatic method consist in fixing the work electrode potential to give as a result the curves illustrated in Figure 2. The galvanostatic method is the inverse to that mentioned above. Steady state methods allow following electrode processes and changes in a system. This can be achieved by recording an electrical parameter upon time whereas the other one is being fixed, they can be: 1) Potentiostatic, in which a potential pulse is applied to the electrode and the current is registered as a function of time. During the experiment, once the double layer is charged, the potential of the electrode remains at a constant value (E_a) over the open circuit voltage (E_{ocp}) and the current decreases as the concentration of the electrodic specie decreases in the solution and is deposited in the working electrode. The described events are depicted in Figure 2. 2) Galvanostatic, when a constant current pulse is applied to the work electrode, the potential is shifted from the equilibrium and changes are registered against time.

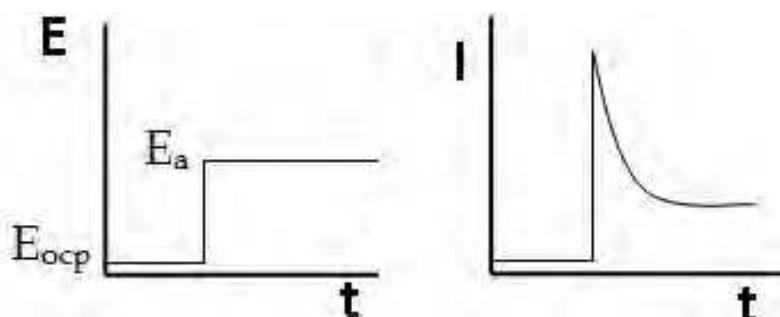


Fig. 2. Potentiostatic polarization and the current response of a typical deposition process of PPy.

2.2 Unsteady state methods

Unsteady state methods allow following electrode processes and changes in a system that do not occur instantaneously. Between non-stationary methods available for studying electrode processes, potential sweep methods are probably the most widely used. They consist in the application of a continuously time-varying potential to the working electrode. The observed current is therefore different from that in the steady state. Resulting this in the occurrence of oxidation or reduction reactions of electroactive species in solution (faradaic reactions), possibly adsorption of species according to the potential, and a capacitive current due to double layer charging. There are two forms of sweep voltammetry techniques named, linear sweep voltammetry (LSV) and cyclic voltammetry (CV). In linear sweep voltammetry the potential is scanned only in one direction, stopping at a chosen value, E_{fin} for example at $t = t_1$ in Figure 3.

The scan direction can be positive or negative and, in principle, the sweep rate can have any value. In cyclic voltammetry, the potential scan is done in two directions, on reaching $t = t_1$ the sweep direction is inverted as shown in Figure 3 and swept until E_{min} , then inverted at t_2 and swept to E_{max} . The faradaic current, I_f , due to the electrode reaction, is registered simultaneously to the applied potential where electrode reactions occur, giving place to a cyclic voltammogram like that shown in Figure 4.

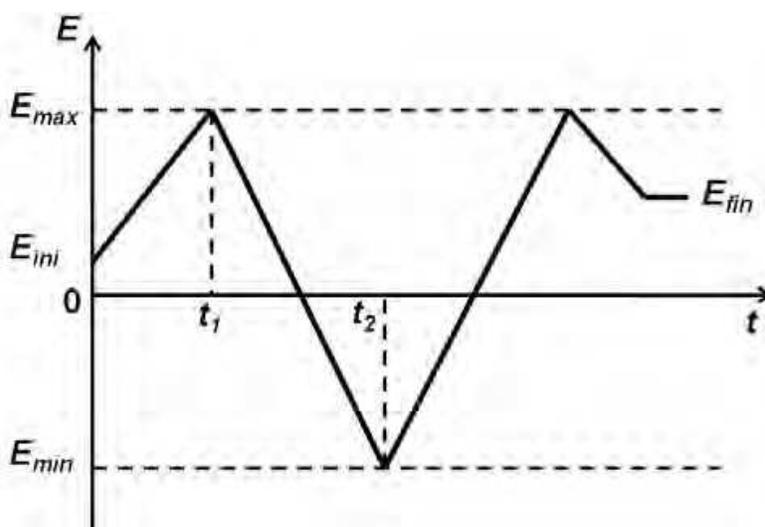


Fig. 3. Variation of applied potential with time in cyclic voltammetry, showing the initial potential, E_{ini} , the final potential, E_{fin} , maximum, E_{max} , and minimum, E_{min} , potentials.

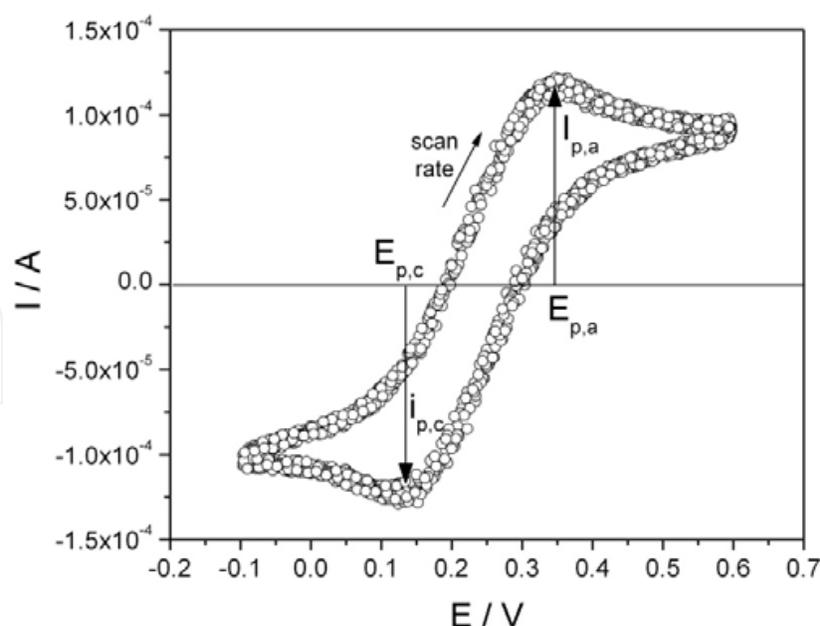


Fig. 4. Typical Cyclic voltammogram for a reversible system.

3. Polypyrrole/ Fe_3O_4 composite films

3.1 General issues Polypyrrole/ Fe_3O_4 films

Several studies have attempted to the development of PPy/ Fe_3O_4 composite films; however there is not still a general consensus about the effect of magnetite on the final composite as well as the type of interaction between the PPy and Fe_3O_4 nanoparticles. Some researchers have found that the presence of Fe_3O_4 in the PPy causes an increase in the conductivity of the composite as compared with pure PPy (Chen et al., 2004; Chen et al., 2003). However, there are others authors claiming the opposite (Deng et al., 2003a; Pailleret et al., 2007). The controversy may be due to many factors such as oxide particle size, dopant agent, electrolyte, method of synthesis, electrodeposition rate, etc.; which influence the properties of the composite leading to changes in the electrical properties when the amount of magnetite incorporated into the polymer matrix is increased. Composites of organic conducting polymer and Fe_3O_4 particles have the advantage of having both good electrical and magnetic properties. In addition of being promising materials as protective coatings, they are attractive to be used in new batteries, fuel and solar cells, capacitors or magnetic materials.

3.2 Electrochemical polymerization of the films

The production of adherent coatings based on conductive polymers chemically synthesized is hampered by its low solubility in common solvents. Polymers obtained by this method cannot be processed by spin or dip coating. This disadvantage can be overcome by electrochemical polymerization, which can simultaneously allow to form and to deposit polymer coatings on the substrate from a monomer–electrolyte solution. Unfortunately, as shown by several previous studies, the attempts to electrochemically polymerize pyrrole on reactive metals such as iron or other oxidizable metals in aqueous medium, present some difficulties. In this case is necessary to find the electrochemical conditions that lead to a partial passivation of the metal and decrease its dissolution rate without avoiding the electropolymerization of the monomer. In acidic medium, no noble metals are preferentially

dissolved due to the polymerization potential of pyrrole, being this higher than the oxidation potential of the metal. These metals can be covered with passive films that prevent their dissolution in acidic medium. However, these passive films are either soluble in the polymerization medium or poorly wetted by the electrolyte-monomer solution and thereby preventing electropolymerization of the monomer. Therefore a coating process that can force simultaneous passivation and polymerization is desirable. Some researchers have developed a one-step in situ passivation and coating of steel for polypyrrole with good adhesion properties (Iroh and Su, 2000, 2002; Ocon et al., 2005; Wencheng and Iroh, 1998). In the same way, PPy/iron oxides composites can be prepared by electrochemical oxidation of the monomer in the presence of dopant anion and the iron oxide particles in suspension. Some works have reported composite films obtained by galvanostatic method on several substrates as: iron, stainless steel, carbon steel, platinum, etc. (Garcia et al., 2002; Montoya et al., 2010; Wencheng and Iroh, 1998). Instead, other electrochemical techniques as constant or variable electric potential have been imposed in order to synthesize the composite coatings. Independently of the electrochemical technique used to film formation the mechanism of electrosynthesis is the same and it involves different stages, as showed in Figure 5: 1. Monomer oxidation. 2. Radical-radical coupling. 3. Deprotonation/Re-aromatization and 4. Propagation or subsequent oxidation. The polymerization is believed to proceed via a radical-radical mechanism (Andrieux et al., 1991), wherein the natural repulsion of the radicals is supposed to be refused by the solvent, the counterion, and even the monomer. Chain growth then continues until the charge on the chain is such that a counterion is able to be incorporated. The backbone has a delocalized π -system and the polymer film incorporate dopant anions, stabilizing the charge on the backbone of the polymer (Ocon et al., 2005). Eventually, as the polymer chain exceeds a critical length, the solubility limit is exceeded, and the polymer can be deposited on the electrode surface. However, in the early stages of polymerization the electrode substrate plays a critical role once the reaction is initiated. For example, when the PPy is electropolymerized on carbon steel by galvanostatic method, using oxalic acid as the electrolyte, three stages can be distinguished in the process of electropolymerization, as can be seen in Figure 6. In the first stage the dissolution of steel is observed, followed by its passivation by the formation of iron oxalate film and iron oxides, and finally the deposition of polypyrrole. Passivation time can be decreased by increasing the applied current, the increased pH and the concentration of pyrrole (Su and Iroh, 1997). Earliest results show that the passive layer has a well-defined crystalline structure, insoluble in water enough to encourage further electropolymerization. It is appropriate to emphasize the formation of iron/oxalic acid system, principally in terms of its complexing and salt-forming reactions (Giacomelli et al., 2004). It is worth noting that the process of electropolymerization of pyrrole on stainless steel is similar to carbon steel if the passive layer of stainless steel is removed prior to the electrosynthesis, otherwise, the time required to start the electropolymerization of the monomer is almost negligible, see Figure 7. During the electrodeposition of PPy and PPy/Fe₃O₄ coatings on stainless steel is possible to see some changes in the registered potentiometric curves. The Figure 7 shows the curves E vs. t for the electropolymerization of pure PPy and PPy/Fe₃O₄ composite films with different concentrations of magnetite present in the electrolyte of the synthesis. It can be observed that the increasing of magnetite content in the polymer decrease the electropolymerization potential. This could indicate that the presence of magnetite reduces the required energy for polymer film formation and prevents the overoxidation of the film during the polymerization process (Montoya et al., 2009).

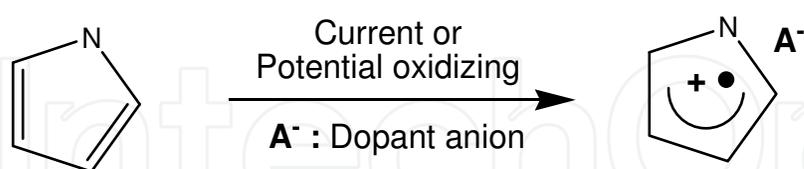
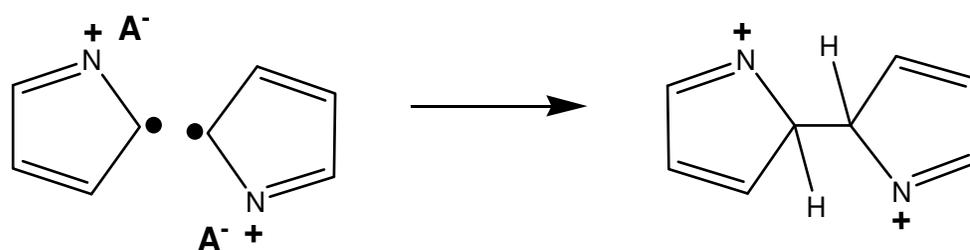
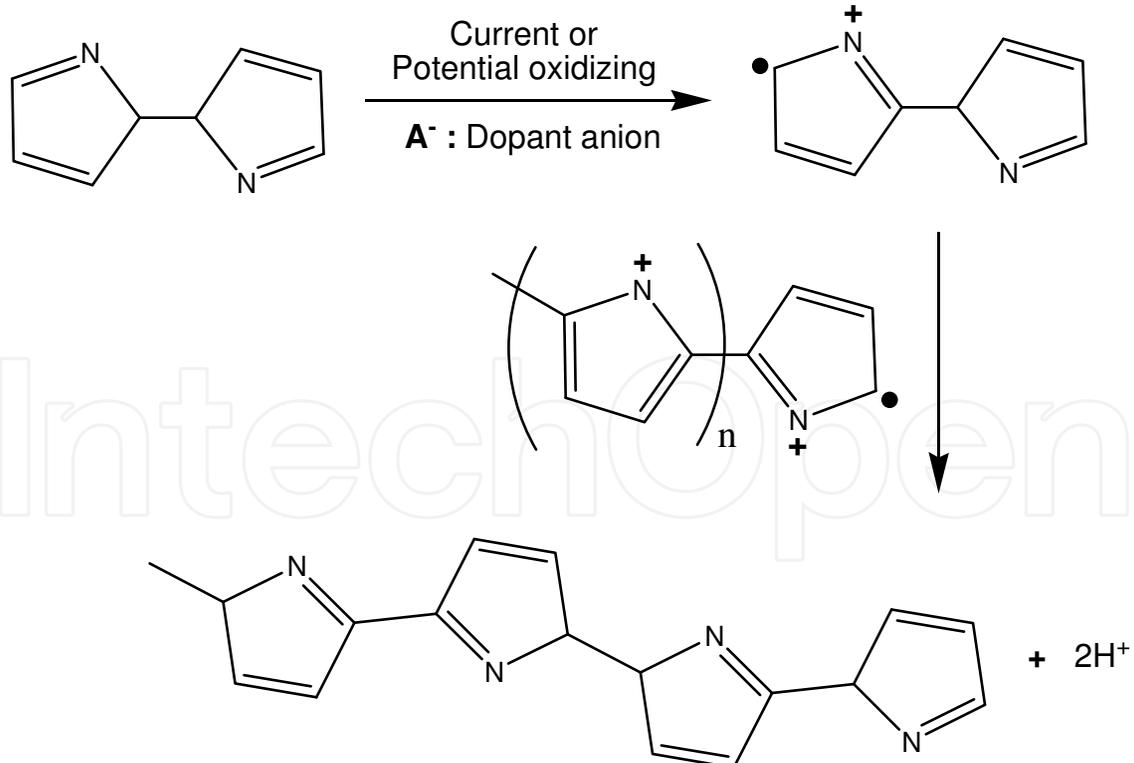
Stage 1**Stage 2****Stage 4**

Fig. 5. Mechanism of formation of polypyrrole by electropolymerization

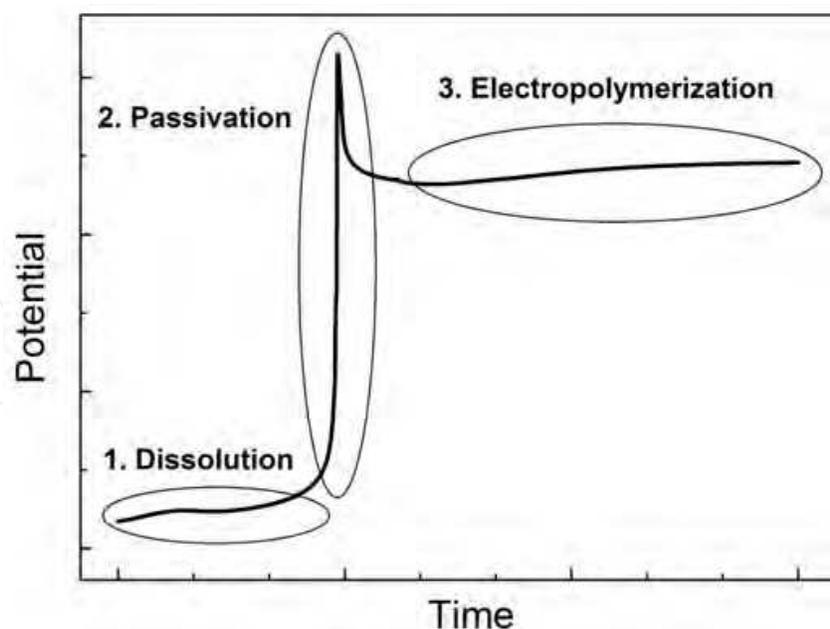


Fig. 6. Potentiometric curve during the formation of Polypyrrole/Fe₃O₄ coatings on carbon steel in oxalic acid by galvanostatic method.

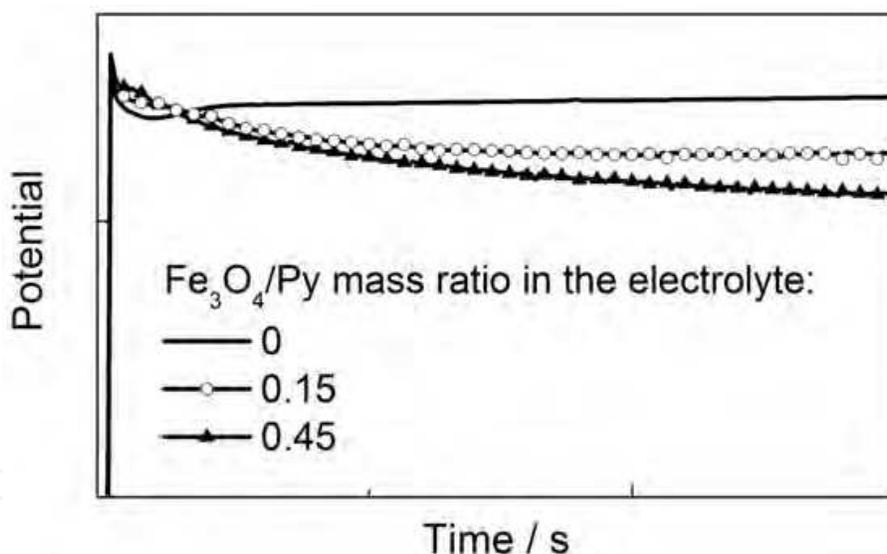


Fig. 7. Potentiometric curve during the galvanostatic electrodeposition of PPy/Fe₃O₄ coatings on stainless steel with several Fe₃O₄/Py mass ratios in the electrolyte of synthesis.

3.3 Physical chemical interaction and stabilization of the polymer

Several studies have shown the interactions between polypyrrole and Fe₃O₄ in polypyrrole-Fe₃O₄ composite films. A recent study examined the effect of the magnetite particles on the structure of the polymer matrix. Films of polypyrrole were synthesized on stainless steel in the presence of magnetite particles (Montoya et al., 2010). The effect of the magnetite particles on the structure of the polymer matrix was determined using Raman spectroscopy and Scanning Electron Microscopy (SEM). Additionally, the changes in the electrical resistance of the films were evaluated over time by electrochemical impedance spectroscopy in solid state. These

results showed that the interaction between the incorporated magnetite and the polymeric matrix, leads to morphological and electronic changes in the composite film respect to pure PPy. It is possible to see in the micrograph of the Figure 8 that the polymer is preferentially deposited as globular chains along the lines of the polished surface. As the content of Fe_3O_4 increases in the polymer matrix, it is possible to observe a change in the coating morphology going from agglomerated globular structures composed of average size about 100nm (Figure 8a) to agglomerates with a star-like conformation (Figure 8b). These results clearly indicate the effect of Fe_3O_4 particles in the morphology of the polymer.

Figure 9 shows the Raman spectra obtained for pure PPy film and $\text{Fe}_3\text{O}_4/\text{Py}$ composite film with a mass ratio in the electrolytic solution of 0.75. The spectra present the characteristic bands already attributed to PPy vibrational modes located at 1592, 1382, 1320, 1252, 1082, 1047, 982 and 931cm^{-1} (Santos et al., 2007). By comparing with reported data by in-situ Raman studies (Furukawa et al., 1988; Santos et al., 2007), it is clear that the polymer is in the oxidized state where both aromatic and quinoid structures coexist indicating a pseudo-equilibrium between polaronic and bipolaronic structures at the same oxidation level as already pointed out by Santos (Santos et al., 2007) and Furukawa (Furukawa et al., 1988). Figure 9 shows that the intensity of the band at 931cm^{-1} decreases when the Fe_3O_4 is in the film. This band is characteristic of the bipolaronic structure (quinoid form) in the oxidized state and is attributed to out-of-plane C-H deformation. Additionally, two bands characteristic of the polaronic structure (aromatic form), at 982 and 1047cm^{-1} , assigned to ring deformation mode and CH in-plane deformation mode respectively, increased when the Fe_3O_4 is present in the composite (Furukawa et al., 1988). Both the bands at 1500 and 982cm^{-1} are assignable to aromatic segments but these are also present at the most oxidized state. The band at 1082cm^{-1} , presents in both spectra is assigned to the most oxidized state, correlated to the bipolaron or dication state. The intensity of this band remains relatively constant for all the obtained composites. According to Yakushi et al. (Yakushi et al., 1983), the evidence of aromatic segments bands when the polymer is oxidized is due to the presence of different conjugation lengths in the PPy films, which are also observed in the composite PPy- Fe_3O_4 .

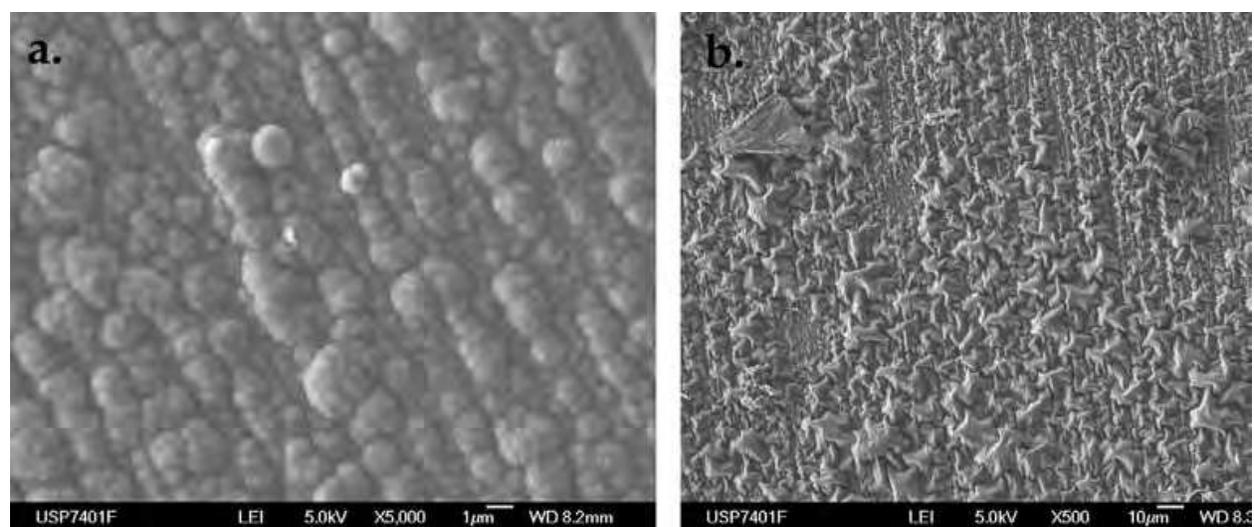


Fig. 8. SEM images of a. pure PPy film and b. $\text{Fe}_3\text{O}_4/\text{Py}$ composite film with a mass ratio in the electrolytic solution of 0.75.

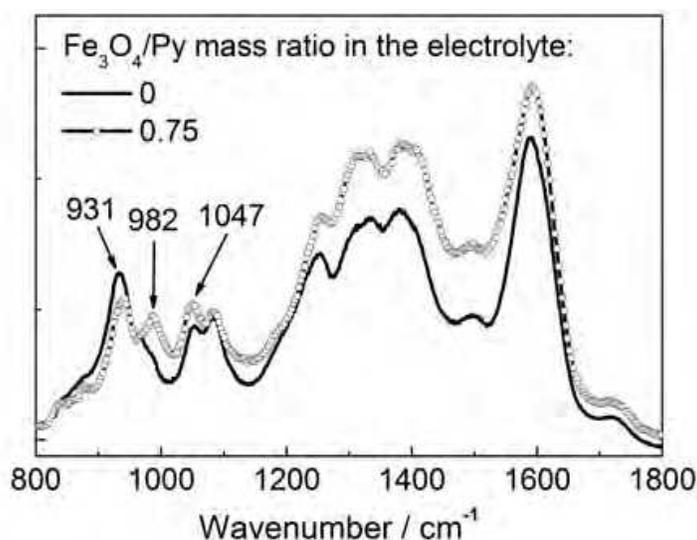


Fig. 9. Raman spectra of PPy film and composite film with a Fe₃O₄/Py mass ratio in the electrolytic solution of 0.75.

The most important evidences in this work are as follows. The incorporation of magnetite into polymeric matrix decreases the electrical resistance of the polymeric films. Additionally, the presence of magnetite into the film not only stabilizes the polaronic form of the polypyrrole, but also preserves the polymer from further oxidation. These results were consistent with previous results showed by Elliott et al. (Elliott et al., 1991); the authors combined resistance and electron spin resonance (ESR) measurements of PPy films and they observed that electric resistance is minimum when the ESR signal is maximum, indicating that polaronic species are the main responsible by charge transportation (Elliott et al., 1991). In the same direction, investigations performed by Deng et al. suggested that the interaction mechanism between the PPy and the Fe₃O₄ may involve the interaction between lone pair electrons of the nitrogen atom in PPy chain with the 3d orbital of iron atom to form a coordinate bond, reducing the energy level interval of the pyrrole ring (Deng et al., 2003). Additionally, the work of Tzong-Ming et al. also shows evidences of the interaction between PPy and Fe₃O₄ nanoparticles (Wu et al., 2007). They observed by UV spectroscopy, a transition from the valence band to the antibonding polaron state in PPy, indicating that the produced PPy was in the doped state. When the spherical structure of PPy-Fe₃O₄ nanocomposites was formed, the characteristic peak assigned to the polaron-p transition was slightly shifted to a smaller wavelength with increasing Fe₃O₄, suggesting the interaction between the quinoid rings of PPy and Fe₃O₄. This is also consistent with the results observed for us by Raman spectroscopy in a recent study (Montoya et al., 2010) and also with the fact that magnetite preserves the PPy film to further oxidation and the PPy-Fe₃O₄ could preserve the conductive state for longer time due to the stabilization of the polaronic form of the oxidized state.

4. Polypyrrole/Pt composite films

4.1 Polypyrrole/Pt films general description

Composite materials based on conducting polymers are alternatives with equal or better efficiency than metals typically used in fuel cell electrodes. These types of materials are considered one of the most promising groups of polymers to manufacture these cells because

their easy application and operation, being PPy one of them. In recent years it has been carried out the electrodeposition of PPy with the incorporation of platinum, silver or gold on substrates such as glassy carbon, gold and platinum. The electrochemical synthesis of PPy/Pt films and their morphological and structural properties are presented here (Marín et al., 2010; Marín et al., 2009). The results in this section show the formation of sandwich-like structures and the important stabilization effect that platinum provided to the polymeric film in terms of electroactive activity. The Polypyrrole/Pt films are a proposed system based on two configurations: two-layer and multiple-layer. The films were obtained by electropolymerization of pyrrole and cathodic deposition of platinum from ammonium hexachloroplatinate salt on stainless steel 304. Moreover, to improve PPy/Pt films, a multiple-layer configuration was obtained by using an electrolytic solution containing pyrrole and platinum salt. Finally the electrocatalytic activity of two-layer and multiple-layer PPy/Pt films was evaluated for methanol oxidation.

4.2 Electrochemical polymerization

The experiments are classified into two groups, two-layer and multiple-layer, as shown in Table 1 and Figure 10. Ammonium Hexachloroplatinate was obtained by hydrometallurgical processes using alluvial platinum (Benner, 1991; Georgieva and Andonovski, 2003) and used as Pt source for the electrochemical synthesis. All potentials reported in this chapter are referred to calomel electrode.

Two-layer PPy/Pt	<ol style="list-style-type: none"> 1. Electrochemical synthesis of PPy films 2. Reduction of Pt (IV) by a potentiostatic method.
Multiple-layer PPy/Pt	Monomer oxidation and platinum reduction alternating.

Table 1. Description of the experiments.

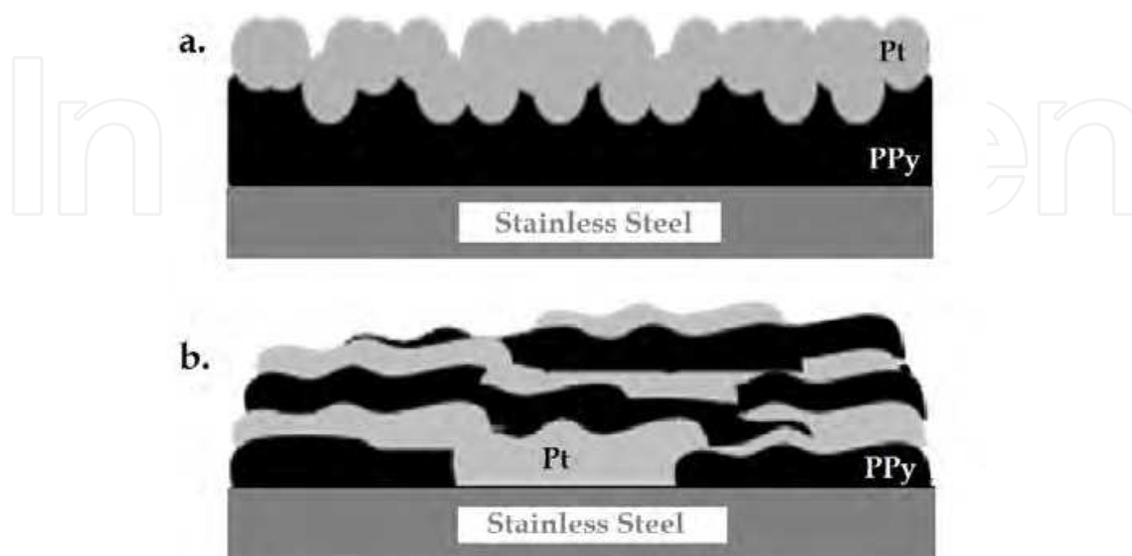


Fig. 10. Schematic representation of PPy composite films a. two-layer, b. multiple-layer.

In the first film configuration the PPy films were obtained by a galvanostatic method, applying 0.001A for 2400s using a 0.1M pyrrole + 0.1M H₂SO₄ electrolyte solution. Once obtained the PPy film, a layer of platinum was cathodically electrodeposited on PPy film in order to obtain the two-layer PPy/Pt (1). The Pt layer was obtained by potentiostatic method from solution containing 0.001M of [(NH₄)₂PtCl₆] and 0.5M of H₂SO₄ and applying -0.2V during 1200s. The multiple-layer PPy/Pt (2) composite films were obtained by potentiostatic method applying 0.5V to get PPy films, and then applying -0.2V to get the platinum deposition using a solution containing 0.1M of Pyrrole, 0.001M of [(NH₄)₂PtCl₆] and 0.5M of H₂SO₄. Each potential was applied during 1200s.

4.3 Characterization

4.3.1 Scanning electron microscopy (SEM)

Figure 11a illustrates how the polymer was formed along the lines of the substrate, showing a globular morphology of sizes ranging from 4 to 5µm with a few smaller outer cores on the surface, which are highlighted on the entire matrix of the polymer. This globular morphology, as previous reported, is typical of polypyrrole when formed by electropolymerization either by potentiostatic or galvanostatic methods (Lehr and Saidman, 2007; Lu et al., 2006; Martins et al., 2008; Nie et al., 2008). In Figures 11b and 11c the same globular morphology is observed. However, in both films there are not small outer cores as in pristine PPy. It is then evident that platinum homogeneously covered the PPy film and copied its morphology. The obtained films were evaluated with EDS analysis to confirm the

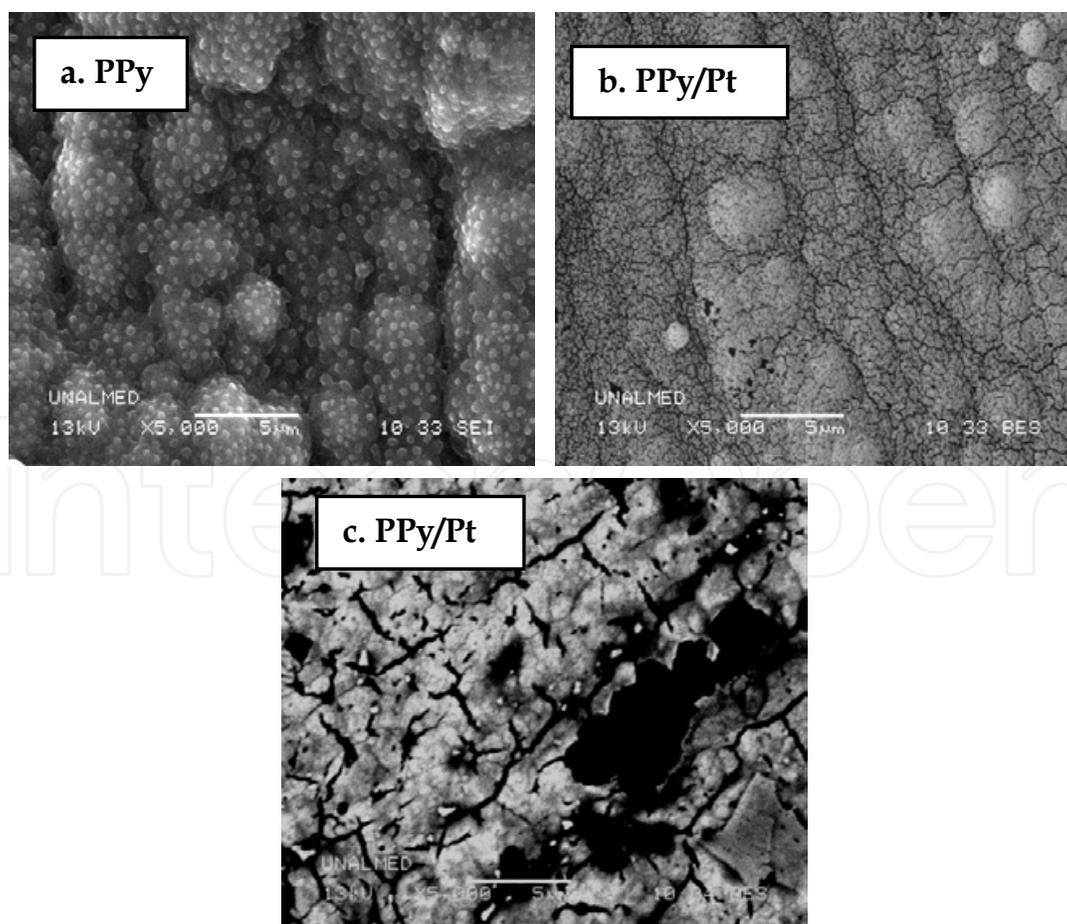


Fig. 11. SEM micrographs of films: a. pure PPy, b. two-layer PPy/Pt, c. multi-layer PPy/Pt.

presence of platinum. Figure 12 shows the results of this analysis. The atomic percentage of Pt is higher than that found for other elements. Fe, Ni and Cr are elements associated with the stainless steel substrate. It is observed that for multiple-layer films, elements of the substrate are in less percentage, given the increase in thickness. In both films it is evident the presence of platinum on the surface of the polymer matrix.

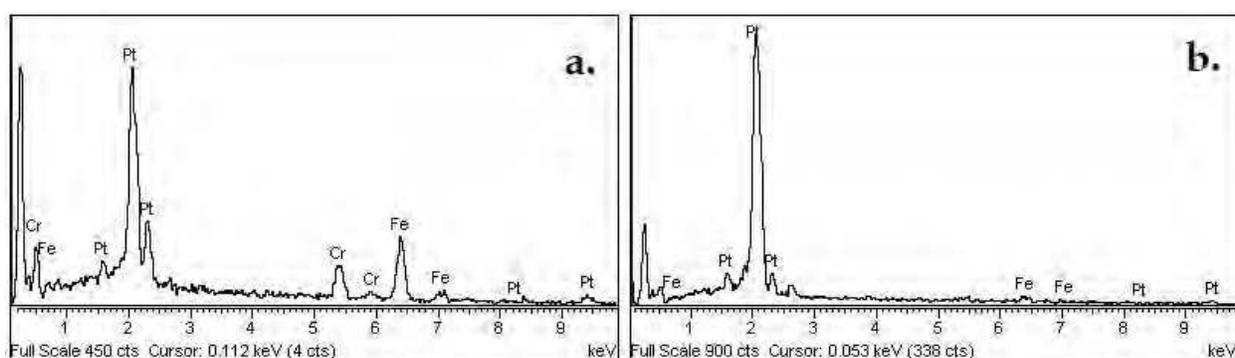


Fig. 12. EDS spectra: a. two-layer PPy/Pt, b. multi-layer PPy/Pt.

Figure 13a shows a SEM micrograph taken at a cross section of the two-layer PPy/Pt film. In this micrograph two layers were clearly observed. The first layer is the PPy and second layer correspond to Pt. The Figure 13b represents a top view of the multi-layer PPy/Pt film. The micrograph shows the effect of electrical potential alternation during the films deposition in short times, giving as a result the formation of discontinuous regions covered by the polymer (black regions) and platinum (bright regions), without being able to cover the entire surface of the substrate. Finally it is expected that both films presented electrocatalytic activity (Bouzek et al., 2001, b; Holzhauser et al., 2005). However, the two-layer films can additionally act as a protective coating for stainless steel substrate, because complete coverage of the metal substrate by PPy.

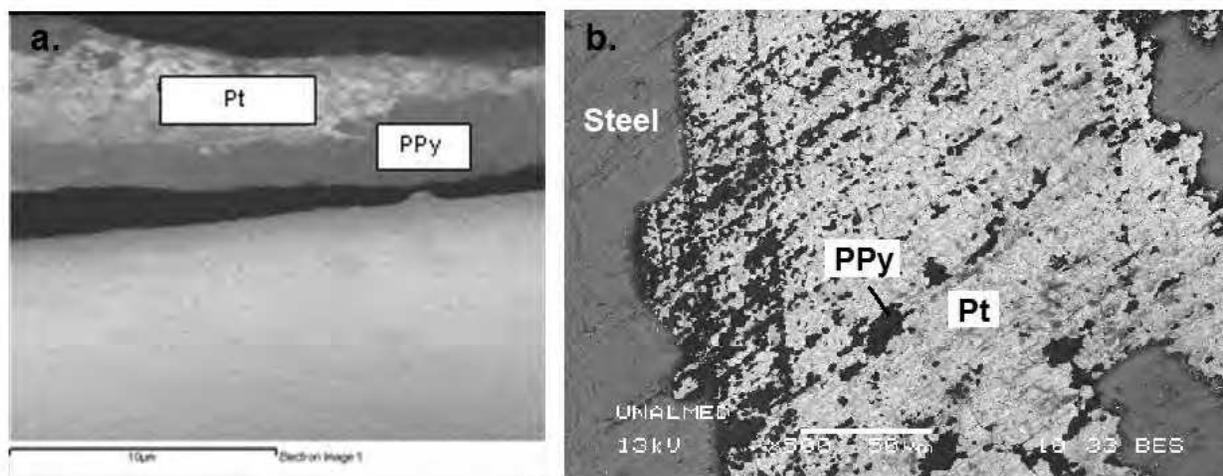


Fig. 13. SEM micrographs of: a. cross-sectional view of two-layer PPy/Pt films, b. top view of multiple-layer PPy/Pt films.

4.3.2 Atomic force microscopy (AFM)

All the obtained films were analyzed by AFM to study their homogeneity, the grain size and surface roughness. The Figure 14a shows a PPy image with granular morphology

heterogeneously distributed all over the surface. Some authors agree that this is the morphology adopted by PPy formed on a metal substrate (Bravo-Grimaldo et al., 2007; Okner et al., 2007). An average grain size is 0.125 μm and a surface roughness of 33.6nm could be calculated, similar to that observed by J. Tamm (Tamm et al., 2004). In the Figure 14b the morphology of a typical two-layer PPy/Pt film is observed. That film showed similar morphology to that for PPy. This is an indication that platinum covers much of the polymer matrix and takes its morphology. Pt reduced the grain size up to 0.083 μm . The surface roughness was less modified and a value of 33.3nm was calculated for this film. Figure 14c shows the morphology for multiple-layer PPy/Pt films and as the two-layer films, they have a granular morphology and platinum copies the polymer. Similar grain size values compared to two-layer film were obtained, and an increase of surface roughness of 10nm was observed.

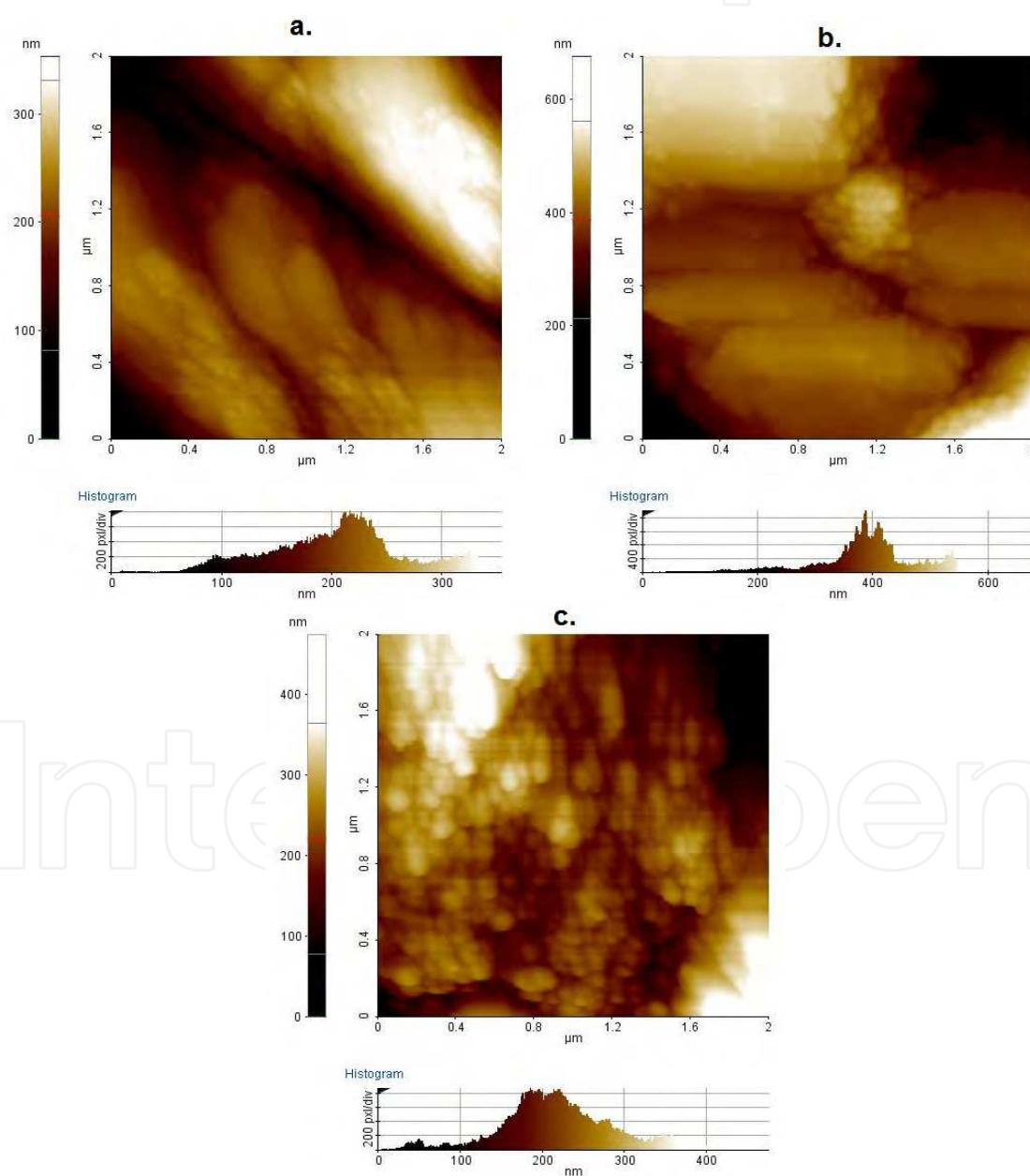


Fig. 14. AFM Image: a. PPy, b. two-layer PPy/Pt, c. multiple-layer PPy/Pt films.

4.3.3 Surface profilometry

This technique was used to obtain accurate results of film thickness. Table 2 reports the thickness data for each system. The obtained results are initially consistent with the patterns shown by Figure 10. The platinum coating deposited on the PPy film had a thickness of about 0.14 μm .

Film	Thickness (μm)
PPy	1.28
Two-layer PPy/Pt	1.42
Multiple-layer PPy/Pt	1.98

Table 2. Thickness of the films.

4.4 Fuel cells applications

Polypyrrole/Pt composite films were evaluated by cyclic voltammetry as anodes for fuel cells applications. The ability of the films to oxidize methanol was measured in 0.5M of H_2SO_4 and 1M of MeOH (Bouzek et al., 2001a; Holzhauser et al., 2005). The cyclic voltammograms were run without going through the over oxidation potential of the polymer, so these were taken from the open circuit potential to 0.8V in the anodic direction and to -0.5V in the cathodic direction.

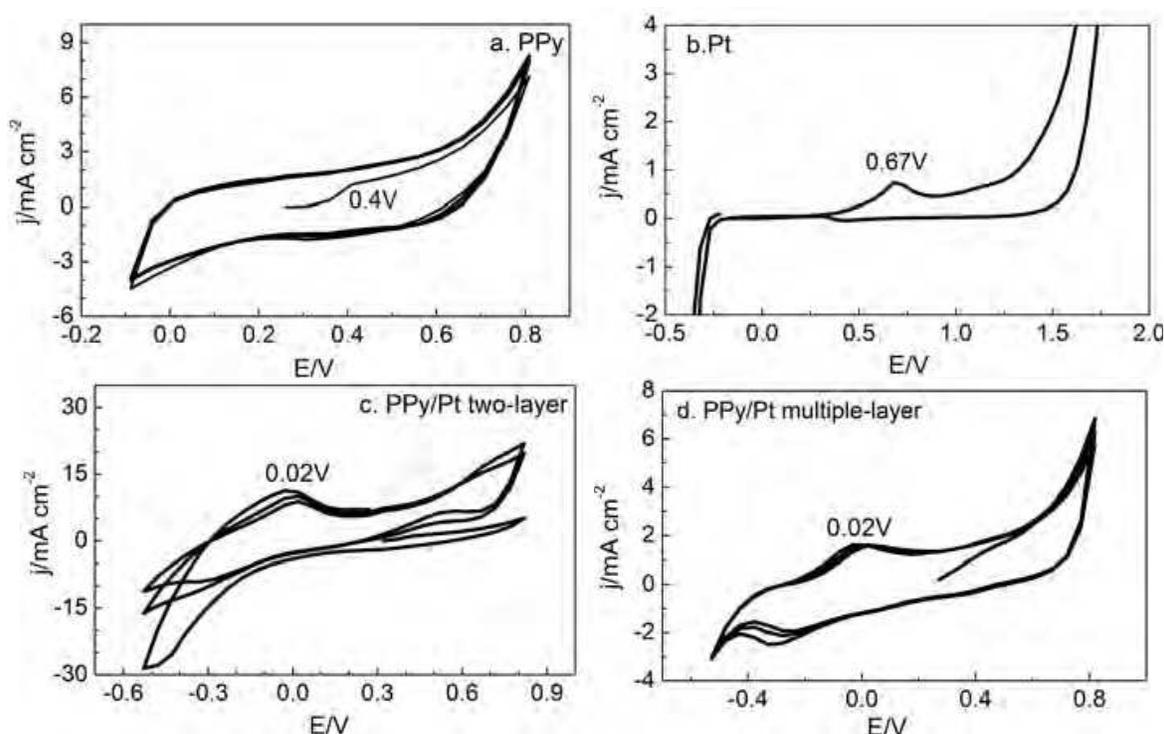


Fig. 15. Cyclic voltammograms of: a. PPy, b. Pt, c. two-layer PPy/Pt and d. multiple-layer PPy/Pt in 0.5 mol.L⁻¹ H_2SO_4 and 1 mol.L⁻¹ methanol at 100 mV/s and atmosphere of N_2 .

Although in both, two-layer and multiple-layer PPy/Pt films, the methanol oxidation occurs at 0.02V, the kinetics of methanol oxidation is different. This is mainly due to the fact that two-layer films presented higher oxidation current densities (11mA.cm⁻²) than those

observed for multiple-layer films (2mA.cm⁻²). The results show that two-layer films are more efficient to oxidize methanol because the more active layer of platinum is deposited on all the surface of the PPy film. While in the multiple-layer films the platinum is deposited heterogeneously all through the film.

5. PPy/Fe₃O₄/Pt composite films

In the present section the effect of the concentration of H₂SO₄ as the electrolyte used in the synthesis of PPy, PPy/Pt, PPy/Fe₃O₄, and PPy/Fe₃O₄/Pt films deposited on 304 stainless steel is evaluated. The oxidation potentials of all films were determined by cyclic voltammetry technique in order to assess the effect of the incorporation of Pt and/or Fe₃O₄ into the conductive polymer matrix. The inorganic particles significantly influence both the oxidation stability and morphology of the PPy matrix. The results showed that the incorporation of platinum and magnetite nanoparticles into the polypyrrole film increase the current density of the electrochemical response and shift the oxidation potential towards more anodic values. Moreover, the deposition of platinum and magnetite allows larger over-potential window to promote redox reactions without compromising the stability to oxidation of the polymer.

5.1 Electrochemical polymerization

Ammonium Hexachloroplatinate was obtained by hydrometallurgical processes of from alluvial platinum (Benner et al., 1991; Georgieva and Andonovski, 2003). This salt was used as Pt source for the electrochemical synthesis. The magnetite particles were obtained by hydrothermal method reported in the literature with some modifications (Deng et al., 2003b; Huang et al., 2005).

The polypyrrole films were obtained by galvanostatic method applying 1mA during 2000s. 0.1M of pyrrole and 0.1M of H₂SO₄ or 0.25M of H₂SO₄ were used as electrolyte. The PPy/Fe₃O₄ films were obtained by galvanostatic method with the same conditions as for PPy films. Before the electropolymerization, Fe₃O₄ particles were dispersed into the electrolyte solution, using an ultrasonic probe during 30 minutes. The PPy/Pt and PPy/Fe₃O₄/Pt composite films were made in two stages, each one in a separate experiment. In the first stage a PPy or PPy/Fe₃O₄ film was obtained by galvanostatic method. The platinum was cathodically electrodeposited on PPy or PPy/Fe₃O₄, from 0.001M of [(NH₄)₂PtCl₆] + 0.5M of H₂SO₄ solution by potentiostatic method applying -0.2V during 1200s. The experiments were classified as shown in Table 3.

Film	[H ₂ SO ₄]	Test
PPy PPy/Pt PPy/Fe ₃ O ₄ PPy/Fe ₃ O ₄ /Pt	0.1M	(1)
PPy PPy/Pt PPy/Fe ₃ O ₄ PPy/Fe ₃ O ₄ /Pt	0.25M	(2)

Table 3. Classification of experiments according to the concentration of the acid used as electrolyte in the polymerization.

5.2 Characterization

5.2.1 Scanning electron microscopy (SEM)

The effect of the electrolyte concentration in the morphology of PPy films was evaluated. In Figure 16 the resulting morphologies of PPy in the experiments (1) and (2) are presented.

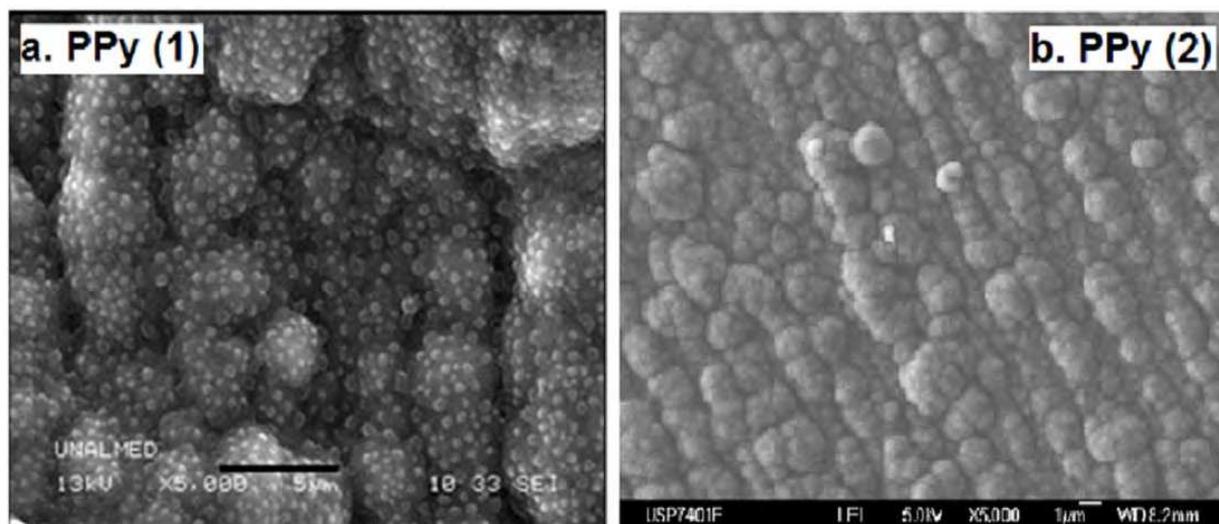


Fig. 16. SEM micrographs of the films: a. PPy (1), b. PPy (2).

Figure 16a shows polypyrrole obtained in 0.1M of H_2SO_4 named as PPy (1). The typical globular morphology is observed (Lehr and Saidman, 2007; Martins et al., 2008). The Figure 16b presents a polypyrrole obtained in 0.25M of H_2SO_4 , PPy (2). The influence of increasing the electrolyte concentration can be clearly observed. A smaller size of about 100 nm was found for the smallest domain. Moreover these films did not show the formation of outer core on the surface.

5.2.2 Cyclic voltammetry

The effect of Fe_3O_4 and Pt particles incorporated into the polypyrrole matrix were evaluated by cyclic voltammetry technique. The oxidation potential of PPy film was analyzed in order to assess the effect of inorganic particles into the film. Figures 17, 18, 19, and 20 shows the PPy, PPy/Pt, PPy/ Fe_3O_4 and PPy/ Fe_3O_4 /Pt cyclic voltammograms evaluated in 0.5M of H_2SO_4 as electrolyte solution for each of the concentrations in which the polymer was obtained, experiments (1) and (2). Figure 17 is composed by three curves. The first one shows the response from stainless steel giving two oxidation current peaks at -0.3V and -1.4 V being the last one the most intense. The second current peak also occurs during the sweep return, resulting in an anodic reactivation process of the substrate. The second and third voltammetry curves show PPy films obtained on stainless steel in solution of 0.1M and 0.25M of H_2SO_4 , respectively. The over oxidation potentials of polypyrrole appeared at 0.9V and 1.1V. These oxidation current peaks are responsible of the enhance presence of bipolarons rather than polarons in the polymer chain (Lamprakopoulos et al., 2004; Radhakrishnan and Adhikari, 2006)

The over oxidation potential of polypyrrole is not influenced by the electrolyte concentration, oxidation current peaks are observed at the same potential in PPy films obtained with both electrolyte concentrations. However the current densities in these potentials are greater for PPy films obtained at 0.25M of H_2SO_4 . This means that the

chemical doping is higher for the PPy (2) at higher electrolyte concentration than PPy (1) obtained at a lower concentration. The sweep return in cyclic voltammometry curves in the PPy films presented a reactivation peak at 1.4V due to the substrate, showing that after the over oxidation potential of the film the steel is exposed to an aggressive media.

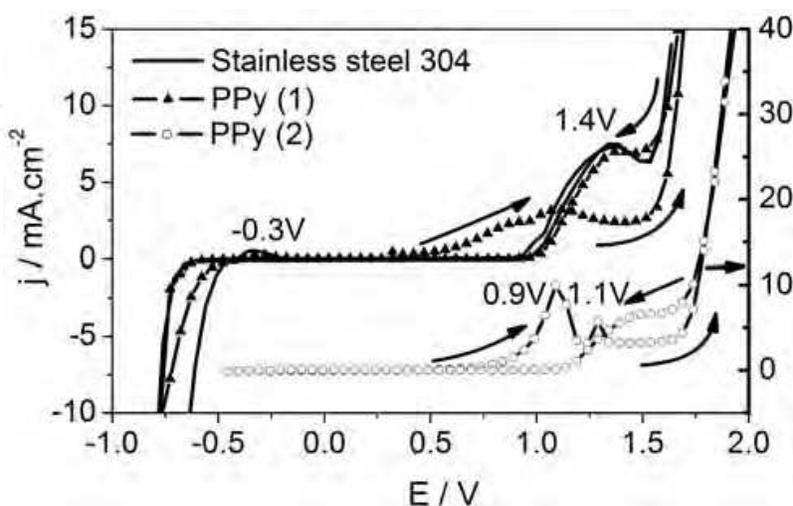


Fig. 17. Cyclic voltammograms of PPy films in the experiments (1) - left axis and (2) - right axis in 0.5 mol.L⁻¹ H₂SO₄ at 5 mV/s.

The Figure 18 shows cyclic voltammograms of PPy/Pt (1) and PPy/Pt (2) composite films in 0.5M of H₂SO₄ electrolyte. Both films presented two oxidation peaks. The first peak in the anodic direction at 0.9V is an over oxidation of the polymer matrix. The second peak in the cathodic direction at 1.4V corresponds to the substrate oxidation process. When comparing the voltammograms in Figures 17 and 18 it can be concluded that although platinum is able to cover all the electrodeposited PPy film, this does not inhibit the oxidation of the polymer. It was observed that both samples of PPy/Pt (1) and (2) presented an over oxidation potential at 0.9V and current density decreases in this potential for PPy (2) film.

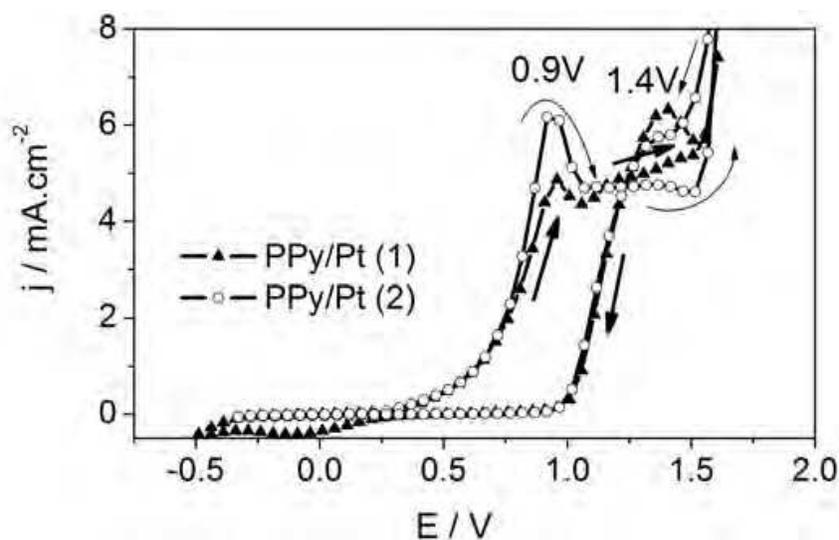


Fig. 18. Cyclic voltammograms of PPy/Pt films in the experiments (1) and (2) in 0.5 mol L⁻¹ H₂SO₄ at 5 mV/s.

Figure 19 shows the voltammograms of PPy/Fe₃O₄ composite films. There are some differences compared to voltammetry response of PPy/Pt films. The first difference is that the oxidation potential of PPy film is shifted to more anodic potentials going from 0.9V to 1.25V for PPy/Fe₃O₄ composite film obtained in 0.1M of H₂SO₄ and from 0.9V to 1.36V for PPy/Fe₃O₄ composite film obtained in 0.25M of H₂SO₄. The observed shift could be associated with a possible redox effect that magnetite provides to overoxidation of the polymer as demonstrated previously (Garcia et al., 2002; Montoya et al., 2009). The second event is an increase of the current density related to polymer oxidation, being considerably higher when the composite film is obtained in an electrolyte solution with high concentration of counter-ions as well as was observed for the PPy and PPy/Pt films. As expected, the PPy/Fe₃O₄ composite film obtained in 0.25M of H₂SO₄ shows greater doping degree of counter-ions than the PPy/Fe₃O₄ composite film obtained in 0.1M of H₂SO₄. From voltammograms of Figure 17 one current peak at 0.4V can be possibly associated to magnetite oxidation. The peak observed for the cathodic sweep at 1.4V was associated with substrate oxidation due to debonding of the film.

Figure 20 shows the voltammograms of PPy/Fe₃O₄/Pt composites films for experiments (1) and (2). In these curves is clearly observed the new positive effect of magnetite due to a shift of the over oxidation potential of PPy to a more cathodic potential at 1.28V. On the other hand, the curves here showed oxidation current densities of the polymer higher than that observed for PPy films. The composite system showed a slightly difference when the electrolyte concentration increased, as observed in the Figure 20. Hence, is likely that the platinum completely covers the surface of the polymer and decreases the counter-ions diffusion through the film when subjected to oxidation-reduction cycles.

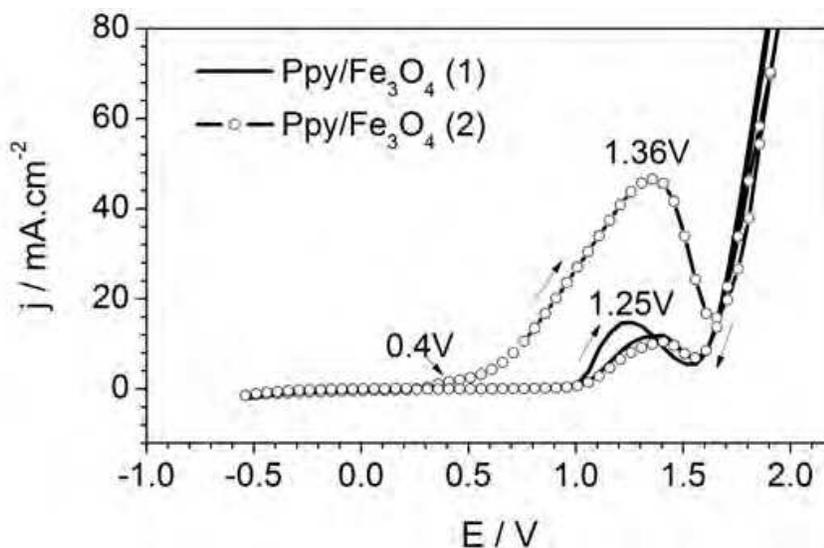


Fig. 19. Cyclic voltammograms of PPy/Fe₃O₄ films in the experiments (1) and (2) in 0.5 mol L⁻¹ H₂SO₄ at 5 mV/s.

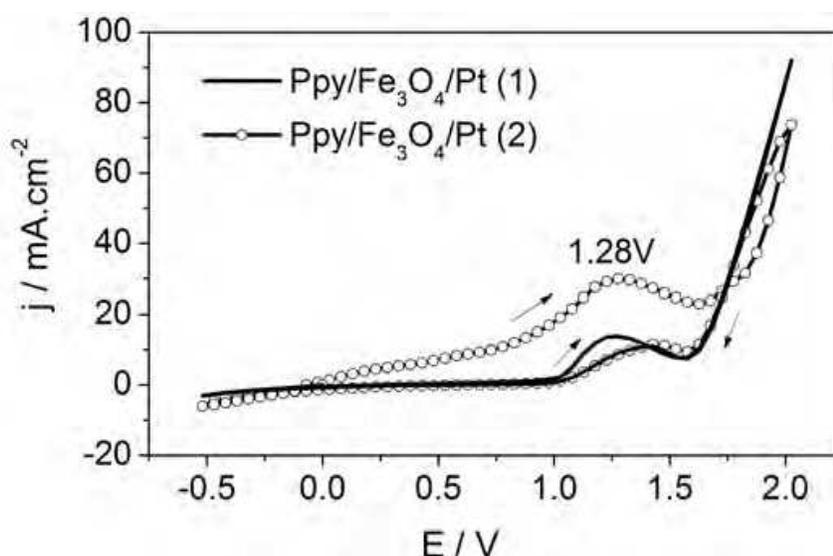


Fig. 20. Cyclic voltammograms of PPy/Fe₃O₄/Pt films in the experiments (1) and (2) in 0.5 mol L⁻¹ H₂SO₄ at 5 mV/s.

6. Conclusions

The addition of Fe₃O₄ to polypyrrole matrix modifies the final structure of the polymer films, as evidenced by SEM and Raman spectroscopy. The observed changes in morphology and structural vibrations of the polymeric matrix after particle incorporation indicate that magnetite interacts with polypyrrole and modifies its properties. The charge transfer process between PPy and Fe₃O₄ causes the stabilization of polaronic segments in decreases the bipolaronic states. This fact occurs in a diminution of the electric resistance of the composite upon Fe₃O₄ load and the preservation of the conductivity when the film is exposed to moisture. The presence of magnetite reduces the required energy for the polymerization and prevents over-oxidation of the polymer during the film formation.

Incorporation of platinum into PPy films does not modify the chemical structure of polymer, however increases the electric conductivity of the composite film. When Pt is incorporated into PPy film the oxidation potential of the polymer is shifted to more positive potential. The increasing of the anodic overpotential window of the composite film makes possible to use these films as catalytic substrates to carry on reactions, like ethanol or methanol oxidation, without significant film deterioration.

The inorganic particles significantly influence both the oxidation stability and morphology of the PPy matrix. Incorporation of platinum and magnetite nanoparticles into the polypyrrole film increase the current density of the electrochemical response and shift the oxidation potential towards more anodic values. Moreover, the deposition of platinum and magnetite allows larger over-potential window to promote redox reactions without compromising the stability to oxidation of the polymer.

7. Acknowledgments

This work is partially supported by the University of Antioquia. The financial support from the Excellence Center for Novel Materials -CENM- and from COLCIENCIAS is also greatly appreciated by the authors.

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