

A New Modified Electrode with a Copolymer of Aniline / Fe(III)-Tetrakis(Para-Aminophenyl)Porphyrin: Test of Its Electrocatalytic Activity Toward the Reduction of Molecular Oxygen and Oxidation of Ascorbic Acid and Sulfite Ion.

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The simultaneous electropolymerization of aniline and Fe-porphyrin in HCl by cycling the potential on glassy carbon (GC) and highly ordered pyrolytic graphite (HOPG) electrodes was studied by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and electrochemical techniques. A conducting copolymer thin film was produced, which was stable and contained a low quantity of porphyrin compared to aniline. Its electrocatalytic activity was tested for the reduction of molecular oxygen and also for the oxidation of ascorbic acid and sulfite anion. This activity was higher than that of the poly-porphyrin and the poly-aniline modified electrodes for these reactions. Here we describe in detail the electropolymerization process and the film morphology. The electrocatalytic behavior of the aniline and porphyrin homopolymers is compared to that of the aniline-porphyrin copolymer.

Keywords: modified electrodes, copolymers, Fe-porphyrin, polyaniline, electrocatalysis

1. INTRODUCTION

Over the past few years the feasibility of obtaining electrode materials with high reactivity and good electrochemical properties for a wide number of reactions of fundamental and applied interest has been widely demonstrated [1-4]. One of the most important research fields in electrochemistry has therefore been the control of the structure and reactivity of electrode/solution interfaces through the

formation of modified electrode surfaces, by incorporating chemically stable molecules of known molecular structure [5,6].

Overall, the modified electrodes are obtained by incorporating some redox species on the electrode surface that are capable of producing rapid and reversible changes in their oxidation states. Thus, such a species acts as redox mediator of an electrochemical reaction between the electrode and an electroactive species present in the electrolyte, modifying the reaction kinetically by lowering its activation energy and decreasing the overpotential corresponding to the reaction on the unmodified electrode [7-11].

There are several experimental methods to obtain these modified electrodes. These techniques have been tested, successfully obtaining surfaces with a high reactivity, and in some cases, with a good selectivity against a particular electrochemical reaction [12]. Such modified electrodes have many applications varying from fuel cells, the development of electrochemical sensors or electrochromic materials [13,14].

Among these experimental routes are physical adsorption or electropolymerization and chemical methods. In this paper we have used the latter method which has certain advantages over the previous procedures because it produces more uniform films which are irreversibly adsorbed on the electrodes and allows a better study of the properties of the adsorbed species. The adsorption takes place through an electrical perturbation such as continuous potential scan, a constant current application, or under the application of a positive enough potential to form an initiator radical.

Electrodes modified with conducting polymers derived from azamacrocyclic complexes of transition metals, such as metalloporphyrins, are widely used in electrocatalytic reactions [15, 16]. These complexes have been deeply studied since they exhibit a high electrocatalytic activity for many reactions of interest and can also be used as models for biological systems [17, 18]. Furthermore, their catalytic activity is known to be greatly increased when they are formed as polymeric films on the electrode surfaces [19-22].

Porphyrins are macrocycles able to form stable complexes with a variety of transition metals. These materials are suitable as molecular systems to modify electrode surfaces for the design of electrochemical sensors. In most cases, the porphyrin-based electrochemical sensors (both amperometric and potentiometric) for the detection of electroactive analytes are based on electrochemical oxidation or reduction of these analytes, mediated by a specific redox couple of metalloporphyrin films [23].

In general, porphyrin complexes are planar molecules (at least the "core"), which can coordinate anions axially in the plane of the molecule. They have a D_{4h} symmetry and 18 π electrons in the ring. The extensive delocalization of the π electrons system gives rise to significant electron conductivity. Otherwise, these systems can be electropolymerized on the electrode surfaces. In the case of tetraminophenylporphyrin complexes, electropolymerization occurs by the oxidation of the amino groups and the subsequent ortho coupling, forming stable films on a conductive substrate [15, 19-22]. The macrocycle substituent groups have the ability to modify the electron density of the system due to their electron donor or attractor character, combined with other properties like the molecular configuration, hydrophobicity or rigidity of the complex. These characteristics may cause steric hindrances that inhibit the catalytic activity or its ability to polymerize [12,16].

One of the possible disadvantages of these modified electrodes is the formation of adducts through metal substrate bonds, which are not broken once the charge transfer is produced, thus inhibiting regeneration of the catalyst. This is one reason why the catalytic activity of porphyrins varies substantially with the nature of the coordinating central metal of the macrocycle, like Fe, Co, Ni, Mn and others [24]

In the family of conductive polymers, aniline is another molecule used to modify electrode surfaces, forming the polyaniline polymer (PANI). It has received considerable attention for its special properties: it is a conducting polymer with high stability, interesting electrochemical and optical characteristics, low cost and easy preparation [25-27]. The characteristics of PANI make it useful as a matrix for the anchoring of other molecules, thus allowing the formation of copolymers with different electrocatalytic properties [28].

The electropolymerization of aniline by continuous potential scanning allows the study of the redox properties of the electrogenerated films and their growth. Furthermore, these synthesis conditions permit us to obtain polymers whose electrochemical properties are more reproducible and stable than those obtained by other synthesis techniques. The electrical conductivity of polyaniline depends on the degree of protonation and the potential applied to the polymer. Thus, PANI passes from a nonconductive state (leucoemeraldine) to a highly conductive state (emeraldine or radical cation).

Additionally, in recent years a wide variety of copolymers have been studied for many different applications [29-46]. Copolymerization can be used as a technique to improve the properties of a material. The characteristics of electrochemical copolymerization are highly dependent on the synthesis conditions, in particular, the mole fraction of each of the monomers involved in the reaction [30, 31, 36-38, 42-45].

In this paper we present copolymerization by the simultaneous electropolymerization of aniline and a Fe-porphyrin in aqueous HCl solution by cycling the potential of the working electrode, thus generating a conductive copolymer on glassy carbon or HOPG. This method improves the mechanical properties, stability and conductivity of the porphyrin films. The films were characterized by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and electrochemical techniques.

In addition, a preliminary study was made of the behavior of the copolymer-modified electrode toward different reactions (electroreduction of oxygen and electrooxidation of ascorbic acid and sulfite ion), showing in all cases a more favorable electrocatalytic activity than that of the pure homopolymers. Our results indicate that for this copolymer there is a synergy between both monomers that provides an electrode with better electroactive characteristics.

2. EXPERIMENTAL

Iron tetra-4-aminophenylporphyrin chloride was obtained from MidCentury Co. and used without further purification, and aniline from Aldrich Inc. The GC and HOPG working electrodes ($A=0.071\text{ cm}^2$ and 1 cm^2 respectively) were purchased from NT-MDT (Moscow, Russia) and from SPI supplies (PA, USA) respectively. Electrochemical experiments were performed in a three-

compartment glass cell. Saturated Ag/AgCl/KCl (sat) was used as reference electrode against which all the potentials are quoted and the counter-electrode was a Pt coil ($A = 14 \text{ cm}^2$). The GC electrodes were polished with $0.25 \mu\text{m}$ alumina and ultrasonicated for 5 min before each experiment. Polymeric films were grown by potentiodynamically cycling the electrode between -0.4 and 0.9 V during 50 cycles at a scan rate 0.1 Vs^{-1} in 0.1 M HCl aqueous solution containing $1 \text{ mM Fe-tetra-4-aminophenylporphyrin}$ and 0.1 M aniline (1:1 in volume). The solution was purged with nitrogen (ultra-pure grade) during each polymerization. After polymerization, the modified electrode was rinsed with ultra-pure water obtained from a Milli-Q purification system. All the experiments were carried out at room temperature and under inert atmosphere, except in the case of the oxygen electroreduction studies. Electrochemical studies were performed using an AFCBP1 Pine Bipotentiostat, along with Pinechem 2.5 software. SEM images were taken with a JEOL JSM 6300 at 20 kV .

AFM measurements were made with a Nanoscope V (Digital Instruments/ Bruker) operating in tapping mode in air at room temperature. Etched silicon tips (RTESP, $215\text{-}254 \text{ kHz}$ and $20\text{-}80 \text{ N/m}$ and TAP150A, $126\text{-}159 \text{ kHz}$ and 5 N/m) were used and images obtained at scan rate $0.5\text{-}1 \text{ Hz}$ after waiting for at least two hours to minimize the thermal drift. Freshly cleaved HOPG was used as substrate. Samples were thoroughly rinsed with Milli-Q water after preparation and dried for several hours under a N_2 current flow before imaging.

Electrochemical experiments measuring electroreduction of oxygen were performed in 0.1 M HCl aqueous solution saturated in O_2 , cycling the potential between 0.7 and -0.7 V . The electrooxidation of ascorbic acid (0.1 M) was done in 0.1 M HCl , cycling the potential between 0.9 and -0.2 V . Finally, electrooxidation of sulfite was in 12% ethanol aqueous solution containing 0.1 M NaCl and $0.1 \text{ M Na}_2\text{SO}_3$, cycling the potential between 1.0 and -1.0 V . All these electrocatalytic studies were carried out on polyaniline-, polyporphyrin- and copolymer-modified electrodes, and a bare GC electrode as control. The potential scan rate (v) was set at 0.1 Vs^{-1} in all cases.

3. RESULTS AND DISCUSSION

3.1 Electropolymerization

Figure 1 depicts the structure of the complex used in this study, where $\text{M} = \text{Fe(III)}$. The charge of the whole molecule is equal to zero because the porphyrin ring has a -2 charge and there is a chloride anion axially bonded to the iron (not shown).

Figure 2A shows the voltammetric response of the electropolymerization of Fe-porphyrin dissolved in HCl on a glassy carbon electrode (PGC). At ca. 1.0 V an irreversible oxidation peak appears, corresponding to the oxidation of amino groups to radical cations responsible for the electropolymerization. A cathodic peak is detected around -0.2 V , coupled with a smaller one (see inset in Fig 2A) in the positive-going potential scan. By comparing these peaks with those found when the electropolymerization is carried out in N,N' -dimethylformamide (DMF) media [47], we can conclude that these peaks correspond to the Fe(III)/Fe(II) redox couple.

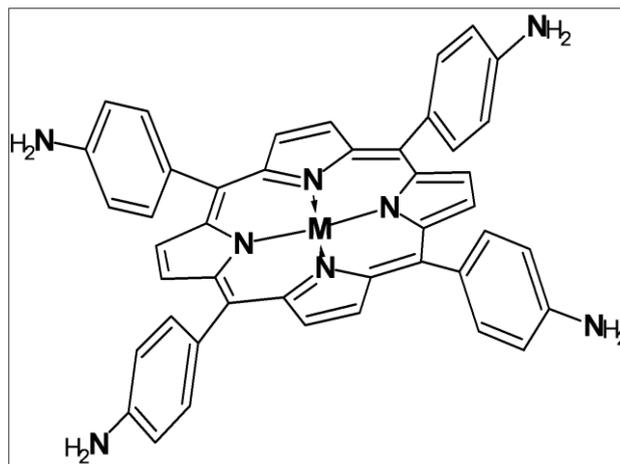


Figure 1. Structure of the complex used in this study, M = Fe(III).

Figure 2B displays the voltammetric response of the electropolymerization of aniline on a glassy carbon electrode (PAGC). In this case, the first redox process, at ca. 0.3 V corresponds to the oxidation of aniline from leucoemeraldine to emeraldine and the second process, at ca. 0.8 V, is due to the oxidation of emeraldine to pernigraniline [48]. The high capacitive current is noteworthy, indicating that this film is thick and porous.

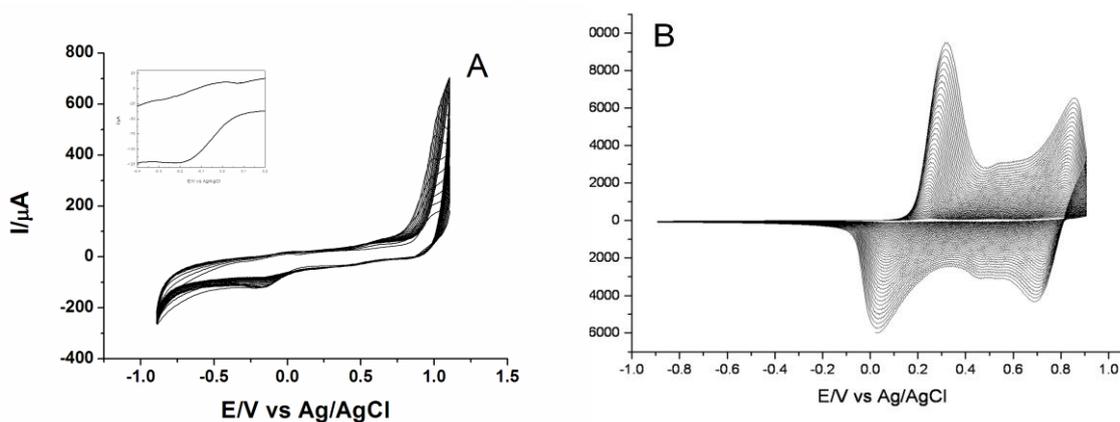


Figure 2. Cyclic voltammograms corresponding to **A)** electropolymerization of Fe-porphyrin dissolved in 0.1M HCl and **B)** electropolymerization of aniline dissolved in 0.1M HCl; 50 cycles between -0.9 and 1.1 V at 0.1 V/s. Inset shows the potential region -0.4 to 0.2V of the redox couple Fe(III)/Fe(II)

The potentials where aniline (ca. +0.7 V) and porphyrin (ca. +1.0 V) begin to oxidize to form a polymer are very different, as shown in Figure 2 (A and B). It is necessary to find the potential limits where both monomers oxidize and form a copolymer. By modifying the HCl concentration, the negative and positive potential limits, the relative concentration of both monomers and the scan rate, it

is possible to find a potential window where all the redox couples appear. If these parameters are not carefully determined, only one of the two homopolymers is obtained. Furthermore, when a copolymer is obtained, it is necessary to optimize all the parameters again to obtain a film where oxygen electroreduction can be achieved at the lowest possible potential.

Figure 3 shows the voltammetric response of the best copolymer on glassy carbon (CPGC) obtained from 0.1 M aniline and 1 mM porphyrin dissolved in HCl 0.1 M. Under these conditions it is possible to prepare a conductive film where all the redox couples from aniline and porphyrin are present. Additionally the redox couple Fe(III)/Fe(II) appears better defined than in Figure 2A but shifted to more positive potentials, suggesting a change in the electron density of the metal centers in the porphyrin.

It should be noted that the morphology of this voltammogram is not as simple as the summed voltammogram of Figures 2A and 2B. This fact is an indication that the porphyrin and the aniline are interacting.

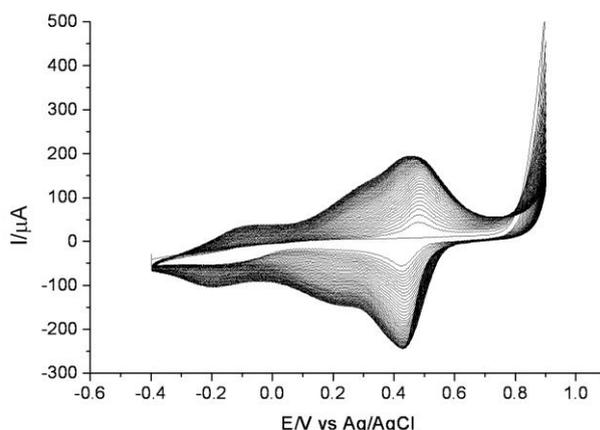


Figure 3. Cyclic voltammograms corresponding to electropolymerization of the copolymer dissolved in 0.1M HCl for 50 cycles between -0.4 and 1.0 V at 0.1 V/s.

The electroreduction mechanism of molecular oxygen on PGC electrodes is centered mainly in the metal, the Fe(II)/Fe(III) redox couple being responsible for the electrocatalytic activities [46,49,50]. This reaction was therefore selected to confirm the formation of the copolymer (see section 3.4) as well as to test the electrocatalytic properties.

In fact, when the CPGC is formed, the oxygen electroreduction wave shifts to more positive potentials. This may be due to enhancement of π -electron delocalization, which increases the electron density of the metal. So this reaction is a very good test to show the formation of these electropolymers, that is, the homopolymer and the copolymer (see Section 3.4).

The main difference between the homopolymer and the copolymer is the change in the electron density of the active site: the metal of the porphyrin. If the copolymer were formed by aniline-porphyrin blocks or by interlaced pure oligomers of aniline and porphyrin, no important differences on

the copolymer electrocatalytic activity would be expected. However, if there is a real copolymerization involving the formation of covalent bonds between aniline and porphyrin molecules, the changes will be more evident. Thus, a change in the reduction potential value for oxygen should confirm copolymer formation (see section 3.4).

Different composites of polyaniline-porphyrin were prepared by successive electropolymerization on a glassy carbon electrode in aniline or porphyrin solutions. In this way two types of modified electrodes were prepared, namely polyaniline/polyporphyrin and polyporphyrin/polyaniline/polyporphyrin electrodes. None of these composites presents electrocatalytic activity toward oxygen electroreduction. These results are consistent with the formation of a true copolymer of porphyrin-aniline under our conditions and that the corresponding film is not merely the result of separate random electropolymerization of the two polymers on the electrode surface.

3.2. Morphological characterization of homo- and copolymers

Figure 4 shows the SEM images of PAGC growth on the GC surface after a different number of potentiodynamic cycles. It can be seen that as the number of cycles increases the continuous growth of the polymer on the surface forms a porous homogeneous film. A similar effect has been observed during the electropolymerization of polyaniline on the bare Al and Al-Pt surfaces [51], where it is compared with how the film morphology varies with the number of cycles.

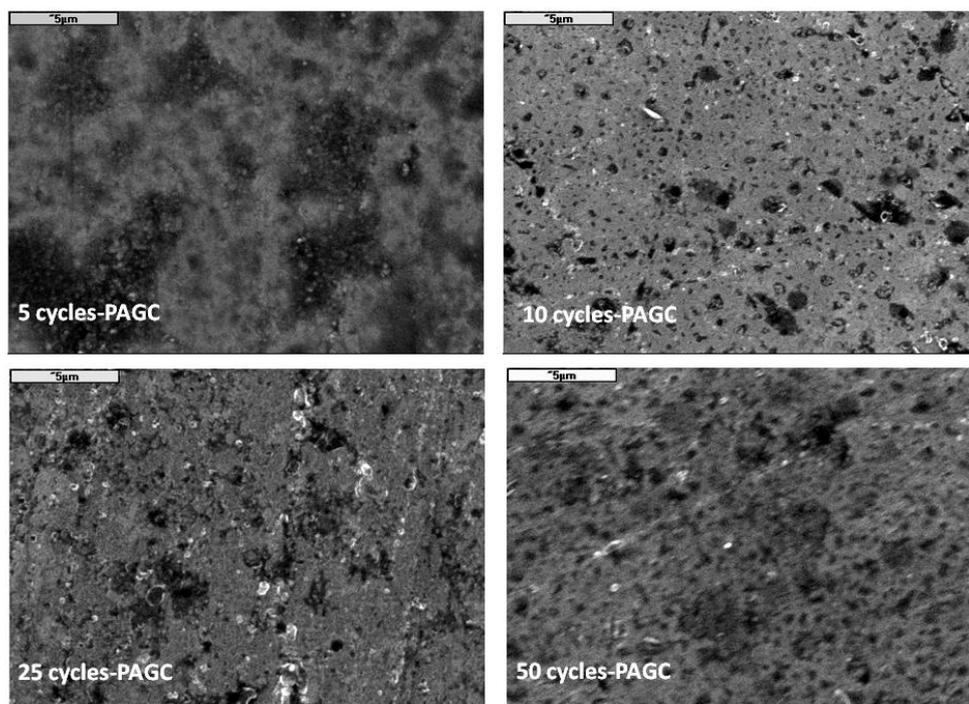


Figure 4. Scanning electron micrographs of a GC electrode modified by growing polyaniline PAGC (x5000) at different numbers of electropolymerization cycles: 5, 10, 25 and 50 respectively.

Figure 5 depicts the growth of PGC. In this case, the film is not homogeneous, in contrast to PAGC, since islands are formed which finally cover practically all the electrode surface. The fact that after 50 cycles of electropolymerization the polished lines in the SEM image of the bare GC are still visible indicates that the film is very thin.

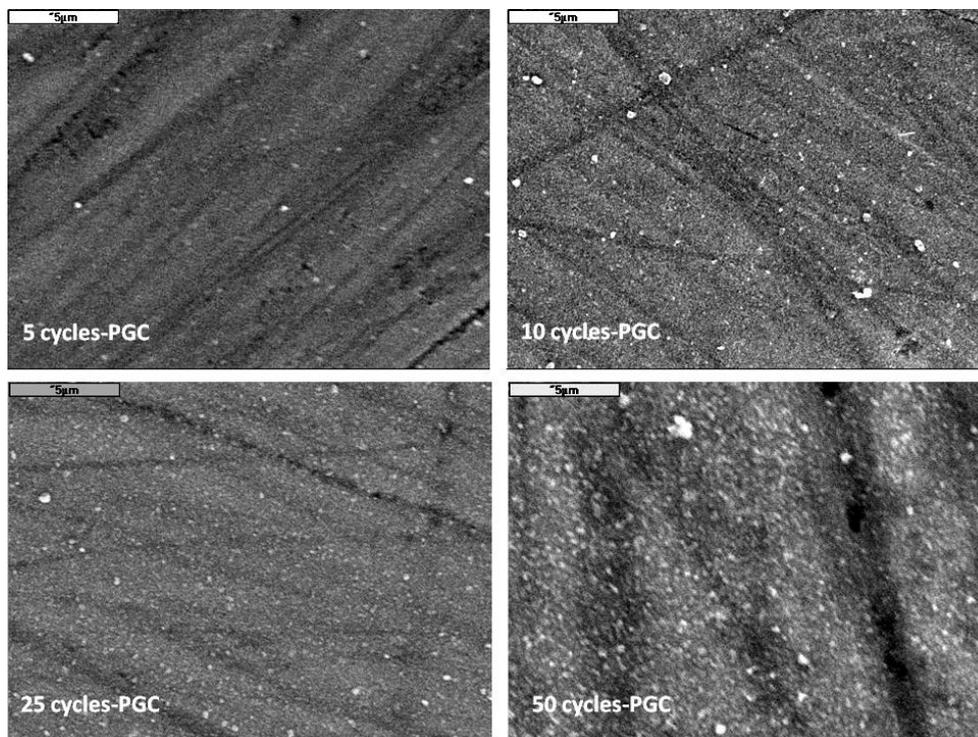


Figure 5. Scanning electron micrographs of a GC electrode modified by growing polyporphyrin (x5000) at different numbers of electropolymerization cycles: 5, 10, 25 and 50 respectively.

Figure 6 shows the growth of the copolymer film (CPGC). At 5, 10 and 25 cycles, the surface of the electrode is totally covered by two types of granules. At 5 and 10 cycles, the growth of the copolymer resembles the growth of the polyporphyrin. However, at 50 cycles a clear difference appears, due to the presence of large granules, which are probably pure polyaniline. This result corroborates one of the tests of copolymerization, where at 25 cycles the CPGC is very similar to the polyporphyrin in its response to the electroreduction of molecular oxygen.

In spite of the lower potential required for the formation of radical cations of aniline compared to porphyrin, it is clear that the difference in solubility of the first oligomers formed on the interface favored the precipitation of polyporphyrin and not that of polyaniline. There is no evidence if the first oligomers are only formed by porphyrin or porphyrins bonded to aniline. However, the similarity between the homopolymer of porphyrin and the copolymer in the first stages of polymerization indicates that the main monomer in both cases is the porphyrin. It seems that, initially, islands of polyporphyrin are formed (maybe with a small number of aniline units) but they collapse forming a single copolymer when the number of cycles is more than 25. A comparable case was observed during

the electropolymerization of iron tetra-3-aminophenylporphyrin on Au in DMF [52]. In our conditions, aniline acts as an adhesive that permits coalescence of the islands. It is important to point out that the stability of the copolymer is so high that it cannot be formed by polyporphyrin unless it is covalently bonded to aniline. In fact, a homopolymer of polyporphyrin can be easily removed from the electrode while the copolymer cannot. To acquire additional information on the initial steps of the electropolymerization, atomic force microscopy images were taken during the first cycles for the three polymers.

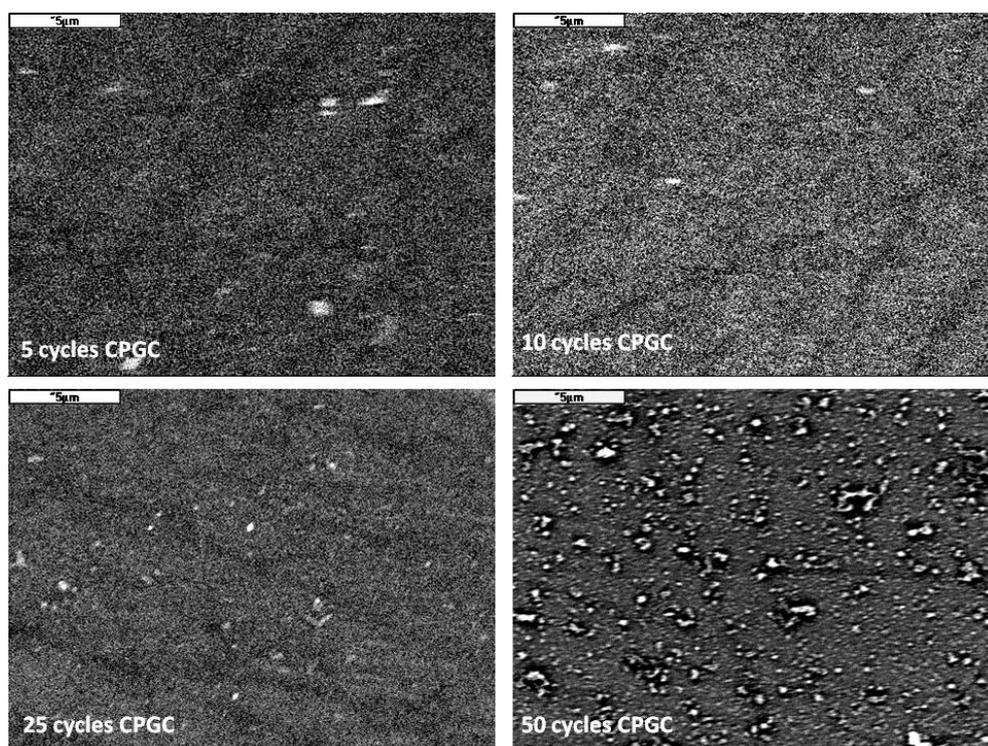


Figure 6. Scanning electron micrographs of a GC electrode modified by growing the copolymer (x5000) at different numbers of electropolymerization cycles: 5, 10, 25 and 50 respectively.

3.3. Atomic force microscopy characterization.

The three polymers included in the present study are able to develop high surface roughness values in a short number of potentiodynamic cycles. This means that their electropolymerization is favored on carbon-based substrates. To achieve good representative AFM images it was necessary to use a very flat carbon-based substrate (HOPG) and limit the number of cycles used in the electropolymerization.

Figure 7 corresponds to the polyaniline-modified HOPG surface after 3 cycles of electropolymerization. Some large isolated particles can be detected, mostly following the step edges of the HOPG surface. These particles grow very fast and in only 3 cycles reach sizes in the order of 50-100 nm long and 20-40 nm high, leaving most of the HOPG surface uncovered.

However, it should be noted that there is also a background of small particles, 15-20 nm wide and only 1-1.5 nm high, homogeneously covering the substrate surface. These particles have been shown to appear as a first step after the first cycle in the aniline electropolymerization. In the successive cycles, the growth of the polyaniline forms the above-mentioned large 3D islands. The roughness value of the polymer surface in Fig. 7 is 3.533 nm

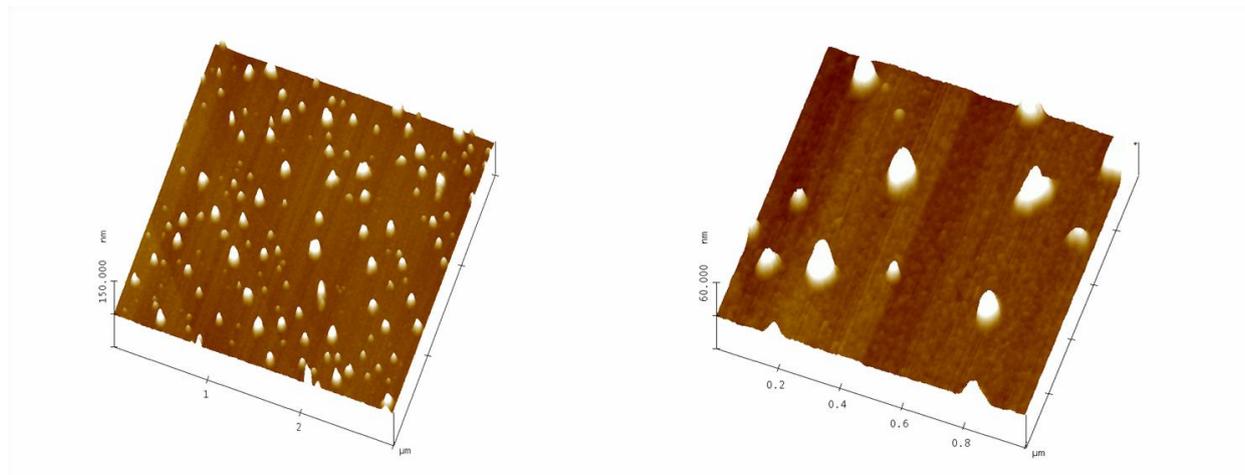


Figure 7. 3 μm x 3 μm (left) and 1 μm x 1 μm (right) AFM images after 3 cycles of electropolymerization of aniline on HOPG.

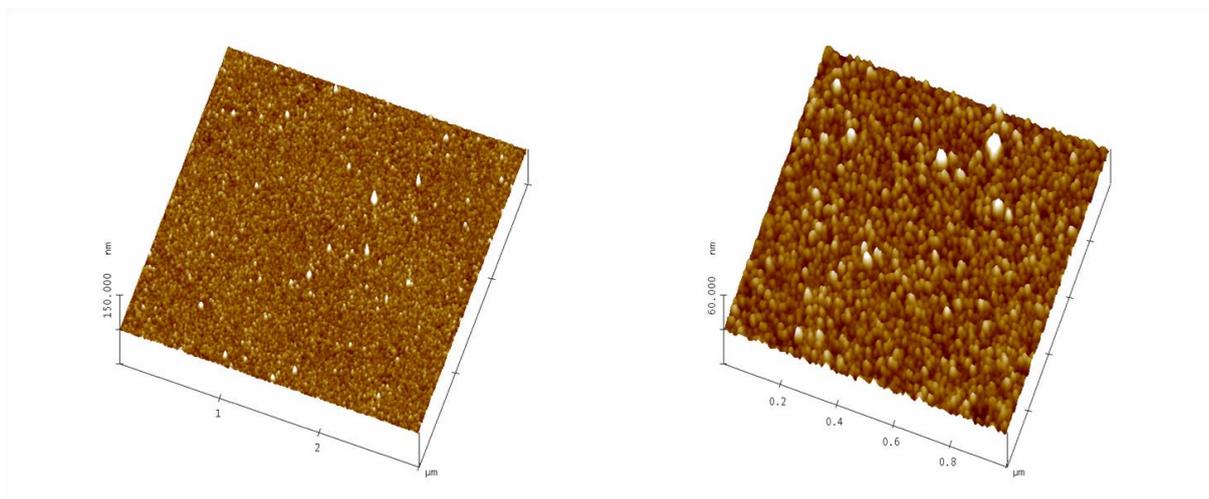


Figure 8. 3 μm x 3 μm (left) and 1 μm x 1 μm (right) AFM images after 3 cycles of electropolymerization of porphyrin on HOPG.

Figure 8 shows the polyporphyrin-modified HOPG surface after 3 cycles of electropolymerization. In this case, the surface appears totally and uniformly covered by polymerized porphyrin particles. These particles are very uniform, 20-30 nm in width and only 4-6 nm in height, and the roughness in Fig. 8 is as low as 1.697 nm. When the electropolymerization of the same porphyrin in DMF at a concentration 10x greater on HOPG, after 50 cycles a very similar film

morphology is seen [53], indicating that the electropolymerization mechanism is independent of the medium the porphyrin is in.

The result after electropolymerization of the aniline-porphyrin copolymer is shown in Fig. 9. The HOPG surface again appears totally and uniformly covered by particles as in the case of the polyporphyrin, but now the size of these particles (ranging 30-50 nm long and 6-10 nm high) is greater than in those of the polyporphyrin (Fig. 8) (the roughness in Fig. 9 rises again to 3.080 nm), although clearly smaller than on the polyaniline modified electrode (Fig. 7).

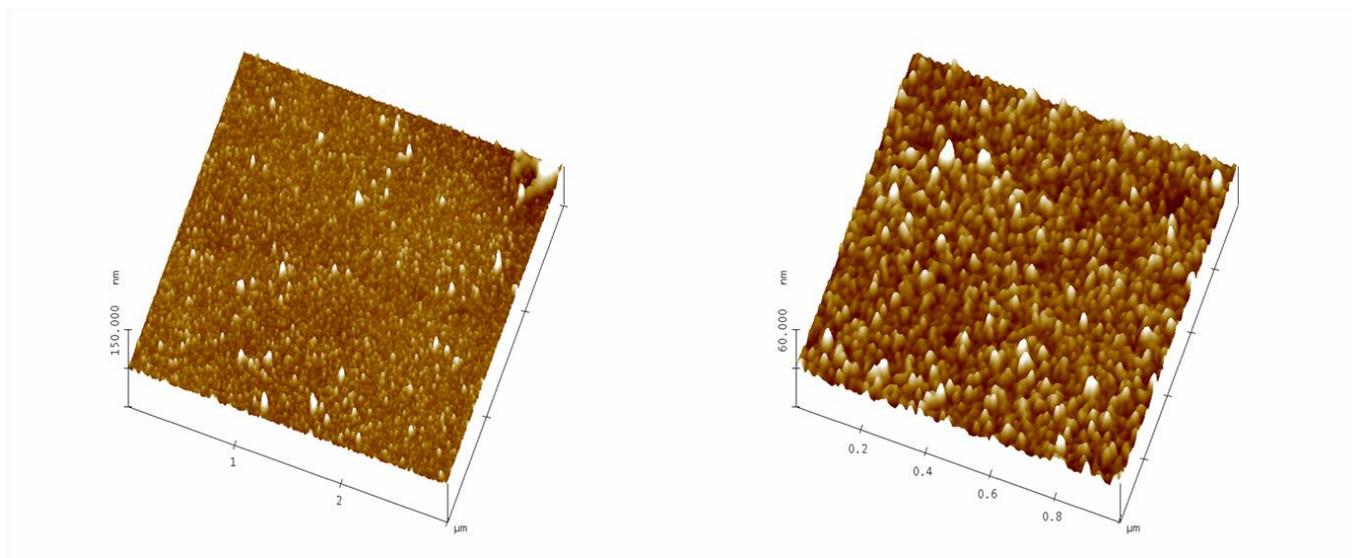


Figure 9. 3 μm x 3 μm (left) and 1 μm x 1 μm (right) AFM images after 3 electropolymerization cycles of copolymer on HOPG.

These results confirm that in the electropolymerization of the copolymer, a different film from those obtained from both the polyaniline and the polyporphyrin electrodes is growing on the HOPG surface. Furthermore, this difference is detected from the very first stage of electropolymerization, indicating that its composition is more complex than the simple addition of the two molecules at the same time. AFM studies with comparable copolymers to this have not been found in the literature.

3.4. Tests of copolymer electrocatalytic activity:

With the aim of determining the electrocatalytic properties of this new electrode and its possible application as a sensor, some preliminary qualitative assays were performed using the ascorbic acid and sulfite electrooxidation reactions, since both substances are commonly used as food additives.

In addition, as noted in section 3.1, the electroreduction of oxygen was studied because it is a test reaction that indicates the formation of the copolymer and the electrocatalytic properties of the polymer toward that reaction, compared to homopolymers.

3.4.1.- Electroreduction of molecular oxygen

Figure 10 compares the three electrodes toward the electroreduction of oxygen. The differences between the two homopolymers and the CPGC are very clear. One of the most important aspects is that the CPGC is much more active in the electroreduction of oxygen than the pure homopolymers, see Table 1. A shift of 125 mV toward positive potential for the polyporphyrin electrode and around 615 mV for glassy carbon was observed. This was also observed on polyaniline/carbon-black composite-supported iron phthalocyanine for the oxygen reduction reaction in an air-cathode microbial fuel cell [46]

As the PAGC does not catalyze this reaction, this result shows that the copolymer formed has a synergic effect between aniline and porphyrin, probably due to the greater delocalization of the charge, which would play a key role in the electroreduction of oxygen. The electrocatalytic activity of the CPGC toward oxygen electroreduction does not correspond to a simple sum of the activity of the homopolymers. Furthermore, the electrocatalytic activity is much greater in the case of copolymer. It is evident that the copolymer is not formed by blocks of homopolymers, but rather there is a radical change in the active site environment that would account for a random copolymerization. It is possible that aniline units covalently bonded to the porphyrin promote the reduction of Fe(III) to Fe(II), which acts as redox mediator in the electroreduction of molecular oxygen.

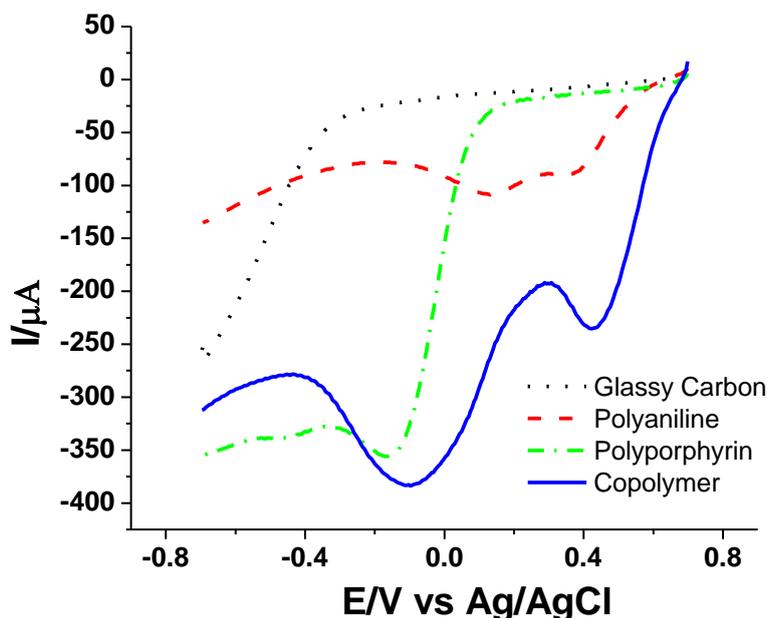
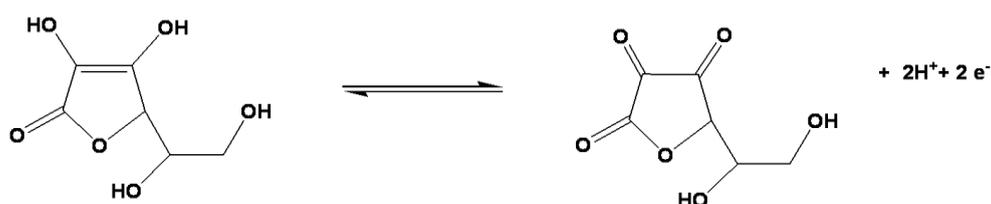


Figure 10. Voltammetric response of the glassy carbon, polyaniline, polyporphyrin and copolymer towards the electroreduction of oxygen in an aqueous solution of HCl 0.1 M, saturated with O₂. Scan rate: 0.1 Vs⁻¹.

Interestingly, on increasing the porphyrin concentration in the electropolymerization solution, the copolymer is not as active as that in Fig. 10. It seems that despite the active center being the Fe ion

of the porphyrin, a significant amount of aniline in the polymer is necessary to enhance its activity. Also, if the concentration of porphyrin is lowered below 0.05 mM, the copolymer loses its activity. It thus seems necessary for porphyrins to be surrounded by anilines to provide a good electrocatalyst toward the reduction of oxygen. The active sites are proportional to the porphyrin units and the enhanced electrocatalytic activity of the copolymer is due to the changes in the electron density of Fe(II) centers becoming more negative through the presence of anilines bonded to the porphyrins. These aniline units act as electron donors for the porphyrin metals.

3.4.2. Electrooxidation of ascorbic acid



Scheme 1. Oxidation of ascorbic acid via two electrons.

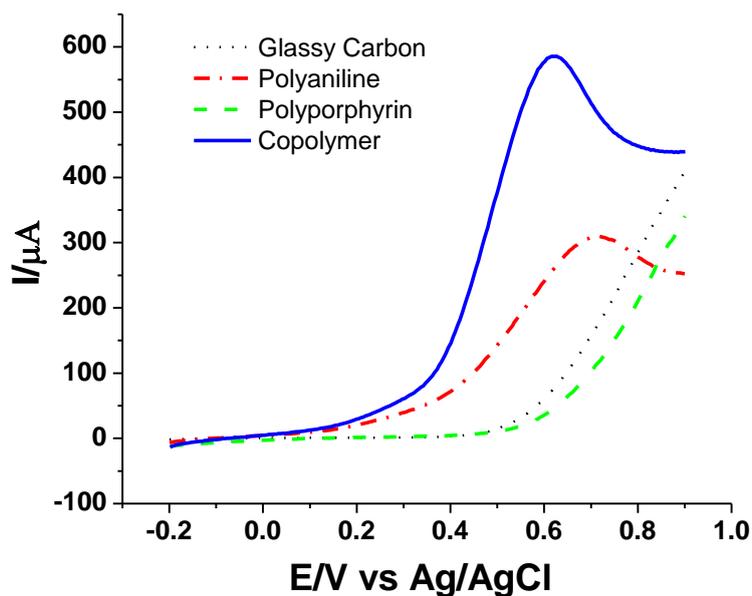


Figure 11. Voltammetric response of the glassy carbon, polyaniline, polyporphyrin and copolymer toward the electrooxidation of ascorbic acid in an aqueous solution of HCl 0.1 M, ascorbic acid 0.1 M. Scan rate: 0.1 V s^{-1}

Figure 11 shows the comparison of the three electrodes toward the electrooxidation of ascorbic acid, and the values of potential and current for the electrooxidation of ascorbic acid on the different modified electrodes are given in Table 1.

In this case, polyporphyrin does not catalyze this reaction but polyaniline does. It acts as a redox mediator for the irreversible oxidation of ascorbic acid via 2 electrons to form dehydroascorbic acid [54-59], see Scheme 1. In contrast to the oxygen electroreduction, in this case, polyaniline is active and polyporphyrin is not. When the central metal in the porphyrin is Mn, a catalytic reaction is however obtained [20]. The copolymer is more active than the polyaniline because the oxidation needs less positive potential. If aniline acts as electron donor for the metal center of porphyrin, then aniline units should become more positive in the copolymer compared to the polyaniline homopolymer. If this is true, the oxidation of the aniline in the copolymer needs more positive potentials to begin, compared to the homopolymer and the oxidation of ascorbic acid should also take place at more positive potentials in the copolymer compared to polyaniline. This does not occur. The role of the aniline units is not as simple as being a donor substituent of polyporphyrin. On the contrary, both aniline and porphyrin units present more electron density when they form a copolymer. Thus, it is clear that very good electron communication between the two kinds of monomers is taking place. The π - π electron system is completely delocalized along the chain and acts as a reservoir or donor of electrons.

3.4.3. Electrooxidation of sulfite.

Sulfite ion is added to some foods, beverages and pharmaceutical products as an inhibitor of enzymatic activity or bacterial growth and as an antioxidant.

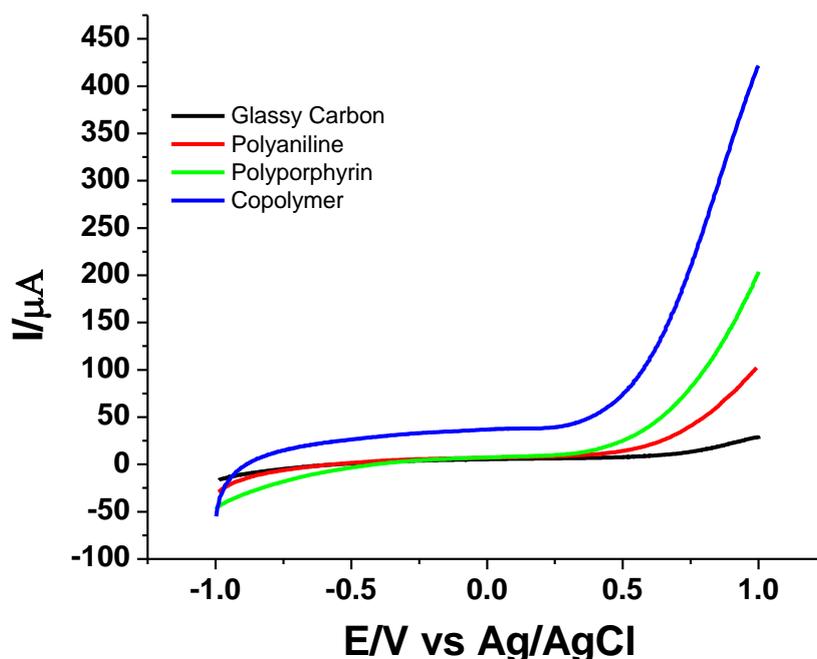


Figure 12. Voltammetric response of the glassy carbon, polyaniline, polyporphyrin and copolymer toward the electrooxidation of sulfite in an aqueous solution of 12 % ethanol, NaCl 0.1 M, purged with N_2 Na_2SO_3 0.1 M). Scan rate: 0.1 Vs^{-1}

A possible application of these electrodes could therefore be their use as electrochemical sensors. To this end, in this experiment the electrooxidation of sulfite is carried out in an ethanol:water mixture 12% v/v, containing 0.1M of NaCl (a wine-model electrolyte).

Figure 12 shows the comparison of the three modified electrodes toward the electrooxidation of sulfite. In this case, polyporphyrin catalyzes the oxidation better than polyaniline. But the copolymer is more active, since it promotes the oxidation at a less positive potential than the polyporphyrin. According to previous results [47,60], the product of the oxidation should be sulfate, formed by an irreversible oxidation process. As a result, the electrochemical response of this copolymer-modified electrode is clearly the best for the electroreduction of molecular oxygen and the two electrochemical oxidations studied.

Table 1. Values of onset potential and peak current corresponding to the electroreduction of oxygen and the electrooxidation of ascorbic acid and sulfite ion on the different modified electrodes.

| Electrodes | GC | PAGC | PGC | CPGC |
|--------------------|------|------------|------|------|
| Oxygen | | | | |
| Potential (mV) | -258 | ----- - | 161 | 276 |
| Current (μ A) | -265 | ----- - | -355 | -382 |
| Ascorbic acid | | | | |
| Potential (mV) | 460 | 150 | 500 | 100 |
| Current (μ A) | 406 | 310 | 340 | 585 |
| Sulfite ion | | | | |
| Potential (mV) | 648 | 430 | 330 | 260 |
| Current (μ A) | 30 | 100 | 200 | 415 |

4. CONCLUSIONS

An aniline-porphyrin copolymer was electropolymerized by cyclic voltammetry on GC and HOPG electrode surfaces, and the optimal experimental conditions for this electrochemical growth process were established. Any variation in these conditions gives rise to a film which is very similar to one of the two homopolymers. The production of a true copolymer was tested through cyclic voltammetry, scanning electron microscopy, atomic force microscopy and different electrocatalytic studies. This film is stable, reliable and grows faster and thicker than any of the two homopolymers alone. Under our conditions, a considerable enhancement in electrocatalytic activity of the copolymer film is obtained. This improvement was tested in different representative electrochemical oxidation and reduction reactions, to permit its use in the design of new electrochemical sensors.

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