

Practical Applications of Poly(*O*-Aminophenol) Film Electrodes

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Abstract: In this paper the different practical applications of poly(*o*-aminophenol) film electrodes in the field of bioelectrochemistry and electrocatalysis are reviewed. Different electrochemical methods employed to prepare sensors based on poly(*o*-aminophenol) are described in detail. Particular emphasis is laid on methods employed to immobilize different macromolecules into the polymer to construct the required biosensor. Also, the electrochemical performance of each sensor is discussed in terms of the different factors that affect its stability, dynamic range and response time.

Keywords: Poly(*o*-aminophenol) films, biosensors, bioelectrochemistry, electrocatalysis.

1. INTRODUCTION

Oxidation of *o*-aminophenol on different electrode materials (gold, platinum, carbon, indium-tin oxide, etc.) in aqueous acid medium was shown to form poly-*o*-aminophenol (POAP) [1-3]. POAP exhibits its maximal electroactivity within the potential range $-0.2 \text{ V} < E < 0.5 \text{ V}$ (*versus* SCE) at pH values lower than 3 [4-7]. The electroactivity of POAP was explained by a redox mechanism that involves an addition/elimination of protons coupled with a reversible electron transfer [4, 5]. Charge-transport processes at POAP films were studied by employing different electrochemical techniques [8-15]. The properties of POAP are favorable to its applications in the field of electrochemical sensors, bioelectrochemistry and electrocatalysis. In this regard, POAP exhibits several advantages with respect to other electroactive polymers. *O*-aminophenol can be *in situ* electropolymerized on different electrode surfaces, and the polymer thickness can be controlled within 10-100 nm due to a self-limiting growth. In addition, the POAP film can be easily regenerated after use. Another interesting characteristic of POAP is the presence of an electron-donating OH group next to the imine nitrogen that increases the electron density at the imine sites. In addition, OH by itself is also a potential coordinating site. These factors combine to provide a strong acceptor binding of POAP with several metal cations. In this regard, POAP was employed to develop stable electrocatalysts for oxygen reduction. Also, POAP is able to immobilize biological macromolecules. It was proved that large amounts of glucose oxidase could be immobilized at POAP films, which is essential to the good performance of an amperometric glucose sensor. Also, employed as material to build amperometric biosensors, POAP has shown to be permselective. In this regard, the interference from electroactive species, such as ascorbic acid and uric acid, which are generally encountered in the determination of a physiological sample, was significantly reduced by the use of a POAP

film. In the following sections, the more relevant practical uses of poly(*o*-aminophenol) are described and discussed in detail considering the influence of different external variables on the electrochemical performance of the polymer in the different developing fields of science in which it was tested. It is expected that despite incompleteness and possible subjectivity, this paper will be helpful to the colleagues who are interested in practical applications of this polymer.

2. AMPEROMETRIC BIOSENSORS BASED ON POLY(*O*-AMINOPHENOL)

Enzyme amperometric biosensors have attracted widespread attention in clinical, environmental, agricultural and biotechnological applications. In recent years, electropolymerized polymers used for generating biosensors have received much attention. Unlike conventional immobilization strategies for biosensors, electropolymerization has no limits in terms of the electrode geometry and area, and offers advantages with respect to thickness control, reproducibility and the uniformity of the polymer film on electrode surfaces with complex geometries. In addition, electropolymerization permits simple electrode regeneration and can easily be extended to the production of microbiosensors. In the optimization of biosensors based on polymer films it is important to understand the factors that affect their stability, dynamic range and response time.

The construction and characterization of a horseradish peroxidase (HRP)-ferrocene modified carbon paste biosensor, using an electrochemically generated POAP membrane for the determination of hydrogen peroxide is reported in [16]. The electropolymerization was carried out by continuous cycling potential scanning (40 cycles) from 0.0 to 0.8 V (*versus* Ag/AgCl) in a fresh acetate buffer solution (0.1 M, pH 5) containing *o*-aminophenol (*o*-AP) (5 mM) at a scan rate of 50 mV s^{-1} . The enzyme electrodes were thoroughly washed after preparation and stored in a phosphate buffer 0.1 M (pH 8) at room temperature when not in use. The amperometric behavior of the HRP-ferrocene electrode coated with POAP was studied in batch conditions (stirred solution) to investigate the influence of several designs and operating parameters on its response characteristics. At a potential

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more negative than -100 mV, a rapid loss of activity was observed due to the irreversible reduction of the immobilized HRP. The calibration curves obtained for the determination of H_2O_2 within the range 2×10^{-6} to 1×10^{-5} allowed calculating the apparent Michaelis-Menten constant (K_m^{app}) of the immobilized enzyme and the maximum apparent velocity ($V_{\text{max}}^{\text{app}}$) according to the Lineweaver-Burk equation (plot of reciprocal values of the current *versus* concentration), which are $K_m^{\text{app}} = 3.9 \times 10^{-5}$ M and $V_{\text{max}}^{\text{app}} = 2740$ nA. In order to elucidate the nature of the biosensor response, several experiments were carried out in [16] using a sensor prepared as described and coupled to a rotating disc electrode. Levich plots were obtained for different H_2O_2 concentrations in a 0.1 M phosphate buffer solution at pH 8. When the angular rotation speed increases, the current eventually reaches a plateau, whose value depends on the concentration of the substrate. The steady-state current was found to be directly proportional to the square root of the angular rotation speed at low concentration of hydrogen peroxide (Levich equation for the limiting current) (Fig. 1). This is indicative of mass transport-controlled conditions. At higher concentrations of hydrogen peroxide a nonlinear behavior was observed, which indicates that the enzyme catalysis rate is slow with respect to convective diffusion and that the sensor works under catalysis controlled conditions (Fig. 2). The responses of the rotating disc electrode prepared in [16] were very rapid. At 3000 rpm, 95% of the steady-state current response could be reached in 2.3 s. The current produced by the electrode was linearly related to the hydrogen peroxide concentration within the range 1×10^{-8} M to 1×10^{-5} M, with a slope, intercept, detection limit (calculated as the concentration corresponding to three times the standard deviation of the estimate) and correlation coefficient of 5.79×10^{-7} nA M

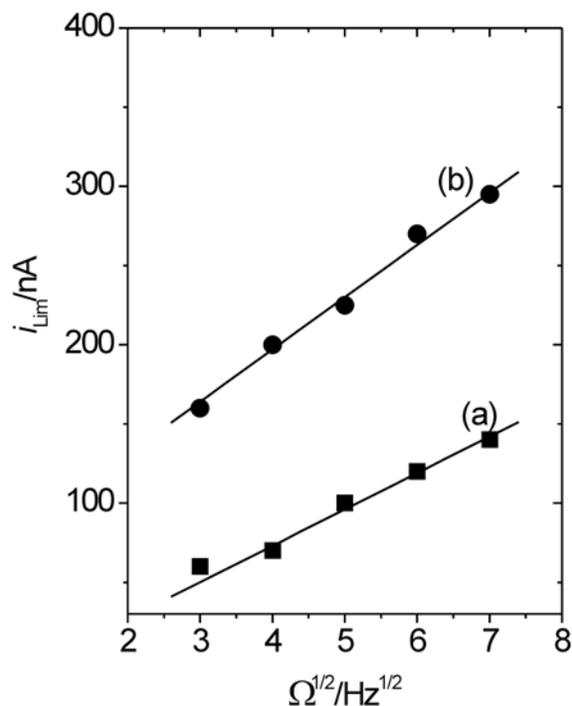


Fig. (1). Levich plots for very low concentrations of H_2O_2 : (a) 4×10^{-7} M, (b) 1×10^{-6} M. The electrolyte was 0.1 M phosphate buffer solution (pH 8).

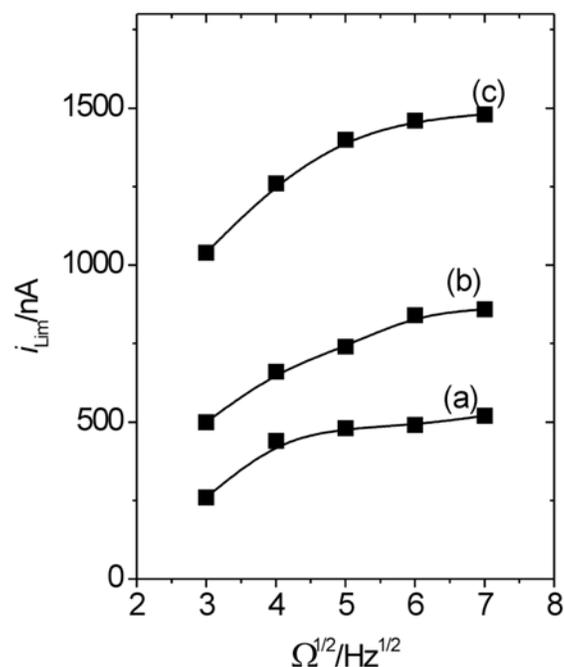


Fig. (2). Levich plots for low concentrations of H_2O_2 : (a) 2×10^{-6} M, (b) 4×10^{-6} M, (c) 8×10^{-6} M. The electrolyte was 0.1 M phosphate buffer solution (pH 8).

1 , -2.44 nA, 8.5×10^{-9} M and 0.9998 ($n=11$), respectively. Nonlinear responses were obtained at higher concentrations (Fig. 3). The stability of the HRP-ferrocene/POAP electrode stored at room temperature in acetate buffer (pH 5) was investigated in batch conditions. A 43% decrease in response was observed after 7 days. The linear dynamic range remains constant during this period of time. The sensor also served as the working electrode in an amperometric detector for flow injection system (FIA). However, in this case a 0.1 M phosphate buffer solution of pH 8 was chosen to improve sensitivity during measurements due to the optimum pH value of soluble HRP (pH 7-8). Rapid return to the base line and short response times were observed. The working electrode exhibited no memory effects. The sensor demonstrates a linear response in the concentration range 1×10^{-8} M to 2×10^{-6} M of H_2O_2 with a slope, intercept and correlation coefficient of 6.47×10^{-7} nA M $^{-1}$, 2.17 nA and 0.9995 ($n=10$), respectively. The detection limit of the method was found to be 7×10^{-9} M. A series of injections of 10^{-5} M of H_2O_2 yielded a standard deviation of 0.8% that remained constant after 300 injections.

An amperometric hydrogen peroxide sensor based on immobilization of hemoglobin (Hb) in POAP films at iron-cobalt hexacyanoferrate (FeCoHCF) films was reported in [17]. A series of FeCoHCF films were electrodeposited on gold electrodes from solutions containing 6 mM $\text{Fe}(\text{CN})_6^{3-}$ with different concentrations of Co(II) and Fe(III). The FeCoHCF film deposited from a solution with an iron molar ratio of 0.4 showed the largest response current to H_2O_2 . Therefore, the optimized FeCoHCF film was combined with a nonconducting POAP film that entraps Hb to construct the biosensor (Hb/POAP/FeCoHCF/Au electrode). The response current (29.8 nA) of the sensor was nearly 40 times that of the Hb/POAP/Au electrode (0.7 nA) and it was also 1.5 ti-

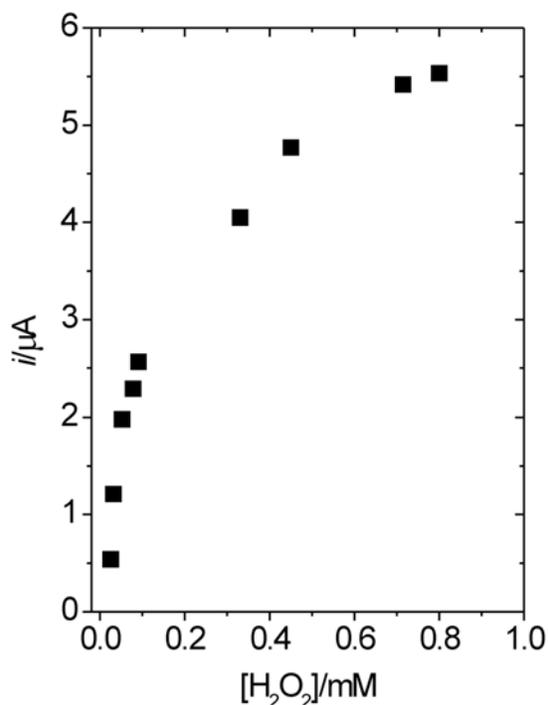


Fig. (3). Calibration plot for the amperometric determination of H₂O₂ in a static system using HRP-ferrocene-poly(*o*-aminophenol) electrode of optimum design. Applied potential 0.050 V vs. Ag/AgCl. Electrolyte 0.1 M acetate buffer (pH 5).

mes that of the POAP/FeCoHCF/Au electrode (20 nA). The Michaelis-Menten constant of Hb in the Hb/POAP/FeCoHCF/Au film was 9.31 mM. These results show that the immobilized Hb in the Hb/POAP/FeCoHCF/Au film exhibits higher catalytic activity and larger response current to H₂O₂ by the mediation of FeCoHCF. In addition, the effects of applied potential, solution pH and electroactive interferent on the response current of the sensor were investigated in detail in [17].

Several amperometric biosensors for glucose based on poly(*o*-aminophenol) (POAP) have been reported in the literature [18-22]. Most of the amperometric biosensors for glucose are based on the electrochemical oxidation of hydrogen peroxide, which is formed in the course of the enzyme-catalyzed oxidation of glucose by dissolved oxygen. In general, electrochemical detection of produced hydrogen peroxide in the presence of oxygen is usually accomplished by the oxidation of hydrogen peroxide at positive potentials (> 0.6 V versus Ag/AgCl). However, all biological fluids contain series of electrochemically active interferents, such as ascorbic acid, uric acid and acetaminophen, which are easily co-oxidized at similar potentials and produce an additional response current. It hinders the quantitative analysis of the produced hydrogen peroxide and the enzyme substrate. Experimental conditions related to the preparation and characteristic of an amperometric glucose biosensor based on the immobilization of glucose oxidase (Gox) in an electrochemically polymerized nonconducting POAP film at Prussian Blue (PB)-modified platinum (Pt) microelectrode are described in [18]. With regard to this microelectrode (Pt/PB/POAP/GOx), while PB acts as a typical electroactive film that exhibits catalytic properties for H₂O₂ oxidation, the

POAP film is a typical nonconducting film that acts as an effective barrier to protect the electrode from fouling. Then, the effect of the interferents decreased significantly due to selective permeability of POAP. Different influential factors on the response characteristic of the Pt/PB/POAP/GOx electrode are discussed in [18]. With regard to the effect of the polymerization cycle number on the polymer film thickness, in general, a thick film shows a long response time and low sensitivity, but results in a wider linear response range. The effect of the pH value of the detection solution on the response behavior of the PB/POAP/GOx electrode operated at 0.6 V was also investigated in [18]. A wide pH range (pH 4.5-8) for the Pt/PB/POAP/GOx electrode can be used, and the maximum of the response current can be observed at pH 7 (Fig. 4). This was attributed to the entrapment of GOx in a POAP film at a PB-modified electrode, making GOx more active at neutral media. Additionally, at pH 5.6 there is a higher response current. In this connection, a maximum of the response current at around pH 5.5 was also reported for the free enzyme. The response current of the enzyme electrode in 1/15 M phosphate buffer solution (pH 7) containing 1 mM glucose as a function of applied potential, which ranges from 0.4 to 0.9 V with 0.05 V increments, was also analyzed in [18] (Fig. 5). When the applied potential is below 0.55 V, the response current increases rapidly with the increase of the applied potential. This means that the response of the enzyme electrode in this potential range was controlled by the electrochemical oxidation of hydrogen peroxide. When the applied potential is over 0.55 V, the response current remains constant, which is explained by the rate-limiting process of the enzyme kinetics and substrate diffusion. A potential value of 0.6 V was chosen for the oxidation operation of the enzyme electrode in [18]. With regard to the effects of interferents, it was observed that the influence of

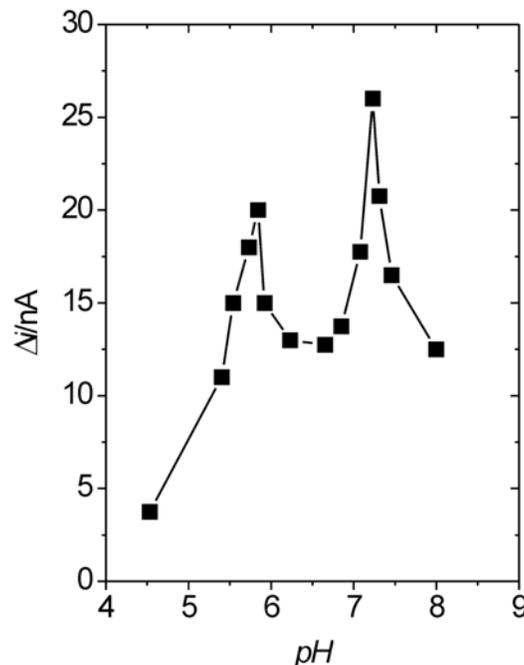


Fig. (4). Effect of pH on the steady-state response current on the Pt/Prussian blue/poly(*o*-aminophenol)/Glucose oxidase electrode at 0.6 V in 1/15 M phosphate buffer solution (pH 7) containing 2 mM glucose ($n = 3$).

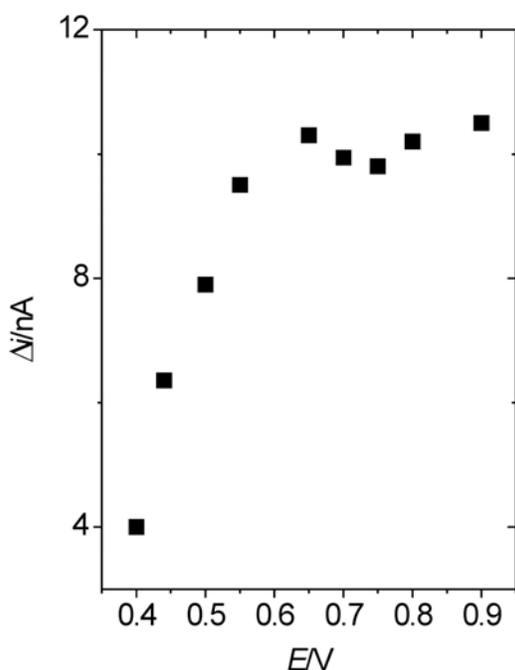


Fig. (5). Effect of the applied potential on the steady-state response current on the Pt/Prussian blue/poly(*o*-aminophenol)/Glucose oxidase electrode at 0.6 V in 1/15 M phosphate buffer solution (pH 7) containing 1 mM glucose ($n = 3$).

ascorbic acid, uric acid and acetaminophen on the glucose response was always small under the testing conditions. Then, it was concluded that those bi-layers of PB and POAP films are very useful to avoid the effects of interferents. A comparison of the Pt/PB/POAP/GOx and Pt/POAP/GOx electrodes for the amperometric determination of glucose was established in [18]. The calibration curve of the biosensor based on the Pt/POAP/GOx electrode for glucose is linear with glucose concentration up to 10 mM, and then a plateau is reached gradually at higher glucose concentrations. The biosensor has a detection limit of 0.02 mM. Additionally, the response of the biosensor to the injection of glucose is very fast (within 5 s). The Pt/PB/POAP/GOx biosensor has a lower detection limit (0.01 mM) and a larger response current. This was attributed to several reasons. Firstly, the surface coverage of enzyme on the Pt/PB/POAP/GOx electrode was higher than on the Pt/POAP/GOx electrode due to increased surface roughness of PB. Secondly, some PB molecules could be oxidized to Berlin green at 0.6 V, which electrocatalyzes the oxidation of hydrogen peroxide. On the other hand, the Pt/PB/POAP/GOx biosensor has a narrower linear range (up to 5 mM). This was attributed to the poor operational stability and high decrease in sensitivity of the PB film. The reproducibility and stability of the Pt/PB/POAP/GOx electrode are also analyzed in [18]. With regard to the reproducibility, it was estimated from the response to 1 mM glucose for five enzyme electrodes at 0.6 V. The results revealed that the sensor exhibits satisfactory reproducibility with a mean change of the response current of 12.6 nA and a relative standard deviation of 4.32%. The stability of the enzymatic biosensor under storage conditions (phosphate buffer of pH 7 at 4 °C) was analyzed in the same buffer solution containing 5.0 mM glucose (Fig. 6). Only 6% decrease of the original current response to glucose was ob-

served in the first continuous 7 days. With the experiment prolonged, a decrease of the response current to glucose was observed. However, 75% response current was still retained after 30 days. This is shown in Fig. (6), where $\Delta i_{ss}/\Delta i_{ss}^0$ is the change between the steady-state current and the background current of a fresh enzyme electrode.

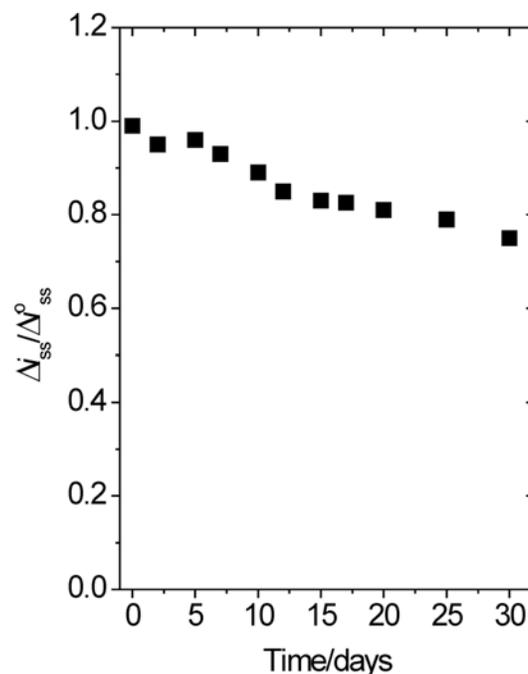


Fig. (6). Stability of the enzyme electrode stored in 1/15 M phosphate buffer solution (pH 7) at 4 °C. Determined by 5 mM glucose in 1/15 M phosphate buffer solution (pH 7).

An amperometric glucose biosensor based on boron-doped carbon nanotubes (BCNT) and POAP films was reported in [19]. Glucose oxidase (GOx) was employed as the model enzyme and immobilized on the BCNT-modified glassy carbon electrode (GC/BCNT) by electrochemical copolymerization of GOx and *o*-AP. Impedance responses of GC/BCNT, GC/BCNT/POAP and GC/BCNT/POAP-GOx electrodes were compared in equimolar 5.0 mM $\text{Fe}(\text{CN})_6^{3-}/\text{K}_4\text{Fe}(\text{CN})_6^{4-} + 0.1 \text{ M KCl}$ aqueous solutions. A semicircle with a small diameter along with a straight line could be seen at the GC/BCNT electrode. However, a semicircle with a much larger diameter could be observed at both GC/BCNT/POAP and GC/BCNT/POAP-GOx electrodes due to the formation of the POAP film. On the other hand, the diameter of the semicircle at the GC/BCNT/POAP-GOx electrode was much larger than that at the GC/BCNT/POAP electrode. This was attributed to the fact that the electron-transfer resistance at the electrode increases with the entrapment of GOx in the POAP film because GOx is the non-conductive macromolecule. These results indicated that the GOx was immobilized on the GC/BCNT electrode by electrochemical copolymerization of *o*-AP and GOx. The performance of the sensor was investigated by electrochemical methods. At an optimum potential of 0.60 V and pH 7, the biosensor exhibits good characteristics, such as high sensitivity (171.2 nA mM⁻¹), low detection limit (3.6 μM), short response time (6 s), satisfactory anti-interference ability and good stability. The apparent Michaelis-Menten constant,

K_m^{app} , was 15.19 mM. The applicability to the whole blood analysis of the enzyme electrode was also evaluated.

An amperometric glucose biosensor that is based on immobilization of glucose oxidase (GOx) in a composite film of POAP and carbon nanotubes (CNT), which are electrochemically copolymerized at a gold electrode, is described in [20]. The Au/POAP/CNT/GOx film was synthesized by placing the Au electrode in a 0.2 M deaerated acetate buffer solution (pH 5) containing 500 U/ml GOx, 5.0 mM *o*-AP monomer and 13 $\mu\text{g/ml}$ of a fresh CNT dispersion and by cycling the potential in the range 0.0–0.8 V (*versus* SCE) at a scan rate of 50 mV s⁻¹. All films used in the experiments were grown for 15 cycles and the resulting enzyme electrodes were thoroughly washed with double-distilled water and stored in phosphate buffer solution (pH 7) below 4°C for future use. In [20] it is indicated that cyclic voltammograms of the copolymerization of *o*-AP, GOx and CNT are similar to that of the polymerization of only *o*-AP. This implies that the the electropolymerization characteristics of *o*-AP monomer are not affected by the presence of GOx and CNT. The influential factors on the response characteristic of the Au/POAP/CNT/GOx electrode were discussed in [20]. With regard to the effect of the applied potential, authors of [20] set the potential of 0.75 V for the oxidation operation of the enzyme electrode. In connection to the effect of the interferences, it is indicated that the response current obtained at various Au/POAP/CNT/GOx electrodes to ascorbic acid decreases significantly as compared to that at the unmodified Au electrode. Again, this result shows that the POAP-modified electrodes can efficiently avoid the interference of ascorbic acid. A similar situation was observed for uric acid and for acetaminophen. Also, in [20] a comparison between the Au/POAP/CNT/GOx and Au/POAP/GOx electrodes for the amperometric determination of glucose was made. Compared with the Au/POAP/GOx biosensor, the Au/POAP/CNT/GOx biosensor has a lower detection limit (0.01mM) and a larger response current. This effect was attributed, firstly, to the fact that the surface coverage of enzyme on the Au/POAP/CNT/GOx electrode was higher than that on the Au/POAP/GOx electrode, due to increased roughness surface caused by CNT. Secondly, CNT has the property of increasing the electron transfer. However, unfortunately, the Au/POAP/CNT/GOx electrode has a narrower linear range (up to 5 mM) than the Au/POAP/GOx electrode. With regard to reproducibility and stability, the results revealed that the sensor has satisfactory reproducibility, with a mean change of the response current of 3.6 nA and a relative standard deviation of 8.4%. The stability of the enzymatic biosensor under storage conditions was analyzed in a phosphate buffer (pH 7) solution containing 2.0 mM glucose. The 75% response current is still retained after 30 days. Such good stability was attributed to the enzyme entrapped strongly in the POAP film that is stable in the neutral medium.

The fabrication and characterization of a glucose sensor based on a polypyrrole-platinum (PPy-Pt) composite-modified glassy carbon electrode (GCE), which was covered by a layer of poly(*o*-aminophenol)-glucose oxidase (POAP-GOx) film, are reported in [21]. For this sensor, firstly PPy was electrochemically deposited on a GCE at a constant potential of 0.80 V (SCE) for 120 s in an aqueous solution of 0.1 M LiClO₄ and 0.1 M carbonate containing 0.15 M pyrrole. Thus, PPy nanowire-modified electrodes (PPy/GCE)

were obtained. After synthesizing the PPy nanowires, Pt nanoclusters were also electrochemically deposited by CV on the PPy/GCE. The PPy-Pt nanocomposite-modified electrode (PPy-Pt/GCE) was then obtained. Pt nanoclusters were deposited from a 0.5 M H₂SO₄ solution containing 2 mM K₂PtCl₆ with a potential scanning from 0.40 to -0.25 V at 50 mV/s for 30 cycles. Then, the glucose sensor was fabricated by electrodeposition of *o*-AP on the PPy-Pt/GCE in a 0.1 M pH 5.6 acetate buffer containing 5 mM of *o*-AP and 2.0 mg/mL GOx by potential scanning between -0.2 and 0.8 V at 50 mV/s for 15 cycles. The prepared electrode was denoted as POAP-GOx/PPy-Pt/GCE. For comparison purposes, the same POAP-GOx deposition was carried out at Pt/GCE and PPy/GCE, and the obtained electrodes were denoted as POAP-GOx/Pt/GCE and POAP-GOx/PPy/GCE, respectively. The morphologies of the PPy nanowires and PPy-Pt nanocomposite were characterized by FE-SEM. With regard to PPy nanowires, a three-dimensional (3D) structure of the matrix with a large number of gaps and pores, which are beneficial to Pt deposition and enzyme incorporation, was observed. With respect to PPy-Pt nanocomposites, it was observed that deposited Pt nanoclusters are not on the surface of PPy but embedded in PPy. Also, XPS spectra obtained for PPy-Pt/GCE indicate the presence of Pt(0). Powder XRD determination was employed to characterize the crystal structure of Pt nanoparticles. Four peaks observed by this technique were assigned to (111), (200), (220), (311) structures of the face-centered cubic lattice of Pt (0), respectively. The mass of deposited POAP was calculated from the integrated charge (Q) passed during electropolymerization based on the Faraday's law. According to the equation $Q = nFAT$ considering a value of 2 for n and 109 for *o*-AP molecular weight. Assuming a value of about 1.30 g/cm³ for POAP density at 25 °C, the POAP thickness was calculated. It was shown that POAP film thickness was 8 nm on bare GCE, 10 nm on PPy/GCE, 20 nm on Pt/GCE and 25 nm on PPy-Pt/GCE for 15-cycle deposition. The amount of GOx entrapped on the film was assumed to be proportional to the formal thickness of the POAP film. The maximum current response at the POAP-GOx/PPy-Pt/GCE was obtained when the polymerization cycle number for POAP-GOx was 15. The effect of applied potential on the current response of the POAP-GOx/PPy-Pt/GCE was also examined in [21]. In order to obtain a large response current and short time response, an operational potential of 0.6 V was employed. As the pH is another variable that affects the current response of the enzyme electrodes, the pH dependence of the response of the POAP-GOx/PPy-Pt/GCE electrode was also investigated. The current increased from pH 4.5–7.0, while it decreased sharply above pH 7.0. The maximum current of the enzyme electrode was obtained at pH 7.0 due to the entrapment of GOx in the POAP film covered on the PPy-Pt nanocomposite, which made GOx more active in neutral solution. Then, neutral buffer solution (pH 7) was selected for glucose detection in [21]. The temperature is also an important factor for the activity of the enzyme. The response of the enzyme electrode was measured between 10 and 60 °C. The current response increased almost linearly with temperature from 10 to 40 °C, but decreased linearly from 40 to 60 °C. The latter was due to the deactivation of GOx. However, the former was attributed to the increase of the activity of the immobilized GOx. Then, 25 °C was selected as operational tempera-

ture in [21]. With regard to the determination of glucose, the response current increased with a higher concentration of glucose and then reached a steady-state value. That is, the response current was linear with glucose concentration up to 13 mM with a limit of detection of 4.5×10^{-7} M ($s/n=3$). For glucose concentrations higher than 13 mM, the response gradually reached a plateau. A fast response time of about 7 s was estimated. Such a fast response was attributed to the thin POAP film and the high dispersion of embedded Pt nanoclusters. A mechanism was proposed for the POAP-GOx/PPy-Pt/GCE electrode polarized at 0.6 V (SCE) in which the added glucose is transferred fast into the POAP film so as to be oxidized by the entrapped GOx in the presence of O_2 . The generated H_2O_2 can penetrate through the POAP film and be electrocatalytically oxidized at the PPy-Pt conducting nanocomposite. According to the Lineweaver-Burk form of the Michaelis-Menten equation, the relation between the reciprocal of the response current (i_s^{-1}) and the reciprocal of glucose concentration (C_g^{-1}) was obtained. The Michaelis-Menten constant (K_m) and the maximum current density (I_m) of the POAP-GOx/PPy-Pt/GCE electrode were calculated, and the values were 23.9 mM and $378 \mu A/cm^2$, respectively. These parameters were also calculated for the other electrodes (POAP-GOx/Pt/GCE and POAP-GOx/PPy/GCE). The K_m value was considered as a criterion for the effective enzyme loading and the electrocatalytic activity for H_2O_2 oxidation. An interference test was also made in [21] for the different electrodes. To this end the amperometric responses of POAP-GOx/PPy-Pt/GCE and POAP-GOx/Pt/GCE to the consecutive additions of glucose, uric acid, ascorbic acid and acetaminophen were analyzed. The current response of 5.5 mM glucose could be observed at POAP-GOx/PPy-Pt/GCE and POAP-GOx/Pt/GCE electrodes. However, the latter response is much smaller than the former. For successive additions of 0.5 mM uric acid, 0.2 mM ascorbic acid and 2.0 mM acetaminophen to the glucose solution, the POAP-GOx/PPy-Pt/GCE electrode had nearly no response current. The POAP-GOx/Pt/GCE electrode could also eliminate the influence of uric acid and ascorbic acid. However, 2.0 mM acetaminophen had significant response. The interference of these electroactive compounds with the glucose response was also examined by finally adding glucose to the mixed solution. The influence of uric acid, ascorbic acid and acetaminophen on the glucose response was small at the POAP-GOx/PPy-Pt/GCE electrode in comparison with the POAP-GOx/Pt/GCE electrode.

In [22] a highly sensitive and stable amperometric glucose biosensor based on POAP is described. It is based on the immobilization of glucose oxidase (Gox) in an electropolymerized *o*-aminophenol (*o*-AP) nonconducting polymer film on a platinized glassy carbon electrode (PGCE). The porous platinum particle matrix of PGCE provides not only a large microscopic surface area for higher enzyme loading but also a desirable microenvironment to transform the enzymatically produced H_2O_2 more efficiently to an electronic signal. The experiments also show that the GOx entrapped in a platinized platinum particle matrix is much more stable than that immobilized on a Pt disk electrode (PDE). After platinization of the GC electrode, the electropolymerization of *o*-AP and the immobilization of GOx were performed in an unstirred deaerated 0.05 M acetate buffer (pH 5.6) containing 0.05 M *o*-AP and 20 mg/mL Gox (500 units/mL) by

scanning between potentials of -0.2 V and 1.0 V (SCE) at a scan rate of 100 mV/s for 10 min. The charge passed for deposition of POAP/GOx was estimated from the anodic peak area to be 5.7-6.0 mC, and the GOx incorporated was about 0.7 units. The POAP film formed under these conditions was permselective and very useful in both preventing the electroactive species from reaching the electrode surface and keeping the biosensor from fouling. In this regard the POAP film can reject the access of ascorbic acid, uric acid, and $Fe(CN)_6^{4-}$ to the platinum surface, while it allows 60% of H_2O_2 to penetrate it. The various experimental parameters in GOx immobilization, including pH of the polymerization solution, the *o*-AP and GOx concentrations, polymerization potential, and deposition time, were explored for optimum analytical performance. The optimization was based on a comprehensive survey of the response of the sensor to glucose, its stability, and its efficient rejection of electroactive species. The response current of 0.05 M glucose on the PGCE/POAP/GOx electrode was about 20 times higher than that on the PDE/POAP/GOx electrode. The linear response of the enzyme electrode to glucose was from 1×10^{-6} to 1×10^{-3} M with a response time of less than 4 s. The detection limit was 5×10^{-7} M at a signal-to-noise ratio of 3. According to the Lineweaver-Burke form of the Michaelis-Menten equation, the apparent Michaelis-Menten constant ($K_m^{\#}$) for the entrapped enzyme was calculated to be 16.4 mM. The PGCE/POAP/GOx electrode exhibited very good long-term stability. The stability of this electrode was evaluated by repetitive (200 times) measurements of its response to 1 mM glucose within a period of 10 h. The sensitivity of the sensor lost only 14.3% after the 200 measurements. With intermittent usage and storage at 4 °C in phosphate buffer for 10 months, the biosensor maintained 50% of its original sensitivity and still displayed an excellent response to glucose. The interference from electroactive species, such as ascorbic acid and uric acid, which are generally encountered in the determination of a physiological sample, was significantly reduced by the use of the POAP film. However, the response of the sensor to ascorbate gradually increased when the sensor was stored for more than 3 months. The current response to 0.1 mM ascorbate on the sensor stored for 10 months is about 5-fold that on the freshly prepared sensor. This was attributed to falling off or dissolution of the film into the solution. The mechanism of GOx incorporation and stability of the biosensors were investigated in [22]. In this work several approaches were employed to fabricate GOx biosensors. These approaches included: (a) adsorption of GOx on PGCE by immersing a PGCE in pH 7 phosphate buffer containing 20 mg/mL of GOx for 10 min, (b) adsorption of GOx on a POAP film by immersing a POAP-coated PGCE in the GOx solution described above for 10 min, (c) application of a POAP coating to Gox-adsorbed PGCE, after step (a) and (d) electropolymerization of *o*-AP and immobilization of GOx simultaneously on PGCE. All sensors fabricated with the methods described above exhibited a response to glucose, but their sensitivity and stability differ considerably from sensor to sensor. The sensor prepared by approach (d) is the most sensitive and stable one. Its response current was about 5-fold higher than that of the sensors prepared with methods (a) and (b), and almost 10-fold higher than that of the sensor prepared with method (c). By comparing the stability of the sensors prepared by approach (d) with (b), authors

of [22] conclude that the quick loss of sensitivity of the GCE/POAP/Gox electrode resulted primarily from the desorption of the Gox adsorbed onto the POAP film surface and that the Gox entrapped within the POAP film is very stable under the storage conditions. From studies on sensitivity, authors of [22] indicate that the characteristics of the platinized surface have great promise for the development of highly sensitive miniature biosensors.

POAP films have also been successfully used in the development of uric acid [23] and lactate [24] biosensors. A uric acid selective biosensor constructed by immobilizing uricase and horseradish peroxidase (HRP) in carbon paste is described in [23]. The response of the electrode is based on the enzymatic reduction of hydrogen peroxide in the presence of uric acid. Uricase and HRP were dispersed in the carbon paste and the optimum paste mixture was determined. Then, POAP was deposited at the working surface area of the electrode acting as a conducting polymer layer. Cyclic Voltammetry was used to characterize the permselective characteristics of the polymer layer. At an applied potential of 50 mV (*versus* Ag/AgCl) a linear response was obtained up to 1×10^{-4} M, with a limit of detection of 3×10^{-6} M. The sensor had a response time of 37 s, a calibration precision of 2.2% ($n = 4$) and an estimated sample frequency of 20 h^{-1} . Responses to the analyte of interest were pH dependent. The sensor was incorporated into a flow injection system for the qualification of uric acid in human serum. Results compared favorably with standard spectrophotometric methods. A reagentless lactate amperometric biosensor, constructed by immobilizing pyruvic transaminase (GPT) and *L*-lactate dehydrogenase (LDH) together with its cofactor nicotinamide adenine dinucleotide (NAD^+) in carbon paste using a poly(*o*-phenylenediamine) (PPD) film is described in [24]. Interference by direct electrochemical oxidation of easily oxidizable substances, such as uric acid, *L*-ascorbic acid, *L*-cysteine, glutathione and paracetamol, was drastically reduced by covering the PPD-modified electrode with a second electrochemically synthesized nonconducting POAP film. The response of the electrode is based on the electrocatalytic oxidation, at low applied potentials, of the enzymatically produced NADH by the conducting PPD film. The bienzyme-double polymeric layer modified electrode, at an applied potential of 0.0 V (*versus* Ag/AgCl), gives a linear response for lactate in the range 6×10^{-7} M– 8.5×10^{-5} M and a response time of 80 s. This sensor was used for the quantification of lactic acid in cider. Results compared favorably with standard spectrophotometric methods.

In [25] voltammetric and amperometric detection of NAD(P)H (dihydronicotinamide adenine dinucleotides) at low applied potentials is shown to be feasible at POAP-modified electrodes without other immobilized electron-transfer mediators. POAP films were grown on paste carbon electrodes by potential-sweep electrolysis in aqueous solutions. The electrode potential was cycled between -0.5 and 0.7 V (*versus* Ag/AgCl) at 50 mV s^{-1} in an oxygen-free 0.1 M acetate buffer of pH 5.0 containing 5×10^{-4} M *o*-aminophenol under a nitrogen atmosphere. The POAP-modified electrodes thus prepared were used for cyclic voltammetry or amperometric measurements of NADH or NADPH in 0.1 M phosphate buffer of pH 7. The uncatalyzed oxidation of NADH at a bare carbon paste electrode in pH 7 phosphate buffer yields a single irreversible peak in cyclic

voltammetry at *ca* 0.5 V (*versus* Ag/AgCl) close to the potentials previously reported for the coenzyme oxidation at other carbon electrodes [26]. The electrocatalytic activity of the POAP-modified carbon paste electrode for the oxidation of NADH was demonstrated by the appearance of an anodic current starting at potentials below 0.0 V giving rise to a pre-wave with a half-wave potential of 200 mV. A second anodic process appears at a potential close to that corresponding to the uncatalyzed NADH oxidation at a bare carbon paste electrode. This last peak practically disappears at low concentrations of NADH. An analogous cyclic voltammetric behavior for NADH was also observed for NADPH. The effect of the potential scan on the pre-wave limiting current and the uncatalyzed oxidation peak current of NADH was also examined for POAP-modified carbon paste electrodes. The peak current was found to be linearly related to the square root of the potential scan rate within the tested range $2\text{--}20 \text{ mV s}^{-1}$, indicating that this process is diffusion-controlled. Nevertheless, the pre-wave limiting current remains constant at different potential scan rates. An entirely analogous behavior was found for NADPH oxidation. Thus, the POAP-modified carbon paste electrode lowers the oxidation overpotential of NADH and NADHP and also, voltammetric observations suggest that the electrocatalytic behavior results from a chemical interaction (reaction) between active sites of the polymer and the adsorbed molecules (NADH or NADHP). In [25] the catalytic amperometric response of POAP-modified electrodes to NADH was evaluated as a function of the composition and pH of the electropolymerization solution, the monomer concentration and the number of potential scan cycles applied to the electrode during polymer film formation (thickness of the polymer). It was found that the catalytic oxidation of NADH does not depend on the electrolyte used (NaCl , Na_2HPO_4 , Na_2SO_4 , 1-heptanesulphonic acid) in the film formation process nor on the film thickness. With regard to the solution pH, POAP-modified electrodes were prepared in background solutions of pH ranging from 1 to 9 at a monomer concentration of 5×10^{-4} M. POAP generated in this pH range always displays catalytic activity but the catalytic current is higher for the film prepared at pH 1 and 3. However, pH 5 acetate buffer was preferred because a significant loss of enzymatic activity occurs when more acidic solutions are used. With regard to potential, the optimum detection potential for NADH and NADPH was determined by measuring the steady-state current obtained in pH 7 phosphate buffer for a stepwise increment in NAD(P)H concentration of 1×10^{-5} at applied potentials increasing from -100 to 700 mV in 50 mV steps. Hydrodynamic voltammograms for the unmodified and POAP-modified carbon paste electrodes were compared. There was not appreciable oxidation of NADH or NADPH at the bare carbon paste electrode up to 0.3 V. For the POAP-modified carbon paste electrode a plateau was obtained for NADH oxidation at potentials between 150 and 300 mV, whereas the NADPH oxidation occurs at more positive potentials close to the uncatalyzed coenzyme oxidation. The potential selected for further investigation was 150 mV. The amperometric response of POAP-modified electrodes to increasing concentrations of NADH and NADPH was investigated using stationary working electrodes in magnetically stirred solutions. NADH was added in increments of 1.0×10^{-8} M to a final concentration of 1.0×10^{-7} M. Calibration plots were obtained in 0.1 M phosphate buffer at pH 7.0 and 0.1 M ace-

tate buffer at pH 5.0. With regard to the catalytic activity of POAP, a current value of about 0.16 nA for 1.0×10^{-7} M NADH at pH 7 was reported. The time required to obtain a steady-state response was less than 15 s. It was remarked that even when POAP-modified carbon paste electrodes are suitable for NADH detection in aqueous solutions, for NADPH detection a polymer such as poly(*o*-phenylenediamine) seems to be more adequate. Authors of [25] also report the application of the electrocatalytic detection of NADH to the development of ethanol and lactate amperometric sensors based on the corresponding dehydrogenase enzyme [alcohol dehydrogenase (ADH) or lactate dehydrogenase (LDH)] and NDA^+ immobilized together in the bulk of a carbon paste electrode covered by an electropolymerized POAP coating. Sensors thus prepared were used for amperometric measurements of ethanol or lactate at 0.15 V (*versus* Ag/AgCl) using a 0.1 M phosphate buffer as background at pH 8.5 for ethanol and pH 9.5 for lactate measurements.

Nonconducting polymers of phenol were also developed to be employed as biosensors. The electropolymerized films of phenol are produced by *ortho*- or *para*- coupling of phenolate radicals generated by oxidation of the phenylate anion. Subsequent reactions produce oligomers and, finally, poly(phenylene oxide) films are polymerized on the surface of the electrode [27, 28]. Bartlett *et al.* [29] reported that the electropolymerization of phenol at a platinum electrode surface gave a thin layer film with a thickness of 38 nm (25 mM phenol, sweep range of 0.00 – 0.95 V *versus* SCE). In this regard, a glucose biosensor was fabricated by repetitive potential cycling of a platinum electrode in an aqueous solution of phenol and glucose oxidase (Gox) [29]. This electropolymerized nonconducting film enables rapid diffusion of substrate and product, and also exhibits selectivity towards interfering species. Electropolymerization of other phenol derivatives is similar to that of phenol. In [27] five phenol derivatives (phenol, 3-aminophenol, 3-methylphenol, 3-nitrophenol and 1,3-dihydroxybenzene) were examined. 3-Aminophenol was found to be the most suitable monomer for creating amperometric glucose biosensors. Both hydroxyl and amino groups were involved in the electropolymerization and, consequently, larger amounts of GOx could be immobilized in this polymer film, which resulted in higher sensitivity to glucose. Also, this glucose biosensor minimized contributions from the easily oxidizable compounds such as uric and L-ascorbic acid. 3-Aminophenol was also electropolymerized on a carbon paste electrode to immobilize ferrocene and horseradish peroxidase for the development of an H_2O_2 biosensor [28]. In [30], also nonconducting polymers of phenol and several phenol derivatives (phenol, acetaminophen, 1,2-dihydroxybenzene, 1,3-dihydroxybenzene, 1,4-dihydroxybenzene, 1,3,5-trihydroxybenzene and 1,2,3-trihydroxybenzene) were synthesized onto Pt anodes. This study illustrates that polyphenol-modified electrodes produce responses that are selective and exceptionally fast, with performances similar to that of uncovered electrodes. The modified electrodes also provide an alternative to standard polymeric membranes, as well as an advantageous one-step process for enzyme immobilization. Polymerization of functionalized monomers enables a more specific chemical interaction between the film and the enzyme to be immobilized. This method was employed with monomers bearing specific groups, such as tyramine, which can enhance the interaction between polymers and electroactive species through the formation of

covalent bonds between either the amino and aldehyde or amino and carboxyl groups. The tyramine electropolymerization mechanism is associated with phenol-group oxidation and subsequent radical formation. Glucose oxidase is covalently attached to free amine groups on the polytyramine film using the coupling reagents 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride and N-hydroxysuccinimide [31]. This method of constructing enzyme biosensors produces reproducible and stable devices.

3. POAP AS A MOLECULAR IMPRINTING MATERIAL FOR SENSOR PREPARATION

Molecular imprinting is a means of synthesizing some polymers with selectivity to some particular molecules (template molecules) developed in recent years. Molecularly imprinted polymers usually have some cavities with a given size and shape and arraying functional groups, so they lend some memorial function to the specific steric structures of template molecules, thus endowing them with good recognition ability. Traditionally, molecularly imprinted polymers prepared by routine methods, such as, castings, *in-situ* polymerization, spin coating, etc., are generally of a thickness over a micron and are poorly homogeneous, influencing the sensitivity and the final design of sensors to a certain degree. In this regard, an electrochemical sensor for nicotine based on the electropolymerization molecular imprinting polymer with *o*-aminophenol as monomer and nicotine as template was analyzed in [32]. Compared with nicotine imprinting membranes, the electropolymerization film of POAP had the following advantages: it was homogeneous, the thickness was of the order of the nanometer and its preparation was simple. Thus, by employing cyclic voltammetry and weak acidity conditions, a sensitive layer was prepared by electropolymerization of *o*-AP on a gold electrode in the presence of the template (nicotine). The sensor exhibited good selectivity and sensitivity to nicotine. The determination limit was 2.0×10^{-7} molL⁻¹, and a linear relationship between current and concentration in the range 4.0×10^{-7} - 3.3×10^{-5} molL⁻¹ was reported. The sensor was also applied to the analysis of nicotine in tobacco samples with recovery rates from 99.0% to 102%. In [33] the preparation and properties of electro-synthesized POAP, as a molecular imprinting material, were studied by *in-situ* Quartz Crystal Impedance method. 2,4-Dichlorophenoxyacetic acid was employed as template molecule. During the polymerization, the changes of frequency (Δf_0), resistance (ΔR_0) and capacitance (ΔC_0) of the equivalent circuit were analyzed on the basis of the Butterworth-Van Dyke model. The thickness shear mode acoustic sensor modified with this material exhibited molecular recognition ability to the template molecule. However, the specificity was not as good as that of the molecularly imprinted polymer prepared by traditional imprinting technology. In the range 4.0×10^{-5} to 2.0×10^{-3} M, a linear relationship between the frequency shift ($-\Delta f_0$) and log C was found from the calibration curve. The determination limit was 1.0×10^{-5} M. Using this electropolymerization technology, the preparation of the sensor was very simple and the reproducibility of preparation was very good.

4. POAP AS ELECTROCHEMICAL GAS SENSOR

The development of a NO sensor based on hybrid films of POAP and the metal complex Ni sulfonated phthalocyanine

is reported in [34]. POAP films were produced by cycling the base electrode (Pt or GC) between -0.25 and 0.7 V (SCE) at 50 mV s^{-1} in a 0.05 M *o*-aminophenol solution in 0.5 M HClO_4 . To incorporate the metal complex, sulfonated nickel phthalocyanine was added to the solution at a 10 μM concentration. The polymerization in presence of the metal complex is faster than with *o*-aminophenol alone, probably due to electrocatalysis of the metal complex or a template effect of the sulfonic groups. After several cycles (> 50) a film of POAP-sulfonated nickel phthalocyanine (POAP/Ni-SuPh) was deposited on the electrode. The modified electrode, tested in a monomer-free solution (0.5 M HClO_4) shows only a peak system at ca. 0.0 V (SCE). The polymer itself did not show redox response in pH 7 solution. The incorporation of the metal complex into the polymer film was tested by *ex-situ* reflection-absorption FTIR spectroscopy. The hybrid film, produced with the metal complex, revealed new bands at 1063 and 1030 cm^{-1} , with respect to those corresponding to POAP. These bands were assigned to stretching of the sulfonate group. The presence of those bands confirms that the complex was incorporated into the polymer film. The bands are retained after cycling in a solution without the complex, even at pH 7. Electrodes modified with the polymer layers were tested for NO electrochemical oxidation. A peak at 0.95 V was observed on the cyclic voltammogram that corresponds to the NO oxidation, and it increases with NO concentration. It was observed that both POAP and POAP/NiSuPh films present higher electrocatalytic activity for NO oxidation than the base substrate (GC). The oxidation current, in the electrode modified with the complex, is higher and the oxidation overpotential is lower, indicating that the Ni complex incorporated into the hybrid film could electrocatalyze NO oxidation. Measuring the peak current was possible to determine the concentration of NO in the solution. The peak current is linear with concentration up to 200 μM (Fig. 7).

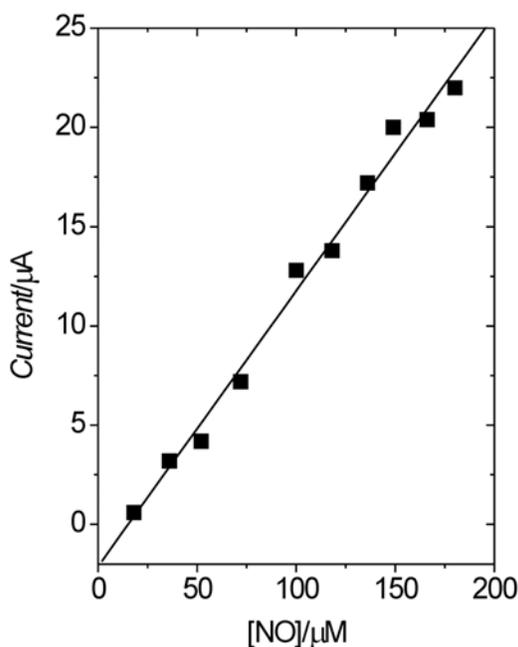


Fig. (7). Relationship between the peak current and NO concentration during oxidation of NO on a poly(*o*-aminophenol)/Ni sulfonated phthalocyanine modified electrode. Electrode area 0.071 cm^2 . Scan rate 0.010 V s^{-1} .

5. THE ELECTROCATALYTIC ACTIVITY OF POAP

The electro-oxidation of methanol in aqueous acid solutions using GC electrodes modified by a thin film of POAP containing dispersed platinum and platinum alloys microparticles was reported in [35]. POAP films were synthesized either by potentiodynamic or potentiostatic methods. In the potentiodynamic procedure the electrode potential was swept between -0.10 and 1.00 V (*versus* SCE) at a scan rate of 20 mV s^{-1} . In the potentiostatic method the electrode potential was fixed at 1.00 V (*versus* SCE) for a given time. In both cases, an aqueous solution containing 0.10 HClO_4 and 0.10 M of *o*-aminophenol was used as electrolyte. The thickness of the deposited films was calculated in each case from the consumed charge during electrodeposition of the POAP films. For a given Q value, the mass of deposited POAP was estimated using the Faraday's law, considering a value of 2 for n and 109 for *o*-aminophenol molecular weight. Assuming a value of about 1.30 g cm^{-3} for POAP density at 20 $^\circ\text{C}$ (*o*-aminophenol density at 20 $^\circ\text{C}$ is 1.283 g cm^{-3} [36]) and the geometrical area of the GC electrode 0.0707 cm^2 , a mean value of 0.52 ± 0.02 μm was obtained for the polymer film thickness. Pt, Pt-Ru and Pt-Sn particles were incorporated into the polymer film by electrochemical deposition from an aqueous sulfuric acid solution containing 2×10^{-4} M H_2PtCl_6 (for the GC/POAP/Pt electrode), 2×10^{-4} M $\text{H}_2\text{PtCl}_6 + 1.5 \times 10^{-4}$ M $\text{K}_2\text{RuCl}_5 \cdot 2\text{H}_2\text{O}$ (for the GC/POAP/Pt-Ru electrode) and 2×10^{-4} M $\text{H}_2\text{PtCl}_6 + 6 \times 10^{-4}$ M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (for the GC/POAP/Pt-Sn electrode) at a constant potential of -0.20 V (*versus* SCE). Thus, the oxidation of methanol was investigated at the GC electrodes covered by a thin film of POAP incorporating Pt or Pt alloy microparticles. After comparing the voltammetric responses of potentiodynamically and potentiostatically synthesized POAP films, the former were preferred to investigate methanol oxidation in [35]. In all experiments the working electrode was submerged in open-circuit position into methanol solution. All voltammograms were recorded by sweeping the potential from 0.0 V to 1.00 V (*versus* SCE) and vice versa without any stay in starting potential. Voltammetric responses of the different electrodes were compared in [35]. Although the Pt loading for both electrodes (GC/Pt and GC/POAP/Pt) was alike, it was observed that the peak current for the oxidation of methanol (0.63 V *versus* SCE) increased from 0.48 mA (GC/Pt electrode) to 1.73 mA (GC/POAP/Pt), confirming the crucial effect of POAP film on the enhancement of Pt microparticle efficiency towards the catalytic oxidation of methanol. Similar results were also obtained when Pt was replaced by Pt-Sn or Pt-Ru alloys, whereas the peak currents increased with respect to that of Pt alone, and this increase was evident in the case of Pt-Sn loading. In this regard, the results show that the presence of the polymer film considerably enhances the catalytic current of methanol oxidation, especially in the case of Pt-Sn microparticles. This was attributed, on the one hand, to the large surface area of the electrode due to the incorporation of Pt and Pt alloy particles into the polymer layer and, on the other hand, to the fact that the catalyst micro and nanoparticles in polymer media are probably less sensitive to poisoning by adsorbed CO species. Chronoamperometric experiments also seem to indicate the existence of an increase in the real surface area of a GC/POAP/Pt electrode with respect to that of a GC/Pt electrode. This surface increase leads to an increase in the overall oxidation currents

in comparison with the same amount of Pt or Pt alloy deposits on the surface of bare electrodes. Thus, the role of the polymeric matrix seems not to be directly connected with an increase of the intrinsic specific activity of electrocatalysts. That is, the film only acts as a good and proper bed for deposition of electrocatalyst particles and increases the electrocatalytic active sites, which in turn causes an increase of the anodic current for methanol oxidation. Different parameters, such as polymer thickness, real surface of the electrode, methanol concentration and temperature, which can affect the electro-oxidation of methanol, were analyzed in [35]. With regard to the POAP thickness, it was observed that for thickness greater than about 0.6 μm , the peak current is independent of the POAP thickness, whereas for lower values the percent of anodic current decrease increases in proportion to the POAP film thickness (Fig. 8). This increase indicates the predominant effect of the electrode matrix nature over that of the polymeric film on the catalysis of methanol oxidation. In other words, the effect of the deposited film on the enhancement of the catalytic current appears when the electrode surface is thoroughly covered by a POAP layer and methanol cannot reach the electrode matrix. In this connection, 200 cycles of potential scan yielding a 0.52 μm thickness for the POAP film were considered as an optimum value. Concerning the effect of the real surface of the electrode, an augmentation of the real surface seems to be the reason why in the presence of POAP the reactivity of the deposited electrocatalyst increases. A chronoamperometric experiment was used in [35] to obtain an estimate of GC/Pt and GC/POAP/Pt electrode area. To this end, chronoamperograms for these two electrodes were recorded in solutions containing 0.10 M methanol and 0.10 M HClO_4 , and by setting the electrode

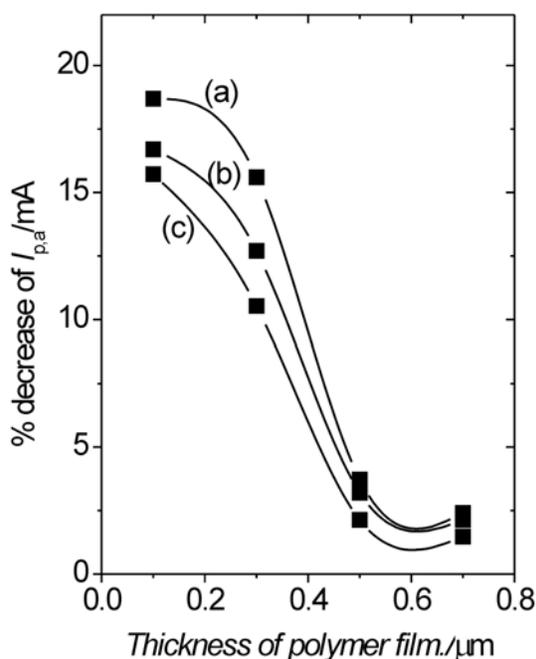


Fig. (8). Plot of the anodic peak current decrease as a function of the polymer film thickness for: (a) glassy carbon/poly(*o*-aminophenol)/Pt electrode; (b) glassy carbon/poly(*o*-aminophenol)/Pt-Ru electrode; (c) glassy carbon/poly(*o*-aminophenol)/Pt-Sn electrode. Solution: 0.10 M HClO_4 + 0.10 M CH_3OH . Pt and Pt alloy loading 0.1 mg cm^{-2} .

potentials at 1.0 V (*versus* SCE). Under these conditions, the measured current was limited by the diffusion of methanol from the bulk solution to the electrode surface and was considered in the light of the Cottrell equation

$$I = nFA D^{0.5} C^* / \pi^{0.5} t^{0.5} \quad (1)$$

where A is the real surface area of the electrode, D is the diffusion coefficient, and C^* the bulk concentration of methanol. Under diffusion control, a plot I *versus* $t^{0.5}$ gives a straight line with a slope equal to $(nFAD^{0.5}C^*/\pi^{0.5})$. The values of this slope were considered as an estimation of A , since the other terms are the same in both experiments. From the slope values it was concluded that the real surface area of Pt microparticles at the GC/POAP/Pt electrode was 2.85 times larger than that of the GC/Pt electrode. This clearly explained the effect of POAP film on the enhancement of electrocatalytic currents. With regard to the electrode stability, the results indicated that by neglecting the weak decrease in peak current during the first 3 weeks, the responses were reproducible up to 60 days, which was indicative of the nearly long-term stability of POAP-modified electrodes.

The simultaneous presence of hydroxyl and amino groups on the POAP backbone should allow the polymer to coordinate with most transition metal cations. In this connection, it was reported that some metal cations increase the catalytic activity of POAP through their incorporation into the POAP matrix. As an attempt to understand the interaction between POAP and metal cations, the formation and characterization of the Ag(I)-POAP system were examined in [36]. The interest in this specific complex arises from observations of its electrocatalytic activity in the dissolved oxygen reduction. In this connection, in [37] POAP was deposited on glassy carbon and Pt. The polymer was synthesized from 0.05 M *o*-aminophenol in a mixture of 1 M H_2SO_4 and 0.5 M Na_2SO_4 by CV. The potential was scanned from -0.2 V to 0.8 V (*versus* SCE) at 100 mVs^{-1} for different numbers of cycles (N). It was observed that complexation between Ag(I) and POAP was a more likely event in thin films, particularly those that were deposited from a single voltammetric cycle ($N = 1$). In order to obtain the complex, thin POAP films were equilibrated in 0.1 M AgNO_3 for 30 min. In the same sense, a stable POAP-Cu(I) electrocatalyst active for the reduction of oxygen was also reported [37].

The electrocatalysis of POAP-coated glassy carbon electrodes for O_2 reduction in acidic aqueous media (pH 1.0) was analyzed in [38]. POAP-coated GC electrodes were prepared by potential-sweep electrolysis at 50 mV s^{-1} in the potential range -0.4 V to 1.0 V (SCE) in 0.2 mol dm^{-3} NaSO_4 aqueous solution (pH 1) containing 50 mmol dm^{-3} *o*-aminophenol under a nitrogen atmosphere. The polymer thus prepared shows a reversible redox response at *ca.* 0.05 V. In O_2 -saturated solution two well-defined reduction peaks were observed at about 0.0 V and -0.65 V. The first reduction peak is only slightly larger compared with that obtained under a nitrogen atmosphere, and the second reduction peak is fairly similar in peak potential to that obtained at a bare GC electrode. Then, it was concluded that POAP exhibits a poor catalytic activity for O_2 reduction. A reaction mechanism of POAP and O_2 was proposed in [38]. On the basis of the mechanism proposed in [38], the poor catalytic activity of POAP for the oxygen reduction was attributed to different reasons. No catalytic formation of H_2O_2 *via* the POAP film

was detected by Rotating Ring-Disk Electrode Voltammetry. The reversible redox response of POAP remained substantially unchanged before and after the POAP film had been held in its reduced state for some time (*e.g.* 30 min) under O₂ atmosphere, suggesting that some of the intermediates proposed in the mechanism given in [38] were scarcely formed.

In [39] authors describe the electrocatalytic behavior of grafted *o*-aminophenol (*o*-aminophenol) towards the oxidation of hydrazine. The kinetics of the mediated electro-oxidation of hydrazine at *o*-AP of the modified GC electrode was investigated using cyclic voltammetry, chronoamperometry, chronocoulometry and rotating disk electrode voltammetry. The application of the modified electrode as electrocatalytic sensor in the amperometric detection of hydrazine is also illustrated in [39].

The electrocatalytic oxidation of glucose and some other carbohydrates on nickel/POAP-modified carbon paste electrodes, such as enzyme-free electrodes in alkaline solution, was investigated in [40]. POAP was prepared by electropolymerization employing a carbon paste electrode bulk-modified with *o*-aminophenol. Cyclic voltammetry in a HCO₄ solution was employed to obtain the polymer films. The Ni(II) ions were incorporated to the electrodes by immersion of the polymer-modified electrodes in 1 M Ni(II) ion solution. Cyclic voltammetry and chronoamperometric experiments were used for the electrochemical study of this modified electrode. A good redox behavior of the Ni(OH)₂/NiOOH couple at the surface of the electrode was observed. The capability of this modified electrode for the catalytic oxidation of glucose and other carbohydrates was proved. The surface coverage of the redox species and catalytic chemical reaction rate constants for each carbohydrate were calculated. Also, the electrocatalytic oxidation peak currents of all tested carbohydrates exhibited a good linear dependence on concentration, and their quantification was done.

6. POAP AS A FERRIC CATION SENSOR IN SOLUTION

In [41] POAP obtained on ITO electrodes by electropolymerization of *o*-aminophenol (0.1 M) in a 0.1 M H₂SO₄ aqueous solution exhibits IR spectra that are indicative of a 1,4-substituted structure. These POAP films were soaked for 24 h in a 0.1 M H₂SO₄ aqueous solution containing 50 mM Fe₂(SO₄)₃, and XPS spectra of the films were again obtained. XPS spectra confirmed the iron ion capture by POAP films. After this cation capture process, the electrode potential of the POAP film was measured in various aqueous solutions containing Zn(II), Ni(II), Cu(II), Fe(II) and Fe(III) ions at different concentrations. The relationship between the electrode potential, *E*, and the logarithm of the concentration, *C*, in the different cations in solutions was obtained (Fig. 9). The electrode showed no potential response to ion concentration for Zn(II), Ni(II), Cu(II) and Fe(II) ions. However, it showed a Nernstian potential response to Fe(III) ions with a slope -57 mV/log [Fe(III)]. The response time was less 10 s, and the response was observed until [Fe(III)] = 10⁻⁴ M. The response to Fe(III) ions in solution was considered indicative of the presence of Fe(II) into the POAP film. The response was attributed to the electron transfer between Fe(II) ions into the film and Fe(III) ions in solution. Then, the following Nernst equation was considered:

$$E = E^{\circ} + 0.059 \log \{ [\text{Fe(III)}]_{\text{solution}} / [\text{Fe(II)}]_{\text{film}} \} \quad (2)$$

where [Fe(II)]_{film} denotes the concentration of Fe(II) ions in the POAP film. It is evident that POAP functions as a potentiometric Fe(III) sensor. However, the concentration sensitivity needs to be enhanced.

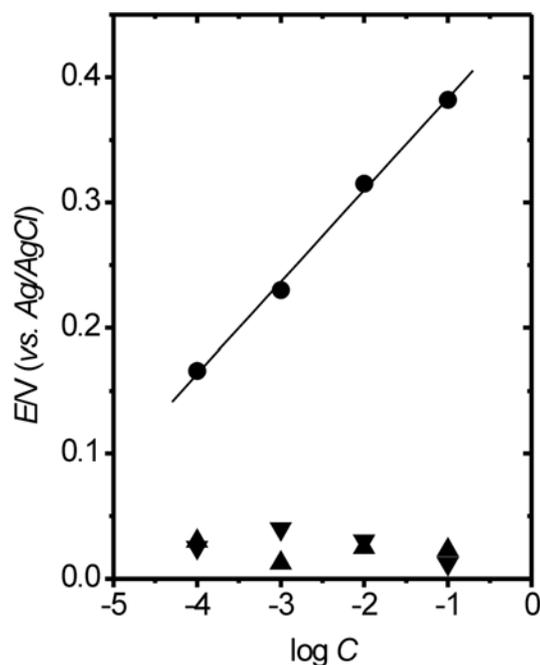


Fig. (9). Relationship between the electrode potential, *E*, and the logarithm of the concentration, log *C*. (●) Fe (III); (▲) Ni(II), (▼) Zn(II).

7. THE COPOLYMER OF *o*-AMINOPHENOL AND ANILINE AND ITS APPLICATIONS

The electrochemical copolymerization of aniline with *o*-aminophenol is described in detail in [42]. Also, in this paper the electrochemical characteristics of the copolymer are analyzed. A solution containing 0.01 M *o*-AP, 0.2 M aniline and 0.6 M H₂SO₄ was used to prepare the copolymer. The cyclic voltammogram of the copolymer is very similar to that of PANI. In this sense, the copolymer in acidic solutions has a good electrochemical characteristic [43]. In order to gain further insights into the electrochemical activity of poly(aniline-co-*o*-aminophenol), the cyclic voltammograms of PANI and the copolymer were compared in 0.3 M Na₂SO₄ solution with pH values in the range from 4.0 to 9.6. Based on changes in the oxidation and reduction currents on the solution pH, it was observed that the electrochemical activity of PANI decreases quickly as the pH value increases in the range from 5.0 to 7.1. This result indicates that PANI is degraded. However, anodic peak current and cathodic peak current for the copolymer decrease slowly with the increase of the pH value within the range from 5.0 to 9.6. In this regard, only a 29% decay of the electrochemical activity of the copolymer film was observed when the copolymer film electrode was transferred from pH 5 to 9.6 of the solution. This indicates that the copolymer film at pH 9.6 has a quite high electrochemical activity. In this connection, the quantity of electricity of the copolymer is 4.2 times larger than that of PANI at pH 5.0. This means that the pH dependence of the

electrochemical activity of the copolymer is much better than that of PANI. Besides, the cyclic voltammogram showed that the copolymer has a good reversibility. The structure of the copolymer based on the FT-IR and XPS spectra is shown in [42]. In [42] it is concluded that even when the conductivity of the copolymer is lower than that of PANI, its properties are favorable to its application in rechargeable batteries and electrocatalysis.

In [44] poly(aniline-co-*o*-aminophenol) was employed as sensor of catechol. In this regard, the copolymer was used as an electron-transfer mediator in the electrochemical oxidation of catechol and also, the effect of various factors (potential, pH, concentration of catechol, temperature and phenolic compounds) on the response current of the sensor was studied. The electrochemical copolymerization was performed on a platinum electrode in a solution containing 0.2 M aniline, 0.01 M *o*-aminophenol and 0.6 M H₂SO₄ using repeated potential cycling between 0.0 and 1.0 V (SCE). A solution of 0.3 M Na₂SO₄ containing different concentrations of catechol was used for the determination of the relationship between the concentration and the response current of the sensor. It was observed that the copolymer in a 0.3 M Na₂SO₄ solution with pH 5 exhibits a good electroactivity in the potential range from 0.0 to 0.6 V. When cyclic voltammograms of the copolymer in the presence of different compounds, such as phenol, catechol, resorcinol and hydroquinone, were compared in the 0.3 M Na₂SO₄ solution with pH 5, it was observed that while phenol could not be oxidized and reduced at the copolymer electrode within the potential range from 0.0 to 0.6 V, an anodic peak at 0.46 V and a cathodic one at 0.33 V appeared for catechol. Also, as compared with a platinum electrode, the copolymer can effectively catalyze the reduction-oxidation of catechol at pH 5. While the oxidation of resorcinol was more difficult than that of catechol at the copolymer, the redox reaction of hydroquinone was easier than that of catechol. Thus, in [44] it was concluded that the copolymer can effectively catalyze the oxidation of catechol, which provides a way of using the copolymer as a sensor to detect this substance. The response current of the sensor in a catechol solution (0.12 M catechol and 0.3 M Na₂SO₄ solution with pH 5) was studied as a function of the applied potential. The operation potential of the sensor was set at 0.55 V. In [44] it was demonstrated that the electrocatalytic oxidation of catechol at a PANI electrode is different from that at the poly(aniline-co-*o*-aminophenol) electrode, which was attributed to the faster electron transfer at the copolymer electrode. That is, the effect seems to be caused by the -OH group of the copolymer chain, which increased the electron-transfer rate between the electrode and catechol in the solution. A mechanism for the catalytic oxidation of catechol at the copolymer is proposed in [44]. The effect of pH on the response current of the sensor was also analyzed. A solution containing 0.04 mM of catechol in 0.3 M Na₂SO₄ was used in the experiments. It was observed that the response current of the sensor increased with pH in the range from 3.0 to 6.0. With regard to the catechol concentration, it was shown that the response current of the sensor changed with the catechol concentration within the range from 5 to 120 μM. A straight line through the origin was obtained between 5 and 80 μM with a correlation coefficient of 0.997. Thus, it was concluded that the sensor can be used to determine the concentration of catechol within this concentration

range. The dependence of the response current of the sensor on the temperature was also analyzed in [44]. The response current increased as the temperature increased. A linear dependence between $\log I$ and T^{-1} was observed. An apparent activation energy (26.6 kJ mol⁻¹) was extracted from the slope of the straight line. This activation energy is low, which is further evidence for the electrocatalytic oxidation of catechol taking place at the copolymer electrode. As was above-indicated, phenol, resorcinol and hydroquinone were employed to study the interference in the determination of catechol. It was demonstrated that while the contribution of phenol and resorcinol to the response current of the sensor can be neglected, the hydroquinone seriously interferes with the determination of catechol. This is due to the fact that the oxidation potential of hydroquinone is lower than that of catechol. Poly(aniline-co-*o*-aminophenol) was also employed as hydrogen peroxide sensor [45].

In [46] the immobilization of uricase with poly(aniline-co-*o*-aminophenol) using the template method is reported. Effects of potential, pH, temperature and substrate concentration on the response current of the copolymer-uricase sensor were studied. Fourier transform-infrared spectra (FTIR), ultraviolet spectra (UV-vis) and scanning electron microscopy (SEM) were used to characterize the biosensor. With regard to the copolymer preparation, firstly, a copolymer uricase electrode was prepared with a one-step process using cyclic voltammetry in a solution containing 0.2 mol dm⁻³ aniline, 0.01 mol dm⁻³ *o*-AP, 0.6 mol dm⁻³ H₂SO₄ and 0.75 mg cm⁻³ uricase. Secondly, the electrode was refluxed in 6 mol dm⁻³ HCl for 24 h to remove uricase from the copolymer, and cavities for immobilizing uricase were left. After that, the potential of the copolymer film was swept to -0.20 V (SCE) in B-R buffer solution, where the copolymer was reduced continuously for 20 min, in order to remove anions from the copolymer film as completely as possible. Then, the reduced copolymer film was removed into B-R buffer containing 0.75 mg cm⁻³ active uricase (pH 8). The potential of the copolymer film was then swept to 0.60 V, where it was continuously oxidized for 30 min. The purpose was to immobilize active uricase into the cavities left before. By comparing cyclic voltammograms of the copolymer film and the copolymer-uricase film in the B-R buffer solution (pH 8) at 60 mV s⁻¹, it was observed that the current of the copolymer-uricase film is less than that of the copolymer film. This was attributed to the fact that the electrode process was controlled by diffusion, and diffusion may have been affected when uricase was entrapped into the copolymer film. This indicates that uricase was doped into the copolymer film using the template method. With regard to the potential effect, the potential was stepped from 0.15 to 0.65 V in 0.05 increments in a B-R buffer solution containing 0.5 mmol dm⁻³ uric acid (pH 8). The response current increased as the potential was increased. However, as the response current was small at low potentials, the biosensor potential was set at 0.4 V. With regard to the pH dependence of the response current, it increased when the pH was increased within the range from 3.0 to 6.0. Even when the conductivity of the copolymer decreased, the activity of the enzyme increased at higher pH, and the latter is dominant, so the response current increased with pH in this range. On the contrary, within the range from 6.5 to 8.5, the decrease of the copolymer conductivity was dominant and it affected the response current more

remarkably than the increase of enzyme activity, so the response current decreased with increasing pH in this range. Then, the response current increased with increasing pH within the range 8.5 to 11.0. This was attributed to the ionization of uric acid, which increases as pH increases in aqueous solutions, and also to the basic formation of uricase that has better catalytic activity than free uricase. These two conditions are favorable for promoting the uricase catalytic reaction. Since the copolymer was not steady above pH 9, the biosensor was set at pH 8.0. With regard to the temperature effect, within the temperature range from 273.15 to 318.15 K, the response current of the biosensor increased as the temperature increased. The temperature of the sensor was set at 45° C, which shows that the copolymer protects uricase and the immobilization material improves the heat stability of uricase. An activation energy was calculated in the B-R buffer solution containing 0.5 mmol dm⁻³ uric acid. A value of 14.28 kJ mol⁻¹ was obtained. With regard to the stability of the sensor, it was observed that the response current of the copolymer-uricase biosensor prepared with the template process only decreased 19% in 50 days, but compared with the PANI-uricase biosensor, the latter decreased 43% in 40 h, which implies that the former has a better stability and also shows that uricase is entrapped into the copolymer structure but not adsorbed on the surface of the copolymer film. The copolymer-uricase biosensor prepared with the template process still maintained good electrochemical activity after 50 days.

The electrochemical synthesis of the copolymer of aniline and *o*-aminophenol and its use in the electrocatalytic oxidation of ascorbic acid is discussed in [47]. Even when the electrochemical copolymerization of aniline and *o*-aminophenol was treated by Mu [42] and Shah and Holtze [48], in [47] it is shown that the copolymer obtained at the ratio 10:1 (An: *o*-AP) not only shows good electrochemical activity in neutral solutions, but also exhibits excellent catalytic function towards the electro-oxidation of ascorbic acid (AA). The chronoamperometric technique was also used to evaluate the diffusion coefficient of AA and the rate constant for the electro-oxidation reaction of AA at the copolymer. The electrochemical copolymerization of An and *o*-AP was performed in [47] by cyclic scanning for 60 cycles within the potential range from -0.2 to 1.1 V (*versus* SCE) at 50 mV s⁻¹ in a solution containing 0.5 mol L⁻¹ sulfuric acid, 0.1 mol L⁻¹ An and various concentrations of *o*-AP. A GC electrode was employed as substrate. With regard to applications of this copolymer in bioelectrochemistry, the electrochemical activity of PANI-OAP/GCE obtained at different concentration ratios (An: *o*-AP) in neutral solution (pH 6.8) was investigated in [47]. When the ratios were 1:1 and 2:1, the copolymer almost had no electrochemical activity because their voltammograms had no anodic and cathodic peaks at pH 6.8. However, broad anodic and cathodic peaks were observed at 0.43/0.05 V and 0.22/-0.1 V for 10:1 and 5:1 ratios, respectively. Even more, the electrochemical activity for the ratio 10:1 was better than that for the ratio 5:1. In this sense, the electrochemical activity of the copolymer is better than that of PANI, because PANI has no redox behavior at pH 6.8. The electrochemical activity of the copolymer at pH > 4 was attributed to the substituted -OH groups in the copolymer chain. On the other hand, the ring-substituted copolymer by the introduction of -OH groups into the PANI backbone is

very stable, so its electrochemical activity is not easily lost. Thus, due to the good electroactivity of the copolymer (ratio An: *o*-AP 10:1) in a wide pH range, the film was used for the electrocatalytic oxidation of AA in neutral media. Cyclic voltammograms of GCE and PAN-OAP/GCE electrodes in 5 x 10⁻⁴ mol L⁻¹ AA solutions were compared in [47]. It was observed that the oxidation peak of AA is broad and irreproducible at about 0.53 V on GCE, and the oxidation current was about 6 µA. In contrast, the oxidation current (16.5 µA) increased greatly and the peak potential shifted negatively to 0.21 V at PAN-OAP/GCE. The increased peak current and the negatively shifted anodic potential for the electro-oxidation of AA indicate the strong electrocatalytic function of the copolymer for AA. The shift in the overpotential was attributed to a kinetic effect, thus a substantial increase in the rate of electron transfer from AA was evident, indicating the improvement in the reversibility of the electron-transfer process. Also, an increase in the anodic peak current with increasing AA concentration was observed on the copolymer. The anodic peak current was linearly dependent on the AA concentration in the range from 5 x 10⁻⁴ to 1.65 x 10⁻² mol L⁻¹, with a correlation coefficient of 0.9998. Further investigation was made into the transport characteristics of AA in the modified electrodes. To this end, cyclic voltammograms of PAN-AOP/GCE at different scan rates in a 5 x 10⁻⁴ mol L⁻¹ AA solution were analyzed. It was observed that the catalytic oxidation peak potential shifts to more positive potential with increasing scan rate, indicating a kinetic limitation in the reaction between the redox sites of the copolymer and AA. However, the cyclic voltammetric peak currents for AA at the copolymer were proportional to the square root of the scan rate in the range from 20 to 180 mV s⁻¹. This indicates that the electrode reaction is controlled by a diffusion process. The effect of pH on the peak current and oxidation potential was investigated on a 2.5 x 10⁻³ mol L⁻¹ AA solution using cyclic voltammetry. The peak potentials shift towards negative potential with a slope of about -57 mV pH⁻¹ within the pH range from 2.0 to 4.0, indicating a 1e⁻/1H⁺ transfer process at this pH range. At higher pH values (4.0-8.0) the slope decreases to about -31 mV pH⁻¹ suggesting a 2e⁻/1H⁺ transfer process at this pH range. Consequently, the overall electrode reaction was classified as an electrochemical reaction followed by a chemical reaction process. The peak current of AA in acid solution is higher than in basic solution, and decreases as the pH increases within the range from 4.0 to 8.0. This was attributed to the instability of AA in basic solutions. From chronoamperometric measurements, a mean value for the diffusion coefficient of AA was determined ($D = 4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). Also, the catalytic rate constant for the reaction between AA and the redox sites of the surface-confined copolymer film was evaluated. The mean value of k in an AA concentration range from 5 x 10⁻⁴ to 1.05 x 10⁻² mol L⁻¹ was 8.3 x 10⁵ cm³ mol⁻¹ s⁻¹. With regard to stability and reproducibility, during the first week the current response had no apparent decrease and in the next 3 weeks it decreased about 15% of its initial value. Repetitive measurements were carried out in solutions containing 5 x 10⁻⁴ mol L⁻¹ AA. The results of 10 successive measurements showed a relative standard deviation of 3.2% for AA, indicating that the modified electrode was not subject to surface fouling by the oxidation products.

The construction of a Zn-poly(aniline-co-*o*-aminophenol) rechargeable battery, as well as the spontaneous oxidation

and protonation of the reduced copolymer in air and aqueous acid solution, is reported in [49]. The copolymer was prepared as described in [42]. The battery was made of a Zn foil electrode, a copolymer electrode as mentioned above and an electrolyte solution consisting of 2.5 M ZnCl₂ and 3.0 M NH₄Cl. This solution was selected due to its large buffer capacity. Since the concentration of oxygen dissolved in the solution depends of the solution depth, the copolymer electrode was immersed in the solution with a fixed depth of 7 mm from the top of the copolymer electrode to the solution surface during the charge-discharge and protonation process. Again, the behavior of the copolymer was compared with that of PANI. In general in solution at pH > 4.4, no well-defined redox peaks appear on the cyclic voltammogram of PANI. However, cyclic voltammograms of the copolymer in the solutions at pH 4.40 and 4.70, exhibit two oxidation peaks and two reduction peaks on each curve, respectively. This difference indicates that the electrochemical activity of the copolymer is better than that of PANI at the corresponding pH values. The potential of each peak shifts slightly with the pH value. This means that the pH dependence of the copolymer is smaller, that is, better than that of PANI. This pH dependence behavior of the copolymer will enable the battery to diminish its capacity loss with an increasing pH value. The shape of the cyclic voltammogram of the copolymer at pH 5.0 is a little different from that at pH 4.40. In this way, the electrochemical activity of the copolymer decreases slightly as the pH increases within the range from 4.40 to 5.00. The effect of pH and charge-discharge current density on the battery characteristics was studied in [49]. It was observed that for a current density of 10 mA, the charging and discharging times at pH 4.40 were a little longer than those at both pH 4.70 and 5.00, and the starting charge voltage increased gradually as the pH value increased within the range from 4.40 to 5.00. Also, charge-discharge curves at other lower current density values (5 and 1 mA, which correspond to 2.5 and 0.5 mA cm⁻² current density values of the copolymer, respectively) were recorded for this battery. Based on the different charge-discharge curves recorded and the weight of the copolymer, the capacity density, energy density and coulombic efficiency of the copolymer were calculated. The capacity density and energy density of the copolymer were affected by the pH at the same charge-discharge current density, but their difference is small in the pH range 4.40-5.00. However, it was found that the capacity density and energy density of the copolymer increase markedly when at the same pH value the charge-discharge current density decreases. This was attributed to the polarization of the electrodes and to the solution resistance. In this connection, the copolymer has a lower conductivity compared with other metal electrodes and a low charge-transfer characteristic at pH > 4, which therefore easily causes the polarization of the copolymer electrode as the charge-discharge current density increases. In [49] it is shown that the copolymer at pH 4.70 and under a discharge of 0.5 mA cm⁻² has the largest capacity density and energy density among the different pH values used, and at various current densities. In this case the capacity density and the energy density of the copolymer for the discharge process were 103.0 A h kg⁻¹ and 120.4 W h kg⁻¹, respectively. A comparison was made between the Zn-copolymer battery and the Zn-polyaniline battery with the same electrolyte solution and in the same charge-discharge

voltage region. It was found that the capacity density and energy density of the copolymer are 31.2% and 39.8% higher than those of PANI, respectively. Even when the pH value of the electrolyte in the Zn-copolymer is a little higher than that in Zn-PANI battery, this small increment is favorable to protecting the zinc electrode from corrosion. Also, in [49] it is shown that the coulombic efficiency of the copolymer depends on the charge-discharge current density. The coulombic efficiency is greater than 98% at the current density of 5 and 2.5 mA cm⁻², and is greater than 94% at 0.5 mA cm⁻². This indicates that the copolymer electrode in aqueous solution has a good stability. Based on the fact that the electrode reaction of the copolymer is related to the acid concentration and that the -OH group of *o*-aminophenol unit can be oxidized and reduced, a charge and discharge reaction for the copolymer was proposed in [49]. Based on the charging time and the coulombic efficiency of the copolymer battery, it was demonstrated that the reduced copolymer (-0.3 V *versus* SCE) cannot be spontaneously oxidized in the 2.5 M ZnCl₂ and 3.0 M NH₄Cl solution with pH 5. Also, in this solution the copolymer cannot be protonated. However, the copolymer can be spontaneously oxidized in air and in 0.2 M H₂SO₄ solution. Also, the protonation process of the reduced copolymer in 0.2 M H₂SO₄ solution was studied with and without bubbling nitrogen. It was observed that the oxidation extent of the reduced copolymer with bubbling nitrogen was lower than without it. So, it was concluded that the spontaneous oxidation of the reduced copolymer was caused by oxygen. The presence of acid plays an important role in the catalytic action of the copolymer oxidation. The structure of the copolymer in the electrolyte solution of pH 5.00 and at -0.3 V is likely similar to that of emeraldine base (PANI), so it can be protonated in the more acidic solution.

The synthesis of poly(aniline-co-*o*-aminophenol) in the presence of ferrocenesulfonic acid using repeated potential cycling in the potential range from -0.10 to 0.86 V (*versus* SCE) is reported in [50]. The aim of this work was to synthesize copolymer nanostructures without using solid templates and especially obtain an electrode consisting of polymer nanostructures. A solution consisting of 0.2 M aniline, 9 mM *o*-AP, 0.3 M ferrocenesulfonic acid and 0.6 M H₂SO₄ was used for the polymerization. A Pt electrode was employed as substrate. On the voltammogram appears an anodic peak at 0.31 V and a cathodic one at 0.28 V, which were attributed to the redox behavior of ferrocenesulfonic acid. As the number of cycles increase, three new peaks appear at 0.20, 0.44 and 0.53 V, and their corresponding cathodic peaks at about 0.00, 0.42 and 0.51 V, respectively. They were attributed to the redox reaction of the copolymer itself. The voltammogram of the copolymer in a 0.2 M H₂SO₄ solution showed evidence of the presence of ferrocenesulfonic acid. In this connection, it was proved that ferrocenesulfonic acid was positively charged and was incorporated into the copolymer film during the copolymerization process. SEM images of the copolymer revealed that films are constructed of interwoven fibers with different diameters. This copolymer can catalyze the electrochemical oxidation of catechol. Also, it was demonstrated that the oxidation potential of catechol increases as the diameter of the copolymer nanostructures increases. It was indicated that there is a higher surface area of the copolymer as compared with the bare Pt electrode, due to smaller average diameters of fibers. In connec-

tion with the electrochemical properties of this copolymer with a nanostructured network, it was proved that it has a fast charge transfer and a good electrochemical activity at $\text{pH} \leq 9.0$ (0.3 M Na_2SO_4 solution). However, the cyclic voltammograms of the copolymers synthesized in the presence and in the absence of ferrocenesulfonic acid are quite different. Even when the former has a good electrochemical activity at $\text{pH} \leq 9.0$, no evident redox peaks were observed on the voltammograms. The difference in the electrochemical properties between copolymers synthesized in the absence and in the presence of ferrocenesulfonic acid was attributed to a small amount of ferrocenesulfonic acid incorporated in the latter one, since ferrocenesulfonic acid plays an important role in enhancing electron-transfer ability. However, it was found that the electrochemical activity of the copolymer synthesized in the presence of ferrocenesulfonic acid is completely lost in 0.3 M Na_2SO_4 solution with $\text{pH} 10.0$.

The direct determination of arsenate based on its electrocatalytic reduction at a poly(aniline-co-*o*-aminophenol) electrode was reported in [51]. The effect of potential, pH , and $\text{As}(\text{V})$ concentration on the electrochemical response of the sensor was examined. The copolymer was deposited on a GC electrode from a solution containing 0.30 M aniline, 5.5 mM *o*-aminophenol and 2.0 M HCl. The potential was controlled at a constant value of 0.79 V (SCE). It was observed that the response current increases as the pH increases within the range from 4.5 to 6.0, a maximum response appears at $\text{pH} 6$, and then, the current response decreases in the range from 6.0 to 7.0. This was attributed to the fact that the nature of arsenate predominates over the effect of pH on the electrochemical activity of the copolymer at $\text{pH} < 6.0$, in which arsenate exists in H_2AsO_4^- form. Thus, a solution of $\text{pH} 6.0$ was employed in the experiments performed in [51]. With regard to potential, it was observed that the response current increases as the applied potential decreases in the range from 0.0 to -0.15 V. However, the response current over -0.15 V decreased as the applied potential was decreased further. This was attributed to the decrease of the electrochemical activity of the copolymer. Then, an optimal potential value for the reduction of arsenate at the copolymer was -0.15 V, which is much less negative than that employed in cathodic stripping voltammetry experiments. A less negative potential is favorable for decreasing the interference of metallic ions in the solution and hydrogen generation at negative potentials. With regard to the temperature effect, it was observed that the response current increased as the temperature increased. An apparent activation energy was calculated, which is low and falls in the range of enzyme-catalyzed reactions. This indicates that the copolymer plays an important role in lowering the activation energy of arsenate reduction, which is an essential issue for the electrocatalytic reaction. On the basis of the above-described results, a 0.10 M NaCl solution with $\text{pH} 6.0$ and an applied potential of -0.15 V (SCE) were chosen as the optimal conditions for the determination of arsenate. Also, it was found that the poly(aniline-co-*o*-aminophenol) electrode has a wide linear response range from 0.994 to 495 M arsenate with a correlation coefficient of 0.995 and a limit of detection of 0.495 M. The sensitivity of the electrode was $0.192 \text{ A M}^{-1} \text{ cm}^2$. The stability of the sensor was tested in a solution containing 0.10 M NaCl and 20 mM arsenate with $\text{pH} 6.0$. No decay of the electrode activity was observed after 10 days. In addition, the copolymer

has good adherence to the GC electrode surface, which ensured that the film would not break up.

8. CONCLUDING REMARKS

Employed as material to build amperometric biosensors, POAP mainly exhibits permselective properties. In this connection, the interference from different electroactive species can be significantly reduced during the analysis of physiological samples by employing a biosensor based on POAP. However, it has also been reported that POAP can act as a conducting layer in some biosensors. As both hydroxyl and amino groups are involved in the electropolymerization process of *o*-aminophenol, large amounts of biological macromolecules such as glucose oxidase could be immobilized in poly(*o*-aminophenol), which results in higher sensitivity of the sensor as compared with sensors based on other polymers. Different influential factors on the response characteristic of biosensors based on POAP are discussed in the literature. With regard to the effect of the polymer film thickness, in general, a thick POAP film shows a long response time and low sensitivity, but has a wider linear response range. In relation to the solution pH , even when POAP is a nonconducting polymer at $\text{pH} 7$, maximum response currents are often observed at neutral media where immobilized biological macromolecules are more active. With regard to the stability of the biosensors containing POAP, it has been pointed out that the quick sensitivity loss of the electrode results primarily from desorption of the macromolecule adsorbed on the polymer film surface. However, in the case of macromolecules such as glucose oxidase entrapped within the polymer film, the sensor was very stable. Also, it has been found that the presence of POAP as material of sensor the oxidation overpotential of some macromolecules decreases, and it has been suggested that the electrocatalytic behavior results from a chemical interaction (reaction) between active sites of the polymer and the adsorbed molecules. In this case POAP acts as an active layer. However, in other cases POAP has a passive role. In this connection, it was demonstrated that POAP enhances the efficiency of Pt and some of its alloys, towards the catalytic oxidation of methanol. In this case the role of POAP is not directly connected with an increase in the specific activity of electrocatalysts. An augmentation of the real surface area of the electrode seems to be the reason why in the presence of POAP the reactivity of Pt and its alloys increases. The simultaneous presence of hydroxyl and amino groups on the POAP backbone also allows the polymer to coordinate with most transition metal cations and with some of their complexes. It was verified that after soaking into a ferric cation solution, POAP captures iron ions. On this basis a potentiometric sensor of Fe(III) was proposed. Also, some metal cations, such as Ag(I) and Cu(I), were incorporated into the POAP matrix, and then, an increase of catalytic activity of POAP towards O_2 reduction was observed. In this regard, a stable POAP-Cu(I) electrocatalyst active for the reduction of oxygen was reported. A hybrid modified electrode was also prepared by electropolymerization of *o*-aminophenol in the presence of sulfonated nickel phthalocyanine. The modified electrode could electrocatalyze NO oxidation and was employed as NO sensor.

The copolymer poly(aniline-co-*o*-aminophenol) exhibits favorable properties to its application in sensors, electrocata-

lysis analytic determinations and rechargeable batteries. The pH dependence of the electroactivity of the copolymer is much better than that of PANI. Poly(aniline-co-*o*-aminophenol) was employed as sensor of catechol and ascorbic acid. In this connection, the copolymer was used as an electron-transfer mediator in the electrochemical oxidation of these compounds. This effect was attributed to a rapid electron-transfer process between the copolymer and the molecule in solution. Also, the immobilization of uricase with poly(aniline-co-*o*-aminophenol) using the template method was possible. It was indicated that uricase was entrapped into the copolymer structure but not adsorbed on the surface as in the PANI-uricase biosensor. In this connection the copolymer-uricase biosensor based on POAP exhibits a better stability as compared with that of the PANI-uricase biosensor. Also, the copolymer was employed in the construction of a Zn-poly(aniline-co-*o*-aminophenol) rechargeable battery. Again, a comparison can be made between the Zn-copolymer battery and the Zn-polyaniline battery with the same electrolyte solution and in the same charge-discharge voltage region. It was found that the capacity density and energy density of the copolymer is 31.2 and 39.8% higher than those of PANI, respectively. The direct determination of arsenate based on its electrocatalytic reduction at a poly(aniline-co-*o*-aminophenol) electrode was also reported. The reduction of arsenate at the copolymer occurred at -0.15 V (SCE), which is much less negative than that employed in cathodic stripping voltammetry experiments. A less negative potential is favorable for decreasing the interference of metallic ions in the solution and hydrogen generation at negative potentials. The synthesis of poly(aniline-co-*o*-aminophenol) in the presence of ferrocenesulfonic acid using repeated potential cycling was also reported. SEM images of the copolymer revealed that films are constructed of interwoven fibers with different diameters. It was proved that ferrocenesulfonic acid was positively charged and was incorporated into the copolymer film during the copolymerization process. This copolymer can catalyze the electrochemical oxidation of catechol. However, the oxidation potential of catechol depends on the diameter of the copolymer nanostructures.

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