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Poly(2-bis-aminophenyldisulfide) and Polythiothene / Platinum-Particles Modified Electrodes. Prospective Applications in Sensing and Electrocatalysis

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In this paper electrode miniaturization with prospective use in electro-catalysis or as sensors is proposed. To this purpose it was postulated that dispersion of metal particles in a polymer matrix increases the effective area, on the same geometric area. In addition, the catalytic effect would significantly improve the sensitivity and detection limit toward the analyte compared to the same electrode material when used in massive form. In this first study, besides of verifying the catalytic properties towards formic acid oxidation, the determination of nifedipine in its OROS (Osmotic Release Oral System) formulation is proposed to test the hypothesis and to lay the groundwork for more concrete proposals regarding this matter. Platinum proved to be the most suitable for nifedipine oxidation, therefore this metal was selected to be dispersed in the polymer matrix. In the current survey 2-bis-(aminophenyldisulfide), APDS, and thiophene, Th, electro-deposited on gold and platinum electrodes respectively. After, platinum dispersion was carried out by applying reduction potentials at the polymer modified electrodes on a hexachloroplatinic acid solution. These composite electrode were then used for HCOOH electro-oxidation. The results also demonstrated, firstly, that the catalytic effect on formic acid is higher when platinum was dispersed into poly-APDS and, secondly, that indeed the used methodology would allow the polymer to increase the metal effective area and thus, the sensitivity for analyte determination. However, the morphology of the polymeric matrix should be optimized as a function of the analyte size before optimizing its use as sensor.

Keywords: modified electrodes, poly(2-bis-aminophenyldisulfide), polythiophene, electropolymerization, platinum particles

1. INTRODUCTION

The development of conductive polymers in recent decades and the numerous studies related to them are largely due to their variety of applications that have proven, based on conductivity, electrochromic or electrical and electronic properties, to be useful to fabricate devices such as light emitting diodes (LED), solar cells, batteries, etc [1-5]. In electro-initiated polymerization reactions, the cell contains a large volume of electrolyte, consisting of a solvent, a soluble salt and the monomer. The electro-polymerization is a fast process: after a few seconds of anodic polarization, the voltage perturbation applied to the working electrode brings about polymer deposition[6]. Therefore, the term conducting polymer in fact refers to the oxidized polymer. The oxidation involves the generation of cation or dication radicals along the polymeric chain (polarons or bipolarones in the physics nomenclature). Hence, an important property of these materials is their doping/undoping ability and that, when performed by electrochemical means, has the advantage of modulating, for instance, its conductivity: in the electrochemical doping the electrode provides the redox charge to the conducting polymer, while ions diffuse toward (or from) the polymer structure from (or toward) the bulk electrolyte to compensate the electrical charge[7].

This interesting property, except conductivity modulation of the material, has been little explored. However, other uses are foreseen, such as removal of charged species, already corroborated and well explored by our research group [2, 8, 9], or then metal particles dispersion within polymeric matrices[10, 11], to attempt its use, for example, in electro-catalysis[12, 13]. The proposed method, based on p-doping process, has proved useful for promoting the catalytic effect of Pt dispersed into polythiophene for formic acid oxidation. Thus, it was postulated this straightforward approach should allow, by simply increasing the effective area, to improve the properties of metal electrodes for the detection of various analytes.

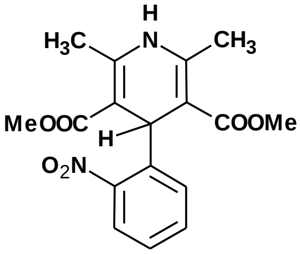


Figure 1. Nifedipine structure. 3,5-dimethyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate

For this first study Nifedipine, NFP, was proposed as analyte, fig. 1. Nifedipine is a vasodilator drug whose side effects, ascribed to sharp changes of plasma concentration, have been reported. This has led to the development of a new formulation, Nifedipine OROS (Osmotic Release Oral System) that enables the administration of a single daily dose of the drug. Thus, the gradual and constant release of the substance into the digestive tract, 24 hours a day, yields a flat plasma values curve, with a pharmacokinetic profile typical of a second generation dihydropyridine, suitable for *angina pectoris* treatment [14, 15]. This makes side effects to decrease and, at the same time, in situ control of the drug concentration is required[16]. Consequently, an amperometric sensor based on a polymer matrix supported on a micro-electrode, would allow the dispersion of a metal to afford an assembly responsive to nifedipine, whose redox properties and mechanism have been extensively studied, in order to count with an electrode of appropriate size and sensitivity for this purpose.

Bearing in mind that the polymer deposit, besides of the general characteristics of stability and cost, must meet requirements such as p-doping ability in order to incorporate the metal following the approach to be discussed below; the p-doping process must proceed at a potential that does not prevent further NFP oxidation, *i.e.* at a potential higher than 1.2 V. It is clear that, among the likely polymeric matrices, thiophene or some substituted anilines fulfill the aforementioned requirements. Nonetheless, thiophene, although it has proven to be suitable as support for electro-catalysis[13], requires stringent experimental conditions for synthesis (totally anhydrous medium). Consequently, it may be - utilized just as "standard" versus another polymeric deposit whose electro-synthesis being easier to achieve, 2-bis-(aminophenyldisulfide), APDS, figure 2.

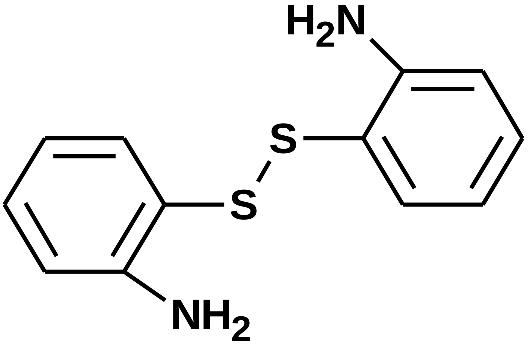


Figure 2. 2-bis-(aminophenyldisulfide) structure, APDS.

Its chemical and electrochemical polymerization and characterization has been previously accomplished by our working group [17, 18]. The compound fulfills the abovementioned requirements and, to the simplicity of aniline derivatives, adds up the presence of sulfur that would guarantee metal ion coordination during oxidation, as observed with thiophene.

2. EXPERIMENTAL

All experiments were performed at room temperature (20° C) under argon atmosphere. The chemicals used in the current work were of analytical grade and used with no further purification. Electrochemical measurements were accomplished on a CHI Instruments Model 900B potentiostat using a conventional three-electrode cell. Platinum and gold discs, 0.07 cm^2 geometric area, were employed as working electrode. A platinum wire was the counter electrode and as reference, an Ag/AgCl wire immersed in a tetramethylammonium chloride solution whose concentration is adjusted so that the potential matches the potential of the saturated calomel electrode, SCE, was utilized [19]. Hence, all potentials quoted here are referred to the SCE.

2.1. Electropolymerization

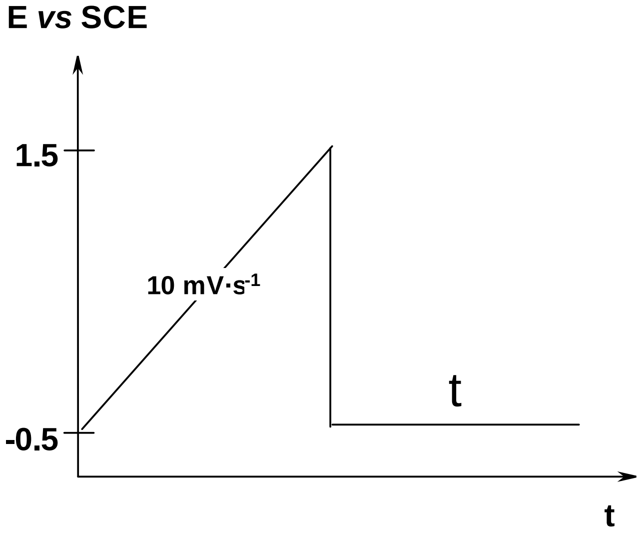
Thiophene, Th, electro-polymerization was accomplished over Pt from monomer solutions in anhydrous acetonitrile, as previously reported[20-22], obtaining a platinum|polythiophene modified electrode, Pt|pTh.

APDS electropolymerization was optimized in order to obtain the greatest p-doping charge; gold was found the most suitable supporting electrode while the working solution consisted of 10^{-1} mol·L^{-1} tetraethylammonium hexafluorophosphate, TEAPF$_6$, in a 60 : 40 mixture of CH_3CN:H_2O and 10^{-2} mol·L^{-1} APDS (monomer). In both cases, characterization and polymerization was accomplished by cyclic voltammetry, CV (successive voltammetric sweeps), obtaining a gold|poly-2-bis-(aminophenyldisulfide) modified electrode, Au|pAPDS.

Scanning Electron Microscopy, SEM, was used to obtain micrographs of the polymeric deposits, employing a LEO Electron Microscopy Inc. Model 1420VP.

2.2. Platinum dispersion

Platinum dispersion over these modified electrodes, Pt|pTh and Au|pAPDS, was performed according to the previously described approach [13], which is illustrated in the potential perturbation program of Scheme 1.



Scheme 1. Potential program applied for the incorporation of platinum particles to the polymeric matrix.

The electrode modified with the polymer deposit was dipped into a 10^{-3} mol·L^{-1} hexachloroplatinic acid solution, H_2PtCl_6, in 10^{-1} mol·L^{-1} KPF_6. The potential was anodically scanned at low rate so that upon p-doping, $PtCl_6^{2-}$ particles are incorporated to counteract the positive charge generated by the partial oxidation of the polymer. Once the anodic limit potential is reached, a -0.5 V potential step was immediately applied for a time, t, necessary to reduce Pt(IV) incorporated during the p-doping. Thus, the obtained Pt(0) remains dispersed within the polymer matrix. The process described and illustrated in Scheme 1 is called platinization cycle, PC, and is repeated as many times as necessary to optimize the desired response.

2.2. Formic acid and NFP oxidation

Formic acid, HCOOH, oxidation over platinum dispersed modified electrodes, Pt|pTh-Pt and Au|pAPDS-Pt, was assessed by cycling them in a 10^{-3} mol·L^{-1} HCOOH and 10^{-1} mol·L^{-1} KPF_6 aqueous solution. This system was selected in order to check the analyte size effect on the reaction rate at both modified electrodes.

Nifedipine oxidation studies over same substrates were carried out in a solution containing 10^{-3} mol·L^{-1} NFP + 10^{-1} mol·L^{-1} $TEAPF_6$ in acetonitrile. CV was also the electrochemical method selected.

3. RESULTS AND DISCUSSION

Optimum conditions were selected to work with NFP. Platinum, copper and gold were attempted as working electrode. As previously reported, platinum displayed the best response; consequently this metal was selected to be dispersed into the polymer matrix in order to test the hypothesis. Figure 3 shows the voltammetric profile, explained by its electrochemical oxidation mechanism [23] depicted in Scheme 2.

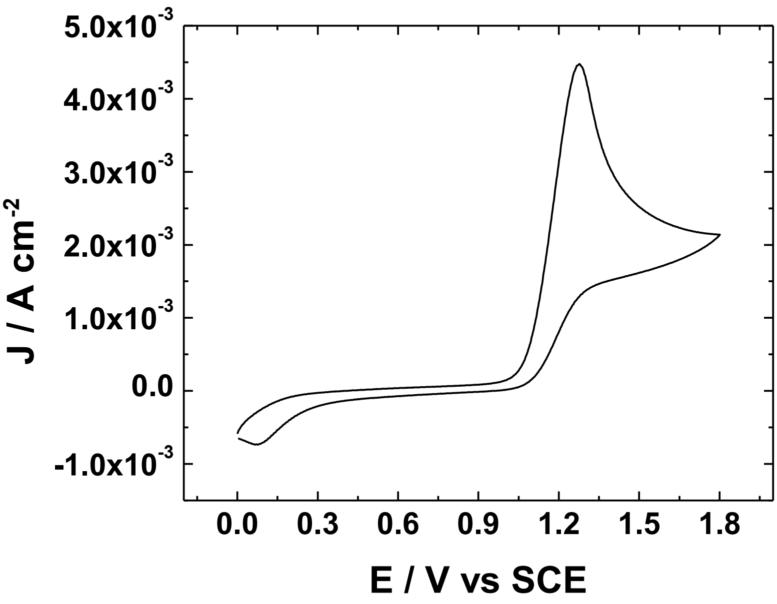
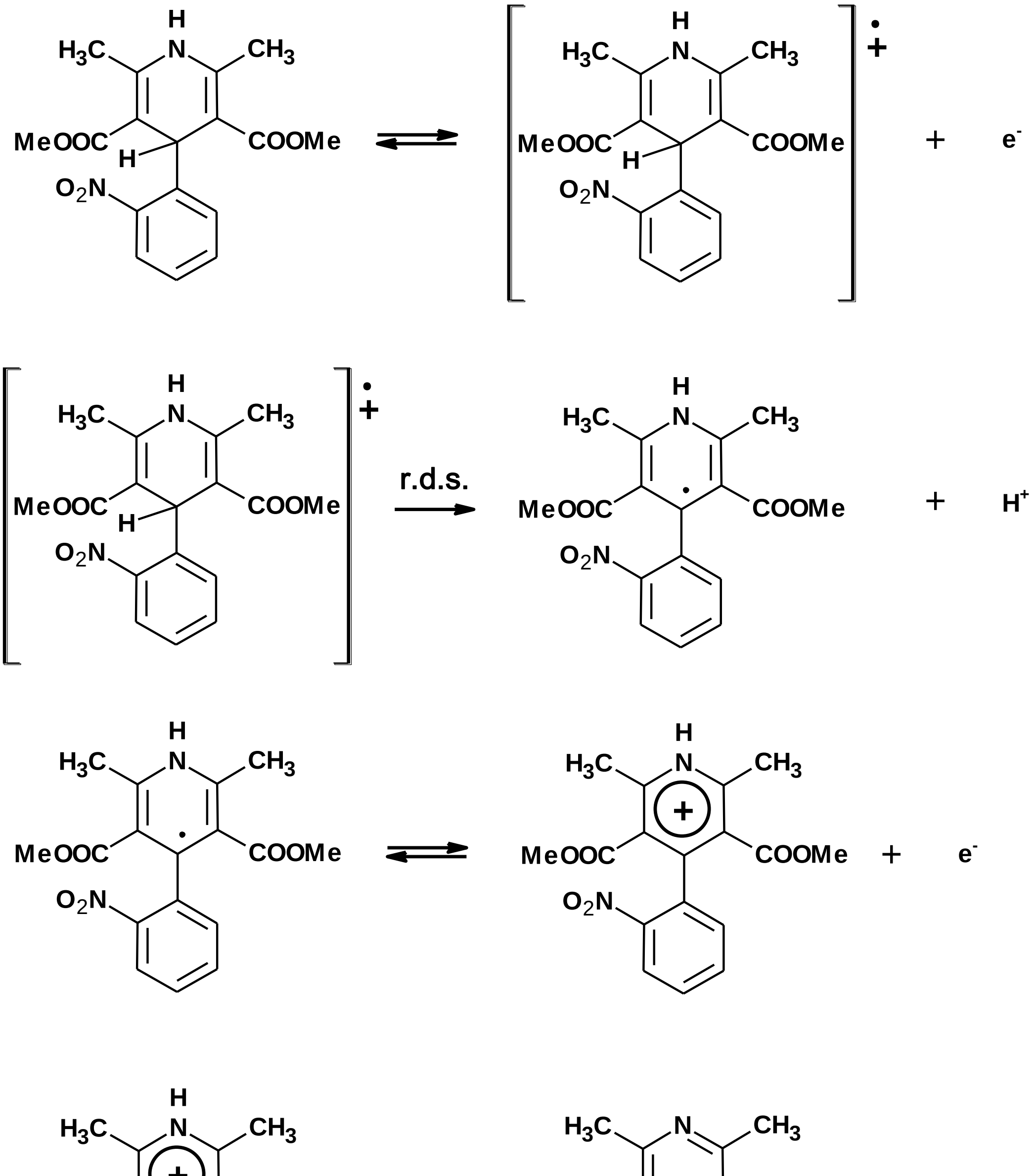


Figure 3. Voltammetric profile of 10^{-2} mol·L^{-1} NFP + 10^{-1} mol·L^{-1} $TEAPF_6$ in acetonitrile, at Pt. Scan rate: 100 mV·s$^{-1.}$



Scheme 2. Proposed mechanism for NFP electrochemical oxidation

Concerning to the electro-polymerization, numerous assays led to the conclusion that the optimal conditions for the proposed goal was the potentiodynamic electro-oxidation at gold in the electrolytic medium described in experimental. Figure 4 depicts, as an example, profiles obtained during APDS electro-polymerization. The continuous current increase as a function of the number of successive potentiodynamic cycles accounts for the conductive coating formation, whose morphology is shown in Fig. 5.

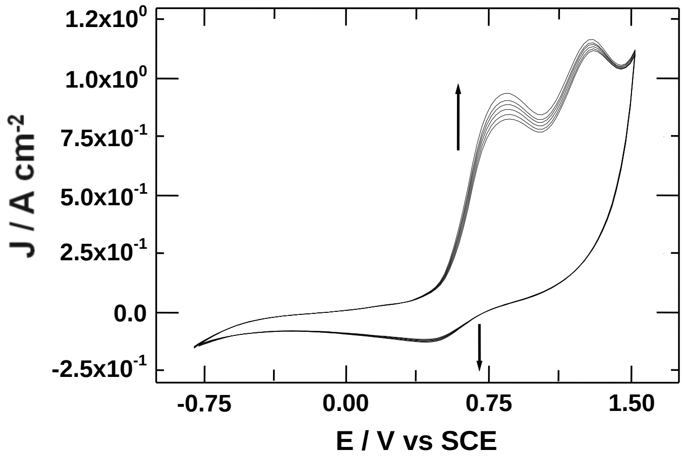


Figure 4. Voltammetric response during the electro-polymerzation of APDS. Interfase: 10^{-2} mol·L^{-1} APDS + 10^{-1} mol·L^{-1} TEAPF$_6$ in a mixture 40:60=water:acetonitrile solution, at Au. Six cycles at 100 mV·s^{-1} scan rate.

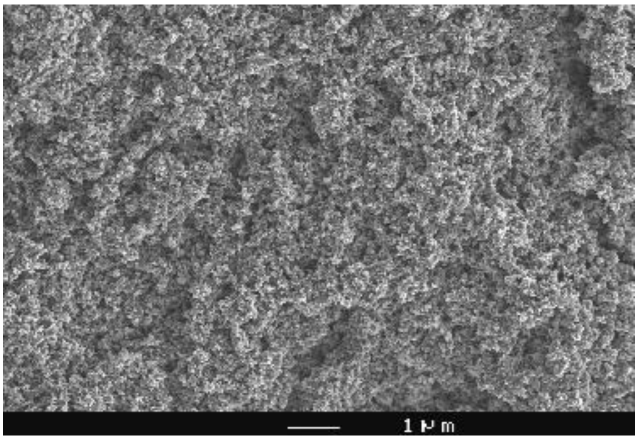


Figure 5. Scanning electron micrograph of poly(APDS) obtained under the optimum conditions set forth herein.

The response of the polymeric matrix modified electrode was studied in supporting electrolyte and 10^{-3} mol·L^{-1} HCOOH solutions, respectively. In both cases, identical stable profiles were attained. This finding demonstrated that the electrode underwent p-doping/undoping, but no response to the acid was observed.

Later, platinization cycling described in the experimental was conducted to incorporate Pt. The procedure was that reported for polythiophene. The response of the modified electrode Pt|pTh-Pt to formic acid was then measured, reproducing the result described therein (Figure. 6, dashed line), that will be used as "standard".

Similar procedure using pAPDS to prepare the Au|pAPDS-Pt modified electrode also demonstrated that two CP were required to obtain the best answer, Figure 6 (solid line).

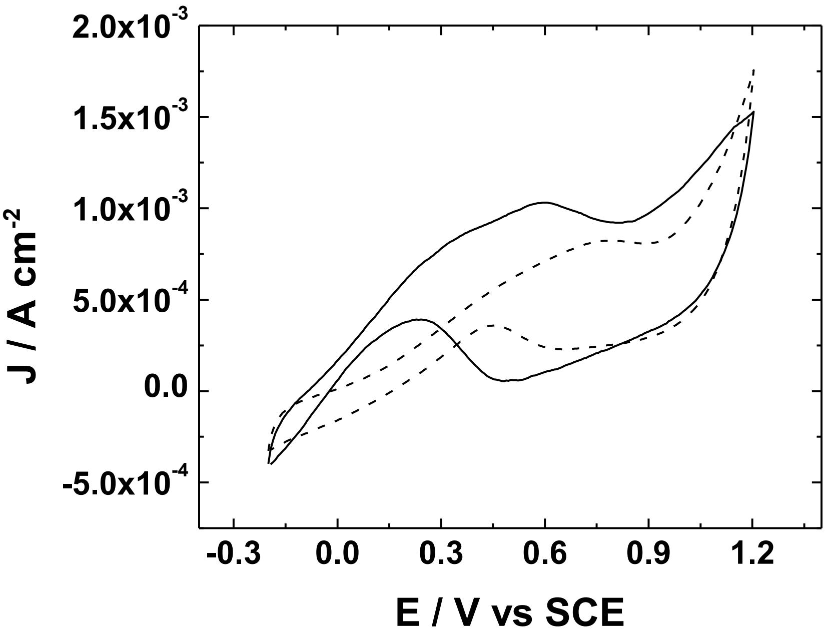


Figure 6. Voltammetric response of 10^{-3} mol·L^{-1} HCOOH + 10^{-1} mol·L^{-1} KPF_6 in water, at (solid) Au|pAPDS-Pt and (dashed) Pt|pTh-Pt electrodes. Scan rate: 100 mV·s^{-1}.

The results in Fig. 6 are a clear signal that indeed the method of platinum "inclusion" into the polymeric matrix is effective since the metal was actually dispersed [13]. Furthermore, it is evident here that Au|pAPDS-Pt catalytic effect is much greater than that achieved on Pt|pTh-Pt.

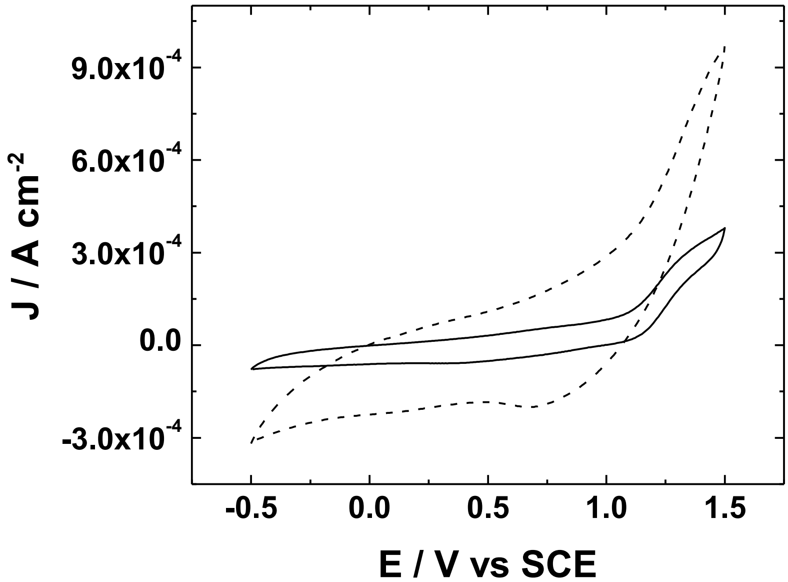


Figure 7. Voltammetric response for Nifedipine oxidation. Interfase: 10^{-3} mol·L^{-1} NFP + 10^{-1} mol·L^{-1} $TEAPF_6$ in acetonitrile, at (solid) Au|pAPDS-Pt and (dashed) Pt|pTh-Pt electrodes. Scan rate: 100 mV·s^{-1}.

This fact was verified by the obtention of both higher current and significant potential decrease that can be attributed to the presence of a greater amount of Pt, although is dispersed in the same form. This would be due to the morphology of the polymeric deposit, whose porosity and higher p-doping level favor metal dispersion.

The modified electrodes were attempted for NFP oxidation. The response is shown in Fig. 7 (solid line) for Au|pAPDS-Pt. On this case, for Pt|pTh-Pt (dashed line) the current was much higher.

Clearly, for these concentration levels, the current obtained on dispersed Pt is less than on massive Pt, contradicting the hypothesis. However, after several trials it was concluded that the problem lies in the analyte size. The porosity is not suitable for these molecules size and prevents their diffusion toward Pt particles dispersed within the polymeric matrix. This was demonstrated by decreasing NFP concentration and performing amperometric measurements at 1.5 V. The result was a narrow range of linearity for a j *vs.* NFP concentration plot. However, currents obtained in this case were higher than those attained at massive Pt.

Consequently, the hypothesis would have proven true, though the pore size of the polymer matrix needs to be increased, perhaps using template during electro-polymerization, to guarantee that suitable amounts of analyte come into the polymer, enabling thus the determination of a wider range of analyte concentration.

4. CONCLUSIONS

It was established that platinum has a suitable response for Nifedipine oxidation. pAPDS was chosen as the polymer matrix to disperse platinum. However, despite varying all the experimental conditions, the expected current response for NFP was not satisfactory. The obtained evidences led to the conclusion that NFP, owing to its large volume, does not diffuse through the polymeric matrix to reach the metal sites where the charge transfer should occur. As far as formic acid electro-oxidation, a molecule much less bulky than NFP, is concerned, pAPDS modified electrodes showed a more significant catalytic effect than when modified with pTh. This is important because involves a cheaper and easier to manufacture electro-catalysis based devices.

Consequently, we concluded that in the near future the following studies should be conducted: optimization of pAPDS modified electrodes for formic acid electro-oxidation; polymer modification of metal electrodes in the presence of "template" to ensure further diffusion of the analyte into the polymeric matrix.

Metal dispersion on the polymeric matrix would effectively increase its sensitivity with respect to the same support electrode geometric area, which is very important having in mind not only the sensitivity increment, but also the miniaturization of any metallic electrode.

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