

# Electrocatalytic oxidation of nitrite to nitrate mediated by Fe(III) poly-3-aminophenyl porphyrin grown on five different electrode surfaces

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Received 1 July 2006; received in revised form 29 November 2006; accepted 30 November 2006

Available online 8 December 2006

## Abstract

Conducting poly-tetrakis(3-aminophenyl) porphyrin-Fe(III) chloride films are prepared by electropolymerization of the complex on five different electrode surfaces: highly oriented pyrolytic graphite (HOPG), glassy carbon (GC), transparent electrode modified with tin oxide doped with indium (ITO), polycrystalline gold (Au(pc)) and monocrystalline Au(1 1 1). The electrocatalytic behaviors of the polymer film-modified electrodes in the nitrite electrooxidation reaction were investigated. The results show that three of the five modified electrodes, HOPG, GC and ITO, have catalytic effect toward the oxidation of nitrite to nitrate. According to the shift of the potential, the activity shows the following order: HOPG  $\approx$  ITO > GC. However, the activity measured as the increase in current between modified and unmodified electrode in the presence of nitrite at a fixed potential shows the following order: ITO  $\gg$  HOPG > GC. In the case of Au(1 1 1) there is a current enhancement when the electrode is covered with the polymer film, but the foot of the oxidation wave appears at more positive potential. For Au(pc) the response in both current or potential is the same whether the electrode is modified or not. On the other hand, after a few cycles in the presence of nitrite, gold-modified electrodes (mono and polycrystalline) lose their activity.

In the cases of HOPG, GC and ITO, the modified electrodes are stable and reproducible systems for the electrooxidation of nitrite.

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**Keywords:** Porphyrin; Electropolymerization; Electrooxidation; Nitrite; Modified electrodes

## 1. Introduction

The nitrite ion is one of the active intermediate species in the nitrogen cycle, resulting from complete oxidation of ammonia or from reduction of nitrate ion. The occurrence of nitrite salts in the environment and their use in food preservation are widespread. However, now there has been increasing concern about the role of nitrite ions in the formation of *N*-nitrosamines, many of which have been shown to be carcinogenic [1–4]. Although naturally occurring concentrations of nitrites are usually of no significance to health, wastes from fertilizers or intentional addition

of nitrites for corrosion control are potential sources of nitrite contamination [5]. For these reasons the determination of nitrite has received considerable attention.

Electrochemical methods offer useful alternatives since they allow faster, cheaper and safer analyses. Therefore, there are methods involving the indirect determination of nitrite by amperometry with bare platinum disc microelectrodes [6,7] or with two platinum wire electrodes in a biamperometric mode [8,9]. A more convenient approach involves direct anodic oxidation of the nitrite ion on a polarized electrode. Accordingly, it is well known that nitrite is oxidized on platinum [10,11], gold [12], glassy carbon [13] and transition metal oxides electrodes [14]. However, the application of these sensors is limited because several species may poison the electrode surface and decrease the electrode's sensitivity and accuracy [15]. Therefore, modification of electrode surfaces with molecular films has been pursued

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with great interest because of the possibility of exploiting the kinetics of interfacial electron transfer in a chemically controlled way. This is a promising approach for imparting selectivity and improving the sensitivity of the electrodes for otherwise slow electrochemical reactions [16]. Furthermore, sometimes it is possible to increase the sensitivity and even the selectivity of the active interfaces by immobilizing materials that form three-dimensional networks, containing suitable electrocatalytic active sites. In this way, it is possible to improve the electrode's activity for modifying materials in which the response is limited by the kinetics of the chemical processes occurring at the active sites [17,18].

Oxidation of nitrite at modified electrodes has been largely described. Methods include the use of thin films of mixed-valence  $\text{CuPtCl}_6$  [19], Iron(III) porphyrin-based polymers [20],  $[\text{Ru}(\text{bipy})_2\text{poly-(4-vinylpyridine)}_{10}\text{Cl}]\text{Cl}$  electrochemical sensors [21], molybdenum oxide layers [22], phthalocyanine-modified electrodes [23–25], chitosan-carboxylated multiwall carbon nanotube-modified electrodes [26], carbon paste electrodes modified with Co(II) porphyrin adsorbed on  $\text{SiO}_2/\text{SnO}_2/\text{phosphate}$  [27], aluminum electrode modified by Pd-pentacyanonitrosylferrate films [28] and Pt nanoparticles and Fe(III) on glassy carbon electrodes [29].

Metalloporphyrin-coated electrodes have shown beneficial features as analytical sensors because they can substantially lower the overpotential for redox processes of several species with slow electron transfer [30–33].

An attractive approach reported in the literature for the modification of electrodes by porphyrin films consists of the electropolymerization of suitable porphyrin–metal complexes [34]. The polymerization of a desirable electroactive monomer is by functionalization of its periphery with groups which, when activated, can participate in polymer coupling reactions by electroreduction or oxidation of the monomer. In particular, amino-substituted porphyrins and derivatives can be electropolymerized [35–42] in order to obtain surface-modified electrodes with the aim of securing potentiometric or amperometric sensors.

In this work we check the electrocatalysis of the oxidation of nitrite to nitrate on five different electrode surfaces: highly oriented pyrolytic graphite (HOPG), glassy carbon (GC), transparent electrode modified with tin oxide doped with indium (ITO), polycrystalline gold (Au(pc)) and monocrystalline Au(111), all of them modified with a polymer of Fe-3-tetra-aminophenyl porphyrin obtained by electropolymerization using cyclic voltammetry.

## 2. Experimental

Tetrakis(3-aminophenyl) porphyrin (TAPP)-Fe(III) chloride were obtained from MidCentury Co. and used without further purification. *N,N'*-Dimethylformamide, DMF (Fluka p.a. >99.5%) was treated with anhydrous  $\text{Na}_2\text{CO}_3$  and then doubly distilled at reduced pressure in an argon atmosphere. Tetrabutylammonium perchlorate, TBAP (Fluka, 99%) was recrystallized from a 2:1 ethanol–water solution and dried at 60 °C under vacuum.

Phosphate pH 7.4 buffer solution (PBS, prepared from 0.1 M NaCl, 2.6 mM KCl, 0.04 M  $\text{Na}_2\text{HPO}_4$  and 0.01 M  $\text{KH}_2\text{PO}_4$ ) was used as base electrolyte. Aqueous solutions were prepared using Milli-Q water and were deoxygenated before each measurement by bubbling argon gas (99.99%). All the experiments were carried out at room temperature.

Electrochemical measurements were made using an Autolab potentiostat-galvanostat (PGSTAT30). The reference electrode was changed depending on the solvent. An Ag/AgCl/1 M TMAcI in  $\text{CH}_3\text{CN}/\text{DMF}$  (3:1) reference electrode was used in DMF solutions whose potential was always measured compared to the SCE, and an SCE reference electrode was used in aqueous solution. All the potentials were quoted with respect to this electrode.

The working electrodes were flame-annealed Au(111) plates ( $0.4\text{ cm}^2$ , Arrandee<sup>TM</sup>), Au spheres ( $0.25\text{ cm}^2$ ) made by melting a gold wire (namely polycrystalline gold, Au(pc)), highly oriented pyrolytic graphite (SPI Supplies) plates, a glassy carbon disc and a transparent electrode modified with tin oxide doped with indium (Delta Technologies). A platinum ring was used as counterelectrode.

Electropolymerization was carried out by consecutive potential cycles (50 cycles) at  $0.2\text{ V s}^{-1}$  in a DMF + 0.1 M TBAP solution containing 0.1 mM (TAPP)-Fe(III) chloride. After the polymerization, the modified electrodes were carefully rinsed with DMF to remove excess electrolyte and finally with Milli-Q water. Then the electropolymerized film was stabilized in a PBS solution by consecutive potential cycles between the potential limits at which nitrite oxidation is carried out.

AFM images (tapping mode) were taken with a Nanoscope Multimode III (Digital Instruments, Santa Barbara, CA). All images were taken in air and at room temperature. The UV–vis experiments were performed using a Nicolet Evolution 300.

## 3. Results and discussion

### 3.1. Preparation of the Fe (TAPP) electropolymerized films

Fig. 1 shows the schematic structure of the metalloporphyrin used in this study. This molecule has a core where the metal has a fifth ligand or contra-ion, chlorine. On the other hand, the phenyl groups are practically perpendicular to the core of the molecule. When the electropolymerization takes place, the amino groups oxidize forming radical cations that attack the neutral molecule in a carbon atom of the phenyl substituents. This kind of polymerization forces torsion in the phenyl groups, allowing conjugation along the entire polymer. Normally, it is easier to electropolymerize this kind of porphyrins when the amino groups are in the “para” or “ortho” position, but in our case, where the amino groups are in the “meta” position, we also get reproducible polymer-modified electrodes.

In all the electrodes the electropolymerization process was carried out exactly under the same conditions, except in the case of HOPG electrodes, where the positive potential limit was set at a smaller value as can be seen in Fig. 2, where the voltammetric response corresponding to the electropolymerization on four

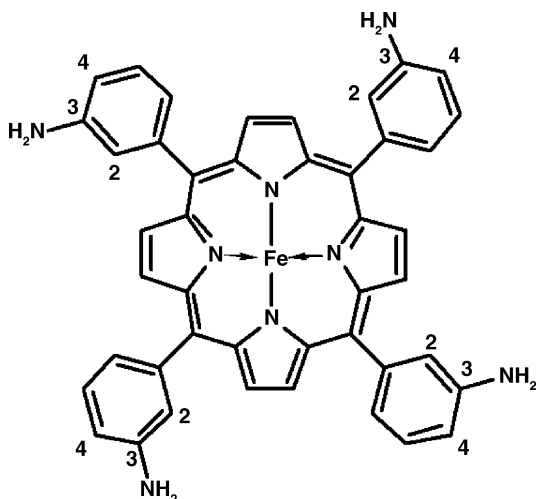


Fig. 1. Structure of tetrakis(3-aminophenyl) porphyrin-Fe(III) chloride: (TAPP)-Fe(III) chloride.

electrodes is shown. Growth of the polymer on Au(pc) was not depicted because its response is very similar to that seen with Au(111). Different voltammetric peaks are developed during the electropolymerization process, and this can be attributed to the oxidation and reduction of the porphyrin ring and to the Fe(III)/Fe(II) couple as has been shown previously [41,43]. On the other hand, the foot of the oxidation wave corresponding to the amino groups is different depending on the surface. In terms of potential it is easier to polymerize on HOPG ( $\approx 0.95$  V), then on ITO ( $\approx 1.04$  V) or GC ( $\approx 1.02$  V), than on Au(111) ( $\approx 1.29$  V). This is the first evidence of a change in the nature of the redox mediator depending on the electrode surface. However, in spite of the potential of the foot of the oxidation wave,

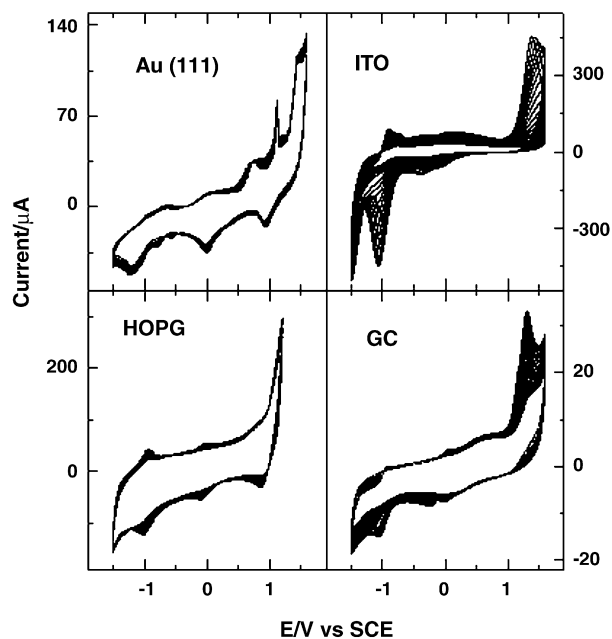


Fig. 2. Voltammetric response of the electropolymerization on four different electrocatalytic surfaces namely Au(111), ITO, HOPG and GC of (TAPP)-Fe(III) chloride (ca. 0.1 mM) in a solution of DMF/0.1 M TBAP at  $0.2 \text{ V s}^{-1}$  and 50 voltammetric cycles, vs. SCE reference electrode.

in all cases the positive potential limit must be at least 1.2 V to form the polymer on the electrode surface.

AFM studies were made at the same time in order to detect some changes in the nature of the polymer film depending on the surface of the electrode. The HOPG and Au(111) surfaces are completely covered by the film after 50 cycles (not shown). For the Au electrodes a more detailed study of the growth of the film has been made [43]. ITO electrodes were also analyzed by AFM, but due to their high surface roughness, the images can give poor information about morphologic changes of the electrode surface. A detailed discussion of the morphology of the films is therefore not possible. However, it is interesting to note that in both HOPG and Au (a good and a poor catalytic system), the surface was completely covered, indicating that in both cases the catalyst is the polymeric film and not the bare surface. In order to check if ITO is also covered by the surface, the UV–vis spectrum of the modified ITO was obtained. The UV–vis spectra of the monomer dissolved in DMF and the polymer grown on the surface of the ITO electrode and immersed in DMF shows the typical broadness of the polymer's Soret band due to the different energies of the oligomers forming the film. The same effect is obtained for the Q bands due to the energy dispersion of each oligomer (not shown) [42]. The difference in absorbance is not indicative of a difference in concentration because the extinction coefficient of the polymer or of the oligomers is not known, and it is probably different from that of the monomer and dependent on the kind of polymerization used to obtain it. It is known that the first layers of an electropolymer (order and morphology) are strongly related to the nature of the electrode surface and the polymerization conditions [44–46]. After the deposition of the first oligomers on the surface, the kind of polymerization (chain length and cross binding) is depending on the nature of the modified surface, i.e., the conductivity and the active sites of the film. As an example, in the case of Au(111), the first potentiodynamic cycles give islands of oligomers with from 4 to 20 molecules forming a 2D coating. The molecules are distorted and the phenyl groups tend to a more planar conformation. After 25 cycles, 3D growth is seen [43]. It is not possible to determine or conclude what is happening on each of the electrode surfaces shown here. From Fig. 2 it is clear that the polymer is different on each surface in spite of using the same conditions during the electropolymerization. However, it is not possible to elucidate the main differences among them. Electrochemical impedance spectroscopy studies are being carried out in order to compare the conductivity and the thickness of each film.

### 3.2. Electrocatalytic oxidation of $\text{NO}_2^-$ by poly (Fe-TAPP)

The voltammetric response of the five modified electrodes in the PBS electrolyte, but in the absence of nitrite, does not show any redox couple, but only a capacitive response (not shown). These kinds of voltammograms are characteristic of polymer-modified electrodes [41], because generally the interfaces are porous and double layers are thick, masking Faradic currents. In spite of the absence of redox couples, it is probable that the active site for the reaction is the iron metal center, because this metal is very electroactive in porphyrins, phthalocyanines and other

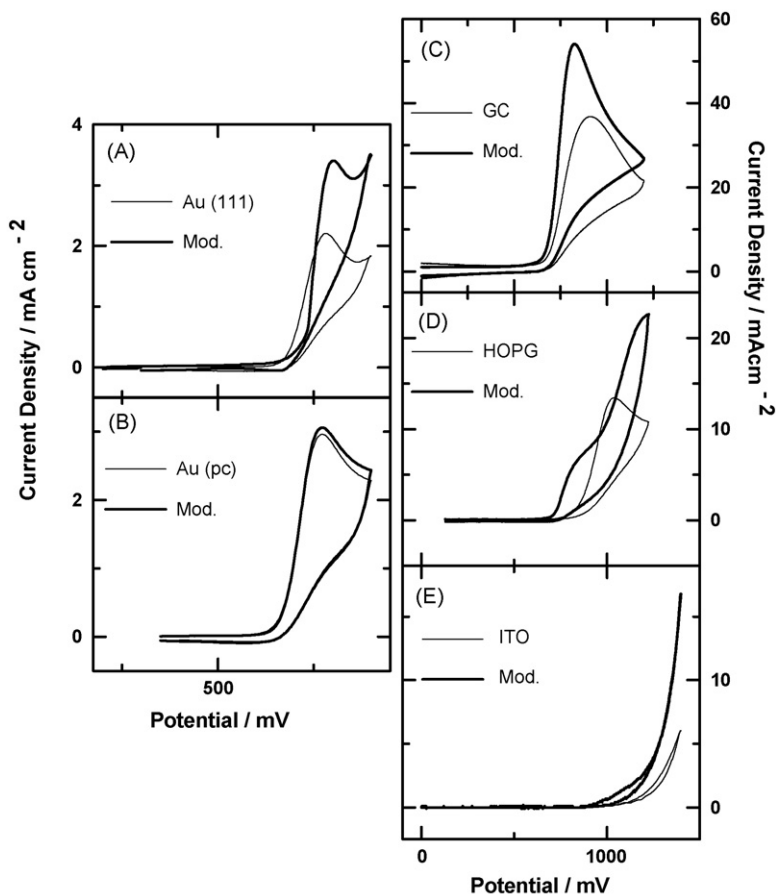


Fig. 3. Voltammetric response of the first cycle at scan rate  $0.1 \text{ V s}^{-1}$  on five different electrodic surfaces in the presence of  $2 \text{ mM}$  nitrite in PBS solution, pH 7.4. In each case (dashed line) represents the response of bare electrodes and (full line) represents the response of modified electrodes: (A) Au(1 1 1); (B) Au(pc); (C) GC; (D) HOPG; (E) ITO, vs. SCE reference electrode.

related complexes [47]. The electrocatalytic efficiency of these modified surfaces has been compared by means of the nitrite electrooxidation reaction ( $2 \text{ mM NaNO}_2$  in PBS solution, pH 7.4). The voltammetric responses of the modified electrodes to the poly (Fe-TAPP) in PBS solution were previously recorded at different potential scan rates and were subtracted from the nitrite oxidation curves. Fig. 3 shows the response of the five modified electrodes under the same conditions compared to the same process on bare electrodes. In all cases an anodic wave corresponding to the electrooxidation of nitrite to nitrate appears. It is important to mention that each voltammogram corresponds only to the response of the nitrite oxidation because in all the systems the current of the blank (modified or unmodified electrode) in the absence of nitrite was subtracted. Except for the gold electrodes (Fig. 3A and B), the modified electrodes shift the potential to more negative values and enhance the current. In the case of the gold electrodes, the behavior is very different for Au(pc) or Au(1 1 1) substrates. In the case of Au(1 1 1) (Fig. 3A) the nitrite oxidation potential is shifted to more positive potentials, but the current increases when the electrode is modified. It seems as if nitrite modifies the surface forming a different kind of polymer that blocks the gold surface but enhances the current. However, in the case of Au(pc) (Fig. 3B), the response of the modified or unmodified electrode is very similar [43]. There

are many explanations for these features. The clean surface of each electrode is different, including the adsorption of water and electrolytes. On the other hand, on each surface a different kind of polymer is probably formed. It is not possible to elucidate double layer effects or porosity of the coating and many other factors that can be playing a role in the final behavior. In fact, depending on the composition of the surface, different kinds of polymers can be obtained [44]. Also, differences in electrocatalytic responses to the oxidation of nitrite of a glassy carbon due to a difference in the method of modifying the surface with a cobalt phthalocyanine was determined [45], indicating all the factors that are playing a role. During polymerization, the grafting of the film would depend on surface defects, the possible affinity of higher filled orbitals of the metal and the chain, and the presence of OH (among other factors) [46]. These few examples indicate the complexity of the analysis of the electrocatalytic behavior of the modified electrodes. However, it may be mentioned that there is no adsorption of nitrite because in all cases the current is under diffusional control. On the other hand, there is an important difference between the behavior of the gold and the other modified electrodes. Both Au(pc)- and Au(1 1 1)-modified surfaces are deactivated in the presence of nitrite after three or four cycles. Deactivation of the gold surfaces is probably due to the oxide layer formed in those substrates at the pH



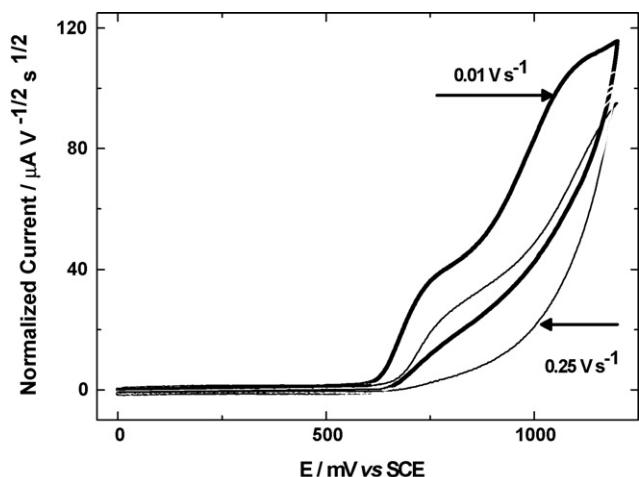


Fig. 4. Voltammetric response of the first cycle, at two different scan rates  $0.01 \text{ V s}^{-1}$  (full line) and  $0.25 \text{ V s}^{-1}$  (dashed line) of HOPG/poly-3-aminophenyl porphyrine of Fe(III) in the presence of 2 mM nitrite in PBS solution, pH 7.4.

of PBS. More detailed studies are being made to elucidate this question.

In the case of HOPG (Fig. 3D), a shoulder appears in the oxidation wave between 0.7 and 0.9 V. In order to check if this shoulder corresponds to an intermediate or to a different reaction product, a 1-h electrolysis at  $E = 0.9 \text{ V}$  was carried out, but bubbles or changes attributed to a new product were not detected. This shoulder probably corresponds to long-lived intermediates formed between nitrite and the metal that require more energy to produce nitrate. Indeed, the reaction has slow kinetics and the electrocatalytic effect is more pronounced at low scan rates, indicating that long-lived intermediates are reacting as shown above.

A study at different scan rate potentials indicates that the enhancement in the electrocatalysis is better at low scan rates, as can be seen in Fig. 4, where the normalized oxidation current of nitrite for modified HOPG is compared at 0.01 and  $0.25 \text{ V s}^{-1}$ .

For modified GC and ITO, the same behavior is obtained (only the response for HOPG is shown, Fig. 4). Probably due to the slow reaction kinetics, there is no clear relation between current and nitrite concentration. Several nitrite concentrations were attempted on modified GC, and as the concentration of nitrite gets higher the current increases but not linearly (not shown). Since the only case in which a well defined  $I_p$  was seen is that of the modified GC electrode (Fig. 3C), this electrode was chosen in order to check if the catalysis is a diffusional process. A series of cyclic voltammograms were obtained at a fixed nitrite concentration, but changing the potential scan rates. The behavior of  $I_p$  versus the square root of the scan rate for modified GC indicates that a linear relationship is obtained at low scan rates, pointing to a mass transport control process for the reduction of nitrite (not shown). It has been reported [25] that in the case of Co-phthalocyanine-GC-modified electrodes used for the oxidation of nitrite, a diffusional transport control process is also obtained over a wider range of scan rates. On the other hand, a plot of  $I_p/\nu^{-1/2}$  versus  $\nu$  needs to have a characteristic behavior [47,48] if the process is catalytic. Fig. 5 shows this behavior

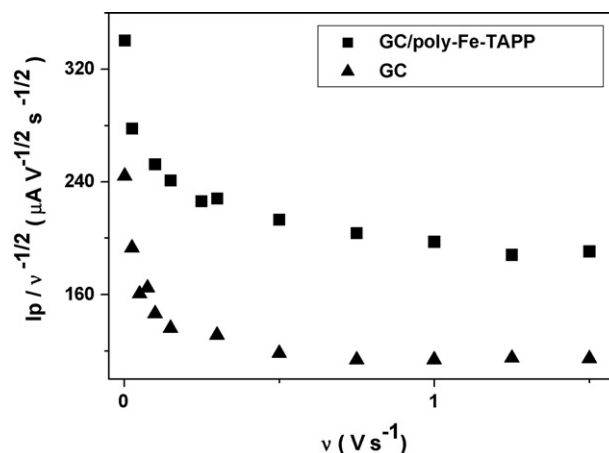


Fig. 5. Plot of  $I_p$  vs. square root of potential scan rate  $\nu^{1/2}$  of GC/poly-3-aminophenyl porphyrine of Fe(III) in the presence of 2 mM nitrite in PBS solution, pH 7.4.

for GC/Fe(III) poly-3-aminophenyl porphyrin and the bare electrode. For all the modified electrodes, the profile of this plot was the same. This profile has the characteristic shape of a typical EC' catalytic process [49,50]. For all the modified electrodes, studies of the oxidation of nitrite at different pH values (range 4–10) were made. Over the whole pH range there are no changes in the electrocatalytic behavior of the electrodes. These results indicate that the  $pK_a$  of the iron active sites of the poly-porphyrin is out of this pH range. On the other hand, in order to elucidate the mechanisms of the catalytic processes, plots of  $E_p$  versus  $\log \nu$  were made for modified and unmodified GC electrodes (not shown). The slope of this plot is  $dE_p/d(\log \nu) = 29.6/(\alpha n')$  mV, where  $\alpha$  is the electrochemical charge transfer coefficient, normally 0.5, and  $n'$  is the number of electrons transferred in the rate determining step of the reaction for irreversible systems [51]. In Fig. 6, we get two linear regions with slopes of 23.9 and 150.8 mV/dec for slow and fast scan rates, respectively. It is interesting to note that the unmodified electrode also shows two linear regions, but at low scan rates the slope is 51.2 mV/dec. This behavior indicates, assuming  $\alpha = 0.5$ , that at low scan rates

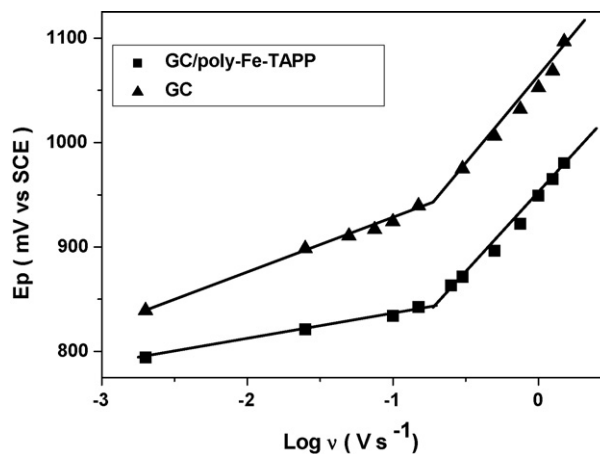


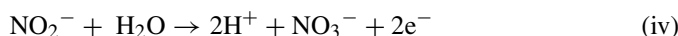
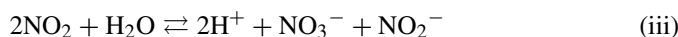
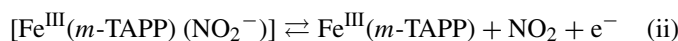
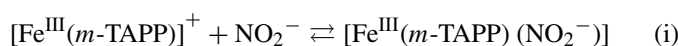
Fig. 6. Plots of  $I_p/\nu^{-1/2}$  vs.  $\nu$  of GC/poly-3-aminophenyl porphyrine of Fe(III) (full square) and no modified GC (full triangle) in the presence of 2 mM nitrite in PBS solution, pH 7.4.

Table 1

Comparative results on the potential of the foot of the oxidation wave and the current at the same potentials for the modified and non-modified electrodes in the presence of 2 mM of nitrite in PBS solution, pH 7.4

Electrode	State of the electrode	$E$ (V) foot of the wave	$E$ (V) where the current was compared	$I$ ( $\mu$ A)
Au	Non-modified	0.623	0.7	49.1
Au	Modified	0.616	0.7	38.8
111-Au	Non-modified	0.639	0.7	73
111-Au	Modified	0.641	0.7	37
HOPG	Non-modified	0.705	0.7	80
HOPG	Modified	0.605	0.7	317
ITO	Non-modified	1.011	1.2	3.2
ITO	Modified	0.910	1.2	23.3
GC	Non-modified	0.681	0.8	67.7
GC	Modified	0.608	0.8	74.8

the electrooxidation in the case of the modified electrode has a chemical slow step after the first electron transfer. At faster scan rates the slope does not have a clear electrochemical significance. The unmodified electrode operates in a different way at low scan rates. Therefore, the following two-step mechanism (electrochemical and chemical) can be proposed for the systems studied here:



The interaction between nitrite and the polyporphyrin is shown in Eq. (i), and it has been reported previously [48,52]. This step involves the interaction of an adduct where nitrite is located in an axial position, as a fifth ligand of the metal center of the porphyrin. The formation of  $\text{NO}_2$  (see Eq. (ii)) is followed by the disproportionation of the nitrogen dioxide to give nitrite and nitrate (see Eqs. (iii) and (iv)) and therefore, nitrate is the sole product.

The electroactive electrodes do not show a clear linear relationship between  $I_p$  and nitrite concentration, probably because of the low kinetics of the reaction (not shown). However, they can be considered as semi-selective electrodes because under the same conditions they do not react with high concentrations of interfering ions:  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{Na}^+$  and  $\text{K}^+$ . Only  $\text{SO}_3^{2-}$  can be oxidized in the same range of potentials by the modified electrodes at  $\text{pH} > 9$  [41]. This study shows that the modified electrodes can be stated as selective with respect to the commonly present interfering ions.

On the other hand, it is not possible to study the electrocatalytic behavior of the monomeric porphyrin because it is insoluble in aqueous PBS buffer solutions. At very low pH, where the porphyrin is soluble, nitrite quickly disproportionates. However, some studies using other porphyrins are being published. For example, Trofimova et al. [32] showed the electrocatalytic oxidation of nitrite mediated by a high-valence manganese porphyrin cation. At pH 7 (PBS buffer solution) they found a current wave that starts at potentials close to 1.1 V versus Ag/AgCl using an ITO electrode. In our case,

the modified ITO electrode shows a catalytic response that appears at potentials close to 0.9 V. The study of the oxidation of nitrite by iron porphyrins (tetraphenylporphyrin and octaethylporphyrin) was made in DMF solution [53]. In this case an adduct is formed between iron and  $\text{NO}_2^-$ . Nitrite is quite stable in the presence of both ferric and ferrous porphyrins. For that reason the redox reaction of nitrite is hindered and the polymer-modified electrodes shown here are interesting as possible nitrite sensors.

Finally, Table 1 compares the current of the modified and unmodified electrodes and the potential corresponding to the foot of the oxidation wave. The electrocatalytic oxidation of nitrite increases with current for modified HOPG, GC and ITO electrodes; also in the case of HOPG and ITO, there are noticeable shifts of potential.

Our results show that three of the five modified electrodes have a catalytic effect toward the oxidation of nitrite to nitrate. In terms of potential, the modified electrodes are in the following order: HOPG  $\approx$  ITO  $>$  GC.

In terms of current, the order is : ITO  $\gg$  HOPG  $>$  GC

In spite of the higher potentials required by the ITO-modified electrode, its behavior as a semi-selective sensor is the same as that of the other modified systems. Then this result is promising in terms of a sensitive and selective electrode.

Also, it is interesting that these three electrodes are very stable. At least during 500 cycles no significant changes in response were seen. Furthermore, the modified electrodes can be stored in air, retaining their electroactivity.

#### 4. Conclusions

The modified electrodes GC, HOPG and ITO show an enhanced electrocatalytic effect toward the oxidation of nitrite to nitrate compared to the bare surfaces. In all cases there are shifts of the potentials to more negative values and an increase in the current. The electrodes are very stable and catalyze the oxidation to nitrate. The best electrodes are HOPG and ITO, but ITO, modified or not, presents the oxidation wave at more positive potentials than the others. It is very noteworthy that the modified polycrystalline gold does not change its behavior when modified or not. This effect can be accounted for because the film

is not very stable and nitrite probably destroys the polymer and reacts with the bare surface. In all cases, long-lived intermediates are probably formed because the catalytic effect is more pronounced at low scan rates. This process is mass-transport controlled at low scan rates and does not depend on the pH in the range studied. Due to the presence of long-lived intermediates, there is no linear relationship between current and nitrite concentration.

## Acknowledgments

This paper was financially supported by the Spanish MEC (Project CTQ2005-03222/BQU), Dicyt-USACH, and Fondecyt (Chile) Projects 1010695 and 1050306, and by Conicyt/Banco Mundial "Redes de Anillos de Investigación". F.A. acknowledges a postdoctoral fellowship from MAE-AECI 05/06, and M.C.G. acknowledges The Cabildo de Tenerife for a 2006-doctoral fellowship.

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