

# Electrocatalytic oxidation of sulfite at polymeric iron tetra (4-aminophenyl) porphyrin—modified electrode

M. Lucero<sup>a</sup>, G. Ramírez<sup>a</sup>, A. Riquelme<sup>a</sup>, I. Azocar<sup>a</sup>, M. Isaacs<sup>a</sup>, F. Armijo<sup>a</sup>,  
J.E. Förster<sup>a</sup>, E. Trollund<sup>a</sup>, M.J. Aguirre<sup>a,\*</sup>, D. Lexa<sup>b</sup>

<sup>a</sup> *Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile*

<sup>b</sup> *BIP, CNRS, 31 Chemin J. Aiguier, 13402 Marseille Cedex 20, France*

Received 2 January 2004; received in revised form 16 April 2004; accepted 16 April 2004

Available online 14 August 2004

## Abstract

The electro-oxidation of sulfite was studied by using a glassy carbon electrode coated with a polymeric film of Fe-tetra-4-aminophenylporphyrin, in a wide pH range. The polymeric complex-modified electrode catalyses the electro-oxidation of sulfite to sulfate in acid and basic media, but it is more active at pH higher than 8.5. The polymer film coating is obtained by cycling the electrode in a solution containing the complex (monomer). The polymerization process takes place after the oxidation of the amino groups via a radical mechanism. When the modified electrode is obtained, the polymeric system needs to be over-oxidized in order to avoid the further oxidation of the remaining amino groups in the potential range where the oxidation of the sulfite takes place. The over-oxidation process destroys the monomer-modified electrode. Then, the electropolymerization of the iron complex is the only way to obtain a catalyst for this reaction with this porphyrin. The specie postulated for the oxidation is Fe(IV). The polymer-modified electrode is very stable and its activity remains almost constant for more than 500 consecutive cycles. Also, its activity remains unchanged during more than 30 days of exposure to air and light. The oxidation process occurs during the anodic and the cathodic potentiodynamic scans, showing that it is only necessary the recovery of the active sites; the formation of Fe(IV) is probably needed to promote the oxidation. However, this regeneration is low and becomes the slow step of the reaction. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Electrocatalytic sulfite oxidation; Poly-Fe-tetra-4-aminophenylporphyrin; Modified electrodes

## 1. Introduction

The oxidation of sulfur containing species is an environmental concern. For this reason, the treatment of these species has drawn the attention of scientists both in the chemical and the biological areas [1,2]. The oxidation of sulfuroxanions—in their homogeneous phase—has been carried out through different methods, chemically and photochemically [3,4]. It has been studied, for example, the auto-oxidation of  $S_4O_6^{2-}$  and  $S_2O_3^{2-}$  catalyzed through different aqueous soluble porphyrins under visible light illumination (419 nm), rendering  $SO_4^{2-}$  as main product [5]. On the other hand, electrochem-

ical techniques emerge as a good alternative for the transformation of pollutant species into reusable products [6]. In this field, electrodes modified by transition metal complexes have been developed [3,5], proving to be good catalysts in homogeneous [3,7] and heterogeneous phases [8]. An example of these complexes is constituted by porphyrins, as they possess redox couples of the metal, which act as active sites. In this work, the iron tetra 4-aminophenylporphyrin was used because it presents qualities, which allow the anchorage to the electrodic surface due to the fact it presents a predominantly planar and aromatic structure with phenyl groups practically perpendicular to the macrocycle [8,9]. This complex includes amino groups in the periphery of the rings, which allows radical-electropolymerization by means of cyclic voltammetry [10]. Moreover, electrochemical records in homogeneous

\* Corresponding author. Tel.: +56 2 6812575; fax: +56 2 6812108.  
E-mail address: [maguirre@lauca.usach.cl](mailto:maguirre@lauca.usach.cl) (M.J. Aguirre).

phase show the possibility to carry out the oxidation of the sulfite ion with soluble iron porphyrins [3], assigning the Fe(IV) specie as the active specie. Fe(IV) in a basic media can be stabilized through hydroxyl groups as Fe(III) porphyrins in organic media [11] although the most common Fe(IV) porphyrin is an oxo-Fe(IV) metal center [12–14]. Even though iron complexes with oxidation states (IV) are not very common, there is enough information available about stable complexes among which iron (IV) is found [12–20].

The electrodic system obtained in this study shows great stability and important catalytic activity for the oxidation of sulfite, in a 3–13 pH range, rendering sulfate as the unique detectable product.

## 2. Experimental

Iron tetra-4-aminophenylporphyrin and its free ligand (Mid-century Co.) were used as received. The NMR, UV–vis and FTIR analysis (not shown) demonstrates that the porphyrin is pure.

### 2.1. Modification of the electrodic surface

#### 2.1.1. Monomer-electrode

The working electrode was modified with the monomer by placing a drop of monomer solution ( $1 \times 10^{-3}$  M) in DMF (dimethylformamide) on the electrode glassy carbon surface. After 1 h the electrode was rinsed with DMF, ethanol and deionized, bidistilled water.

#### 2.1.2. Polymer-electrode

Polymeric films were grown by potentiodynamically cycling the glassy carbon electrode in a  $1 \times 10^{-3}$  M Fe-tetra-4-aminophenylporphyrin (or the free ligand) containing, tetrabutylammoniumperchlorate, TBPA as electrolyte (0.1 M) and DMF as solvent, between  $-0.9$  and  $+1.15$  V versus Ag/AgCl during 50 cycles at  $0.2$  V  $s^{-1}$ . After polymerization, the modified electrode was rinsed with DMF, ethanol, and then with bidistilled water.

#### 2.1.3. Over-oxidization process

After the polymer-modified electrode is obtained it is necessary to over-oxidize it so as to avoid the oxidation response of the free amino groups that appear in the same potential range for the sulfite oxidation. To carry out the over-oxidation, the modified electrode is cycled in aqueous solution at the same pH where the oxidation of sulfite is measured. For example, at pH 9.55, the polymer-modified electrode is repetitively cycled between  $-1.0$  and  $+1.0$  V versus Ag/AgCl, until a stable profile without any redox couple is obtained.

#### 2.1.4. Instrumentation

Electrochemical experiments were performed in a three-compartment glass cell, one for each of the electrodes: the

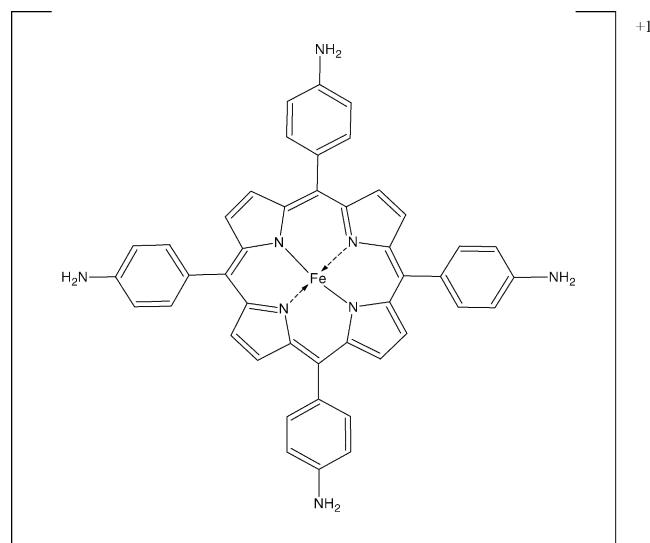


Fig. 1. Structure of the iron tetra(4-aminophenyl)porphyrin. The oxidation state of the iron is (III) and the complex is a salt: iron(III) tetra(4-aminophenyl)porphyrin chloride.

working electrode, a disc of glassy carbon ( $A = 0.071$  cm<sup>2</sup>); the reference, saturated Ag/AgCl, to which all the potentials are quoted; and the counter electrode, a Pt coil ( $A = 4$  cm<sup>2</sup>). All measurements were carried out in aqueous solutions of different pHs. The solutions were purged with pure N<sub>2</sub> before and during each measurement. The cyclic voltammetry measurements were carried out in an AFCBP1 Pine bipotentiostat connected to a rotating disk unit. In order to detect dithionate as a possible product, an Analytikjena Specord S 100 UV–vis spectrophotometer was used. The method employed was the titration of a solution containing 0.1 M sulfite and black ink (from an Epson C42 UX printer) with the resulting solution of 5 h electrolysis of a 0.1 M sulfite solution at pH 9.5. If dithionate is present in the solution, the intensity of the absorbance of the colored solution decreases. Previously, a calibration curve was done. The calculated detection limit was  $1 \times 10^{-6}$  M. The range of pH studied was 3–13 and the electrolyte for pH 13 was obtained mixing solutions 0.1 M of Na<sub>2</sub>CO<sub>3</sub> and NaOH. For pH 11–8, mixtures of solutions 0.1 M of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> were used. For solutions between pH 7 and 6, the solutions were 0.1 M of NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>. A mixture of solutions 0.1 M HCl and 0.1 M NaOH were used for pH 3.

## 3. Results and discussion

Fig. 1 shows the structure of the complex used to modify the glassy carbon electrode. Phenyl groups, which are substituted with amino groups in para position, are practically perpendicular to the macrocycle, but this fact does not hinder the electropolymerization to obtain a conductive film [21]. The irreversible oxidation of the amino groups gives origin to the electropolymerization. In this work, the free

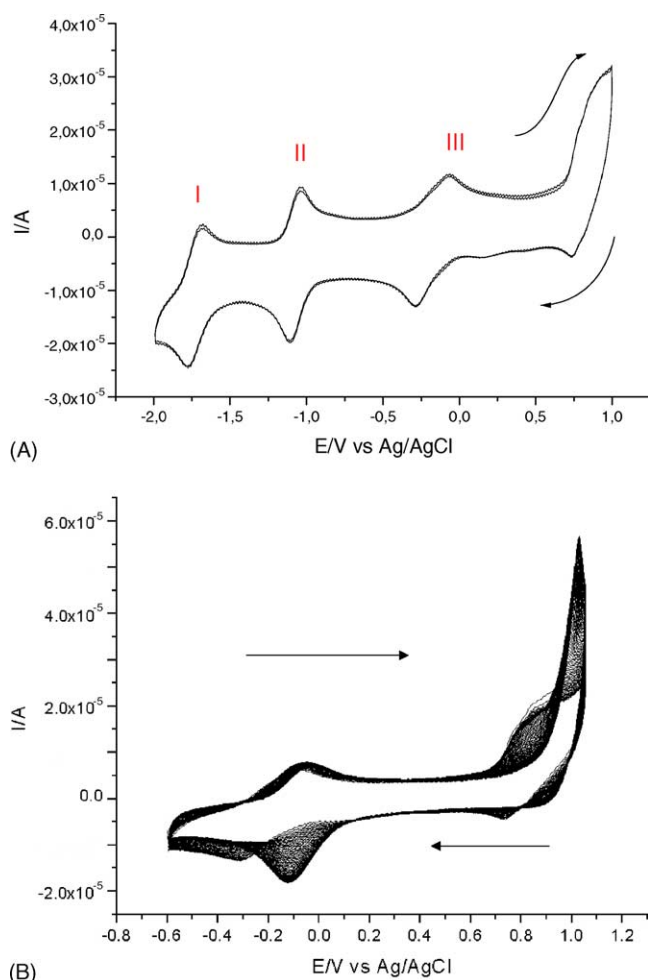


Fig. 2. (A) Voltammetric response of the monomer, iron tetra(4-aminophenyl)porphyrin, (ca. 1 mM) in a solution of DMF/0.1 M TBPA purged with  $N_2$ . Scan rate:  $0.2 \text{ V s}^{-1}$ . Arrows indicate the direction of the scans. (B) Voltammetric response of the electropolymerization of the iron tetra(4-aminophenyl)porphyrin, (ca. 1 mM) in a solution of DMF/0.1 M TBPA between  $-0.9$  and  $+1.15 \text{ V}$  vs. Ag/AgCl during 50 cycles at  $0.2 \text{ V s}^{-1}$ . Arrows indicate the direction of the scans.

ligand and the iron complex were used to obtain polymeric films. Fig. 2A shows the voltammetric response of the iron porphyrin (monomer) in DMF solution, where three redox reversible couples are shown. The redox couples of the porphyrins can correspond to high or low spin states, depending on the macrocycle, the solvent and the redox couples that have been assigned to pure metal or metal-ligand transfers [22]. Using the most common assignment, peak I corresponds to a ligand process, peak II to the Fe(II)/Fe(I) couple, and peak III to the Fe(III)/Fe(II) couple [22]. The last irreversible-oxidation peak corresponds to the response of the amino group. Fig. 2B exhibits the voltammetric response of the electropolymerization of the Fe-porphyrin. Fig. 3 shows the response of the monomer and the polymer modified electrodes in aqueous media. The monomer exhibits only an ill-defined semi-reversible redox couple at ca.  $-0.6 \text{ V}$ , corresponding to the Fe(III)/Fe(II) process. The polymer shows a

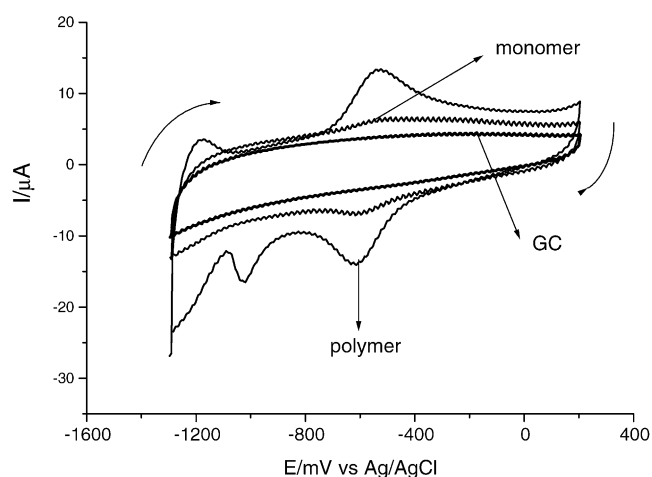
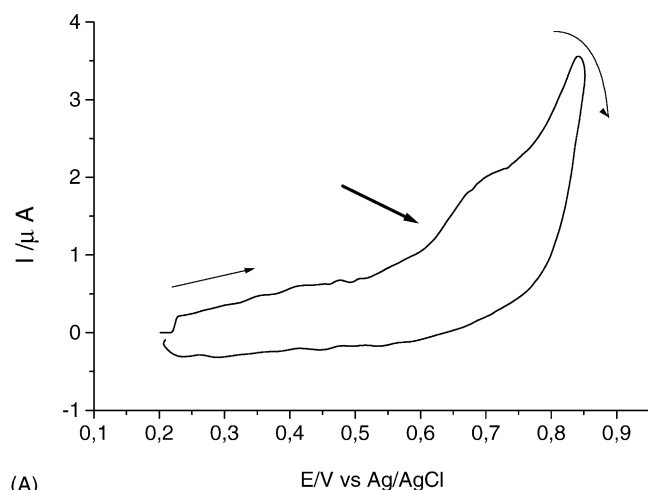
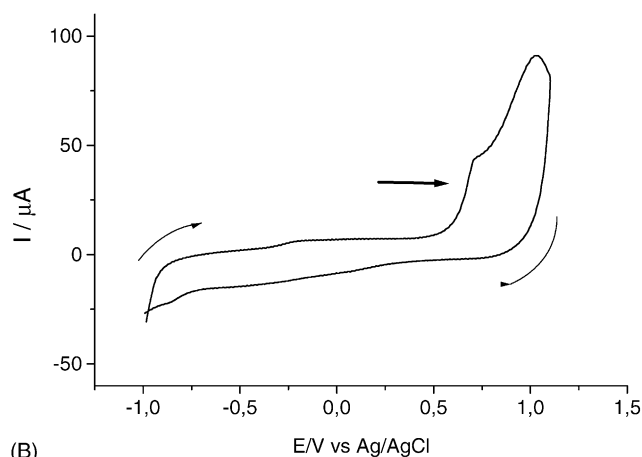


Fig. 3. Voltammetric response of the polymer-modified electrode, the monomer-modified electrode and the glassy carbon in an aqueous solution of NaOH 0.1 M (pH 13) purged with  $N_2$ . Scan rate:  $0.2 \text{ V s}^{-1}$ . Arrows indicate the direction of the scans.

better-defined response and a charge comparable to that of the monomer. The polymer also exhibits a semi-reversible peak at ca.  $-0.5 \text{ V}$  corresponding to the Fe(III)/Fe(II) couple and a cathodic signal at ca.  $-1.0 \text{ V}$  that can be due to the reduction of oxidized amino groups or linkages formed during the electropolymerization. Also, at negative potentials a ligand redox-couple appear [23]. The polymer-modified electrode is stable in DMF and in aqueous solution. No noticeable change was observed in the voltammetric profile at least after 500 cycles in both organic and aqueous solutions between the same potential limits used during the electropolymerization (not shown). The activity also remains practically unchanged during a month (time when it was proved) and exposed to air and light. Fig. 4 compares the response of two different iron porphyrins at positive potentials. Fig. 4A exhibits the voltammetric response of iron tetra-4-aminophenylporphyrin and Fig. 4B, of iron-tetra-4-sulfonatedphenyl porphyrin. In both cases, at positive limits, where an irreversible oxidation appears, there is a shoulder at ca.  $+0.5 - 0.7 \text{ V}$  versus Ag/AgCl probably corresponding to the formation of the Fe(IV) specie [15–20]. The last irreversible peak is attributed to the oxidation of the amino groups in the first case and to the oxidation of sulfonate groups in the second case. In the case of the sulfonate groups the oxidation process probably originates radical species as shown in their electropolymerization [24], with a mechanism similar to that presented by porphyrins substituted by amino or OH groups [25]. After the polymer-modified electrode is obtained, it is necessary to over-oxidize it so as to avoid the oxidation response of the free amino groups that appear in the same potential range for the sulfite oxidation. Indeed, the response of the monomeric or polymeric-modified electrode—when not over-oxidized—only shows one high irreversible wave at positive potentials. This signal probably corresponds to both, the oxidation of sulfite and the oxidation of the amino groups. Both oxidations practically appear at the same potentials, as shown by the response



(A)



(B)

Fig. 4. (A) Voltammetric response of the tetra-sulfonated Fe(III) porphyrin adsorbed on glassy carbon, in aqueous solution at pH 9.5 (under  $N_2$ ). Scan rate:  $0.1 \text{ V s}^{-1}$ . The arrow indicates the begin of the Fe(IV) formation. Arrows indicate the direction of the scans. (B) Voltammetric response of the tetra-amino Fe(III) porphyrin adsorbed on glassy carbon, in aqueous solution at pH 9.5 (under  $N_2$ ). Scan rate:  $0.1 \text{ V s}^{-1}$ . The arrow indicates the begin of the Fe(IV) formation. Arrows indicate the direction of the scans.

of the sulfite oxidation on glassy carbon, and the oxidation of the amino groups when sulfite is not presented. The response of the irreversible oxidation of the aminoporphyrin increases and a broadening is also observed when sulfite is added to the solution (not shown) but there is no possibility to separate both signals. To carry out the over-oxidation, the potential of the modified electrode is cycled in aqueous solution at the same pH where the oxidation of sulfite is measured. For example, at pH 9.55, the potential of the electrode is repetitively cycled between  $-1.0$  and  $+1.0 \text{ V}$  versus Ag/AgCl, until a stable profile is obtained (see Fig. 5). This profile does not show the characteristic oxidation peak corresponding to the oxidation of the amino groups and does not show any redox couple. On the other hand, the monomer-modified electrode is destroyed during the over-oxidation process, probably forming soluble species that diffuse to the bulk of the solution. The over-oxidized polymer modified-electrode shows a negative

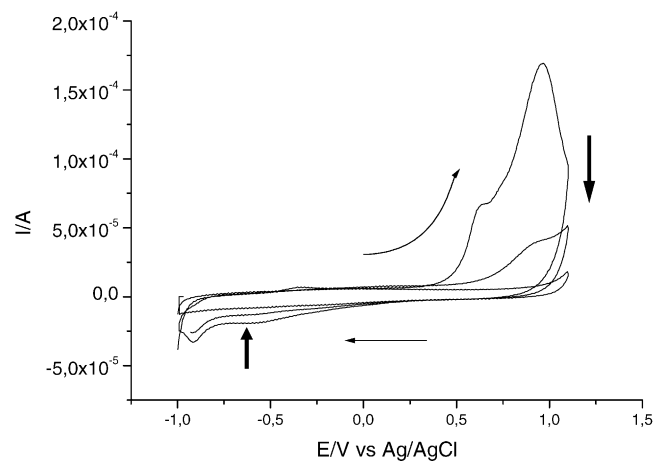


Fig. 5. Voltammetric response of the over-oxidation of the polymer-modified electrode in an aqueous solution of pH 9.55 purged with  $N_2$ . Scan rate:  $0.2 \text{ V s}^{-1}$ . The bold arrows indicate the changes during the successive cycles. Narrow arrows indicate the direction of scans.

shift in the potential at the beginning of the oxidation wave corresponding to the sulfite reaction compared with the bare electrode at all the pHs studied. There is also a small negative shift (ca.  $50 \text{ mV}$ ) compared to the mixed wave (oxidation of sulfite and amino groups) showed by the non-oxidized monomer or polymer toward the oxidation of sulfite (not shown). On the other hand, when the bare electrode is cycled to the same positive limit where the polymer is over-oxidized, the glassy carbon is oxidized. Its surface generates some active sites that enhance the reduction of molecular oxygen (not shown). Those active sites catalyze the oxidation of sulfite at potentials higher than those observed with the polymer (ca.  $250 \text{ mV}$ ). The active sites also show an oxidation peak at the positive limit in absence of the sulfite, attributed to their oxidation or the oxygen evolution reaction. This “blank” current was subtracted to the currents showed in the following figures. Then, the following responses only correspond to the oxidation of sulfite. For the polymer, the best response is obtained at pH 8.5–13. At pH 9.55, for instance, the over-potential diminishes in ca.  $200 \text{ mV}$  compared to the glassy carbon. Although the catalytic effect is small, the obtained electrode is very stable, as mentioned above. Unfortunately, the turnover number cannot be measured because it is not possible to estimate the quantity of catalysts used. The voltammetric response is predominantly capacitive; therefore, it is not possible to infer the mass of porphyrins from this data.

Results show that the current increases with the pH (at constant potential). There is an oxidation process that takes place during the direct and the reverse scans, showing that the surface recovery is the only requisite for the oxidation of sulfite (see Fig. 6). However, the scan rate is too high for a total recuperation of the surface, and the oxidation that takes place during the reverse scan is very low compared to the direct scan.

Fig. 7 compares the response of the polymerized ligand, the polymerized iron complex and the bare electrode toward

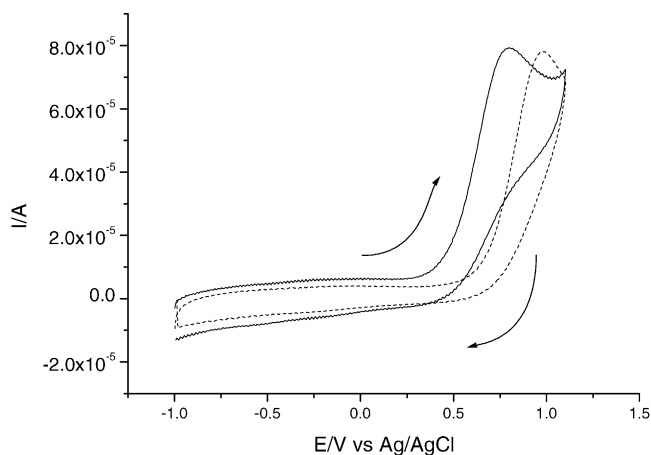


Fig. 6. Voltammetric response of the polymer-modified electrode (continuous line) and the glassy carbon (dashed line) toward the oxidation of sulfite in an aqueous solution of pH 9.55, purged with  $N_2$ . ( $SO_3^{2-}$ ) = 1 mM. Scan rate:  $0.2 V s^{-1}$ . The arrows indicate the direction of the scan. During the reverse scan, there is also an oxidation current.

the electro-oxidation of sulfite at pH 9.55. The potential where the oxidation of sulfite begins does not correspond with the couple Fe(III)/Fe(II) and does not correspond with the potential where the ligand promotes this reaction. Indeed, the oxidation wave appears at potentials closer to the shoulder shown in Fig. 4 [3,15–20], attributed to the formation of Fe(IV) species.

On the other hand, sulfate is the unique detected product of the reaction. As mentioned in literature the reaction of the radical  $SO_3^{\cdot -}$  could generate dithionate [26] although this reaction is favored in acid media. However, in this case, dithionate was not detected. It is possible that radicals  $SO_3^{\cdot -}$  rapidly react with OH generating sulfate. OH is an intermediate of the reaction of evolution of oxygen that probably occur at the potentials where the oxidation of sulfite takes place.

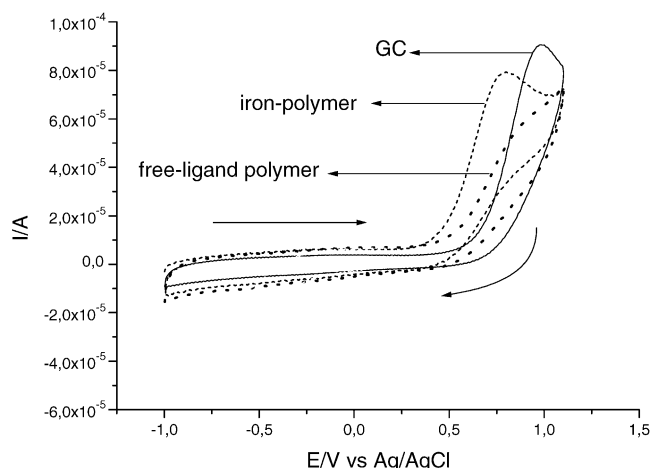


Fig. 7. Voltammetric response of the iron-polymer, the free ligand-polymer and the glassy carbon toward the oxidation of sulfite in an aqueous solution of pH 9.55, purged with  $N_2$ . ( $SO_3^{2-}$ ) = 1 mM. Scan rate:  $0.2 V s^{-1}$ . Arrows indicate the direction of the scans.

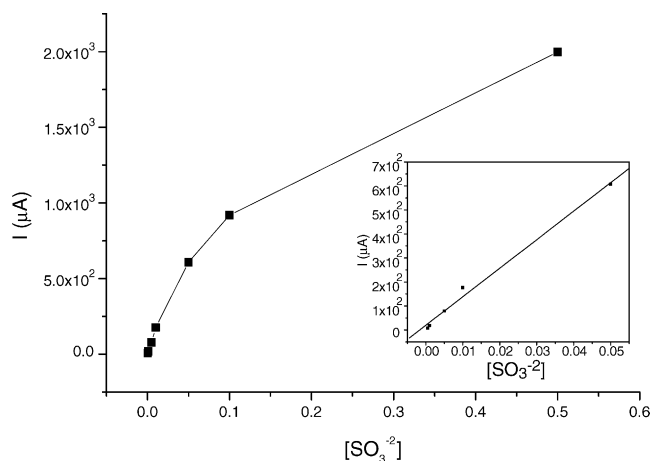


Fig. 8. Plot of  $I$  (current of the peak) vs. sulfite concentration for the polymer-modified electrode. Data taken at pH 9.55.

The detection of products was carried out after electrolysis at controlled potential (the potential of the foot of the oxidation wave, at each pH) during five hours. After the electrolysis, barium chloride was added to an aliquot of the solution and a precipitate was formed. This precipitate was weighted and then dissolved in a solution of HCl 0.1 M. In this solution, the barium sulfite was re-dissolved and the remaining precipitate corresponded to sulfate. The spectrophotometric method (described on the Experimental Section) used to detect dithionate does not show its presence within the detection limits.

On the other hand Tafel slopes values are very high (ca. 300–500 mV/decade, indicating that there is a kinetic impediment in the reaction. So, high energies are necessary to increment the current in one order of magnitude. On the other hand, the plot of  $I$  versus (sulfite) (see Fig. 8) deviates from linearity at high concentrations of sulfite showing a saturation-like behavior. As mentioned before, it can be explained as a slow recuperation of the active sites for the reaction. In accordance with this explanation, the polarization curves do not show a diffusional plateau, indicating that the reaction is not controlled by mass transport at high overpotentials. It seems that, in spite of the applied potential; the chemical step is very slow, hindering the recuperation of the active sites. On the other hand, as mentioned above, the reaction is very sensitive to the concentration of  $OH^-$ , increasing the current and decreasing the overpotential at pH higher than 8.5. A possible explanation for this behavior is that the formation of active iron species requires  $OH^-$  ions in order to increase their stability. If Fe(IV) is the active specie, it is possible that it appears as an oxo species [12–14], especially due to the over-oxidation imposed to the polymer. However, it is also possible that  $OH^-$  groups will stabilize the iron (IV) cation besides the oxo formation. Also, it is possible that when  $OH^-$  originates a radical, it reacts with a radical-sulfonate, forming sulfate as product. In order to determine the order in  $OH^-$ , the following relationship can be used:  $(\delta E / \delta pH)_i = -m(\delta E / \delta \log i)_{pH}$ , where  $m$  is the  $OH^-$  order [27], where  $(\delta E / \delta \log i)_{pH}$  is

the Tafel slope. If the Tafel slope does not change, it is possible to use this relationship to obtain  $m$ . In this case, it is necessary to interpolate  $E$ , at constant  $i$ , from a graph containing the Tafel curves obtained at different pHs. Then, the slope of the plot of  $E$  versus pH is  $m$  times the Tafel slope. Using the data obtained in the pH range 9–11, an order equal to one in  $\text{OH}^-$  is obtained. That could indicate that the  $\text{OH}^-$  stabilizes the active iron species. On the other hand,  $\text{OH}^-$  oxidized (as a radical) could participate in forming sulfate, as mentioned before. However, a radical–radical interaction is a very fast reaction and must occur after the rate-determining step.

#### 4. Conclusions

Fe-tetra (4-aminophenyl)porphyrin, when electropolymerized and over-oxidized, is an efficient electrocatalyst for the conversion of sulfite into sulfate. In fact, the electrodic system obtained showed great stability and important catalytic activity for the oxidation of sulfite, in 3–13 pH range, rendering sulfate as the unique detectable product. It diminishes the overpotential required in glassy carbon in almost 200 mV at pH 9.5. The polymeric-modified electrode is very stable and operates in a wide range of pH. The couple responsible for the catalysis is probably Fe(IV)/Fe(III) as can be determined by the potential where the reaction begins. The recovery of the active sites is slow, and at high concentrations of sulfite, there is no linear correlation between the current of the oxidation and the concentration. This slowness prevents the use of this electrocatalyst for the amperometric sensor of sulfite at high concentrations. However, there is a good linearity at low concentrations. The reaction depends on the  $\text{OH}^-$  concentrations at pH higher than 8.5. The electrode modified by layers of the monomer is not stable and cannot be used for this reaction.

#### Acknowledgements

Authors acknowledge Fondecyt (project 1010695) financial support. M.L., G.R., I.A. and A.R. acknowledge Conicyt Doctoral Fellowship. G.R. acknowledges a fellowship (AT-403139) for thesis research.

#### References

- [1] C. Lion, L. Da Conceicao, H. Sayag, C.R. Acad. Sci. Ser. II. C. 2 (1999) 57.
- [2] M.H. Ali, M. McDermott, Tetrahedron Lett. 43 (2002) 6271.
- [3] S.-M. Chen, S.-W. Chiu, Electrochem Acta 45 (2000) 4399.
- [4] N. Rea, B. Looock, D. Lexa, Inorg. Chim. Acta 312 (2001) 53.
- [5] S.-M. Chen, J. Molec. Cat. A: Chem. 112 (1996) 277.
- [6] O. Chailapkul, P. Aksharanandana, T. Frelink, Y. Einaga, A. Fujishima, Sens Actuators, B: Chem. 80 (2001) 193.
- [7] M.F. Zippies, W.A. Lee, T.C. Bruice, J. Am. Chem. Soc 108 (1986) 4433.
- [8] E. Trollund, P. Ardiles, M.J. Aguirre, S.R. Biaggio, R.C. Rocha-Filho, Polyhedron 19 (2000) 2303.
- [9] B.D. Berezin, Coordination compounds of porphyrins and phthalocyanines, John Wiley & Sons, New York, 1981.
- [10] R.W. Murray, Ann. Rev. Matter Sci. 14 (1984) 145.
- [11] C.M.C.P. Manso, C.R. Neri, E.A. Vidoto, H.C. Sacco, K.J. Ciuffi, L.S. Iwamoto, Y. Iamamoto, O.R. nascimento, O.A. Serra, J. Inorg. Biochem. 73 (1999) 85.
- [12] C.C. Guo, J.X. Song, X.B. Chen, G.F. Giang, J. Molec. Catal. A: Chem. 157 (2000) 31.
- [13] H. Fujii, Coord. Chem. Revs. 226 (2002) 51.
- [14] W. Nam, M.H. Lim, S.Y. Oh, Inorg. Chem. 39 (2000) 5572.
- [15] R. Boulatov, J.P. Collman, I.N.M. Shiryayeva, C.S. Sunderland, J. Am. Chem. Soc. 124 (2002) 11923.
- [16] Ibid, Supplementary information.
- [17] J.P. Collman, R. Boulatov, C.J. Sunderland, I.M. Shiryayeva, K.E. Berg, J. Am. Chem. Soc. 124 (2002) 10670.
- [18] Ibid, Supplementary Information.
- [19] T.W. Kaaret, G.-H. Zhang, T.C. Bruice, J. Am. Chem. Soc. 113 (1991) 4652.
- [20] B. He, R. Sinclair, B.R. Copeland, R. Makino, L.S. Powers, I. Yamazaki, Biochemistry 35 (1996) 2413.
- [21] G. Cornejo, G. Ramírez, M. Villagrán, J. Costamagna, E. Trollund, M.J. Aguirre, J. Chil. Chem. Soc. 48 (2003) 49.
- [22] K.M. Kadish, E. Van Caemelbecke, G. Royal, Electrochemistry of Metalloporphyrins in Nonaqueous Media “The Porphyrin Handbook”, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), Electron Transfer, Vol. 8, Academic Press, 2000, pp. 38–55 (and references therein).
- [23] G. Ramírez, E. Trollund, J.C. Canales, M.J. Canales, F. Armijo, M.J. Aguirre, Bol. Soc. Chil. Quím. 46 (3) (2001) 247–255.
- [24] M.S. Ureta-Zañartu, C. Berríos, J. Pavéz, J. Zagal, C. Gutiérrez, J.F. Marco, J. Electroanal. Chem. 553 (2003) 147.
- [25] T. Malinski, Porphyrin-Based Electrochemical Sensors, The Porphyrin Handbook, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), Applications: Past, Present and Future, Vol. 6, Academic Press, 2000, p. 234.
- [26] T. Ozawa, T. Kwan, Polyhedron 4 (1985) 1995.
- [27] J. Bard, L.R. Faulkner (Eds.), Electrochemical Methods, Fundamentals and Applications, John Wiley & Sons, New York (USA), 1980, p. 151.