J Solid State Electrochem (2010) 14:1065–1072
DOI 10.1007/s10008-009-0916-0

ORIGINAL PAPER

Nafion/tetraruthenated porphyrin glassy carbon-modified electrode: characterization and voltammetric studies of sulfite oxidation in water–ethanol solutions

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Received: 14 April 2009 / Revised: 28 July 2009 / Accepted: 3 August 2009 / Published online: 26 August 2009

Abstract In this work, the modification of a glassy carbon electrode with tetraruthenated porphyrins electrostatically assembled onto a Nafion film, previously adsorbed on the electrode surface, is reported. This modified electrode was characterized by scanning electron microscopy–energy-dispersive X-ray, Raman spectroscopy, UV-Vis spectroelectrochemistry, and cyclic voltammetry. The Nafion film onto the glassy carbon electrode shows a smooth disposition; when the tetraruthenated porphyrin is incorporated on the Nafion film, the complex is adsorbed in a homogeneous way. The modified electrode catalyzes HSO_3^- oxidation in water–ethanol solutions and shows an enhanced stability compared with the electrode modified with the dip coating method. Rotating disk electrode experiments showed a kinetic limitation to the electron transfer controlled by charge propagation in the film. *I*/*E* curves show a Tafel slope of 120 mV/decade corresponding to a first electron-transfer reaction, depending on the potential, as the determining step. Spectroelectrochemical experiments demonstrated that Ru(II) is the active site for the electrocatalysis.

Keywords Sulfite · Tetraruthenated porphyrins · Modified electrodes · Nafion membranes · Electrocatalysis

Introduction

The sulfite anion has been extensively used in the food and beverages industries [1]. In the wine industry, the SO_3^{2-} anion is used as an antioxidant and antiseptic agent, the SO_2 gas being the active specie [2]. One of the most used analytical methods worldwide in the wine industry is a classical volumetric method based in the titration of SO_3^{2-} with I_2 (Ripper's method) [3]. When red wines are analyzed, starch used as an indicator originates problems with the detection of the end point of the titration. The other method employed consists in the volatilization of SO_3^{2-} to SO_2. The gas is oxidized, in acid media, to SO_4^{2-} and then titrated as H_2SO_4 [4, 5]. But this method is time consuming and may involve loss of samples and consequently loss of precision [6].

Electronic supplementary material The online version of this article (doi:10.1007/s10008-009-0916-0) contains supplementary material, which is available to authorized users.

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From the explanations above, the need to develop new methods is understood, which need to be precise, accurate, fast, and inexpensive. Considering that the wine industry in Chile is one of the most important economical activities, the design of modified electrodes with sensing capabilities to S(IV) oxoanions is of great relevance.

With this idea in mind, electrochemistry appears as a powerful tool offering a variety of techniques. Indeed, electrochemical methods have been broadly used in the determination of sulfite. These methods can be classified into two major groups: potentiometric [7–9] and amperometric [10, 11]. In the first case, chemical transformation from SO_3^{2-} to SO_2 is necessary, and the determination as a gas diffusion electrode either in flow or static analysis has been performed [10, 12–15]. In the second case, several methods involve the amperometric detection with enzyme-modified electrodes, but in these cases low stability is one of the main drawbacks [12, 16].

A novel way to examine this problem using electrochemical techniques is the use of glassy carbon electrodes modified with macrocyclic complexes containing transition metals [17–21]. This kind of electrodes are usually selective because previous to the electron transfer the analyte coordinates to the active center (normally the central metal ion), forming an adduct. The potential at which the adduct reacts depends on the metallic center, substituents in the periphery of the macrocycle and the electrodic surface modified by the complex [17–21].

Metallic porphyrins have catalytic activity towards the oxidation of sulfite at basic pH [22]. Polymerized Ni protoporphyrins in an arranged submonolayer allow the analysis of sulfite ion either in stationary or flow injection analysis. In this case, the results show a linear range until 9 μg ml^{-1} and a limit of detection of 0.15 μg ml^{-1}, showing that with this kind of electrochemical method it is possible to achieve high sensibilities [23].

In 1993, Toma et al. [24] prepared a supramolecular porphyrin containing four units of $[Ru(bpy)_2\ Cl]^+$ (bpy= 2,2′bypyridine) coordinated to pyridinic moiety of a Co(III) meso-(pyridyl)porphyrin (CoTRP), i.e., a tetraruthenated porphyrin [25]. From this point, this group has presented an astonishing amount of work related with this kind of porphyrins [24–29]. The main characteristic of these complexes is that they are able to produce numerous redox processes working as a pump of electrons, for example, the Ru(III)/Ru(II) redox couple presents a four-electron simultaneous voltammetric wave. However, the authors have explained that one of the most important problems in the use of these compounds is related to its high positive charge (4+), making them very soluble in water, redissolving the complex from the electrode to the test solution. Several efforts have been developed to solve this problem, for example, the incorporation of large amounts of triflate ion into the test solution and building up of layer by layer-modified electrodes with water-soluble negative phthalocyanines or porphyrins, as well as the design of conducting polymers giving different results but improving the stability of the electrode in all the cases [30, 31]. One of the ways that have not been explored to our best knowledge is the use of films produced with ionomeric membranes to anchor these complexes onto the surface of glassy carbon electrodes.

It is known that chemically inert ionomeric membranes such as Nafion can be used to produce films onto several electrodic surfaces [32–36]. Nafion is a tough, chemically inert, gas-permeable ionomer material fabricated in thin films by copolymerization of tetrafluoroethylene and sulfonyl fluoride vinyl ether. Its microscopic structure comprises a chemically inert hydrophobic skeleton of perfluorinated alkyl chains from which ramifications via the ether bond arise. These lateral chains end hydrophilic sulfonate groups resembling the polar heads of surfactant molecules [36]. Modified electrodes with Nafion® and charged porphyrins have been used in the electrocatalytic oxidation of nitrite and nitric oxide and the reduction of oxygen among others [32–36].

The aim of this paper is to prepare and characterize a modified electrode formed by a glassy carbon electrode coated with a Nafion film where a Co tetraruthenated porphyrin is adsorbed; the electrocatalytic properties of this modified electrode are tested toward the oxidation of HSO_3^- in water–ethanol solutions resembling a wine sample with the purpose of designing a suitable electrochemical sensor for the former analyte.

In this paper, Nafion polymer was used as a support of TRP's complexes, immobilized by electrostatic and hydrophobic interactions. The electrode was characterized by microscopic, spectroscopic, and electrochemical methods regarding the study of the oxidation of HSO_3^- in water–ethanol solutions. Also, a comparison with the traditional dip coating method of modification is presented; an evaluation is made on the stability of this modified electrode. On the other hand, rotating disk electrode (RDE) voltammetry and UV-Vis spectroelectrochemistry were used to understand the kinetic factors affecting the oxidation of HSO_3^- with this modified electrode in this medium.

Experimental

Materials

All chemical reagents were of analytical grade. Nafion® 117 solution (5 wt.% alcohol solution) was purchased from Fluka Chemica. Cobalt(II) acetate, 5,10,15,20 tetrapyrydil

21H, 23H porphine, tetrabutylammonium hexafluorophosphate ($TBAPF_6$), sodium perchlorate, and sodium sulfite were purchased from Sigma-Aldrich. Lithium chloride was purchased from Fisher Scientific.

Electrochemical-grade ammonium hexafluorophosphate (NH_4PF_6) was purchased from Alfa Aesar. Solvents acetonitrile (ACN), *N*,*N′*-dimethylformamide, methanol, ethanol, acetone, and glacial acetic acid and neutral alumina were purchased from Merck.

The precursor complex *cis*-dichloro (2,2′-bipyrydine) ruthenium(II) dihydrate was prepared following the procedure described in the literature [37]. The supramolecular complexes of Co(II) and free metal center μ-{*meso*-5,10,15,20-tetra(pyridyl)porphyrin}tetrakis{bis(bipyridine)(chloride) ruthenium(II)} $(PF_6)_4$ (CoTRP) were prepared by the method described by Toma et al. [25]. The purity of this compound was checked by optical absorption spectroscopy, elemental analysis, and ^{1}H nuclear magnetic resonance (^{1}H-NMR).

Apparatus

The UV-visible spectra were recorded on a Shimadzu Multispec 1501 spectrophotometer; ^{1}H-NMR spectra were registered on DMSO-d^6 samples on a Bruker Avance 400 instrument; cyclic voltammetry (CV) experiments were carried out using a potentiostat CH Instrument 620B model. RDE experiments were carried out with a speed control unit CTV101 Radiometer Analytical and a BM-EDI101 Radiometer Analytical rotation unit. The Raman spectra were recorded with a Renishaw Raman Microscope System RM1000 equipped with a diode laser (providing the 633-nm laser line) microscope. The spectra shown here were obtained by using a ×10 objective. Morphologic characterization was performed by scanning electron microscopy (SEM)–energy-dispersive X-ray on a JEOL 6400 SEM equipped with Oxford Link Isis EDX detector.

Cell and electrodes

CV was performed in a three-electrode Pyrex glass cell. Working electrodes were glassy carbon disks, purchased from CH Instruments (r=1.5 mm) and Radiometer Analytical (r=3 mm); auxiliary electrode was a Pt wire, and reference electrode was Ag/AgCl both from CH instruments. For spectroelectrochemical experiments, an indium tin oxide (ITO) electrode from Delta Technologies was utilized (A=1.89 cm^2).

In the case of CV performed in organic solvents, a modified Luggin capillary containing a Pt wire as a bridge was used to avoid any contact between the solution containing the complex and the aqueous solution.

After each experiment, the GC electrode was polished with 0.3-μm alumina slurry (Struers). The electrode was rinsed with double-distilled deionized water and cleaned in an ultrasonic water bath for 30 s to remove any remaining alumina and then rinsed again with abundant deionized water.

The aqueous electrochemical experiments were performed in a water–ethanol solutions containing 0.02 M tartaric acid, 0.1 M $NaClO_4$, and 12% ethanol; the pH was fixed at 3.5 with drops of 0.1 M NaOH. Variable sulfite concentrations were obtained, diluting a mother extract in the water–ethanol solutions [38].

Procedure for the preparation of the modified electrodes

GC/CoTRP-modified electrode The GC electrode was immersed into a 1-mM methanolic solution of the complex for 4 min. After that, the electrode was left to dry at room temperature for 10 min. The electrode was then rinsed with abundant deionized water and used without further modifications.

GC/Nf/CoTRP-modified electrode Five microliters of 1% Nafion solution diluted in methanol was placed on the surface of the GC electrode, and it was allowed to dry at room temperature (drop coating). The electrode was dipped into a 1-mM methanolic solution of the complex for 4 min (dip coating). The electrode was left to dry at room temperature; after 10 min, the electrode was rinsed with deionized water. The electrode modified with this procedure was placed in the electrochemical cell without further modifications.

Results and discussion

Electrochemical characterization of complex in organic solvent

The cyclic voltammetric behavior of CoTRP (see Fig. 1 in a 1 mM ACN and 0.1 M $TBAPF_6$ solution) was recorded at 100 mV s^{-1}. The results are in good agreement with those reported previously by the Toma and Lexa groups; see Table 1 [38–42].

Characterization of modified electrode

Figure 2 shows the Raman characterization of GC/Nf/CoTRP-modified electrode. Figure 2a displays the Raman spectrum of solid CoTRP complex where the main bands correspond to 1,369-, 1,249-, and 404-cm^{-1} vibrational peaks associated with porphyrin skeletal modes, 1,500- and 1,318-cm^{-1} vibrational peaks associated with vibrational modes of bipyridine ligand, 1,217- and 1,020-cm^{-1} vibra-

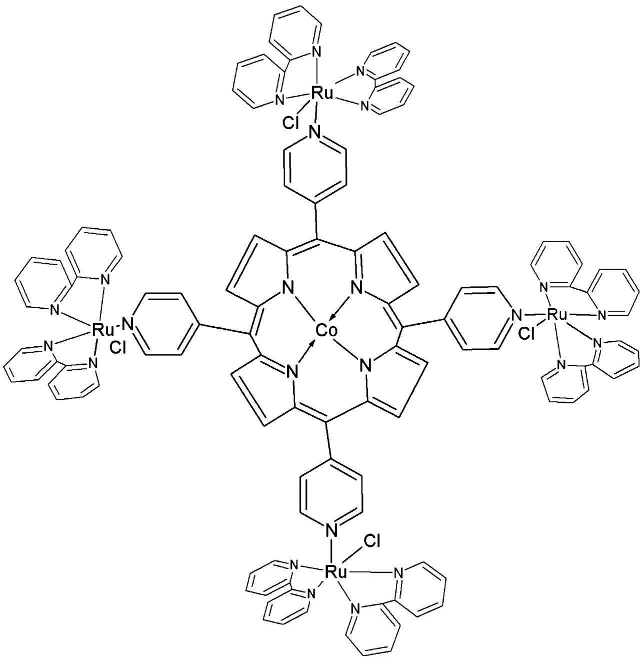

Fig. 1 Structure of μ-{*meso*-5,10,15,20 tetra(pyridyl)porphyrin}tetrakis{bis(bipyridine) (chloride) ruthenium (II)}$(PF_6)_4$ (CoTRP)

tional modes corresponding to pyridine or porphyrin vibration strongly coupled with the π ring, and finally 1,608 and 1,564 cm^{-1} involved in bridging the pyridine and bipyridine groups [43, 44]. Whereas Fig. 2b shows Raman spectrum of the modified electrode, no remarkable differences are observed, indicating that CoTRP complex does not change its structure, and no new bonds are formed between the sulfonate groups and CoTRP complex.

Additionally, SEM characterization of GC/Nf/CoTRP-modified electrode can be seen in the "Electronic supplementary material." When CoTRP complex is placed, after the Nafion film formation on the GC surface, a thick and rough coating is observed, indicating that the complex is distributed in a homogeneous way without preferences for specific sites in the film [36, 40, 45].

Voltammetric studies of HSO_3^- oxidation in water–ethanol solution using modified electrodes

Figure 3a displays the cyclic voltammograms corresponding to GC/CoTRP-modified electrode in water–ethanol solution in the absence and presence of 1 mM HSO_3^-, at pH=3.5 and recorded at 100 mV s^{-1}.

Table 1 Redox potentials (V vs. Ag/AgCl de CoTRP) in ACN solution

Compounds	Porph$^{(-/-2)}$	Porph$^{(0/-)}$	Co$^{(3+//2+)}$	Ru$^{(3+//2+)}$
CoTRP	−1.1[a]	−0.44[a]	0.37[a]/0.37[b]	0.85[a]/0.84[b]

[a] This work

[b] [39, 40]

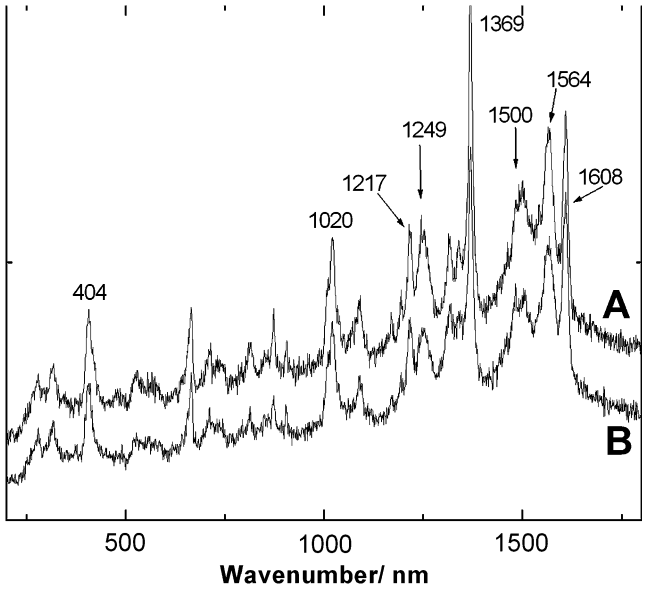

Fig. 2 Raman spectra of the **a** solid CoTRP and **b** modified electrode GC/Nf/CoTRP, both excited with 633-nm laser line

When the supporting electrolyte does not contain HSO_3^- anion, an anodic peak at *approximately* 0.8 V corresponding to the Ru(III)/Ru(II) redox couple is observed; the voltammetric peak is electrochemically quasireversible with a ΔEp=0.125 V. At negative potential, no other redox processes are observed. The behavior of Ip$_{a,c}$ vs v shows a linear relationship, indicating that the redox process of the confined species in the film is adsorption-controlled (not shown). When 1 mM of HSO_3^- is added to the solution, an enhancement in the Ip$_a$, i.e., Ru(III)/Ru(II) redox process, is observed. This enhancement of the current is associated with the oxidation of HSO_3^- to SO_4^{2-} [38].

As a stability test, GC/CoTRP-modified electrode was cycled 100 times in 1 mM HSO_3^- water–ethanol solution; GC/CoTRP was rinsed, and a new CV was performed in a solution containing only supporting electrolyte; the current of the Ru(III)/Ru(II) redox process decreases its intensity by 17%, compared to the initial curve without HSO_3^-. In fact, the charge under the voltammetric peak changes from 17.5 to 15 μF after the continuous swept of the electrode. This fact suggests that the GC/CoTRP-modified electrode lost its original activity for a leaching of the complex to the solution, indicating a low stability.

Figure 3b is equivalent to Fig. 3a, but, now, the GC/Nf/CoTRP-modified electrode is used. Several differences can be observed comparing with GC/CoTRP-modified electrode. The area under the voltammetric peak is bigger than the analogous GC/CoTRP, indicating a larger amount of active complex adsorbed. Therefore, the oxidation of HSO_3^- reaches an Ip$_a$ of 78 μA. Also, when the stability

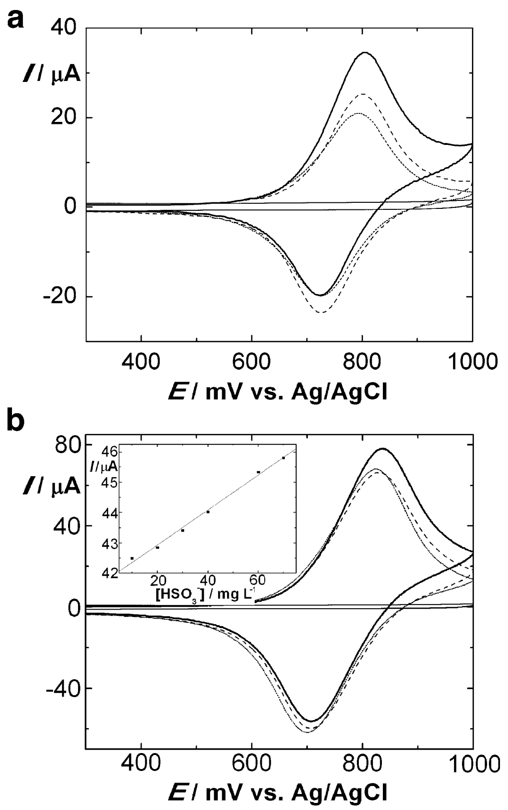

Fig. 3 **a** Cyclic voltammograms of GC/CoTRP-modified electrode at pH 3.5 in water–ethanol solution. GC/CoTRP initial test (*straight dash line*), GC/CoTPRP final test (*short dash line*), GC/CoTRP with 1 mM HSO_3^- (*thick solid line*), glassy carbon electrode without HSO_3^- (*thin solid line*). Scan rate 100 mV s^{-1}. **b** Cyclic voltammograms of GC/Nf/CoTRP-modified electrode at pH 3.5 in water–ethanol solution. GC/Nf/CoTRP initial test (*straight dash line*), GC/Nf/CoTPRP final test (*short dash line*), GC/Nf/CoTRP with 1 mM HSO_3^- (*thick solid line*), glassy carbon electrode without HSO_3^- (*thin solid line*). Scan rate 100 mV s^{-1}. *Inset*: plot of peak current vs HSO_3^- concentration

test is performed to GC/Nf/CoTRP-modified electrode, the current of the Ru(III)/Ru(II) redox couple is practically the same compared to the original voltammogram, even though the GC/Nf/CoTRP-modified electrode was left in laboratory conditions for 90 days, and the voltammetric peak of Ru (III)/Ru(II) redox couple keeps its original intensity; in this case, the Nafion film provides a stable support to the complex CoTRP.

The Ip_a current shows a linear relationship with the concentration of HSO_3^- (see the inset in Fig. 3b) [38]. This electrode presents a linear range from 0 to 70 mg l^{-1} with a limit of detection of 7.7 mg l^{-1}.

In order to detect HSO_3^- in real wine samples, several interferences should be considered; among them, phenolic compounds are the main group [46–48]. Indeed, in red wine, at least two families of phenolic compounds are present; simple compounds such as caffeic, gallic, and vanillic acids and also more complex structures such as polyphenols and flavylium cation derivatives which include anthocyanin structure. These compounds present oxidation processes very dependent on their structures, phenolic acids present oxidation processes around 0.4 V vs Ag/AgCl. In anthocyanins, the oxidation processes is shifted to more positive potentials at *approximately* 0.65 V vs Ag/AgCl [46–48]. Thus, these two families of organic components in wine may possibly be considered interferences to the determination of HSO_3^- using GC/Nf/CoTRP-modified electrode. However, it has been informed recently that there is a suitable sample treatment considering column chromatographic separations [49]. This method is currently under research in our laboratory.

Spectroelectrochemistry studies of HSO_3^- oxidation in water–ethanol solutions using modified electrodes

In general, the electronic spectra of porphyrins are characterized by several π–π* transition bands; the most remarkable are those related with a broad absorption band at approximately 430 nm (Soret Band) and four to one less intense Q bands, depending on whether the porphyrin is metal free or not, since metallated porphyrins present a minor symmetry [50].

Coordination of peripheral complexes disturbs the porphyrin π system, and this effect has been shown to be strong enough to influence significantly the electronic spectra of the chromophores constituting those supramolecular porphyrins. In organic solvent (ACN), CoTRP exhibits a porphyrin Soret band and the two Q bands at 434, 546, and 594 nm, respectively, and the bands of peripheral complexes at 298 (bpy π–π*), 354 (MLCT2), and 490 nm (MLCT) [39].

Figure 4a displays the spectroelectrochemical behavior of an ITO electrode modified by the same procedure explained in the experimental part for glassy carbon electrode. The spectrum of ITO/Nf/CoTRP-modified electrode at open-circuit potential shows a Soret band at 437 nm, two Q bands at 555 and 595 nm, respectively, and the bands of peripheral complexes at 298 (bpy π–π*), 354 (MLCT2), and 490 nm (MLCT). After the application of 0.8 V, the band at 298 nm, associated with the pπ → pπ* transition centered in the bipyridine ligand, is split into two peaks 302 and 313, respectively; the MLCT band assigned as a Ru → bpy centered at the region 480–500 nm decreases its intensity. These spectroscopic changes are consistent with the oxidation of the $Ru(bpy)_2Cl^+$ moieties. Finally, the increase and small blue shift of the Soret band during the constant application of potential is an indicative of an electronic coupling among $Ru(bpy)_2Cl^+$ moieties and the porphyrin unit [40, 51].

On the other hand, the spectroelectrochemical results in the presence of HSO_3^- (see Fig. 4b) show that the Soret

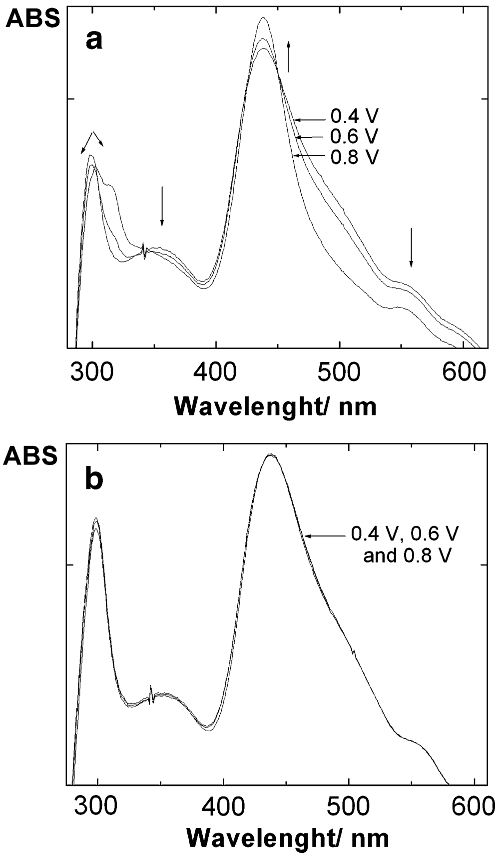

Fig. 4 Spectroelectrochemistry of GC/Nf/CoTRP-modified electrode at pH 3.5 in water–ethanol solution. Applied potentials: 0.4, 0.6, and 0.8 V. **a** Without HSO_3^-, **b** with 1 mM HSO_3^-

band and bpy ligand are practically the same after the application of constant potential (0.8 V). This fact could imply that the addition of HSO_3^- inhibits the oxidation of the peripheral Ru units. Keeping the oxidation state of the peripheral metal as 2+, in this case, the peripheral metal might be working as an electron relay, indicating that the active species in the CoTRP complex is Ru(II). Moreover, the formation of intermediary species between Ru(II) moieties and HSO_3^- is not observed, in contrast to other cases of Co(II) porphyrins or other related macrocycles without the peripheral substituent complexes [52, 53].

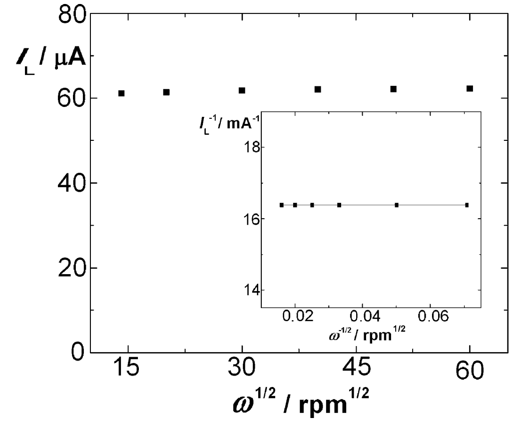

Fig. 5 Levich plot. *Inset*: Koutecky–Levich plot of GC/Nf/CoTRP-modified electrode at pH3.5 in water–ethanol solution containing 1 mM HSO_3^-

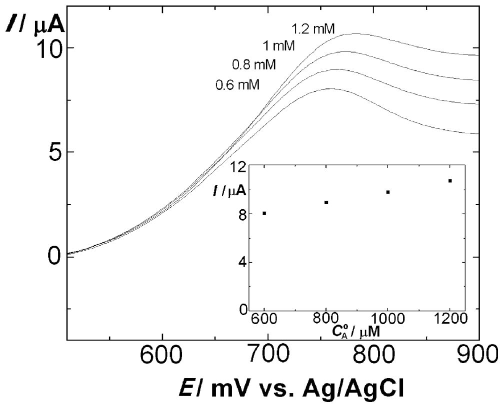

Fig. 6 RDE voltammetry of the GC/Nf/CoTRP-modified electrode at pH 3.5 in water–ethanol solution in the presence of increasing amounts of sulfite. *Inset* plot $C_A°$ vs I_L

In order to elucidate the electrochemical mechanism that controls the oxidation of HSO_3^- in these modified electrodes, RDE experiments were performed. From the *I–E* polarization curves, it is possible to produce Levich plots that correlate I_L versus $\omega^{1/2}$, where I_L, the limiting current, represents the current of the plateau and ω is the electrode rotation rate (see Eq. 1):

$$I_L = 0.62\, n\, F\, D^{2/3} \upsilon^{1/6} c^{\infty} \omega^{1/2} \tag{1}$$

where F is Faraday's constant; D is the diffusion coefficient; ν is the kinematic viscosity of the solution, and C is the bulk concentration [54–56]. Figure 5 displays the I_L vs $w^{1/2}$ diagram (Levich plot). A linear behavior of the limiting current is observed with the inverse of the square

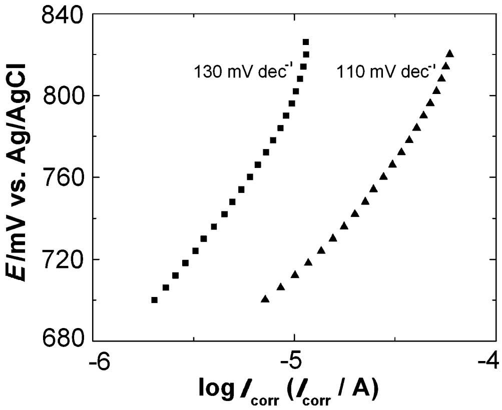

Fig. 7 Tafel plots for the HSO_3^- oxidation on the GC/Nf/CoTRP-modified electrode in water–ethanol solution, *square*: GC/CoTRP (130 mV dec^{-1}); *triangle*: GC/Nf/CoTRP (110 mV dec^{-1}). Sweep rate 5 mV s^{-1}

root of rotation rate, and the intercept does not pass through the origin; these facts involve a kinetic factor more important than the diffusion of the HSO_3^- anion to the electrodic surface. On the other hand, a Koutecky–Levich plot (see the inset in Fig. 5), i.e., I_L^{-1} vs $w^{-1/2}$, clearly shows that the limiting current does not depend on the rotation frequency, with a slope of *approximately* 0 and an intercept at 61 μA.

According to the Andrieux-Saveant theory [57–62] about kinetics in modified electrodes with polymer-electroactive coatings, I_L in RDE is governed for five characteristic currents: i_A the mass transfer rate of the substrate A, in solution to a bare electrode which in this case is HSO_3^- anion; i_S is the mass transfer of the substrate A in the film; i_E is defined as the effective charge transfer rate via a mediator which in this case is the Ru^{III}/Ru^{II} redox couple; i_k is the rate of the cross-exchange reaction between HSO_3^- and the mediator, and finally i_P is the mass transfer rate of the substrate across the film solution interface. However, in most experimental systems, only one or two of these contributions become important; then, according to Saveant and coworkers, three limit situations are achieved:

Case R, the cross-exchange reaction
Case S, the mass transfer of the substrate within the film
Case E, charge propagation (via mediator) through the film

Several diagnostic criteria have been developed to determine through Koutecky–Levich plots the kinetic factor with major contribution; in the present work, a linear Koutecky–Levich plot with a slope=0 is a clear indication that the factor governing the kinetics of the process is the charge propagation through the film. A complementary experiment is shown in Fig. 6 where the plot *I* vs *E* at different concentrations of HSO_3^- at 1,600 rpm is displayed; the current is proportional to the concentration (see the inset in Fig. 7); however, the plot shows a straight line that does not pass through the origin. This behavior corroborates the slow charge propagation in the film [54].

Additionally, Fig. 7 presents the Tafel plots for the oxidation of HSO_3^- at 3,600 rpm, where the *I–E* curves correspond to low-polarization region. These plots present slopes of 138 and 116 mV decade^{-1} for GC/CoTRP- and GC/Nf/CoTRP-modified electrodes. These values verify that a first electron-transfer reaction, depending on the potential, is the determining step [63].

Conclusions

A simple and stable modification method of a glassy carbon electrode has been developed by adsorption of Co(II) tetraruthenated porphyrin onto Nafion films previously formed on the electrodic surface. After the adsorption of the complex on the Nafion film, the structure of the CoTRP complex does not undergo any changes, and the formed film presents a thick morphology. From CV experiments, a linear correlation between *I*pa and the concentration of HSO_3^- anion is observed. Considering that the amount of HSO_3^- in wines in many countries present a range between 10 and 40 mg l^{-1}, it is considered that these results are in good accordance with the methods currently in use, suggesting a potential use of GC/Nf/CoTRP-modified electrode as sensor to HSO_3^-, after a suitable pretreatment of the sample, in the wine industry. In addition, from RDE experiments, it was possible to observe that a diffusional control is not governing the electron-transfer process of oxidation of HSO_3^- on GC/Nf/CoTRP-modified electrode. Moreover, complementary results indicate that the charge propagation in the film is the main kinetic factor affecting the whole oxidation process. On the other hand, Tafel slope indicates that the rate-determining step is the first electron transfer without a previous chemical path. Finally, spectroelectrochemical results show that Ru moieties are working as electron relays where no adduct or intermediary complex formation can be observed in the timescale of the experiment [52–54].

Acknowledgements This work was supported by the program “Anillo Bicentenario de Ciencia y Tecnología CONICYT” ACT No. 24. AECID and A/012666707 PCI projects. KC is grateful to CONICYT for the doctoral scholarship.

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