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Electrocatalytic oxidation and reduction of S(IV) Species by 5,10,15,20-Tetrakis-Tetraferrocenylporphyrin-Modified Electrodes.

J.P. Muena[*], *M. Villagrán, M.J. Aguirre*

Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, USACH, Av. Bernardo O'Higgins 3363, Estación Central, Santiago, Chile.
[*]E-mail: juan.muena@usach.cl

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5,10,15,20-tetrakis-tetraferrocenylporphyrin ($TFcPH_2$) free ligand was synthesized and characterized by spectroscopic (UV-Vis, ^{1}HNMR, FT-IR) and electrochemical (cyclic voltammetry) techniques. The electrocatalytic oxidation of S(IV) species in aqueous media mediated by two modified electrodes was studied. In both cases, tetraferrocenylporphyrin was used to modify electrodes. Glassy carbon electrode was modified by *drying-drop* method, whereby a drop of concentrated solution ($\approx 10^{-4}$ M) of the porphyrin was applied to the electrode surface and allowed to dry (DDE electrode), and carbon-paste was modified with solid porphyrin (CPE electrode). DDE electrode shows electrocatalytic activity toward the sulfite oxidation only for one cycle. Loss of activity of this modified electrode was attributed to the formation of a stable adduct between the porphyrin and the product of the oxidation of sulfite. However, $TFcPH_2$ absorbed on glassy carbon electrodes shows electrocatalytic activity toward the sulfite reduction in acid media. The catalytic current peak was linearly dependent on the sulphite concentration over concentration 0.03 – 1.4 mM, and the detection limit is 22μM under optimized conditions.

Keywords: Ferrocenyl Porphyrin, Electrocatalysis of S(IV), Modified Electrodes, Carbon Paste Electrodes, Amperometric Sensor

1. INTRODUCTION

There is an increasing demand for simple, inexpensive and rapid analytical test to determine the concentration of biological and environmental compounds. Particularly, electrochemical techniques have been studied for these applications and much interest has been centered on the use of carbon as an inexpensive substrate for electrochemical techniques. But owing to the often impractically high activation overpotential that is required for the oxidation or reduction at a carbon surface, it rarely lends itself to direct environmental analysis; one field that offers great scope is chemically modified electrodes (CMEs)[1-4], where working electrodes have been achieved through judicious surface modifications with various redox mediators, that facilitate charge transfer between the electrode and an electroactive species in solution at much lower potentials than it would be possible otherwise. Among the various mediators used for electrode modifications, the porphyrins macrocycles have attracted the attention as excellent electron transfer mediators, due to their high stability, and the redox potentials can be modified by changing the metal coordinated at the macrocycle[5-13].

On the other hand, the sulfite is commonly used in the food industry as apreservative, but high levels of sulfite produce poisonous effects on asthmatic people, gastrointestinal problems, and mutagenic and Co-mutagenic effects [14]. For this reason, it becomes necessary to look for simple methods for sulfite determination to facilitate the quality control of food industry products. Also, it is known that the ion sulfite (SO_3^{2-}), when dissolved in water, balances with the ion bisulphite (HSO_3^-) and sulfur dioxide (SO_2), whose relative concentrations depend on the pH of the solution. For pH between 7 and 10 used in present study the dominant electroactive species is the ion sulfite and pH< 2.0, being sulfur dioxide the dominant electroactive species[14].

In this research it was synthetized, spectroscopic, and electrochemically characterized the ligand 5, 10, 15, 20-tetrakis-tetraferrocenylporphyrin (there after $TFcPH_2$). This substituted porphyrin isused to study the electrocatalytic oxidation and reduction of the S(IV) species in aqueous media. The drying-drop and carbon paste electrodes were prepared using 5, 10, 15, 20-tetrakis-tetraferrocenylporphyrin ($TFcPH_2$) as electron transfer mediator.

2. EXPERIMENTAL

2.1. Apparatus

IR-TF spectra (KBr pellet) were recorded between 4000 and 400 $cm^{-1}$by a spectro photometer Bruker IFS- 66V.

UV-visible spectra were recorded in dichloromethane (CH_2Cl_2) solutions using a Specord S100 along with Aspec Plus software.

Voltammetric characterization was performed using a CH 604Cbipotentiostat. All the voltammetric measurements were carried out in a conventional three-electrode cell at room temperature 20°C.

Reagents:

For electrochemical experiments, dichloromethane p.a. from Merck and tetrabutyl ammonium perchlorate (TBAP)99% from Across-Organics, were used without further purification. All solutions were prepared by using deoxygenated and doubly distilled water. All other chemicals were of analytical grade and used as provided. A home-made Britton Robinson buffer was used in each voltammetric experiment. Sodium sulfite was from Merck.

2.2. Preparation and spectroscopic characterization of 5,10,15,20-tetrakis-tetraferrocenylporphyrin (TFcPH$_2$).

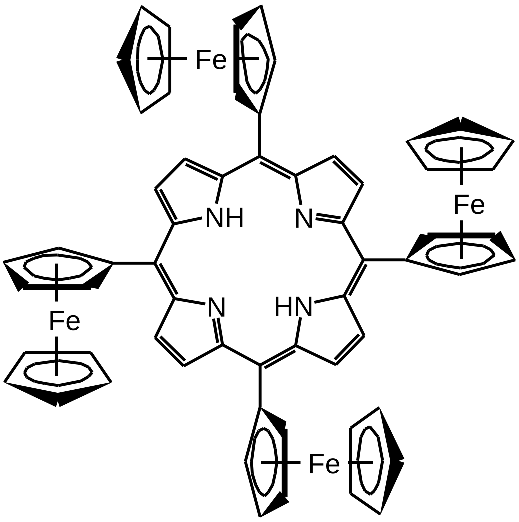

Figure 1. Molecular structure of 5,10,15,20-tetrakis-tetra ferrocenylporphyrin.

5,10,15,20-tetrakis-tetra ferrocenylporphyrin (Fig. 1) was synthesized and characterized as previously described [15-17]. A mixture of ferrocenecarboxaldehyde (2.4 g, 10 mmol) with pyrrol (0.71 mL, 10mmol) and 68 µL of mild acid catalyst ($BF_3{\cdot}Et_2O$) in CH_2Cl_2 (150 ml) was stirred for 20 h at 20°C under nitrogen atmosphere. After this period, 2.16g of chloranil was added to oxidize the porphyrinogen to porphyrin. The mixture was stirred and refluxed for 3.5 h at 20°C under nitrogen atmosphere. After solvent evaporation, the residue product was purified by using a chromatographic column of silica gel (230-400 mesh) and CH_2Cl_2–$CHCl_3$ (40 : 60 v/v) as the eluent to give 30% yield. ^{1}H-NMR spectrum showed the characteristic signals reported by Nemykin et al[16]: one singlet at 9.6ppm corresponding to thepyrrol protons, 0.49ppm N-H protons of the porphyrin ring, 3,9ppm signal assigned to the unsubstituted cyclopentadienyl ring, two triplet at 4,7 and 5,3ppm assigned to the substitued cyclopentadienyl ring. UV-visible spectrum, in CH_2Cl_2 (ε x 10^{-3} $cm^{-1}M^{-1}$): 433nm (83,50); 664nm (9,44); 728nm (8,31). Infrared spectrum: 3432.2cm^{-1} (νN–H); 3086.2 cm^{-1} (νC-H$_{pyrrol}$), 1465 cm^{-1} (νC-H$_{cp}$); 2921.4 cm^{-1} (νC-H$_{pyrrol}$); 1548 cm^{-1} (νC=N); 796.2 cm^{-1} (porphyrin ring). These spectroscopic results confirm the molecular structure proposed for TFcPH$_2$ shown in Figure 1.

2.3. Preparation of the Modified Electrodes.

To prepare a drying-dropelectrode, DDE, 40 µl of TFcPH$_2$ solution (0.1mM in CH_2Cl_2 or DMF) was transferred to cover the glassy carbon electrode surface (diameter = 6.85 mm) and solvent was evaporated at room temperature. The electrode was rinsed with dichloromethane several times and used as working electrode (Fig. 2).

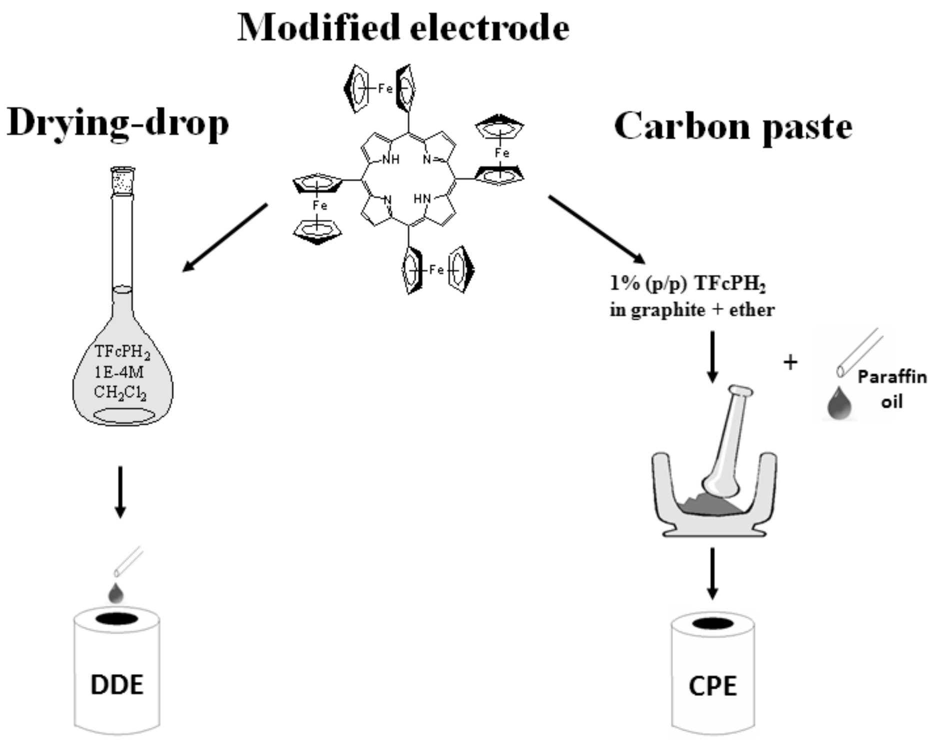

Figure 2. Preparation of the modified electrodes.

To prepare the Carbon-Paste Electrode, CPE,1% (w/w) mixture of $TFcPH_2$ to total weight of graphite powder was prepared by dissolving $TFcPH_2$ in diethyl ether. Then the mixture (solution and graphite powder) was hand-mixed in an agate-mortar. Diethyl ether was evaporated and paraffin oil was added until a homogeneous paste was obtained. A portion of this paste was packed into a cavity of a Teflon tube (ca. 3 mm internal diameter). The electric contact was established through a stainless steel screw. The surface of the electrode was smoothed with a spatula (Fig. 2).

DDE and CPE electrodes were used as working electrodes. The auxiliary electrode was a platinum wire. All potentials were measured versus a Ag/AgCl/KCl(saturated)reference electrode.

The glassy carbon electrode surface was polished with 0.05 mm alumina powder on a wet polishing cloth. The polished electrode was rinsed with doubly distilled water several times.

Britton Robinson buffer solution adjusted to pH = 9 (oxidation) and 2.0 (reduction) was used as test solution.

3. RESULTS AND DISCUSSION

3.1. Electrochemical response of $TFcPH_2$.

The voltammetric response of the $TFcPH_2$was carried out using a glassy carbon electrode on a solution of 0.1 mM [$TFcPH_2$] and 0.1M tetrabuthyl ammonium perchlorate (TBAP) as supporting electrolyte in dichloromethane (CH_2Cl_2) (Fig.3). Peaks II and IV correspond to the oxidation (0.86V) and reduction (0.46V) of the ferrocenyl sustituents in the prophyrin ring respectively. It is interesting to notice that the oxidation and reduction of the four ferrocenyl groups of the porphyrin present different energies.

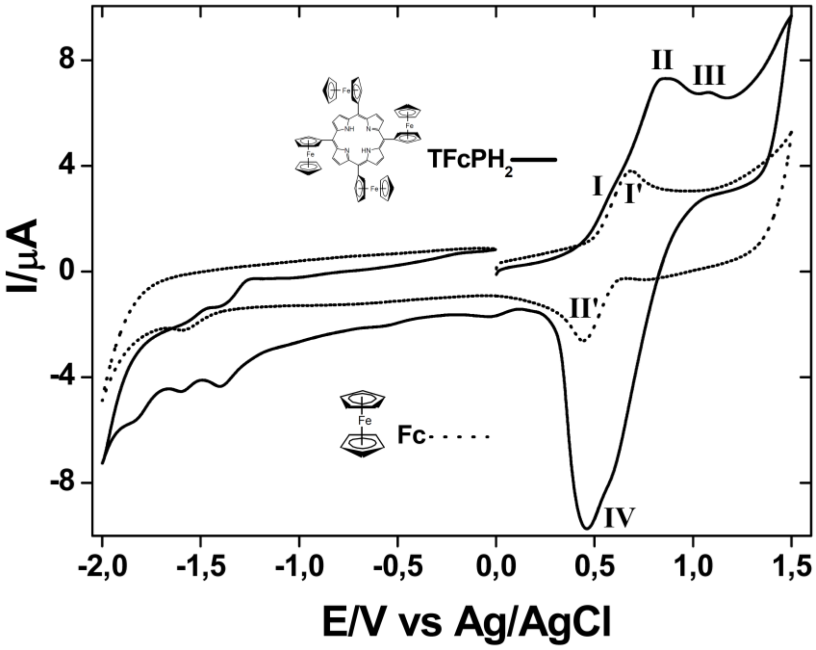

Figure 3. Cyclic voltammetry for $TFcPH_2$ (continuous line) and Ferrocene (dashed line) in CH_2Cl_2 solution containing tetrabutyl ammonium perchlorate (TBAP) under nitrogen. Scan rate 100 mVs^{-1}

The oxidation peak shows at least three overlapped signals. On the other hand, the reduction wave shows an ill-defined shoulder. Therefore, ferrocenyl sustituents in the porphyrins are not equivalent from an electrochemical point of view. For comparison, the voltammetric response of ferrocene is shown in Figure 3.

This ferrocene shows only one oxidation wave (I') and one reduction wave (II') located at 0.69V and 0.44V respectively. The ΔEp for ferrocene is 245 mV while, for a higher current wave in $TFcPH_2$ ligand, the ΔEp is about 400 mV. This indicates that the oxidation of ferrocenyl groups gives rise to a species having a higher chemical difference if compared with the ferrocene specie. The signal IV shows a stripping peak reported for ferrocenyl polymers, dendrimers and ferrocenyl substituted phthalocyanines [21-24]. On the other hand, in the cathodic region, four redox processes corresponding to the porphyrin ring [21,26] are shown.

3.2. Voltammetric characterization of DDE and CPE

Figure 4 shows the response of the DDE modified electrode. In the anodic region there is one oxidation peak associated to the reduction peak corresponding to the couple FeIII/II in the ferrocenyl substituents. The oxidation wave behavior clearly indicates a diffusional control for the electron transfer process. This behavior is demonstrated in the inset of the Figure 4 where the relationship between Ipa and the square root of the scan rate is a straight line. On the other hand, the inset B shows that after a critical scan rate the system becomes more and more irreversible. These facts can be attributed to a porous film covering the modified electrode.

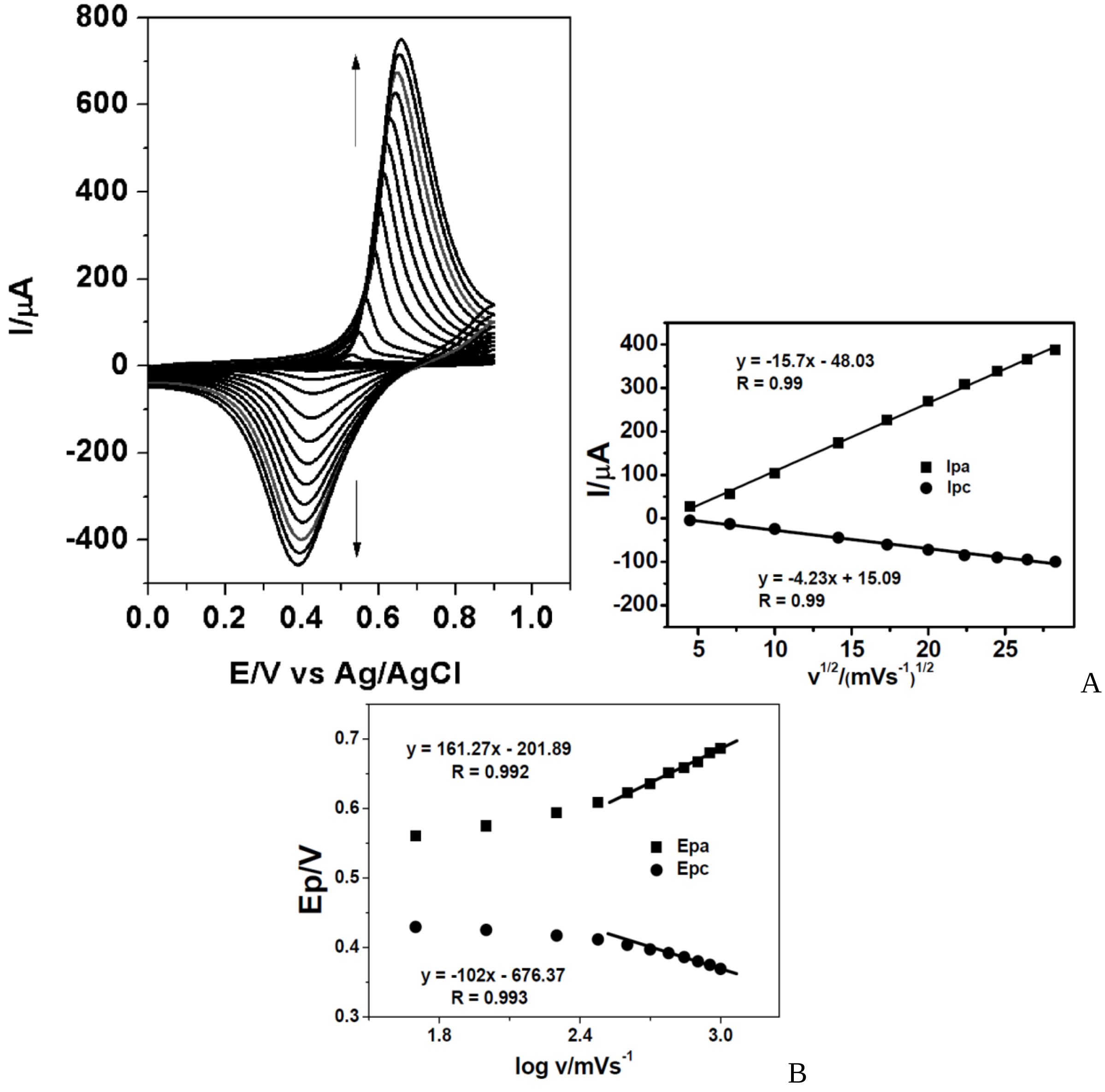

Figure 4. Voltammetric response of the drying-drop modified electrode TFcPH$_2$/GC A) Ip vs v$^{1/2}$; B) Ep vs log v.

The voltammetric behavior of CPE is very similar to that of DDE as shown in Figure 5. In fact, one oxidation wave and its corresponding reduction wave appear at practically the same potentials. Insets A and B show also the same behavior. The enhancement of the irreversibility with the scan rate indicates that the electron transfer is diffusion-controlled and this diffusion implicates a time that is longer than the critical scan rate where the potential begins to change.

Application of the Modified Electrodes as Electrocatalyst for S(IV) Oxidation in Basic Media.

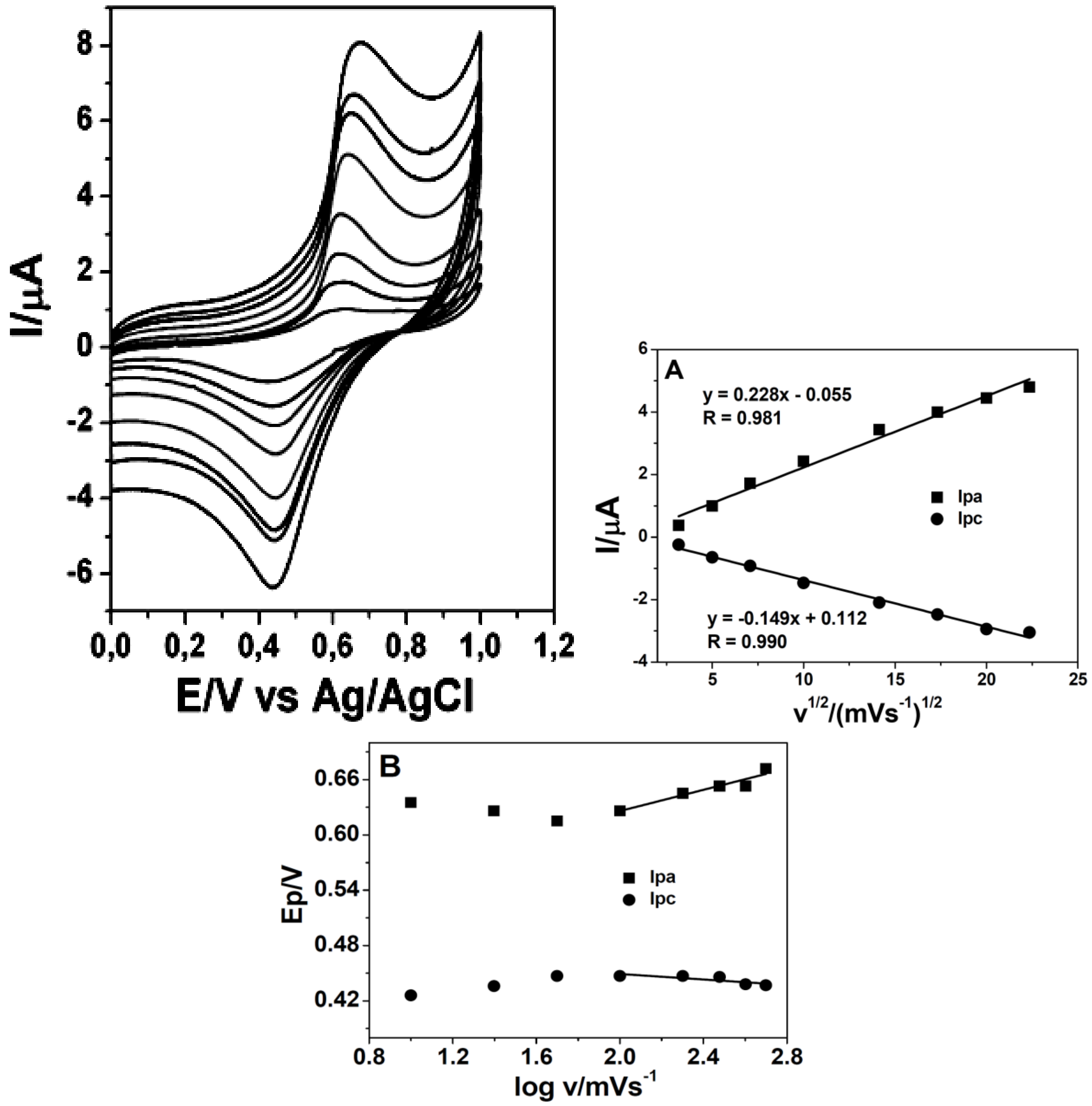

Figure 5. Voltammetric response of the carbon paste /TFcPH$_2$ modified electrode. A) Ip vs v$^{1/2}$; B) Ep vs log v.

3.4.1. DDE electrodes.

Figure 6 shows the electrooxidation of sulfite mediated by DDE electrode at different pHs. Also, at the best pH (pH = 9) a comparison with the blank (glassy carbon and DDE electrodes in the absence of sulfite) shows clearly that DDE electrode catalyzes the oxidation of sulfite if compared to the bare glassy carbon, as it is shown by the increasing current and the shifting of the potential. In spite of this catalytic response, this electrode cannot be used as sensor because it loses its activity for the second cycle. This loss is attributed to a poisoning of the electrode by one of the sulfite oxidation product that inhibits the activity of the porphyrin. Normally, this fact is due to the formation of a stable adduct [27].Therefore, under the experimental conditions used here DDE can not be used as an amperometric sensor.

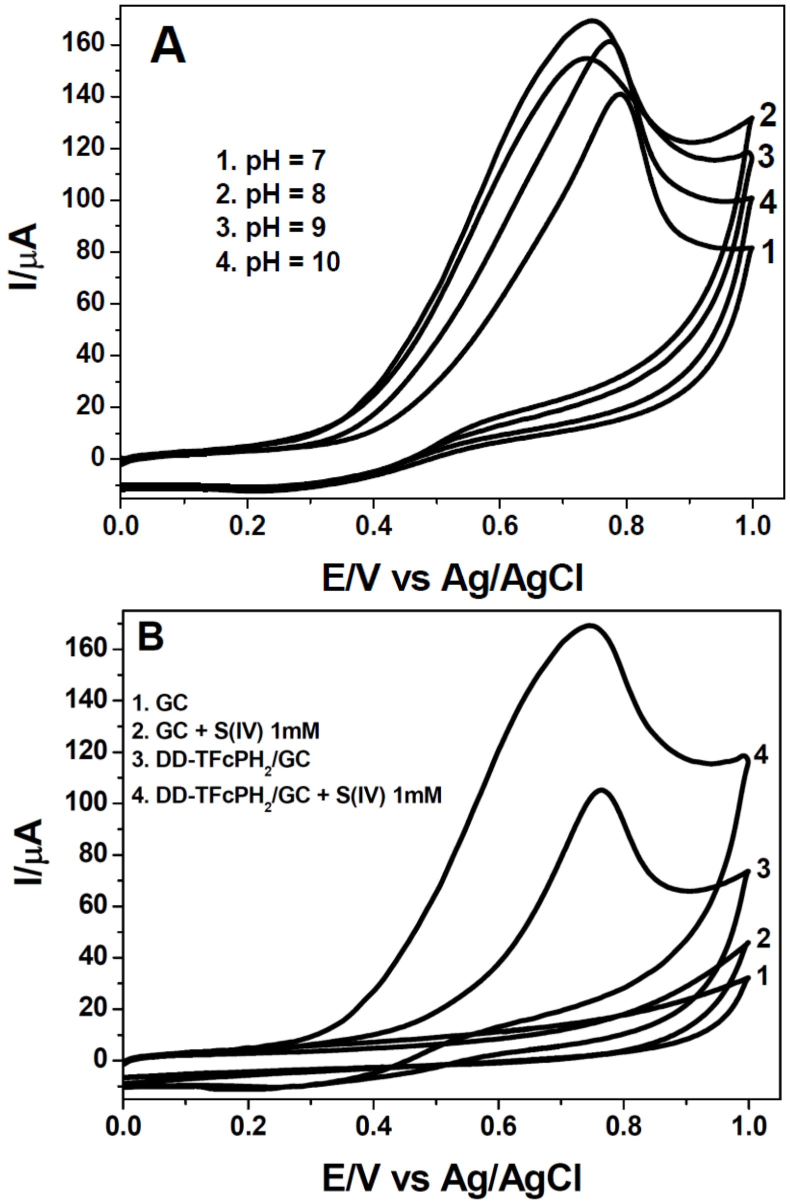

Figure 6. Electro-oxidation of sulfite using drying-drop TFcPH$_2$/GC modified electrode: A) different pHs (7,8,9,10); B) best pH = 9.

3.4.2. CPE electrodes.

This electrode shows electrocatalytic activity for the oxidation of sulfite as shown in Figure 7. However, two oxidation waves appear. They are not attributed to different active sites, because this electrode's response shows, in absence of sulfite, a unique oxidation wave for the ferrocenyl groups. These two waves correspond to the oxidation of two different S(IV) species: sulfite and bisulfate. They coexist at those basic pHs. As in the first case, this modified electrode loses its activity after the first cycle.

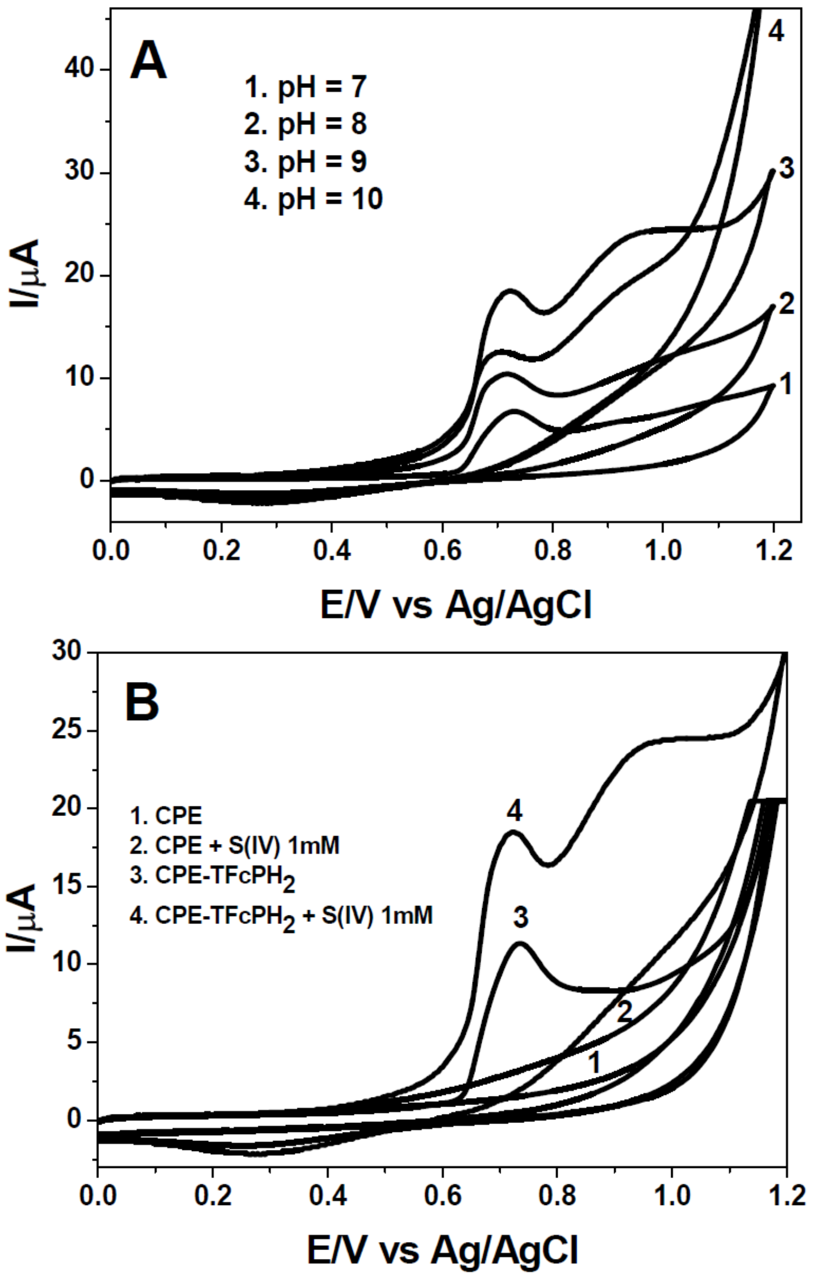

Figure 7. Electrocatalytic response of carbon paste/TFcPH$_2$modified electrode as redox mediator for sulfite oxidation: A) pH (7,8,9,10); B) best pH = 9.

3.5. Application of the Modified Electrodes as Electrocatalysts for S(IV) Reduction in Acid Media.

3.5.1. DDE modified electrode.

Figure 8A shows the electroreduction of S(IV) (HSO_3^-, SO_3^{2-}, SO_2) species using DDEelectrode at different pHs. The high catalytic current is obtained at pH= 2.0. The catalytic current decreases as the pH increases, pointing out that the modified electrode reduces SO_2 species with high selectivity. Figure 8B shows that the voltammetric response of DDE modified electrode for the SO_2 reduction at pH=2.0, where the reduction process begins at -0.34V vs Ag/AgCl, 80 mV, shifted to more positive potentials compared to the bare glassy carbon. Cyclic voltammograms of DDE electrode at various scan rates in the presence of sulfite indicate that the peak current for sulfite electrocatalytic reduction is proportional to the square root of scan rate (not shown) indicating that the reaction is a diffusion-controlled process [28].

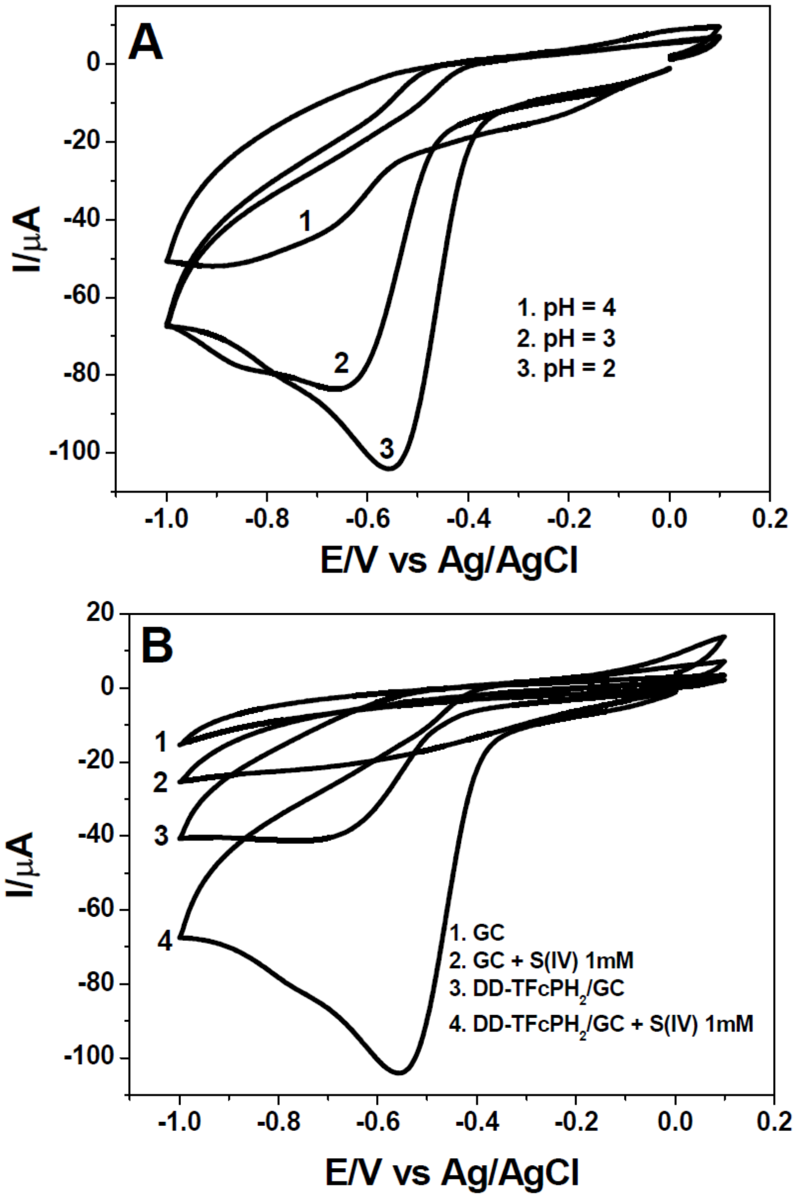

Figure 8. Electroreduction of sulfite using drying-drop TFcPH$_2$/GC modified electrode: A) different pHs; B) best pH = 2.0.

The non-linear curve of current function (current normalized by the square root of the scan rate (ip·$v^{-1/2}$)vs v (Fig. 9) confirms the catalytic process mediated by the DDE modified electrode [28].

The Tafel slope for the reduction mediated by DDE electrode is 180 mV/dec, suggesting that the rate-limiting step is the first electron transfer depending on the potential (corresponding to 120 mV/dec), but kinetic complications are taking place.

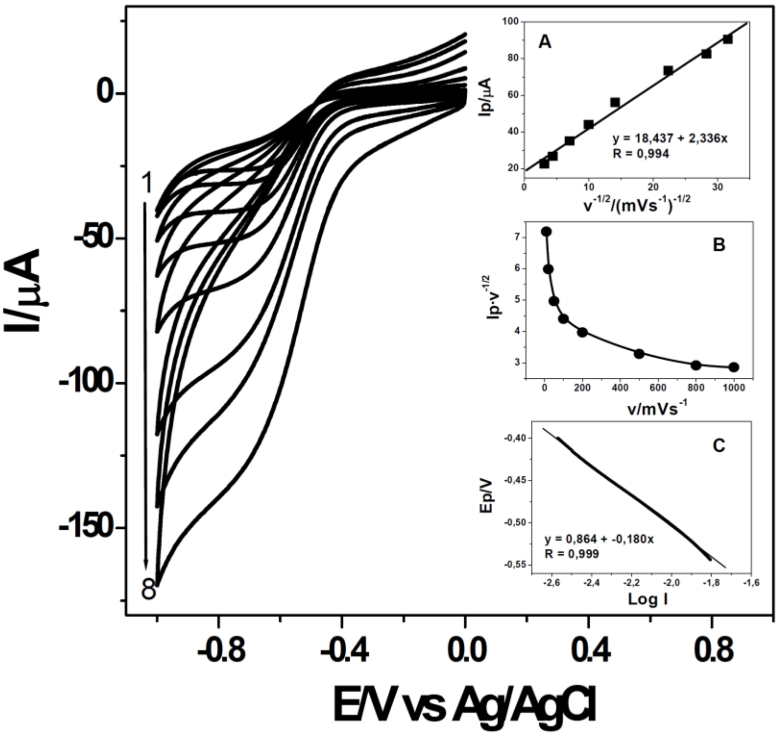

Figure 9. Electroreduction of S(IV) using TFcPH$_2$/GC modified electrode at pH = 2, at different scan rate (10, 20, 50, 100, 200, 500, 800, 1000 mVs^{-1}). Insets: A) Ip vs v$^{1/2}$; B) normalized current (Ip/v$^{1/2}$) vs v; C) Ep vs log I.

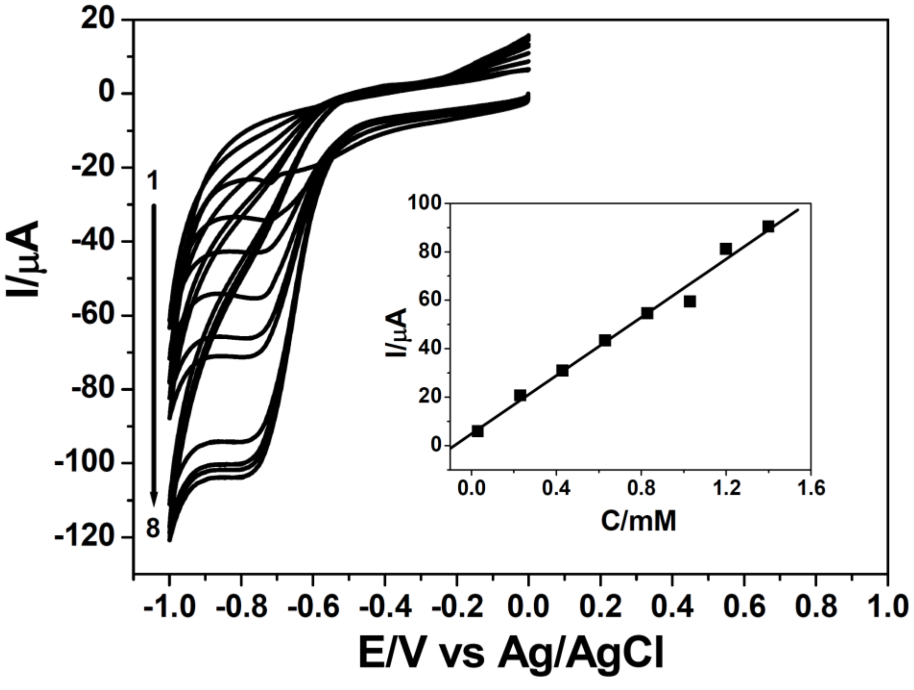

Figure 10. Electroreduction of S(IV) using TFcPH$_2$/GC modified electrode at pH = 2, at different concentration (0.03, 0.2, 0.4, 0.6, 0.8, 1.0, 12,1.4 mM). Inset: Calibration plot illustrating the linear response to S(IV) (Ip/ μA vs C/mM).

In the case of CPE electrode, it practically does not electrocatalyze the reduction of sulfite species at pH 2. There is not a shift in the potential compared to the non-modified carbon-paste electrode and the enhancement in the current is not important (not shown).

DDE modified electrode is a stable (more than 20 cycles each day during one week exposed to air) amperometric sensor. Cathodic currents for the different concentrations of sulfite were recorded in order to obtain the typical analytical curve. The curve in figure10 shows very good linearity from 0.03 to 1.4 mM with a detection limit of 22 μM.

4. CONCLUSIONS

DDE and CPE modified electrodes catalyze the oxidation of sulfite at pHs ranging from 7 to 10 showing the best results at pH 9. Both electrodes lose their activity after the first potentiodynamic cycle. DDE modified electrode electrocatalyzes the reduction of sulfite. It is stable at least during one week. It behaves as an amperometric sensor of sulfite from 0.03 to 1.4 mM at pH 2.

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