

Progress in Electrochemistry Research

Contributors

C. M. V. B. Almeida

Paolo Bertoncello

S. H. Bonilla

Cyril Delacôte

Mathieu Etienne

Germà Garcia-Belmonte

B. F. Giannetti

Dmitry G. Shchukin

Dmitry V. Sviridov

Alain Walcarius

Magdalena Nuñez

NOVA

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PROGRESS IN ELECTROCHEMISTRY RESEARCH

Magdalena Nuñez
Editor



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**PROGRESS IN ELECTROCHEMISTRY
RESEARCH**

PREFACE

Electrochemistry is the branch of chemistry that deals with the chemical action of electricity and the production of electricity by chemical reactions. In a world short of energy sources yet long on energy use, electrochemistry is a critical component of the mix necessary to keep the world economies growing. Electrochemistry is involved with such important applications as batteries, fuel cells, corrosion studies, hydrogen energy conversion, bioelectricity. Research on electrolytes, cells, and electrodes is within the scope of this old but extremely dynamic field.

Chapter 1 presents CPfEs, new and simple electrodes, which may be used to achieve the electrochemical response of ground solids or insoluble samples. The new electrode avoids the use of binders or other agents overcoming major deterioration problems. The investigation of metal adsorption on mineral surfaces is also presented. An interesting application for CPfEs is the exploratory studies on fuel cells catalysts shown in order to emphasize the versatility of the electrode.

The utilization of the Langmuir-Blodgett (LB) technology for the fabrication of engineered supramolecular thin films has received an exceptional development in these last years due to possibility of different applications in materials science ranging from nanotechnology to biosensors. The materials fabricated by LB technology provide an accurate control of the order at the molecular level. The main objective of Chapter 2 is to give an overview of the electrochemical properties of a particular class of polymeric thin films such as conducting polymers and ionomer polymers and describe the potentialities of some recent electrochemical technique for nanotechnological applications mainly scanning electrochemical technique (SECM) and SECM combined to Langmuir trough.

Conjugated polymers like polyaniline, polypyrrole, polythiophene, etc. do not only possess unique electroconductive properties and electrochemical activity but can also act as conductive hosts to create multifunctional nanocomposites of guest-host type where polymer matrix represents both an effective conductive support and a good dispersion media maintaining homogeneous distribution of embedded nanomaterial. Chapter 3 summarizes electrochemical characteristics, chemical properties, and structural parameters of the conducting polymers modified by the embedment of different inorganic nanophases. The role of the domain structure inherent in the conducting polymers in formation of electrocatalytic properties of nanocomposites and spatial separation of the photogenerated electrons and holes in case of nanocomposite-based photocatalytic systems is also discussed.

In Chapter 4, the authors report on a correlation between ionic diffusivity and electrode morphology of several polymer films [polypyrrole, polydicarbazole and poly(3,4-ethylenedioxythiophene)] deposited by electrochemical methods. Our approach takes advantage of the relationship between the characteristic diffusion frequency ω_d and the diffusion thickness l , $\omega_d = D/l^2$, to convey information on the electrode structure. This chapter deals mainly with the response of polypyrrole films, for which a transition between two types of deposition mechanism from nuclei growth at initial polymerization stages (thinner, more regular layers) to 1-D transversal growth after nuclei overlapping (thicker, porous structures) is reported. In addition to polypyrrole, the impedance response of other types of electronically conducting polymer films are outlined.

The implication of silica-based organic-inorganic hybrid materials, displaying an ordered structure at the mesoporous level, in electrochemical science is presented in Chapter 5. A general overview is provided in a first part on the basis of two complementary approaches: (1) the use of electrochemical methods to characterize the properties of these rather new materials, and (2) the exploitation of their attractive features to build voltammetric and amperometric sensing devices. Selectivity of the sensor and the effect of possible interference from other metal ions are also discussed.

CONTENTS

Preface		vii
Chapter 1	The Versatile Carbon Paraffin Electrodes (CPfEs): Applications from Natural Minerals to Fuel Cell Catalysts <i>C.M.V.B. Almeida, S. H. Bonilla and B. F. Giannetti</i>	1
Chapter 2	Electrochemistry of Polymeric Thin Films Prepared by Langmuir-Blodgett Technique <i>Paolo Bertoncello</i>	67
Chapter 3	Nanoengineered Composites Based on Conducting Polymers <i>Dmitry G. Shchukin and Dmitry V. Sviridov</i>	91
Chapter 4	Analysis of Conducting Polymer Electrode Morphology from Ion Diffusion Impedance Measurements <i>Germà Garcia-Belmonte</i>	123
Chapter 5	Interest of Mesoporous Organic-Inorganic Hybrids in Electroanalysis: General Overview and Sensor Application for Mercury Binding to Thiol-Functionalized Silica-Based Materials <i>Mathieu Etienne, Cyril Delacôte and Alain Walcarius</i>	145
Index		185

Chapter 1

THE VERSATILE CARBON PARAFFIN ELECTRODES (CPfEs): APPLICATIONS FROM NATURAL MINERALS TO FUEL CELL CATALYSTS

*C. M. V. B. Almeida, S. H. Bonilla and B. F. Giannetti**

LaFTA - Laboratório de Físico-Química Teórica e Aplicada
Instituto de Ciências Exatas e Tecnologia da Universidade Paulista
R. Dr. Bacelar 1212, Cep 04026-002, São Paulo, Brazil

ABSTRACT

This chapter presents CPfEs, new and simple electrodes, which may be used to achieve the electrochemical response of ground solids or insoluble samples. The new electrode avoids the use of binders or other agents overcoming major deterioration problems. Cyclic voltammograms of the chosen minerals are presented in order to illustrate the versatility of the electrode use. Voltammetric studies performed with mineral mixtures show the perspective for studying ores as they are found in nature. The investigation of metal adsorption on mineral surfaces is also presented. Two examples were chosen. The first focused on silver ions adsorption distinguishes the search for better performances for hydrometallurgical processes. The second explores the ability of iron sulfides to retain heavy metals and illustrates the use of CPfEs on the research applied to environmental issues. The use of CPfEs on the investigation of the semiconducting properties of solids was carried out to exemplify the use of CPfEs to determine band gap energies, capacitances measurements and to evaluate the effect of an adsorbed ion on the semiconducting properties of a solid sample. An interesting application for CPfEs is the exploratory studies on fuel cells catalysts shown in order to emphasize the versatility of the electrode.

Key words: carbon paraffin electrodes (CpfEs), ground minerals, electrochemical response, semiconducting properties, fuel cells electrocatalysts, metal ions adsorption

* biafgian@unip.br

PART 1. INTRODUCTION

The most popular electrode to study hardly soluble compounds is based on a carbon paste. These electrodes have been extensively used because of their advantages, such as ease preparation and large potential window. Surface renewal and modification are also simple.

The invention of carbon paste electrodes (CPEs) was a significant step toward solid-state electro analysis. The first CPEs were composed of carbon with an organic binder, as Nujol or silicone oil. With the solid to be analyzed added into the paste, the electrodes, now called “modified CPEs” or “carbon paste electro active electrodes – CPEEs”, were employed to determine redox potentials of organic insoluble compounds [1] and to investigate the electrochemical behavior of minerals [2,3]. However, these electrodes have some inherent problems. For example, the silicon oil binder causes deterioration and the binder viscosity has a significant effect on the electrode performance [4]. The use of carbon paste electrodes (CPE) prepared mainly by direct mixing of electro active compounds is well described in an excellent review [5].

Electrolytic binders, such as sulfuric acid, were also successfully used for investigating the electrochemical behavior of minerals and oxides [6,7], but the oxidation of the sample in the presence of the electrolytic binder means that CPE’s lifetime is limited. Despite of some experimental problems, easy to solve in research laboratories, the carbon paste electrodes enhanced the possibilities to investigate the electrochemical properties of insoluble solids and poorly soluble materials.

The methodology to immobilize mechanically solid particles on carbon surfaces (VMP – Voltammetry of Microparticles) was developed by Scholz et al. [8]. This technique is based on the mechanical immobilization of solid particles at the surface of carbon or metal electrodes without the use of binders. The graphite electrode impregnated with paraffin is gently rubbed on the ground sample, which is transferred to the electrode surface. This electrode permits the direct analysis of solid ground samples without pretreatments or time-consuming deposition procedures. The limitation of this electrode, easily manageable, is its preparation. The paraffin could cover part of the particles. For qualitative analysis, this limitation causes no harm, however it is not possible to control the active area exposed, which impedes quantitative determinations.

In this chapter, it is presented a new and simple electrode, which may be used to achieve the electrochemical response of ground solids or insoluble samples. In a sense, this electrode may be considered a combination of CPEs and VMP electrodes, as it uses carbon powder and paraffin for its construction. In order to show the use and the versatility of this new electrode, called CPfE (carbon paraffin electrode), a series of examples is presented.

Some advantages of CPfEs can be listed:

- I. it avoids the use of binders or other agents overcoming major deterioration problems,
- II. ease preparation,
- III. low cost,
- IV. large potential window,
- V. easy modification,
- VI. excellent electrical conductivity, and

- VII. the use of solid particles of the same size guarantees the current values reproducibility, that is, similar surface areas are obtained.

With the purpose of illustrating the advantages of CPfEs, several examples are shown using mainly cyclic voltammetry. This technique may be considered the basis for most studies on solid-state redox systems. The potential of the working electrode is scanned linearly between two limiting values (E_a , the anodic potential limit and E_c the cathodic potential limit), the current is recorded and valuable information about the reversibility, and the nature of reaction products is obtained. Cyclic voltammograms of the chosen minerals pyrite, pyrrhotite and arsenopyrite, are presented in Parts 3.1 to 3.3. Exploratory studies carried out with pyrite and pyrrhotite are followed by a more detailed study of arsenopyrite, in order to illustrate the versatility of the electrode use. Part 4 shows voltammetric studies performed with mineral mixtures. The possibility of analyzing mixed solids offers the perspective for studying ores as they are found in nature. The investigation of metal adsorption on mineral surfaces is illustrated in Part 5. Two examples were chosen. The first focused on silver ions adsorption distinguishes the search for better performances for hydrometallurgical processes. The second explores the ability of iron sulfides to retain heavy metals and illustrates the use of CPfEs on the research applied to environmental issues. Part 6 exemplifies the use of CPfEs on the investigation of the semiconducting properties of solids. The electrode permits the determination of band gap energies, capacitance measurements and to evaluate the effect of an adsorbed ion on the semiconducting properties of the solid sample. An interesting application for CPfEs is shown in Part 7, where exploratory studies on fuel cells catalysts are shown in order to emphasize the versatility of the electrode.

PART 2. ELECTRODE PREPARATION

The preparation of solid samples for electrochemical experiments is not a simple procedure. For analytical practices, the electrode construction should be simple, easily reproducible and reliable. However, each solid sample has its own characteristics and it is necessary to guarantee a suitable electric contact with the current collector.

The CPfEs consist of 1.0 g graphite and 1.2 g paraffin wax (solidification point 68-74 °C) containing the desired quantity of the solid sample. For the construction of the electrodes, a brass or copper wire with diameter 3.0 mm was immersed in the mixture graphite/paraffin heated at 70 °C, Fig. 1(1). Then, the solid sample is placed in a Teflon cavity with diameter 4.5 mm, Fig. 1(2) and the extremity of the wire covered with the hot mixture was immediately pressed on the solid particles placed in the mould. The resulting set is a sample disk with diameter nearly 4.0 mm, which covers the graphite surface almost completely, Fig. 1(3). The lateral parts of the electrode were then covered with Teflon tape to avoid contact with solution, Fig. 1(4).

The particles mechanically immobilized on the graphite/paraffin mixture are very stable. Besides the mechanical immobilization, the cooling process of the mixture in contact with the particles improves the solid stabilization. Thus, the electrode can be vigorously washed before its transfer to the electrochemical cell and can also rotated to perform hydrodynamic experiments. Finally, the electrode-tip covered with solid particles can be easily removed

after every measurement and the brass wire can be used immediately to make a new electrode.

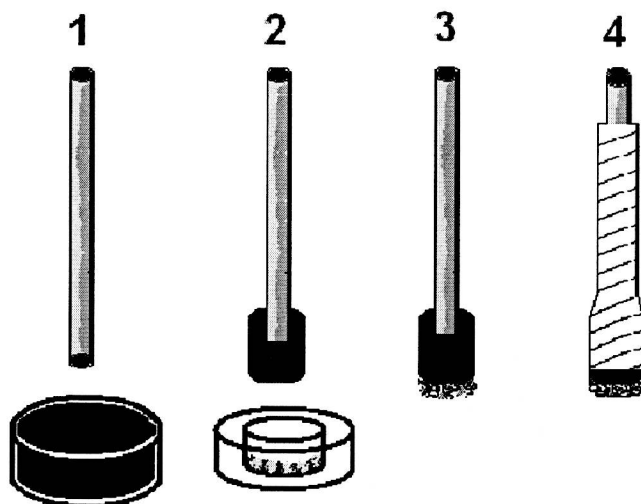


Figure 1. Schematic representation of the electrode construction.

2.1. Experimental Procedure

Potentiodynamic measurements were carried out in a standard electrochemical cell. Nitrogen was bubbled through the cell to deaerate the solution. The reference electrode was a reversible Ag/AgCl electrode placed in a Luggin-Haber capillary and the counter electrode was a platinized platinum wire of large area.

The mineral natural samples of FeS₂, FeS and FeAsS investigated are from Morro Velho Mine, in Minas Gerais, Brazil. The mineral characterization was performed by X-ray fluorescence spectrometry and powder X-ray diffraction was carried out on the samples to confirm the crystal structure. The CPfE surface with 5 mg of ground mineral is a disc with diameter nearly 4 mm, which covers the graphite surface almost completely. The electrolyte, 0.5 M acetic acid/sodium acetate, pH = 4.5 was prepared from p.a. grade reagent and triply distilled water. The choice of this electrolyte is due not only to its pH value next to that found under weathering conditions [9, 10], but because it acts as a pH buffer and controls the ionic strength of the solution. The voltammetric curves were obtained with freshly prepared electrodes allowed to reach the open circuit potential, E_{oc} , which equals the E_{oc} measured in water [11]. The open circuit potential varies with time because of the interaction between the mineral and the electrolyte [12]. The variation is negligible after 5 min of immersion. This time was taken into account in each experiment. Potentials quoted in Parts 3 to 7 are given on the standard hydrogen scale. All experiments were carried out at 25°C with scan rate 20 mV s⁻¹.

The voltammetric characterization of the catalysts for fuel cells was carried out at the scan rate of 100 mV s⁻¹, always under inert N₂ atmosphere. The working electrodes were

constructed from the following electro catalysts: nano-dispersed Pt (commercial E-Tek) and nano-dispersed Pt/Ru onto C support. The experimental procedures applied in the present study involve cyclic voltammetry experiments of the electro catalysts in H_2SO_4 1 M medium prepared from p.a. grade reagent and triply distilled water. The results are compared with those obtained from the same technique but with the adding of methanol and ethanol. The experimental procedure includes the working electrode stabilization until a constant profile through cycling between the selected potential limits. The potential limits chosen for every catalyst depend on their stability. Potentials quoted in Part 7 are given on the Ag/AgCl scale.

2.2. Influence of the Minerals Particle Size

Some solids can be studied in a variety of particle sizes, which can influence the results. Before initiating the study of the electrochemical behavior of minerals, a standard particle size was selected. With this purpose, CPfEs were constructed with 5 mg of ground natural pyrite, FeS_2 . The pyrite was hand ground in an agate mortar and pestle. The material was sieved to isolate a desired fraction to assure the reproducibility of the current values. In order to compare the data with that obtained from the carbon paste electrode and with others found in literature [13, 14], a compact crystal electrode was constructed (Fig. 2). A selected crystal of pyrite was cut to size and mounted in polyester resin with one surface exposed. The exposed surface was polished wet on 600-grit silicon carbide paper.

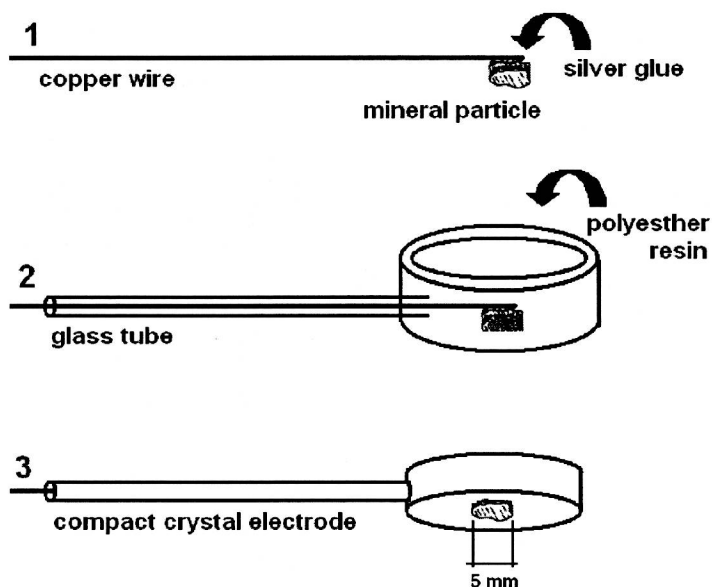


Figure 2. Schematic representation of the crystal sample electrode.

SEM micrographs of the pyrite crystal sample (geometric area of 19.6 mm^2) and of the carbon paste electrode containing pyrite particles $< 210 \text{ }\mu\text{m}$ fixed on the CPfE are shown in Figure 3. It can be seen that the graphite/paraffin mixture exposed to the solution is minimal.

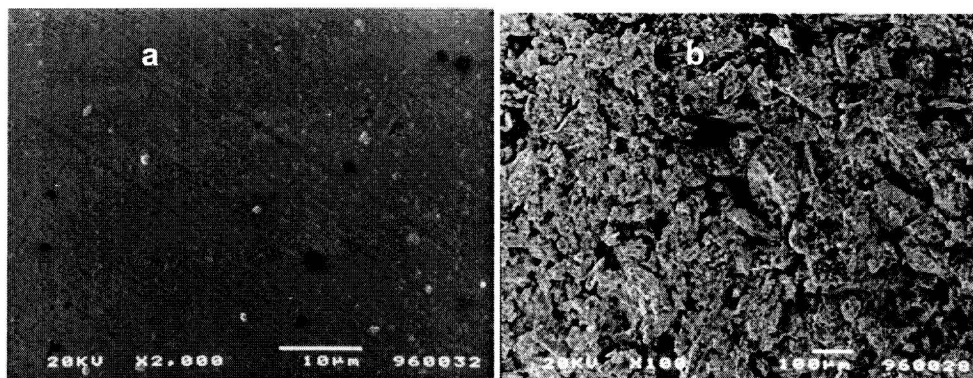


Figure 3. SEM micrographs of the electrodes: (a) polished and (b) CPfEs containing pyrite particles $< 210 \text{ }\mu\text{m}$.

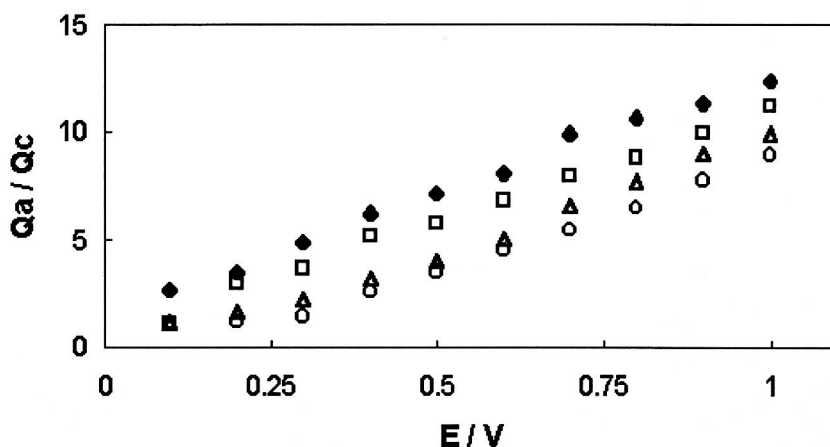


Figure 4. Dependence of Q_a/Q_c on the anodic end point potential. (◆) polished electrode, (□) particles $< 210 \text{ }\mu\text{m}$, (Δ) $210 \text{ }\mu\text{m} <$ particles $< 250 \text{ }\mu\text{m}$ and (○) particles $> 250 \text{ }\mu\text{m}$. Potential quoted to SHE.

Fig. 4 shows the relation between anodic charges (Q_a) and cathodic charges (Q_c) as function of the anodic end point potential. It can clearly be seen that with increasing particle size the relative anodic current, decreases possibly due to the change in surface area. The area of the ground electrodes is about 20 times larger than that of the polished ones, even without taking into account the roughness of each particle [15]. The results in Fig. 4 show further that ground particle electrodes, even with larger area, present smaller anodic currents than those that were mechanically polished. As the electrodes are not polished, pyrite particles may be partially covered by iron hydroxides/oxides formed in air during grinding. Preparation, grinding and prolonged oxidation of pyrite in air favor the formation of iron oxide/hydroxide,

in contrast to the natural weathering process of pyrite, which produces mainly a basic iron sulfate similar to jarosite and also iron oxide/hydroxide [13, 16-18]. A detailed explanation of the influence of the particle size on electrochemical response is reported in [15]. The mineral fractions used in this chapter to exemplify the electrode performance are less than 210 μm , in size.

PART 3. ELECTROCHEMICAL BEHAVIOR OF MINERALS

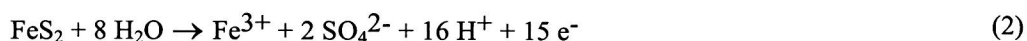
3.1. Electrochemical Behavior of Pyrite

Considerable research has been carried out on the oxidation of pyrite using a wide range of methods. Many of these relate to metallurgical processing because enhancement of pyrite oxidation may improve the recovery of metals from sulfide ores. In this regard, pyrite has been studied mostly by electrochemical techniques [10, 12, 14, 15, 19, 20]. There is also wide interest in the knowledge of surface properties as the oxidation state of the sulfide mineral surface can not only influence interactions with flotation collectors but also impart hydrophobicity or hydrophobility to the mineral surface [21, 22], due to the presence of sulfur or iron hydroxides, respectively. In this respect Fourier transform infrared spectroscopy [23], X-ray photoelectron spectroscopy [24-26] and Raman spectroscopy [27, 28] were used. The role of the semiconducting properties on the anodic dissolution of semiconducting sulfide minerals was also studied [13, 23, 29, 30], in order to give an explanation for the very limited dissolution rate of the mineral at potentials a little more positive than the open circuit potential.

Voltammograms obtained from both pyrite electrodes (the polished and the CPfEs, Fig 5 a and b) with the sweep potential starting from the open circuit potential. The curve obtained from the ground electrode is similar to that obtained from the crystal sample, except for anodic current peak A_1 and the open circuit potential, which is more negative and corresponds to the system Fe(II)/Fe(III), Equation 1. Current peak A_1 is also observed when massive specimen is used as electrodes, but only during the second cycle, and is related to the formation of Fe(III) species on the electrode surface [14, 21]. Taking into account that the pyrite particles may be partially covered by iron oxides/hydroxides formed in air during grinding [15], the presence of current peak A_1 and the more negative potential is expected.



The other aspects of the voltammogram of pyrite are identical to the voltammograms found in the literature [13, 14] (Fig. 1). The oxidation reactions of the mineral are fairly well discussed in literature and the overall reaction may be represented as



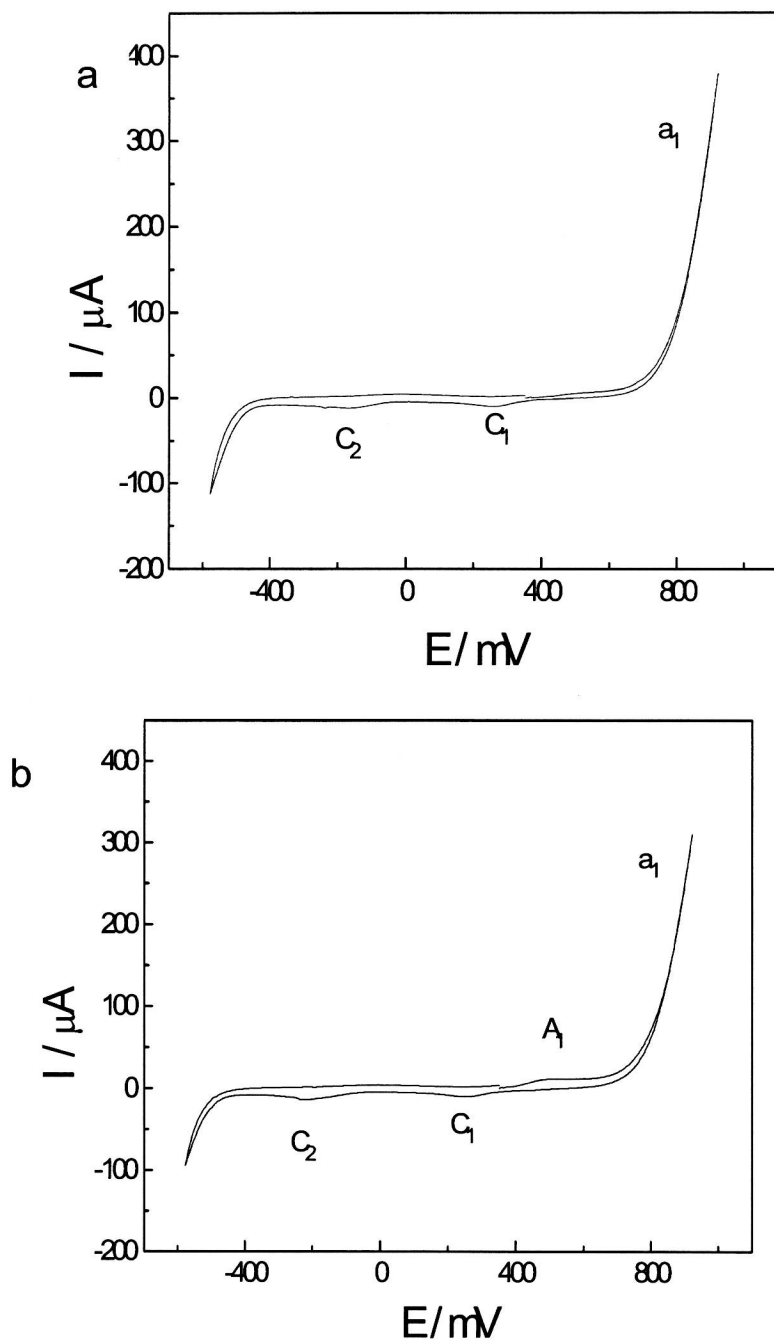


Figure 5. Voltammograms of (a) the pyrite crystal sample and (b) CPfEs pyrite electrode, in acetic acid/acetate buffer, pH = 4.5, sweep rate 20 mV s^{-1} , at 298 K. E_i : open circuit potential, $E_a = 0.95 \text{ V}$. Potential quoted to SHE.

In the reverse scan, two current peaks are observed. Peak C_1 was attributed to the reduction of the iron oxide/hydroxide species formed during the oxidation. Peak C_2 was

associated with the reduction of sulfur species [14, 19] in accordance with the following reaction:



3.2. Electrochemical Behavior of Pyrrhotite

Pyrrhotite is a major species among iron sulfides in nature, but there are only a few studies concerning its electrochemical behavior [14, 31-34]. Hamilton and Woods [14], in a more detailed work, studied the pyrrhotite dissolution at pH 4.6, 9.2 and 13.0 employing cyclic voltammetry. Their report shows that elemental sulfur is the main product of the mineral oxidation and that sulfate yield depends on pH. There is also a small number of surface analytical investigations of pyrrhotite reported [35-38], many of these relating to the nature of the reactions occurring at the interface between pyrrhotite and air or water during weathering.

Figure 6 shows the cyclic voltammogram obtained from the pyrrhotite CPfEs with the sweep potential starting from the open circuit potential, E_{oc} and three anodic current peaks are observed. The curve obtained is similar to that obtained by Hamilton and Woods [14] and Mikhlin [34] except that both studies limited the upper potential limit to 0.8 V. Under these conditions, the anodic dissolution of pyrrhotite results in the formation of ferrous ions and an iron deficient phase. The anodic peak a1 was attributed to the formation of elemental sulfur [14]:

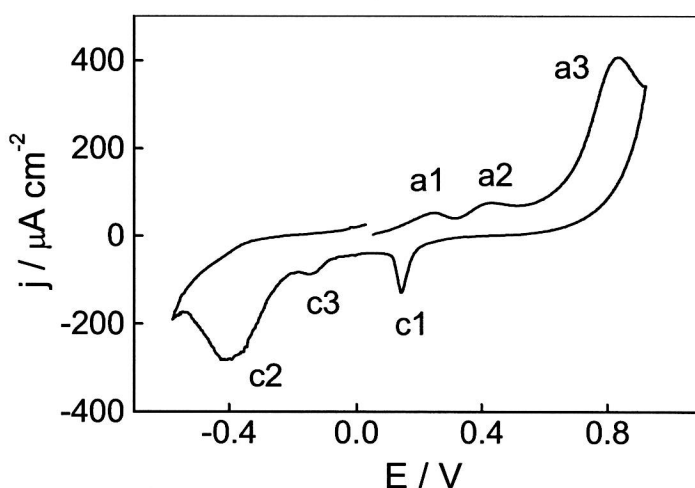
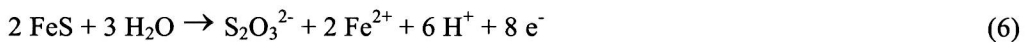


Figure 6. Cyclic voltammogram of the pyrrhotite CPfE: $E_i = E_{oc}$, $E_a = 0.922 \text{ V}$, $E_c = -0.6 \text{ V}$, $E_f = E_{oc}$, $\nu = 20 \text{ mV s}^{-1}$. Potential quoted to SHE.

During this step, as ferrous ions go to the solution, the accumulation of sulfur on the electrode surface is expected to occur. This accumulation can be interpreted as being due to the formation of an elementary sulfur layer or to the formation of an iron-deficient surface [14].

As amount of sulfur on the surface increases, it becomes more difficult for Fe^{2+} ions to diffuse and a high concentration of ferrous ions remains at the mineral surface. Increasing the potential, part of the Fe^{2+} is oxidized, forming Fe^{3+} (peak a2, at 0.45 V). However, the accumulation of Fe^{2+} can reduce the concentration of protons near the electrode increasing the local pH, and favoring the formation of thiosulfate as proposed by Paul et al [39] for the anodic dissolution of galena. The following reactions are thermodynamically possible [40]:



When the potential is scanned further than 0.8 V, a third anodic peak appears. The anodic current peak a3 may be associated with the oxidation of the intermediates formed, leading to sulfate formation.



In the reverse scan (Fig. 6), three cathodic current peaks are observed. Peak c1 has usually been assigned to the reduction of ferric oxy-hydroxides to Fe^{2+} species, at 0.2 V [14,34]. Current peaks c2 and c3 had been considered relative to the reduction of the layer rich in sulfur/intermediates at the electrode surface. The intermediates, possibly reduced in peak c3 domain, act as a precursor in the formation of elementary sulfur [37]. Other authors associate these peaks with the presence of iron atoms that remain in the sulfur film, which constitutes the iron-deficient phase [28]. However, it is not possible to attribute each peak observed to a determined process using voltammetry alone. A larger peak c2 at about 0.35 V is also observed. Similar peaks were observed in various electrolytes for pyrrhotite and other metal sulfides and were assigned to the reduction of elemental sulfur to H_2S [14, 41] or to the reduction of a metal-deficient layer [38].

3.3. Electrochemical Behavior of Arsenopyrite

The arsenopyrite present in ores is generally discarded as solid waste during mining operations [42, 43]. The mineral is an inconvenient impurity whose dissolution may create environmental problems due to the contamination of water by soluble arsenic compounds. Like many other conducting and semiconducting solids, arsenopyrite undergoes dissolution by an electrochemical mechanism [11, 44-50]. The treatment of arsenopyrite usually involves flotation processes and several studies found in literature are directed to the investigation of the mineral dissolution in alkaline media [11, 44-46].

Arsenopyrite is also worthy of attention because it is abundant and difficult to leach. Most of the works about electrochemical oxidation of arsenopyrite in acidic media have been