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ELECTROCHEMICAL BEHAVIOUR OF GOLD AT THE CARBON PASTE ELECTRODE: APPLICATION TO THE GOLD ORE ANALYSIS

M. Diaw[1*], D. Lemordant[2], O. Sock[1] and O. Sarr[3]

[1]Laboratoire d'Electrochimie et des Procédés Membranaires, Ecole Supérieure Polytechnique, BP 5085 Dakar-Fann, Université Cheikh Anta Diop, Dakar, Senegal
[2]Laboratoire de Physicochimie des Interfaces et des Milieux Réactionnels, EA2098, Université de Tours, Faculté des Sciences, Parc Grandmont, 37200 Tours, France
[3]Laboratoire de Chimie Minérale et Analytique, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Senegal

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ABSTRACT. Electroanalysis of gold and gold derivatives incorporated in a carbon paste electrode has been shown to be a useful tool for gold speciation. This technique allows a rapid access to the oxidation state of gold in the composite under study. Voltammetric studies have been conducted on metallic gold, gold oxide and gold(III) solutions in hydrochloric and sulphuric acids. Moreover the analysis of a gold ore has been performed in order to investigate the possibility of determining the presence of gold in pyrite gangue.

KEY WORDS: Carbon paste electrode, Electrochemistry of gold, Gold ores, Pyrite

INTRODUCTION

Gold is usually inert toward oxidation because of its high oxidation potential (1.4 V/SHE). The oxidation of gold as Au(III) is only achieved in complexing media like hydrochloric acid or cyanide solutions. The analysis of metallic gold or gold in ores can be realized by the incorporation of a solid sample of the element in a carbon paste electrode. This technique has been already applied to the analysis of precious metals like palladium [1, 2] and platinum [1, 3] and allows the determination of the state of oxidation of the element [1-8] by monitoring the potential applied to the electrode against a reference electrode and recording the current. In addition quantitative results can be obtained by mean of coulometric measurements [5]. The aim of this work is to investigate the voltammetric behaviour of gold and some of its derivatives (Au_2O_3, Au(III) and gold ore) in the presence of an aqueous acid media (HCl and H_2SO_4 solutions).

The carbon paste can be prepared from a fine mixture of the sample under study with carbon powder and a binder. The electrochemical reactions occurring in the paste can be quantitative or partial, depending on whether the binder is an electronic conductor or not [5]. The potential at which the electrochemical reactions are observed depends on the nature of the binder. Moreover, significant shifts in oxidation or reduction potentials are noted when ions produced upon oxidation of the incorporated element can form a stable complex with one component of the binder. This explains the performance of this technique applied to palladium and platinum. In order to test the efficiency of the carbon paste electrode technique for gold, the electrochemical behaviour of gold associated with minerals in ore has been studied. The gold ore used contains mainly sulphur in pyrite (98%), and some minor constituents.

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[*] Corresponding author. E-mail: diawmahy@yahoo.fr

EXPERIMENTAL

The carbon paste electrode was prepared by mixing 40-50 mg of ultra-pure graphite powder (Johnson-Matthey) with the sample under study (0.1 to 3 mg of powdered solid) and 30-50 μL of hydrochloric acid (2 M) or sulphuric acid (2 M). The homogenized mixture was then introduced at the open end of a U-shaped glass tube sealed, at its bottom, by a vitreous carbon disk designed to ensure the electrical contact [7]. A fine layer of sand covered the carbon paste mixture in order to avoid diffusion of particles toward the electrolyte. The carbon paste electrode was used as the working electrode in a classical three-electrode system, consisting of a KCl saturated calomel reference electrode (SCE, from Tacussel XR 110) and a platinum electrode as an auxiliary electrode (Tacussel XM 110). The three electrodes were immersed in a closed cell containing hydrochloric or sulphuric acid as electrolyte. In all cases, the electrolyte was of the same nature and composition as that used as binder in the carbon paste. In the following, all potentials are referred to the SCE electrode.

The cyclic voltammograms were obtained with the aid of a synchronous motor (Tacussel type PIL 101 T) driven potentiometer (Tacussel PRT 30-0.1) and a recorder (Asea Brown Boveri (ABB) model SE 790). In order to achieve quantitative oxidation or reduction of the electroactive material, low voltage scan rate was used (0.5 mV/s or 2.5 mV/s). All the cyclic voltammograms have been obtained by voltage scanning from the null current potential, towards oxidation or reduction. The compounds under study, gold, gold derivatives and the other minerals, are described in Table 1.

Table 1. Compounds under study, solubility and sources.

Compound	Solubility in water at 20 °C	Solubility in HCl	Source
Gold (metal)	Insoluble	Insoluble	Aldrich chemicals
Gold(III) oxide (Au_2O_3)	Insoluble	Slightly soluble[1]	Aldrich chemicals
Gold(III) chloride (atomic absorption standard solution)	Soluble	Soluble	Aldrich chemicals
Pyrite	Slightly soluble	-	Geological purity
Gold ores	-	-	Geological purity

RESULTS AND DISCUSSION

Gold and its derivatives

Gold(III) in HCl (5 M). The cyclic voltammogram relative to a gold(III) solution in hydrochloric acid (5 M) is displayed in Figure 1. Starting from the equilibrium potential (E_0 = 670 mV), the cyclic voltammogram exhibits a reduction peak at E_{pc}= 480 mV during the forward scan and an oxidation peak at E_{pa} = 800 mV during the reverse scan. The measurement of the oxidation peak area reveals that 2.7 electrons per mole of Au are exchanged during this electrochemical process, corresponding to a transformation of the initial gold present in the carbon paste up to 90%. This indicates that gold(III) is initially reduced to metallic gold on the carbon paste and subsequently reoxidated in the form of a tetrachloro-complex $AuCl_4^-$ [9]. The equilibrium potential of the system Au(III)/Au evaluated as $(E_{pa} + E_{pc})/2$ is 640 mV is in accord with literature value for this system (E° = 750 mV).

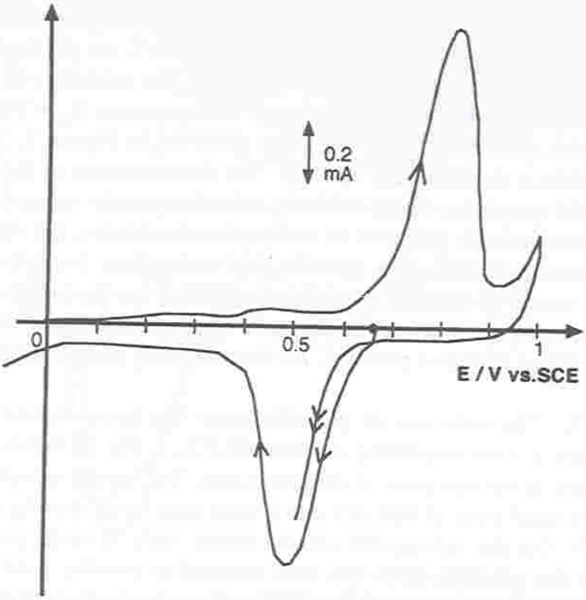

Figure 1. Electrochemical behaviour of gold(III) in 5 M HCl. Graphite powder: 44.9 mg; binder: gold(III) in 5 M HCl (33 μL). Scan rate: 2.5 mV/s; E_0 = 670 mV; E_1 = 0; E_2 = 1000 mV.

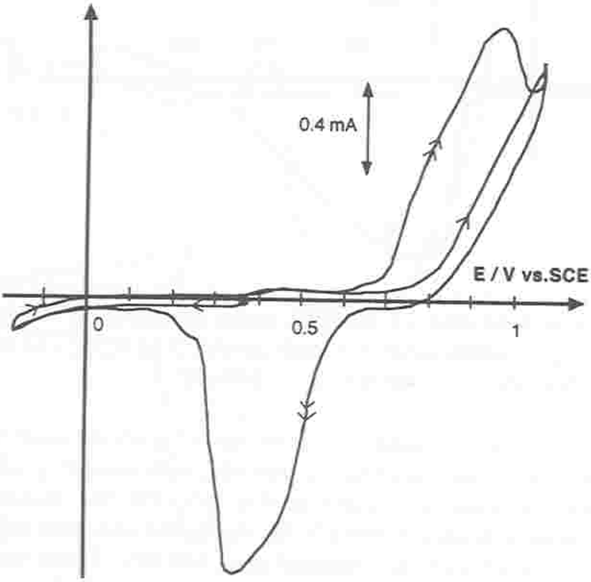

Figure 2. Electrochemical behaviour of metallic gold in 2 M HCl. Graphite powder: 50 mg; metallic gold: 1 mg; binder: 2 M HCl (40 μL). Scan rate: 2.5 mV/s; E_0 = 370 mV; E_1 = -150 mV; E_2 = 1100 mV.

Metallic gold. The electrochemical behaviour of metallic gold at the carbon paste electrode is presented in Figure 2. The cyclic voltammogram has been run in hydrochloric acid (2 M) as electrolyte. Starting from the equilibrium potential E_0 = 370 mV, no electrochemical reaction occurs during the first cathodic sweep. On the reverse scan, the oxidation of gold is observed starting at 670 mV. The corresponding reduction peak is observed at E_{pc} = 370 mV. The shape of the obtained reduction peak is different from that observed in Figure 1. The width of this peak is larger and exhibits a shoulder near 450 mV. The determination of the peak area shows that only 7 % of the gold sample have been oxidized and subsequently reduced.

All these observations indicate that after an uncompleted oxidation, the metallic sample has been reduced on different nucleating sites: metallic gold and carbon. It can be deduced that the reduction of gold(III) occurs at different potentials depending on the nature of the nucleation site. During the second anodic sweep, the oxidation is observed at 960 mV for gold deposited on carbon (see Figure 1) and at higher potential, for the remaining metallic gold (see Figure 2).

Gold(III) oxide (Au_2O_3). The reduction of gold(III) oxide has been studied in a complexing medium (HCl, 2 M) and a non-complexing medium (H_2SO_4, 2 M). In Figure 3 is reported the voltammogram obtained in the presence of sulphuric acid. Two peaks are obtained during the first cathodic sweep: a small peak at 820 mV and a very large peak starting at 700 mV with a maximum at 250 mV. On the subsequent anodic sweep, only a small peak at 970 mV is recorded. This means that gold(III) oxide has been reduced to metallic gold which can not be reoxidized in this non-complexing medium in the investigated potential window. The nature of the system responsible of the small corresponding anodic and reduction peak has not been determined and is attributed to impurities present in gold(III) oxide (technical, purity 85-86%).

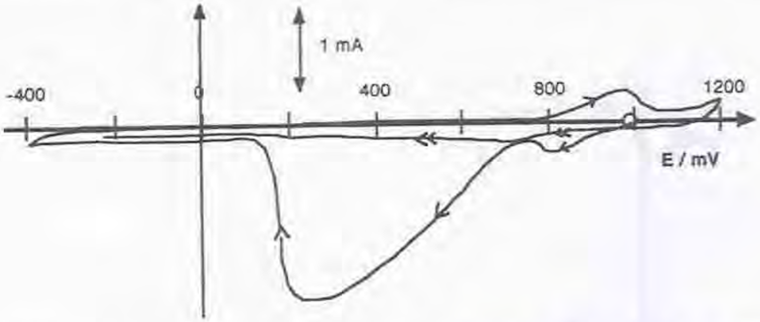

Figure 3. Electrochemical behaviour of gold(III) oxide as Au_2O_3 in 2 M H_2SO_4. Graphite powder: 43 mg; gold(III) oxide: 0.43 mg; binder: 2 M H_2SO_4 (35 µL). Scan rate: 2.5 mV/s; E_0 = 1000 mV; E_1 = -400 mV; E_2 = 1200 mV.

In Figure 4 is reported the electrochemical behaviour of gold(III) oxide in the presence of HCl. Starting from an equilibrium potential of 680 mV, reduction of gold(III) oxide occurs immediately. The peak potential is located at 430 mV. On the reoxidation sweep, the corresponding anodic peak is situated at 900 mV. On the second reduction sweep, the maximum peak height is shifted toward cathodic potential near 410 mV. These results indicate that gold(III) oxide has been first reduced to metal and reoxidized as tetrachloroaurate anions as the equilibrium potential $(E_{pa} + E_{pc})/2$ = 665 mV is very near from the standard potential of the $AuCl_4^-$/Au system. On the second reduction, $AuCl_4^-$ anions are reduced and this explains the observed shift in potential.

In hydrochloric acid, the reduction of gold(III) oxide occurs with coulombic yield near 90% when the amount of oxide in the paste is less than 1%.

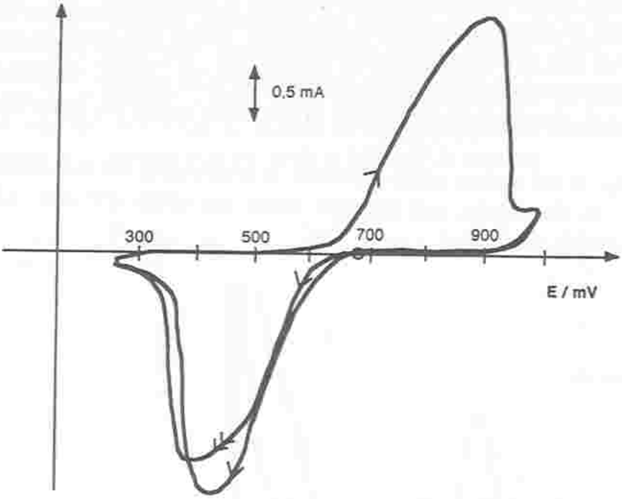

Figure 4. Electrochemical behaviour of gold(III) oxide as Au_2O_3 in 2 M HCl. Graphite powder: 46 mg; gold(III) oxide: 1 mg; binder: 2 M HCl (37 µL). Scan rate: 0.5 mV/s; E_0 = 680 mV; E_1 = 250 mV; E_2 = 1000 mV.

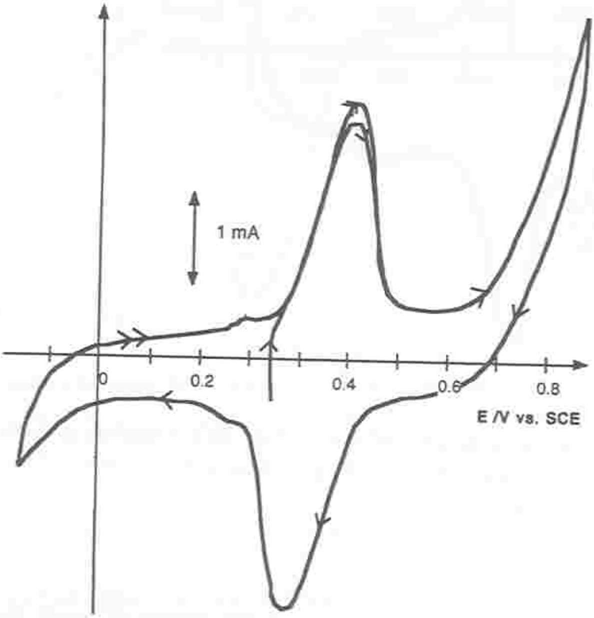

Figure 5. Electrochemical behavior of pyrite in 2 M HCl. Graphite powder: 50.7 mg; pyrite: 0.5 mg; binder: 2 M HCl (40 µL). Scan rate: 2.5 mV/s; E_0 = 325 mV; E_1 = 950 mV; E_2 = -150 mV.

Pyrite. As the main component of gold ores is pyrite, the electrochemical behaviour of this mineral incorporated in the carbon paste has been studied. The behaviour of pyrite of geological purity is represented in Figure 5. Hydrochloric acid (2 M) was used as the binder of the paste. From the zero current potential (325 mV), two peaks are registered, respectively, at 500 mV during the anodic sweep and at 370 mV during the cathodic sweep. The mean potential (E_{pa} + E_{pc})/2 is equal to 435 mV corresponds fairly well to the Fe(III)/Fe(II) system. Moreover, this electrochemical system has been already put in evidence in cordierite using the same technique [1, 2].

The incorporation of pyrite in the carbon paste electrode is responsible for the reduction of the electrochemical window, as the anodic and cathodic limits are +900 mV and -150 mV, respectively, in the presence of this compound.

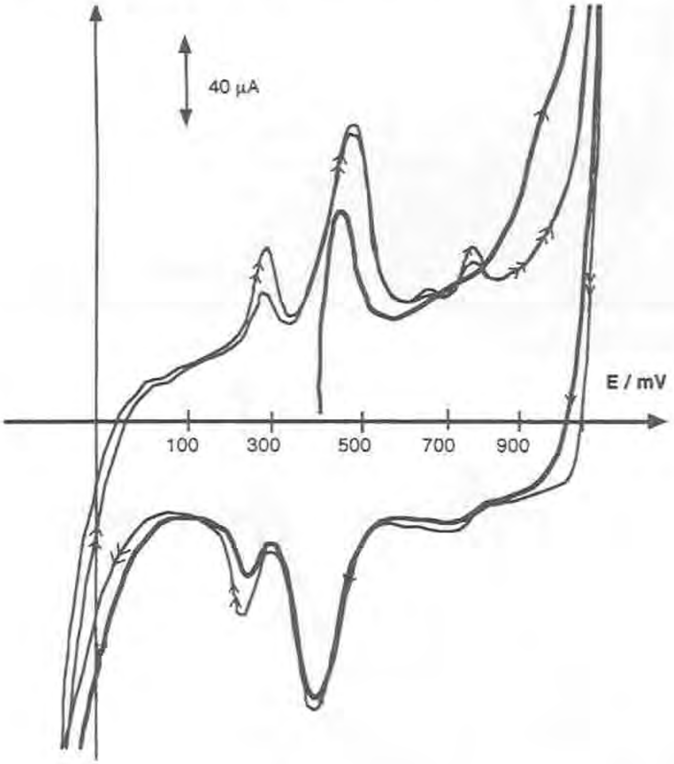

Figure 6. Electrochemical behaviour of beige gold ore in 2 M HCl. Graphite powder: 49 mg; beige gold ore: 0.7 mg; binder: 2 M HCl (40 μL). Scan rate: 2.5 mV/s; E_0 = 407 mV; E_1 = 900 mV; E_2 = -150 mV.

Gold ores

Previous studies have shown that the present ore contains large amount of pyrite, nearly 98% [10, 11]. It is only slightly soluble in water [12]. As an attempt to reduce the intensities of the peaks due to the presence of pyrite, the powdered ore was treated with hydrochloric acid for a 24 hours period before the electrochemical investigation. In Figure 6 is reported an example of the voltammogram obtained from a treated gold ore (beige color) incorporated in the carbon paste. As shown in the voltammogram, all the pyrite has not been eliminated (E_{pa} = 480 mV and E_{pc} = 390 mV). Near 265 mV is observed a quasi-reversible electrochemical system linked to the presence of unknown chemicals in the gangue. The anodic peak at 760 mV is attributed to metallic gold. The corresponding cathodic peak can not be observed owing to the presence of large amount of remaining pyrite. Its potential value and the fact that in sulphuric acid medium it does not appear support the assessment of the peak at 760 mV to metallic gold. Moreover, taking on ore from another source (gray color), the presence of gold is also detected by the presence of the 760 mV peak as shown in Figure 7 and its absence in H_2SO_4. In the same voltammogram, it is notable that the peak at 265 mV is missing.

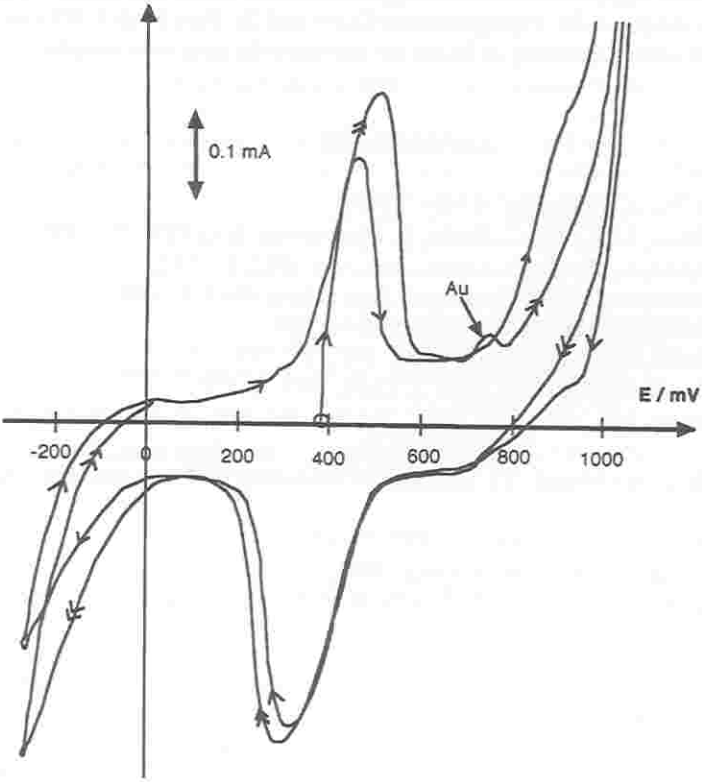

Figure 7. Electrochemical behaviour of gray gold ore in 2 M HCl. Graphite powder: 49 mg; beige gold ore: 0.7 mg; binder: 2 M HCl (40 μL); Scan rate: 2.5 mV/s; E_0 = 407 mV; E_1 = 900 mV; E_2 = -150 mV.

CONCLUSION

The use of carbon paste electrode immersed in an hydrochloric acid solution is a useful tool to investigate the behaviour of metals and metals ions. This study shows that the state of gold in a mineral matrix can be easily determined if the electrochemical systems present in the gangue are well separated from that of gold. In the case of the ores investigated, the presence of gold can be analytically detected but quantitative measurement of the gold content is difficult in the present conditions owing to the presence of pyrite. The use of another complexing medium, such aqueous thiourea or cyanide in basic solution has now to be investigated to obtain quantitat results. Nevertheless, the carbon paste method appears as an attractive method for analyz minerals as it is not time consuming and can be easily applied in developing countries.

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