

# Electrochemical dissolution of calaverite ( $\text{AuTe}_2$ ) in thiourea acidic solutions

S. AGUAYO SALINAS, M. A. ENCINAS ROMERO

*Departamento de Ingeniería Química y Metalurgia, Universidad de Sonora, Hermosillo, 83200, México*

I. GONZALEZ

*Departamento de Química, Universidad Autónoma Metropolitana, Unidad Iztapalapa, México*

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Cyclic voltammetric studies of carbon paste electrodes of a synthetic gold telluride, calaverite ( $\text{AuTe}_2$ ), in acidic aqueous thiourea solutions indicate that for potentials of about 0.4 V vs SCE adsorbed thiourea decomposes to formamidine disulphide, while gold from calaverite oxidizes and complexes with thiourea. The chemical oxidation of calaverite with the formamidine disulphide produced occurs in parallel with these electrodic processes. Additionally, for potentials in the vicinity of 0.5 V vs SCE tellurium from calaverite transforms to telluril ion,  $\text{HTeO}_2^+$ . A passive film of tellurous acid  $\text{H}_2\text{TeO}_3$  forms at potentials around 0.7 V vs SCE whereas at potentials above 0.9 V vs SCE the formation of gold oxides and hydroxides is apparent. Reduction of calaverite occurs at potentials less than  $-0.7$  V vs SCE. Other cathodic peaks are associated to the reverse processes of the anodic decomposition stages.

Keywords: *calaverite, electrochemical dissolution, thiourea, gold telluride*

## 1. Introduction

Telluride ores are the only gold minerals other than metallic gold and Au–Ag that are of some economic significance [1]. They have a wide geographic distribution and occur in several geological environments. Only on one location more than 20 such occurrences have been reported [2]. These minerals are grouped within the so-called refractory gold ores along with sulphide and carbonaceous ores [3]. The refractory nature of the last two is relatively clear, for example, sulphides consume both oxygen and cyanide whereas carbonaceous ores adsorb dissolved gold by ‘preg-robbing’. For tellurides the refractoriness is not very clear, however [4, 5]. It has been known that ores containing gold tellurides are less amenable to standard cyanidation and it is an accepted industrial practice that a preoxidation step is necessary for the treatment of these refractory ores. Tellurium can be recovered from the oxidized material by sodium sulphide leaching and sodium sulphite precipitation, as practiced at Emperor, Fiji [1].

Electrochemical experiments have been performed on the thermodynamics and kinetics of gold tellurides dissolution [6]. In alkaline solutions containing cyanide, the rate of gold telluride dissolution increases with increasing pH and strength of oxidant. Initially, the oxidation proceeds via the formation of the gold–cyanide complex,  $\text{Au}(\text{CN})_2^-$  and tellurous acid,  $\text{H}_2\text{TeO}_3$ . On the other hand, in relatively strong acid media the initial oxidation products are metallic gold

and telluril ion,  $\text{HTeO}_2^+$ . At higher oxidation potentials ( $> 0.50$  V vs SCE) and higher pH ( $> 2.0$ ) the dissolution is controlled by the formation of a passive film of  $\text{H}_2\text{TeO}_3$ .

Thiourea has been proposed as an alternative to cyanide for the treatment of sulphidic, cyanide-consuming precious metal ores, or for use in locations where environmental concerns make the use of cyanide difficult [7–10]. Thiourea leaching is a relatively nontoxic process, poses a rapid dissolution rate for gold and silver, slow dissolution rate of impurities and high selectivity [11]. Moir [12] and later Plaksin and Kozukhova [13] proposed the use of thiourea in the extraction of gold. Thiourea leaching has been used to treat an antimony-rich concentrate in New South Wales (Australia) and has been investigated as a process option for the treatment of several other ores [14–16], but no large scale commercial process has been developed. The potential applications for thiourea in gold leaching have been discussed and reviewed [17–22].

The objective of this work is to examine the electrochemical dissolution behaviour of synthetic calaverite,  $\text{AuTe}_2$ , in thiourea acidic solutions by using cyclic voltammetry.

## 2. Experimental details

Calaverite,  $\text{AuTe}_2$ , was prepared by fusion of stoichiometric mixtures of high purity gold and tellurium in evacuated silica tubes held at  $452^\circ\text{C}$  for 15 d [23].

X ray diffraction and fluorescence revealed the presence of  $\text{AuTe}_2$  only.

The working electrode consisted of a carbon electroactive paste made by a mixture of three components, spectrochemically pure carbon, the electroactive substance: calaverite, tellurium or gold ( $d_p = -120 + 105 \mu\text{m}$ ) and nujol as a binder. Firstly, the carbon was thoroughly wetted with the binder in a proportion kept constant at 5 g/2 ml for all experiments. Then, the desired carbon paste–electroactive species mixture was blended in a porcelain mortar to obtain a homogeneous paste. The ratio of electroactive substance to carbon paste was kept constant at 20% for all experiments. The paste bearing the electroactive material was laid as a 4 mm thick layer over a carbon paste mass, which had been previously filled and pressed into a cavity of a Teflon vessel. The surface of the working electrode was then smoothed with a spatula and excess paste was removed with a tissue paper. The surface of the electrode was renewed after each experiment by removing about 2 mm of the paste. Electrical connection to the carbon paste was made via a copper rod placed at the bottom of the Teflon vessel.

Electrochemical experiments were carried out in a 500 ml cell. The flanged cover of the reactor consisted of sockets for the working electrode, a thermometer, inert gas entrance, a platinum auxiliary electrode and a Luggin probe with a saturated calomel electrode (0.2412 V vs NHE at 25 °C). All potentials were measured and are reported against the saturated calomel electrode (SCE).

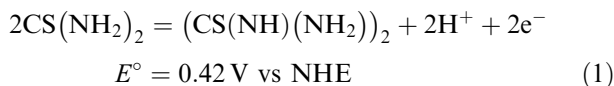
Electrochemical measurements were made using a potentiostat/galvanostat model PAR 273 in interface with a computer equipped with the PAR 270 electrochemical analysis system. All measurements were carried out at 25 °C in previously deoxygenated solutions prepared from AR grade chemicals and triply distilled water.

### 3. Results and discussion

#### 3.1. Cyclic voltammetry

A typical voltammogram of calaverite in an acid solution of thiourea is shown in Fig. 1. In the positive going potential scan, from the open circuit potential of 0.11 V, at least three anodic current peaks (A1, A2 and A3) are identified. Reversing the cycle, an additional anodic peak (A4) and three cathodic peaks (C1, C2 and C3) are observed. Comparison of this voltammogram with the one initiated in the cathodic direction (Fig. 2) indicates that the cathodic peaks C1 and C2 should be associated to the reduction of the oxidation products of calaverite. Furthermore, for experiments under stirring conditions, cathodic peaks C1 and C2 were absent which indicates that the oxidation products of calaverite are soluble species.

The first anodic peak A1 ( $E_{pA1} = 0.41 \text{ V}$ ) may be assigned to several processes occurring sequentially. One is associated to the partial decomposition of thiourea to formamidine disulphide (all potential values are standard reduction potentials):



According to several investigators [24–32] a prerequisite for Reaction 1 appears to be the adsorption of thiourea, as tautomeric thiourea, via the sulphur atom onto the oxide-free metal atom in the electrode surface. According to Kirchnerova and Purdy [26], during the first oxidation step of thiourea a weak adsorption is evident on both glassy carbon and platinum electrodes. The proposed mechanism considers the formation of a radical from adsorbed thiourea by a one-electron transfer reaction, and the recombination of two of those adsorbed radicals with formation of formamidine disulphide [25].

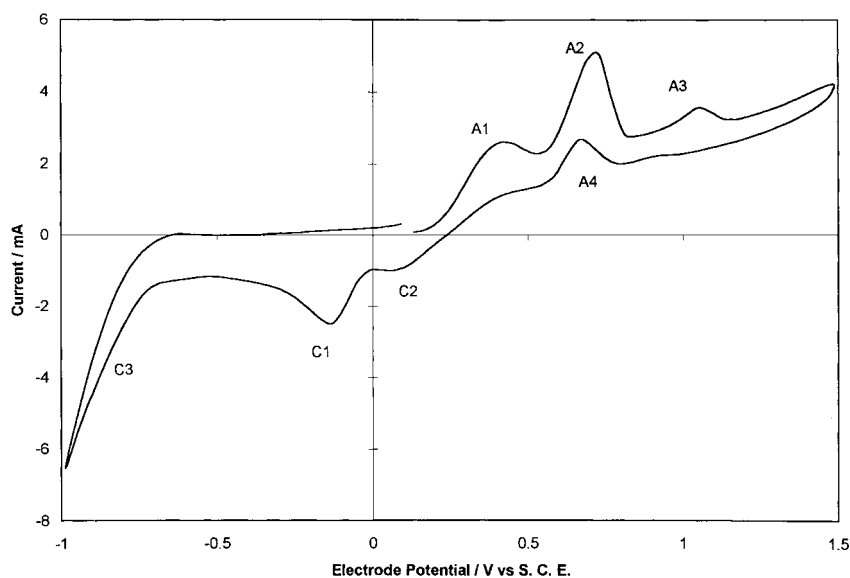


Fig. 1. Cyclic voltammogram of carbon paste–calaverite electrode in the anodic direction. Conditions:  $\text{H}_2\text{SO}_4$  0.1 M +  $\text{CS}(\text{NH}_2)_2$  0.1 M,  $50 \text{ mV s}^{-1}$ .

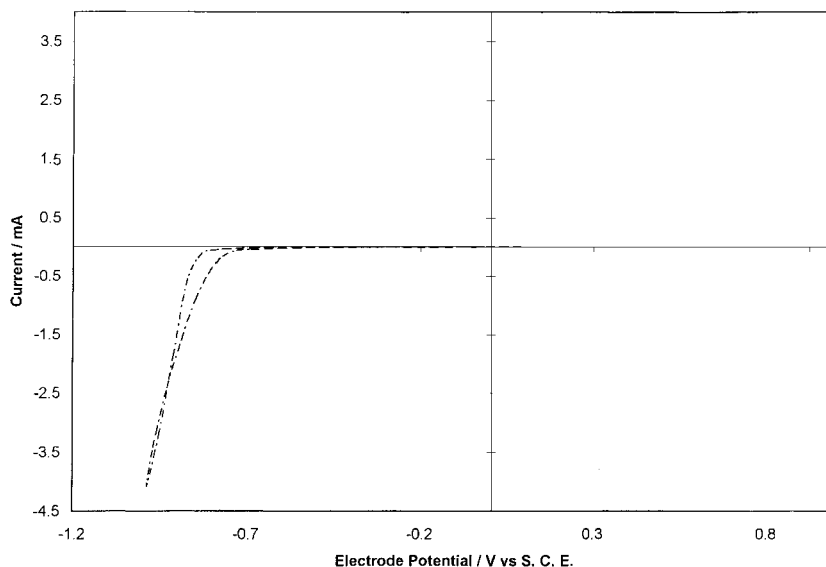
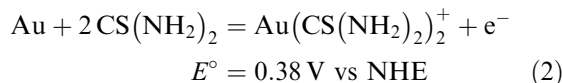


Fig. 2. Cyclic voltammogram of carbon paste-calaverite electrode in the cathodic direction. Conditions:  $\text{H}_2\text{SO}_4$  0.1 M +  $\text{CS}(\text{NH}_2)_2$  0.1 M,  $50 \text{ mV s}^{-1}$ .

In carbon paste electrodes, decomposition of thiourea to formamidine disulphide occurs at a threshold potential of about 0.2 V as Fig. 3 depicts. This potential is within the range where peak A1 is observed. In addition, Fig. 4 demonstrates that peak A1 depends strongly on thiourea concentration. Therefore, it is postulated that initially thiourea molecules adsorbed on the calaverite surface undergo oxidation to formamidine disulphide according to Reaction 1.

Electrochemical studies have shown that the most active dissolution of gold in thiourea acid solutions is obtained at redox potentials from 0.1 to 0.15 V [33–37]. Increasing the redox potential increases the consumption of thiourea. This could be partially related to the degradation of thiourea to formamidine

disulphide according to Reaction 1. Voltammograms for gold-carbon pastes in sulphuric acid and in acidic thiourea solutions were obtained. Figure 5 establishes that the anodic dissolution of gold in acidic thiourea solutions occurred for potentials near to 0.15 V (A1\*), according to the reaction:



This anodic peak is not well defined in the cyclic voltammogram (Fig. 1) due to the onset of thiourea decomposition. Therefore, another process occurring at A1 corresponds to the oxidation and complexation of gold from calaverite through the following reaction:

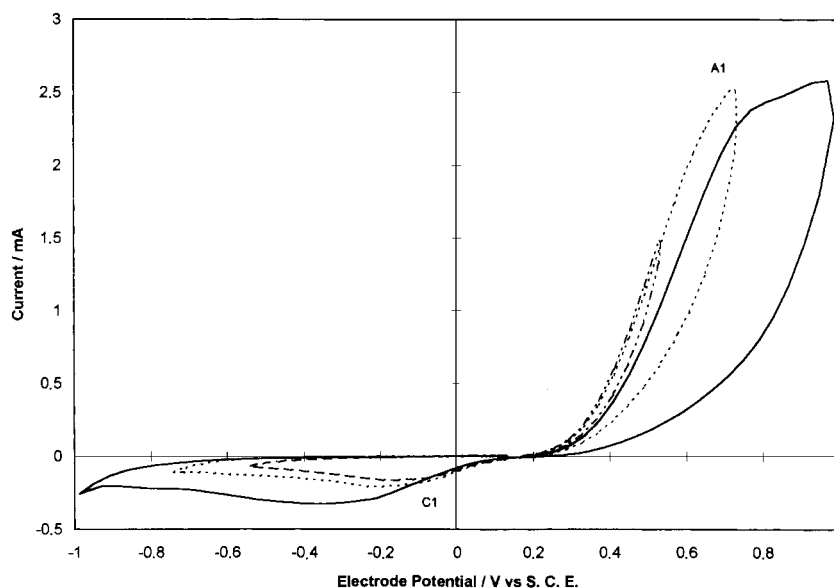


Fig. 3. Cyclic voltammograms of carbon paste electrode showing the threshold potential for thiourea decomposition and the effect of switching potential. Conditions:  $\text{H}_2\text{SO}_4$  0.1 M +  $\text{CS}(\text{NH}_2)_2$  0.1 M,  $50 \text{ mV s}^{-1}$ . Switching potential: (---) 0.5 V, (.....) 0.7 V and (—) 1.0 V.

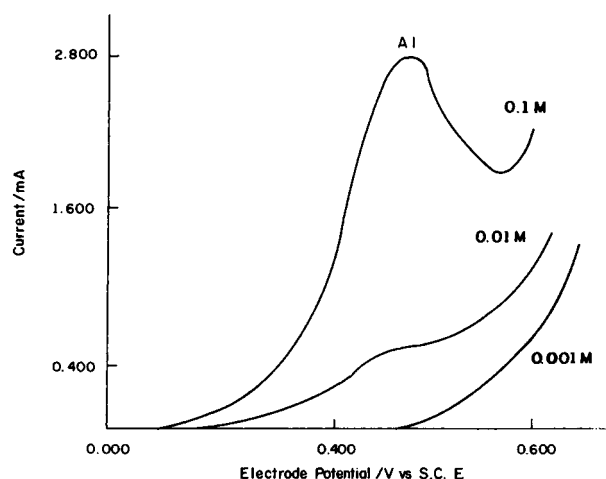
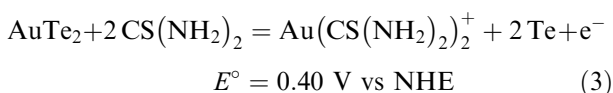
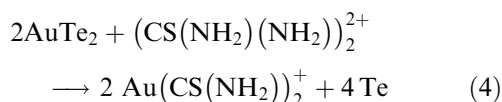


Fig. 4. Linear voltammograms of carbon paste-calaverite electrode showing the effect of thiourea concentration in the first anodic peak of calaverite oxidation. Conditions:  $\text{H}_2\text{SO}_4$  0.1 M  $50 \text{ mV s}^{-1}$ .



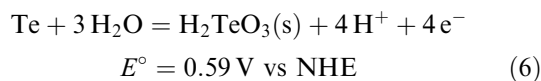
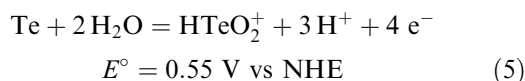
Furthermore, according to several investigators [40, 41], formamidine disulphide itself acts as the oxidant and supplies some of the complexing agent at the same time for the dissolution of gold. Hence, the following chemical reaction is occurring once formamidine disulphide has formed:



The Eh-pH diagram for the calaverite-thiourea system depicted in Fig. 6 demonstrates that metallic tellurium can coexist with the gold-thiourea complex in thiourea acidic aqueous solutions [39]. This dia-

gram compares favorably with those reported by others [21, 40].

Experiments with tellurium carbon paste electrodes indicate that a different dissolution behaviour is observed whether thiourea is present or not. Figure 7 presents voltammograms for the oxidation of tellurium in the absence and presence of thiourea. For the main oxidation peak A1\*\*, current densities are three times lower for sulphuric acid solutions than those in acidic thiourea solutions. Moreover, in the presence of thiourea an oxidation prewave is observed at threshold potentials of about 0.25 V. Another difference relates to the shape of the main cathodic peak C1\* which becomes broader when thiourea is present. The voltammogram in the presence of sulphuric acid resembles partially to that reported by Jayaskera with bulk electrodes in perchloric acid [6]. However, passivation for the first oxidation peak was more evident in that work. This difference in response to the formation of passive films is typical between bulk and carbon-paste electrodes [42]. The main oxidation step A1\*\* can be related to the oxidation of tellurium to telluril ion and formation of tellurous acid according to the following reaction scheme [6]:



Consequently, for the calaverite-carbon paste the second anodic peak A2 ( $E_{pA2} = 0.175 \text{ V}$ ) is connected to the decomposition of the tellurium formed according to Reactions 3 and 4, via Reactions 5 and 6. In addition, tellurium from unreacted calaverite can also be oxidized through the following reactions:

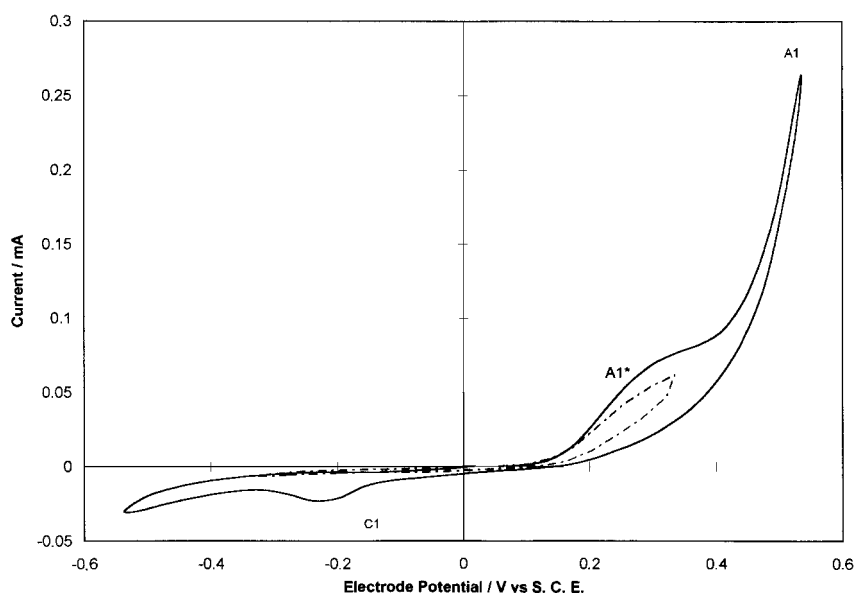


Fig. 5. Cyclic voltammograms of carbon paste-gold electrode showing the threshold potential for gold dissolution and the effect of switching potential in peak C1. Conditions:  $\text{H}_2\text{SO}_4$  0.1 M +  $\text{CS}(\text{NH}_2)_2$  0.1 M,  $50 \text{ mV s}^{-1}$ . Switching potential: (---) 0.35 V and (—) 0.55 V.

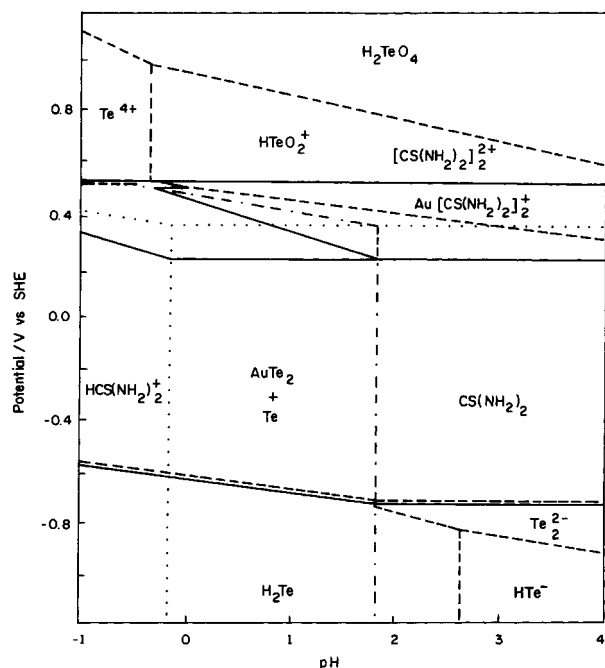
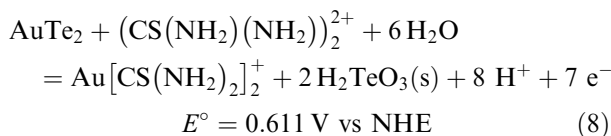
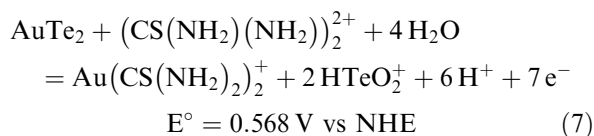


Fig. 6. Potential-pH diagram for the  $\text{AuTe}_2 - \text{CS}(\text{NH}_2)_2 - \text{H}_2\text{O}$  system at 298 K. Activities of dissolved species: (i) gold species =  $10^{-5}$  M, (ii) tellurium species =  $10^{-4}$  M, and (iii) thiourea species =  $10^{-4}$  M except  $[\text{HCS}(\text{NH}_2)_2] = 10^{-2}$  M and  $[\text{CS}(\text{NH}_2)_2] = 10^{-1}$  M.



Peak A3 ( $E_{\text{pA}3} = 1.05$  V) can be associated with the formation of gold oxides and hydroxides, soluble in thiourea solutions.

Reversing the cycle, an anodic peak A4 is observed at potentials near 0.7 V. This peak was also present in the anodic dissolution of tellurium carbon paste electrodes as Fig. 7 shows. This kind of behaviour is related to the formation of a soluble film whose growing rate decreases as its thickness increases [38]. Thus, the anodic peak A4 is linked to a reactivation of the electrode due to the chemical dissolution of the passive film of tellurous acid [6].

Regarding the cathodic peaks C1 and C2, they are connected to the reduction of the soluble products formed during the oxidation of calaverite at A1, A2 and A3. These peaks were not present either when the voltammogram was initiated in the cathodic direction nor when the working electrode was rotated. This was further confirmed by a number of tests made by varying the inversion potential.

Several reduction processes are related to the cathodic peak C1 ( $E_{\text{pC}1} = -0.136$  V). Those associated to the reverse of reactions occurring at A1 and to the reduction of the telluril ion and tellurous acid passive film formed at A2.

The cathodic wave C2 ( $E_{\text{pC}2} = 0.060$  V) appeared only when the preset anodic switching potential was greater than about 0.9 V. Therefore, it could be linked to the reduction of gold oxides or hydroxides produced at A3.

Peak C3 appeared at threshold potentials about -0.7 V. It was the only perturbation produced when the sweep was initiated in the cathodic direction, either under stirring or quiescent conditions. It is probably mostly due to hydrogen evolution although some calaverite may be reduced by the following reaction:

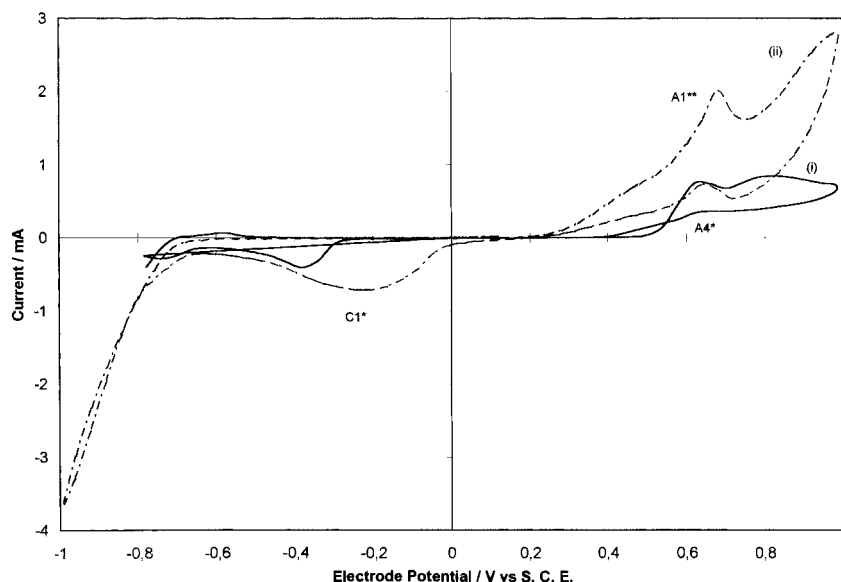
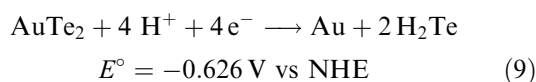


Fig. 7. Cyclic voltammograms of carbon paste-tellurium electrode in: (i)  $\text{H}_2\text{SO}_4$  0.1 M,  $50 \text{ mV s}^{-1}$  and (ii)  $\text{H}_2\text{SO}_4$  0.1 M +  $\text{CS}(\text{NH}_2)_2$  0.1 M,  $50 \text{ mV s}^{-1}$ .

#### 4. Conclusions

Cyclic voltammetry of the gold telluride, calaverite, in acidic thiourea aqueous solution reveals the presence of three anodic peaks A1, A2 and A3. The first peak can be assigned to two electroodic processes. For potentials less or equal than about 0.4 V, the processes include decomposition to formamidine disulphide of the thiourea adsorbed on the calaverite surface, and oxidation and complexation of gold. Additionally, a chemical reaction involving the oxidation of gold with formamidine disulphide is occurring in parallel with the above electroodic reactions.

The second anodic peak is linked to the oxidation of the tellurium to telluril ion, for potentials less than 0.7 V and formation of a passivating film of tellurous acid for higher potentials. At that potential range, gold continues dissolving and complexing and formamidine disulphide decomposition is occurring.

The third anodic peak corresponds to the formation of gold hydroxides that might be relatively soluble in the thiourea solution.

An anodic peak A4, is observed while reversing the cycle at potentials near 0.7 V. This peak is related to the decomposition of the original surface, which continues reacting once the chemical dissolution of the surface film has occurred.

Cathodically, calaverite decomposes to metallic gold and hydrogen telluride at potentials greater than  $-0.7$  V (C3). Two more cathodic peaks are observed, one at 0.060 V (C2) and another at  $-0.136$  V (C1). These two peaks are related to the reverse of the anodic processes occurring at A3 and A1 and A2 respectively.

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