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ELECTROCHEMICAL BEHAVIOUR OF TELLURIUM AND SILVER TELLURIDE AT ROTATING GLASSY CARBON ELECTRODE

M. TRAORE, R. MODOLO and O. VITTORI*
Laboraroire d'Electrochimie Analytique, Département de Génie Chimique et Chimie Appliquée (C.N.R.S U.A. 417), I.S.I.D.T.—Université LYON I—43, Boulevard du 11, Novembre 1918, 69622 Villeurbanne, France.

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Abstract—Electrodeposition of tellurium and silver is performed at rotating glassy carbon disc electrodes. First the mechanism of deposition of tellurium is investigated, and a well defined wave may be observed close to -0.4 V/*sce*. On the plateau of this wave a small peak may be noticed at -0.7 V/*sce*, and is due to reduction of Te(0) into Te($-$II), but a chemical reaction occurs simultaneously between Te($-$II) and Te(IV), reaching the electrode by convection and diffusion, to lead again to Te(0), and consequently the thickness of the deposit increases. Conversely, with a non-rotating electrode, the Te(IV) species reach the electrode only by diffusion and in lesser amounts than in the above case; so the peak at -0.7 V/*sce* is large since the tellurium deposit dissolves by reduction into Te($-$II).

The electrodeposition of silver telluride Ag_2Te is investigated with several concentration ratio of Ag(I) and Te(IV). One may observe the progressive changes in the shape and magnitude of the oxidation peaks of Ag and Te. For a Ag(I)/Te(IV) ratio close to 0.8 it has been observed that quasi pure Ag_2Te is obtained. The elementary composition of the deposit was confirmed by X-ray analysis.

INTRODUCTION

An economic method of obtaining stable polycrystalline electrodes with high light conversion yields is essential for photovoltaic cells applied to the use of solar energy. Electrodeposition is the commonest method since it allows control of the parameters influencing the composition of the film, and consequently of the photovoltaic properties. During these last years many papers dealing with this object have been published. These mainly concern mixed metal–semiconductor compounds, more precisely metal–tellurium deposition[1–9]. The most thoroughly investigated compound is undoubtedly cadmium telluride because of its low band gap value *ie* 1.5 eV[4].

Such electrosynthesis requires a good knowledge of the semiconducting material, but unfortunately there are only a few papers on the study of tellurium alone. The earlier work of Lingane and Niedrach[10–11] was related to the polarographic behaviour of the (IV) and ($-$II) oxidation states of tellurium. These authors showed that, except for strongly alkaline medium, the reduction of tellurous acid occurs *via* a 4 electron process as follows:

$$H_2TeO_3 + 4\,H^+ + 4e^- \rightarrow Te + 3H_2O.$$

In strongly alkaline medium the ($-$ II) oxidation state may be obtained:

$$TeO_3^{2-} + 2H_2O + 6e^- \rightarrow Te^{2-} + 6OH^-.$$

In addition these authors point out the presence of a sharp and intense maximum on the wave plateau of acidic or neutral pH. This maximum was attributed to the Te/Te($-$II) couple but some difficulties in a correct interpretation arise.

More recently Sella *et al.*[12] using a tin oxide electrode, and Carbonnelle *et al.*[13] using a glassy carbon electrode have studied the behaviour of Te(IV) in acidic medium. The reduction of Te(IV) occurs *via* 4 electron process, leading to Te(0). At more negative potentials, elemental tellurium, Te(0), is reduced to Te($-$II), and a reaction between Te(IV) and Te($-$II) appears to give Te(0) deposited on the electrode.

In the present paper we are concerned with the reduction of Te(IV) in the presence of silver. We confirm some of the results of Sella *et al.*[12] and Carbonnelle *et al.*[13] but the reduction of the tellurium deposit by reaction with the Te($-$II) and formation of polytelluride Te_2^{2-} is not unambiguously verified.

The use of a rotating disc electrode (*rde*) leads to a constant flux of species towards the electrode surface, and avoids the concentration decrease in the vicinity of the electrode which occurs with a non-rotating device. We also proposed several experimental conditions for performing electrosynthesis of silver telluride from dilute electrolytic baths, in contrast to the initial method of Panicker *et al.*[1] subsequently used by other authors[3, 4].

EXPERIMENTAL

A GSTP3 signal generator, a PRT 30–0.1 potentiostat, and an EDI rotating disc electrode were used for recording the cyclic voltammograms (SOLEA–TACUSSEL, France) A XY IF 3802 recorder was associated to the above apparatus (IFELEC, France).

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*Author to whom correspondence should be addressed.

Classical three electrode circuitry was used, with a *sce* as reference, a platinum wire as auxilliary and the *rde* as the working electrode. The diameter was 0.2 cm.

All the reagents were of analytical grade (MERCK, Germany or PROLABO, France). Tellurium dioxide is weighed and first dissolved in the minimum of aqueous 1 M NaOH and then adjusted to pH 1 with $HClO_4$. Oxygen was removed by bubbling pure nitrogen through the solution. X-Ray spectroscopy was performed using a D 500 model X-Ray spectrometer (SIEMENS, Germany).

RESULTS AND DISCUSSIONS

In the majority of the experiments, the starting potential is $+1.1$ V/*sce*, and the first scan is applied towards cathodic values.

The typical current–potential curve obtained with tellurous acid in 0.1 M $HClO_4$ is given in Fig. 1. Two reduction waves are evident (V_1 and V'_1) the half wave potentials of which are -0.45 and -0.25 V/*sce*, respectively and two oxidation peaks (a_1 and a_2) the peak potentials being 0.45 and 0.70 V/*sce* respectively. In addition a small peak C_1 may be observed on the plateau of wave V_1 which is the first wave recorded when the potential sweep is applied from $+1.1$ to -0.9 V/*sce*.

The point where the potential sweep is reversed is of great importance to the presence of peak a_2 (Fig. 1). When this potential is less cathodic than -0.6 V/*sce*, *ie* before peak C_1 appears, then peak a_2 is absent. Conversely, if the reverse potential is more negative than -0.6 V/*sce*, then peak C_1 appears on the cathodic sweep and peak a_2 is observable after peak a_1. As shown in Fig. 2, peak a_1 is in fact the addition product of two coalescing peaks. This may be demonstrated by progressively changing the reverse potential from -0.3 to -0.9 V/*sce*. If the reverse potential is -0.5 V/*sce*, then the deposit is very thin and the more anodic peak, *ie* a_1, corresponds to a first layer with special properties due to the carbon–tellurium interface. Thus it appears that it is easier to dissolve electrochemically deposited tellurium when coated on tellurium, than this particular layer. Peak a_1 which corresponds to thicker deposits obtained at -0.6, -0.75 and -0.9 V/*sce* progressively masks the small a'_1 peak.

Study of peak C_1 at -0.7 V/sce

Peak C_1 situated at -0.7 V/*sce* (Fig. 1), has two interesting features: (i) it appears on the plateau of the wave V_1 when the limiting current is reached; (ii) its symmetry a surface process rather than a diffusional one. Such a surprising peak was observed at a *dme* by Lingane and Niedrach[11] who described the phenomenon, and outlined the formation of brown elemental tellurium in the vicinity of the electrode. They also described the reaction of Te($-$II) with Te(0) coated on the drop leading to polytelluride ions. Our experiments on a carbon electrode tend to confirm the interpretation of Carbonnelle who suggests that Te($-$II) reacts with Te(IV) on reaching the electrode leading again to coated Te(0).

In effect, when the cathodic sweep is reversed before peak C_1 appears then the areas under the waves and the peaks are identical, indicating that there is no loss of tellurium and the electrical charges are the same. However, if the reverse potential is then made more negative than -0.6 V/*sce*, then this equality cancels (Table 1). When potential sweeps are applied from $+0.1$ to -0.9 V/*sce* in solutions, both with and without tellurous acid, with a previously tellurium covered electrode, we observe that for a stationary electrode a very important peak C'_1 appears, exactly at the peak potential of C_1, and in oxidation a peak a_3 at -0.65 V/*sce* is noticed. A small peak C_2 is also

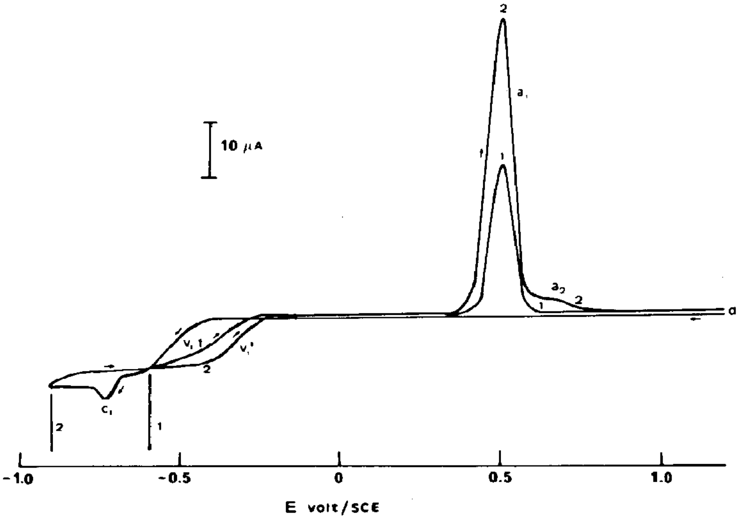

Fig. 1. Cyclic voltammetric curve for 4×10^{-5} M Te(IV) in 0.1 M $HClO_4$ at 2000 rpm. Potential sweep rate 20 mV s^{-1}.

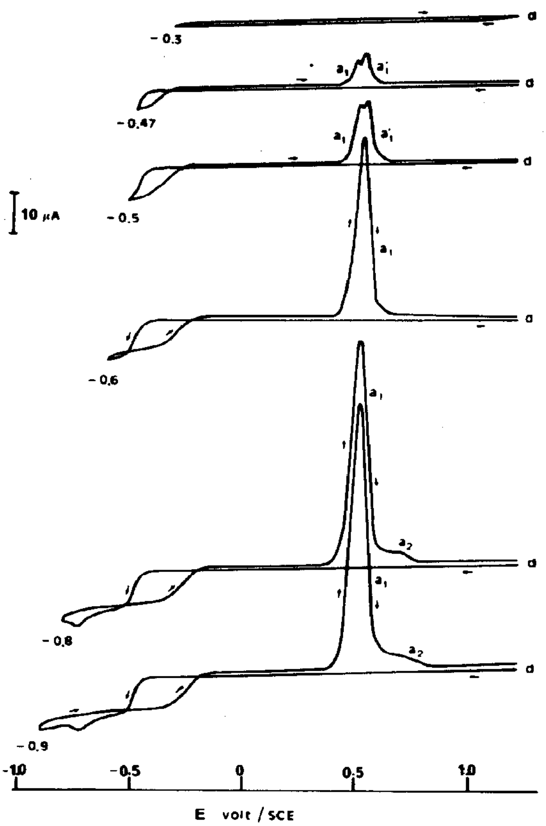

Fig. 2. Cyclic voltammetric curves for 4×10^{-5} M Te(IV) in 0.1 M $HClO_4$ with decreasing reverse potential. Same conditions as Fig. 1.

observed at the same potential that wave V'_1, if tellurous acid is present. This is quite normal with a pre-coated electrode (Fig. 3).

Thus it seems possible to describe peak C_1 by the following equation; in acidic medium:

$$Te(0) + 2e^- + 2H^+ \rightarrow H_2Te. \qquad (1)$$

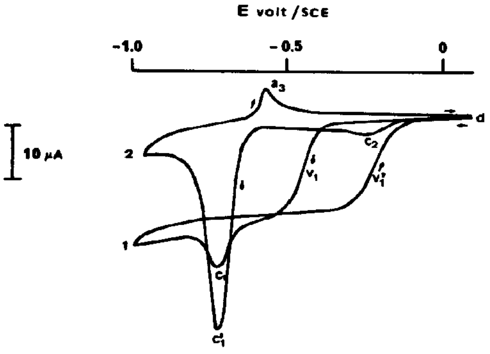

Fig. 3. Cyclic voltammetric curves for 8×10^{-5} M Te(IV) in 0.1 M $HClO_4$ from +0.1 to −1.1 V/*sce*, $v = 20$ mV s^{-1}.
(1) Rotating rlectrode; 2000 rpm.
(2) Stationary electrode previously coated with an electrodeposit of tellurium.

Peak a_3 results from oxidation of Te(−II), (H_2Te) with the same equation as above.

The areas of peaks C'_1 and a_3 are very different, suggesting a loss of H_2 Te by a subsequent chemical step rather than by diffusion, which is too slow a process:

$$2H_2Te + H_2TeO_3 \rightarrow 3Te(O) + 3HO. \qquad (2)$$

As shown in Fig. 4, peak a_3 does not appear with a *rde*, since H_2TeO_3 arrives at the electrode more quickly than in the stationary case. We suggest in addition that tellurium obtained in this way is slightly more difficult to oxidize that tellurium directly deposited from Te(IV) into Te(0) and gives peak a_2 in Fig. 1.

Similar tellurium behaviour was observed in H_2SO_4 with a stationary glassy carbon electrode, and in our laboratory we have also conducted similar studies on selenium[14]. This interpretation of the nature of peak C'_1, C_1 and a_3 has been confirmed by other experiments as follows:

A glassy carbon electrode first covered with tellurium by classical electrodeposition from +0.1 to −1.0 V/*sce* is rinsed and then immersed in 0.1 M $HClO_4$ without any tellurous acid. A cathodic sweep

Table 1. Variation of the ratio between the oxidation peak area and the sum of the areas under the reduction waves during a cyclic scan

Potential range V/*sce*		Supporting electrolyte	Ratio A_{peak}/A_{wave} (%)
Start	Reverse		
+1.2	−0.6	0.1 M $HClO_4$	100
+1.2	−0.85	*idem*	65.9
+1.2	−1.00	*idem*	60
+1.2	−0.6	0.1 M HCl	98.6
+1.2	−0.7	*idem*	85.9
+1.2	−0.85	*idem*	64.2
+1.2	−0.6	0.5 M CH_3COOH	98.7
+1.2	−0.7	*idem*	98.3
+1.2	−0.8	*idem*	58.7
+1.2	−0.9	*idem*	58

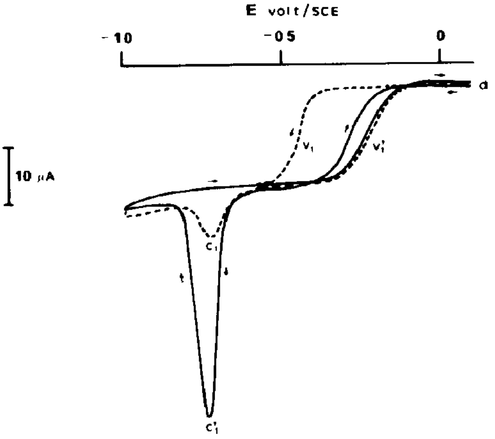

Fig. 4. Same conditions as for Fig. 3 for a tellurium coated electrode with $\omega = 2000$ rpm.

from -0.5 to -1.0 V/*sce* is applied. Peaks C'_1 and a_3 are observed (Fig. 5a). An anodic sweep from $+0.1$ to $+1.4$ V/*sce* is then applied and only a very small quantity of tellurium is apparent from peak a_1 (Fig. 5b).

A carbon paste electrode with 5 % (w/w) of tellurium powder (99.999 %, ALDRICH) is immersed in 0.1 M $HClO_4$ and a cathodic sweep from $+0.1$ to -1.0 V/*sce* is applied. A large current starts to flow at about -0.7 V/*sce*. Because of hydrogen evolution this curve is stopped at -0.9 V/*sce* and the carbon paste is dislocated and falls.

Thus Equation (1) seems to be fully demonstrated.

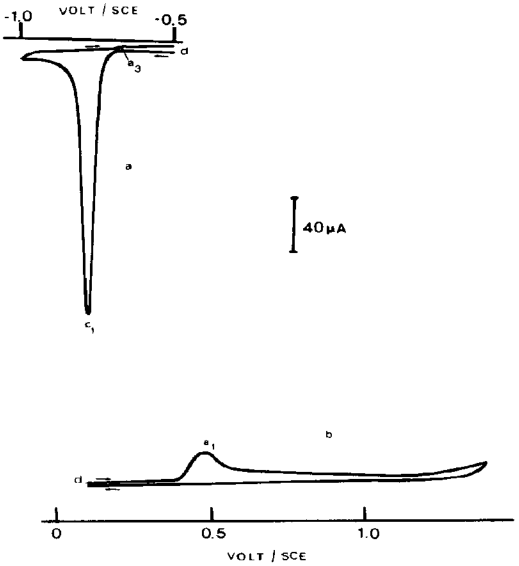

Fig. 5. Cyclic voltammetric curve with a tellurium coated electrode,
(a) From -0.5 to -1.0 V/*sce*; $v = 2$ mV s^{-1}.
(b) From $+0.1$ to 1.4 V/*sce* following (a).

Study of waves V_1 and V'_1 and peak a_1

These two waves are due to tellurous acid reduction. Te(IV) is more easily reduced on tellurium than on carbon since wave V'_1 is less cathodic than wave V_1 by about 150 mV. For a stationary electrode peak C_2 looks like that of a classical diffusion controlled step (Fig. 6). For a rotating electrode the limiting currents are proportional to the tellurous acid concentration and to $\omega^{1/2}$ (ω being the rotating speed of the electrode) following the Levich criterion (Figs 7 and 8). X-Ray analysis of elementary tellurium deposited at -0.4 V/*sce* shows that it crystallized in the compact hexagonal system. Two reduction schemes are possible.

1st mechanism:

$$H_2TeO_3 + 6e^- + 6H^+ \rightarrow H_2Te + 3H_2O, \qquad (3a)$$

$$2H_2Te + H_2TeO_3 \rightarrow 3Te + 3H_2O. \qquad (3b)$$

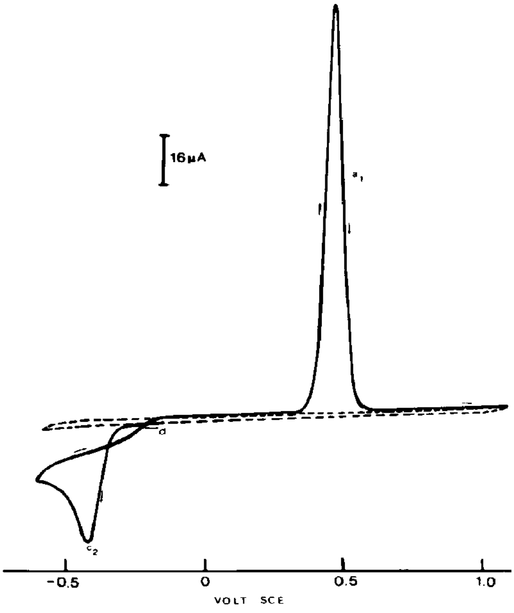

Fig. 6. Cyclic voltammetric curve for 3.3×10^{-4} M Te(IV) in 0.1 M $HClO_4$ with a stationnary electrode. $v = 20$ mV s^{-1}.

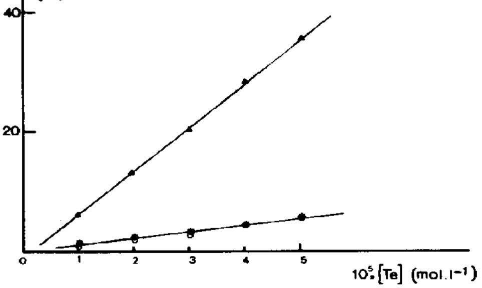

Fig. 7. Variation of peak and wave currents with tellurium concentration. ▲ = peak; ✱ and O = waves.

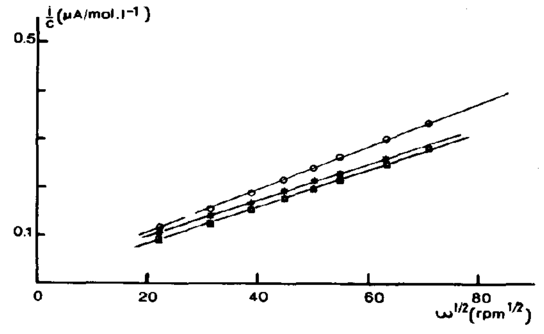

Fig. 8. Variation of i/[Te(IV)] versus $\omega^{1/2}$ for the reduction waves [Te IV] = 4×10^{-5} M (Δ); 8×10^{-5} M (✱); 10^{-4} M (□); 1.5×10^{-3} M (O).

Notice that Equation (3b) is identical to Equation (2). Such a mechanism has been established for selenium (IV) at the *dme*[11] and was confirmed later on platinum and carbon[14].

2nd mechanism

$$H_2TeO_3 + 4H^+ + 4e^- \rightarrow Te + 3H_2O \qquad (4)$$

From the above study on peaks C_1 or C'_1 at -0.75 V/*sce* it appears that reactions 3a and 3b are not possible when the potential is less cathodic than -0.6 V/*sce*. And also, with the first mechanism one may expect a great influence of the diffusion of H_2TeO_3 towards the electrode surface. So for dilute solution the 6 electron step Equation (3a), has to be observed, using the Levich criterion. But in fact for solutions ranging from 4×10^{-5} to 10^{-3} M Te(IV) the same electronic transfer is observed (Fig. 8) and the second mechanism seems to be more realistic.

The electronic transfer coefficients determined by Tafel slope applied to the rising part of the waves V_1 and V'_1 are respectively $\alpha = 0.280$ and $\alpha = 0.143$ with $n = 4$. Recently Sella *et al.*[12] found $\alpha = 0.19$ for wave V'_1.

Peak a_1 is attributed unambiguously to the oxidation of Te(O) to Te(IV) as in Equation (4). The height of the peak is proportional to the amount of tellurium provided the deposition potential is never more cathodic than -0.6 V/*sce*, and its shape is not influenced by stirring (Fig. 7).

Electrodeposition of silver and tellurium

The study of silver in 0.1 M $HClO_4$ is given in Fig. 9. Two reduction waves are apparent, V_2 at -0.05 V/*sce* and V'_2, which result from deposition of silver on silver, and an oxidation peak a_4 at $+0.35$ V/*sce*.

When, for a given Ag^+ concentration, increasing amounts of Te(IV) are added we observe important modifications in the shape of waves and peaks. First two waves appear, V_3 at -0.25 V/*sce* and V'_3 at -0.15 V/*sce* (Fig. 9) and second, the peak a_4 decreases while a new peak, a_5 appears at $+0.55$ V/*sce*, a potential more anodic than that of pure tellurium Te(O) ($+0.45$ V/*sce*). Peak a_4 at last disappears and the tellurium peak close to $+0.45$ V/*sce* becomes measurable. At this time peak a_5 stays quasi-constant.

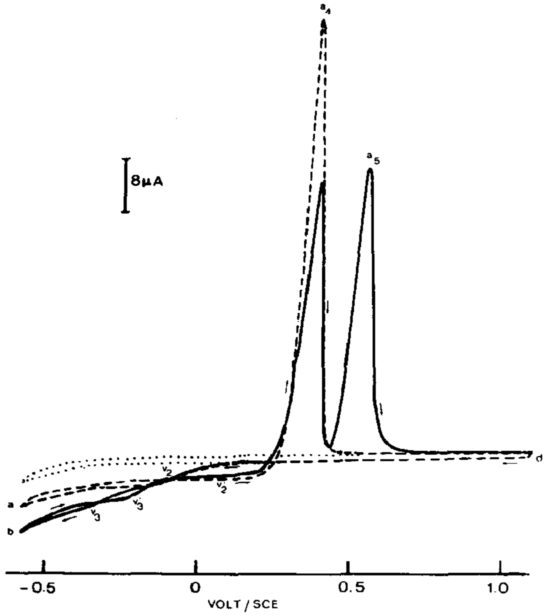

Fig. 9. Voltammetric curves $Ag^+ = 8 \times 10^{-5}$ M with (a) = [Te(IV)] = 0; (b) = [Te(IV)] = 2×10^{-5} M; v = 20 mV s^{-1}; ω = 2000 rpm.

Similarly progressive addition of silver, Ag(I), in a solution with a fixed Te(IV) concentration leads to the appearance of increasing waves for electroreduction of silver and a shift towards more anodic values of the reduction wave of Te(IV).

In oxidation we observe the progressive decrease of the Te(0) redissolution peak and the presence of the peak at $+0.55$ V/*sce*, the height of which initially increases with the addition of Ag(I) to the bulk. In contrast the electrodissolution peak of silver is only noticed when the $[Ag^+]/[Te(IV)]$ ratio is close to 1. Then, peak a_5 at $+0.55$ V/*sce* becomes constant even when more Ag^+ ions are added (Fig. 10).

X-Ray analysis of the deposit shows that Ag_2Te is present. This may be interpreted as follows:

Because of the reduction potentials of these two elements, there is first the deposition fo silver on glassy carbon, by Equation (5). Then Te(IV) is reduced on the silver deposit with formation of Ag_2Te as described by Equation (6):

$$Ag^+ + e^- \rightarrow Ag, \qquad (5)$$

$$H_2TeO + 2Ag + 4H^+ + 4e^- \rightarrow Ag_2Te + 3H_2O. \quad (6)$$

This reaction shows that Ag_2Te formation is governed by the initial amount of silver on the electrode. When the initial amount of silver is very small then no dissolution peak for silver may be observed because all silver atoms have reacted to give Ag_2Te. As the silver deposit increases, reaction (6) is limited because probably only the few layers of silver in contact with the bulk may lead to Ag_2Te and so the peak a_5 reaches a maximum value. The unreacted silver still present leads to the silver peak.

These conclusions may be verified with the set of experiments described below:

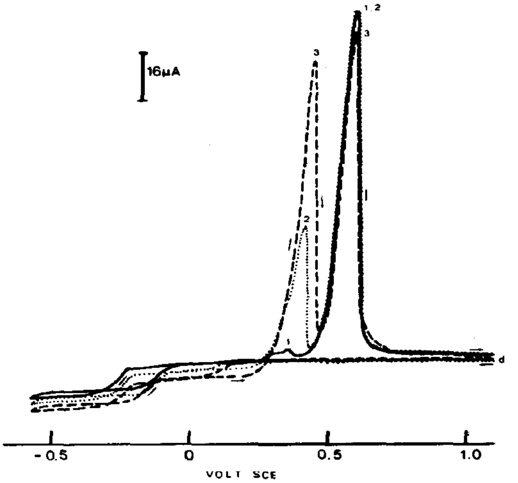

Fig. 10. Cyclic voltammetric curves for 5×10^{-5} M Te (IV) with increasing concentration of Ag^+: $[Ag^+] = (1)\ 4 \times 10^{-5}$ M; (2) 7×10^{-5} M (3) 1.1×10^{-4} M. Other conditions as in figure 1.

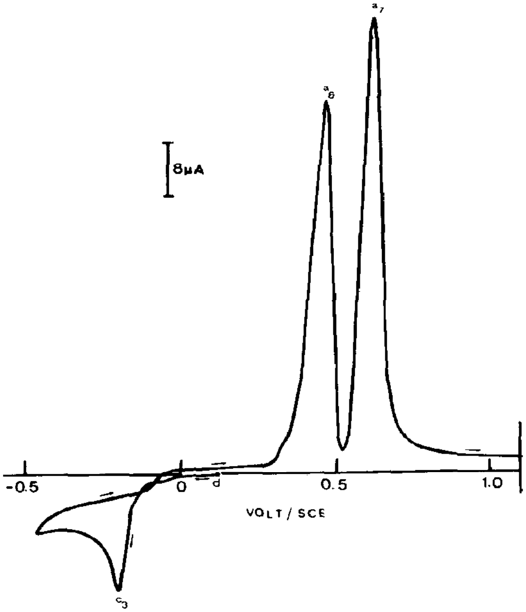

Fig. 11. Voltammetric curve for 2×10^{-4} M Te(IV) in 0.1 M $HClO_4$ with a stationary, previously silver coated electrode. Starting potential = +0.1 V/*sce*.

A glassy carbon electrode covered with silver in a solution containing only Ag^+ ions is rinsed and immersed in a 3×10^{-4} M tellurous acid solutions and the potential is applied from +0.1 to −0.5 and after to +1.1 V/*sce* (Fig. 11). One may observe with a stationary carbon disc that the peak C_3 corresponds to the electrodeposition of species related to H_2TeO_3 since no silver ions are present. In oxidation one may observe two well defined peaks a_6 and a_7 at +0.45 and +0.6 V/*sce*, potentials very closed to that of a_4 and a_5 previously described. Thus there is a reaction between solid silver and H_2TeO_3 during the reduction of Te(IV), as in Equation (6).

As a conclusion we may outline the possibility offered by electrodeposition in the modulation of the ratio of the deposited species *ie* Ag, Te, and Ag_2Te, and the main result of this study seems to be the electrodeposition of quite pure Ag_2Te for a ratio $[Ag^+]/[Te(IV)]$ close to 0.8 as shown in Fig. 10.

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