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Electrochemical research on tellurium deposition from acid sulfate medium

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Abstract The telluryl ion (HTeO_2^+) reduction process from acid sulfate medium, on in situ generated tellurium electrodes, was investigated by means of different electrochemical techniques. The kinetic study revealed the existence of two Tafel slopes, thus indicating that the deposition mechanism changes with the applied potential and the kinetic parameter values pointing to this process is irreversible at 25 °C. Moreover, the HTeO_2^+ electrochemical reduction is preceded by adsorption of the electroactive species on the electrode surface. In addition, the activation energies for both the activation and the diffusion processes were evaluated.

Keywords Tellurium electrodeposition · Kinetics · Adsorption · Pulsed current

Introduction

Tellurium has great practical applications in the semiconductor industry since this element is the raw material for the production of thermoelectric devices and photosensitive materials [1, 2, 3, 4, 5]. The preparation of semiconductor materials composed of more than one element can be made in several ways [6, 7, 8]; in the case of the electrochemical method to obtain these materials, little attention has been devoted to study the individual

behavior of the elements present in such semiconductor materials. The lack of this information frequently avoids that the electrochemical processes to prepare semiconductors can be enhanced. Thus, it is clear that a formal study of the deposition process for obtaining a semiconductor material should be, firstly, focused to study the individual deposition process of the components in the same chemical medium, as it has been pointed out in other works [9, 10].

In the particular case of tellurium, this element is by itself a semiconductor material and when it reacts with some other specific elements, it can lead to the formation of other types of semiconductor [1, 2, 3, 4, 5, 11, 12]. Therefore, it is important to know the deposition mechanism of this element since this information should allow improvement of the electrochemical processes for obtaining semiconductor materials based on tellurium.

Studying tellurium electrochemical behavior is specially complex in view of the fact that this element can be present in several oxidation states [13] and its electrochemical reduction is a multielectronic process. Investigations about tellurium behavior have been carried out in both aqueous [14, 15] and non-aqueous [16, 17] media, and various electrochemical techniques have been used to perform such research [18, 19, 20, 21, 22]. In the majority of works published up to now, it is assumed that, in acid medium and at low pH, the HTeO_2^+ reduction process to give elementary tellurium takes place in one step with the transfer of four electrons [23, 24]. Later reduction of tellurium at more negative potentials leads to the H_2Te species and, simultaneously, the hydrogen evolution reaction starts [25, 26]. Nevertheless, other authors have proposed a different route for the telluryl ion electrochemical reduction and the following mechanism has been suggested: by a six-electron transfer, the HTeO_2^+ is firstly reduced to form the H_2Te^+ species; later, a chemical reaction between this species and the telluryl ion gives elementary tellurium [27, 28, 29, 30, 31]. Some debate about the tellurium deposition mechanism has emerged from these two points of view and, until now, there is still some doubt about which of

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the two pathways is the best to describe the attained results.

Therefore, in this work we intend to contribute to the knowledge and understanding of the HTeO_2^+ reduction process; to this end, a systematic study of tellurium electrodeposition on solid tellurium electrodes has been performed and the results obtained from a technique were confirmed by using other electrochemical techniques. The study was made starting from an acid aqueous solution and different electrochemical techniques in stationary and non-stationary diffusion regimes were used. This investigation is mainly focused on the kinetic and mechanistic aspects of the reduction process, besides the detection and characterization of the possible collateral phenomena coupled to the charge transfer. In order to avoid electrode contamination and uncertainty in the obtained electrochemical information, this study has been carried out using solid tellurium electrodes prepared in situ.

Experimental

Chemical reagents of analytical grade (Aldrich) and triply distilled/deionized water were used during this work. A millimolar solution of TeO_2 and 0.5 M K_2SO_4 was used and sulfuric acid was added until the pH of the solution was 2. In the case of aqueous solutions and $\text{pH} < 5$, it has been shown from thermodynamic considerations [13] that the dissolution of TeO_2 leads to formation of the stable species HTeO_2^+ ; therefore, in this work this ion is assumed as the soluble electroactive species. Besides, with the purpose of guaranteeing the formation of such species, the prepared solutions were stabilized by thermal treating (50 °C) during several hours, which allowed us to obtain reproducible results.

A conventional three-electrode electrochemical cell made of glass (Pyrex) was used, with a capacity of 100 mL and designed to maintain an oxygen-free atmosphere. The working solution was purged with nitrogen for at least 30 min before each experimental series and the nitrogen flow was maintained over the solution during the development of the same.

Platinum disk electrodes (2 mm diameter) embedded in a cylindrical Teflon base (13 mm diameter) were used. The electrodes were covered with a tellurium thin film and immediately utilized as working electrodes. An electrode of $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (saturated) (SSE, 0.64 V vs. NHE at 25 °C) was used as reference and all potentials in this work are referred to this electrode. The counter electrode was a platinum gauze of large area with regard to the working electrode. The working temperature was controlled at 25 °C, but, when telluryl reduction was analyzed at different temperatures, the reference electrode was placed outside of the electrochemical cell, maintained at constant temperature (25 °C) and connected to the cell by means of a glass tube (fritted glass in the tip) filled with supporting electrolyte.

For the electrochemical experiments, two potentiostat/galvanostats were used, each one controlled by means of a computer: a Par model 273A and a Radiometer model VoltaLab 32. To impose the constant hydrodynamic regime, a Pine controller model AF-MSRX, able to apply a rotation rate of the working electrode up to 10,000 rpm, was used.

Preparation of the working electrodes

By using alumina of different sizes (from 1 to 0.05 μm) the platinum disk electrodes were mechanically polished to a mirror, then underwent cleaning with deionized water and ultrasonic vibration to remove the alumina traces, and finally rinsed with deionized

water. The platinum electrodes treated in this way were subjected to a galvanostatic deposit of tellurium (approximate thickness of 500 nm) under the following conditions: cathodic current density 796 $\mu\text{A cm}^{-2}$, deposition time 24 min, temperature 25 °C, and electrode rotation rate of 500 rpm. This procedure was used to obtain solid tellurium electrodes generated in situ and, in this way, contamination problems were avoided. Once the working electrodes were prepared, we proceeded to study the electrochemical system $\text{HTeO}_2^+/\text{Te}$ by means of different electrochemical techniques.

In the case of electrochemical measurements carried out at a slow potential scan rate or in the case of pulsed techniques of long duration, a new electrode was always used to avoid the influence of roughening of the electrode surface. With pulsed techniques of short duration, several experiments were carried out with the same electrode.

Results and discussion

The telluryl electrochemical reduction was firstly analyzed by using the linear potential sweep voltammetry technique in a non-stationary diffusion regime. Potential scans in the cathodic direction were applied to the working electrode starting from its equilibrium potential in the electrolytic solution (−140 mV) and the potential scans rates (ν) were varied from 5 to 1000 mV s^{-1} . The obtained current-potential (j versus E) curves showed a gradual variation as the potential scan rate was increased (Fig. 1). As can be seen, the measured current is negligible when the overpotential (η) is low and only when this is in the order of −500 mV is the beginning of the reduction process observed, thus indicating that this process is, in principle, very slow. For more negative η values, the typical voltammetric peak in the measured current density was observed and its height increased as ν did also. Besides this, a gradual displacement of the peak potential toward more negative values was observed as ν was increased.

The measured peak current densities (j_p) showed a linear variation when these were plotted against $\nu^{1/2}$ (insert in Fig. 1), which means that the process is controlled by diffusion [32]; from the slope of the curve in the same plot the diffusion coefficient for the electroactive species was evaluated. An interesting aspect to be discussed is the fact that, when the curve of j_p vs. $\nu^{1/2}$ was extrapolated to $\nu^{1/2} = 0$, the curve did not pass through the origin and provided a positive ordinate. This result can be due to some phenomenon that systematically contributes to increase the total current and the same phenomenon can also cause the measured current to be abnormally higher in the activation region of the j vs. E curves (zone A, Fig. 2). This behavior can be the originated, among other factors, of the presence of adsorbed electroactive species on the electrode surface [33], a possibility that was afterward investigated by means of other electrochemical techniques (see below).

The absolute value of the difference between the cathodic peak potential and the cathodic half-peak potential, $|E_{pc} - E_{pc/2}|$, plotted against $\log \nu$ showed an almost constant value of −75 mV. If the electrochemical process is considered as irreversible [32], such a

Fig. 1 Linear sweep voltammograms for telluryl reduction in acid sulfate medium: *a*, 10; *b*, 30; *c*, 90; *d*, 175; *e*, 300; *f*, 500; and *g*, 700 mV s^{-1} . *Inset*: variation of the absolute value of j_p vs. $v^{1/2}$

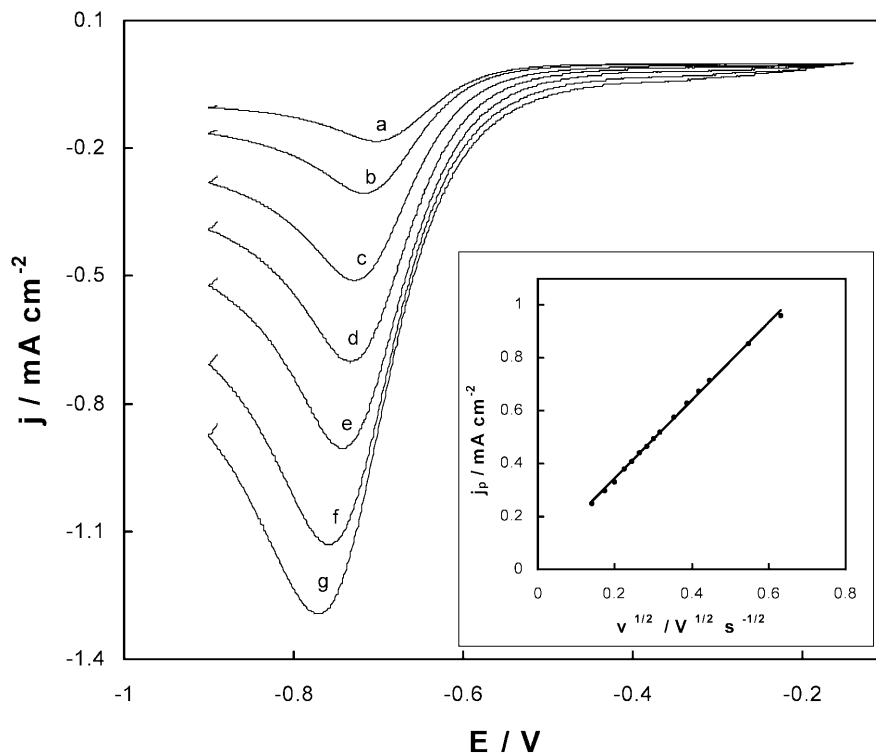
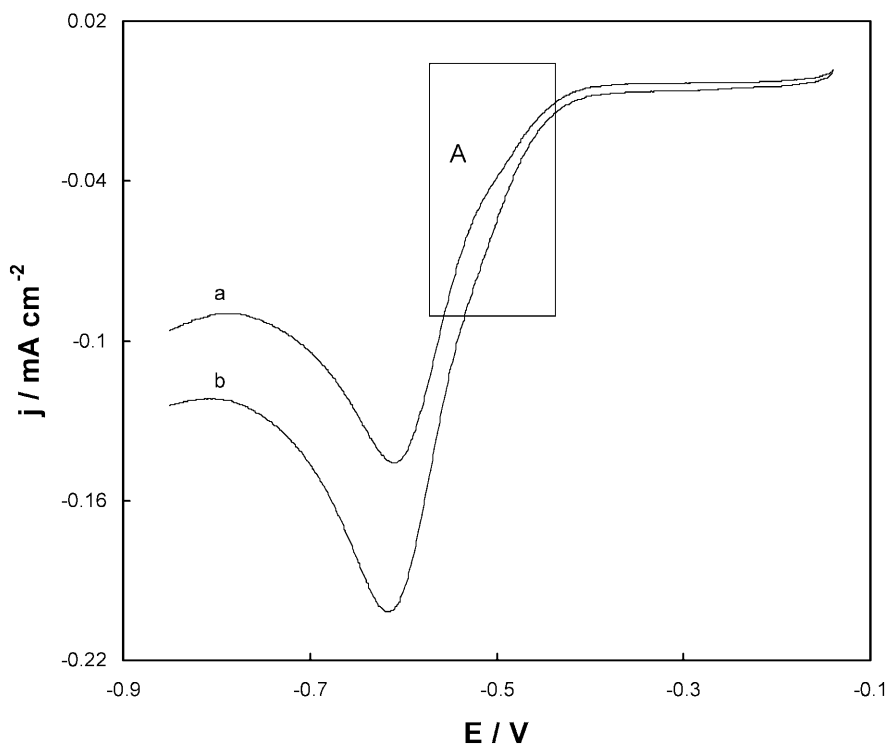


Fig. 2 Linear sweep voltammograms for HTeO_2^+ reduction in acid sulfate medium: *a*, 20; *b*, 30 mV s^{-1}

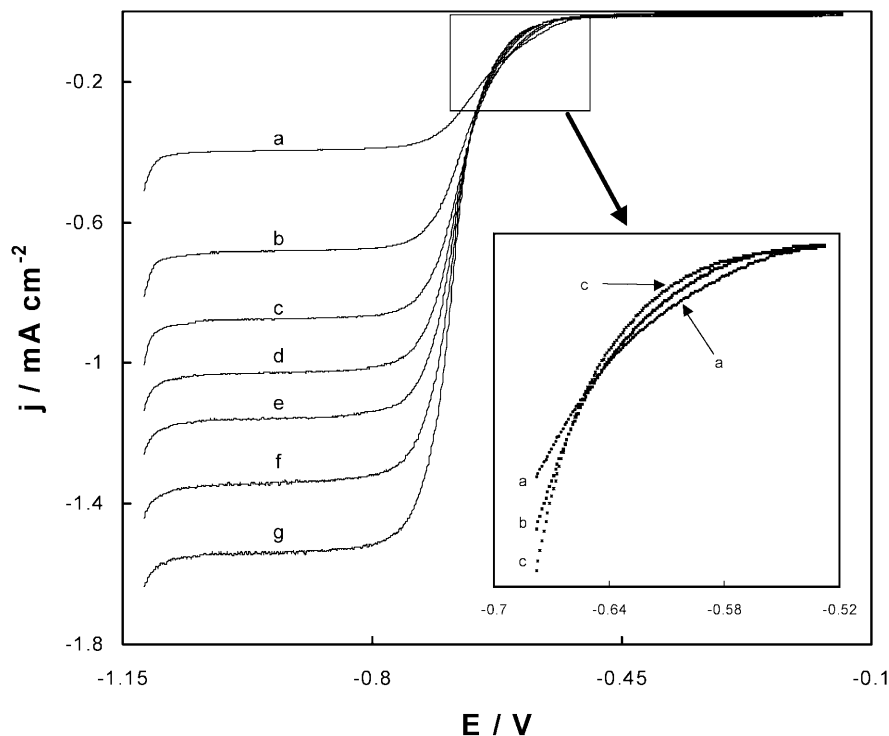


difference gives 0.16 for the charge transfer coefficient (α) for a transfer of four electrons. This value is corroborated below.

The rotating disk electrode technique (RDE) was used to study the tellurium electrochemical deposition process in the stationary diffusion regime. By applying an elec-

trode rotation rate (ω) of between 100 and 1800 rpm and a constant potential scan rate (2 mV s^{-1}), j vs. E potentiodynamic curves were obtained (Fig. 3). In these curves it is observed again that a great overpotential is required for starting the telluryl reduction process. In general, as the electrode rotation rate is increased the current density

Fig. 3 Potentiodynamic curves in the stationary diffusion regime for telluryl reduction at 2 mV s^{-1} : *a*, 100; *b*, 300; *c*, 500; *d*, 700; *e*, 900; *f*, 1200; and *g*, 1600 rpm. *Inset*: details at the foot of the wave: *a*, 300; *b*, 700; and *c*, 1600 rpm



grows. However, just at the foot of the wave, and for a short potential interval, the opposite behavior is observed; that is to say, at low ω values the current is higher than at high ω values (see insert in Fig. 3). This phenomenon could be explained in terms of an adsorption phenomenon of the electroactive species on the electrode surface, in such a way that, with strong agitation, this species is partially expelled from the electrode surface before the charge transfer reaction happens. It should also be noticed that such a phenomenon appears in the same overpotential region where the slight inflections obtained in voltammetry without agitation are observed.

At high overpotentials the j vs. E curves showed different current plateaus for a wide potential interval; such plateaus correspond to the limiting current densities (j_{lim}) whose values increase as the electrode rotation rate is increased. In these kinds of curves, the hydrogen evolution begins at potentials more negative than -1.10 V . When the j_{lim} values were plotted against $\omega^{1/2}$, a linear relationship was obtained (Fig. 4), thus indicating that the process is limited by mass transport of the electroactive species, as predicted by the Levich equation [34]:

$$j_{\text{lim}} = 0.620nFD^{2/3}\nu^{-1/6}C_0^*\omega^{1/2} \quad (1)$$

where n is the number of electrons involved in the reduction process (in this case, $n=4$), F is the Faraday constant, D is the diffusion coefficient of the electroactive species, ν is the kinematic viscosity ($0.0094 \text{ cm}^2 \text{ s}^{-1}$ for this medium) [35], and C_0^* is the bulk concentration of the electrochemically active species.

From the slope of the Levich-type plot the apparent diffusion coefficient for the electroactive species was estimated as $D=3.33 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is slightly

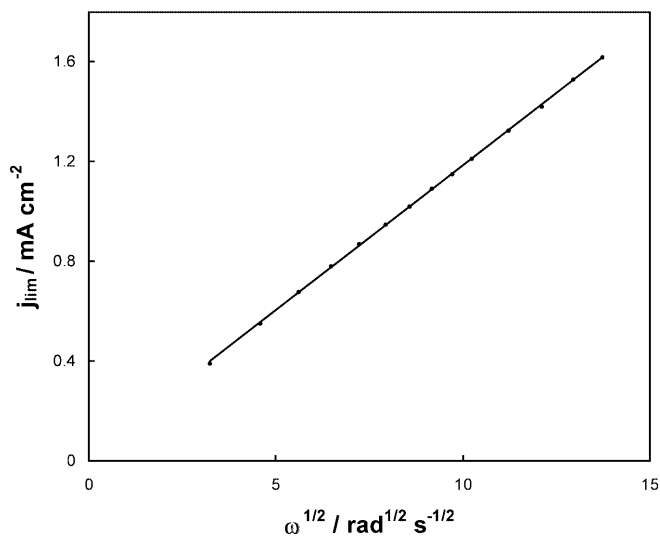


Fig. 4 Variation of the cathodic limiting current density with agitation

smaller than that reported in the literature for a similar electrolytic medium [21, 33]. Nevertheless, this value agrees well with the one previously obtained by means of the potential scan voltammetry technique without agitation. Here also the extrapolation of the curve j_{lim} vs. $\omega^{1/2}$ to $\omega^{1/2}=0$ provided a positive ordinate slightly higher than zero, which confirms the existence of other phenomena coupled to the charge transfer process, thus increasing the current density [34].

In order to evaluate the kinetic parameters of the electrochemical process, the same curves shown in Fig. 3 were used. The current densities free from the diffusional

contribution, j_k , were evaluated by plotting j^{-1} vs. $\omega^{-1/2}$ for several fixed overpotentials (Fig. 5) and extrapolating to $\omega^{-1/2}=0$, in accordance with the following expression [36]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1.61\nu^{1/6}}{nFD^{2/3}C_0^*\omega^{1/2}} \quad (2)$$

From the intercepts the j_k values were obtained; with these values for each overpotential it was possible to estimate the kinetic parameters by using the rate equation related to the cathodic process in the activation zone, the Tafel equation [36]:

$$j_k = j_0 \exp\left[-\frac{\alpha nF}{RT}\eta\right] \quad (3)$$

which is a function of α , η , and the exchange current density defined [36] as $j_0 = nFk_0C_0^{(1-\alpha)}$, where k_0 is the rate constant for the process.

Figure 6 shows the Tafel-type curve and two regions (A and B) can be appreciated where $\log j_k$ vs. η is linear. Such behavior can be due to a change in the reduction mechanism of the electroactive species with regard to the applied potential during the electrodeposition process [37, 38]. From the slope of the fitting curve in the activation region (zone A, Fig. 6) the α value was obtained as 0.17; from the intercept the following values were assessed: $j_0 = 2.95 \times 10^{-7} \text{ mA cm}^{-2}$ and $k_0 = 2.30 \times 10^{-10} \text{ cm s}^{-1}$. This α value confirms the value previously obtained from the linear sweep potential technique in a non-stationary diffusion regime and, in addition, such a value agrees well with that reported by other authors [28, 33]. On the other hand, the obtained k_0 value makes clear that the electrochemical reduction process of the HTeO_2^+ ions, on a solid tellurium electrode, can be certainly assumed as an irreversible process [32, 36].

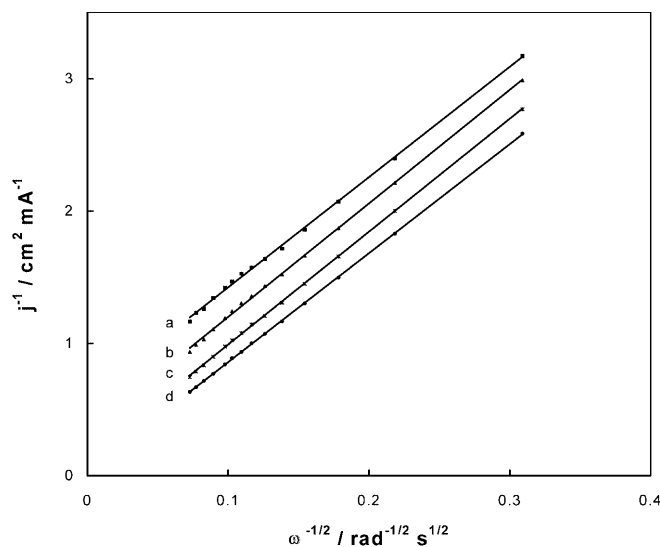


Fig. 5 Plot of j^{-1} vs. $\omega^{-1/2}$ for some overpotentials: a, -550; b, -560; c, -580; and d, -640 mV

The slope change observed in the Tafel-type plot (Fig. 6) has been usually associated with a change in the deposition mechanism of the electroactive species [37, 38] and in this case it can be at least discussed in terms of two possibilities. The first one is based on the following idea: in a former step the reduction of the HTeO_2^+ ions leads to tellurium; once this elemental tellurium is initially formed, then a second reduction process generates the species H_2Te ; after that, this new species reacts with the telluryl ion to give elemental tellurium again [11, 15, 18]. This reaction sequence should mean, according to some authors [25, 29], a change in the reaction mechanism. However, we not found any experimental evidence for such a sequence and, on the contrary, we have observed that the H_2Te is only formed at very negative potentials near to -1.10 V. Nevertheless, forming this species causes, simultaneously, the degradation of the working electrode. This phenomenon is seen as a black trickle in the vicinity of the electrode and, after a few seconds, such a trickle dissolves in the electrolytic solution.

The second possibility concerns the fact that the deposition process can involve an adsorption step of the electroactive species. This possibility has been discussed in several works [26, 33, 39] and we think it is a better explanation for our results. In such a situation, the deposition mechanism first involves an adsorption step and then the reduction of the adsorbed species (zone A, Fig. 6), while at high overpotentials (zone B, Fig. 6) the stage of adsorption is not significant for the global process. Consequently, additional electrochemical techniques were applied to study the telluryl reduction process in view of the importance of settling, beyond doubt, the presence of adsorbed species on the electrode surface; these results are discussed below.

An interesting aspect of the j vs. E curves (Fig. 3) is their variation with respect to temperature. For that

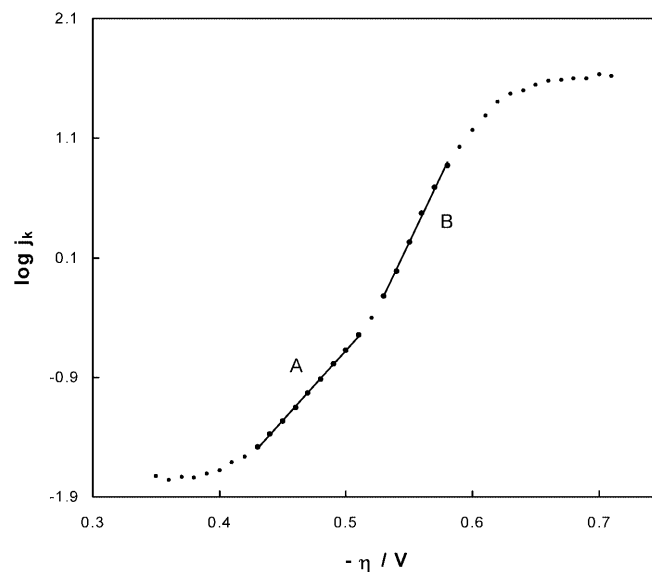


Fig. 6 Tafel plot for HTeO_2^+ reduction at 25 °C; j_k in mA cm^{-2}

reason, potentiodynamic curves in a stationary diffusion regime were obtained between 15 and 75 °C for a well-defined hydrodynamic condition, $\omega = 300$ rpm, and a slow potential scan rate of 2 mV s^{-1} ; such curves are shown in Fig. 7. In these curves it can be appreciated that, once the electrochemical reduction starts, for any applied potential the measured current increases as the temperature is increased and, contrary to the constant temperature experiments (25 °C, Fig. 3), the curves do not present any anomaly at the foot of the wave. Therefore, the temperature increase favors the charge transfer reaction. This is equally valid in the limiting current region of the j vs. E curves (Fig. 7), where a small plateau is also observed at approximately -1.05 V (more clear in curves f and g), which corresponds to the formation of the gaseous compound H_2Te [14]. It has already been mentioned that this phenomenon occurs at room temperature at very negative potentials, but its effect on the current is clearer when the temperature is higher (as shown in Fig. 7).

The curves in Fig. 7 allowed us to evaluate the activation energy (E_a) of the reduction process (in both activation and diffusional regions) by means of the Arrhenius-type equation for the current density [40]:

$$j = A \exp(-E_a/RT) \quad (4)$$

where A is the frequency factor, R is the universal gas constant, and T is the absolute temperature. By plotting the limiting currents (from Fig. 7) in the form $\ln j$ vs. T^{-1} (curve 1, Fig. 8), the activation energy of the diffusional process was estimated. A similar procedure was followed for the evaluation of the activation energy of the electron exchange process when this takes place under activation

control (curve 2, Fig. 8). The values of such energies are, respectively, 12.5 and 23.5 kJ mol^{-1} , which are within reasonable values for both processes [41, 42, 43].

With the aim of deepening our knowledge about the reduction mechanism of the telluryl ions on solid tellurium electrodes, and in order to demonstrate and to quantify the presence of adsorbed electroactive species on the electrode surface, chronoamperometry and chronopotentiometry electrochemical techniques in a non-stationary diffusion regime [44], as well as the pulsed current electrolysis technique [45], were applied.

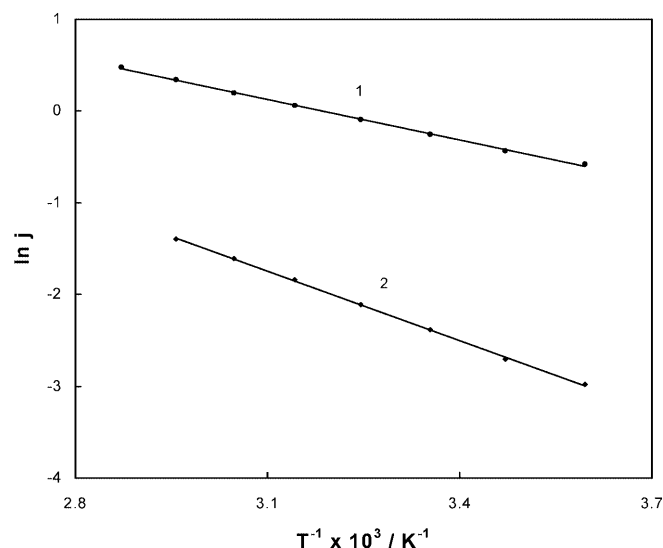
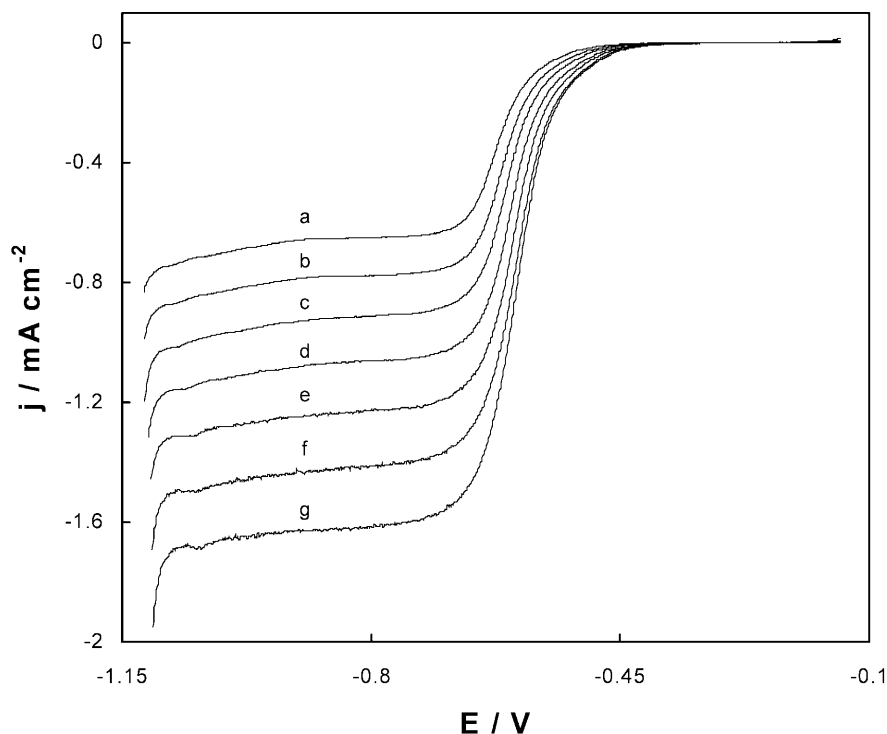


Fig. 8 Arrhenius plot for HTeO_2^+ reduction: 1, diffusional control; 2, activation control ($E = -500 \text{ mV}$); j in mA cm^{-2}

Fig. 7 Effect of temperature on telluryl reduction at 2 mV s^{-1} and $\omega = 300$ rpm: a, 15; b, 25; c, 35; d, 45; e, 55; f, 65; and g, 75 °C



In the case of the chronoamperometry technique, different overpotentials were applied (-20 to -960 mV) to the working electrode during different time intervals t (550–5000 ms) and the corresponding current-time (j vs. t) responses were registered. The electrochemical process is of a diffusional nature and when a high overpotential was applied (-740 mV), in such a way that the process was under diffusional control, the expected behavior according to the Cottrell equation [44]:

$$j = \frac{nFD^{1/2}C_0^*}{\pi^{1/2}t^{1/2}} \quad (5)$$

was not satisfied at short times after the start of the experiment, that is to say, a linear relationship in the j vs. $t^{-1/2}$ plot was not fulfilled at short times ($t < 500$ ms), as it is clear in the right side of the plot shown in Fig. 9. In this region ($t < 500$ ms) the measured current is higher than that expected according to the Cottrell relationship (dashed line). This effect at short times also establishes that the product $jt^{1/2}$, which is known as the chronoamperometric constant [36] (equivalent to the more commonly mentioned chronopotentiometric constant), shows a maximum when it is plotted against $\log t$ (insert in Fig. 9). In the literature, several explanations have been proposed to interpret the deviation observed in such a constant. They are [46]: oxide existence or oxide formation, double layer charging, and the adsorption of electroactive species on the electrode surface. In this work, special care has been taken to avoid the formation of oxides on the electrode surface and, for this reason, the electrodes have been prepared in situ. The double layer charging can be discarded because all the chronoamperometric responses have been corrected by

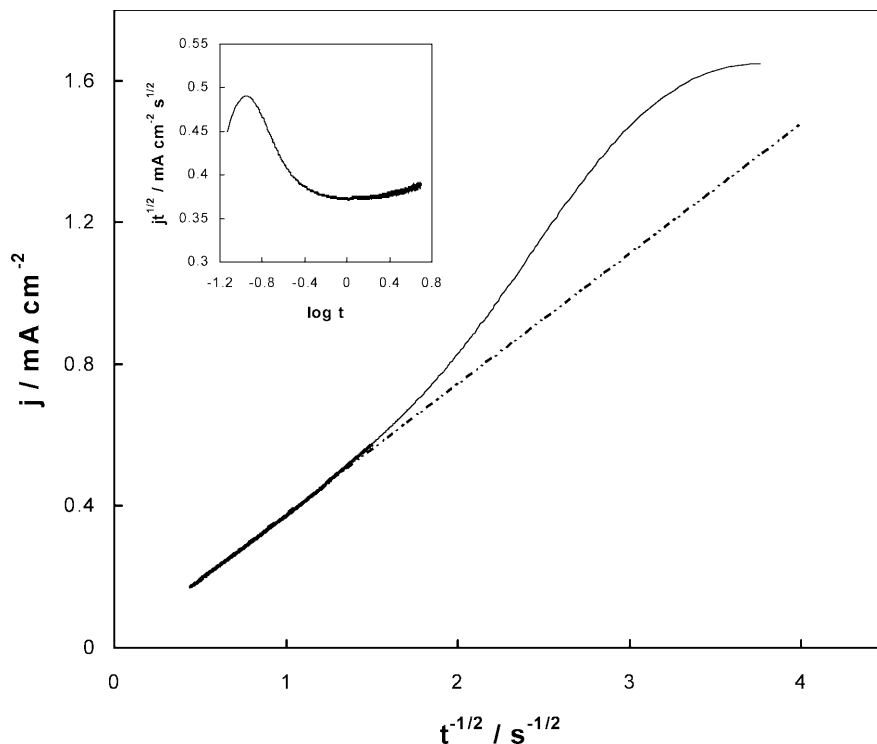
subtracting the contribution to the total current originating from the corresponding blank experiment, that is to say, the experiment carried out in the supporting electrolyte at the same operating conditions for each experiment.

The experimental results presented until here seem to indicate that the deviation in the j vs. $t^{-1/2}$ curve, at short times, could be due to the reduction of adsorbed electroactive species on the electrode surface. However, we proceeded to look for more experimental evidence before attributing the observed behavior to the adsorption phenomenon.

Thus, we proceeded to the study of the reduction process by means of the chronopotentiometry technique in a non-stationary diffusion regime. In this case, cathodic current steps were imposed (0.095 to 3 mA cm $^{-2}$) on the working electrode during different time intervals (70 to 0.3 s). Some typical potential-time (E vs. t) responses are shown in Fig. 10. In such responses it is observed that when the current step is applied, the potential of the working electrode moves toward the characteristic value for telluryl reduction (-600 mV), and it varies with time toward slightly more negative potentials as the concentration of the electroactive species is depleted on the electrode surface. Once the surface concentration of the HTeO_2^+ species falls to zero, the electrode potential moves toward potential values that are more negative; such values correspond to H_2Te generation and simultaneously to hydrogen evolution.

The E vs. t responses showed well-defined transition times (τ) that satisfy the Sand equation [44]. Moreover the $j\tau$ vs. j^{-1} plot according to the expression [47]:

Fig. 9 Plot of j vs. $t^{-1/2}$ for the electrochemical reduction of telluryl ion in acid sulfate medium. Potential steps from -140 to -880 mV. *Inset*: chronoamperometric constant as a function of time; t in s



$$j\tau = \frac{n^2 F^2 \pi D C_0^{*2}}{4j} + nF\Gamma_0 \quad (6)$$

showed a linear relationship with a positive ordinate that proves the existence of adsorbed electroactive species on the working electrode surface [36, 47]. From the intercept the quantity of the adsorbed species was evaluated as $\Gamma_0 = 1.55 \times 10^{-10} \text{ mol cm}^{-2}$, which is smaller than the necessary quantity to form a monolayer.

By using the pulsed current electrolysis technique [45], a final proof about the existence of adsorbed electroactive species on the electrode surface was obtained. In this case, the working electrode was subjected to a constant pulsed current train until the E vs. t response reached a stationary electrolysis state at a constant rotation rate (1000 rpm) of the working electrode. Several current densities between 1.25 and 3 times the limiting current density (j_{lim} for the imposed hydrodynamic condition) were imposed with fixed pulse (t_{on}) and pause (t_{off}) times; during t_{off} the imposed current was zero. Also, for the same current density the pulse time was varied while maintaining the pause time fixed, and vice versa.

Figure 11 shows a typical E vs. t response for such experiments obtained at the following conditions: cathodic current density 1.81 mA cm^{-2} ($1.5 j_{\text{lim}}$) applied during 280 ms followed by zero current during 2 s. Under these conditions it is expected that the electroactive species consumed in each pulse be regenerated during the zero current condition. At the beginning of the experiment there is only a stabilized electrode at the

equilibrium potential; once the current step is applied, the E vs. t response shows the appearance of a transition time (τ) in each pulse that evolves until reaching a stationary electrolysis state in which the transition time no longer changes.

From the series of consecutive pulses shown in Fig. 11, the first one and the last one (pulse 10) have been expanded and superimposed in Fig. 12. Pulse 10 represents the stationary state of electrolysis, a situation

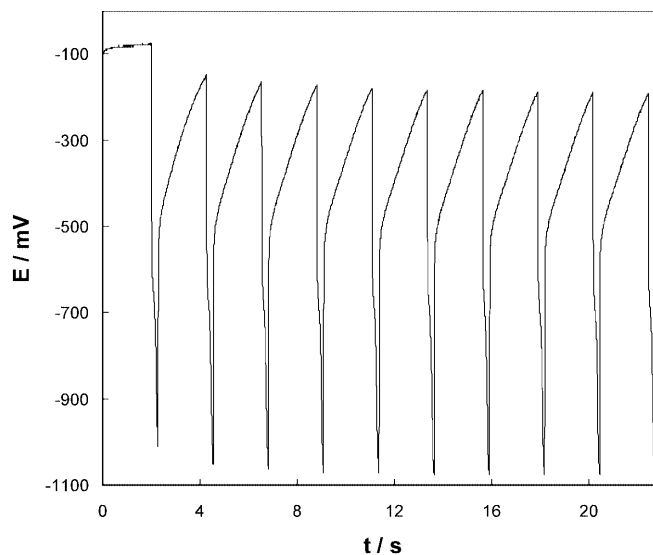


Fig. 11 Potential-time response after application of a cathodic pulsed current: 1.81 mA cm^{-2} during 280 ms and 0 mA cm^{-2} during 2 s; $\omega = 1000 \text{ rpm}$. For clarity, only 10 cycles are shown

Fig. 10 Chronopotentiometric curves for different cathodic current pulses: *a*, 700; *b*, 763; *c*, 827; and *d*, 891 $\mu\text{A cm}^{-2}$

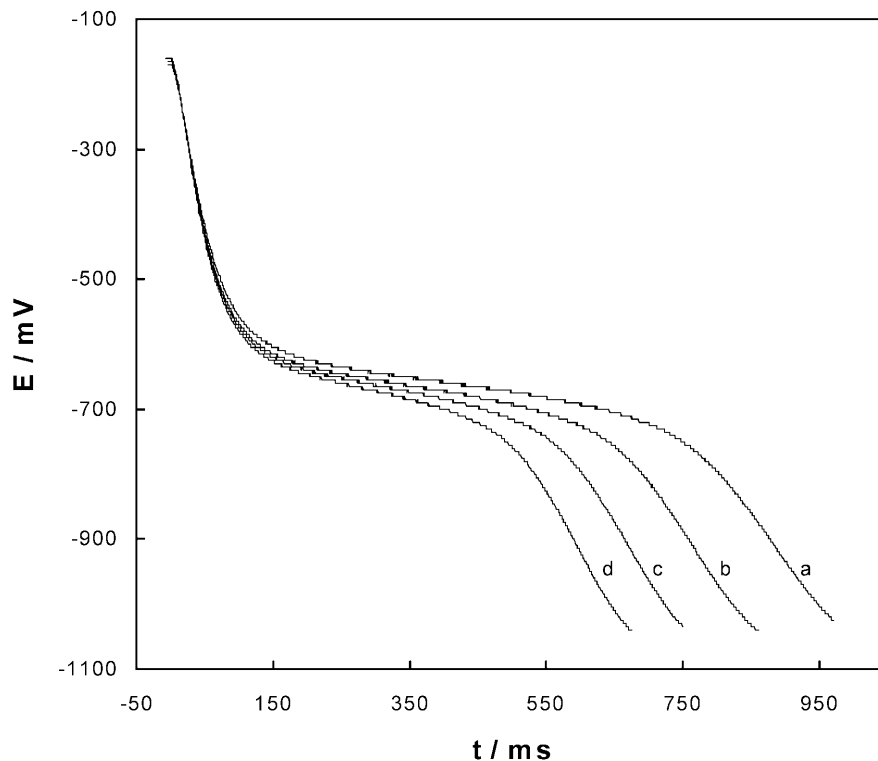
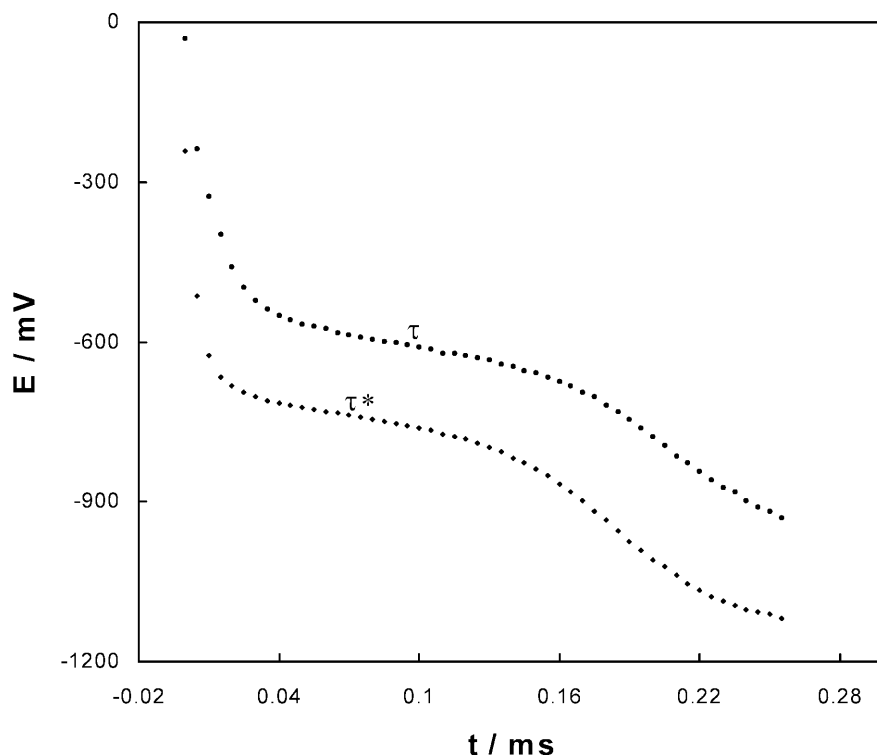
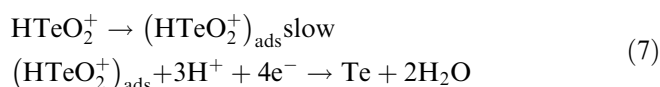


Fig. 12 E vs. t plots obtained by pulsed electrolysis (from Fig. 11). τ : transition time for the first pulse; τ^* : transition time in the electrolysis stationary state



that is reached after four or five consecutive pulses. For clarity, pulse 10 in Fig. 12 was slightly displaced toward more negative potentials. It is clear that the transition time for the first pulse (τ) is longer than that corresponding to the stationary electrolysis state (τ^*) and this is indicative of the existence of adsorbed electroactive species at the start of the experiment. The adsorbed electroactive species is not recovered during the pause time in spite of the large value for t_{off} ; in consequence, the adsorption step of the telluryl ions is the slow step of the reduction process. From the difference between the transition times, $\tau - \tau^*$, and by following a similar procedure to that employed by Paunovic and Schlesinger [48], it was possible to estimate the quantity of adsorbed species as $\Gamma_0 = 2.57 \times 10^{-10} \text{ mol cm}^{-2}$. This value is very similar to that achieved by means of the chronopotentiometry technique and confirms the previously obtained result. Moreover, this is within the typical values attained for solid electrodes [49].

The use of different electrochemical techniques has allowed us, firstly, to show that the telluryl reduction process is preceded by an adsorption step of the electroactive species and, secondly, to demonstrate that such adsorption on the electrode surface is a slow process. With these results the mechanism for the HTeO_2^+ reduction process in acid sulfate medium (pH 2) and at room temperature (25 °C) can be visualized as:



This reaction sequence is particularly appropriate in the rising part of the Tafel plot (region A, Fig. 6); however, at more negative overpotentials the process seems to proceed in another way.

Conclusions

Telluryl ion electrochemical reduction in acid sulfate medium was studied by means of electrochemical techniques in stationary and non-stationary diffusion regimes on solid tellurium electrodes generated in situ. The measurements led to the following kinetic parameters: $\alpha = 0.17$, $j_0 = 2.95 \times 10^{-7} \text{ mA cm}^{-2}$, and $k_0 = 2.30 \times 10^{-10} \text{ cm s}^{-1}$, thus demonstrating that the electrochemical process is irreversible at 25 °C. The reduction process involves an adsorption step of the electroactive species on the working electrode surface and the quantity of adsorbed species has been estimated by means of chronopotentiometry and the pulsed current electrolysis technique; its value is smaller than the corresponding one needed to form a monolayer. The reduction mechanism changes with the applied potential and the kinetics of the process is improved with the temperature increase. The temperature effect study on the reduction process allowed us to evaluate the apparent activation energy for both the diffusional and the activation control processes; the values are respectively 12.5 kJ mol^{-1} and 23.5 kJ mol^{-1} . Finally, the diffusion coefficient of the electroactive species was almost the same for all the applied techniques.

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