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Tellurium underpotential deposited ad-atoms on Au electrodes: A new electrodeposition mechanism using an electrochemical quartz crystal nanobalance

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ABSTRACT

Interfacial phenomena involved in the underpotential deposition of tellurium layers were studied with an electrochemical quartz crystal nanobalance (EQCN) in perchloric acid solution (pH = 1). The *in situ* study of the oxidation kinetics showed that the oxidation of the Te layer deposited neighbor a Te_{ads}/Au provides evidence of TeO_{2ads} formation with the incorporation of oxygen to induce the formation of H_2TeO_3. From the calculations of the first tellurium layer (82 ng cm^{-2}), the mass expected for the second layer deposited in underpotential control was found. Moreover, the oxidation of Te_{ads} followed a bi-functional mechanism involving the oxygen incorporated before the tellurium oxidation at high overpotentials. The combination of powerful interfacial methods (cyclic voltammetry and EQCN) gives a new perspective on tellurium electrodeposition and leads to a comprehensive understanding of the interfacial architecture.

1. Introduction

Since the landmark paper by Sauerbrey [1], Electrochemical Quartz Crystal Nanobalance (EQCN) has been used in several studies [2–9], mainly for rigid deposits [10]. The change in the resonant frequency of the oscillating crystal is proportional to the change in mass per unit area (A) of the deposit on the working electrode, as described by the Sauerbrey equation. This technique has been used in studies on metal electrodes [3,5,10], conductive metal oxides [11], sensors [6,9], biosensors [7–13] and electroactive polymers [14–16]. This technique has been used extensively to study electrodeposition processes [3,5,10] such as UPD [17–20].

Underpotential deposition (UPD) is applied to better control the structural quality of deposits and requires studies on surface reactions, which are the basis of electrodeposition and an ongoing part of the development of new material growth cycles [19]. UPD provides a straightforward approach for controllably and reproducibly modifying the structure and composition of metal electrodes with a layer of foreign metal [19–28].

Semiconductor compounds have been produced using electrochemical atomic layer electrodeposition (ECALE) [19 and references therein], and UPD is the main process in the ECALE cycles. These compounds frequently contain tellurium. Te films are used in several devices, such as solar cells [29], hydrogen generation [30], thermoelectric power generation and cooling [31]. Most recently, chalcogenides films have been employed in NO sensors [32].

In most papers on the tellurium UPD process on gold, the authors [20,21,33–42] consider the presence of $HTeO_2^+$ in acid media as a precursor of Te_{ads}. At low pH, the telluryl ion may be electrochemically reduced to give elementary tellurium via a process that occurs in one step with the transfer of four electrons [43]. On the other hand, Te underpotential deposition process can be based on H_2TeO_3 as a precursor of Te_{ads} due the dissociation constants of acids of tellurium and the equilibrium constants of dissolution of $HTeO_2^+$ and H_2TeO_3 [44].

The present work proposes a new mechanism for Te UPD on gold using EQCN from the oxidizing step after the formation of the maximum recovery of tellurium in an UPD potential. H_2TeO_3 was assumed to be the precursor of elementary tellurium in a process that occurs in two steps that involve the formation of Au_2Te_{ads} and $Au_2Te_{ads}Te$.

2. Experimental

2.1. Chemicals

TeO_2 (99.99% purity) and perchloric acid (Suprapur) were obtained from Merck and used as received. Millipore-Q purified

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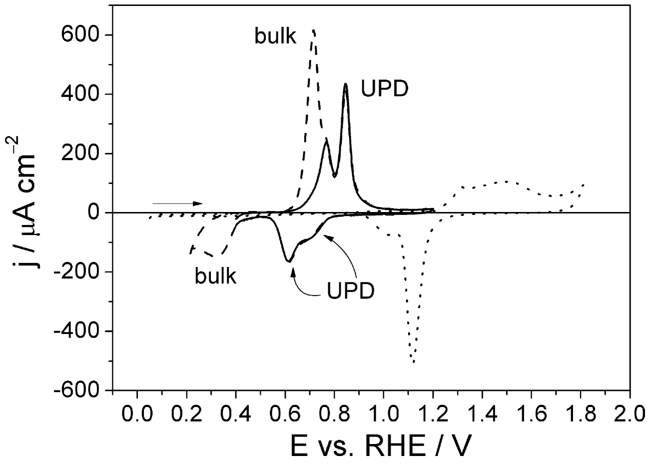

Fig. 1. Cyclic voltammogram for the Au-EQCN electrode in 1.0 mM TeO_2 + 0.1 M $HClO_4$. The dotted line represents the response in 0.1 M $HClO_4$. In the presence of 1.0 mM TeO_2 + 0.1 M $HClO_4$, the solid line (E_i = 0.4 V) and dashed line (E_i = 0.2 V) are the results after 600 s of polarization. Scan rate = 0.10 V s^{-1}.

water was used to prepare all solutions. Before the experiments, it was deaerated with high-purity N_2 (White Martins SS), and the experiments were performed at room temperature.

2.2. Equipment and apparatus

The electrochemical instrumentation consisted of a potentiostat/galvanostat EG & G PARC model 273 linked to an IBM-type PC-486 microcomputer and to a quartz crystal analyzer (QCA 917 Seiko EG & G PARC), both interfaced with a GPIB interface. The appropriate software was employed from M270 EG & G PARC.

The working electrode (Au-EQCN) was a 9 MHz AT-cut quartz crystal electrode. Both sides of the quartz crystal were covered with thin gold films on a Ti adhesion layer, but only one of these faces was exposed to the electrolyte. The electrochemical area was calculated to be 0.35 cm^2 based on measurements of the voltammetric charge related to the reduction of a complete monolayer of gold oxide, following the Trasatti and Petrii procedure [45]. This procedure gives a roughness factor (R) value of 1.75 for the Au-EQCN electrode. The reference electrode utilized in this work was a hydrogen electrode in the same solution (RHE), and the auxiliary electrode was a Pt foil with a geometric area of 1 cm^2.

The sensitivity factor of EQCN crystal was obtained as 830 Hz μg^{-1} as described elsewhere [46].

3. Results and discussion

3.1. Voltammetric profile during the electrodeposition of tellurium

Fig. 1 shows the voltammetric profile of Te in perchloric acid solution on Au. Initially, the electrode was polarized for 600 s at two different potentials (0.2 and 0.4 V) and swept in the positive direction. When the polarization was performed at 0.2 V (dotted line), the presence of two well-defined peaks was observed, which corresponds to the oxidation of bulk Te (0.77 V) and Te UPD (0.85 V) [38,40]. When the potential was fixed at 0.4 V and swept in the positive direction, two peaks were also observed. However, the peak at 0.75 V was hidden by the peak attributed to the Te bulk process. For this reason, the assignment of the voltammetric peak at 0.75 V associated with UPD process is explored in following section.

Previous studies have shown that the UPD of tellurium on gold electrodes occurs in multiple activity states [41].

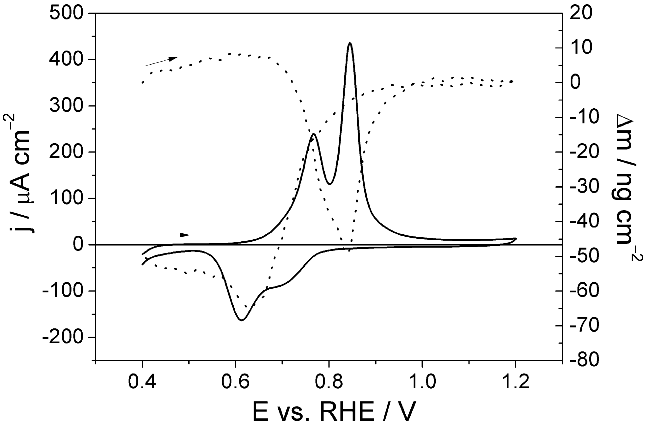

Fig. 2. Voltammetric profile for the Te UPD process. The cyclic voltammogram (full line) and mass variation profile (dotted line) for the oxidation and reduction of the Te layer on to Te_{ads}/Au and Te_{ads} on Au. Scan rate = 0.10 V s^{-1}.

According to others studies [33–43], the first step is the deposition of a Te monolayer, where each Te ad-atom occupies the sites of two gold atoms on the substrate. The second step is the deposition of Te in the other active state, that forms an epitaxial layer. The charge involved in the formation of the first monolayer of Te on Au is close to 249 μC cm^{-2} (see Fig. 2 at 0.85 V – oxidation peak). The amount of Te_{ads} on the Au surface corresponds to a 0.64 monolayer, given that a complete tellurium monolayer on Au, where each Te ad-atom occupies two Au atoms involves 390 μC cm^{-2} [47–49]. Thus, it can be suggested that the first submonolayer of Te on Au has some free-Te gold active sites.

Subsequently, there is a deposition layer of Te neighbor to the Te previously deposited on Au. The charge involved in the formation of the Te layer deposited neighbor to Te_{ads}–Au is approximately to 172 μC cm^{-2} (see Fig. 1 at 0.77 V – oxidation peak). At this point, the charge correlated with this coverage should be related to the charge of the first monolayer of Te free from immediate neighbor on Au (249 μC cm^{-2}). Therefore, the coverage of Te neighbor deposited on Te_{ads}–Au is 0.44 monolayers.

Fig. 2 shows the mass variation profile during the tellurium UPD process. The behavior of the oxidation of Te ad-atoms deposited from UPD on gold and the layer of Te formed afterwards was unexpected.

The end of the cycle was used to begin the sweep (after 600 s of polarization at 0.4 V). The mass variation between the end and the start of the sweep was 50 ng cm^{-2}. Given the theoretical mass variation expected in the formation of the UPD layer of Te on Au, this value can be calculated by assuming that, on a polycrystalline Au surface, there are 2.0×10^{-9} mol of Au atoms/cm^2 available. Thus, with a molar mass of Te of 127.6 g mol^{-1}, it is possible to find a theoretical value of 127.6 ng cm^{-2}, given that each Te_{ads} occupies two Au sites. This value is then associated with the reduction of Te^{4+} from the solution and the formation of a full monolayer of Te_{ads} on to Au surface. However, according to the voltammetric data, 0.64 monolayers of Te_{ads} formed; hence, the theoretical value must be 82 ng cm^{-2}. This value is very important to obtain the expected mass variation of the coverage of Te deposited neighbor to Te_{ads}–Au.

The experimental voltammetric data showed that the coverage was 0.44 monolayers for the oxidation peak at 0.77 V; the experimental value obtained from Fig. 3 (considering the mass variation between the end and the start – 50 ng cm^{-2}) is in agreement with the relationship between (0.7×127.6) ng cm^{-2}, following the same calculations used above and charge density according to the CV data for the Te layer deposited neighbor to Te_{ads}–Au. This step of the mechanism will be explored in the following section.