Voltammetric and Surface Conductance Study of the Deposition and Stripping of Mercury on Gold

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The voltammetric and surface conductance (SC) responses of thin gold film electrodes during the deposition and stripping of mercury in 0.1 M $HClO_4$ solutions have been measured for (i) the potential region corresponding to the underpotential deposition (upd) and stripping (ups), (ii) the formation and stripping of the Hg-Au bulk alloy, and (iii) the deposition and stripping of bulk Hg(0). The analysis of the experimental results shows that the upd mercury grows by an island mechanism up to $\vartheta \sim 0.7$. Linde's surface rule suggests the formation of an interstitial surface phase in this coverage range. The formation of bulk Hg-Au alloy occurs when $\vartheta = 1$ but in the absence of bulk Hg(0). During the stripping of the alloy, the SC is only sensitive to the surface concentration of the Hg(upd) species. Only a relatively small amount of alloy is stripped off during the stripping cycle. It has been verified that the penetration of the mercury atoms into the bulk depends on the grain boundaries concentration. The changes in SC during the formation of bulk Hg(0) indicate that it is a more dense surface phase than the Hg(upd) surface phase.

Introduction

The deposition and stripping of mercury on gold have been studied recently by several workers.[1-4] The main conclusions of those works can be briefly summarized as follows.

In the potential range comprised between about 1.0 and 0.4 V vs SCE, underpotential deposition (upd) and stripping (ups) of the equivalent of up to a monolayer of Hg on Au occur. The faradaic charge required to strip a complete monolayer is 340 $\mu C \cdot cm^{-2}$.[1] However, Sherwood and Bruckenstein[1] and Lindstrom and Johnson[2] showed, employing different electrochemical techniques, that the apparent number of exchanged electrons during the stripping reaction lies between 1.6 and 1.7. This means that, as extreme cases, either the adsorbed mercury retains a positive partial charge between 0.3 and 0.4 or the monolayer can be considered to be composed of Hg(0) and Hg(I) in a 4:1 ratio.

The partially charged mercury adatoms can be further reduced at about 0.25 V. The oxidation of this reduced mercury occurs only in the absence of deposited bulk mercury (see below).[3]

An anodic scan after mercury has been deposited at potentials more cathodic than the reversible one, either from concentrated or from stirred solutions, shows a stripping peak at about 0.45 V. This has been attributed to the dissolution of a monolayer of bulk Hg(0) with $n = 1$.[3]

When the electrode potential is repeatedly cycled or held at potentials more cathodic than the reversible one, a bulk Hg-Au alloy is formed.[3] The stripping of this alloy shows a broad peak at about 0.7-0.8 V. It has been claimed that the formation of this alloy requires the prior deposition of bulk Hg(0).[3] We will show here that this is not the case.

On the other hand, surface conductance (SC) has proved to be useful to investigate adatom adsorption both in the gas phase[5-8] and in electrochemistry.[9-14] The SC response allows one to infer about the adatom/substrate bonding and the adatom surface structure.[13-15]

In this work, we report a voltammetric and SC study of the mercury deposition and stripping including the underpotential, the bulk Hg-Au alloy, and the bulk Hg(0) formation reactions.

Experimental Section

Electrodes. Thin gold film electrodes were vacuum deposited onto optically polished acrylic substrates. The evaporation conditions and electrical contacts were described previously.[16] Electron diffraction patterns of the electrodes show they are composed of crystallites with a majority of (111) orientations with small contributions of (110) and (100), in that order. SEM analysis showed that the mean crystallite size is

* Author to whom correspondence should be addressed.
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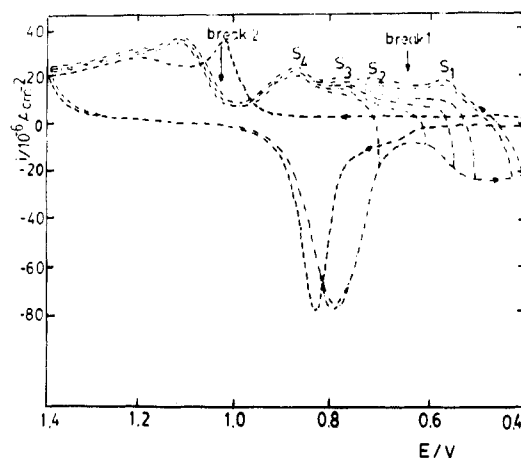
Figure 1. I/E response in the upd and ups potential region for different cathodic limits, $E_{c,l}$: (- - -) 0.1 M $HClO_4$; (- · -) 2 × 10^{-5} M Hg(II) + 0.1 M $HClO_4$. $v = 2 \times 10^{-2}$ V s^{-1}.

about 0.5 μm.[16] The roughness factor of the electrodes was estimated as previously reported and was about 1.6.[17]

Some experiments were performed with polycrystalline gold electrodes (Johnson Matthey 99.999%) and others were carried out with nonoriented single crystals obtained by melting a Au wire in the flame so as to obtain a sphere of about 2 mm in diameter.[18]

Instrumentation and Cells. The voltammetric experiments were performed with a potentiostat (LyP, Model M-5), a ramp generator (LyP), and an X-Y_1-Y_2 recorder (Hewlett-Packard, Model 7046B).

The circuitry and cells to measure the SC as well as the measuring method have been described previously.[19]

Chemicals. The solutions were prepared from AR grade chemicals (Merck). Water from Milli-Q (Millipore) was further distilled twice, the first in an alkaline solution of $KMnO_4$.

A SCE reference electrode was used throughout. The experiments were carried out at room temperature in deareated solutions.

Results and Discussion

Voltammetric and Resistometric Response in the upd and ups Region. The I/E responses for the blank and test solutions for different cathodic limits, $E_{c,l}$, within the upd region are shown in Figure 1. The voltammogram shows the four stripping peaks (labeled S_1 to S_4 in Figure 1) characteristic of the ups of Hg on Au.[1] The integration of the anodic charge between 1.0 V and $E_{c,l}$ allows the faradaic charge for the ups process to be determined. After correction for the roughness factor determined in ref 17, the monolayer charge is 340 ± 1 μC·cm^{-2}. This value coincides well with that reported by Sherwood and Bruckenstein.[1]

The $\Delta R/R$ response as a function of potential is shown in Figure 2, both for the blank and the test solutions. Starting from the anodic limit at 1.4 V, both responses coincide until the potential corresponding to the gold surface oxide reduction is reached ($E \simeq 0.95$ V). From there on, in the test solution, $\Delta R/R$ increases, showing that some species are progressively adsorbing on the electrode surface. Note that in this potential region $\Delta R/R$ depends on the scan direction. This is due to the fact that in the cathodic scan Hg(upd) can only form on the surface sites free from surface oxide. Once all the sur-
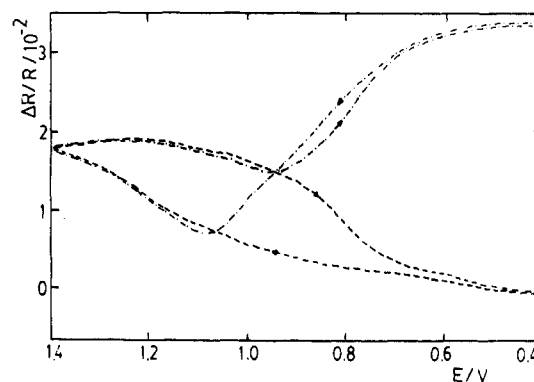
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Figure 2. $\Delta R/R$ vs E response in the upd and ups potential region: (- - -) 0.1 M $HClO_4$; (- · -) 2 × 10^{-5} M Hg(II) + 0.1 M $HClO_4$. $v = 2 \times 10^{-2}$ V s^{-1}.
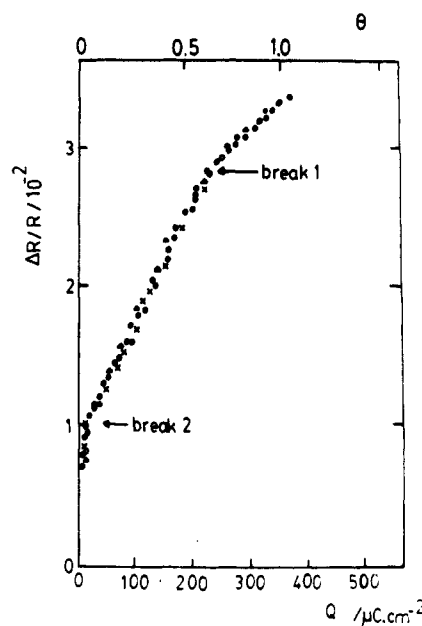

Figure 3. $\Delta R/R$ vs Q and ϑ.

face oxide has been reduced, $\Delta R/R$ becomes independent of the potential scan direction, thus showing that the surface process is reversible even though this cannot be seen in the voltammetric response. Holding the potential in this potential range shows no change in $\Delta R/R$ with time, indicating that the surface process is at equilibrium.

In Figure 3, $\Delta R/R$ is plotted as a function of the surface coverage of the Hg(upd) species, $\vartheta_{Hg(upd)}$. In order to calculate $\vartheta_{Hg(upd)}$, the surface concentration of Hg(upd), $\Gamma_{Hg(upd)}$, was found from

$$\Gamma_{Hg(upd)} = Q/n_{app}F \tag{1}$$

where Q is the anodic stripping charge and n_{app} is the apparent number of exchanged electrons in the stripping reaction and was taken from ref 1, $n_{app} = 1.7$. The maximum coverage was also taken from ref 1, $\Gamma_{Hg(upd),max} = 2.03 \times 10^{-9}$ g atom cm^{-2}.

Figure 3 shows three straight lines. The first one involves a very small coverage and corresponds to a potential region where the ups superimposes with the beginning of the gold surface oxide formation reaction. Since it is not possible to find the contribution of each reaction, we will not consider this portion. The second straight line goes up to $\vartheta \simeq 0.7$. Considering that n_{app} is constant in the range $0.9 > E > 0.4$ $V^{1,2}$ and according to

previous interpretations of $\Delta R/R$ vs ϑ plots (see refs 13 and 14), this behavior suggests an island-type growth with a constant surface structure up to $\vartheta \simeq 0.7$. Note that this coverage range comprises only the peaks S_2 to S_4. Since the atomic radii of the adorbate are bigger than that of the substrate, a change from a conmensurate to an inconmensurate surface structure should occur for a coverage $\vartheta < 1$.[20] We propose $\vartheta \simeq 0.7$ as the coverage at which this transition occurs.

In a previous work, Linde's rule as applied to surface impurities was verified for Cd, Tl, Pb, and Bi on gold:[13,14]

$$\Delta R/R\vartheta = a + bZ^2 \qquad (2)$$

where $\Delta R/R\vartheta$ is the slope of the linear portion at low coverages in the $\Delta R/R$ vs ϑ plot and a and b are constants. According to Geus,[21] $Z = z_{ad} - z_{sub}$ for substitutional impurities and $Z = z_{ad}$ for interstitial ones, z_{ad} and z_{sub} being the number of valence electrons for the adsorbate and substrate, respectively. The experimental value of $\Delta R/R\vartheta$ for mercury on gold is 2.88×10^{-2}, which is higher than that corresponding to $Z = 1$ in the substitutional case ($z_{ad} = 2$ and $\Delta R/R\vartheta = 0.9 \times 10^{-2}$, see Figure 5 of ref 14). Instead, it coincides well with that expected for $Z = 2$, which would mean that either the effective valence of mercury is $z_{ad} = 3$ or the adsorbed mercury is behaving as an interstitial surface impurity. Since it is difficult to interpret a value of $z_{ad} = 3$, this would mean the adsorbed mercury is behaving as an interstitial impurity. However, for Hg in the liquid state, the topmost core states (5d) are unusually close to the conduction band (6s).[22] According to Evans et al.,[23] this cause the phase shift, η_2, to be exceptionally large. In turn, this would cause a large scattering cross section for the electrons, which could be responsible for the large $\Delta R/R\vartheta$ observed even when the substitutional case is considered.

Since beyond the reversible potential part of the faradaic charge is employed to oxidize the Hg–Au alloy, it is not possible to determine the surface concentration of the adsorbed species, and there is no purpose in analyzing quantitatively the $\Delta R/R$ vs ϑ plot for $\vartheta > 1$.

Voltammetric and Resistometric Behavior at Potentials More Cathodic Than the Reversible Potential. (a) Formation of the Hg–Au Bulk Alloy. In order to investigate the response of the Hg–Au alloy, the potential was first cycled between the limits $1.4\ V < E < 0.4\ V$ until a stable I/E profile was reached and then scanned into the cathodic region and held at $E_{c,l}$ for different holding times, t_h. Care had to be taken since large t_h resulted in the disintegration of the film. The voltammetric response (Figure 4) shows how the broad anodic peak, B, characteristic of the stripping of Hg from the Hg–Au alloy, increases with t_h. Note that under the present experimental conditions (low Hg(II) concentrations and no stirring of the solution) the anodic peak at about 0.45 V corresponding to the stripping of bulk Hg(0) does not appear. This is at variance with the suggestion of previous workers,[3] who postulated that the formation of Hg–Au alloy required the "prior deposition of the bulk Hg(0) in the equivalent of $\vartheta_{Hg(0)} = 1$".
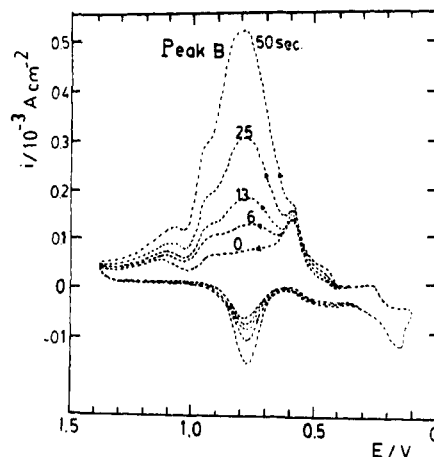

Figure 4. I/E response for different t_h in seconds: $E_{c,l} = 0.1$ V vs SCE. The experimental conditions were the same as in Figure 1.
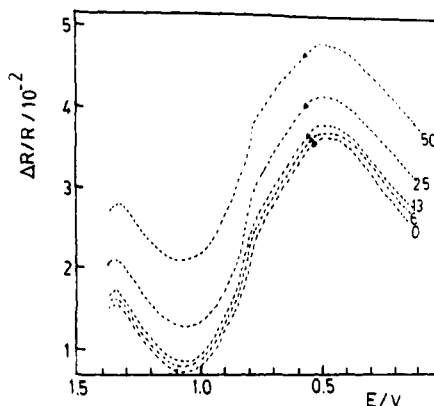

Figure 5. $\Delta R/R$ vs E response for the experiment in Figure 4.

In order to establish the possible contribution of grain boundaries to the diffusion path of the mercury atoms into gold, we repeated the experiments mentioned above employing massive polycrystalline gold and single crystal gold electrodes. We found the height of the stripping peak, at constant t_h, decreases in the order: thin film > polycrystalline > single crystal. This indicates that the penetration depth decreases in the same order, thus showing grain boundaries play an important role in this process.

The $\Delta R/R$ response for the stripping of the Hg–Au alloy shows a small shift of the initial value with t_h (Figure 5). This is related to the change of the bulk conductivity of the film as the alloy is formed. The potential dependence of $\Delta R/R$ during the anodic scan is independent of t_h. This shows that the SC is detecting only (or mostly) the surface concentration of adatoms and that it does not change significantly during the stripping of the alloy. It is further noticed in Figure 5 that the initial shift in $\Delta R/R$ produced during the potential holding at $E_{c,l}$ is maintained during the stripping scan. This shows that only a relatively small amount of the alloy is being stripped off during the anodic scan, in agreement with the findings of Schadewald et al.[3] However, it is not necessary to invoke differences in the solid-state diffusion rates for the deposition and stripping processes since during the first stripping cycle the Hg still will continue diffusing into the bulk of the gold electrode.

(b) Formation of Bulk Hg(0). Previous workers[3] have attributed the anodic peak at 0.4–0.45 V (peak A, Figure 6) to the stripping of one monolayer of bulk Hg(0). We have found that this peak does not appear in the

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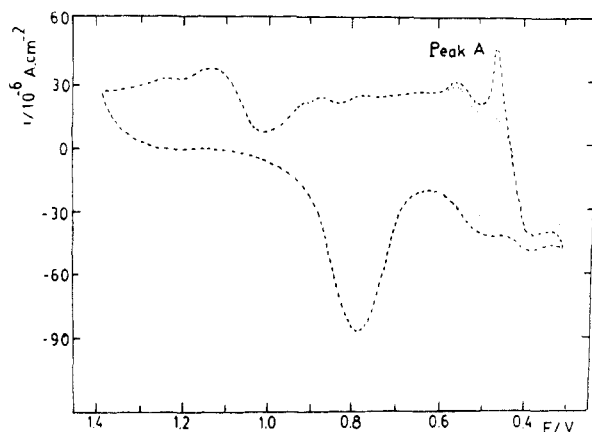(23) Evans, R.; Greenwood, D. A.; Lloyd, P.; Ziman, J. M. *Phys. Lett.* **1969**, *30A*, 313.

Figure 6. I/E response: (···) in the absence of bulk Hg(0) deposition, 2×10^{-5} M Hg(II); (- - -) in the presence of bulk Hg(0) deposition, 2×10^{-3} M Hg(II). $v = 2 \times 10^{-2}$ V s^{-1}.

Figure 7. $\Delta R/R$ vs E response for the experiment described in Figure 6: (···) in the absence of bulk Hg(0); (- - -) in the presence of bulk Hg(0).

absence of stirring or in diluted solutions ($c_{Hg(II)} < 10^{-4}$ M; Figure 6). This phenomena was observed both with massive gold and with thin-film electrodes. It can be understood by considering that there are two processes competing for the Hg adatoms: the formation of the Hg–Au alloy and the buildup of an oversaturation concentration necessary to start the nucleation of the bulk Hg(0), the former being faster than the latter. Since neither of them nor the charge transfer reaction is rate determining, in order to start the nucleation process it is necessary to have the high fluxes of Hg(II).

In Figure 7 the $\Delta R/R$ responses as a function of E are shown in the absence and in the presence of bulk Hg(0). In the latter case, $\Delta R/R$ shows a big diminution when bulk Hg(0) is formed. This response is similar to that reported by Rath[11] for the deposition of bulk Pb on gold. In a previous work,[14] it was shown that the more dense a surface phase is, more specularly the conduction electrons are reflected by the surface; that is, the smaller would be the resistance change as compared with that of the uncovered surface. Therefore, the bulk Hg(0) is a more dense surface phase than the Hg(upd) layer.
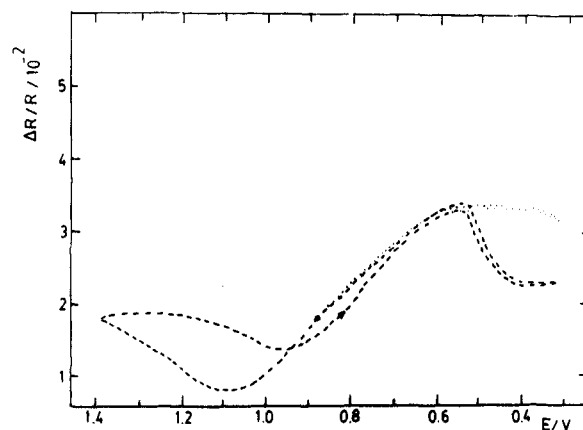
Conclusions

From the present work, the following conclusions can be drawn:

(1) In the upd and ups region, the SC changes show that the Hg(upd) is formed after the surface gold oxide is reduced. The reaction is reversible, and at equilibrium. Hg(upd) grows by an island mechanism up to $\vartheta \simeq 0.7$. The application of Linde's surface rule suggests the formation of an interstitial surface phase.

(2) The formation of bulk Hg–Au alloy occurs only when $\vartheta = 1$ irrespective of the presence of bulk Hg(0). The penetration of the mercury atoms into the bulk depends on the grain boundaries concentration of the gold electrode. During the stripping of the alloy, the surface concentration of Hg(upd), as detected by SC, remains the same as in the absence of bulk alloy. Only a relatively small amount of the latter is stripped off the electrode during one stripping cycle.

(3) The formation of bulk Hg(0) is accompanied by a decrease of the SC, which shows that it is a more dense surface phase than Hg(upd).