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## AN IRIIDIUM-BASED MERCURY-FILM ELECTRODE

### PART I. SELECTION OF SUBSTRATE AND PREPARATION

S.P. KOUNAVES \* and J. BUFFLE

*Department of Inorganic and Analytical Chemistry, University of Geneva, 30, quai E. Ansermet,  
1211 Geneve 4 (Switzerland)*

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#### ABSTRACT

A mercury-film electrode with iridium as the substrate has been developed. Various metals were considered as potential electrode substrates, but only iridium was found to possess the desirable properties as a Hg-film substrate. After testing several pretreatment procedures the recommendation is to polish with 1  $\mu\text{m}$  diamond, rinse with chromic acid and cathodize at  $-2.0$  V vs. SCE. Different deposition conditions and solutions were tested for optimizing the conditions of film formation. The use of a square-wave deposition potential and  $0.1$  M  $\text{HClO}_4$  as electrolyte resulted in a dramatic improvement in the formation of a stable Hg film. Finally a complete procedure is given for the formation of a stable Hg film on iridium.

#### INTRODUCTION

With the arousing of environmental consciousness has come an increasing demand on analytical chemistry to provide the means not only to determine which and how much of an element is present, but also to characterize the role and reactivity of the different forms in which it occurs [1,2]. The distribution of an element or component over all its physico-chemical forms or species is referred to as its speciation.

Electrochemical methods offer versatile and efficient approaches for the measurement and characterization of dissolved trace-metal species [3–5]. Since many metals of interest in the environment occur at total concentrations between  $10^{-8}$  to  $10^{-10}$  M, most speciation studies in natural waters have been done using anodic stripping

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\* Present address: Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, U.S.A.

voltammetry (ASV). The remarkable sensitivity of ASV is due to a predeposition step during which the metal ions of interest in the solution are reduced and concentrated into a mercury film electrode. Reoxidation and measurement of the metal is then performed by a positive-going potential sweep [6].

Currently the most important limitations for theoretically sound interpretations of speciation data obtained from such techniques are linked to the deposition step, in particular the electrode geometry, reproducibility and hydrodynamics. An ideal electrode should be mechanically stable, chemically inert, and possess a high hydrogen overvoltage. Hanging-mercury-drop (HMDE) or mercury-film (MFE) electrodes possess some of these properties and have therefore generally been used in the past for voltammetric studies. However, both electrodes have serious limitations for speciation studies (ref. 7, pp. 8–11). The HMDE faces several problems, particularly in terms of its relative “massiveness” with respect to internal diffusion and the rather uncontrolled and non-uniform solution hydrodynamics/diffusion at its surface during deposition. The MFE utilizes as a substrate either (i) a metal such as Pt, Au, Ni or Ag, all of which form an “amalgam-film electrode”, or (ii) an inert material such as glassy carbon, graphite or boron carbide, all of which form a “mercury-droplet-film electrode” [8].

The ideal configuration would be a true thin mercury film formed on an appropriate substrate with a controlled flow of solution over its surface during stripping and deposition (e.g. rotating disk electrode). This substrate should: (i) possess good wettability by mercury, in order to promote film formation and mechanical stability, and (ii) be chemically inert with respect to mercury and all metals to be reduced in the mercury. It seems, though, that finding an “appropriate” substrate on which to form a mercury film has been, to the frustration of many electrochemists, a rather unattainable goal.

## EXPERIMENTAL

### *Instrumentation*

The electrochemical system has been described previously [7]. It consists of a microcomputer-controlled potentiostat (Motorola EXORset + Tacussel PRG5), a custom-built medium-exchange/flow-through plexiglass cell, and an inverted polarizing microscope (Leitz Epivert) allowing in-situ observation and photography of the electrode surface.

The working electrode assembly was a Tacussel EDI-55442 rotating disk electrode (RDE) with a 1 cm Teflon tip into which a 2 mm dia.  $\times$  10 mm long iridium cylinder (99.9% purity, Heraeus GmbH) was press-fitted. The electrodes were polished initially with diamond spray pastes (Surfex, Metzger & Co, Switzerland) of decreasing size, the smallest of them being 1  $\mu$ m, until a mirror-like surface could be seen under the microscope at 250 $\times$ . After polishing the electrode was rinsed with diamond spray solvent (Blue Diamond Spray Solvent, Metzger & Co). Further pretreatments will be described later. The electrode was rotated at 1500 rpm during the experiments unless indicated otherwise. The counter electrode was a 2 mm dia.

× 2 cm long Pt rod. The reference electrode, to which all potentials are referred, was a SCE (238 mV vs. SHE) filled with a saturated NaCl solution and equipped with a 0.1 M NaNO<sub>3</sub> bridge.

### *Reagents*

All chemicals used were analytical reagent grade (Merck). The Hg(II) used for film formation was prepared by dissolution of triply distilled mercury in nitric acid, followed by dilution with 0.1 M HClO<sub>4</sub> to give 10<sup>-3</sup> M Hg(II), unless indicated otherwise.

All solutions were prepared with 18 MΩ water from a Millipore brand ion-exchange system.

High-purity (99.95%) nitrogen gas (Carbagas) was used to purge oxygen from the solutions and to maintain a nitrogen blanket during experimentation.

### SELECTION OF AN APPROPRIATE SUBSTRATE

At first glance, it would appear that the only materials which are capable of supporting a mercury film are those which are soluble in, and/or form a compound with, mercury. However, it is also possible to utilize the long-range attractive interactions (due to London–Van der Waals forces, dipole moments, and coulombic forces) which also exist at the interfaces. These forces can provide a means of forming a stable mercury film in cases where no reaction and/or solvation occurs.

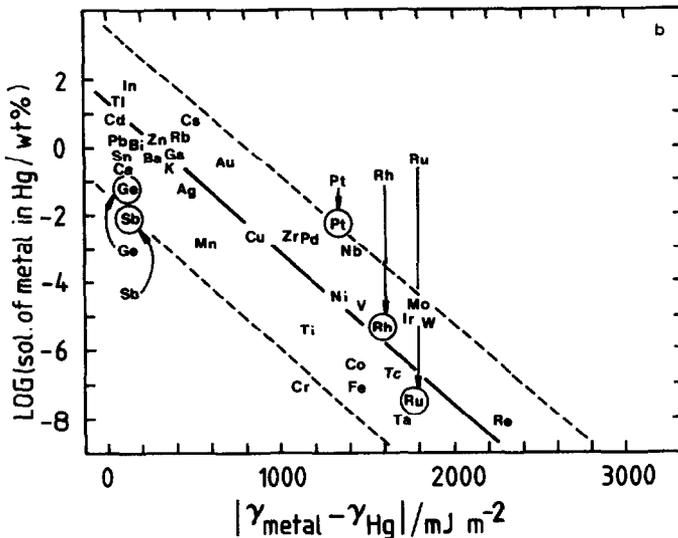
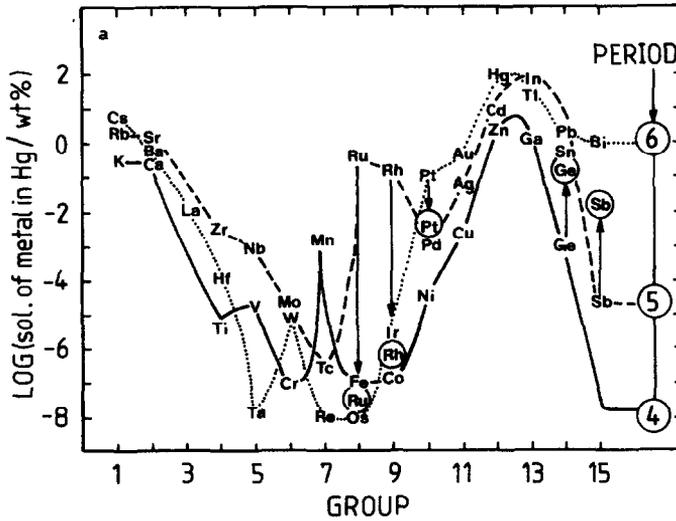
The selection of the substrate material was based initially on the low solubility of the substrate in mercury, and the non-chemical interaction of the substrate with mercury, as indicated by the electrochemical work function. It should be remarked at this point that, because of the requirement of having an electrically conducting substrate, we ruled out, beforehand, a substantial number of elements, leaving mainly the transition metals.

### *Solubility of substrate material in mercury*

The values for the metals' solubilities in mercury were taken mainly from Vydra et al. [9] and Guminski and Galus [10]. By necessity, the definition of solubility is not very rigorous or precise. A metal which shows *high* solubility, may do so not because it is "soluble", but because it undergoes a chemical reaction, forming an intermetallic compound, thus appearing to be solvated. On the other hand, a metal may show *low* solubility because its rate of solvation is extremely low or because of some passivation effect occurring at the interface. These and other experimental problems are responsible for many of the differences found between solubility values in the literature [10]. For practical electrochemical purposes we consider metals as being "soluble" if their solubility is > 10<sup>-4</sup> weight %, and "insoluble" if their solubility is < 10<sup>-6</sup> weight %.

No general laws have yet been found from which one can predict the solubility of any metal in mercury. However, during our efforts to find some type of relationship to make such predictions, the combination of two sets of correlations resulted in just such a possibility.

Generally, the more periodic properties that two elements have in common (atomic size, electronegativity, valence, etc.), the greater is the probability that they will be soluble in each other. Thus, one type of correlation known is between an element's position in the periodic table with respect to mercury and its solubility in



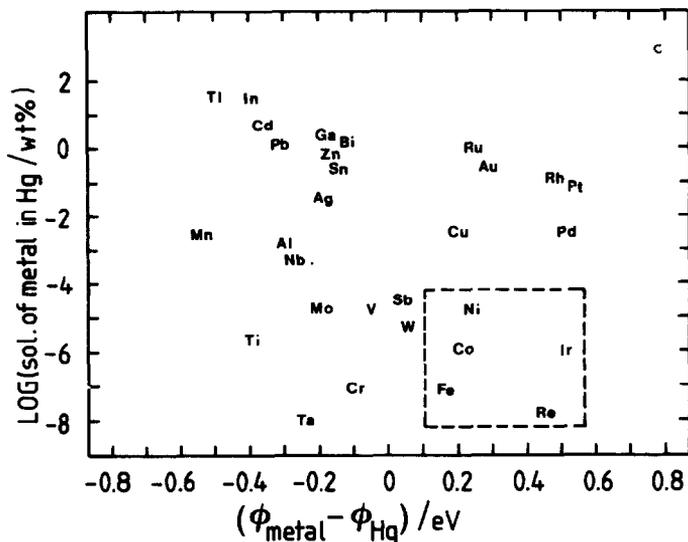


Fig. 1. The solubility of period 4, 5 and 6 elements in mercury (25°C) as a function of: (a) their position in the periodic table group; (b) the surface Gibbs energy difference between the metal and mercury; (c) the difference in the work function  $\Delta\phi$  of the metal and mercury.

mercury. Such a correlation is shown in Fig. 1a. As can be seen, the metals *most soluble* in mercury are those nearest to it in the periodic table between groups IB and IVA, and those *least soluble* lie further away between groups IVB and VIII B.

Another correlation was conceived on the basis of the surface Gibbs energy,  $\gamma$ . Very qualitatively, one might expect that any associations in a solution would tend to restrict the motion of the atoms and thus the entropy,  $S$ , of the system should decrease, i.e.  $S \propto 1/\text{solubility}$ . At the same time, from the thermodynamic definition of Gibbs energy ( $G = E - TS$ ) we have that  $\gamma \propto -S$ , so we would expect that  $\gamma \propto -1/\text{solubility}$ . A plot of the solubility as a function of the surface Gibbs energy, shown in Fig. 1b, gives just such a correlation.

The two sets of data are independent of each other and can be used as a cross-check for solubility. This was demonstrated clearly in the case of the solubility of iridium, which was given by Vydra et al. (ref. 9, p. 59) as 0.001 weight % at 20°C, which we used initially. In both graphs, the value appeared to be too high by two orders of magnitude. After several further literature searches and inquiries, and being ready to give up this idea, we found recent values that indicate the upper limit for the solubility of iridium in mercury to be no more than  $10^{-5}$  weight % at 500°C [10]. The solubility at 20°C is at least an order of magnitude lower. (As an interesting point, we note that there are several other elements for which the same situation may exist: e.g. "correcting" the solubilities for Rh, Ru, and Pt in either plot (circled symbol), also "corrects" them in the other.) In terms of solubility, we were then left with about fifteen pure metals as possible substrates.

### *Interactions between substrate and mercury*

The interaction between the mercury and the substrate is expressed electrochemically as the underpotential of deposition. This deposition underpotential,  $E_u$ , can exist either due to a chemical reaction between the first layer of mercury and the substrate, or due to the above mentioned attractive forces. It has been shown [11] that when chemical interactions between substrate and mercury can be discounted,  $E_u$  is related directly to the electrochemical work function,  $\phi$ . The greater the difference in  $\phi$ , the greater will be the polarity and thus the attractive-force bonding of the mercury and substrate. In other words, due to this stronger bonding of substrate and mercury, a large  $\Delta\phi$  favors film formation over distinct three-dimensional nucleation.

Figure 1c shows a plot of the solubility data [9,10] as a function of the work function,  $\Delta\phi$  [12]. The important item to note is that the metals at the bottom right-hand corner should be very good candidates for forming a mercury film on their surfaces, especially in terms of non-solubility and maximum attractive-force bonding. However, we also found it necessary to eliminate Re, Ni, Co and Fe, since, according to their electrochemical equilibrium diagrams [13], they all undergo dissolution or some type of reaction at the pHs and potentials where mercury deposition would take place.

Thus, iridium was selected as the substrate of choice on the basis of its low solubility in mercury and the non-chemical interaction of its surface with mercury. Iridium also possesses many other properties desirable in an electrode substrate: it is quite hard and can be polished to a flat mirror-like surface, it is immune to attack by any of the acids, and it has good electrical conductivity. A more detailed description of the selection process and also of other alloy substrates tested can be found in ref. 7.

### SELECTION OF SURFACE PRETREATMENT

We established six electrode pretreatments to be tested. All pretreatments included the polishing procedure described above as their initial step. The pretreatments tested were as follows:

(I) The electrode was washed with deionized water only. Thus, we had at most a partial air/water-oxidized monolayer.

(II) In addition to treatment I, the surface was washed with concentrated  $\text{HNO}_3$  for 5 min, and then rinsed with deionized water (chemically oxidized surface).

(III) Same as II, except that the electrode was washed for 30 min in concentrated  $\text{HNO}_3$ .

(IV) Same as I, but with the addition of anodization at +1.5 V for 5 min in 1.0 M  $\text{HNO}_3$  (electrically oxidized surface).

(V) Same as I, but with the addition of cathodization at -2.0 V for 5 min in 1.0 M  $\text{HNO}_3$  (electrically reduced surface).

(VI) Same as IV, but after the anodization the surface was cathodized at -2.0 V for an additional 5 min (electrically oxidized then reduced surface).

To compare the effect of these various pretreatments, we have used the following criteria:

(a) The measurement of the contact angle,  $\theta$ , which depends on the relative values of the mercury/iridium, iridium/solution, and mercury/solution interface surface energies. Since we wanted to find the pretreatment which would result in a surface that would promote Hg-film formation, we were looking for the smallest possible value of  $\theta$ , corresponding to a maximum wetting of the iridium surface by the mercury.

(b) Hg(II) reduction potential and usable potential range of the film.

(c) Microscopic morphology of the deposited mercury (film vs. droplets).

#### Contact angle measurements

The results for the determination of the contact angle [7] are summarized in Table 1. The value given in each case is the average of two measurements.

As expected,  $\theta$  was the largest ( $\approx 130^\circ$ ) for the electrode with the least pretreatment (I). The smallest value of  $\theta$  ( $121^\circ$ ) was found for the cathodization (V). Thus, we concluded that negative polarization was more effective than either concentrated  $\text{HNO}_3$  or anodization for reducing the contact angle.

No literature data can be found for the contact angle of mercury on iridium in air; therefore, we have no way of evaluating whether the contact angle obtained ( $\approx 121^\circ$ ) should be thought of as an accurate value for mercury on iridium (in air),

TABLE 1

Pretreatment effects on contact angle and reduction potential for mercury at the iridium electrode

Pretreatment <sup>a</sup>	Contact angle /degrees <sup>b,d</sup>	Reduction potential /mV (vs. SCE) <sup>c,d</sup>
I. Rinsed with water (air-oxidized)	130	+ 230
II. 5 min/conc. $\text{HNO}_3$ (chem. oxidized)	129	+ 210
III. 30 min/conc. $\text{HNO}_3$ (chem. oxidized)	128	+ 190
IV. Same as 1 plus 5 min/1 M $\text{HNO}_3$ + 1.5 V (elec. oxid.)	129	+ 180
V. Same as 1 plus 5 min/1 M $\text{HNO}_3$ - 2.0 V (elec. red.)	121	+ 170
VI. Same as 4 plus 5 min/- 2.0 V (elec. oxid. + red.)	125	+ 190

<sup>a</sup> All pretreatments include the initial polishing step.

<sup>b</sup>  $\pm 0.5^\circ$ .

<sup>c</sup>  $\pm 5$  mV.

<sup>d</sup> Average for two measurements with identical pretreatments, same electrode.

or whether to consider it only as a relative value to be used in judging the efficacy of the pretreatment. For platinum [14] and palladium [15] the contact angles are given as  $38^\circ$  and  $40^\circ$ , respectively. Considering the much higher solubility of these metals in mercury as compared to that of iridium (Fig. 1a), the value of  $\theta = 121^\circ$  for iridium appears reasonable.

#### *Pretreatment effects on Hg(II) reduction potential*

Together with the contact angle measurements, we also recorded a cyclic voltammogram for each pretreatment, paying special attention that the reduction curve was taken on the first negative-going scan. The electrodes were prepared using exactly the same pretreatments as those used for the contact angle measurements.

The solutions used contained  $0.1\text{ M HClO}_4 + 10^{-4}\text{ M Hg(II)}$  in deionized water, and were purged with  $\text{N}_2$  for 30 min before starting. The cyclic voltammograms were all recorded at  $20\text{ mV/s}$  starting at  $+700\text{ mV}$  to a vertex of  $-200\text{ mV}$ , and using the RDE with  $\omega = 1000\text{ rpm}$ .

Figure 2 shows, as an example, a cyclic voltammogram made after pretreatment I. The half-wave potential,  $E_{1/2}$ , for the reduction of Hg(II) is at  $\approx 230\text{ mV}$ . The anodic peak at  $460\text{ mV}$  is due to the bulk oxidation of mercury (a more detailed description of the Hg/Ir surface chemistry can be found in ref. 16).

The results of the determination of the half-wave reduction potential of Hg(II),  $E_{1/2}$ , for each pretreatment, are summarized in Table 1.

#### *Selection of a pretreatment*

Figure 3 shows the relationship between the contact angle,  $\theta$ , and the reduction potential,  $E_{1/2}$ , for the set of pretreatments (I–VI in Table 1). The oxidation and

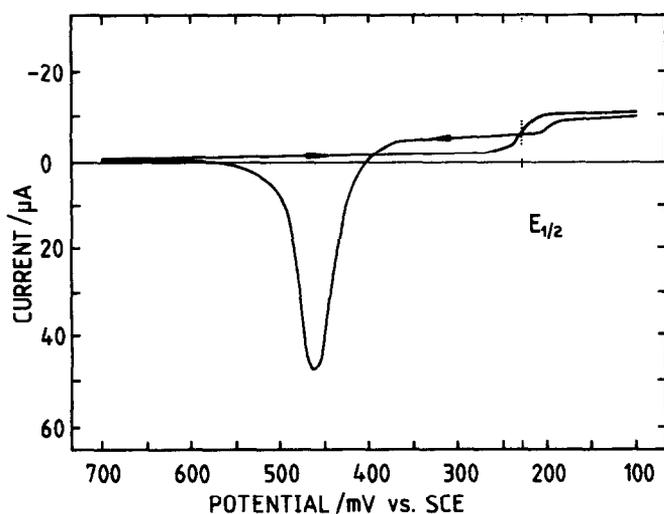


Fig. 2. Cyclic voltammogram of mercury on the iridium substrate electrode, conditions as given in text.

reduction pretreatments both affect the surface similarly in terms of  $E_{1/2}$ , but somewhat differently in terms of  $\theta$ .

For both types of *oxidation* pretreatments, acid and electrical (II–IV), there is a substantial decrease of  $E_{1/2}$  ( $\approx 50$  mV), especially with increasing oxidation strength, but only a small decrease of  $\theta$  ( $\approx 2^\circ$ ). On the other hand, the cathodization pretreatment (V) shows the largest decrease of all for both  $E_{1/2}$  and  $\theta$  ( $\approx 60$  mV and  $9^\circ$ ).

The above behavior suggests that both the chemical and electrochemical oxidation pretreatments produce an oxide layer on the iridium surface. This layer makes it more difficult (i.e., requires more energy) for the reduction of Hg(II), but makes no difference in the ability of Hg to spread on the surface (no decrease in  $\theta$ ). This means that eventually, when some nuclei are formed, the reduction of Hg(II) will continue on these nuclei ( $\text{Hg(II)} \rightarrow \text{Hg(0)}$ : +400 mV) [16] rather than on the oxide-coated surface. This situation is not favorable for the formation of a homogeneous mercury film.

The cathodization (V) most probably reduces the oxide layer, making it easier for mercury to spread once it is deposited ( $\theta$  decreases), but not seeming to make any difference for the reduction of Hg(II) onto a new surface. For the combined anodization/cathodization (VI), we have probably only partially reduced the anodized surface, hence, it exhibits a midway behavior.

Thus, from the above-mentioned results, a cathodized surface needs more energy for the reduction of Hg(II) than a surface which is polished only, but it seems to provide a better substrate on which to form a well-spread mercury film.

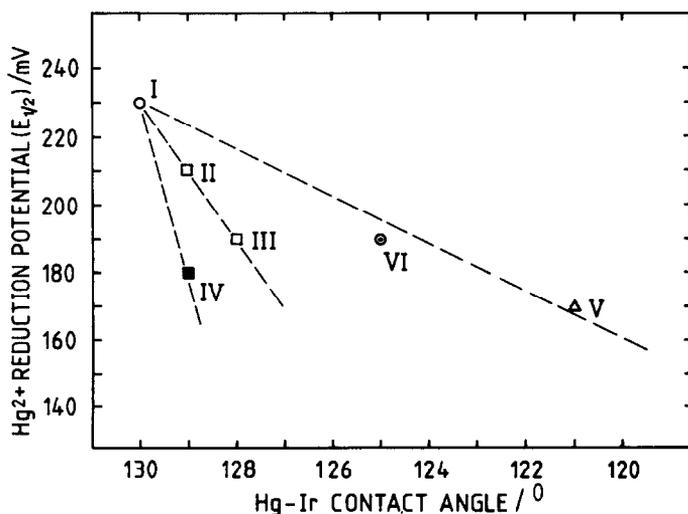


Fig. 3. The relationship between the contact angle,  $\theta$ , and the mercury reduction potential,  $E_{1/2}$ , for each pretreatment described in Table 1: (I) none; (II,III) acid oxid.; (IV) elect. oxid.; (V) elect. reduced; (VI) elect. oxid. and reduced.

## SELECTION OF ELECTROLYTE

The effect of the solution matrix on Hg film formation was studied in two ways: Firstly, in terms of the usable potential range of the iridium, relative to the redox potential of water and secondly, by looking at several types of deposition–solution composition such as neutral, basic, acid, and complexing.

The diagram in Fig. 4 shows the experimental potential limits for the iridium substrate in several different electrolytes. The limits are arbitrarily defined as the point where the oxidation or reduction yields a current density in excess of  $30 \mu\text{A}/\text{cm}^2$ . The data were taken under the following conditions: a potential scan of  $4 \text{ mV}/\text{s}$ , the RDE rotating at  $1000 \text{ rpm}$ , and the reference electrode being a SCE with a  $\text{NaNO}_3$  bridge for the perchlorate-containing solutions. The limits exhibited by all the electrolytes tested with iridium do not present any major problems, and any of them would fulfil our requirements on the basis of the potential range for  $\text{Hg(II)}$  reduction.

The effect of the seven deposition solutions (S1–S7) tested for the formation of a Hg film are summarized in Table 2. For both  $\text{KNO}_3$  and  $\text{HNO}_3$ , the mercury was always deposited as small droplets distributed uniformly over the surface (Fig. 5a). With longer deposition times, the droplets coalesced to form domed patches (Fig. 5b) and eventually a single large semisphere covering the entire surface (but never a true film).

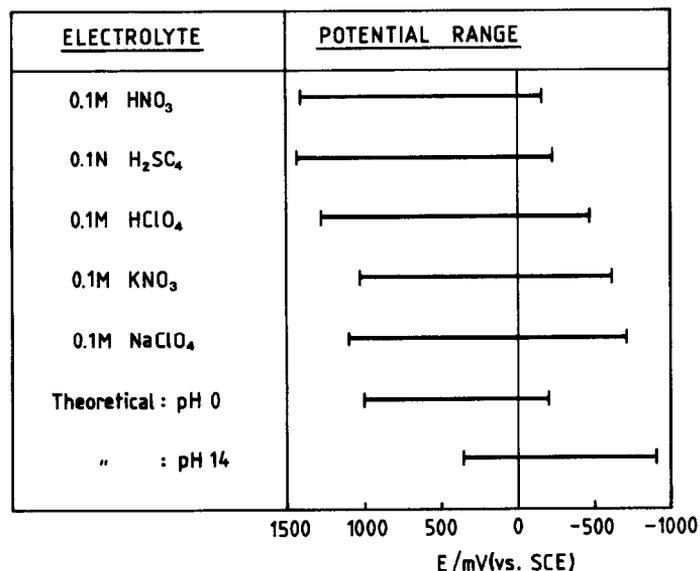


Fig. 4. The upper and lower potential limits for the iridium substrate in various electrolytes. Scan rate  $4 \text{ mV}/\text{s}$ . Limits are defined as the potential for which  $i = \pm 1 \mu\text{A}$ .

TABLE 2

Effect of deposition solution on the formation of a mercury film on an iridium substrate ( $\text{Hg(II)} = 0.001 M$ ,  $\omega = 1000 \text{ rpm}$ )

Solution <sup>a</sup>	Deposition time/min	Potential /mV vs. SCE	Result
S1: 0.1 M $\text{KNO}_3$	10	-1000	Droplets, 2400/mm <sup>2</sup>
	90	-100	Semispheres, 80/mm <sup>2</sup>
S2: 0.1 M $\text{KNO}_3$ + 0.05 M EDTA	90	-200/-1500	Flat patches
	300	-1000	Blackish film
S3: 0.1 M $\text{KNO}_3$ + 0.0001 M NTA	90	-1500	100 $\mu\text{m}$ domed patches, 10/mm <sup>2</sup>
S4: 0.1 M $\text{KNO}_3$ + 0.05 M en	30	-1600	50 $\mu\text{m}$ domes, 8/mm <sup>2</sup>
S5: 0.1 M $\text{HNO}_3$	10-90	-200/-1500	Droplets only, 200-2500/mm <sup>2</sup>
S6: 0.1 M $\text{HClO}_4$	10-30	-200/-400	Hg film 50% of the time, rest droplets
S7: 0.5 M $\text{NH}_4\text{OH}$ + 0.05 M EDTA	30-300	-200/-1500	Flat patches with black crust

<sup>a</sup> en: ethylenediamine; NTA: nitrilotriacetic acid; EDTA: ethylenediaminetetraacetic acid.

Solutions containing ethylenediamine, EDTA or NTA, which form respectively slow, inert and labile complexes with  $\text{Hg(II)}$ , were used to test the effect of complexation and concentration polarization (which is less with inert complexes than labile ones). Nevertheless, in all cases the deposition of mercury occurred very slowly and with the same morphology. After 90 min the entire surface was covered with a thin deposit of mercury, which however was neither uniform nor smooth and

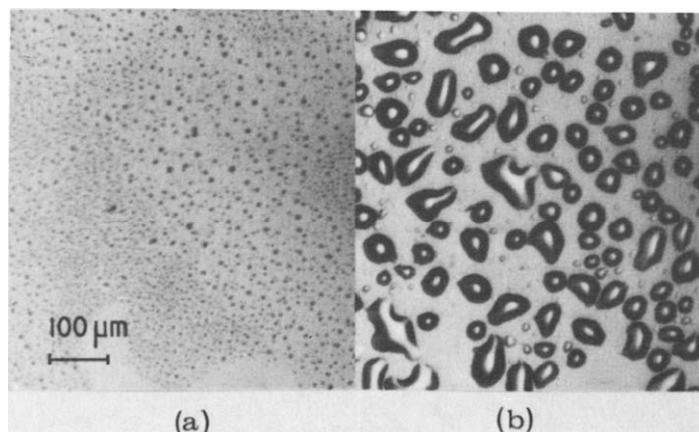


Fig. 5. The morphology of the mercury film for both  $\text{KNO}_3$  (S1) and  $\text{HNO}_3$  (S5) with the RDE ( $\omega = 1000 \text{ rpm}$ ) in the potential range -200 mV to -1500 mV after: (a) 10 min, (b) 60-90 min.

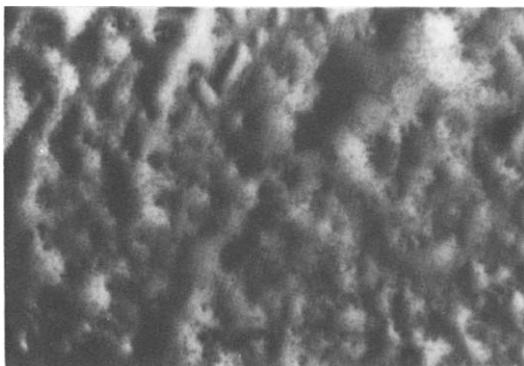


Fig. 6. The morphology of the mercury film in solutions containing ethylenediamine, EDTA or NTA. In all cases the deposition of mercury occurred very slowly and with the same result. After 90 min the entire surface was covered with flat non-uniform patches of mercury.

consisted of flat patches (Fig. 6). Prolonged deposition for up to 5 h caused degradation of the surface and a solid black film to form over the surface.

$\text{HClO}_4$  was the only electrolyte with which a completely flat or semispherical film could be formed. However, even in this case, we had only a 50% success rate. The remaining attempts resulted in a coverage similar to that shown in Fig. 5.

#### USE OF A SQUARE-WAVE POTENTIAL FOR Hg-FILM DEPOSITION

In order to improve the uniformity of the Hg film on iridium, we investigated the use of square-wave deposition potentials. This technique is sometimes used in metallurgy to give smooth solid depositions [17], but to our knowledge has not been applied to Hg-film formation for analytical purposes.

Figure 7a shows the calculated diffusion-layer profile expected after the application of a dc potential. Due to the thinner diffusion layer on any raised surface feature (such as deformations or Hg nuclei) the flux of  $\text{Hg(II)}$  ions is greater and thus results in faster deposition of Hg at these points. At the same time the increase in flux causes an increase in current, which in turn alters the potential field, creating an electrically "shielded" region around what is now a growing mercury droplet. This effect is thus responsible for an "amplification" of the surface roughness. The theory of the diffusion-layer interaction with microprofiles (with and without convection) has been discussed in detail by Kardos [18].

The application of a square-wave potential will produce a much thinner diffusion layer, whose thickness depends on the frequency, and is constant over the entire surface [17]. With higher frequencies, the diffusion layer can be thin enough to follow the microprofile to such an extent that surface deformations are not amplified (Fig. 7b).

The diffusion layer becomes constant when its thickness reaches the same order

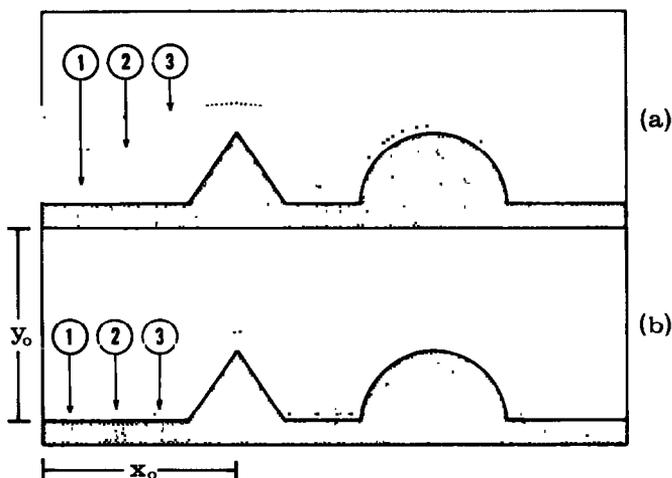


Fig. 7. The diffusion-layer profile (where  $C(t) = 0.5 C(t = 0)$ ) for a model diffusion field ( $x$  by  $y$  cm) in which there are several surface features. Lines 1–3 are for times of  $0.1y^2/D$ ,  $5y^2/D$ , and  $10y^2/D$  s respectively, after application of: (a) a dc potential; (b) a square-wave potential with a frequency of  $100(D/y^2)$  Hz.

of magnitude as the radius of curvature of the protruding or receding surface features. The thickness of the diffusion layer,  $\delta$ , is given by:

$$\delta = (D\pi/0.367\nu)^{1/2} \quad (1)$$

where  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ), and  $\nu$  the frequency (Hz). Thus, one can define a minimum frequency above which there is no amplification of the surface features. Since most of the surface will bear the markings of the final diamond polishings (3 and  $1 \mu\text{m}$ ), and the initial mercury nuclei will be  $< 1 \mu\text{m}$ , we should be able to obtain a minimum of surface feature amplification using frequencies greater than 1000 Hz.

A square-wave potential was applied using a GSTP Signal Generator (Tacussel, Lyon, France). The solutions, containing  $0.1 M \text{HClO}_4 + 0.01 M \text{Hg(II)}$ , were purged with  $\text{N}_2$  for 30 min, and deposition was performed for 5 min with the RDE at  $\omega = 1500 \text{ rpm}$ . The square-wave potential used had an amplitude of 700 mV p-p and a positive base of +410 mV. This latter limit was chosen so as to cause a slight oxidation of the mercury [16], thus destroying part of the diffusion layer. The amplitude was chosen to provide a sufficiently negative pulse to re-nucleate any available surface sites.

The results for the application of different frequencies are shown in Fig. 8. A definite change in the deposition was noticed starting at about 50 Hz. As expected, the mercury became more and more spread out in the form of flat patches, and the first signs of a film were evident at about 500 Hz. A true film was deposited at 2000 Hz. No change was noticed again until approx. 10000 Hz, at which point the

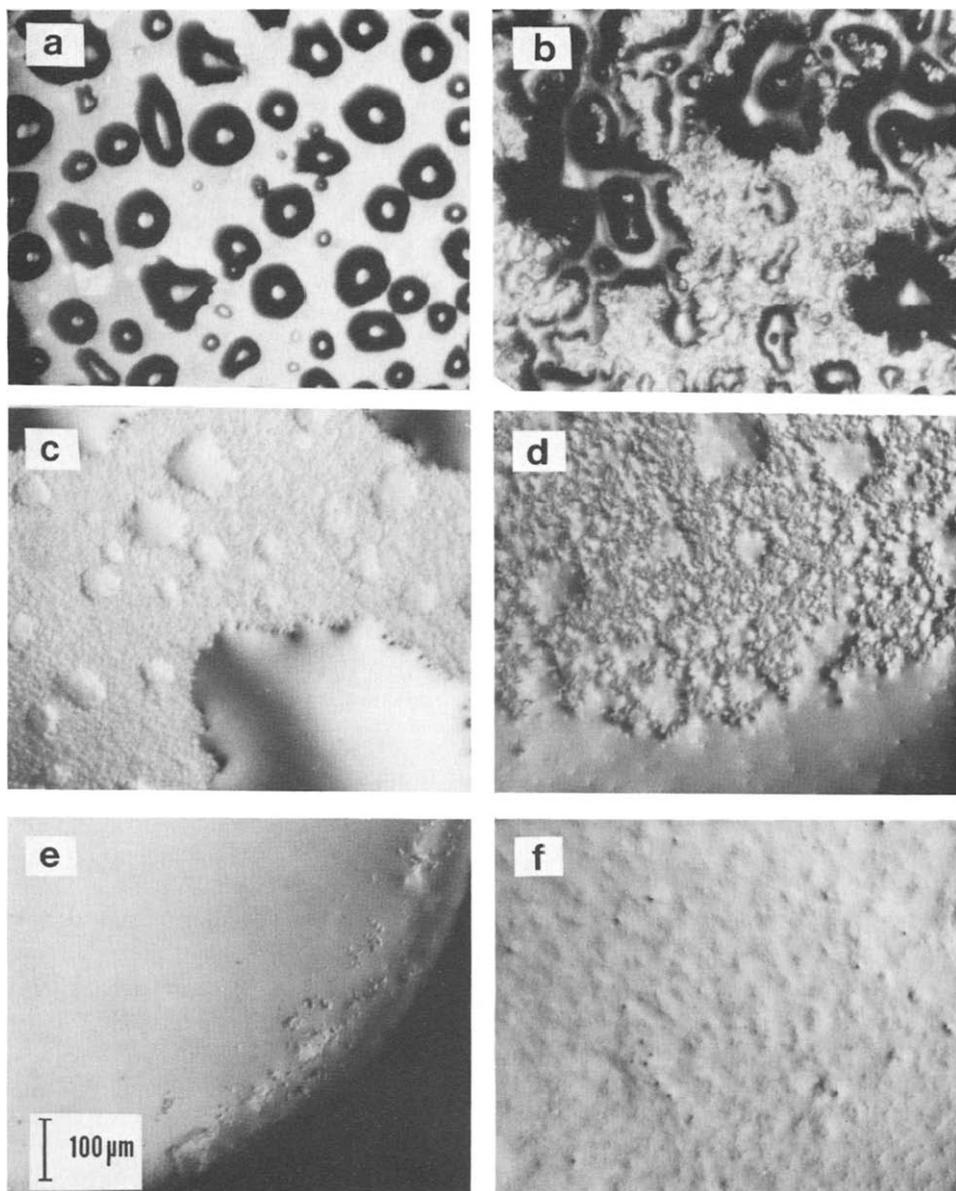


Fig. 8. Photomicrographs of the iridium electrode surface covered by mercury deposited at various square-wave frequencies (conditions described in text): (a) Dc potential; (b) 50 Hz; (c) 100 Hz; (d) 500 Hz; (e) 2000 Hz; (f) 10000 Hz.

surface was still covered by a film, but seemed to be thinner and had more deformities. This condition remained unchanged until 20000 Hz, at which point the film reverted back to the same condition as at 500 Hz. We attribute this behavior to

the possibility that the electrical components of the circuitry and cell may not be capable of responding to frequencies above 5000 Hz and thus the actual applied potential and current distribution at the surface of the iridium may be decreased and/or distorted.

For square-wave amplitude and/or base potential values increasingly greater than or less than those selected above, the Hg film decreased in quality. For values higher than 100 mV, no Hg film was formed.

Interestingly, the same procedure applied to a glassy-carbon substrate, under identical conditions, failed to produce a Hg film. Additional experiments on other substrates are being planned and will be reported in future papers.

#### DEPOSITION PROCEDURE FOR A MERCURY FILM ON IRIDIUM

##### *General considerations*

Unlike Hg films on Pt and Au, which are formed by an amalgamation process, the Hg film on Ir depends on weaker forces to maintain it in place [16]. For this reason, the preparation and use of the iridium mercury-film electrode (Ir-MFE) requires a little more time and care. This is nowhere near being a problem, however, when the end result is a Hg-film electrode, which is just that, and not a Pt/Hg alloy-film electrode. Furthermore, with a computer-controlled system, the flow and exchange of solutions, the application of potentials and the experimental sequence in general are easy to control, requiring a minimum of operator effort.

Keeping in mind the results and conclusions arrived at above, we give here a basic procedure which has, 8 out of 10 times, resulted in a stable long-term mercury film.

It should be noted at this point that, in our experience with Hg films, we surmise that a truly flat film probably cannot exist at thicknesses of more than  $1\ \mu\text{m}$  [7]. A film of about  $20\ \mu\text{m}$  may look very flat to the naked eye or even under a normal light microscope, but when viewed under a polarizing microscope it becomes evident that the surface is slightly convex. This seems reasonable, since rough calculations show that even for a  $1\ \mu\text{m}$  flat Hg film, we already have  $\approx 4000$  layers of Hg atoms. Considering the high surface tension of Hg, it seems unlikely that 4000 layers of Hg atoms could be kept from pulling together into a configuration of least surface tension: a semisphere (and still maintain an Ir-Hg surface bonding). In preparing a Hg film, we must be aware that at some thickness, it will cross over from a truly flat film, to a semispherical film.

The procedure and results given below are for a thin, flat mercury film ( $< 1\ \mu\text{m}$ ), because it is more useful but more difficult to prepare than a thicker, semispherical film ( $> 5\ \mu\text{m}$ ). The latter can be prepared using the same procedure, but once it is formed it will tend to act more like a mercury drop.

The procedure consists of three basic parts: (1) pretreatment of the iridium substrate surface, (2) deposition of the mercury, (3) medium exchange and electrode storage.

### *Pretreatment*

The procedure is carried out each time a Hg film is to be deposited. The electrode surface is: (1) Polished for 1 min with 1  $\mu\text{m}$  diamond spray, with the RDE rotating at about 1000 rpm; (2) rinsed with "blue diamond solvent", followed by acetone and deionized water; (3) placed in concentrated chromic acid, for 5 min, while rotating at  $\approx 1000$  rpm; (4) rinsed with deionized water and placed quickly and directly into a deoxygenated deposition electrolyte, containing only 0.1  $M$   $\text{HClO}_4$ , and no mercury; (5) cathodized by applying  $-2.0$  V (vs. SCE) for 5 min, with the RDE rotating at 3000 rpm or more while simultaneously applying a stream of nitrogen gas bubbles in such a way as to "scrub" the evolving hydrogen gas bubbles off the active electrode surface; and (6) kept in the electrolyte and maintained at 0.0 V (vs. SCE) until the deposition step.

### *Deposition of mercury*

The deposition steps should be carried out as soon as possible after the pretreatment. One should then proceed as follows: (1) The electrode circuit is disconnected, and either an addition or a solution exchange is done, to give a mercury concentration of 0.01  $M$  (still in 0.1  $M$   $\text{HClO}_4$ ). The exchange solution should be deoxygenated prior to coming into contact with the electrode. (2) With the RDE rotating at 1500 rpm, a 2000 Hz square-wave potential with a 50 mV baseline and an amplitude of  $\pm 350$  mV is applied. The deposition time should be selected for the film thickness desired. (Note: calibration studies indicated that the effective (rms) dc current recorded during a deposition was always in agreement with the charge used for the deposition, and can thus be used to calculate the film thickness.) (3) Once the deposition is finished, the electrode circuit is opened and the deposition solution is replaced as quickly as possible (using flow-through) by a pre-deoxygenated 0.1  $M$   $\text{HClO}_4$  solution, and a dc potential of 0.0 V (vs. SCE) is applied.

At this point, our experience has shown that a film is formed about 8 out of 10 times. One may then use the medium-exchange method and proceed with the sample analysis, bearing in mind always to maintain the potential at 0 V (vs. SCE) when the electrode is not being used for analysis. If the Hg was deposited in a "patchy" manner, the dc potential is increased gradually to about  $-900$  mV, while the electrode surface is observed through the microscope. The semifilm can be made to spread out, and by "playing" with the potential between  $-100$  and  $-900$  mV, the film can usually be made to take form within 10 or 20 min. If a true film is not formed at this point, the entire procedure should be repeated starting with the pretreatment.

### *Electrode storage*

Mercury films made during this research have been kept for as long as two weeks without showing any signs of deterioration, by keeping them in a solution of 0.1  $M$   $\text{HClO}_4$  with an applied potential of about  $-50$  mV (vs. SCE) and under slow nitrogen-gas bubbling (about 6 bubbles/min). If the electrode circuit is left open for more than 10 h, a surface oxide starts to form. This oxide is usually visible only by

microscopic observation. Electrodes have been left in air for several days without showing visual deterioration of the film, *but* once placed back in solution the film invariably reverts to the droplet form and cannot be made to re-form a film again under any condition.

#### CONCLUSIONS

These initial studies have shown that the use of an iridium substrate and a square-wave mercury deposition potential offer a new and novel method for the preparation of a true mercury-film electrode. The preparation and use of the Ir-MFE requires more time and patience than Pt-, Ag-, or glassy carbon-based electrodes, but again, for certain analytical techniques such as speciation studies, a well-defined Hg-film surface may be worth the effort.

A detailed description of the voltammetric stripping behavior and limitations of the Ir-MFE, with several metal ions, can be found in Part 2 of this paper [19].

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