

Fig. 14. Change in discharge capacity vs. cycles

a pasted-type lead-acid battery during deep charge and discharge cycles can be prevented by compression on the positive plates with glass mats. With high compression, the structural changes in the active mass become smaller and the cycle life of the cell increases remarkably. The structural change takes place due to the stress caused mainly by the volume change of the active mass during charge and discharge cycling, and consequently the active mass gradually expands with cycling. The rate of expansion is higher in the early stages of cycle testing. Once the coralloid structure is formed, it absorbs the stress of the volume change. It is considered that the reason why the cycle life increases by compression is due to the suppression of structural changes in the positive active mass and the considerable suppression of the decrease in the cohesion between PbO₂ particles.

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High Speed Gold Plating: Anodic Bath Degradation and Search for Stable Low Polarization Anodes

C. G. Smith* and Y. Okinaka*

Bell Laboratories, Murray Hill, New Jersey 07974

ABSTRACT

Two kinds of anodic bath degradation occur in high speed gold plating: the oxidation of cyanoaurate(I) to cyanoaurate(II) ion resulting in a decrease in plating current efficiency, and the oxidation of citrate ion causing a loss of buffer capacity. These oxidation reactions can be minimized by replacing the conventional platinum or platinum-coated anode with a low polarization anode such as the so-called "dimensionally stable anode (DSA[®])." However, the ordinary DSA with a coating consisting of RuO₂ and TiO₂ is not sufficiently stable under the conditions of this application. This paper describes results of three studies: (*i*) analysis of laboratory data for the rate of Au(III) accumulation to develop a method for predicting the concentration of citrate buffer capacity as a function of bath operating conditions; and (*iii*) an extensive search for a more stable low polarization anode, which led to the development of a coating consisting of IrO₂ and Ta₂O₅ with barium as the additive.

Gold plating technology has advanced significantly in recent years. Automated machines now plate gold selectively to minimize its usage, and at high speeds to maximize throughput and thus to minimize capital outlays. To maintain the process under high speed conditions, the control of plating bath characteristics becomes significantly more important. The degradation of bath characteristics occurs much more rapidly in high speed processes than in conventional low speed processes.

Two types of bath degradation have been found to take place. Both result from anodic reactions occurring at the conventional platinum or platinized titanium anodes. Oxidation of the cyanoaurate(I) ion to the cyanoaurate(III) ion leads to a decrease in current efficiency (1). The destructive oxidation of citrate buffers also occurs. Degradation products apparently do not affect the nature of the deposit (2). However, a hitherto unrecognized effect is a resultant loss of buffer capacity. As the initial capacity decreases, a point is eventually reached at which loss of control of the interfacial pH at the cathode occurs.

In the previous work (1, 3), it was shown that the rate of Au(III) formation is significantly lower at the so-called "dimensionally stable anode (DSA®)" (4). This well-known type of anode usually consists of a titanium substrate coated with a mixture of a precious metal oxide, such as RuO₂, and a valve metal oxide, typically TiO₂. The RuO₂-based anode,

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however, has a limitation that its useful life is too short for practical high speed plating applications.

This paper is concerned with three aspects of high speed gold plating. (i) Laboratory data for the rate of Au(III) accumulation have been analyzed mathematically to derive expressions useful for extending laboratory results to scaled-up production conditions. (ii) The magnitude of loss of buffer capacity of citrate-based systems has been evaluated theoretically and experimentally. It is shown that citrate degradation occurs at a much lower rate on DSA than on a platinum anode. (iii) Mixed metal oxide coatings much more stable than the RuO₂-TiO₂ combination have been developed. It is shown that coatings consisting of IrO2 and Ta2O5, particularly with barium as additive, provide electrodes with considerably extended lifetimes. Since the usefulness of these electrodes in gold plating results from their very low anodic polarizations (low oxygen overpotentials) as demonstrated in this communcation, they will be called "low polarization anodes."

Experimental

Plating apparatus and Au(III) analysis.—The rate of Au(III) accumulation during plating with various anode materials was measured for a high speed, additive-free hard gold (AFHG) bath operated at 40°C. This bath (5) consisted of a pH 7 phosphate buffer containing 100 g/liter KH₂PO₄ and 28 g/liter KOH, and 30 g/liter Au(I) added in the form of $KAu(CN)_2$. A polarographic method (6) was used to analyze the bath for total gold and Au(III). The plating apparatus has been described previously (1). The cathode was a copper cylinder rotating at 3600 rpm, and the anode a concentric cylinder 3 cm in inside diameter and 2 cm in height. The volume of the plating solution was 250 ml, and the temperature was maintained at 40°C by circulating water through a jacketed glass vessel. The bath was replenished every one-eighth turnover (a turnover defined as completed when the amount of gold initially present has been plated out and this amount of gold replenished) to limit a variation in total gold between 26 and 34 g/liter.

Measurement of citrate degradation.-The functional property of importance of a buffer is its buffer capacity, which characterizes the effectiveness with which a constant hydronium ion concentration is maintained. As the buffer capacity is proportional to the concentration of buffer, it can be expected that, in citrate-based gold plating baths, the buffer capacity will decrease as citrate ions are oxidized at the anode. In the present work, the decrease in buffer capacity, rather than the increase in degradation products, is considered as a measure of the degree of citrate degradation.

The rate of citrate buffer degradation was determined by measuring the "integral buffer capacity" as a function of electrolysis time. The integral buffer capacity, $C_{\rm H}$, is defined as

$$C_{\rm H} = C_{\rm b} \int \frac{\beta}{C_{\rm br}} dp {\rm H}$$
 [1]

where β is the buffer value (7) which is a differential ratio given by

$$\beta = \frac{db}{dpH}$$
[2]

where db is an increment of strong base in gram equivalents. A solution has a unit buffer value when a liter of it will take up 1g equivalent of strong alkali per unit increase in pH. Other symbols are explained in the list attached at the end of the text. Theoretically, the integral buffer capacity should be equal to the hydrogen content for the first three dis-

sociation states of citric acid available to react with KOH and, therefore, can be calculated from the dissociation constants of citrate species. The values calculated for a total citrate concentration of 1M at different pH values are given in Table I. The integral buffer capacity for a given solution is obtained by multiplying these normalized values by the total citrate concentration. Thus, if the citrate concentration decreases due to the decomposition at the anode, the integral buffer capacity decreases proportionally. Experimentally, the integral buffer capacity as a function of electrolysis time was determined as follows. Eighty milliliters of a pH 4.5 mixture of 74 g/liter acid $(H_3C_6H_5O_7 \cdot H_2O)$ and 111 g/liter base $(K_3C_6H_5O_7)$ \cdot H₂O) was electrolyzed at 30 C in a 100 ml cell equipped with an anode (2 cm^2) and a large cylindrical stainless steel cathode (3 cm in diameter and 2 cm in height). Small samples were withdrawn at various times and titrated to pH 7.6 with 1M KOH.

Preparation of anodes.-Binary oxide anodes were prepared by thermal decomposition of coatings of chloride mixtures on titanium substrates (8). The chloride mixtures were prepared by mixing desired volumes of 0.06M platinum metal chlorides in 2.4M HCl and 0.06M valve metal chlorides in methanol. The titanium disks, 1.27 cm in diameter, formed at an end of titanium rods, were used as substrates for anode aging experiments. The substrates used for citrate degradation experiments were titanium sheets, 1×1 cm. In the Au(III) formation experiments titanium cylinders, 0.13 cm thick, measuring 3 cm in inside diameter and 2 cm in height were used. These substrates were dry honed and etched in 2.4M HCl at 70°C for 15 min immediately prior to application of coatings. Unless mentioned otherwise, oxide coatings were produced by first applying three coats of the chloride mixtures and baking at 450°C for 20 min, followed by repeating the process of chloride application and baking two additional times. The baking process converts the chlorides into oxides, and the temperature used will be called conversion temperature. The final baking was done for 1 hr. Ternary oxide anodes were prepared in the same manner with the addition of the third component in the form of either chloride or nitrate.

Anode aging experiments.—Accelerated aging tests were performed at 30° C by electrolyzing the pH 4.5 citrate buffer or the pH 7 phosphate buffer at a constant cell voltage. For convenience, four anodes were tested simultaneously in the same cell. A common, four-sided stainless steel cathode was used, and the anodes were each located with a 3 cm anodecathode separation. Initial currents were adjusted with variable resistors in series with each anode.

Results and Discussion

Au(III) accumulation.-Rates of accumulation of Au(III) and resulting decreases in plating current efficiency are shown in Fig. 1. The anode current density used was approximately 150 mA/cm². These results are similar to those presented earlier (1),

Table I. Calculated integral buffer capacity of 1M citrate at various pH values

(pK values use	$d: pK_1$	= 3.13	pK₃ =	4.76, pKs	=	6.40)
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pH	H₃R (M)	H2R- (M)	HR-2 (M)	R-3 (M)	Integral buffer capacity*
4.5	0.07	0.61	0.32	0.004	1.74
5.0	0.01	0.36	0.61	0.02	1.36
5.5	0.002	0.14	0.76	0.10	1.04
7.0	0.0	0.001	0.20	0.80	0.20

* The units are mols of H per liter (per mol of citrate).

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Fig. 1. Accumulation of Au(III) during gold plating from AFHG bath with various anodes and corresponding decrease in plating current efficiency. (Anode current density, 150 mA/cm².)

with additional results for a 50:50 Ir: Ta oxide coated anode and an iridium metal anode. For a fraction pof the total gold existing as Au(III), the current efficiency η is given by

$$\eta = \frac{1}{1+2p}$$
[3]

A surprising result is that while the $IrO_2-Ta_2O_5$ anode gave a low Au(III) accumulation rate similar to that observed with the RuO₂-TiO₂ anode, the accumulation rate with iridium metal was identical to that with platinum. Figure 2 shows polarization curves for oxygen evolution in the citrate buffer (30°C, pH 4.5). The shift to high potentials for the iridium metal anode is possibly due to the formation of a passive surface film. These results support the interpretation proposed previously (1) that the faster accumulation of Au(III) observed with the platinum anode results from the higher potential at this anode.



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The rate of Au(III) formation in grams per hour for a given plating system can be calculated from the experimental results presented in Fig. 1 by considering the differential mass balance for Au(III) in the plating system. The observation that the accumulation rate of Au(III) depends on anode potential implies that its formation rate at the anode is independent of Au(I) concentration above a certain critical concentration. With this assumption, the mass balance gives.

$$\frac{\partial (pC_{\mathrm{au}}^*V)}{\partial t} = F_{\mathrm{a}} - v_{\mathrm{d}}pC_{\mathrm{au}}^* - \frac{3600IM}{\mathbf{F}} \frac{p}{1+2p} \quad [4]$$

This equation is not valid for very low Au(I) concentrations, where p approaches unity, and the formation rate would approach zero. The second term on the right represents Au(III) lost to dragout. The last term is for the reduction of Au(III) to Au at the cathode and was derived by assuming that the reductions of Au(I) and Au(III) to Au are the only reactions that must be considered, and that Au(I) and Au(III) reduction rates are both mass transport limited. Assuming further that the total gold concentration C_{au}^* is constant, the equation is nondimensionalized by using the dimensionless time T

$$T = t/\alpha_0; \quad \alpha_0 = \frac{C_{\rm au} * V}{7.35I}$$
 [5]

The characteristic time α_0 is the time it takes to complete one turnover of gold at 100% current efficiency. Substitution of T gives

$$\frac{dp}{dT} = C_1 - C_2 p - \frac{p}{1+2p}$$
[6]

The constants in Eq. [6] are

$$C_1 = \frac{F_a}{7.35I}; \quad C_2 = \frac{v_d C_{au}^*}{7.35I}$$
 [7]

The constant C_2 is the dragout in fraction of the total electrolyte volume per turnover. The experimental results indicate that at large T, p approaches a steady-state value. This steady-state value, p_{ss} , can be obtained from Eq. [6]

$$p_{\rm ss} = \frac{[C_4^2 + 8C_1C_2]^{\frac{1}{2}} - C_4}{4C_2}$$
 [8]

where the constant C_4 is

$$C_4 = 1 + C_2 - 2C_1$$
 [9]

An approximation to Eq. [6], which should be valid for small p, is

$$\frac{dp}{dT} = C_1 - (1 + C_2)p$$
 [10]

With the initial condition $p = p_i$ at T = 0, the solution to Eq. [10] is

$$p = C_3 + (p_i - C_3) \exp(-(1 + C_2)T)$$
 [11]

where the constant C_3 is defined by

$$C_3 = \frac{C_1}{1 + C_2}$$
 [12]

Equations [11] and [12] are suitable for determining rates. For zero dragout $(v_d = 0 \text{ and hence } C_2 = 0 \text{ and } C_3 = 3C_1)$, and with no initial Au(III) $(p_1 = 0)$, Eq. [11] can be rearranged to give

$$F_{\rm a} = \frac{7.35Ip}{1 - e^{-T}}$$
[13]

Experiments were conducted under the conditions described above for three anodes: platinum, a 35:60:5

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Ir: Ta: Ba composition, and a 65:30:5 Ir: Ta: Ba composition. The anode current density was varied from 35 to 210 mA/cm². The Au(III) percentage, p, at one-half turnover was substituted into Eq. [13] to determine formation rates. The formation rate was normalized by the anode area, and these results are presented in Fig. 3. The rate varies linearly with current density for platinum between 30 and 250 mA/cm² and for the Ir-Ta-Ba anodes below 75 mA/cm².

To estimate Au(III) accumulation in a production facility, an electrolyte volume of 80 liters, an anode area of 800 cm², and total machine currents of 12 and 20A will be considered. The rate of Au(III) formation, F_{a} , corresponding to these conditions was calculated for various anodes using the data in Fig. 3. These results are presented in Table II.

Equation [6] was solved numerically using the Runga-Kutta-Gill algorithm (9, 10). The results for the platinum and 35% Ir oxide anodes, with a gold concentration of 30 g/liter and 5% dragout per turnover, are presented in Fig. 4. Also shown is the accumulation of Au(III) predicted by the approximate Eq. [11]. The approximate analytical solution agrees with the exact numerical solution up to one-half turnover, which validates the procedure used to determine rates. While the steady-state value predicted from Eq. [11] agrees quite well for low formation rates, characteristic of the iridium oxide anode, the value for large formation rates is a very poor approximation. Therefore, the steady-state value given by Eq. [8] should always be used. Steady state is obtained after about five turnovers. The exponential term in Eq. [11] could be used as an approximation for the time to reach steady state.

The effect of dragout in reducing Au(III) accumulation as calculated by using Eq. [6] is illustrated in Fig. 5. The difference in steady-state values for 5 and 10% dragout per turnover is relatively small. The formation of Au(III) at the anode is balanced chiefly by its reduction at the cathode.

Steady-state values of Au(III) for the platinum, 35% Ir and 65% Ir oxide anodes are presented in Table III. The difference between the 35 and 65%

I (A)	Anode*	F_{a} (g/hr)
12	35:60:5 Ir:Ta:Ba	6.06
20	35:60:5 Ir:Ta:Ba	9.47
12	65:30:5 Ir:Ta:Ba	7.13
20	65:30:5 Ir:Ta:Ba	11.14
12 20	Pt	42.7 67.1

Table II. Au(III) formation rates

* Area, 800 cm².

Table III. Steady-state Au(III) percentages (p_{ss}) and plating current efficiencies (η)*

I (A)	Anode	Dragout (%)	p== (%)	η (%)
20	35% Ir	5.0	6.8	88
20		10.0	6.5	88
12		5.0	7.4	87
12		10.0	7.0	87
12	65% Ir	5.0	8.7	86
12		10.0	8.4	86
20	Pt	5.0	90.1	36
20		10.0	81.1	38
12		5.0	98.5	34
12		10.0	88.5	36

• Steady state achieved after five turnovers. Values of p_{**} calculated using numerical solution to Eq. [6] and F_* values given in Table II. Current efficiencies calculated from Eq. [3].



Fig. 3. Au(III) formation rates for various anodes. (AFHG bath, 30 g/liter Au, pH 7.0, 40°C.)



Fig. 4. Au(III) accumulation predicted from exact numerical solution to Eq. [6] and from approximate analytical solution, Eq. [11]. (Formation rate, $F_{\rm a}$, given in Table II. Electrolyte volume 80 liters, 12A plating current, 30 g/liter Au.)

iridium oxide anodes is relatively minor, compared with the steady-state values for the platinum anode.

Citrate buffer degradation.—Figure 6 shows the percentage of the initial integral buffer capacity as a function of electrolysis time at an anode current density of 100 mA/cm². Under the accelerated conditions of this experiment (see Experimental section) all of the citrate was decomposed after 24 hr with the platinum anode, while no change was apparent with the IrO_2 -Ta₂O₅ anode. Rate constants for the buffer degradation at the platinum anode are presented in Table IV.

For actual plating baths, changes in the citrate concentration and hence in the buffer capacity result from three factors: degradation at the anode, loss by



Fig. 5. Variation of Au(III) accumulation with dragout. (Solid curve, 5% per turnover; dashed curve, 10% per turnover. Electrolyte volume 80 liters, 12A plating current, 30 g/liter Au.)



Fig. 6. Degradation of citrate during electrolysis with 50:50 Ir:Ta oxide anode. (Citrate buffer, pH 4.5, 30°C, 80 ml volume, anode current density 100 mA/cm². The ordinate is the percent of the integral buffer capacity.)

dragout of the plating solution, and addition of citric acid, which is made to maintain pH. A mass balance including these three contributions can be used to

Table IV. Rate of citrate oxidation at Pt anode

* K_a (Eq. [16]) = $k_a(I/A)A = k_aI$.

<i>i</i> (mA/cm ²)	Oxidation rate (mols/hr-cm ²)	ka* (mols/hr-A)
50	0.00023	0.0023
100	0.00048	0.0048
200	0.00142	0.0142

predict the change in citrate concentration with time. It should be noted that the experimentally determined rate constants presented in Table IV characterize only the anodic degradation. Dragout rates vary with the plating system and also need to be determined experimentally. The rate of citric acid addition is related to the cathodic current efficiency as shown below.

The cathodic current efficiency of a citrate-based, cobalt-containing gold plating bath can be as low as 35%, even in the absence of Au(III) (1). The low efficiency in this case is due to simultaneous hydrogen evolution. To estimate the rate of citric acid addition required to maintain pH, it is assumed that the only cathodic processes involved are Au(I) reduction and hydrogen evolution. The Au(III) formation and its reduction will not be considered here. The overall change in hydronium ion concentration is due to three processes: (i) hydrogen evolution, (ii) formation of HCN from CN- liberated from the Au(CN)2complex, and (iii) acid formation accompanying oxygen evolution at the anode. The net change can be related to the current efficiency and system amperage as

$$\Delta H^{+} = j_{3} - j_{1} - j_{2} = \frac{I}{F} [1 - (1 - \eta) - 2\eta] = -\frac{\eta I}{F}$$
[14]

where the subscripts 1, 2, and 3 refer to the above three processes, respectively. To balance this net loss of hydronium ions, citric acid is added. In view of the fact that citric acid has three dissociatable hydrogen atoms, the rate of citric acid addition necessary to maintain pH is given by

$$j = \frac{3600}{3F} \eta I = 0.0124 \eta I \mod/hr$$
 [15]

As already mentioned, the change in total citrate concentration results from addition of citric acid, degradation at the anode, and loss by dragout. The differential mass balance for these three contributions is

$$\frac{\partial C_b V}{\partial t} = 0.0124 \eta I - K_a - v_d C_b \qquad [16]$$

Substituting the dimensionless concentration θ and time T defined as

$$\theta = \frac{C_{\rm b}}{C_{\rm bo}}; \quad T = \frac{t}{\alpha} \quad [17]$$

into Eq. [16] yields

$$\frac{\partial\theta}{\partial T} = \frac{0.0124\alpha\eta I}{C_{\rm bo}V} - \frac{\alpha K_{\rm a}}{C_{\rm bo}V} - \frac{\alpha v_{\rm d}}{V}\theta \qquad [18]$$

By defining α in turnovers of gold as in Eq. [5]

$$\alpha = \frac{C_{\rm au}^* V}{7.35 In}$$
[19]

Eq. [18] becomes

$$\frac{\partial\theta}{\partial T} = K_4 - K_3\theta \qquad [20]$$

The constants in Eq. [20] are

$$K_3 = \frac{C_{\rm au} * v_{\rm d}}{7.35 I_{\rm \eta}}; \quad K_4 = K_1 - K_2$$
 [21a]

where

$$K_1 = \frac{0.0124C_{au}^*}{7.35C_{bo}}; \quad K_2 = \frac{K_a C_{au}^*}{7.35I\eta C_{bo}}$$
 [21b]

The solution to Eq. [20] with the initial condition $\theta(t=0) = 1$ is

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$$\theta = \frac{K_4}{K_3} + \left[1 - \frac{K_4}{K_3}\right] \exp(-K_3 T)$$
 [22a]

From Eq. [1] it can readily be shown that the dimensionless concentration θ is also a dimensionless integral buffer capacity. As the reference concentration C_{bo} is chosen as the initial citrate concentration, θ is the dimensionless capacity relative to the initial value. The integral buffer capacity at a given pH can be obtained by multiplying θ by the initial buffer capacity, which is the product of the normalized capacities given in Table I and the initial buffer concentration

$$C_{\rm H} = \theta C_{\rm bo} \int \frac{\beta}{C_{\rm br}} dp {\rm H}$$
 [22b]

Equation [22] should be useful for the application of the degradation rates given in Table IV to production conditions. For the purpose of illustration, the dragout rate is chosen to maintain a constant salt concentration in the plating bath by balancing the rate of citric acid addition with dragout

$$v_{\rm de}C_{\rm b} = 0.0124 \eta I$$
 [23a]

Combining Eq. [23a] with the expression for K_3 (Eq. [21a]) yields

$$K_3 = 0.0169 \frac{C_{au}}{C_{bo}}$$
 [23b]

It should be noted from a comparison of Eq. [18] and Eq. [20] that K_3 is the dragout ratio per turnover. For a gold content of 30 g/liter and an initial total citrate concentration of 1M, Eq. [23b] yields $K_3 = 0.051$, indicating that a dragout of 5.1% per turnover is required to maintain the citrate concentration constant. At smaller dragout rates, the buildup of salts would eventually cause components to precipitate out.

At current densities lower than 100 mA/cm^2 , the degradation rate is linear with current density (Table IV). When the current is expressed in amperes, we may write

$$K_{\rm a} = 0.0048I$$
 [24]

As an approximation for greater current densities, it is assumed that a second linear region lies between 100 and 200 mA/cm^2 . In this region

$$K_{\rm a} = 0.0094I - 0.00046A$$
 [25]

A gold plating system is now considered with 30 g/liter Au, an initial citrate concentration of 1M, an anodic current density less than 100 mA/cm², and the dragout for maintaining constant citrate concentration equal to 5.1% per turnover. Equations [22] and [24] yield

$$\theta = 1 - \frac{0.39}{\eta} + \frac{0.39}{\eta} e^{-0.051T}$$
 [26]

Integral buffer capacities as a function of time are presented in Fig. 7 for cathodic current efficiencies of 80, 60, and 30%. It is seen that with Pt anode the buffer capacity for efficiencies of 60 and 80% eventually reaches a greatly reduced steady-state value after approximately 60 turnovers. At 30% efficiency, the capacity rapidly drops to zero. The capacity of a plating system using IrO_2 -Ta₂O₅ anodes remains constant, because citrate does not degrade at these electrodes.

Search for stable low polarization anodes.—The RuO_2 -TiO₂ anode has gained wide-spread usage in the chlor-alkali industry (4, 8). In this application, the predominant anode reaction is the evolution of chlorine, and the electrode is very stable. However, when this electrode is used in electrolysis systems where the anode reaction is oxygen evolution (such as in the gold plating), the useful life of the electrode is



Fig. 7. Decrease in integral buffer capacity with time for various cathodic current efficiencies, η . (Initial total citrate concentration 1M, 30 g/liter Au, 5.1% per turnover dragout, anodic current density < 100 mA/cm².)

limited because of the increase in electrical resistivity with use (8).

Two properties of the anode coatings are important. The electrode should have a low potential for oxygen evolution to minimize bath degradation. The coating should also exhibit good electrical conductivity to be useful at high current densities. Many metal oxides have multiple valence states. It is expected that the minimum potential required for oxygen evolution is the equilibrium potential of the lower oxide/higher oxide couple (11). Literature values for this potential as well as the type of conductivity of the oxides are given in Table V. The oxide couples indicated are attainable during anodic polarization. In addition, Ru(IV) is oxidized to Ru(VIII) at 1.39V, and Ir(IV) is oxidized to Ir(VI) at 2.06V (vs. the normal hydrogen electrode). These data indicate that Ir, Os, Ru, Ni, and Co should exhibit lower potentials for oxygen evolution than Pt, Rh, or Pd. Osmium was excluded from study because of the very low (130°C) boiling point of OsO4. Nickel and cobalt oxides were not investigated because of their poor conductivity (11).

Binary oxides.—The four platinum group metal oxides chosen as being representative of active oxides were those of Ir, Ru, Rh, and Pt. Oxides of five valve metals, Ti, Ta, Nb, Hf, and Zr were selected as binders.

Figure 8 shows representative current-time behavior observed with various binary oxide systems. Initial current densities were adjusted to 200 mA/

Table V. Redox potentials and conductivity types of metal oxide couples

Oxide couple	E vs. NHE (V) •	Conductivity type
Ir ₂ O ₃ /IrO ₂	0.93	Metallic**
Ru ₂ O ₃ /RuO ₂	0.94	Metallic**
050%/0504	1.00	Metallic**
Ni ₂ O ₃ /NiO ₂	1.43	Semiconductor*
	1.45	Semiconductor*
Rh ₂ O ₃ /RhO ₂	1.73	Semiconductor**
PtO ₂ /PtO ₃	2.00	Semiconductor**
PdO ₂ /PdO ₃	2.03	Semiconductor**

* Ref. (11). ** Ref. (12).



Fig. 8. Stability of iridium oxide-valve metal oxide anodes. (50 m/o 1rO₂, citrate buffer, pH 4.5, 30°C.)

 cm^2 for anodes containing Ir and Rh and 150 mA/ cm^2 for those containing Ru and Pt. In the constant cell voltage experiments, anode degradation is indicated by a decrease in current density. Relative electrode stabilities for twenty different binary systems are given in Table VI. Iridium oxide was found to be the most stable active oxide for this application. In addition, the active metal oxide-binder metal oxide combination is extremely important. The Ir-Ta oxide system has the greatest stability under the conditions used. It should be noted that this system is also known to be highly stable in sulfuric acid (13).

For the Ir-Ta system, four factors have been found to have major effects on electrode stability: coating thickness, current density, composition of the coating, and free cyanide in the plating bath. Tests were conducted at the initial current density of 100 mA/cm^2 in the citrate buffer with the 50:50 Ir:Ta composition. Electrode life was defined as the time at which the current density drops to one-half of its initial value. The energy dispersive x-ray spectrometer (EDAX) attachment to the scanning electron microscope was used to characterize film thickness. The intensity of the detected signal is proportional to the amount of iridium present in the volume of the coating per unit area. The ratio of the major Ir peak to the major Ti substrate peak was selected as a measure of the coating thickness for the same coating

Table VI. Stability of binary metal oxide anodes*

Active oxide	Binder oxide	$i (t=0) (mA/cm^2)$	i (t = 50 hr) (mA/cm2)
I =0		200	200
$1rO_2$	1 a205	200	134
	HfO	200	62
	ZrO ₂	200	54
	TiO ₂	200	46
BbO.	TaoOr	200	147
101102	Nb ₂ O ₅	200	58
	HfO ₂	200	42
	ZrO ₂	200	30
	TiO2	200	30
BuOa	HfO ₂	150	82
	TiO ₂	150	46
	Ta ₂ O ₅	150	46
	Nb ₂ O ₅	150	10
	ZrO ₂	150	10
PtO ₂	Nb ₂ O ₅	150	20
	HfO ₂	150	13
	Ta2O5	150	11
	TiO ₂	150	4
	ZrO ₃	150	4

* Citrate buffer (30°C, pH 4.5), 2 μm thick films, 50:50 molar ratio of active oxide to binder oxide.



Fig. 9. Electrode life as a function of coating thickness. (50:50 Ir:Ta, citrate buffer, pH 4.5, 65°C, 100 mA/cm².) (EDAX ratio is the ratio of major Ir peak to major Ti peak, normalized by the value giving 100 hr of electrode life.)

composition, and it is plotted against the electrode life in Fig. 9, in which the initial peak ratio of 3 corresponds to 1 μ m in thickness as calculated from the amount of the coating material applied and bulk densities of the oxides. At least for thin films, electrode life is directly proportional to film thickness.

A critical current density has been observed for ruthenium-based anodes (14). At electrode potentials above the potential corresponding to this critical current, RuO_2 is oxidized to higher valence species. A similar critical current density was found to exist for IrO_2 . Figure 10 shows that above approximately 300 mA/cm², the Ir-Ta system is unstable. Below the critical value, electrode life is not strongly dependent on current density.

Electrode life depends greatly on the Ir: Ta ratio in the oxide mixture. Life tests were performed in the citrate buffer at 65° C and in the phosphate buffer



Fig. 10. Stability of Ir-Ta binary oxide anodes as a function of initial current density. (50:50 Ir:Ta, citrate buffer, pH 4.5, 65°C.)

at 40°C, and the results are shown in Table VII. The initial current density was 200 mA/cm². In the phosphate buffer a 70 mol percent (m/o) Ir composition gave the longest life, while in the citrate buffer a 40 m/o Ir composition was most durable. The amount of iridium in the coatings was normalized by dividing the major Ir peak by the major Ti substrate peak. A second normalization, which was made to allow comparison of electrode service life independent of coating thickness, was to divide the Ir/Ta ratio by the ratio for the composition giving the longest service life.

Free cyanide is liberated from the cyanoaurate(I) complex at the cathode during gold plating. This cyanide escapes relatively rapidly from the bath as HCN at pH 4.5, but can accumulate significantly at pH 7.0, especially in high speed plating conditions. Experience with a phosphate-buffered bath indicates that the concentration can build to about 0.2 g/liter CN⁻. To observe the effect of free cyanide, tests were performed in the phosphate buffer with a concentration of 0.5 g/liter. These results are also presented in Table VII. It is seen that the electrode stability is greatly reduced. Ternary metal oxide systems were subsequently investigated in order to overcome this problem.

Ternary oxide systems.—To determine which ternary systems would be more resistant to free cyanide than the binary Ir-Ta system, a mol ratio of 60:40 Ir: Ta, which had the minimum stability in Table VII, was used. With a 10% additive level, this yields a 54:36:10 Ir: Ta: additive composition. As IrO_2 is the dominant active component of the film, it is necessary to find an additive which stabilizes the IrO_2 phase of the oxide mixture. A preferred class of additives would be those which form mixed metal oxides with iridium. Alkaline earth and rare earth metals (group IIa and group IIIb) are known to form iridates (7). A second class of additives would be those which form solid solutions of oxides, of which the IrO_2 -SnO₂ system is an example. A third criterion used was the solubility product of the metals with OH- anions (less soluble oxides would be more stable). Metals in groups VIb, VIIb, IIb, IIIb, and IVa, tend to form insoluble oxides.

Life tests were performed in the pH 7 phosphate buffer containing 0.5 g/liter CN- at 40°C with an initial current of 150 mA/cm². Addition of oxides of other group VIII metals, Ru, Co, Ni, Rh, Pd, and Pt, gave shorter electrode lives. Furthermore, effects of

Table VII. Stability of Ir-Ta oxide anodes

Mol % Ir	Bath	Ir*/Ti (EDAX ratios)	Ir**/Ti (EDAX ratios)	Life (hr)	Life*** (hr)
40	Phosphate(a)	1.34	1.08	515	477
50		1.57	1.26	350	223
60		2.35	1.88	460	245
70		1.25	1.00	725	725
40	Citrate(b)	0.11	1.00	425	425
50		0.08	1.38	262	190
60		0.12	0.92	33	36
70		0.07	1.57	29	19
40	Phosphate(c)	0.60	0.94	40	43
50		0.44	0.69	22	32
60		0.82	1.28	65	51
70		0.64	1.00	106	106
80		0.83	1.30	70	54
85		0.62	0.97	26	27
90		0.34	0.53	75	144

Normalization for Ir content using ratio of major EDAX

peaks, Ir to Ti (substrate). ** Ir/Ta ratio relative to ratio giving longest service life. *** Normalized life obtained by dividing actual life by Ir**/Ta

ratio. (a) pH 7.0, no CN-, 40°C. (b) pH 4.5, no CN-, 65°C. (c) pH 7.0, 0.5 g/liter CN-, 40°C.

the addition of Mg, Ca, Sr, Ba, Li, K, Cs, Cr, Mn, Fe, Cd, Ga, In, Tl, Ge, Sn, Bi, Sc, Y, La, and Ce were investigated. After 20 hr, only electrodes containing Ba, Ca, Cr, Sc, or Sn had current densities at least equal to the initial value of 150 mA/cm². Of these, chromium and tin were found to have a detrimental catalytic effect; the electrode potential was higher in the presence of these elements than in their absence. It was concluded that the preferred additive for the Ir-Ta system is barium. Life tests indicated that 5-20 m/o compositions of barium are useful under high speed gold plating conditions. With an approximate loading of 0.1 mg/cm² of iridium, an electrode life of 275 hr was obtained at 100 mA/cm² for a composition of 50:40:10 Ir:Ta:Ba as compared to 30 hr in the absence of barium.

Use of a conversion temperature (see Experimental section) of 450°C was found to be critical for good electrode stability, as shown in Table VIII. Samples were prepared for x-ray powder diffraction measurements by converting metal chlorides to oxides on a quartz substrate. Conversion temperatures of 450° and 350°C were used, followed by final baking at 450°C for 1 hr. Table IX presents results for the conversion temperature of 450° C and the compositions of 50:50 Ir:Ba and 50:40:10 Ir:Ta:Ba. The majority of d-spacings for the Ir-Ba samples are not found in the JCPDS listings for the distinct oxides IrO_2 or BaO, indicating that a new compound is formed, presumably $BaIrO_3$. The 50:40:10 Ir:Ta:Ba sample yielded d-spacings corresponding to IrO_2 and the tentatively identified barium iridate. When the conversion temperature of 350°C was used, no BaIrO3 was observed. Distinct BaO was present in oxides containing 50:20:30 Ir:Ta:Ba as indicated by d-spacings at 3.11 and 2.77Å. The amount of BaO

Table VIII. Effect of conversion temperature on electrode stability in cyanide-containing phosphate buffer

(50 m/o Ir, 10 coats, final bake for 1 hr at 450°C, initial current 150 mA/cm², 0.5 g/liter CN-, pH 7.0, 40°C.)

Mol %		Commenter to a second		
Та	Ва	(°C)	i (t = 50 hr) (mA/cm ²)	
50	0	350	55	
40	10	350	39	
50	0	450	85	
40	10	450	124	

Table IX. X-ray powder diffraction data

(Sweep rate, 1 deg/min; time constant, 40; 45 kV; 14 mA; copper Ka radiation.)

Ir 50	:Ba):50	Ir:Ta:Ba 50:40:10		IrO₂•	BaO•
d (A)	I/I 1	d (A)	I/I1	d (A)	d (A)
5.53 4.17 3.91	68 39 37	5.57 4.21 4.02	14 16 12	<u></u>	
3.39 3.20 3.05 2.85	19 100 90 42	3.20 3.06 2.86	74 38 26	3.18	3.20 3.11 2.77••
2.59 2.49 2.41 2.35	79 57 55 73	2.60 2.50 2.41 2.35	100 24 19 18	2.58	2.59
2.25 81 2.00 21 1.98 25	81 21 25	2.28	22	2.25	2.23 2.12 1.96** 1.81
		1.71 1.59	29 14	1.70 1.59	1.68 1.55 1.50
		1.42	16	1.42 1.35 1.29	1.40 1.33 1.24

* d-spacings for IrO₂ and BaO taken from JCPDS files 15-870 and 26-176A (or 22-1056 as indicated by **), respectively.

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Conclusions

Two types of plating bath degradation occur at significant rates on conventional platinum or platinized titanium anodes in high speed gold plating processes. The oxidation of Au(I) to Au(III) can lead to a rapid decrease in plating current efficiency. In the AFHG bath the initial value of 100% can decay to 33% after only six turnovers. In citrate-buffered baths, the oxidation of citrate ions results in a loss of buffer capacity and subsequently a loss of control of the interfacial pH at the cathode. The theoretical analysis presented indicates that the most important parameter influencing the integral buffer capacity is the cathodic current efficiency, because, in the citrate system, the cathodic hydrogen evolution is the major cause of plating inefficiency. When additives such as cobalt are used as hardening agents, the cathodic current efficiency can be as low as 35% because of preferential hydrogen evolution. With such a low cathodic efficiency, loss of control of the interfacial pH can occur very rapidly.

The rates of oxidation of both Au(I) and citrate ions are much smaller at DSA-type low polarization anodes. For the additive-free hard gold bath the steady-state percentage of Au(III) occurring in a process using these anodes is 8% with a cathodic current efficiency of 85%. At these anodes the rate of citrate degradation is essentially zero, and citratebased baths are stable at all current efficiencies.

A low polarization anode with RuO_2 as the active oxide is unstable for high speed gold plating applications. Anodes containing IrO2 have a much longer service life. In particular, the three-component system Ir-Ta-Ba has a superior service life. Based on x-ray diffraction studies, the effect of Ba addition is attributed to the formation of a compound between BaO and IrO₂, presumably BaIrO₃.

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LIST OF SYMBOLS

 $\stackrel{A}{C_{\mathrm{au}}}$

anode area, cm² gold (I) concentration in mols/liter

- Cb, Cbo citrate concentration, mols/liter. The subscript o refers to the initial concentration reference buffer concentration for integral
- $C_{\rm br}$ buffer capacity definition, 1M citrate
 - integral buffer capacity, mols H+/liter Faraday constant, 96,500 C/mol-equiv. Au(III) formation rate, g/hr
- $C_{\rm H} F$
- \overline{F}_{a}
- fa Au(III) formation rate per unit anode area, g/hr-cm² total plating current, A
- I
- j Ka flux to electrode surface
 - rate of citrate degradation, mols/hr
- k_{a} rate of citrate degradation per unit anode area, mols/hr-cm²
- М atomic weight of gold (= 197)
- \boldsymbol{m}

GOLD PLATING

- multiplier to v_{de} fraction of total gold as Au (III) $p \\ T$
- dimensionless time; t/α dragout rate, liters/hr
- v_{d}
- dragout rate to balance citric acid addition $v_{
 m de} V$
- volume of plating solution, liters
- reference time, hr/turnover α, α_0
- buffer value, mols H+/liter ß
- cathode current efficiency for Au(I) plating η dimensionless buffer concentration, C_b/C_{bo} . Also dimensionless integral buffer capacity

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