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Cyanoaurate(III) Formation and Its Effect on Current Efficiency in Gold Plating

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ABSTRACT

The cyanoaurate (III) ion has been found to form and accumulate in acidic or neutral gold plating baths containing cyanoaurate(I) as the source of gold. This trivalent gold species brings about a decrease in plating current efficiency because its reduction to gold metal requires three faradays per mole, whereas only one faraday is consumed to reduce one mole of Au(I). The accumulation of Au(III) should therefore be minimized to produce gold deposits with a thickness unaffected by bath age. This paper describes various methods for achieving this objective, which include the use of the so-called "dimensionally stable anode" and a techniqe of chemically reducing Au(III) to Au(I).

Thickness control in gold plating has become increasingly important in recent years because of the necessity for saving gold by plating only a minimal thickness required for specific applications. Since deposit thickness is directly proportional to plating current efficiency, it is important to have knowledge of factors affecting the latter. It is recognized that the current efficiency of both soft and hard gold plating from acidic or neutral cyanoaurate(I) baths tends to decrease with increasing extent of bath use, and generally extrinsic contaminants are believed to be responsible for the efficiency deterioration.

During the course of our recent work to develop a polarographic method for analyzing gold plating solutions (1), significant amounts of cyanoaurate(III) ions, $Au(CN)_4^-$, were found in extensively used production baths. It has been established that this species is produced as a result of a reaction at the anode, generally platinum or platinized titanium, and that it is, at least partly, responsible for the decrease in plating current efficiency because of the greater quantity of electricity required to reduce Au(III) than Au(I).

In the present work, the relationship between current efficiency, Au(III) content, and bath age has been

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studied, and methods for minimizing the formation and accumulation of Au(III) have been investigated.

Experimental

Plating Solutions

Results obtained with two different types of plating solutions are described in this paper: a conventional cobalt-containing hard gold bath (denoted as CoHG) and a high speed, additive-free hard gold bath (AFHG) (2). Make-up compositions and optimum operating conditions of these baths are listed in Table I. During the bath aging experiments, the plating solutions were analyzed for total gold and Au(III) and for Co²⁺ using, respectively, the polarographic and colorimetric methods described previously (1), and the total gold and cobalt concentrations were maintained within approximately $\pm 10\%$ by periodic addition of appropriate salts. The pH was kept constant within ± 0.1 unit by adding citric phosphoric acids for CoHG and AFHG baths, respectively.

Apparatus

CoHG .- A jacketed glass plating cell containing 300 ml of the CoHG plating solution was used. A rigid flat anode (platinum unless noted otherwise) measuring 3.8 imes 3.8 cm was placed vertically at the center of the cell, and two copper sheets with the same dimensions plated

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Ion	Form of salt added	CoHG	AFHG
Au(CN)2-	KAu(CN)2	8.2 g/liter	30 g/liter
Co ²⁺	CoSO ₄	100 ppm as Co	
Citrate	$K_{3}C_{6}H_{5}O_{7} \cdot H_{2}O$ and $C_{6}H_{9}O_{7} \cdot H_{2}O$	0.52M	
Phosphate	KH ₂ PO ₄ and KOH	_	1.23M
	Condition		
pH Temp. Current Agitation		4.0 32°C 10 mA/cm² Mild	7.0 40°C 250 mA/cm² Vigorous

with strike gold were immersed on both sides of the anode with cathode-to-anode separation of about 3.2 cm. The solution temperature was maintained at 32°C by circulating constant-temperature water. Mild agitation was provided with a magnetic stirrer.

AFHG.—A rotating cylinder electrode system with a stationary, concentric cylindrical anode (Fig. 1) was used to plate AFHG at high speed. The substrate was a sheet of copper, 2.1 imes 6.5 imes 0.005 cm, coated with a thin flash of gold strike. It tightly wrapped the stainless steel portion of the rotating cathode as illustrated in Fig. 1. The ends of the substrate were folded into the vertical narrow groove, and a small Teflon key made to fit snugly into the groove was inserted to hold the substrate securely in place. The rotating cathode was fabricated by first attaching a short piece of stainless steel rod (1 cm in radius and 2.1 cm in height) to a rotating disk electrode core purchased from Pine Instruments Company, Grove City, Pennsylvania (Cat. No. DT-101-AA), followed by potting in epoxy resin and machining. This cathode design allowed quick, easy installation and removal of the substrate. The cylindrical anode had an inner radius of 1.46 cm, and was placed on a Teflon support in a glass plating cell. The volume of the plating solution was 1 liter. The solution temperature was maintained at 40°C by circulating it with a pump through an external heat exchanger.



Fig. 1. Rotating cylinder electrode with demountable film substrate.

The cathode was rotated at 3600 rpm, which was well above the critical speed (822 ppm)¹ necessary to obtain turbulent flow. This high rotation speed was necessary to obtain hard, bright deposits at the plating rate (typically a minimum of 2.54 μ m in 16 sec) required for practical high speed plating, for example, in continuous strip plating of electrical connector terminals.

Experimental Results

Current Efficiency, Bath Age, and Au(III) Content

CoHG .--- Many actual production baths, including both citrate-based and organophosphonate-based baths, were analyzed for Au(III) and found to contain up to 25% of total gold in the form of Au(III). In the laboratory aging experiment carried out at 300 mA (~10 mA/cm² at both anode and cathode) with the apparatus described in the preceding section, the rate of accumulation of Au(III) was quite slow; for example, after ten bath turnovers² the Au(III) content was only about 5% of the total gold. In order to facilitate the study of the effect of Au (III) content on plating current efficiency, it was necessary to age the bath under accelerated conditions. It was found that Au(III) accumulates much more rapidly if plating is performed with a high initial gold concentration without cobalt present and the solution is subsequently heated (see Discussion section). Thus, a citrate buffer containing KAu(CN)₂ only (20.5 g/liter as Au) was first electrolyzed continuously at 32°C and 300 mA for 3 hr, and then the solution was heated at 60°C for 1 hr. The analysis of the resulting solution showed that the total gold concentration decreased to 8 g/liter, and that the Au(III) content amounted to 24% of the total gold. CoHG baths containing different amounts of Au(III) were prepared by diluting the above solution with the citrate buffer and adjusting the concentrations of total gold and cobalt to 8.2 g/liter and 100 ppm by adding $KAu(CN)_2$ and $CoSO_4$, respectively. Plating current efficiencies of these baths were measured at the cathode current density of 10 mA/cm² at $32^{\circ}C$ with mild agitation. The results are shown in Table II. A significant decrease in plating current efficiency is seen with increasing Au(III) content. The "calculated efficiency" was obtained by multiplying the initial current efficiency observed in the absence of Au(III) by the theoretical fraction of initial current efficiency, which was calculated by taking account of the difference in number of electrons involved in reducing Au(I) and Au(III)

Fraction of initial current efficiency

=

$$= \frac{[Au(I)] + [Au(III)]}{[Au(I)] + 3[Au(III)]} = \frac{1}{1 + 2x}$$
[1]

where x is the Au (III) content of the bath expressed by

$$x = \frac{[\operatorname{Au}(\operatorname{III})]}{[\operatorname{Au}(\operatorname{I})] + [\operatorname{Au}(\operatorname{III})]}$$
[2]

¹For this electrode system the critical Reynolds number at which the transition from laminar to turbulent flow occurs is given by (3) Re(crit.) = $(r_0 - r_1)r_1\omega\nu^{-1} = 3960$, where r_0 is the inner radius of the anode, r_1 the radius of the rotating cylinder electrode, ω the angular rotation speed, and ν the kinematic viscosity. With $r_0 = 1.46$ cm, $r_1 = 1.00$ cm, $\nu = 10^{-2}$ cm² · sec⁻¹, the above Re(crit.) value can be achieved when $\omega = 86.1$ rad/sec = 822 rom. 822 rpm

² A bath turnover is defined as completed when the amount of gold initially present has been plated out and this amount of gold replenished.

Table II. Effect of Au(III) on plating current efficiency of CoHG bath (10 mA/cm², 32°C)

Au (TTT) //actal Au	Current efficiency, %		
Au (111)/total Au, %	Observed	Calculated	
0	40.0	(40.0)	
10.7 24 0	34.5 32.1 20 8	35.7 32.9	

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The good agreement between the observed and calculated efficiencies implies that the decrease in current efficiency brought about by Au(III) can indeed be accounted for by the greater number of electrons required to reduce Au(III) than Au(I).

AFHG.—In the high speed AFHG system the Au (III) buildup and accompanying current efficiency deterioration occurs more rapidly as the bath is aged. Results obtained with the platinum anode are represented by curves 1 and 1 in Fig. 2, in which changes in current efficiency and Au (III) content are plotted against the total weight of gold plated out from 1 liter of the plating solution and the number of bath turnovers. The cathodic current density used in this experiment was in the range of 230-300 mA/cm², while the corresponding current density at the platinum anode was 150-200 mA/cm². It is seen that the initial efficiency of greater than 90% decreased to only about 50% after four bath turnovers, during which the Au (III) content of the bath increased to almost 25%.³

From the results obtained with both CoHG and AFHG baths, it is clear that if plating current efficiency is desired to be maintained on the level of 90% of the initial efficiency, Au(III) content should not be allowed to exceed about 5% of total gold. In the case of CoHG this Au(III) level was reached after about 10 bath turnovers, whereas for AFHG it took only two-thirds of a turnover. Although the rate of Au(III) accumulation is likely to be controllable to some extent, for example, by increasing the anode area to decrease the anodic current density, it is clearly desirable to establish a method to compensate for the Au(III) effect, or to minimize or eliminate the formation and accumulation of Au(III).

Methods of Controlling Deposit Thickness

Adjustment of plating parameters.—The most obvious method of maintaining the deposit thickness con-

³ Theoretically, the minimum efficiency achievable should correspond to 33.3% of the initial efficiency, which should occur when all Au(I) is converted into Au(III), *i.e.*, when x = 1 in Eq. [1].



Fig. 2. Variation of plating efficiency and Au(III) content with bath age (AFHG bath). (Curves 1, 1': Pt anode; curves 2, 2': RuO_2/TiO_2 anode; curves 3, 3': Au anode.)

stant with changing current efficiency is to adjust either the plating current or the plating time. A general relationship between current efficiency and Au (III) content can be calculated as already explained for CoHG (Table II). Figure 3 shows this relationship, where the ordinate is the fraction of initial current efficiency, or the ratio of current efficiency at a given Au (III) content to that in its absence. The curve was calculated from Eq. [1], and the points are experimental. The agreement is considered to be fair. This relationship is valid for both CoHG and AFHG baths (and for any other gold plating baths), and can be used for adjusting plating current or time based on the results of total gold and Au (III) analyses.

This approach is simple but suffers from certain limitations. For example, the current adjustment method results in a continuous increase in current density at the anode, which in turn is expected to accelerate the accumulation of Au(III) and hence the plating efficiency deterioration. The method relying on the adjustment of plating time is applicable to batch plating, but not to continuous strip plating in which the substrate travels at a fixed speed.

Use of other anodes.—It was found that the Au(III) accumulation and accompanying current efficiency deterioration can be decreased significantly by replacing the platinum anode with an anode of the type often called "dimensionally stable anode" (DSA®), which is now widely used for chlorine production (4). This electrode, which is made typically by coating a titanium metal base with a mixture of RuO₂ and TiO₂, has anodic overvoltages considerably lower than platinum does for the evolution of chlorine (4) as well as oxygen (5). The initial study was carried out with CoHG bath using a RuO₂/TiO₂ anode obtained from Magneto-Chemie B.V., Schiedam, The Netherlands. During eleven bath turnovers, no detectable amount (<0.2%) of Au(III) was found, whereas with paltinum 5.4% of Au(III) was found at the conclusion of the experiment performed under identical conditions. It was noted in these experiments that the yellow discoloration usually observed with CoHG baths operated with platinum anodes was much less intense for the solution aged with the RuO_2/TiO_2 anode. This appears to indicate that citrate ions are more stable at this anode.

The anode used with high speed AFHG bath was prepared using the procedure described by Janssen et al. (6). The results of the aging experiment carried out with this anode in AFHG bath are compared in Fig. 2 (curves 2 and 2') with those obtained with other anodes. The Au(III) concentration never exceeded



Fig. 3. Relationship between fraction of initial current efficiency and Au(III) content. (Points are experimental, line is calculated.)

 $\sim 5\%$ of total gold, and the efficiency remained greater than 89% (as compared to the initial efficiency of 93%) over the period of four bath turnovers. It is recognized that "dimensionally stable anodes" have a limited life as does platinized titanium depending on electrolysis conditions, coating composition, and the method of preparation. Results of our investigation concerning the life of anodes under the conditions of gold plating will be described elsewhere (7).

It was found that a gold anode also brings about the same beneficial effect. The level of Au(III) accumulation was even lower than that observed with the RuO₂/TiO₂ anode, and the current efficiency remained essentially unchanged at the initial level (curves 3 and 3', Fig. 2). The reason why the gold anode works is that gold dissolves preferentially over the oxidation of Au(I) to Au(III). Under the conditions of high speed plating, the concentration of free cyanide becomes quite high because of its rapid formation at the cathode. It was actually found that the gold anode loses its weight quite rapidly. Under our experimental conditions the rate of anode dissolution was such that a 0.38 mm (0.015 in.) thick anode would not last more than 100 hr of continuous plating. For this reason, a gold anode is not likely to be practical.

Chemical reduction.—Many common reducing agents are capable of reducing cyanoaurate(III) to cyanoaurate(I), but for the present application it is important to choose one which does not leave undesirable reaction products after treatment. Hydrazine was selected here for this reason (see Discussion section).

A CoHG bath, 100 ml, containing 20% of total gold in the form of Au(III) was treated with 0.25 ml of 85% hydrazine hydrate (N₂H₄ · H₂O) at 75°C for 4 hr. Then, additional 0.25 ml of hydrazine was added, and heating was continued for 4 more hours. This treatment reduced about 90% of the Au(III) to Au(I). The initial current efficiency of this bath was 29%, which improved to 40% upon hydrazine treatment. No apparent difference was noted on the deposits from the hydrazine-treated bath and from the fresh bath. The addition of large excess hydrazine, e.g., 2 ml, greatly accelerated the reaction; however, the plating done after this treatment yielded discolored deposits.

The AFHG bath aged with platinum anode was also treated with hydrazine and the aging experiment continued. The hydrazine treatment-plating cycle was repeated several times under various treatment conditions. An optimum set of conditions found was to add about an equimolar amount of hydrazine hydrate and heat the bath at $75^{\circ}-80^{\circ}$ C for 1-3 hr depending on Au (III) content of the bath. When the Au (III) content was high (>15%), it was necessary to repeat the treatment in order to bring it down to <2%. The decrease in Au (III) concentration upon hydrazine treatment and the accompanying recovery of current efficiency are illustrated in Fig. 4.

Active carbon treatment.—Carbon treatment is conventionally carried out for removing organic contaminants. It was found that this treatment also removes Au(III) effectively. Active carbon (Darco Red Label), 0.25g, was added in 10 ml of a CoHG bath containing 14% of total gold in the form of Au(III), and the mixture heated at 90°C for 30 min. This treatment removed approximately 80% of the Au(III). However, about 29% of Au(I) was also lost. The loss of gold by carbon treatment is generally known, and for this reason this purification procedure should preferably be avoided. It is also known that carbon treatment does bring about a recovery of plating current efficiency. The experimental result described above shows that it is, at least partly, due to the removal of Au(III).

Discussion

Mechanism of Au(III) formation.—No detailed study has been carried out to establish the mechanism of the



Fig. 4. Recovery of plating current efficiency and Au(III) content upon hydrazine treatment of aged AFHG bath.

formation of $Au(CN)_4^-$. However, the following experimental observations should be noted: (i) A laboratory-aged CoHG bath was analyzed for $Au(CN)_4^-$ by the polarographic method immediately after termination of electrolysis for 3 hr at 32°C and after heating in boiling water for 1 hr. The height of the Au(III) wave found after heating was nearly twice that observed before heating. (This post-heating effect was used for the accelerated aging described in the Experimental section.) It was also noted that the wave height increased significantly when a freshly electrolyzed CoHG bath was allowed to stand overnight at room temperature. (ii) Electrolysis of a fresh CoHG bath was carried out in an H-type cell in which cathode and anode compartments are separated by a sintered glass disk. A platinum sheet was used as the anode, while the cathode was a copper sheet. After electrolysis, the solution in each compartment was analyzed polarographically. Only the solution in the anode compartment showed the presence of Au(III). These two experimental results indicate that $Au(CN)_4$ forms as a result of a slow homogeneous chemical reaction involving an intermediate species produced at the anode. The identity of this intermediate has not been established.

Effect of anode material.—In order to obtain some insight into the mechanism of the effect of anode material on Au (III) formation, polarization measurements were made at 32° C for CoHG bath as well as for the citrate buffer without gold and cobalt present. Results obtained with platinum and RuO₂/TiO₂ anodes are compared in Fig. 5. In both solutions potentials were higher in the plating solution than in the buffer. It is also seen that the potential ranges for the RuO₂/TiO₂ anode are about 0.5V lower than those for platinum in both solutions over the entire current range investigated. Quali-



Fig. 5. Polarization curves for Pt and RuO_2/TiO_2 anodes in CoHG bath and in pH 4 citrate buffer at 32°C.

tatively, these results are expected from the known polarization behavior in strongly acidic solutions (8, 9). Because of the lack of identity of the reaction intermediate, no mechanistic interpretation can be offered for the observed anode effect on Au(III) formation. However, it is of interest to compare the potential ranges for the two electrodes with the equilibrium potential of the Au(III)/Au(I) couple

Au(CN)₄⁻ + 2e⁻ = Au(CN)₂⁻ + 2CN⁻;
$$E_{1^{\circ}} = +0.90V$$
 [3]

Since the standard potential $E_{1^{\circ}}$ was not found in the literature, it was calculated from the following values

$$Au(CN)_2^- + e^- = Au + 2CN^-;$$

A

$$E_{2}^{\circ} = -0.60 V (10)$$
 [4]

$$Au^{3+} + 3e^- = Au; \quad E_{3^\circ} = +1.50V (10)$$
 [5]

$$Au^{3+} + 4CN^{-} = Au(CN)_{4}^{-}; K = 10^{56} (11)$$
 [6]

Furthermore, using $K = 1.62 \times 10^9$ (12) for the stability constant of HCN, the equilibrium potential for a typical plating solution with pH = 4 containing 0.04M $Au(CN)_2^-$, 0.0004M $Au(CN)_4^-$ [1% of Au(I)], and 0.01M free cyanide (a typical concentration of HCN plus CN⁻) was calculated from E_1° to be equal to +1.26V (or +1.02V vs. SCE). An increase in the ratio of Au(III) to Au(I) by a factor of 10 (to 10%) shifts the potential by 0.03V in the positive direction. Comparison of these equilibrium potentials with the polarization curves in Fig. 5 shows that the oxidation of $Au(CN)_2^-$ to $Au(CN)_4^-$ is possible at both platinum and RuO_2/TiO_2 at practical current densities (>10⁻² A/cm²). The faster accumulation of Au(III) observed with the platinum anode may be anticipated from the higher potential at this anode. A further discussion of this subject will be given in a subsequent paper dealing with the behavior of various other anode materials (7).

The oxygen evolution at ruthenium metal was found to take place at potentials which are lower by additional 0.1-0.2V than at the $\text{RuO}_2/\text{TiO}_2$ anode. An experiment with a ruthenium-plated platinum electrode showed, however, that ruthenium metal dissolves significantly at current densities greater than ~30 mA/ cm².

Reaction with hydrazine.—The reaction between hydrazine and Au(III) accompanies the evolution of colorless gas. From this fact and a comparison of E° values for the Au(CN)₄^{-/Au(CN)₂⁻ couple (reaction [3]) and various half-reactions of hydrazine (10), the}

overall reaction is likely to be either or both of the following two reactions

$$2Au(CN)_4^- + N_2H_5^+ = 2Au(CN)_2^-$$

$$+ N_2 \uparrow + 4HCN + H^+$$
 [7]

$$3Au(CN)_4^- + N_2H_5^+ + H_2O$$

$$=3Au(CN)_{2}^{-} + N_{2}O \uparrow + 6HCN + H^{+}$$
 [8]

where $N_2H_5^+$ is the protonated form of hydrazine which is predominant in the pH range under consideration $[N_2H_5^+ = N_2H_4 + H^+, K = 1.02 \times 10^{-8} (10)]$. By using relevant thermodynamic data (10), the ΔG° values for reactions [7] and [8] have been calculated to be -154 and -138 kcal, respectively. The very large values reflect the combined effect of the strong oxidizing power of Au(CN)₄⁻ and the large numbers of electrons involved in these reactions (4 for [7] and 6 for [8]).

In order to obtain insight into the mechanism of these reactions, a kinetic study was carried out by following the disappearance of Au(III) after the addition of large excess hydrazine. The conventional firstorder plot shown in Fig. 6 was obtained at 40°, 50°, and 60°C with an AFHG bath containing a total gold concentration of 30.5 g/liter (0.155M) and an initial Au(III) content of 13.9% (0.0215M). Concentrated hydrazine (85% N_2H_4 H_2O) was added to make the initial concentration equal to 0.215M. It is seen that the linear relationship holds only after about 7 min. A similar set of curves was obtained at 60°C with three different hydrazine concentrations as shown in Fig. 7. The slopes of these curves are approximately proportional to hydrazine concentration. Higher order analyses did not yield consistent results at different temperatures and hydrazine concentrations. Thus, the initial deviation from linearity appears to indicate the presence of some mechanistic complications which become less significant with increasing reaction time. For the linear range, the above results lead to the conclusion that the overall reaction consists of multiple steps including a rate-determining step which is first order with respect to both



Fig. 6. Semi-logarithmic plot of Au(III) concentration against time after addition of excess hydrazine at different temperatures. (AFHG bath; total Au, 0.155M; initial Au(III), 0.0215M; hydrazine, 0.215M).



Fig. 7. Semi-logarithmic plot of Au(III) concentration against time after addition of different amounts of hydrazine at 60°C. (Same bath as for Fig. 6.)

Au(III) and hydrazine. It is likely then that hydroxylamine is formed as an intermediate

$$Au(CN)_{4}^{-} + N_{2}H_{5}^{+} + H^{+} + 2H_{2}O \rightarrow Au(CN)_{2}^{-} + 2NH_{3}OH^{+} + 2HCN \quad [9]$$

This reaction is followed by

$$Au(CN)_{4}^{-} + 2NH_{3}OH^{+} \xrightarrow{\kappa_{2}} Au(CN)_{2}^{-} + N_{2} + 2HCN + 2H_{2}O + 2H^{+}$$
[10]

and/or

$$2Au(CN)_4^- + 2NH_3OH^+ \rightarrow 2Au(CN)_2^- + N_2O + 4HCN + H_2O + 2H^+$$
 [11]

This type of reaction sequence is known to be encountered fairly often [e.g., "consecutive, competitive second-order reaction" (13)], and it can be shown readily that under the conditions of constant [H+] (buffer), constant $[N_2H_5^+]$ (large excess), and $k_1 \ll$ k_2 and/or k_3 , the reaction becomes first order with respect to $[Au(CN)_4^-]$. The last condition has been verified experimentally; namely, the disappearance rate of Au(III) observed with hydroxylamine (added as hydrochloride) as the reducing agent was at least an order of magnitude faster than that found with hydrazine.⁴ The Arrhenius plot shown in Fig. 8 was obtained for the pseudo first-order rate constants calculated from the slope of linear portion of the curves in Fig. 6. The activation energy was found to be equal to $10.2 \text{ kcal mole}^{-1}$.

Finally, it should be noted that hydrazine has been described in the literature as an additive for gold plating baths. It is said to harden electroplated gold (14) presumably due to its influence on grain size (15). In addition, Winters (16) showed that hydrazine acts as an "oxygen scavenger" and increases the current effi-



Fig. 8. Arrhenius plot derived from Fig. 6

ciency of soft gold plating. Presumably, a similar effect is expected for hard gold plating, but the discoloration of deposits by excess hydrazine noted previously precludes its use for this purpose.

Summary and Conclusions

1. Cyanoaurate(III) ions form and accumulate in acidic or neutral gold plating baths with platinum anodes as the baths are aged. The accumulation of the Au(III) species leads to a significant decrease in plating current efficiency.

2. Methods based on adjusting plating current or time to maintain a constant deposit thickness with steadily decreasing plating efficiency are not always applicable. As a simple and more general approach, it is recommended to replace the platinum anode with a low polarization anode such as the so-called "dimensionally stable anode." Although this electrode does not completely prevent the formation of Au (III), it is possible to maintain the Au (III) concentration at a level low enough to obtain a current efficiency greater than 90% of the initial level.

3. Hydrazine is useful for reducing Au(III) to Au(I) without forming undesirable reaction by-products.

4. Treatment with active carbon removes the Au (III) species, but this method suffers from the disadvantage that significant amounts of Au(I) are also removed.

Finally, it should be remembered that the current efficiency of hard gold plating is influenced by many other variables besides Au(III). Concentrations of Au(I), Co^{2+} , pH, temperature, agitation conditions, and impurities all affect the current efficiency. Therefore, it is important to control these variables as well as Au(III) concentration in order to maintain a stable current efficiency and to produce a constant deposit thickness.

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[•] Hydroxylamine would be preferred to hydrazine for this reason. However, the former is available only in the form of saits, such as hydrochloride or sulfate, which would introduce unwanted anions into the bath.

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Steady-State Characteristics of Oxygen **Concentration Cell Sensors Subjected to** Nonequilibrium Gas Mixtures

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ABSTRACT

Oxygen sensors, based on membrane concentration cells, are to be used in a feedback control system on automobiles. For proper control function, the sensors should develop voltages corresponding to equilibrium oxygen partial pressures in engine exhaust, even when substantial deviations from chemical equilibrium actually exist in the bulk exhaust stream. This is accomplished through use of catalytic electrodes that are supposed to equilibrate local oxygen concentrations at the membrane surface and measure the emf developed across the concentration cell. This paper explores physicochemical factors influencing the emf across concentration cell oxygen sensors in the presence of surface reactions that are not necessarily in chemical equilibrium. Specifically, we report an isothermal kinetic analysis linking emf to (i) mass transfer between the bulk gas and boundary layers; (ii) adsorption, desorption, and chemical reaction on the catalyst/electrode surface. With nonequilibrium bulk gas mixtures, our analysis indicates that cell emf corresponds to equilibrium oxygen partial pressures when two restrictions are met: (i) mass transfer between bulk gas and surface boundary layers is slow relative to the rate of surface reactions; (ii) the reactant gases have identical mass transfer coeffiof surface reactions; (ii) the reactant gases have identical mass transfer coeffi-cients. Experimental studies of ZrO_2 oxygen sensors with platinum catalyst/ electrodes are also reported. Voltage/composition curves for O_2 /alkane systems deviate substantially from those calculated for chemical equilibrium. This reflects a relatively poor platinum catalytic efficiency for alkane oxidation. Following recent work by Takeuchi *et al.*, a "mass transfer shift" of voltage/ composition curves was observed at 600°C with the O_2/H_2 and the O_2/D_2 systems. This result, which follows from our kinetic analysis, reflects the sub-stantially different mass transfer coefficients of the reactant gases. In a second stantially different mass transfer coefficients of the reactant gases. In a second set of experiments, gas mixtures were equilibrated chemically before reaching the sensor by passing them over a secondary platinum catalyst. Stoichiometric voltage/composition curves were obtained under these conditions.

Oxygen sensors are being developed for engine control systems on automobiles (1-3). The basic concept involves sensing oxygen partial pressures in engine

Key words: solid electrolyte, gas electrode, control systems, kinetics.

exhaust, then using this information to control the airto-fuel ratio entering the engine. In this way, engine efficiency is optimized while exhaust emissions are controlled.

Sensors based on oxygen concentration cells have been extensively investigated for this control operation.

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