

Gold Electrocrystallization from a Spent Thiosulfate-Sulfite Electrolyte

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Although there are several electrolytes in the market for gold electrodeposition, a thiosulfate-sulfite mixed ligand bath has been recently developed specially for microelectronics applications. The main driver for the development of this electrolyte is long-term sustainability. At the end of a gold electrodeposition process, the spent electrolyte can contain a significant amount of gold in solution. This study has been initiated to study the feasibility of gold recovery from a used thiosulfate-sulfite electrolyte. In our work, we have used glassy carbon and graphite as electrodes. The two different forms of carbon were chosen due to the difference in their structures. It was found that at the early stages of the reduction process, the deposition of gold on glassy carbon exhibits an instantaneous nucleation. At longer times, the deposition follows the classical progressive nucleation phenomenon. Deposition of gold on graphite does not follow the classical nucleation phenomenon. Particle sizes and density can be controlled by varying the deposition potentials and time. This work is expected to elucidate information on the electrochemical behavior of a spent electrolyte at carbon electrodes, as well as studying their microstructural properties, which is likely to govern the utility of recovered gold.

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The emergence of gold-based connectors in microtechnology has initiated the need to search for new electrolytes because existing gold deposition processes have been found to be incompatible with photoresists or other process steps.¹⁻⁵ For long-term utility, interest has grown in developing nontoxic electrolytes in place of the conventional cyanide-based baths. One such alternative electrolyte is a solution containing thiosulfate and sulfite, which was initially proposed by Osaka and co-workers.¹ The bath was reported to be stable without additives and contained phosphoric acid as buffering agent. As the electrolyte was proposed for microbump technology, thallium ions were added to decrease hardness and improve surface morphology of the gold deposits. However, thallium raised the toxicity of the process, and an effort to reduce this was attempted by other researchers.

More recently, a bath containing only thiosulfate and sulfite as ligands was formulated by Newcastle University using aurochloric acid as the starting salt.² It was found that complexation by thiosulfate led to formation of $Au(S_2O_3)_2^{3-}$, a relatively stable complex, and the sulfite acted as a buffer and stabilized the solution.² The bath is found to be stable at near-neutral pH, showed good compatibility with positive photoresists, and proved to be satisfactory for an industrial process.³

However, as the bath aged, changes in electrochemical behavior were observed, mainly the formation of gold particles which precipitated from solution.^{4,5} An electrochemical investigation showed that gold reduction occurred at lower cathodic overpotentials.⁶ A Tafel analysis showed that the charge-transfer coefficient was higher, presumably due to irreversible changes within the electrolyte. This change was not solely due to a decrease in gold [Au(I)] concentration, which was found to be about 8-9 g/L or ~0.05 M upon analysis.

Clearly, for economic and environmental reasons, it is crucial that gold can be recovered from the spent electrolyte. Currently, there is no information available concerning gold recovery from thiosulfate-sulfite electrolytes. It can also be envisaged that the recovery process would have enhanced value if the recovered gold could have applications; for example, supported gold nanoparticles have great potential in the field of catalysis.^{7,8} In the electronics field, gold is used on connectors and contacts due to its high corrosion resistance.^{8,9} Applications have also been reported for gold nanoparticles as sensors in the biomedical sector^{8,10} and broadly used in advanced coatings, exploiting its variation of colors depend-

ing on the particle sizes.^{10,11} This work was carried out mainly to investigate if gold could be recovered from a spent thiosulfate-sulfite electrolyte, and to determine the microstructure of the obtained deposits/particles.

Although relatively little information is available on electrodeposition from thiosulfate-sulfite solutions containing Au(I), there have been a number of electrocrystallization studies using plating baths containing Au(III) in chloride, ^{12,13} citrate, ¹⁴ and borate. ¹⁵ References 12-14 suggest that gold electrocrystallization occurs by threedimensional nucleation followed by diffusion-controlled growth. Examination of gold nucleation on glassy carbon from chloride solutions¹² indicated that in the early stages progressive nucleation occurs, whereas at longer times instantaneous nucleation takes place. Electrodeposition on highly oriented pyrolytic graphite (HOPG) does not follow the classical nucleation phenomena.¹² Those electrocrystallization studies showed that crystal size and density could be controlled by variation of deposition potentials and times.¹³

In this work we have investigated the electrocrystallization of gold on glassy and graphitic carbon, mainly because they are easily available, inexpensive, and are used for metal recovery in industry.¹²⁻¹⁵ The choice of glassy carbon allows us to examine the microstructure when the substrate has no preferred texture, whereas the graphitic electrode allows us to examine when the substrate has a well-established structure. We have examined the effect of electrode potential on particle size, nucleation density, and microstructure.

Theory

Equations describing two- or three-dimensional nucleation and crystal growth process occurring on a foreign substrate have been discussed extensively.¹⁶⁻¹⁸ In many studies of the deposition of metals, this process is described in terms of localized hemispherical nucleus. At the early stage of electrochemical nucleation, there is an increase in current, reflecting an increase of electroactive area due to formation of new nuclei and also the increase in each particle size. During this period, each nucleus grows independently of each other. The deposition current at this stage can be described as

$$f_n(t) = \alpha t^n$$
[1]

The current of a single hemispherical nuclei growing under planar and spherical diffusion are given by Eq. 2 and 3 for instantaneous nucleation and Eq. 4 and 5 for progressive nucleation, respectively

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$$i(t) = \frac{8zFM^2c^3D^{3/2}}{\rho^2\pi^{1/2}}N_0t^{1/2}$$
[2]

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$$i(t) = \frac{zF\pi M^{1/2} (2Dc)^{3/2}}{\rho^{1/2}} N_0 t^{1/2}$$
[3]

$$i(t) = \frac{16zFM^2c^3D^{3/2}}{3\rho^2\pi^{1/2}}AN_0t^{3/2}$$
[4]

$$i(t) = \frac{4zF\pi M^{1/2}(Dc)^{3/2}}{3\rho^{1/2}}AN_{\rm o}t^{3/2}$$
[5]

After this initial stage, further growth of crystallites or mature nuclei on the electrode surface cannot be considered entirely as independent of each other.¹⁹ The diffusion zone of each nucleus begins to overlap with the diffusion zone of neighboring nuclei and this behavior is described by the Avrami theorem.¹⁷ A concept of the extended area, θ_{ex} , where θ_{ex} is the area covered by the centers assuming that no overlapping of nuclei, is introduced

$$\theta_{\rm ex} = N\pi kDt$$
 [6]

Because the centers are randomly distributed on the surface, the diffusion zone of each nuclei will overlap and the area covered by diffusion zones, θ , can be related to θ_{ex} by the expression

$$\theta = 1 - \exp(-N\pi kDt)$$
^[7]

Based on the law of conservation of mass, the amount of material entering the diffusion zone is equal to the amount being incorporated into the growing nuclei.^{18,19} Therefore, the current density flowing to the whole electrode surface for the case of instantaneous nucleation is

$$I(t) = \frac{nFD^{1/2}c\theta}{\pi^{1/2}t^{1/2}} = \frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-N\pi kDt)]$$
[8]

where
$$k = \left(\frac{8\pi cM}{\rho}\right)^{1/2}$$

If nucleation is progressive, the current density is

$$I(t) = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} \left[1 - \exp\left(\frac{-A\pi k'Dt^2}{2}\right) \right]$$
[9]
where $k' = \frac{4}{3} \left(\frac{8\pi cM}{\rho}\right)^{1/2}$

Equations 8 and 9 predict that the current passes through a maximum before it falls and approaches the limiting diffusion current. These equations can be simplified further by using reduced variables as given by Eq. 10 and $11^{19,20}$

$$\frac{I^2}{I_m^2} = \frac{1.9542}{t/t_m} \{1 - \exp[-1.2564(t/t_m)]\}^2$$
[10]

$$\frac{I^2}{I_m^2} = \frac{1.2254}{t/t_m} \{1 - \exp[-2.3367(t/t_m)^2]\}^2$$
[11]

Experimentally measured current transients can be reduced to a dimensionless form by plotting I^2/I_m^2 vs $(t/t_m)^{-1}$ and comparing the results with a theoretical plot of instantaneous and progressive nucleation.

Experimental

Two types of carbon electrodes were used, glassy carbon and rigid graphite (Goodfellow Cambridge Ltd., U.K.). Both types of electrodes were 99.5% pure with 1 mm thickness. The electrode was cut into 1 cm² square and attached to a copper wire using silverloaded epoxy adhesive and hardener (RS components, U.K.). In order to avoid metal deposition on copper wire and silver paste used for contact, the metallic area was covered using a multipurpose silicone sealant (Dow Corning Ltd., U.K.).

The predominant species in gold thiosulfate-sulfite aged plating bath is Au⁺. The bath mainly consists of Au(S_2O_3)₂³⁻ complex as

well as trace amounts of Na⁺ ions. The concentration of Au species was 8.981 g/L. pH of the electrolyte was determined to be 5.23, and this value was found to be stable throughout the process. All electrochemical experiments were performed in a three-electrode H-cell. The cell was separated into the anode and cathode compartment by a glass frit. 45 ± 1 mL volume of aged gold thiosulfate-sulfite plating solution was equally divided in each compartment.

A potentiostat (Sycopel Scientific) controlled by a computer was used to carry out the experiments. The working electrode was mounted in the cell and held in place by the use of a metal clip. $2.0 \times 2.5 \text{ cm}^2$ platinized titanium sheet was used as the auxiliary electrode. All potential measurements were made with respect to a saturated mercurous sulfate electrode (SMSE).

Cyclic voltammetry (CV) was performed to determine the potential for gold nucleation. Cathodic potential is swept between 0 and -1.4 V at scan rates ranging from 5 to 100 mV s⁻¹. Current-time transients for studying the nucleation and growth of gold were accomplished by applying the potentials from the rest potential to the deposition potentials of lower than -0.7 V for duration of 60 s. Prior to each voltammetry and chronoamperometry measurement, the carbon surface was gently polished using wet silicon carbide paper grit 4000 (Struers Ltd., U.K.) and then washed thoroughly with distilled water before being transferred to the experimental cell. The electrode was used immediately after being polished.

Scanning electron microscopy (SEM) analysis for the gold deposits was recorded using a JEOL model 5300 LV SEM at an acceleration voltage of 25 kV. All images are obtained using the secondary electron detector. Image analysis was performed by manually counting the particle density and diameter. In order to determine the phases present on the electrode surface, X-ray diffraction (XRD) patterns were obtained using a Philip X'Pert Pro diffractometer, scanning at 50 kV and 25 mA with Cu k α radiation. The patterns were interpreted using standard methods for powder diffraction.

Results

Cyclic voltammetry.—Figure 1a and b shows CVs for glassy carbon and graphite electrodes, respectively, obtained at a scan rate of 5 mV s⁻¹. Both voltammograms are characterized by two cathodic peaks or shoulders, a first peak close to -0.5V (vs SMSE) followed by another peak close to -0.85 V for the glassy carbon and -0.9 V for the graphite. Unlike deposition on metallic substrates,^{4,6} the peaks are not sharp. Prior studies of gold deposition from fresh thiosulfate, sulfite, and mixed thiosulfate-sulfite electrolytes on a gold surface have shown that a reduction peak is observed at potentials below -0.8 V.^{4,21,22} However, gold deposition was observed only at significantly lower potentials, i.e., -1.5 V. Clearly, our results show that gold deposition occurs at less cathodic overpotentials on carbon.

In our experiments, when the electrode potential was held just above -0.5 V for a certain period of time, the color of the plating solution changed from colorless and transparent to blackish toward the end of the experiment, and black precipitates gradually formed in the cathode compartment. Visual observations revealed no traces of deposited gold on the substrate, and the blackish layer on the electrode surface was easily removed using a clean cloth and distilled water. Therefore, it is apparent that direct reduction of the complex Au⁺ occurs at more negative potential, and in order to initiate the formation of adherent and stable nuclei on carbon, an overpotential more negative than -0.75 V is required.

A set of CVs at scan rates varying between 5 and 100 mV s⁻¹ was carried out to determine if the deposition was governed by diffusion.^{17,23} The linear correlation between the return peak current density and the scan rates for both types of carbon electrodes, as shown in Fig. 2, suggests a diffusion-limited process. The diffusion coefficient was calculated using Randles-Sevcik equation, as presented in equation 12.¹⁷ The best-fit line for each data set is determined by linear regression analysis and yielded diffusion coefficients of 1.835×10^{-6} cm² s⁻¹ for gold deposition on glassy carbon

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Figure 1. CV of gold on stationary (a) glassy carbon and (b) graphite electrodes at scan rate 5 mV $\rm s^{-1}.$

and $3.37\times 10^{-6}\,{\rm cm}^2\,{\rm s}^{-1}$ for gold on graphite. These values are nearly an order of magnitude greater than those observed in the fresh electrolyte 4

$$I_{\rm p} = (2.69 \times 10^{-5}) n^{3/2} c_{\rm o} D^{1/2} v^{1/2}$$
 [12]

Chronoamperometry.— In the case of gold nucleation on glassy carbon electrode, three regions of interest were typically identified in the current transients, as shown in Fig. 3a. For the first 2 s after application of a potential, there is a sharp decay in the current, mainly due to capacitive charging^{14,19} and decay of local currents.¹⁴ The capacitive current increased with applied potential, but the time required for the decay decreased. In our analysis, current data for the first 2 s were, therefore, not used.



Figure 2. Randles-Sevcik plots of gold on glassy carbon and graphite.



Figure 3. (a) Current-time transient for nucleation of gold on glassy carbon at (a) $\eta = -0.850$ V and (b) $\eta = -0.925$ V. (b) Current-time transient for nucleation of gold on graphite at $\eta = -1.050$ V.

After the initial decay, the current transient exhibited a hump or a shoulder (for potentials greater than -0.850 V). As the applied potential is lowered, this current maximum became more pronounced and its height and position increased as the applied potential became more cathodic, as predicted by classic nucleation phenomenon. ^{16,18,19,24} At longer time intervals, the current reached a plateau of -0.003 A cm⁻².

The potentiostatic current transient of gold on graphite, an example of which is presented in Fig. 3b, also exhibited an initial current decay. However, unlike gold deposition on glassy carbon, no current maximum was observed in the transient, showing that classic nucleation phenomenon is not followed. The long-term current transient data approached a current density of -0.005 A cm⁻², which is somewhat higher than that of glassy carbon. This could be due to a higher surface area of graphite.

Deposit characterization.— Figures 4 and 5 contain representative SEMs of gold nanoparticles on glassy carbon and graphite electrodes, respectively. Both figures show the deposits after 60 s of potential application. These images illustrate the influence of overpotentials on crystal distribution and size. As shown in the images of gold nucleation on glassy carbon, deposition at -0.775 V yields a smaller number of nuclei. Notably, the nuclei are of nearly the same size, the average size being 680 ± 10 nm. At intermediate overpotential, two distinct nuclei sizes are visible, with average particle sizes of 650 and 160 nm. As the applied potential is lowered, homogeneous nanocrystals ranging in diameter from 80 to 100 nm are obtained. A manual image analysis showed that the range of crystal diameter had a relative deviation of less than 1% for potentials below -1.0 V.

It has been indicated from previous studies of metal deposition on graphite that the Au nanoparticles are preferentially deposited along the step edges.^{25,26} To avoid this, seals were made alongside



Figure 4. SEM images of gold on glassy carbon as a function of deposition overpotentials: (a) -0.775, (b) -0.925, (c) -1.075, and (d) -1.200 V.

the edges so that a uniform spread of particles is obtained on the surface. When a constant potential within the range $-0.9 < \eta < -1.2$ V is applied to the electrode, the average size of the particles on graphite remained more or less uniform, at about 100–110 nm throughout the potential range. In the same potential range, electrodeposited gold nuclei obtained on glassy carbon were less uniform, and decreased from 200 to 85 nm as the potential was lowered. This result shows that the size of gold nuclei deposited on the graphite surface is not strongly influenced by potentiostatic pulse.

In order to determine the density of gold nuclei, 15 areas were randomly chosen from the micrographs of the substrate surface with each of the areas being 1 μ m². The values, as a function of overpotential, are listed in Table I. As expected, the density of nuclei increased with increasing overpotential for gold reduction. These nuclei density values are an order of magnitude 10¹-10² smaller compared to those reported for gold deposition from chlorides,¹² which could be due to the difficulty of reduction from sulfite-based electrolytes.

Figure 6 shows the distribution of Au nuclei at an overpotential of -1.2 V for short (1 s), intermediate (10 s), and long (100 s) deposition times. Although the images obtained at short time were

 Table I. Nuclei density of gold on glassy carbon and graphite

 electrodes as a function of overpotentials.

Substrates	η (V)	Average particle density calculated from SEM $(10^{-8}/\mathrm{cm}^{-2})$
Glassy	-0.775	4
carbon	-0.925	8
	-1.075	13
	-1.200	19
Graphite	-0.950	20
	-1.200	22
	-1.350	25

during the current decay, it can be seen that nuclei are deposited during the period of capacitive charging. The images presented indicate that the electrodeposition of Au on glassy carbon for 1 s results in uniform coverage of Au nuclei having a relatively uniform size of 80 ± 5 nm. It is also observed that each nuclei grows independently during this stage. At the intermediate period, there is some coalescence of Au crystals and at longer times, large aggregates having diameter ranging from 100 to 300 nm are obtained.

Figure 7 shows that the graphite electrode itself is rough and is characterized by craters. Numerous nuclei are formed on the planar areas, and it is clear that coalescence of the nuclei occurs even before the first second has elapsed. Between 1 and 10 s, a fraction of the Au nanoparticles continues to grow to over 90 nm while other nuclei remain in the range between 80 and 90 nm. After 100 s, the graphite surface is almost completely covered by Au nuclei of 100 -300 nm, which have clearly coalesced from smaller nuclei. The appearance of gold deposited on graphite is more powdery than that observed for glassy carbon.

XRD patterns, as shown in Fig. 8a and b, show a face-centered cubic (fcc) crystallographic orientation for glassy and graphitic carbon, respectively. Au(111) is the preferred texture. Both deposits were obtained at the same plating conditions ($\eta = -1.2 \text{ V}$, T = 298 K); hence, the intensities of all the Au peaks are similar. It is also evident that no impurities are detected. In both cases, carbon peaks were detected because the gold film was thin. The average size of the Au particles, calculated using the Scherrer equation, was found to be between 15 and 30 nm, somewhat smaller than those obtained by SEM.



Figure 5. SEM images of gold on graphite as a function of deposition overpotentials: (a) -0.95, (b) -1.20, and (c) -1.35 V.



Figure 6. SEM images of gold on glassy carbon as a function of deposition time: (a) 1, (b) 10, and (c) 100 s.



Figure 7. SEM images of gold on graphite as a function of deposition time: (a) 1, (b) 10, and (c) 100 s.

Discussion

Cyclic voltammetry.—Our CV results show that gold reduction proceeds on carbon at less cathodic overpotentials than on gold substrates.⁴ This is attributed to the lack of adsorption of sulfur compounds on carbon. It is well known that sulfur-based com-







Figure 9. Cottrell plot of the current-time transient of (a) gold on glassy carbon at $\eta = -0.850$ V and (b) gold on graphite at $\eta = -1.050$ V.

pounds adsorb strongly on gold, and that some adsorption occurs on the gold surface when gold is polarized in an electrolyte containing sulfur-based ligands. This result shows that gold can be reduced from the solution at relatively low overpotentials and that carbon would serve as a useful electrode for gold recovery from spent solutions.

Chronoamperometry.-Diffusion phenomena.-The chronoamperometry results from the steady-state region of j vs t data (region 3) can be used to calculate diffusion coefficients at various overpotentials using the Cottrell equation. As shown in Fig. 9, the current is indeed found to be linear with respect to $t^{-1/2}$ for glassy carbon, as predicted by the Cottrell equation. For deposition potential range $-0.775~V < \eta < -0.925~V,$ diffusion coefficients were found to increase between 6.24×10^{-6} and $3.00 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ from low cathodic overpotentials to the higher values, as shown in Table II. While the lower value is similar in magnitude to the value obtained from the Randles-Sevcik equation, the difference between the diffusivity at low and high overpotentials is nearly an order of magnitude. It can be conceived that there are different species of gold within the aged solution, which reduce at different overpotentials, although we assume that only $Au(S_2O_3)_2^{3-}$ species are involved in the reduction process. This assumption, in turn, could be reflected through changing diffusivity.

The diffusivity of gold can also be calculated from the current maximum and the time at which the maximum is observed¹⁹ in region 2, using the following equation

$$D = \frac{I_{\rm m}^2 t_{\rm m}}{0.1629 (zFc)^2}$$
[13]

The diffusion coefficients for gold on glassy carbon calculated from chronoamperometry measurements using Eq. 13 are also presented in Table II, which show reasonable agreement with the ones obtained from the Cottrell analysis.

Table II.	Values of	of diffusion	coefficients	of gold	deposition	on
glassy ca	rbon calc	ulated by d	ifferent metl	10ds.		

η (V)	Diffusion coefficient calculated from Cottrell plot (cm ² s ⁻¹)	Diffusion coefficient calculated from Eq. 13 $(cm^2 s^{-1})$
-0.775	6.24×10^{-6}	1.76×10^{-5}
-0.850 -0.925	1.53×10^{-5} 3.00×10^{-5}	2.18×10^{-3} 4.57×10^{-5}

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Figure 10. Linear dependence between j and $t^{1/2}$ corresponds to the early stage of gold deposition on glassy carbon at overpotentials (a) -0.775, (b) -0.800, (c) -0.825, (d) -0.850, and (e) -0.875 V.

In the absence of a classic nucleation curve for graphite, the current transient data for gold deposition after 3 s was used to determine the diffusion coefficient of gold species. As shown in Fig. 9, the dependence of *j* is linear with respect to $t^{-1/2}$, as was found for glassy carbon. When a Cottrell analysis was applied for the deposition potential range $-0.80 \text{ V} < \eta < -1.35 \text{ V}$, diffusion coefficients ranging from 4.06×10^{-6} to $3.13 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, were obtained, which are in agreement with the values obtained for glassy carbon.

Nucleation phenomena.— The nucleation characteristics of gold were analyzed using data from the rising part as well as the current maximum observed in region 2 of the current time transient. At the early stage of electrochemical nucleation on glassy carbon, SEM results already showed that the nuclei are widely spaced. Thus it was assumed that there was no interaction between nuclei during this time. The experimental j vs t data, therefore, can be analyzed using Eq. 2 for the regime well before the maximum in the observed current transient.

The result in Fig. 10 shows that a plot of j vs $t^{1/2}$ observes linearity in the region well before the current maximum in the current transient, indicative of hemispherical growth under instantaneous nucleation. The slopes of j vs $t^{1/2}$ plots can be used to determine the nuclei density, N_o , using Eq. 2 and 3 for planar and spherical diffusion, respectively, and the diffusivity at the respective overpotential. The values of the absolute number of nuclei at particular overpotentials calculated using both equations are shown in Table III. Because this analysis does not allow us to distinguish between the two diffusion processes, a second check against electron micrographs has to be made. It is apparent that the nuclei density calculated using Eq. 2, i.e., for planar diffusion, is in good agreement with the results obtained from microscopy.

As the radii of nuclei increase, diffusion zones begin to overlap.^{19,27} This part of the current transient is represent by the

Table III. N_0 and AN_0 values of gold deposition on glassy carbon.

$N_{\rm o}$	values	at early	stages	of	deposition
	for dif	ferent di	iffusion	pr	ocesses

m (V)	Spherical diffusion $(10^{-3}/\text{cm}^2)$	Planar diffusion $(10^{-8}/\text{cm}^2)$	AN_{o} values calculated from dimensionless transient (cm ⁻² s ⁻¹)
	(10 /em)	(10 /em)	
-0.775	6.42	12.6	1.57×10^{3}
-0.800	9.20	18.1	3.29×10^{3}
-0.825	6.46	12.7	8.53×10^{3}
-0.850	16.54	32.4	3.76×10^{4}
-0.875	19.93	39.1	1.64×10^{5}
-0.900	32.22	63.2	1.93×10^{5}
-0.925	25.58	50.2	4.99×10^{5}



Figure 11. Dimensionless current-time transient for nucleation of gold on glassy carbon at $\eta = -0.850$ V and corresponding theoretical curves for instantaneous and progressive nucleation.

current maximum, which is located between regions 2 and 3. This portion of the current transient is interpreted by plotting a dimensionless (or reduced) current transient, I^2/I_m^2 vs the dimensionless inverse time, $(t/t_m)^{-1}$. Such a plot for glassy carbon at an overpotential of -0.85 V is shown in Fig. 11. Because the dimensionless current is plotted as a function of dimensionless inverse time, the short time data of Fig. 3a translates to the larger values of $(t/t_m)^{-1}$ in Fig. 11.

As shown in Fig. 11, the reduced data for short time current transient is well represented by Eq. 2, which described instantaneous nucleation. The data representing current maximum of the dimensionless current transient is best represented by Eq. 11, which describes progressive nucleation. Using the mean value of diffusion coefficient and k' value obtained from Eq. 9, values of AN_0 for the entire range of overpotentials were calculated using Eq. 14 and presented in Table III. The nucleation rate constant, A (s⁻¹), was calculated to range between 7.85×10^{10} and 6.24×10^{12} s⁻¹, and these values agree well with the reported values¹⁵

$$I_{\rm m} = 0.4615 z F D^{3/4} c (k' A N_{\rm o})^{1/4}$$
[14]

Our analyses indicate that the early stages of nucleation of gold are characterized by instantaneous nucleation, which changes to progressive nucleation as time proceeds. Different behavior was observed for gold reduction from different electrolytes. In the case of gold nucleation from plating baths containing Au(III) in chloride^{12,13} and citrate,¹⁴ the electrocrystallization mechanism changes from progressive nucleation at the early stages to three-dimensional instantaneous nucleation at longer times.

As shown in the potentiostatic current transient of gold on graphite, Fig. 3b, no current maximum was observed in the transient; therefore, no classic nucleation analyses could be carried out. This characteristic was affirmed by the observed microscopy images of graphite, which show that the graphite surface is rough and characterized by craters. Gold was distributed unevenly on the surface, which is indicative that some part of the electrode behaved as a nonplanar surface.

Conclusion

The electrodeposition of gold was studied from gold thiosulfatesulfite aged electrolyte. Electrochemistry and microscopy analysis have been applied to characterize Au⁺ crystals deposited on the carbon substrates. CV investigation suggests that the nucleation of gold on carbon electrodes occurs at a significant rate only at overpotentials more negative than -0.75 V.

Current-time transients of gold on glassy carbon show that during the early stages of the reduction process, the deposition exhibits an instantaneous nucleation of nonoverlapping particles. With increasing time, the diffusion zones begin to overlap and the deposition follows the classical progressive nucleation phenomenon. Current-time transients of gold on graphite electrode do not follow the classical nucleation phenomenon.

Microscopy observations demonstrate that the particle size and density can be controlled by varying the deposition potentials and time. Deposition at less cathodic overpotentials yields a smaller number of large particles. As the applied potential is lowered, homogenenous Au crystals ranging in diameter from 80 to 100 nm are obtained. The particle density on both carbon surfaces increases with overpotential, signifying the increase in number of nucleation sites. It is also evident that single crystals can be obtained shortly after applying a potential, whereas at longer times the particles tend to coalesce and form larger aggregates having diameters ranging from 100 to 300 nm. XRD shows peaks characteristic of fcc, and the preferred orientation of gold deposits on both carbon surfaces is (111).

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List of Symbols

- A nucleation rate constant
- concentration
- D diffusion coefficient
- Faraday's constant F
- deposition current i_n deposition current
- peak current $I_{\rm n}$
- $I_{\rm m}$ current maximum
- current density
- peak current density j_p
- electron transfer rate constant for instantaneous nucleation
- k'electron transfer rate constant for progressive nucleation
- М molar mass of deposit
- nuclei density N_o
- overpotential η
- pi π

- ρ density of bulk deposit
- t time
- maximum time $t_{\rm m} \\ \theta$
- area covered by diffusion zones
- θ_{ex} extended area
- scan rate υ
- number of electron transferred Z,

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