

Electrochemical Study of the Gold Thiosulfate Reduction

Anne M. Sullivan*^a and Paul A. Kohl*

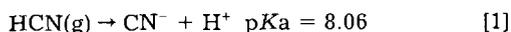
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100, USA

ABSTRACT

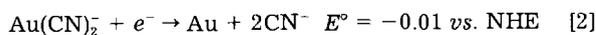
The electrochemical reduction of gold thiosulfate has been studied and compared to the reduction of gold cyanide. Gold thiosulfate is a potential replacement for gold cyanide in electro and electroless plating baths. Gold thiosulfate has a more positive reduction potential than gold cyanide and eliminates the use of cyanide. The standard heterogeneous rate constant, transfer coefficient, and diffusion coefficient for gold thiosulfate reduction were found to be 1.58×10^{-3} cm/s, 0.23 and 7×10^{-6} cm²/s, respectively. The effect of sulfite as an additive to gold thiosulfate solutions was examined.

Introduction

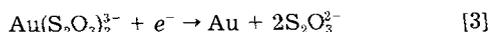
Gold is used as a conducting material for interconnections and electrical contacts in the microelectronics industry. Gold is chosen for its corrosion resistance, thermal conductivity, ductility, and purity. It can be deposited by physical vapor deposition, or by electrochemical methods. The electroless deposition of gold requires a reducing agent to reduce the gold complex. Gold cyanide is the most widely used gold complex in electro and electroless plating processes.¹⁻⁷ The primary disadvantages of using cyanide complexes are (i) the presence of cyanide in solution, wastewater, and the atmosphere raises environmental and safety concerns, (ii) the negative redox potential makes the formulation of electroless baths particularly difficult, and (iii) the low exchange current density of cyanide complexes limit the rate of deposition.^{8,9} The gold cyanide complex decomposes in the absence of excess cyanide ions at pH < 3.1.⁸ The pKa of HCN is 9.46 and the equilibrium constant for HCN(aq) going to HCN(g) is $10^{1.4}$, making the pKa for HCN(g) 8.06¹⁰



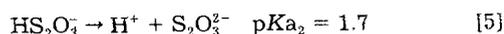
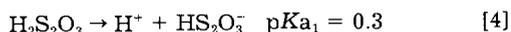
The stability constant for Au(CN)₂⁻ is 10³⁹, making the standard reduction potential for the gold cyanide complex -0.01 V vs. normal hydrogen electrode (NHE)^{11,12}



If cyanide ions accumulate in the plating bath during the reduction of Au(CN)₂⁻, they will shift the equilibrium potential to more negative values following a Nernstian behavior. Often, high pH baths are used to avoid the undesirable evolution of HCN. Consequently, alkaline, gold cyanide electroless baths contain excess cyanide in order to maintain a relatively constant concentration of cyanide. The excess cyanide shifts the redox potential further negative, requiring a reducing agent with a very negative redox potential. These disadvantages of gold cyanide have motivated a search for alternative gold complexes. Gold thiosulfate has been investigated in a nonalkaline electroless bath.^{13,14} Its stability constant is lower than the gold cyanide complex (pKa = 10²⁸), and gold thiosulfate is stable in solution over a wide range of pH.^{11,12} The reduction of gold thiosulfate was confirmed as¹⁵



The accumulation of thiosulfate in an electroless bath process affects the gold thiosulfate reduction potential by shifting it to more negative potentials, as predicted by the Nernst equation.¹³ The electroreduction of gold thiosulfate is affected by protonation of the thiosulfate in acid solutions¹⁵



Sulfite has been used as an additive in gold thiosulfate electroless baths; however, the reason for adding sulfite to the electroless bath with excess thiosulfate present was not explained.^{14,16} The stability constant for gold sulfite is smaller than that of the thiosulfate complex (pKa = 10¹⁰).¹⁶⁻¹⁹ Sulfite protonates in neutral and acidic solutions, making the gold sulfite unstable.^{20,21} Thus, gold sulfite plating baths are usually used at pH > 8.¹⁶⁻¹⁸

In this paper electrochemical reduction parameters for gold thiosulfate have been evaluated, and the effect of excess sulfite on the reduction of gold thiosulfate has been shown.

Experimental

A conventional three-electrode design was used in the cyclic voltammetry experiments. A gold disk working electrode (0.196 cm²) and a Pt wire counterelectrode were used. The reference electrode was a saturated calomel electrode (SCE), placed within 1 cm distance from the working electrode. The Pine Instrument AFASR rotating ring-disk electrode (RRDE) rotator and an EG&G PAR Model 175 universal programmer and sweep generator were used with an EG&G Model 366 bi-potentiostat. The current and potential measurements were recorded with an HP7090A X-Y-Y recorder.

Aqueous citrate mixtures (0.4 M citric acid monohydrate and 1 M potassium hydroxide, 0.4 M citric acid monohydrate, and 0.6 M potassium hydroxide) were used as buffered pH stock solutions. All chemicals were reagent grade. The potassium gold (I) cyanide was obtained from Engelhard (East Newark, NJ) sodium gold (I) thiosulfate was obtained from A. D. Mackay Chemicals (Red Hook, NY), and sodium sulfite was obtained from Fischer Scientific. All cyclic voltammetric experiments were performed at room temperature with an initial 5 min nitrogen gas purge.

The overpotential due to solution resistance was estimated for the experiments. Excess potassium chloride (1.2 N KCl) was used as the supporting electrolyte in all voltammetric experiments. The solution resistance for 1.2 N KCl, with the reference and working electrodes less than 2 cm apart, was calculated to be 32 Ω. The uncompensated solution resistance of a 1.2 N KCl solution was measured with an EG&G PAR Model 273 potentiostat to be 30 V ± 2 V. The overpotential due to solution resistance is approximately 8 mV for $i_d = 0.25$ mA. Therefore, measured characteristic potentials are subject to 8 mV (iR_s) variation. Voltammo-grams were digitized and corrected for background current before measured potentials were quantified.

Results and Discussion

The reduction of gold thiosulfate was studied as an alternate gold complex for plating baths. The reduction voltammograms of 0.01 M gold thiosulfate and 0.01 M gold cyanide are compared in Fig. 1. The reduction voltammograms were obtained on a stationary gold electrode at pH 4.8 and 6.4. The potential sweep rate was 100 mV/s. The voltammograms for gold thiosulfate reduction were the same at the two pHs. The gold thiosulfate reduction voltammogram has a larger peak current than the gold

* Electrochemical Society Active Member.

^a Present address: AMP Incorporated, Harrisburg, PA 17105-3608, USA.

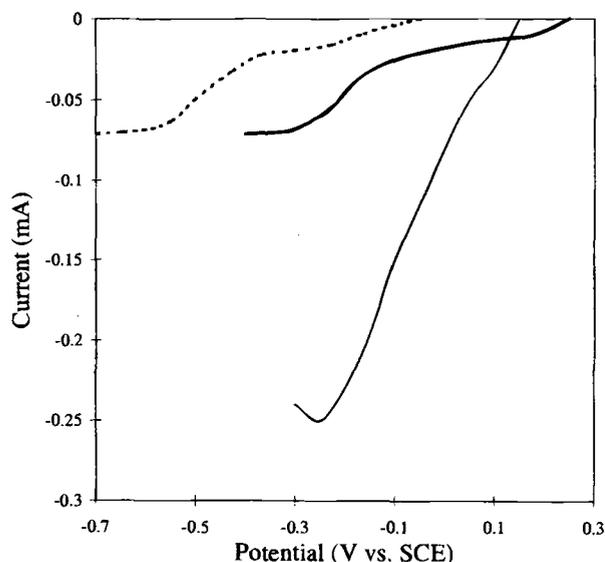


Fig. 1. The reduction voltammogram for 0.01 M gold(III) thiosulfate and 0.01 M gold cyanide. At 100 mV/s, 25°C on a stationary gold disk (0.196 cm²). (---) gold cyanide at pH 6.4, (—) gold cyanide at pH 4.7, (- · -) gold thiosulfate at pH 6.4 and at pH 4.7.

cyanide reduction voltammogram under similar conditions, Fig. 1. At pHs greater than 4, the free thiosulfate concentration is not effected by pH, because it is essentially fully deprotonated, as shown in Eq. 4 and 5. The slope of the gold thiosulfate current-potential curve is greater than that of gold cyanide. The electroreduction of gold thiosulfate occurs at potentials more positive than the electroreduction of gold cyanide at pH 6.4, Fig. 1. The potential for the reduction of gold cyanide shifts with pH, because of the change in free cyanide concentration below pH 8. The gold cyanide reduction voltammogram shifts to more negative potentials with pH until the cyanide becomes essentially fully deprotonated above pH 9.

The effect of thiosulfate buildup during gold deposition and the subsequent effect of thiosulfate concentration on the gold thiosulfate reduction voltammogram were determined in a previous investigation.¹³ The addition of excess thiosulfate shifts the reduction potential of gold thiosulfate to more negative potentials, as predicted by the Nernst equation.

The addition of sulfite as a complexing agent was studied in the gold thiosulfate solution (pH 6.4, 25°C). The reduction voltammograms of 0.03 M gold thiosulfate with varying excess sulfite concentration were obtained at a stationary gold electrode at a potential sweep rate of 100 mV/s, Fig. 2. The reduction of gold thiosulfate shifts in the negative direction as the sulfite concentration increases. The reduction of 0.03 M gold thiosulfate solution shifts negatively by approximately 100 mV with the addition of 0.05 M sulfite. Similar potential shifts with the addition of sulfite were reported for gold chloride solutions with excess thiosulfate.¹⁸ Kato *et al.* did not attempt to explain this effect of sulfite on the gold reduction voltammograms.¹⁸ An asymmetric complex may have formed with thiosulfate ions and sulfite ions. Alternatively, sulfite may adsorb onto the gold substrate, or become involved in the reaction intermediates shifting the reduction voltammogram to more negative potentials. The exact mechanism by which sulfite affects the electroreduction of gold thiosulfate remains unclear.

The reduction of 0.01 M gold thiosulfate was investigated using a rotating gold electrode at different rotation rates. Voltammograms were obtained at a potential sweep rate of 100 mV/s (pH 6.4, 25°C). The reduction of gold thiosulfate has an onset potential near 0.15 V vs. SCE, and reached a limiting current near -0.2 V vs. SCE, as shown

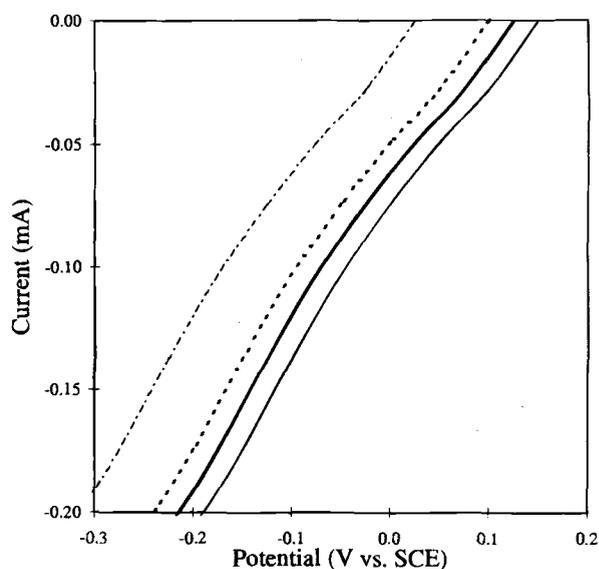


Fig. 2. Current-potential variation of 0.03 M gold(III) thiosulfate with sulfite addition. At 100 mV/s, pH 6.4, 25°C on a stationary gold disk (0.196 cm²): (—) zero excess sulfite, (---) 0.005 M excess sulfite, (- · -) 0.01 M excess sulfite, (· · ·) 0.05 M excess sulfite.

in Fig. 3. The limiting current increased with rotation rate. The currents measured at a rotating disk electrode can be separated into mass transfer controlled, kinetic controlled, and mixed controlled regimes. A reversible electron transfer reaction has a cathodic limiting current which is directly proportional to $\omega^{1/2}$, where ω is the electrode rotation rate in s⁻¹.²¹ A nonlinear relationship between the limiting current and $\omega^{1/2}$ indicates that the limiting current is dependent on kinetics and mass transport²¹

$$1/I = 1/I_1 + 1/I_k \quad [6]$$

Where I_1 is the mass-transport limited current (A) and I_k is the kinetically limited current (A). The limiting current controlled by mass transfer follows the Levich equation²¹

$$I_1 = 0.62 nFAD^{2/3} \nu^{-1/6} \omega^{1/2} C \quad [7]$$

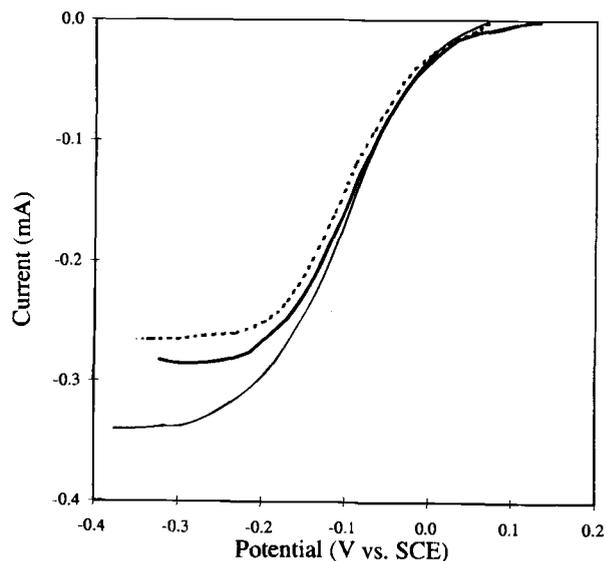


Fig. 3. Current-potential variation of 0.01 M gold thiosulfate with rpm. At 100 mV/s, pH 6.4, 25°C on a stationary gold disk (0.196 cm²): (- · -) 50 rpm, (—) 100 rpm, (- · -) 200 rpm.

where A is the electrode surface area (cm^2), D is the diffusion coefficient (cm^2/s), ν is kinematic viscosity (cm^2/s), C is concentration (mol/cm^3) of the electroactive species, F is Faraday's constant, and n is the number of electrons. The kinetically controlled current is dependent upon the heterogeneous rate constant, $k_t(E)$ (cm/s), and the potential, $E(\text{V})$.

$$I_k = nFACk_t(E) \quad [8]$$

Plots of $1/I$ vs. $1/\omega^{1/2}$ at different potentials allow evaluation of k_t . The heterogeneous rate constant, k_t , is related to the standard heterogeneous rate constant, k_o (cm/s), and the transfer coefficient, α (nondimensional)

$$k_t = k_o \exp[-\alpha F/RT(E - E^{o'})] \quad [9]$$

where $E^{o'}$ is the formal reduction potential.

The currents were measured at different potentials and rotation speeds, and used to determine the kinetic constants for the electrochemical reduction of gold thiosulfate. Currents were measured at six potentials (-0.35 , -0.25 , -0.2 , -0.15 , -0.1 , and -0.05 V vs. SCE) and a linear plot of I^{-1} vs. $\omega^{-1/2}$ at the limiting current shows nonzero y -intercepts, as shown in Fig. 4. The kinetically controlled current, I_k , was calculated from the y -intercepts of the linear plots in Fig. 4 and the heterogeneous rate constants were calculated at each potential.

The determination of the standard heterogeneous rate constant, and transfer coefficient, Eq. 9, requires an accurate value of the gold thiosulfate standard formal potential. The reduction of gold thiosulfate is an irreversible reaction. The determination of the standard potential is more difficult for irreversible reactions than reversible ones because relationships like the Tafel equation cannot be used to find the standard potential.

The standard formal potential of gold thiosulfate has been reported by Pouradier and Gadet to be 0.15 V vs. NHE (-0.09 V vs. SCE).^{12,22} The standard formal potential was experimentally determined here by measuring the rest (equilibrium) potential of gold in gold thiosulfate solutions at various thiosulfate concentrations.²² The standard formal potential was calculated by correcting the rest potential for different gold thiosulfate and thiosulfate concentrations. Fluctuations in the rest potential with small changes in reactant concentrations and electrode

surface anomalies add uncertainty to the previously reported value of the gold thiosulfate standard formal potential.

In this study, the rest potential of 0.01 M gold thiosulfate was measured as a function of thiosulfate concentration. Care was taken in preparing solutions of specified concentrations and in reproducing the surface conditions of the electrode. The activity coefficients of gold thiosulfate were assumed to be one. The standard formal potential was calculated using the rest potentials and gold thiosulfate and thiosulfate concentrations. The average standard formal potential for the electroreduction of gold thiosulfate is -0.09 V vs. SCE ± 0.005 V vs. SCE ($\pm 2\sigma$). The experimental standard formal potential determined in this investigation agrees well with the experimental standard formal potential reported in literature.

A third determination of the standard formal potential was made by using the Nernst equation for the reduction of gold ions to gold and using a literature value for the stability constant for gold thiosulfate, $pK_a = 10^{28}$.^{10,11,18} The standard formal potential for the reduction of gold ions to gold is 1.44 V vs. SCE.¹¹ The Nernst equation for the gold (I) ion reduction to gold was corrected for the complexation of gold ions with thiosulfate. The problem with this method is the uncertainty in the stability constant. From the Nernst equation and gold thiosulfate stability constant of 10^{28} , the standard formal potential for gold thiosulfate is calculated to be -0.22 V vs. SCE.

The standard heterogeneous rate constant and transfer coefficient for the gold thiosulfate reduction were determined using a standard formal potential of 0.09 V vs. SCE and the experimental data show in Fig. 4. A plot of $\ln k_t$ vs. $(E - E^{o'})$ has an intercept equal to $\ln k_o$, and the slope is proportional to the transfer coefficient, as can be seen from Eq. 9. Figure 5 shows the relationship between $\ln k_t$ and $(E - E^{o'})$. The calculated standard heterogeneous rate constant is 1.58×10^{-3} cm/s with an error of 0.8×10^{-3} cm/s ($\pm 2\sigma$). This calculated standard heterogeneous rate constant for gold thiosulfate is high in comparison to two silver complexes, silver(I) cyanide (6.66×10^{-8} cm/s) and silver(I) iodide (2.4×10^{-4} cm/s).²³ The calculated transfer coefficient is 0.23 with a standard error of 0.02 ($\pm 2\sigma$). Silver cyanide and silver iodide have transfer coefficients of 0.61 and 0.84 , respectively.²³ The low transfer coefficient of gold thiosulfate indicates that the activation complex is more structurally similar to the reactant, a bidentate complex, than the products.

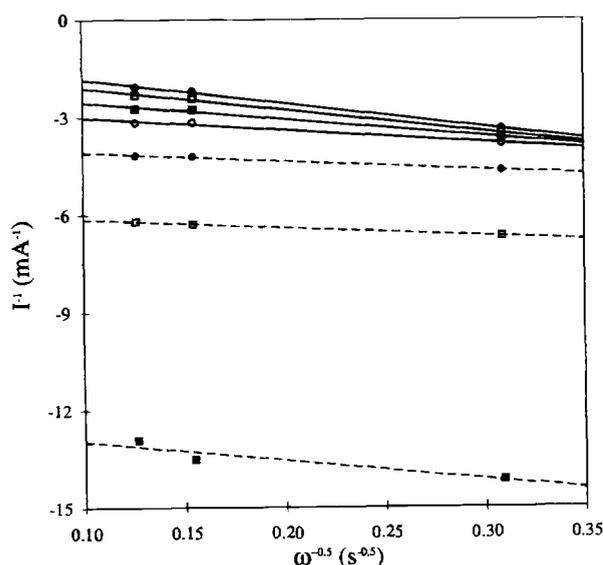


Fig. 4. Inverse current variation with inverse rotation rate for the reduction of 0.01 M gold(I) thiosulfate. At 100 mV/s, pH 6.4, 25°C on a gold disk. (●) -0.35 V vs. SCE, (□) -0.3 V vs. SCE, (■) -0.25 V vs. SCE, (○) -0.2 V vs. SCE, (●) -0.15 V vs. SCE, (□) -0.1 V vs. SCE, (■) -0.05 V vs. SCE.

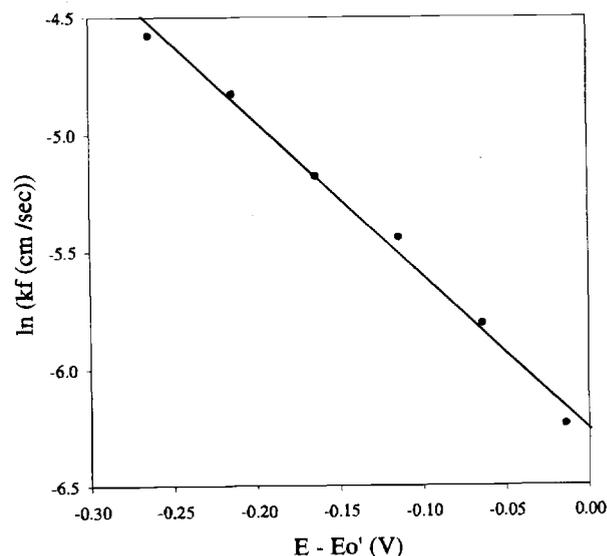


Fig. 5. Logarithmic variation of electrochemical rate constant with potential for the reduction of 0.01 M gold(I) thiosulfate. At 100 mV/s, pH 6.4, 25°C on a gold disk (0.196 cm^2).

The intercepts of the $1/I$ vs. $\omega^{-0.5}$ allows the determination of the kinetic parameter and Tafel region for each rotation rate.²⁴ The Tafel plots at 400 and 600 rpm, had slopes of -0.34 and -0.32 V/decade, respectively, in the potential range from -0.05 to -0.35 V vs. SCE as shown in Fig. 6. Two Tafel slopes were observed for gold cyanide complexes at 60°C . For soft gold, the slopes were -0.35 V/decade (-0.50 to -0.95 V) and 0.154 (-0.95 to -1.1 V). For nickel hardened gold, the Tafel slopes were -0.47 V/decade (-0.50 to -0.80 V) and -0.186 V/decade (-0.95 to -1.1 V). The change in slopes was attributed to a change in mechanism for the reduction of the gold complex. The higher Tafel slopes observed at more positive potentials, were due to reduction through an adsorbed AuCN complex, whereas the lower Tafel slopes (higher currents) at more negative potentials, were due to the direct reduction of the $\text{Au}(\text{CN})_2^-$ complex.²⁴

Gold thiosulfate reduction was studied as a function of concentration at a potential sweep rate of 100 mV/s and an electrode rotation rate of 200 rotations per minute (rpm) at 25°C in a citrate buffer at pH 6.4 . A mass transport limited current is observed in each case, as shown in Fig. 7. The limiting current increases with concentration and a plot of the limiting current as -0.25 V vs. SCE against gold thiosulfate concentration is linear as shown in Fig. 8.

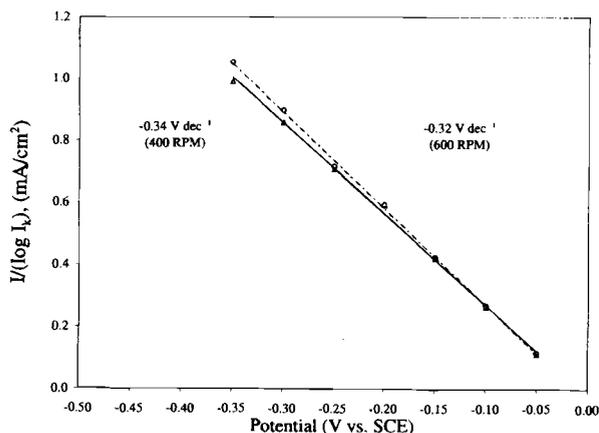


Fig. 6. Tafel plot for gold (II) thiosulfate at two rotation rates.

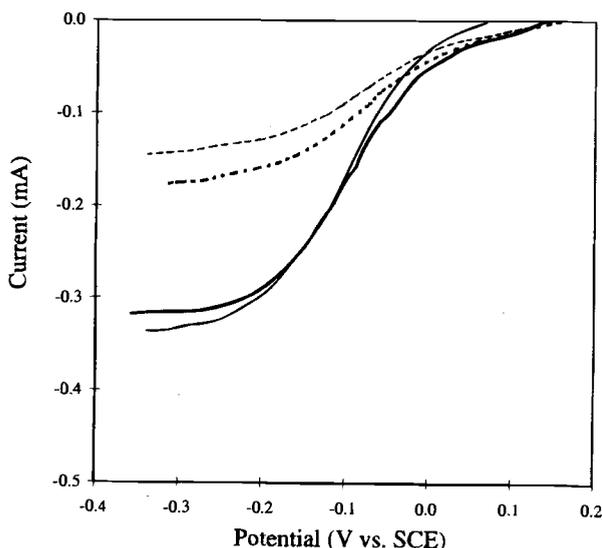


Fig. 7. Current-potential variation of the reduction of gold(II) thiosulfate with concentration. At 100 mV/s, 200 rpm, pH 6.4 , 25°C on a gold disk (0.196 cm²) (—) 0.01 , (---) 0.009 , (· · ·) 0.005 , and (- · - ·) 0.004 M gold thiosulfate.

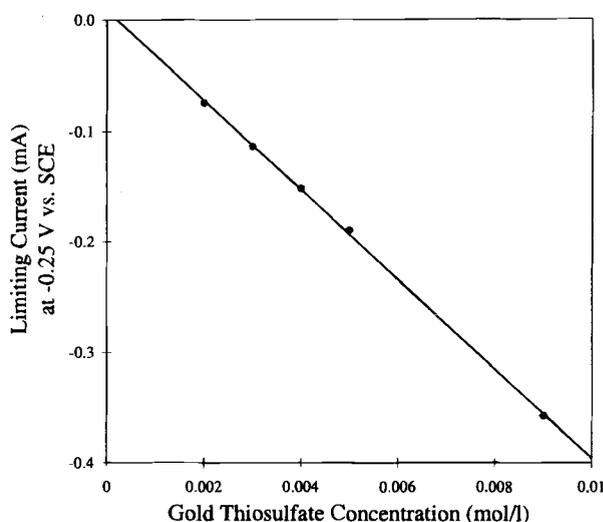


Fig. 8. Limiting current variation with concentration for the reduction of gold(II) thiosulfate. At 100 mV/s, 200 rpm, pH 6.4 , 25°C on a gold disk (0.196 cm²).

At a stationary electrode, a single diffusion limited peak at -0.912 vs. SCE, was observed (100 mV/s). A linear relationship between peak currents and $v^{1/2}$ over a wide range of sweep rates is seen in Fig. 9.²¹

$$I_p = 2.99 \times 10^5 n(\alpha n_a)^{1/2} ACD^{1/2}v^{1/2} \quad [10]$$

From the slope of the I_p vs. $v^{1/2}$, the diffusion coefficient was found to be 7.01×10^{-6} cm²/s with an error of 0.13×10^{-6} cm²/s ($\pm 2\sigma$). The calculated gold thiosulfate diffusion coefficient is lower than the estimated diffusion coefficient of thiosulfate, 1.08×10^{-5} cm²/s.^{14,25} However, the size of the hydrated gold thiosulfate complex is larger than the size of the hydrated thiosulfate ion.

Summary

A qualitative comparison between gold cyanide and gold thiosulfate reduction shows that the gold cyanide electroreduction reaction is kinetically slower. Gold thiosulfate is reduced at 0.15 V vs. SCE. The electroreduction of gold thiosulfate is independent of pH for values above 4.

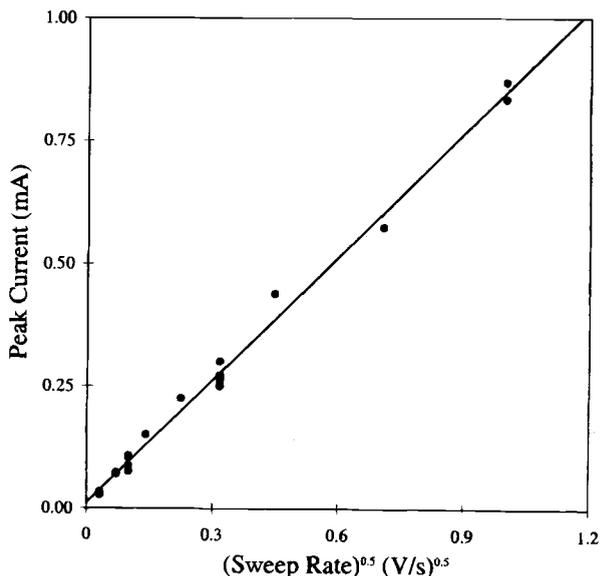


Fig. 9. Peak current variation with square root of the potential sweep rate for the reduction of 0.01 M gold(II) thiosulfate. At pH 6.4 , 25°C on a stationary gold disk (0.196 cm²).

The standard heterogeneous rate constant for gold thio-sulfate was found to be 1.5×10^{-3} cm/s and, the transfer coefficient was 0.23. Gold thiosulfate has a low diffusion coefficient of 7.01×10^{-6} cm²/s.

Manuscript submitted Aug. 30, 1996; revised manuscript received Feb. 6, 1997.

The Georgia Institute of Technology assisted in meeting the publication costs of this article.

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Further Investigation of the Reduction of Alkyl Bromides at p-InP Photocathodes Hot or Thermalized Electrons?

Markus D. Groner, David K. Watts, and Carl A. Koval*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, USA

ABSTRACT

Electron transfer from p-InP photocathodes to competing electron acceptors, oxidized metallocenes, and dibromoethylbenzene (DBEB), in acetonitrile solutions was investigated in order to access the limitations associated with detecting hot electrons in such systems. Low and highly doped p-InP electrodes were investigated under various illumination conditions and acceptor concentrations. Collection experiments showed that the fraction of photocurrent which reduced DBEB decreased from one to zero as oxidized metallocene, decamethylferrocenium⁺ (DFER⁺) or dicarbomethoxycobaltocenium⁺ (DCMC⁺), was added to a DBEB solution. Mott-Schottky data revealed a corresponding decrease in the negative shift of the bandedges under illumination which went to zero at the same metallocene concentrations at which DBEB reduction was no longer detected. Voltammograms revealed hysteretic double waves in cases where the metallocene was not present in large enough concentrations to accept all electrons. The data indicate that the rate constants for reduction of DFER⁺ or DCMC⁺ by conduction-band electrons are at least two orders of magnitude larger than for reduction of DBEB. Although previous research on these interfaces was interpreted as evidence for reduction of DBEB by hot electrons at highly doped p-InP electrodes, these results indicate that it would be difficult to distinguish between hot and thermalized photoreduction mechanisms in these systems.

Introduction

The efficiency of photoelectrochemical cells could be improved if charge carriers with significantly greater energy than the bandedge (*i.e.*, hot carriers) reacted efficiently with redox species in solution. When a photon creates an electron-hole pair in a semiconductor, the energy separation between these hot charge carriers is initially equal to the energy of the photon, but vibrational relaxation due to electron-phonon collisions causes the electron to undergo rapid thermalization which decreases this energy separation down to that of the bandgap. The ability

to utilize all the light energy would allow for theoretical conversion efficiencies of 66% in a single bandgap device, as opposed to the conventional limit of 33% for single bandgap devices operating at thermal equilibrium.¹ Many papers have been published suggesting evidence for nonthermalized charge carriers in liquid-junction cells.¹⁻⁶ While hot electrons are well documented in the solid state,⁷ the question as to whether they can be utilized in liquid junction cells is still under discussion.^{8,9}

Recently our group reported that hot electrons could be detected in a photoelectrochemical cell consisting of a p-InP photocathode and an acetonitrile solution containing decamethylferrocene/decamethylferrocenium (DFER^{+/0})

* Electrochemical Society Active Member.