Electro-oxidation of Ascorbic Acid in an Aqueous Citrate Buffer Solution

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Ascorbic acid is a non-toxic reducing agent with potential applications in the electroless deposition of metals. Reducing agents can be consumed through (i) homogeneous reactions in solution (*e.g.*, reaction with gold thiosulfate, oxygen or peroxide) and (ii) heterogeneous surface reactions, leading either to the deposition of metal or non-metal depositing reactions. The chemical and electrochemical oxidation of ascorbic acid has been investigated in an aqueous citrate solution at pH 6.4 and 25 °C to quantify its consumption rate in electroless processes. Ascorbic acid undergoes a homogeneous reaction with dissolved oxygen in a pseudo first-order reaction having a rate constant of (1.75×10^{-3})/min. This is equivalent to consuming five percent of the initial ascorbic acid concentration in 30 min. Hydrogen peroxide is one of the possible side products of ascorbic acid oxidation. The addition of hydrogen peroxide on gold surfaces does not significantly accelerate the reaction between dissolved oxygen and ascorbic acid. The diffusion coefficient was found to be 6.46×10^{-6} cm^2/sec.

Electroless deposition is a process used to produce thin films of metal in selected areas without having to provide a ground-plane of metal or make electrical contact to the surface being plated. During electroless processes, a metal complex is electro-reduced simultaneously with electro-oxidation of a reducing agent. The two half-reactions occur without an external potential source and, ideally, occur only on the desired surfaces. The most critical characteristics of the reducing agent are its:

- Redox potential
- Solubility
- Possible side reactions

The reducing agent must oxidize at potentials more negative than the reduction potential of the metal complex, and at a rate suitably fast, so as to make the electroless process useful. If the reducing agent undergoes side reactions, either homogeneously in solution or heterogeneously on surfaces, it must be replenished at an accelerated schedule. Undesirable side-products must be handled accordingly. Reducing agents commonly selected for electroless processes have the following electrochemical characteristics:

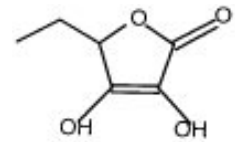
- A redox potential negative of that of the metal complex
- A high heterogeneous rate for oxidation on specific metal surfaces leading to the deposition of metal
- A low homogeneous rate of oxidation.

In addition, it is desirable for the reducing agent to be non-toxic and to form benign products.

The chemical reactivity of the reducing agent can have a large impact on the electroless deposition behavior, replenishment schedule and ease of use. For example, the hydrolysis of borohydride at pH <9 homogeneously consumes the reducing agent, and limits the lifetime of gold cyanide/borohydride electroless baths.[1-4]

Borohydride, hydrazine, hydroxylamine and hypophosphite are common reducing agents in the electroless plating of gold, nickel and silver.[1-14] L-Ascorbic acid, a lactone, has been used in electroless processes, particularly at lower pH.[4,15-17] L-Ascorbic acid is non-toxic and can be used at room temperature. The rate of its decomposition and other side reactions in electroless processes, however, have not been investigated.

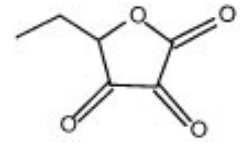
L-Ascorbic acid is the generic name for L-threo-2-hexenono-1,4,lactone, and has the structure of a 2,3-enediol-L-gulonic acid:[18-19]



Ascorbic acid has two acid protons with equilibrium constants of $pKa_1 = 4.04$ and $pKa_2 = 11.34$.[20] The oxidation of ascorbic acid, H_2A, is a chemical reaction followed by a two-electron transfer process.[21]

$$H_2A = HA^- + H^+ \quad (1)$$
$$HA^- = DA + H^+ + 2e^- \quad (2)$$

The final product, DA, is dehydroascorbic acid, $C_6H_6O_6$. Dehydroascorbic acid is a heterocyclic compound with three ketone groups:[18,19]



According to Mushran and Agrawal, the redox potential for this system has been reported to be 0.185 V vs. NHE at 21 °C and pH 7.[21] Various values of the standard redox potential have been reported under different conditions for its electrochemical oxidation.[22] Accordingly, the electrochemical route to the oxidation of ascorbic acid involves deprotonation of the acid (pH ranges between 5 and 10 are desirable), followed by two electron transfer steps.

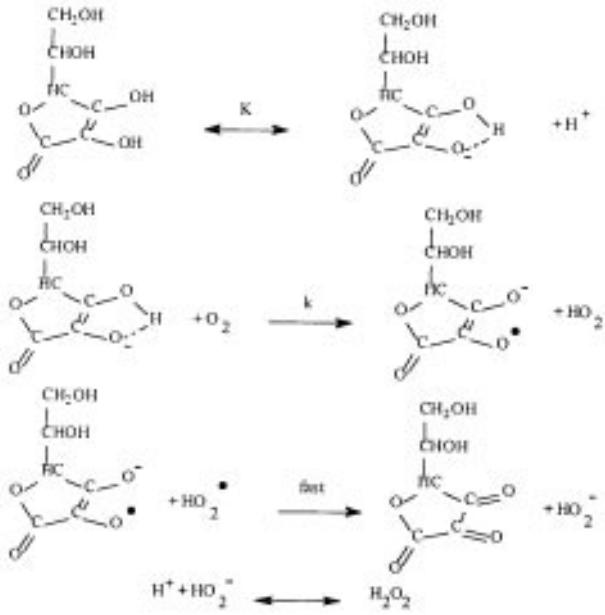
There are two known ascorbic acid side reactions of interest; they can be affected by the presence of metal surfaces, as would occur during electroless plating. The first reaction involves dissolved oxygen in an ascorbic acid solution.

$$H_2A + O_2 \longrightarrow DA + H_2O_2 \quad (3)$$
$$HA^- + O_2 \longrightarrow DA + HO_2^- \quad (4)$$

Ascorbic acid in its monoprotonated and diprotonated forms react with oxygen homogeneously.[23,24] Dehydroascorbic acid and hydrogen peroxide are produced in this homogeneous reaction.[20,25,26] Pseudo-first-order rate constants have been

calculated at different solution conditions. The rate constant is reported to be 1.8 x 10^{-3}/min at pH 9.0 and 25 °C and 1.4 x 10^{-3}/min at pH 6.0 and 25 °C.[20,27] Researchers have claimed that the fast rate of oxygen dissolution maintains a constant concentration of dissolved oxygen in solution and the reaction rate is independent of oxygen concentration.[20,28]

The ascorbic acid oxidation mechanism in the absence of a catalyst is shown here, as proposed by Khan, where K is the equilibrium constant for the deprotonation and k is the rate constant for the homogeneous reaction.[20]

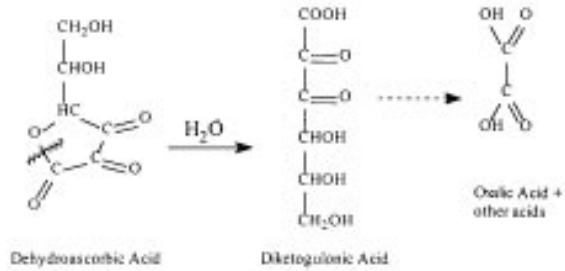


The monoprotonated form of ascorbic acid reacts with oxygen to form an ascorbate radical and a peroxide radical.[20] The peroxide radical quickly reacts with the ascorbate radical to form dehydroascorbic acid and hydrogen peroxide.[20]

The second side reaction of interest involves hydrogen peroxide, a product from the homogeneous oxidation of ascorbic acid. Hydrogen peroxide further reacts with ascorbic acid in a slower reaction, producing dehydroascorbic acid and water.[26,29]

$$H_2A + H_2O_2 \text{ —> } DA + H_2O \qquad (5)$$

Dehydroascorbic acid rapidly hydrolyzes in water to 2,3-diketogulonic acid, which oxidizes to oxalic acid.[27-31]



In this paper we evaluate the homogeneous decomposition of ascorbic acid via several chemical routes, and evaluate the heterogeneous consumption rate. Because ascorbic acid can decompose via several different routes, knowledge of these rates is important for developing electroless bath replenishment schedules. This analysis serves as an example of a general approach that can be taken in evaluating electroless baths.

Experimental Procedure

A conventional three-electrode design was used in the cyclic voltammetry experiments. A gold disk working electrode (0.196 cm^2) and a Pt wire counter-electrode were used. The reference electrode was a saturated calomel electrode (SCE), placed within one cm of the working electrode. A rotating ring disk electrode (RRDE) rotator[a] and a universal programmer and sweep generator[b] were used with a bi-potentiostat.[c] The current and potential measurements were recorded with an X-Y-Y recorder.[d]

Aqueous citrate mixtures (0.4 M citric acid monohydrate and 1 M potassium hydroxide) were used as buffered pH stock solutions. All chemicals were reagent grade. Excess potassium chloride (1.2 N KCl) was used as the supporting electrolyte in the voltammetric experiments. All cyclic voltammetric experiments were performed at room temperature. Voltammograms were digitized and corrected for background current before measured potentials were quantified.

The concentration of ascorbic acid was monitored electrochemically by obtaining intermittent oxidation voltammograms at a rotating gold electrode. A refrigerated constant temperature recirculator was used to maintain the temperature of the ascorbic acid solutions. The rotating gold electrode was immersed in the solution approximately 20 sec prior to onset of the

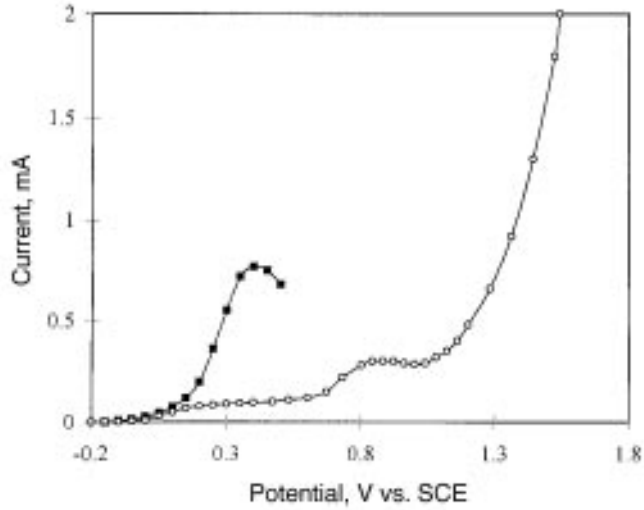


Fig. 1—Voltammograms of the citrate buffer solution ❍ (pH 6.4) and 0.01 M ascorbic acid; 100 mV/sec, 25 °C on a stationary gold disk.

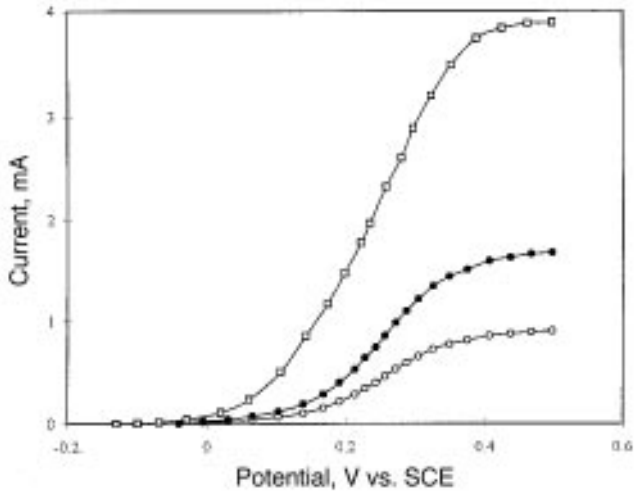


Fig. 2—Voltammograms of 0.01 M ❍ 0.02 M ●, and 0.05 M ❑ ascorbic acid in the citrate buffer solution (pH 6.4); 100 mV/sec, 200 rpm, 25 °C on a gold disk.

electro-oxidation and removed immediately after obtaining the voltammogram. The initial 20 sec were necessary for reaching equilibrium at the solution/electrode interface before the electrochemical experiment. Total immersion time of the gold electrode was less than 90 sec.

Results and Discussion

Electrochemical Oxidation of Ascorbic Acid

Electrochemical oxidation of ascorbic acid was investigated in a citrate buffer (pH 6.4) on a stationary gold electrode at 25 °C. An oxidation voltammogram of 0.01 M ascorbic acid at pH 6.4 was obtained at a potential sweep rate of 100 mV/sec within three min of ascorbic acid dissolution. The voltammograms were corrected for uncompensated solution resistance. Figure 1 shows the anodic voltammogram of the buffer solution at pH 6.4 and 25 °C. The current at potentials just positive of 0.85 V vs. SCE are a result of gold oxidation. The sharp increase in anodic current at potentials positive of 1.0 V vs. SCE results from evolution of oxygen. The oxidation of 0.01 M ascorbic acid has a single peak near 0.3 V vs. SCE, as shown in Fig. 1. The anodic onset potential of 0.01 M ascorbic acid occurs near -0.15 V vs. SCE. Accordingly, the potential region of interest for ascorbic acid oxidation is between -0.15 V and 0.5 V vs. SCE.

Electrochemical oxidation of ascorbic acid was investigated at different concentrations in a citrate buffer (pH 6.4) on a rotating disk gold electrode at 25 °C. Oxidation voltammograms were obtained at a rotation rate of 200 rpm and a potential sweep rate of 100 mV/sec within three min of ascorbic acid dissolution. The anodic current resulting from ascorbic acid oxidation increases with increasing concentration, as shown in Fig. 2. The onset potential of ascorbic acid is near -0.15 V vs. SCE. The anodic current appears as a single wave approaching a limiting value at potentials positive of 0.4 V vs. SCE. The limiting current varies linearly with ascorbic acid concentration and has a correlation coefficient of 0.997, as shown in Fig. 3.

The electro-oxidation of ascorbic acid is assumed to follow the mechanism proposed in the literature and stated in Eqs. (1) and (2).[21] The ascorbic acid oxidation therefore follows a C_rE_r, mechanism (n = 2, where n is the number of electrons). The limiting current of the electron transfer reaction in the C_rE_r mechanism provides valuable information that can be used to evaluate:

- the impact of the preceding chemical reaction on the electrochemical reaction rate
- the diffusion coefficient of ascorbic acid

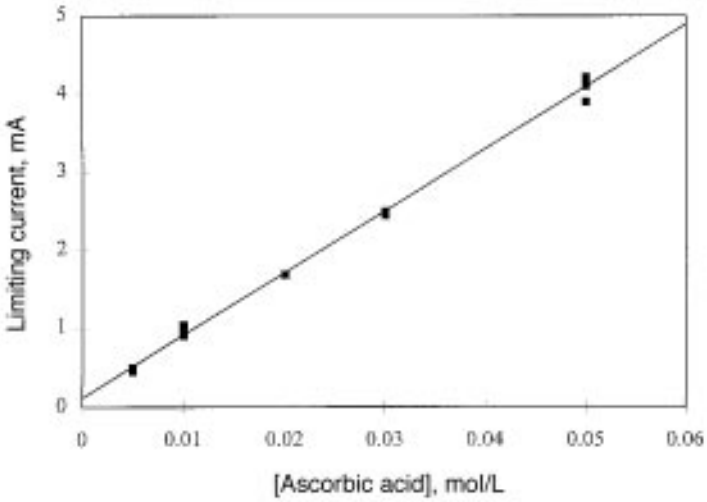


Fig. 3—Limiting current variation with ascorbic acid concentration; 100 mV/sec, 200 rpm, 25 °C, pH 6.4 on a gold disk.

At low rotation rates, the limiting current is predominantly controlled by the mass transfer of ascorbic acid to the electrode. The chemical reaction occurs sufficiently fast enough not to be a limiting factor in the electrochemical reaction. As the rotation rate increases, the limiting current becomes dependent upon both the diffusion layer thickness and the chemical reaction rate. At very high rotation rates, the diffusion layer thickness becomes negligible and the current is controlled by the conversion of H_2A to HA^-.

Oxidation of ascorbic acid was studied at low rotation rates to isolate the electrochemical reaction and eliminate any interference from the preceding chemical reaction. The Levich equation describes the limiting current, i_{lim}, at low rotation rates.[32]

$$i_{lim} = 0.62nFAD_0^{2/3}\upsilon^{-1/6}\omega^{1/2}C_0 \qquad (6)$$

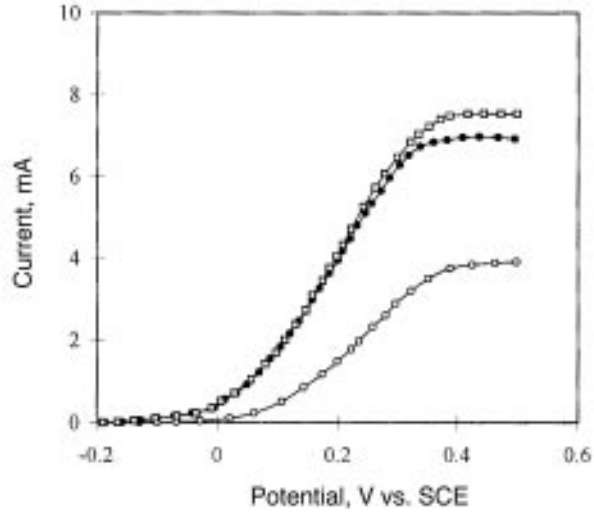


Fig. 4—Voltammograms of 0.05 M ascorbic acid in a citrate buffer solution (pH 6.4) at 200 rpm ❍, 500 rpm ●, and 600 rpm ❑; 100 mV/sec, 25 °C on a rotating gold disk.

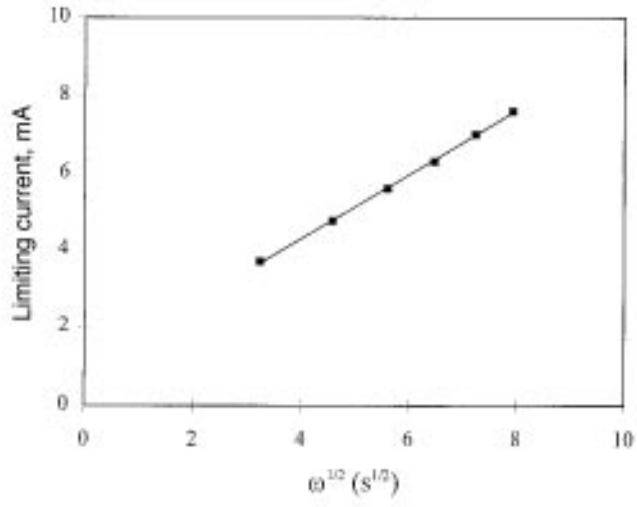


Fig. 5—Limiting current variation with the square root of the rotation rate, ω/sec, for 0.05 M ascorbic acid in a citrate buffer solution (pH 6.4); 100 mV/sec, 25 °C on a rotating gold disk.

where ω is the rotation rate, D_0 is the diffusion coefficient, C_0 is the species concentration, A is the surface area of the electrode and υ is the kinematic viscosity of the solution. If the chemical reaction is slow in relation to the mass transfer rate, the plot of the limiting current vs. the square root of the rotation rate will not follow the Levich equation and will not be linear.

The ascorbic acid oxidation reaction in a citrate buffer (pH 6.4) was investigated on a rotating gold disk electrode at different rotation rates. Oxidation voltammograms shown in Fig. 4 were obtained with a potential sweep rate of 100 mV/sec at 25 °C within three min of ascorbic acid dissolution. An increase in rotation rate increased the limiting current significantly. The limiting current for the ascorbic acid oxidation varies linearly with the square root of the rotation rate in the 100 to 600 rpm range (see Fig. 5). The linearity seen in Fig. 5 is characteristic of a mass-transfer-controlled reaction.-Mechanisms such as C_rE_r commonly behave as a reversible electrochemical reaction controlled by mass transfer at low rotation rates.[32] The ascorbic acid oxidation reaction follows the Levich equation under these experimental conditions. Accordingly, the chemical reaction is fast, in comparison to the mass transfer of ascorbic acid across the diffusion layer, when $Re \leq 393$ ($\omega r_1^2/v$ at 600 rpm).

The Levich equation was used to calculate an experimental diffusion coefficient of $6.46 \times 10^{-6} \pm 2.2 \times 10^{-7}$ ($\pm 2\sigma$) cm^2/sec. The diffusion coefficient of ascorbic acid was measured by Jiang and Dong in a linear rotation scan study with a rotating pyrolytic graphite disk electrode.[22] The ascorbic acid diffusion coefficient in a deaerated, pH 7.2 buffer solution, was reported to be 6.34×10^{-6} cm^2/sec.[22] The diffusion coefficient found in this investigation is within two percent of the experimental diffusion coefficient reported by Jiang and Dong. Diffusion coefficients of electroactive species in aqueous solutions are generally higher, in the range of 1 to 2×10^{-5} cm^2/sec. The bulky structure and subsequent lower mobility of ascorbic acid may explain its low diffusion coefficient.

Homogeneous Oxidation of Ascorbic Acid

The consumption rate of ascorbic acid in homogeneous oxidation reactions was investigated in a citrate buffer solution (pH 6.4). The chemical oxidation of ascorbic acid was studied in three sets of experiments, designed to simulate electroless bath conditions and determine the effect of each bath condition on the consumption of ascorbic acid. The effect of the presence of an immersed gold substrate or an additional co-oxidant in the ascorbic acid solution was investigated by monitoring the ascorbic acid concentration. The homogeneous oxidation of ascorbic acid was studied under the following conditions:

- without a catalyst
- with a gold substrate as a heterogeneous catalyst
- with hydrogen peroxide as a co-oxidant

The homogeneous oxidation of ascorbic acid was expected to exhibit pseudo-first-order kinetics, based on past investigations.[20,27] The concentration of dissolved oxygen was assumed to be constant (see Ref. 20). All citrate buffer solutions (pH 6.4) were exposed to air for at least one day prior to experimentation. Mild agitation of the solutions was controlled by use of a magnetic stir bar or a rotating disk electrode. Ascorbic acid concentration was monitored with time by using cyclic voltammetry.

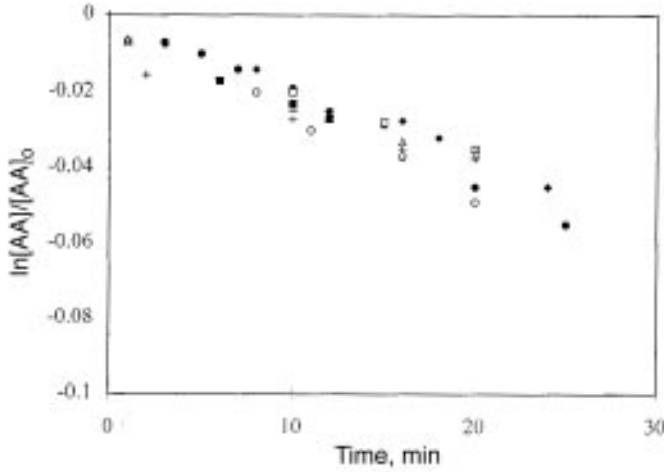


Fig. 6—Variation of the natural log of the normalized ascorbic acid concentration vs. time for ascorbic acid: 0.02 M ○, 0.04 M ●, 0.05 M ❑, 0.08 M ◊, 0.1 M Δ; 0.05 M ♦ ascorbic acid with gold substrate in solution, 0.05 M + ascorbic acid with 0.05 M hydrogen peroxide initially in solution; in a citrate buffer solution (pH 6.4) at 30 °C.

Results from the homogeneous oxidation of ascorbic acid confirm that the rate is pseudo-first-order at dissolved oxygen concentration. That is, the natural logarithm of ascorbic acid concentration varies linearly with time, as shown in Fig. 6. Experiments were done with several initial ascorbic acid concentrations. The ascorbic acid concentration decreased by five percent in 30 min. The slope of the data set was used to calculate a first-order rate constant of $1.75 \times 10^{-3} \pm 3.184 \times 10^{-4}$ ($\pm 2\sigma$)/min. This value of the first-order rate constant at pH 6.4 is close to those reported at other pH values. The rate constants at pH 6 and 9 have been reported to be 1.4×10^{-3}/min and 1.8×10^{-3}/min, respectively.[20,27] It should be noted that at higher temperatures, the homogeneous air oxidation rate constant will increase and the solubility of oxygen in the bath will decrease. At decreased oxygen levels, this reaction may become mass-transfer-limited and the dissolved oxygen concentration will be dependent upon agitation. At 30 °C, the homogeneous oxidation reaction is kinetically controlled (*i.e.*, independent of agitation rates).

Because ascorbic acid can undergo oxidation via peroxide [Eq. (5)] the consumption rate of ascorbic acid in the hydrogen peroxidation reaction is of interest. The concentration of ascorbic acid with added hydrogen peroxide was monitored, using the rotating disk electrode. The oxidation of ascorbic acid in the presence of hydrogen peroxide did not occur faster than in the presence of dissolved oxygen, as shown in Fig. 6.

In a separate set of experiments, the rate of oxidation of ascorbic acid was evaluated in the presence of a gold substrate. The addition of a gold substrate had no significant effect on the consumption of ascorbic acid (see Fig. 6). The results show that ascorbic acid is primarily oxidized by dissolved oxygen and is unaffected by the presence of hydrogen peroxide or a gold substrate. Consequently, the primary route to the chemical oxidation of ascorbic acid is by oxidation via dissolved oxygen and not via peroxide intermediates. The presence of gold surfaces, as would be present during electroless plating, had no noticeable effect on the homogeneous chemical decomposition route. The replenishment schedule for ascorbic acid need consider only the heterogeneous rate consumption resulting in electroless plating, and the homogeneous oxidation via oxygen (with a pseudo-first-order rate constant, given above) that can be altered by purging the solution of dissolved air and solution drag-out.

Conclusions

Ascorbic acid is a non-toxic reducing agent with a redox potential suitable for electroless processes. Ascorbic acid is electrochemically oxidized on an oxide-free gold substrate in a two-electron-transfer reaction. The diffusion coefficient was measured to be 6.46 x 10^{-6} cm^2/sec. The homogeneous oxidation of ascorbic acid proceeds via dissolved oxygen and is not affected by peroxide intermediates or the presence of gold surfaces. The rate constant for the homogeneous air oxidation was measured to be 1.75 x 10^{-3}/min, which is a five percent decrease in ascorbic acid concentration in 30 min at 30 °C. The rate increases with higher temperature; however, the solubility of oxygen decreases with temperature. Because the homogeneous oxidation reaction is kinetically controlled, a higher agitation rate should increase the electrochemical reaction rate without affecting the homogeneous oxidation rate. At this rate, frequent replenishment of ascorbic acid is necessary for long term use of an ascorbic acid electroless bath.

[a] *Model AFASR, Pine Instruments.*
[b] *Model 175, EG&G Princeton Applied Research, Princeton, NJ.*
[c] *Model 366, EG&G Princeton Applied Research, Princeton, NJ.*
[d] *Model 7090, Hewlett Packard, Palo Alto, CA.*

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