UCRL-LR-106479
Distribution Category UC-401

Initial Study of the Complete Mediated Electrochemical Oxidation of Ethylene Glycol

Joseph C. Farmer, Robert G. Hickman, Francis T. Wang,
Patricia R. Lewis, and Leslie J. Summers

Manuscript date: January 10, 1991

LAWRENCE LIVERMORE NATIONAL LABORATORY
University of California • Livermore, California • 94551

Contents

Abstract 1
Introduction 1
Process Chemistry and Reaction Kinetics 1
- Loss of Ag(II) by Reduction with Water 2
- Oxidation of Ethylene Glycol by Ag(II) 3
- Oxidation of Aldehyde 5
- Oxidation of Formic Acid by Ag(II) 6
- Quantitative Values of Equilibrium and Rate Constants 7

Model of the Rotating-Anode Electrochemical Reactor 8
- Differential Mass Balance for Ag(II) 8
- Generation Term 8
- Loss of Ag(II) in Bulk Anolyte 10
- Loss of Ag(II) at Anode Surface 11
- Maximum Possible Steady-State Ag(II) Concentration 11
- Numerical Integration of Differential Equations 11
- Predictions Based on the Model 11

Experimental Measurements of Overall Rates of Oxidation 14
Summary and Conclusions 17
Acknowledgments 17
References 18

Initial Study of the Complete Mediated Electrochemical Oxidation of Ethylene Glycol

Abstract

Mediated electrochemical oxidation (MEO) may be used in the future for ambient temperature destruction of hazardous waste and for converting mixed (hazardous and radioactive) waste to transuranic (TRU) waste. We have studied the MEO of ethylene glycol in an electrochemical reactor. The reactor had a rotating anode that was usually operated below the limiting current for Ag(II) generation. Rates of carbon dioxide generation were measured. A dynamic model of the rotating-anode electrochemical reactor was developed to predict the concentrations of ethylene glycol, carbon dioxide, chemical intermediates, and Ag(II) as functions of time. Intermediates are believed to include formaldehyde and formic acid.

Introduction

Mediated electrochemical oxidation (MEO) may be used for ambient temperature destruction of hazardous waste and for converting mixed (hazardous and radioactive) waste to transuranic (TRU) waste. Ag(II), generated by the anodic oxidation of Ag(I), can be used to oxidize organics dissolved in an aqueous phase.[1–6] Dissolved organics are ultimately converted to carbon dioxide and water in such a process. For mixed waste, Ag(II) also enhances the dissolution of actinide contamination for subsequent removal by ion exchange. Ambient temperature oxidation of mixed wastes avoids the possibility of high-temperature actinide volatilization during incineration.

We have studied the complete MEO of ethylene glycol to carbon dioxide. Partial oxidation of ethylene glycol had been studied previously.[6]

The electrochemical reactor used in this study had a rotating anode that operated well below the limiting current for Ag(II) generation. Rates of carbon dioxide generation were measured. A dynamic model of the rotating-anode electrochemical reactor was developed to predict the concentrations of ethylene glycol, carbon dioxide, chemical intermediates, and Ag(II) as functions of time. Intermediates may include formaldehyde and formic acid. Plausible reaction paths are shown in Fig. 1. Note that the overall reaction involves alternating hydrogen-extraction and oxygen-addition steps. Other experimental measurements were made to support the model and are also discussed. For example, we have determined the diffusivity of Ag(I) under relevant conditions.

Process Chemistry and Reaction Kinetics

Ag(II), in the form of Ag^{2+}, is generated by the anodic oxidation of Ag^{+}:

$$Ag^{+} \longrightarrow Ag^{2+} + e^{-} . \qquad (1)$$

In the absence of organics, most of the Ag(II) is present as a dark brown nitrate complex, $AgNO_3^{+}$:[7,8]

$$Ag^{2+} + NO_3^{-} \longrightarrow AgNO_3^{+} . \qquad (2)$$

The anodic reaction is balanced by the cathodic reduction of nitric acid:

$$HNO_3 + 2H^{+} + 2e^{-} \longrightarrow HNO_2 + H_2O . \qquad (3)$$

The nitric acid is regenerated by the chemical reaction of nitrous acid with oxygen:

$$2HNO_2 + O_2 \longrightarrow 2HNO_3 . \qquad (4)$$

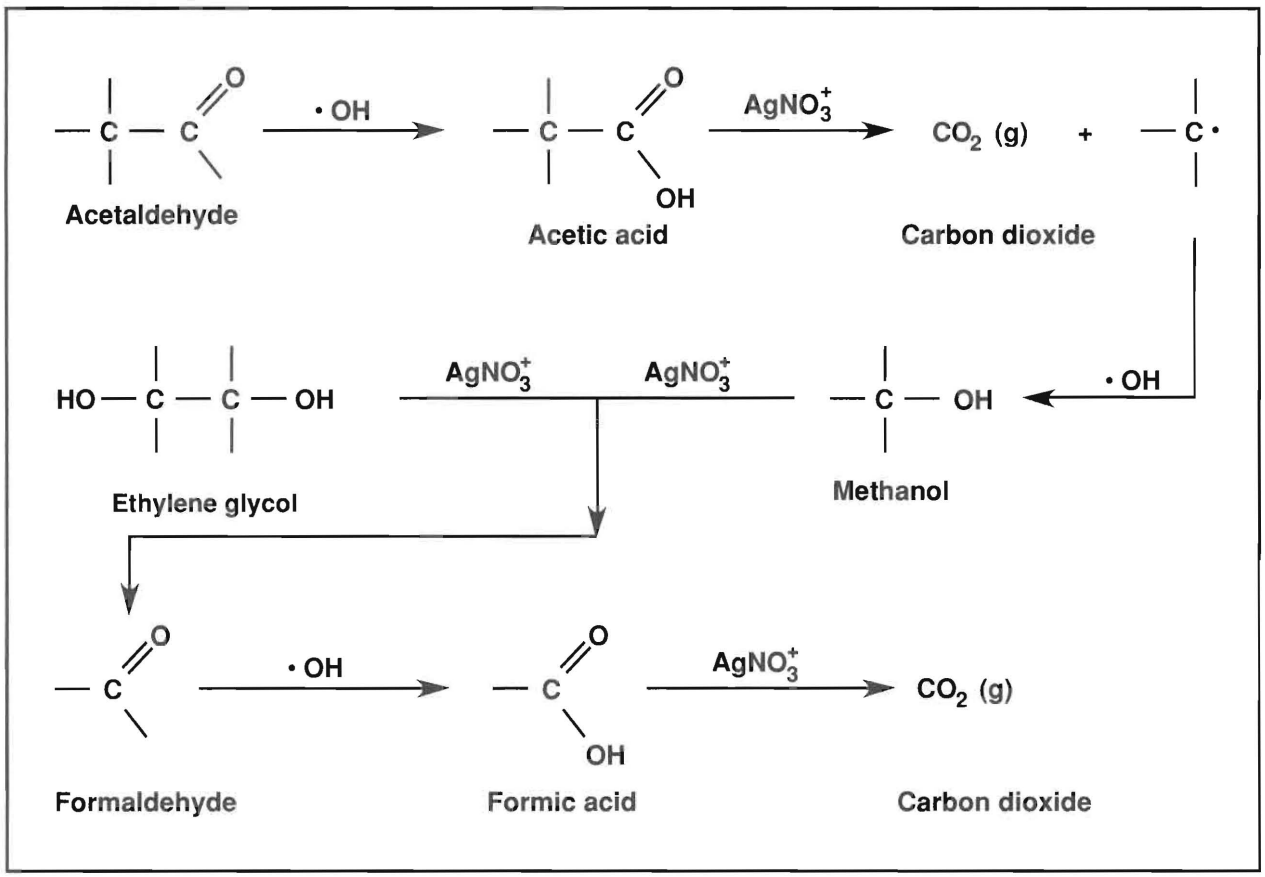

Figure 1. Plausible reaction paths for ethylene glycol and acetaldehyde involving possible intermediates such as formaldehyde and formic acid.

After generation, Ag(II) can be lost by any one of several homogeneous reactions. For example, consider the reaction with water:[7,8]

$$4AgNO_3^+ + 2H_2O \longrightarrow 4Ag^+ + O_2 + 4HNO_3 . \quad (5)$$

Ag(II) also reacts with dissolved organics to produce carbon dioxide, CO_2. The overall reaction for the oxidation of ethylene glycol is

$$10AgNO_3^+ + (CH_2OH)_2 + 2H_2O \longrightarrow 10Ag^+ + 2CO_2 + 10HNO_3 . \quad (6)$$

Formic acid is believed to be an intermediate formed during the oxidation of ethylene glycol; however, this has not yet been verified. Oxidation of this intermediate involves only two electrons and is relatively easy:

$$2AgNO_3^+ + HCOOH \longrightarrow 2Ag^+ + CO_2 + 2HNO_3 . \quad (7)$$

Oxidation of benzene is much more difficult since at least thirty electrons are required:

$$30AgNO_3^+ + C_6H_6 + 12H_2O \longrightarrow 6CO_2 + 30Ag^+ + 30HNO_3 . \quad (8)$$

Loss of Ag(II) by Reduction with Water

The kinetics of Ag(II) reduction by water have been thoroughly studied by Po, Swinehart,

Substituting the equilibrium expression for $[Ag\text{-}(CH_2OH)_2^{2+}]$, Eq. 29:

$$\frac{d[(CH_2OH)_2]}{dt} = -kK_{eq}K_1[Ag^{2+}][(CH_2OH)_2] . \quad (35)$$

The equilibrium expression for Ag^{2+}, Eq. 33, is substituted into the rate expression for the oxidation of ethylene glycol by Ag(II), Eq. 35:

$$\frac{d[(CH_2OH)_2]}{dt} = \frac{-kK_{eq}K_1[Ag(II)][(CH_2OH)_2]}{\left\{1 + \frac{K_h}{[H^+]} + K_4[NO_3^-] + K_{eq}K_1[(CH_2OH)_2]\right\}} . \quad (36)$$

Assuming that all of the Ag^{2+} is complexed, we find that

$$\frac{d[(CH_2OH)_2]}{dt} = \frac{-kK_{eq}\,K_1[Ag(II)][(CH_2OH)_2]}{\left\{\frac{K_h}{[H^+]} + K_4[NO_3^-] + K_{eq}\,K_1[(CH_2OH)_2]\right\}} . \quad (37)$$

The partial oxidation of diols by oxidizing agents such as HIO_4 is discussed by Morrison and Boyd.[9] The generalized unbalanced reaction is

$$(RCHOH)(R'CHOH) + HIO_4 \rightarrow RCOOH + R'COOH . \quad (38)$$

In this case, the oxidizing agent extracts a proton and provides oxygen to the aliphatic carbon atoms. The electrophilic action of the HIO_4 weakens the C—C bond, thereby promoting disintegration of the molecule. From a mechanistic point-of-view, this reaction is very different from the one involving Ag(II), since oxygen is probably not provided directly by the $AgNO_3^+$ complex.

Oxidation of Aldehyde

The oxidation of ethylene glycol generates either two molecules of formaldehyde or an aldehyde-like intermediate. This intermediate is then oxidized by oxygen-bearing species generated during the reduction of Ag(II) by water:

$$CH_2O + \tfrac{1}{2}O_2 \rightarrow HCOOH . \quad (39)$$

We assume that the empirical rate of reaction is

$$\frac{d[CH_2O]}{dt} = -k_2''\,[CH_2O][Ag(II)]. \quad (40)$$

The rate of generation of the oxygen-bearing species, represented by "O," is proportional to the rate of Ag(II) reduction by water:

$$\frac{d[O]}{dt} = 2k_{II}[Ag(II)]^2. \quad (41)$$

Therefore, we expect that the maximum electrochemically enhanced rate of oxidation of formaldehyde (or aldehyde-like intermediate) is

$$\frac{d[CH_2O]}{dt} < \frac{d[O]}{dt} . \quad (42)$$

The oxidation of formaldehyde by a hexavalent chromium compound, H_2CrO_4, is discussed by Morrison and Boyd.[10] The general reaction is

$$RCHO + H_2CrO_4 \longleftrightarrow (RHCOOH)(CrO_3H) , \quad (43)$$

followed by

$$(RHCOOH)(CrO_3H) \longleftrightarrow RCOOH + H_2CrO_3 . \quad (44)$$

Cr(VI) is reduced to Cr(IV). Unlike Ag(II), this Cr(VI) compound can provide oxygen directly to the aldehyde molecule. In addition to Cr(VI), Tollen's reagent can be used to oxidize aldehydes.[10] The overall (unbalanced) reaction is

$$RCHO + Ag(NH_3)_2^+ \longrightarrow RCOOH + Ag . \quad (45)$$

This reaction is used to detect aldehydes and is probably analogous to the oxidation of aldehydes by Ag(II). Oxygen is not supplied directly by the Tollen's reagent, $Ag(NH_3)_2^+$.

Oxidation of Formic Acid by Ag(II)

The next step toward the complete conversion of ethylene glycol to carbon dioxide probably involves the oxidation of formic acid. The oxidation of formic acid by Ag(II) is relatively simple and the kinetics have been investigated by Miller and Morrow.[10] We assume that the reaction step represented by Eq. 46 is rate limiting and that the reaction step represented by Eq. 47 is very fast:

$$Ag^{2+} + HCO_2^- \xrightarrow{k_1} Ag^+ + HCO_2\bullet \ . \qquad (46)$$

$$Ag^{2+} + HCO_2\bullet \longrightarrow Ag^+ + H^+ + CO \ . \qquad (47)$$

The rate expression for oxidation of formic acid is

$$\frac{d[HCOOH]}{dt} = -k_1[Ag^{2+}][HCO_2^-] \ . \qquad (48)$$

The dissociation of formic acid, Eq. 49, and the complexation of Ag^{2+} with nitrate ion, Eq. 50, are assumed to be at equilibrium.

$$HCOOH \xleftrightarrow{K_3} H^+ + HCO_2^- \ . \qquad (49)$$

$$Ag^{2+} + NO_3^- \xleftrightarrow{K_4} AgNO_3^+ \ . \qquad (50)$$

From the equilibrium between HCO_2^- and HCOOH, we know

$$[HCO_2^-] = \frac{K_3[HCOOH]}{[H^+]} \ . \qquad (51)$$

By substituting Eq. 51 into Eq. 48, the following rate expression for the oxidation of formic acid is derived:

$$\frac{d[HCOOH]}{dt} = \frac{-k_1K_3[Ag^{2+}][HCOOH]}{[H^+]} \ . \qquad (52)$$

In addition to the equilibria represented by Eqs. 49 and 50, others may also be important. For example, we should consider equilibria for $Ag\text{-}(CH_2OH)_2^{2+}$ and $AgOH^+$. From the equilibrium between Ag^{2+} and all forms of Ag(II), Eq. 33, we know

$$[Ag^{2+}] = \frac{[Ag(II)]}{\left\{1 + \left(\frac{K_h}{[H^+]}\right) + K_4[NO_3^-] + K_{eq}K_1[(CH_2OH)_2]\right\}} \ . \qquad (53)$$

By substituting Eq. 53 into Eq. 54, the rate equation for formic acid oxidation becomes

$$\frac{d[HCOOH]}{dt} = \frac{-k_1K_3[Ag(II)][HCOOH]}{\left\{1 + \frac{K_h}{[H^+]} + K_4[NO_3^-] + K_{eq}K_1[(CH_2OH)_2]\right\}[H^+]} \ . \qquad (54)$$

If $[Ag\text{-}(CH_2OH)_2^{2+}]$ and $[AgOH^+]$ are ignored, the equation becomes

$$\frac{d[HCOOH]}{dt} = \frac{-k_1K_3[Ag(II)][HCOOH]}{\{1+K_4[NO_3^-]\}[H^+]} \ , \qquad (55)$$

which can be found in the literature.[10] The rate of CO_2 evolution is simply

$$\frac{d[CO_2]}{dt} = \frac{-d[HCOOH]}{dt} \ . \qquad (56)$$

The maximum overall rate of loss of Ag(II) is calculated from the sum of individual rates of reaction:

$$\sum_{j=1}^{3} m_j r_j = 2\left\{\frac{d[(CH_2OH)_2]}{dt} + \frac{d[O]}{dt} + \frac{d[HCOOH]}{dt}\right\} \qquad (57)$$

where r_j is the rate of reaction of the j-th species with Ag(II) and m_j is the corresponding stoichiometric coefficient of Ag(II).

Quantitative Values of Equilibrium and Rate Constants

Values of equilibrium and rate constants for the oxidation of ethylene glycol and formic acid have been found in the literature, for at least one temperature. Data are summarized in Table 1.

The temperature dependence of a typical equilibrium constant, K, is

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{58}$$

where ΔH° and ΔS° are the enthalpy and entropy changes, respectively. If the equilibrium constant is known at two temperatures, we can write

$$\ln \frac{K}{K'} = \frac{\Delta H^\circ}{R}\left(\frac{T - T'}{T\,T'}\right). \tag{59}$$

The enthalpy change is then

$$\Delta H^\circ = R\left(\frac{T\,T'}{T - T'}\right)\ln \frac{K}{K'}. \tag{60}$$

For example, values of K_h at 283 K (10°C) and 293 K (20°C) can be used to estimate the enthalpy, ΔH° = 11,961 cal/mol. The temperature-dependent expression for K_h is

$$K_h = 0.15 \times 10^{-3} \times \exp\left[\frac{6020(T - 283)}{(283 \times T)}\right] (\text{mol cm}^{-3}). \tag{61}$$

Similar temperature dependence is assumed for the other equilibrium constants:

$$K = 2.3 \times 10^{5} \times \exp\left[\frac{6020(T - 283)}{(283 \times T)}\right] (\text{cm}^3\ \text{mol}^{-1}), \tag{62}$$

$$K_3 = 1.8 \times 10^{-7} \times \exp\left[\frac{6020(T - 298)}{(298 \times T)}\right] (\text{mol cm}^{-3}), \tag{63}$$

and

$$K_4 = 9.4 \times 10^{2} \times \exp\left[\frac{6020(T - 298)}{(298 \times T)}\right] (\text{cm}^3\ \text{mol}^{-1}). \tag{64}$$

The Ahrenius-like temperature dependence of a typical reaction rate constant is

$$\ln \frac{k}{k'} = E_a\,\frac{(T - T')}{T\,T'}. \tag{65}$$

If we assume reasonable activation energies, 25 kcal/mol, for the rate constants, k and k' can be written as

$$k = 13.8 \exp\left[\frac{12582(T - 283)}{(283 \times T)}\right] (\text{s}^{-1}) \tag{66}$$

and

$$k_1 = 3.9 \times 10^{8} \times \exp\left[\frac{12582(T - 298)}{(298 \times T)}\right] (\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}). \tag{67}$$

Table 1. Values of equilibrium and rate constants from literature.

Constant	Value	Units	T(°C)	Reference
K	0.15×10^{-3}	mol cm^{-3}	10	[6]
	0.31×10^{-3}	mol cm^{-3}	20	[6]
K_1K_{eq}	2.32×10^5	cm^3 mol^{-1}	10	[6]
K_3	1.77×10^{-7}	mol cm^{-3}	25	[5]
K_4	0.94×10^3	cm^3 mol^{-1}	25	[5]
	3.90×10^3	cm^3 mol^{-1}	25	[5]
k	13.8	s^{-1}	10	[6]
k_1	3.9×10^8	cm^3 mol^{-1} s^{-1}	25	[5]
k_2''	1.0×10^5	m^3 mol^{-1} s^{-1}	25	assumed

The rates of individual organic oxidation reactions have not yet been verified. Future studies may include spectrophotometric studies of Ag(II)-organic reactions. Activation energies will be determined during these more fundamental studies.

Model of the Rotating-Anode Electrochemical Reactor

A theoretical model of the rotating-anode electrochemical reactor has been developed that accounts for both generation of Ag(II) by anodic oxidation of Ag(I),[11] as well as simultaneous loss of Ag(II) by reaction with water[7,8] and organics.[5,6] Ag(II) generation is limited by the Ag(I) mass-transport rate at the anode surface. The maximum possible flux can be calculated from the Nusselt number, which can be estimated from the Reynolds and Schmidt numbers. A dimensionless correlation for rotating cylinders was used.[12] The anolyte is assumed to be turbulent and well mixed. The model is capable of dealing with two scenarios, high and low ethylene glycol concentrations, respectively. At high organic concentrations, Ag(II) is completely consumed in a thin film of anolyte at the anode surface. At low organic concentrations, significant levels of Ag(II) exist in the bulk anolyte and oxidation reactions occur in the entire liquid volume. Ordinary differential equations representing transient concentrations are integrated simultaneously by application of a fourth-order Runge-Kutta algorithm.

Differential Mass Balance for Ag(II)

The dynamic model for the rotating-anode electrochemical reactor is based on a differential mass balance for Ag(II) and organics. The rate of accumulation of the i-th reactant in the anolyte is equivalent to the difference between generation and loss terms:

$$V \frac{dC_i}{dt} = \text{Generation} - \text{Loss}. \tag{68}$$

where V is the volume of anolyte and C_i is the concentration of the i-th species.

Generation Term

The generation of Ag(II) is due to the anodic oxidation of Ag(I) at the surface of the cylindrical anode as shown in Fig. 2. This rate of generation is proportional to the current density, i, and the surface area of the cylindrical anode:

$$\text{Generation of Ag(II)} = (\pi d_R L)\frac{i}{\mathcal{F}} . \tag{69}$$

where d_R is the diameter of the anode, L is the length of the anode, and $\mathcal{F}$ is Faraday's constant. The maximum possible current density, known as the limiting current, i_L, is proportional to the diffusion-limited flux of Ag(I) to the anode surface, $N_{Ag(I)}$:

$$i_L = \mathcal{F} N_{Ag(I)} . \tag{70}$$

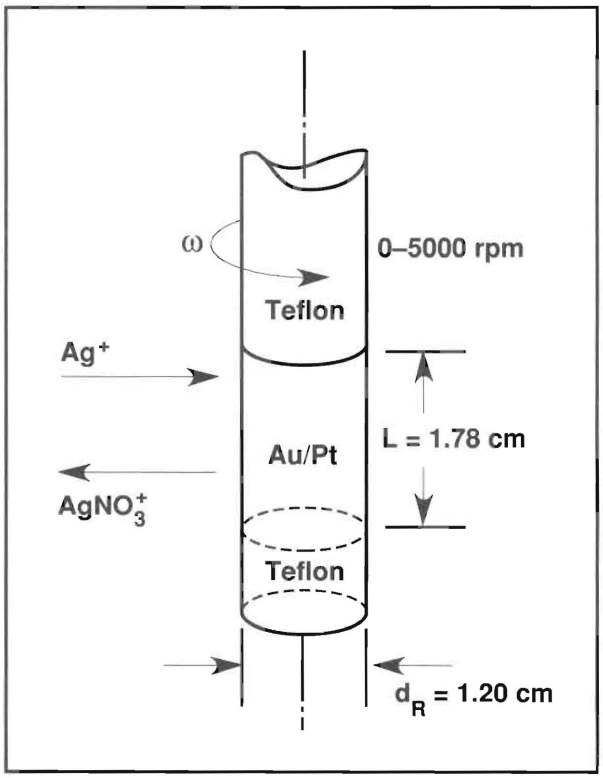

Figure 2. Sketch of rotating anode used for the Ag(II)-mediated electrochemical oxidation of ethylene glycol.

The flux is limited by the rate of Ag(I) transport through a Nernstian boundary layer separating the bulk electrolyte and the surface of the anode. The flux can be increased by reducing the thickness of the boundary layer which is usually done by increasing hydrodynamic flow. Hydrodynamic effects on flux are taken into account in the Nusselt number, Nu, for the anode:

$$N_{Ag(I)} = Nu\, D\, \frac{[Ag(I)]}{d_R} \,. \tag{71}$$

The dimensionless correlation for the Nusselt number of a rotating-cylinder anode is[12]

$$Nu = (0.0791) Re^{0.7} Sc^{\,0.356} \tag{72}$$

where Re and Sc are the Reynolds and Schmidt numbers respectively. The Reynolds number for a rotating cylinder is

$$Re = \frac{\omega\, d_R^{\,2}}{2\,(\mu/\rho)} \tag{73}$$

where ω is the angular frequency of rotation, d_R is the diameter of the anode, and ρ and μ are the density and viscosity of the anolyte, respectively. The Schmidt number represents the intrinsic transport properties of Ag(I) in the electrolyte and is calculated from μ, ρ, and D, the diffusivity of Ag(I):

$$Sc = \frac{(\mu/\rho)}{D} \,. \tag{74}$$

The Reynolds and Schmidt numbers can also be written in terms of the kinematic viscosity, ν, which is defined as μ/ρ.

The diffusivity of Ag(I) must be known before the limiting current can be estimated. A rotating disk electrode (RDE) was used to determine the limiting current for anodic oxidation of Ag(I). The RDE was polarized at +0.85 volts relative to a stable (pseudo) reference electrode, Pt in 3.25 M HNO_3. The rotation speed was varied from 25 to 1000 rpm. The diffusivity was estimated by fitting the Levich equation[10] to data like that shown in Figs. 3a and 3b. Note that $D^{2/3}$ is proportional to the slope of the plots, B.

$$B = 0.62(2\pi)^{1/2}\, \mathcal{F} D^{2/3} (\mu/\rho)^{-1/6} [Ag(I)] \,. \tag{75}$$

Data was obtained for several temperatures (4, 21, and 40°C). Results are summarized in Table 2. The diffusivity was found to obey the following empirical relationship:

$$D = 0.581 \times 10^{-5} - 0.304 \times 10^{-7}\, T - 0.279 \times 10^{-9}\, T^2 + 0.113 \times 10^{-9}\, T^3 \tag{76}$$

where, in this particular case, T is the anolyte temperature in degrees Centigrade (°C). The diffusivity has a greater dependance on temperature than expected. To calculate the diffusivity from the slope, the density and the viscosity must be known. Empirical

Table 2. Estimation of diffusivity from RDE data.

T(°C)	[Ag(I)](M)	B(C/cm$^2\sqrt{s}$)	D(cm^2/s)	Regression coefficient
4	0.01	1.100×10^{-3}	0.686×10^{-5}	0.976
	0.033	2.765×10^{-3}	0.527×10^{-5}	0.994
	0.05	4.494×10^{-3}	0.494×10^{-5}	0.995
21	0.01	1.137×10^{-3}	0.602×10^{-5}	0.982
	0.033	3.877×10^{-3}	0.694×10^{-5}	0.995
	0.05	4.928×10^{-3}	0.533×10^{-5}	0.990
40	0.01	1.737×10^{-3}	1.142×10^{-5}	0.997

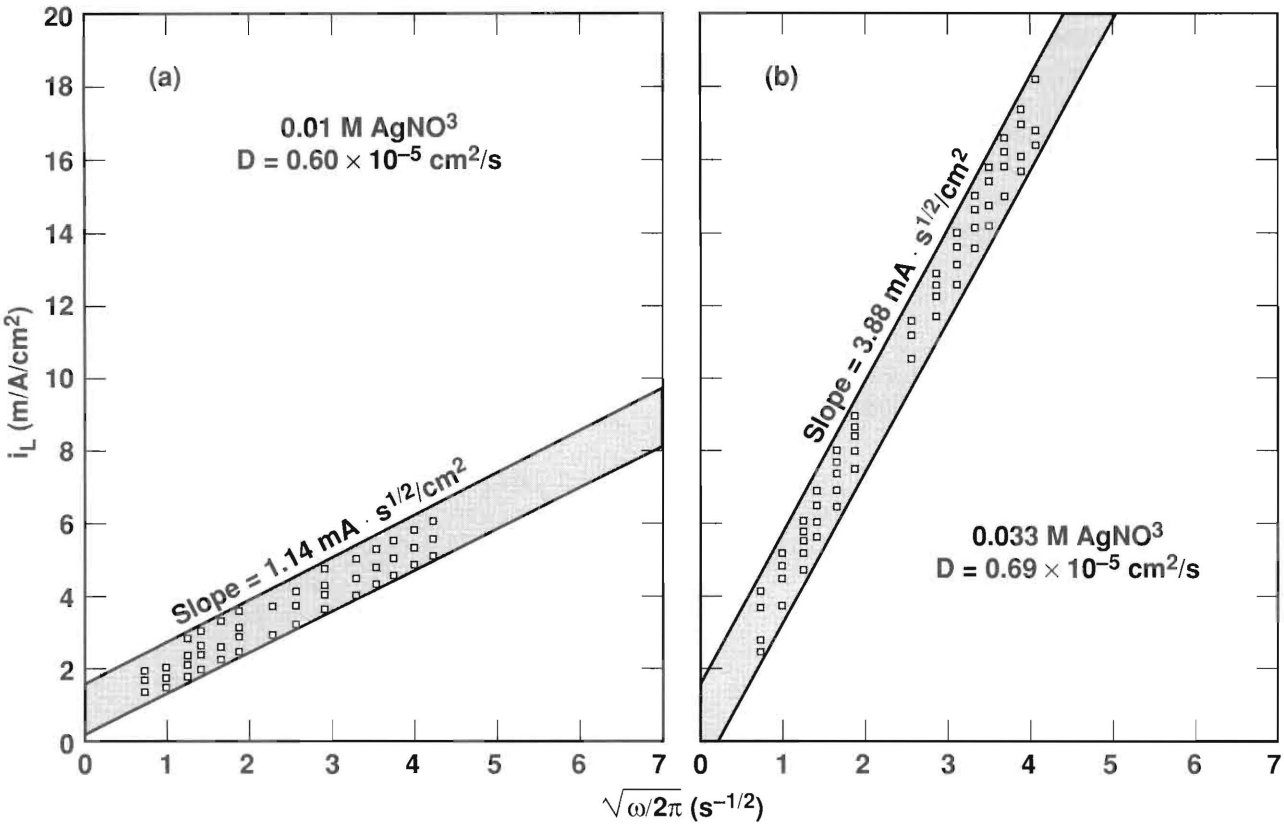

Figure 3. (a) Limiting current of a platinum rotating disk electrode vs the square root of the rotation speed. The electrode had an active diameter of 0.127 cm. The electrode consisted of 0.01 *M* $AgNO_3$ and 3.25 *M* HNO_3 at 21°C. (b) Plot similar to that shown in (a), except the $AgNO_3$ concentration is 0.033 *M*.

expressions for the density and the viscosity of nitric acid have been established by fitting data published in various references:[13,14]

$$\rho = (1 + 0.6741\, X^{1.0988}) \exp[49.20(1/T - 1/293)]\ (\text{gm cm}^{-3})\ . \tag{77}$$

$$\mu = (1 + 3.2043\, X^{1.9037}) \exp[1723.24(1/T - 1/293)]\ (\text{cP})\ . \tag{78}$$

where X is the weight fraction of HNO_3 in the water-acid solution.

Loss of Ag(II) in Bulk Anolyte

After generation, Ag(II) can be reduced by any of several homogeneous reactions. The total rate of loss is proportional to the sum of all rates of reaction:

$$\text{Loss of Ag(II)} = V \sum_{j=1}^{m} m_j r_j\ . \tag{79}$$

Reduction of Ag(II) by water and other important chemical reactions have already been discussed. The differential equation used to predict the transient concentration of Ag(II) can be written as

$$V \frac{d[\text{Ag(II)}]}{dt} = (\pi d_R L)\,(i/\mathcal{F}) + V \sum_{j=1}^{m} m_j r_j\ . \tag{80}$$

This formulation is best when there is a significant concentration of Ag(II) in the bulk anolyte.

Loss of Ag(II) at Anode Surface

At high concentrations of organics, all of the Ag(II) reacts in a thin film of anolyte at the anode surface. The volume-average rate of oxidation of the i-th organic near the anode surface is

$$r_{s,i} = (1/V)\,(\pi\, d_R\, L)\,(i/\mathcal{F})\frac{k_i C_i}{\sum_{j=1}^{m} m_j k_j C_j} \,. \qquad (81)$$

Maximum Possible Steady-State Ag(II) Concentration

The maximum possible Ag(II) concentration can be reached in the absence of organics. This steady-state concentration can be calculated by setting the accumulation term in the differential mass balance, $d[\mathrm{Ag(II)}]/dt$, to zero. This condition requires that the rates of Ag(II) generation and loss be equivalent:

$$(\pi\, d_R\, L)(i_L/\mathcal{F}) = V\, k_{II}[\mathrm{Ag(II)}]^2 \,. \qquad (82)$$

Recall that the limiting current is

$$i_L = \mathcal{F} D\, [\mathrm{Ag(I)}]\, Nu/d_R \,. \qquad (83)$$

Also recall that the second order rate constant, k_{II}, is

$$k_{II} = \frac{\alpha}{\{1 + \beta\, [\mathrm{Ag(I)}]\, [\mathrm{H^+}]^2\}} \,. \qquad (84)$$

Substitution of the expressions for i_L and k_{II} into Eq. 82, the steady-state equation that defines the maximum possible Ag(II) concentration, leads to the following quadratic:

$$[\mathrm{Ag\,(II)}]^2 \left\{\frac{V\alpha}{\pi\, L\, D\, Nu} - \beta\, [\mathrm{H^+}]^2\right\}$$

$$\times\ [\mathrm{Ag(II)}]\{2\,\beta\, [\mathrm{H^+}]^2\, [\mathrm{Ag(I)}]_o + 1\}$$

$$-\ [\mathrm{Ag(I)}]_o\{\beta\, [\mathrm{H^+}]^2\, [\mathrm{Ag(I)}]_o + 1\} = 0 \qquad (85)$$

where $[\mathrm{Ag(I)}]_o$ is the initial concentration of $AgNO_3$. At any instant, $[\mathrm{Ag(I)}]_o$ is equivalent to [Ag(I)] and [Ag(II)]. The solution of this quadratic is

$$[\mathrm{Ag(II)}] = \frac{\sqrt{B^2 - 4AC} - B}{2A} \,, \qquad (86)$$

where

$$A = \frac{V\alpha}{\pi\, L\, D\, Nu} - \beta\, [\mathrm{H^+}]^2 \,,$$

$$B = \{2\,\beta\, [\mathrm{H^+}]^2\, [\mathrm{Ag(I)}]_o + 1\} \,,$$

and

$$C = -\,\{[\mathrm{Ag(I)}]_o(\beta\, [\mathrm{H^+}]^2\, [\mathrm{Ag(I)}]_o + 1)\} \,.$$

Numerical Integration of Differential Equations

The system of ordinary differential equations represented by Eq. 68 and Eq. 80 can be integrated numerically by application of a fourth-order Runge-Kutta algorithm, as discussed by Carnahan and Wilkes:[15]

$$C_{i,m+1} = (h/6)\{k_{1,i} + 2k_{2,i} + 2k_{3,i} + k_{4,i}\} \,, \qquad (87)$$

where $C_{i,m+1}$ represents the concentration of the i-th reactant at time t_{m+1}, h is the time increment from t_m to t_{m+1},

$$k_{1,i} = f\,(t_m;\, C_{i,m}) \,,$$

$$k_{2,i} = f\,(t_m + \{h/2\};\, C_{i,m} + \{h/2\}k_{1,i}) \,,$$

$$k_{3,i} = f\,(t_m + \{h/2\};\, C_{i,m} + \{h/2\}k_{2,i}) \,,$$

and

$$k_{4,i} = f\,(t_m + h;\, C_{i,m} + hk_{3,i}) \,.$$

The function of $f(t_m;\, C_{i,m})$ is equivalent to dC_i/dt. This algorithm is simultaneously executed for all reactants, including Ag(II), ethylene glycol, formaldehyde, formic acid, and carbon dioxide.

Predictions Based on the Model

Predictions based on the model are shown in Fig. 4. The assumed conditions are comparable to those used in our experiments. The electrolyte is 90 ml of 0.5 M $AgNO_3$, 3.25 M HNO_3, and 0.2 M ethylene glycol at 22°C. The rotating anode has a diameter of 1.2 cm and a length of 1.78 cm. The rotation speed is 1500 rpm. The current is either 336 or 673 mA. Calculations for an anolyte

temperature of 70°C were also done but are not shown. Conditions are summarized in Table 3. Predictions for 336 mA and 22°C are shown in Figs. 4a and 4b. Predictions shown in Fig. 4a assume that the ethylene glycol is converted to carbon dioxide via two intermediates, formaldehyde and formic acid. The rate of reaction of ethylene glycol with Ag(II) is large and consumes essentially all available Ag(II) at the anode surface. The point of complete glycol conversion coincides with the point of maximum formaldehyde concentration. After all of the glycol is reacted, there is enough Ag(II) available at the anode surface to oxidize formaldehyde to formic acid; thus, the formic acid concentration begins to increase. The maximum formic acid concentration is reached when the rates of generation and loss of formic acid are equivalent. The model predicts that the glycol will be completely oxidized to carbon dioxide after 14.25 hours. At this point, Ag(II) begins to accumulate in the bulk anolyte and reaches a steady-state concentration of almost 0.1 *M*. As discussed earlier, the steady state Ag(II) concentration is established when the rates of Ag(II) generation and loss from reaction with water are equivalent. This is possible after complete oxidation of the dissolved organics. In contrast to the predictions shown in Fig. 4a, the predictions shown in Fig. 4b assume that the ethylene glycol is instantaneously converted to carbon dioxide. In this case, there is no accumulation of formaldehyde or formic acid in the bulk electrolyte. Again, the time required to completely convert the ethylene glycol to carbon dioxide, is 14.25 hours and is limited by the Ag(II) generation rate.

Predictions for 673 mA and 22°C are shown in Fig. 4c and 4d. Qualitatively, results are similar to those for 336 mA and 22°C. However, the oxidation occurs twice as fast. All of the glycol is converted to carbon dioxide after about 7 hours. Predictions for 70°C are not shown, but are qualitatively similar to those for 22°C. There are quantitative differences, however. For example, the steady-state concentration of Ag(II) at 70°C, which is reached after complete oxidation of the organics, is lower than it is at 22°C.

Figure 5a shows calculated values of the maximum-possible steady-state Ag(II) concentrations in the absence of organics and at various combinations of anolyte temperature and anode speed. Calculations are based on Eq. 87. The maximum-possible steady-state Ag(II) concentration increases gradually with rotation speed and becomes less sensitive to temperature as the temperature increases. Figure 5b shows corresponding values of the limiting current density, i_L. Higher limiting current densities are reached at higher temperatures, due to the increase in diffusivity with temperature.

Table 3. Conditions assumed for predictive calculations.

T(°C)	$A \cdot i$ (mA)	Re	Sc	Nu	i_L(mA/cm^2)	i/i_L
22	336	11,510	1,582	758	189	0.265
22	673	11,510	1,582	758	189	0.530
70	336	25,470	108	509	840	0.060
70	673	25,470	108	509	840	0.119

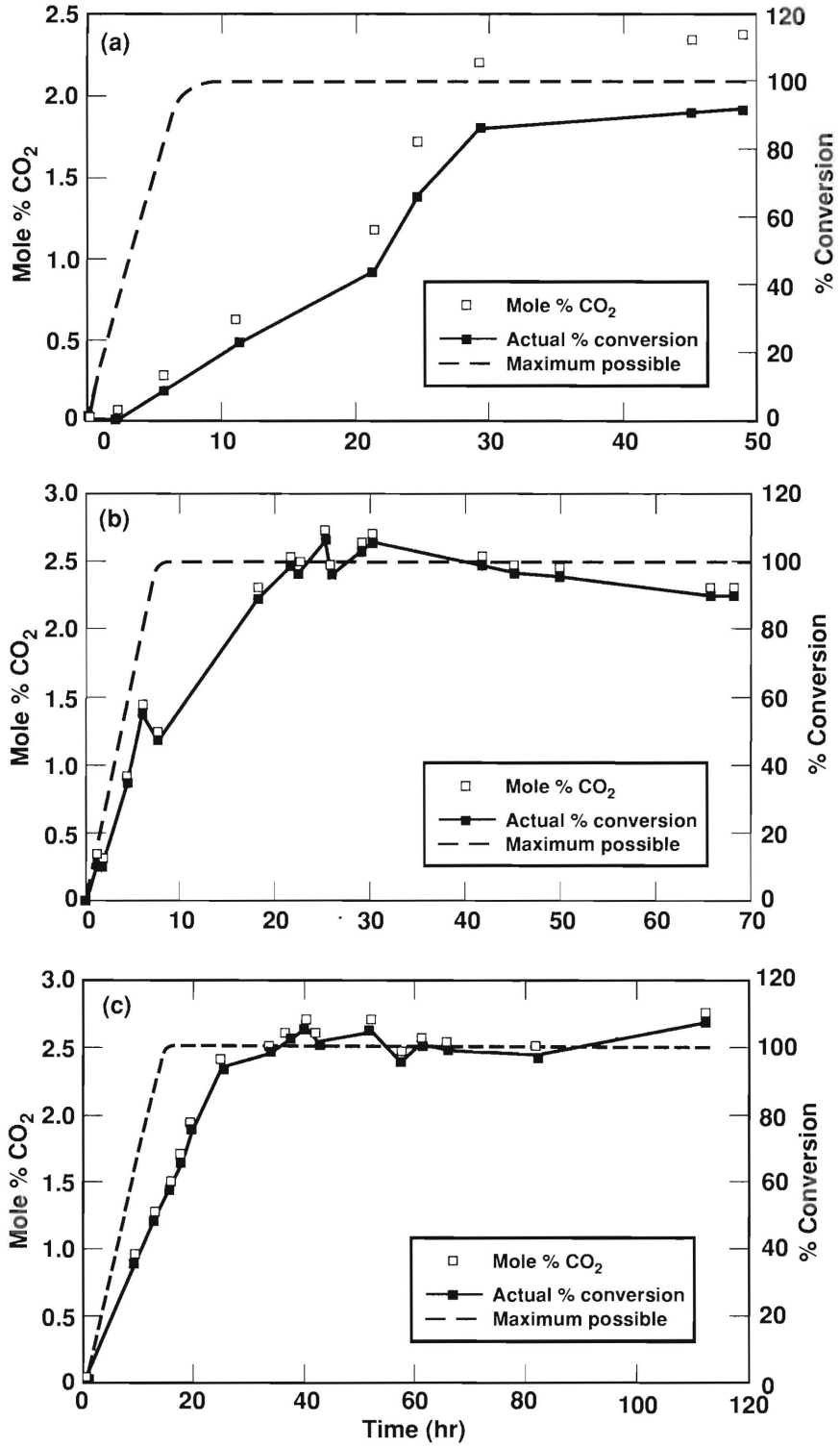

Figure 6. (a) Carbon dioxide evolution during the mediated electrochemical oxidation of ethylene glycol by Ag(II). The electrochemical reactor was charged with 90 ml of 0.5 *M* $AgNO_3$, 3.25 *M* HNO_3, and 0.2 *M* ethylene glycol. The anode was a rotating gold cylinder having a diameter of 1.2 cm and a length of 1.78 cm. The anolyte temperature, rotation speed of the anode, and cell current were 22°C, 1500 rpm, and 673 mA, respectively. These conditions correspond to 53% of the limiting current for Ag(II) generation. Carbon dioxide concentrations, as well as ethylene glycol conversions calculated from the concentrations, are shown. (b) Data from experiment at same conditions as Fig. 6a, except at 70°C. A current of 673 mA corresponds to 11.9% of the limiting current at 70°C. (c) Data from experiment at same conditions as Fig. 6a, except at 336 mA and 70°C. A current of 336 mA corresponds to 6% of the limiting current at 70°C.

Table 4. Times required for ethylene glycol conversion.

T(°C)	$A \cdot i$ (mA)	i/i_L	Actual (h)	Predicted (h)	Efficiency (%)
22	673	0.530	>27	7.11	<26
70	673	0.060	20	7.11	36
70	336	0.119	37	14.25	39

Table 5. Times required for formic acid conversion.

T(°C)	$A \cdot i$ (mA)	i/i_L	Actual (h)	Predicted (h)	Efficiency (%)
22	673	0.530	12	1.3	11
70	673	0.119	5	1.3	26

Such inefficiency will have a profound effect on process economics and will have to be studied in greater detail. Compare the times required for conversion at 336 mA and 22°C to that required for conversion at 336 mA and 70°C. The time required for conversion is independent of temperature and is proportional to cell current. We conclude that the oxidation rate is limited by the Ag(II) generation rate.

Formic acid is probably an intermediate in the mediated electrochemical oxidation of ethylene glycol. Therefore, we decided to include formic acid in our experimental study. Data was obtained at the same conditions as summarized in Table 3. Results are shown in Fig. 7 and summarized in Table 5.

The actual time required to convert formic acid to carbon dioxide was much longer than expected. As in the case of ethylene glycol, Ag(II) generated in the electrochemical cell was not used efficiently to oxidize the formic acid substrate. The process is about 26% efficient at 70°C, based on the rate of generation of Ag(II). Despite low efficiency, formic acid is converted to carbon dioxide more quickly than ethylene glycol.

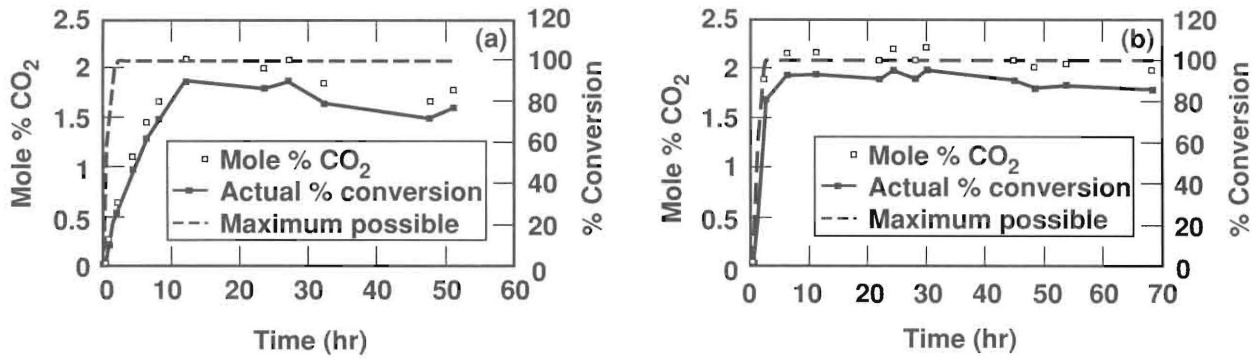

Figure 7. (a) Carbon dioxide evolution during the mediated electrochemical oxidation of formic acid by Ag(II). The electrochemical reactor was charged with 90 m. of 0.5 M $AgNO_3$, 3.25 M HNO_3, and 0.36 M formic acid. The anode was a rotating gold cylinder having a diameter of 1.2 cm and a length of 1.78 cm. The anolyte temperature, rotation speed of the anode, and cell current were 22°C, 1500 rpm, and 673 mA, respectively. These conditions correspond to 53% of the limiting current for Ag(II) generation. Carbon dioxide concentrations, as well as ethylene glycol conversions calculated from the concentrations, are shown. (b) Data from experiment at same conditions as Fig. 7a, except at 70°C. A current of 673 mA corresponds to 11.9% of the limiting current at 70°C.

Summary and Conclusions

We have studied the MEO of a typical aliphatic organic in a rotating-anode electrochemical reactor. Complete oxidation of the organic was demonstrated and significant insight into the MEO process has been gained. A model has been developed that is based on published kinetic rate constants and measured mass-transfer coefficients. Predictions agree qualitatively with experimental data. By adjusting model parameters, taking into account the observed inefficiency in the process, quantitative agreement can be achieved. This model can be used as a basis for designing large-scale electrochemical reactors. Dimensionless correlations for other types of electrochemical reactors can also be incorporated into the model.

Acknowledgments

The technical guidance of Hao-Lin Chen and Leonard Gray is gratefully acknowledged. The authors thank David R. Gardner for the editing and production coordination of this manuscript.

References

1. D. F. Steele, "Electrochemical Destruction of Toxic Organic Industrial Waste," *Platinum Metals Review*, **34**, 1 (1990) 10-14.
2. E. J. Wheelwright, L. A. Bray, J. L. Ryan, "Apparatus and Method for Dissolving Hazardous Waste Materials by Catalyzed Electrochemical Dissolution," International Application No. PCT/US89/01374, Published Under the Patent Cooperation Treaty, April 3 (1989); International Publication No. WO 89/10981, November 16 (1989).
3. P. M. Molton, A. G. Fassbender, S. A. Nelson, J. K. Cleveland, "Hazardous Organic Waste Destruction by Electrochemical Oxidation," presented at 13th Annual Environmental Quality R&D Symposium, Battelle Pacific Northwest Hazardous Waste RD&D Center, Richland, Washington, November (1988).
4. R. C. Schothorst, G. Den Boef, "The Application of Strongly Oxidizing Agents in Flow Injection Analysis, Part IV. Silver (II)," *Analytica Chimica Acta*, **169** (1985) 99-107.
5. L. Miller, J. I. Morrow, "Kinetics of the Oxidation of Formic Acid by Silver(II) in Nitric Acid Media," *Inorganic Chemistry*, **15**, 8 (1976) 1797-1799.
6. E. Mentasti, L. J. Kirschenbaum, "Oxidation of Organic Compounds by Silver (II). Reactions of Aliphatic Diols and α-Hydroxy Acids," *Inorganica Chimica Acta*, **134** (1987) 283-288.
7. H. N. Po, J. H. Swinehart, T. L. Allen, "The Kinetics and Mechanism of the Oxidation of Water by Silver(II) in Concentrated Nitric Acid Solution," *Inorganic Chemistry*, **7**, 2 (1968) 244-249.
8. J. C. Farmer et al., "Design of Electrochemical Reactor for Enhanced Dissolution of Plutonium Oxide," presented at *The 178th Meeting of the Electrochemical Society*, Seattle, WA, *Extended Abstracts*, Vol. 90-2, Abs. No. 724, October 14-19 (1990) 1031-1032.
9. R. T. Morrison, R. N. Boyd, *Organic Chemistry*, 3rd Ed., Allyn & Bacon, Inc., Boston, MA, 1973, p. 538.
10. Ibid., pp. 634-635.
11. M. Fleischmann, D. Pletcher, A. Rafinski, "The Kinetics of the Silver (I)/Silver (II) Couple at a Platinum Electrode in Perchloric and Nitric Acids,"*Journal of Applied Electrochemistry*, **1** (1971) 1-7.
12. J. S. Newman, *Electrochemical Systems*, Prentice Hall, Englewood Cliffs, New Jersey (1973) 324-326.
13. A. V. Wolf, M. G. Brown, P. G. Prentiss, "Concentrative Properties of Aqueous Solutions, No. 38, Nitric Acid," *CRC Handbook of Chemistry and Physics*, 61st Ed., R. C. Weast, M. J. Astle, Eds., Chemical Rubber Company Press, Boca Raton, Florida (1980) D-247.
14. C. O. Bennet, J. E. Myers, *Momentum, Heat, and Mass Transfer*, McGraw-Hill, San Francisco (1974) 775, 777.
15. B. Carnahan, J. O. Wilkes, *Digital Computing and Numerical Methods*, John Wiley and Sons, New York (1973) 389-391.