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Initial Study of Halide-Tolerant Mediators for the Electrochemical Treatment of Mixed and Hazardous Wastes

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Patricia R. Lewis, Leslie J. Summers, and Linda Foiles**

June 20, 1991



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Abstract

Mediated electrochemical oxidation is an ambient-temperature aqueous-phase process that can be used to oxidize organic components of mixed (hazardous and radioactive) wastes. Problems associated with incineration, such as high-temperature volatilization of radionuclides, are avoided. Historically, Ag(II) has been used as a mediator in this process. Fe(VI) and Co(III) are attractive alternatives to Ag(II) since they are tolerant of halide ions liberated during the destruction of halogenated organics. Quantitative data has been obtained for the complete oxidation of ethylene glycol by Fe(VI) and Co(III). Though ethylene glycol is a nonhalogenated organic, this data has enabled engineers to make direct comparisons of activities of Fe(VI), Co(III), and Ag(II). Very good quantitative data for the oxidation of ethylene glycol by Ag(II) had already been collected.

Introduction

We are developing an ambient-temperature aqueous process, known as mediated electrochemical oxidation (MEO), for the treatment of mixed wastes. Mixed wastes may contain both organic and radioactive components. MEO can be used to oxidize organic components of mixed wastes, thereby reducing the total volume that has to be transported and stored. Treatment of mixed wastes in a condensed phase at ambient temperature prevents high-temperature volatilization of radionuclides, a problem that may be encountered during incineration.

In previous studies, electrochemically-generated Ag(II) has been used to completely oxidize dissolved organics such as ethylene glycol and benzene.¹⁻⁴ Ag(II) is a very effective oxidizing agent for the destruction of nonhalogenated organic compounds. Unfortunately, halide ions liberated during the destruction of

halogenated organics react with Ag(II) to form insoluble precipitates. Therefore, it has been necessary to investigate other mediators (powerful oxidizing agents) that are tolerant of halide anions. Fe(VI) and Co(III) satisfy this criteria.

As a first step in the investigation, we have studied the MEO of ethylene glycol by Fe(VI) and Co(III). Quantitative data already exists for the oxidation of ethylene glycol by Ag(II) and can be used as a basis of comparison. The reactor had a rotating-cylinder anode that was operated well below the limiting current for mediator generation. Rates of carbon dioxide evolution were measured. It is believed that ethylene glycol is converted to carbon dioxide via two intermediates, formaldehyde and formic acid.¹ Gas chromatography with mass spectrometry (GC/MS) was used to determine reaction intermediates.

Measurements of Carbon Dioxide Evolution

Ethylene glycol was oxidized to carbon dioxide at near-ambient temperature in an electrochemical reactor charged with 40 ml of anolyte. Three different anolyte compositions were explored: (a) 0.5 M $\text{Co}(\text{NO}_3)_2$, 3.25 M HNO_3 , and 0.22 M ethylene glycol; (b) 0.5 M $\text{Fe}(\text{NO}_3)_3$, 3.25 M HNO_3 , and 0.22 M ethylene glycol; and (c) 0.5 M $\text{Fe}(\text{NO}_3)_3$, 8 M HNO_3 , and 0.22 M ethylene glycol. The anode was a platinum rotating-cylinder having a diameter of 1.2 cm and a length of 1.78 cm. The rotation speed of the anode was maintained at 1500 rpm. The cell current was maintained well below the limiting current for mediator generation, approximately 673 mA. Elevations of the anolyte temperature above ambient (38–64°C) were due to ohmic heating in the cell. A stationary platinum cathode was separated from the anode by a perfluorinated sulfonic acid cation-exchange membrane (Nafion 117). Reactions were conducted in a closed vessel so that all carbon dioxide could be captured. The volume of this container was 38.2 liters, which corresponds to approximately 1.5 moles of gas at ambient temperature and pressure. Carbon dioxide concentrations in the gas phase were periodically determined by mass spectrometry and used to calculate percentage conversion of the organic substrate.

Cobalt System. Measurements of carbon dioxide evolution during mediated electrochemical oxidation of ethylene glycol by Co(III) were made during two experiments and are shown in Figs. 1a and 1b. Calculated conversions ranged from 90 to 120%. The uncertainty may be due to errors in calibration of the mass spectrometer that was used to measure gas-phase concentrations of carbon dioxide. We conclude that all of the ethylene glycol charged to the reactor was converted to carbon dioxide. If the process were 100% efficient, the ultimate conversion should have occurred after 3.8 hours. In the second experiment, almost 10 hours were required to reach the ultimate conversion (calculated as 120%). This is indicative of relatively poor process efficiency (approximately 40%). In similar experiments with Ag(II), complete conversion was achieved after 3.8 hours, which indicated 100% process efficiency (utilization of cell current).

Anolytes containing $\text{Co}(\text{NO}_3)_2$ are pink or rose in color. In the absence of organics, the anolyte color changes to turquoise or dark blue

color after conversion of Co(II) to Co(III) by anodic oxidation. In the presence of organics, the anolyte color remains pink or rose. This observation leads us to believe that Co(III) must be completely consumed by reaction with ethylene glycol in a thin layer of anolyte near the anode.

Some Co(II) diffuses through the Nafion membrane that separates the anolyte and catholyte; the catholyte turns pink during experiments. The concentration of Co(II) at the beginning of the run was determined to be 0.44 M by inductively coupled plasma with mass spectrometry (ICP-MS). Recall that anolyte was believed to have 0.5 M Co(II), based upon the weight of $\text{Co}(\text{NO}_3)_2$ added to the electrolyte. The concentration of Co(II) in the anolyte dropped to 0.3 M by the end of the experiment. Apparently, 32% of the Co(II) diffused through the Nafion membrane during 20–25 hours of operation. The concentration of Co(II) in the catholyte was determined to be 0.17 M at the end of the first experiment. At the end of the second experiment, the concentration of Co(II) in the catholyte was determined to be 0.10 M. A very small volume of immiscible brownish green liquid appeared on the surface of the catholyte during the second experiment. The concentration of Co(II) in this immiscible liquid was determined to be approximately 0.05 M.

In experiments with Co(II)/Co(III), very little NO_x (dark brown gas) was generated in the cathode compartment. Since NO_x is dark brown, it is easily visible. In contrast, large amounts of NO_x were generated during experiments with both Ag(I)/Ag(II) and Fe(III)/Fe(VI).

Iron system. During the first experiment with Fe(VI), the anolyte concentration was 0.5 M $\text{Fe}(\text{NO}_3)_3$, 3.25 M HNO_3 , and 0.22 M ethylene glycol. Measurements of carbon dioxide evolution are shown in Fig. 2a. An ultimate conversion of 67–71% was reached after approximately 8 hours of operation. Approximately 3.8 hours would be required at 100% efficiency. Process efficiency appears to be lower with Fe(VI) than with Ag(II). Substantial quantities of Fe(III) migrated through the Nafion membrane to the catholyte. During approximately 30 hours of operation, the concentration of Fe(III) in the anolyte dropped from 0.5 M to 0.17 M (both determined with ICP-MS). The pH of the catholyte approached neutrality during the experiment. Consequently, most of

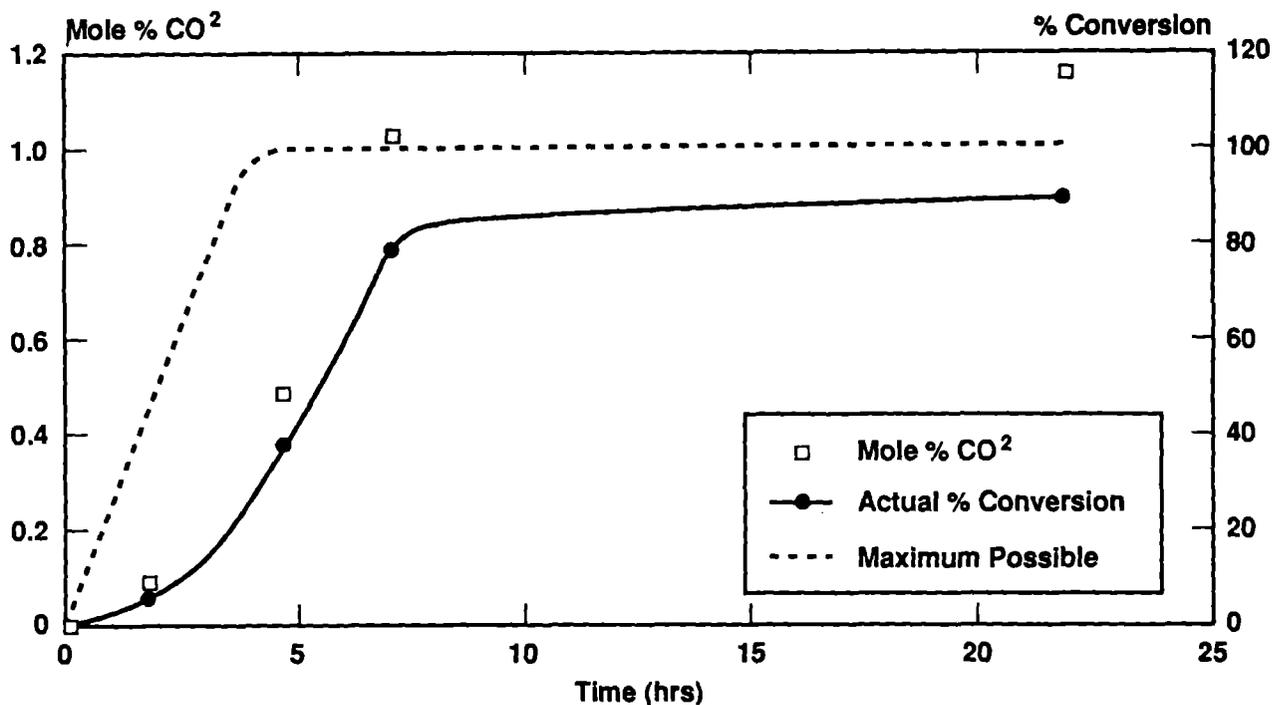


Figure 1. (a) MEO of ethylene glycol by Co(III) at 673 mA and 38°C. The anolyte was 40 ml of 0.5 M $\text{Co}(\text{NO}_3)_2$, 3.25 M HNO_3 , and 0.22 M ethylene glycol. A platinum rotating-cylinder anode (1.2 cm dia. \times 1.78 cm) was used. The rotation speed was 1500 rpm.

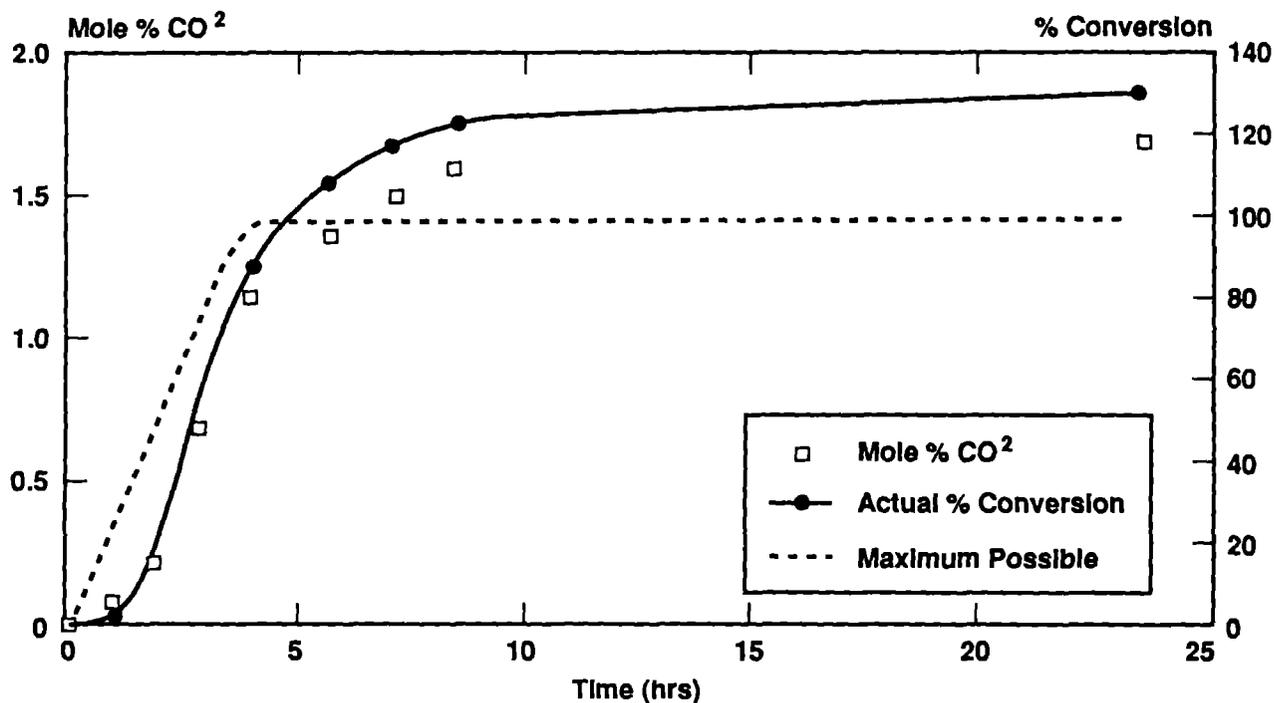


Figure 1. (b) This experiment was identical to (a), except for the steady-state anolyte temperature of 42°C.

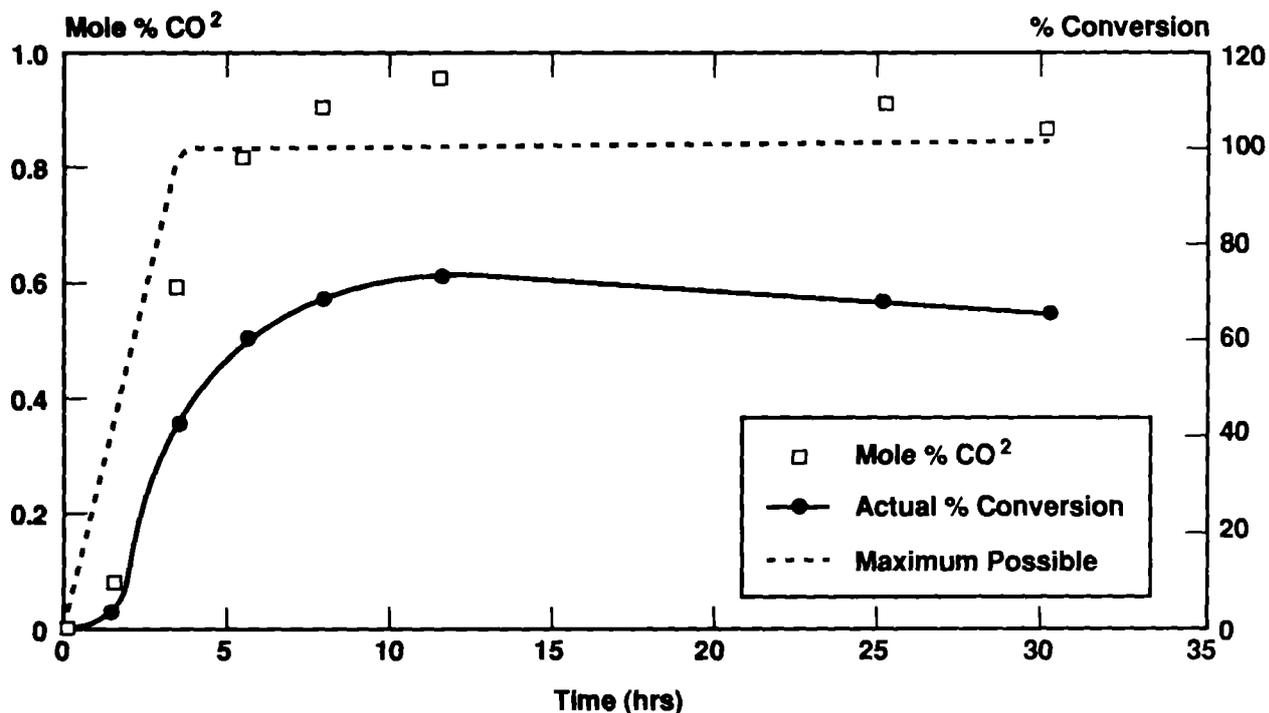


Figure 2. (a) MEO of ethylene glycol by Fe(VI) at 673 mA and 38–64°C. The anolyte was 40 ml of 0.5 M Fe(NO₃)₃, 3.25 M HNO₃, and 0.22 M ethylene glycol. A platinum rotating-cylinder anode (1.2 cm dia. × 1.78 cm) was used. The rotation speed was 1500 rpm.

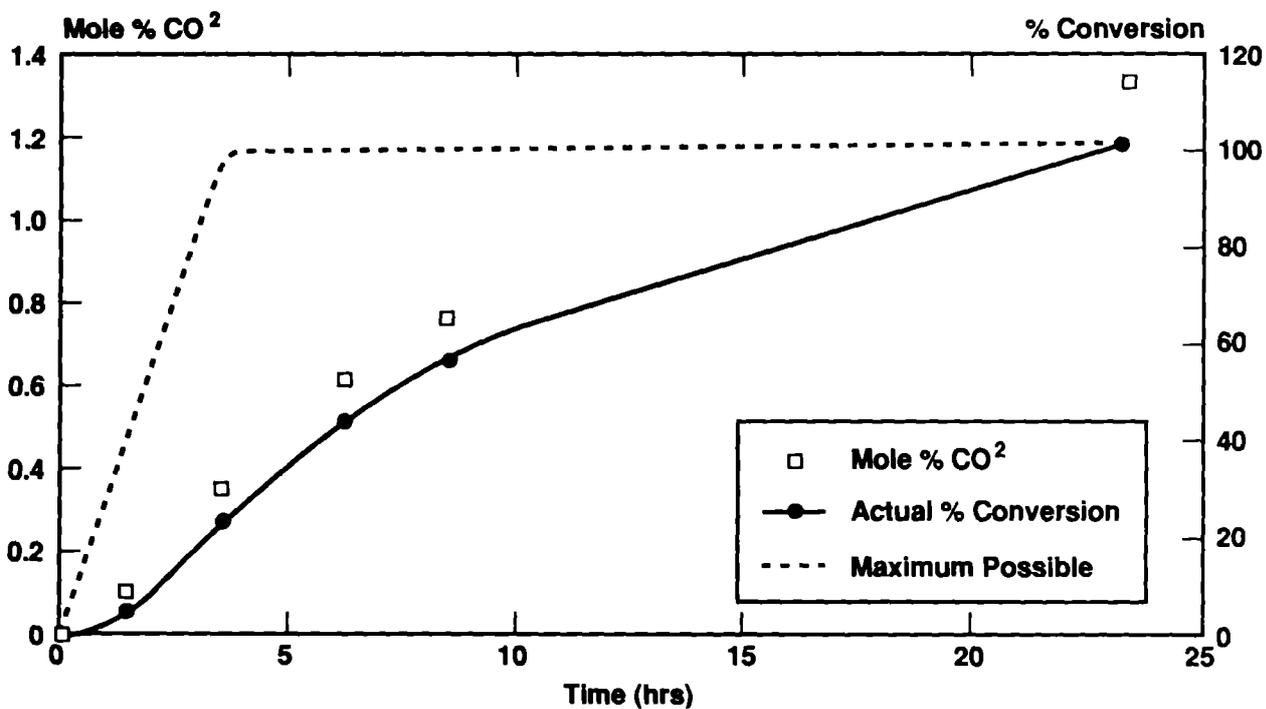


Figure 2. (b) This experiment was identical to (a), except for the HNO₃ concentration of 8 M and the steady-state anolyte temperature of 38°C.

the Fe(III) in the catholyte precipitated as oxide, believed to be Fe_2O_3 . Some Fe_3O_4 was found deposited on the cathode. Low efficiency and low ultimate conversion observed during the first experiment with Fe(VI) may be due to the loss of Fe(III) from the anolyte.

During the second experiment with Fe(VI), the anolyte concentration was 0.5 M $\text{Fe}(\text{NO}_3)_3$, 8 M HNO_3 , and 0.22 M ethylene glycol. By increasing the acid concentration, migration of Fe(III) was reduced and problems associated with precipitation were eliminated. Measurements of carbon dioxide evolution are shown in Fig. 2b. An ultimate conversion of 101% (calculated) was reached after approximately 24 hours of operation. The time required to reach the ultimate conversion is longer at 8 M HNO_3 than at 3.25 M HNO_3 . The oxidation of ethylene glycol probably relies on hydroxyl free radical ($\cdot\text{OH}$). By increasing the concentration of acid, the rate of reduction of Fe(VI) by water may be reduced. The rate of

oxidation of water may also be slowed since the reaction of Fe(VI) with water may be responsible for the formation of $\cdot\text{OH}$.

No mediator. Two experiments were conducted without mediator [Fe(VI) or Co(III)]. See Figs. 3a and 3b. Initial anolyte concentrations were 3.25 M HNO_3 and 0.22 M ethylene glycol. During the first experiment, a gold rotating-cylinder anode was used. After operating 4 hours at 673 mA, a final conversion of 36% was achieved. A steady-state anolyte temperature of 36°C was maintained. Significant corrosion of the gold anode was observed. During the second experiment, a platinum rotating-cylinder anode was used. After operating 8 hours at 673 mA, an ultimate conversion of 50% was achieved. A steady-state anolyte temperature of 35°C was maintained. Significant corrosion of the platinum anode was not observed. Organics can be destroyed by direct anodic oxidation.

GC/MS Analyses of Intermediates

Gas Chromatography with Mass Spectrometry (GC/MS) was used in an attempt to identify reaction intermediates in the anolyte. The conversion of ethylene glycol to carbon dioxide is believed to involve both formaldehyde and formic acid as intermediates. GC/MS analyses on sample extracts were performed on a Hewlett-Packard (H-P) 5890/5970 benchtop GC/MS system running on RTE/6. The column was a Stabilwax-DA with an inner diameter of 0.25 mm, a length of 30 meters, and a film thickness of

0.5 microns. Ethylene glycol was partially oxidized at 673 mA and 38°C. An anolyte sample without preparation (neat) was injected directly into the instrument. The temperature of the chromatograph was ramped from 40°C to 240°C at a rate of 2°C/min. Any formaldehyde present in the sample was obscured by CO_2 and N_2O which elute at 1.8–3.0 minutes (Fig. 4a). Formic and acetic acids were detected at 43.52 and 39.79 minutes, respectively (Fig. 4b). Clearly, formic acid is the major constituent.

Summary

Several important preliminary conclusions have been drawn from these experiments. These are enumerated below:

1. The complete conversion of ethylene glycol to carbon dioxide by Fe(VI) and Co(III) has been demonstrated. Unfortunately, the efficiency of MEO with Fe(VI) and Co(III) appears to be lower than with Ag(II). Better CO_2 evolution data are needed to quantify differences.

2. Both formic and acetic acids were detected in the anolyte prior to complete conversion

of the ethylene glycol to carbon dioxide. Acetic acid was present at a relatively low concentration. Formic acid is an expected intermediate formed during the MEO of ethylene glycol and was present at a higher concentration.

3. The conversion of ethylene glycol to carbon dioxide by anodic oxidation without any mediator was also demonstrated.

4. Gold anodes undergo significant corrosion in the presence of ethylene glycol and nitric acid.

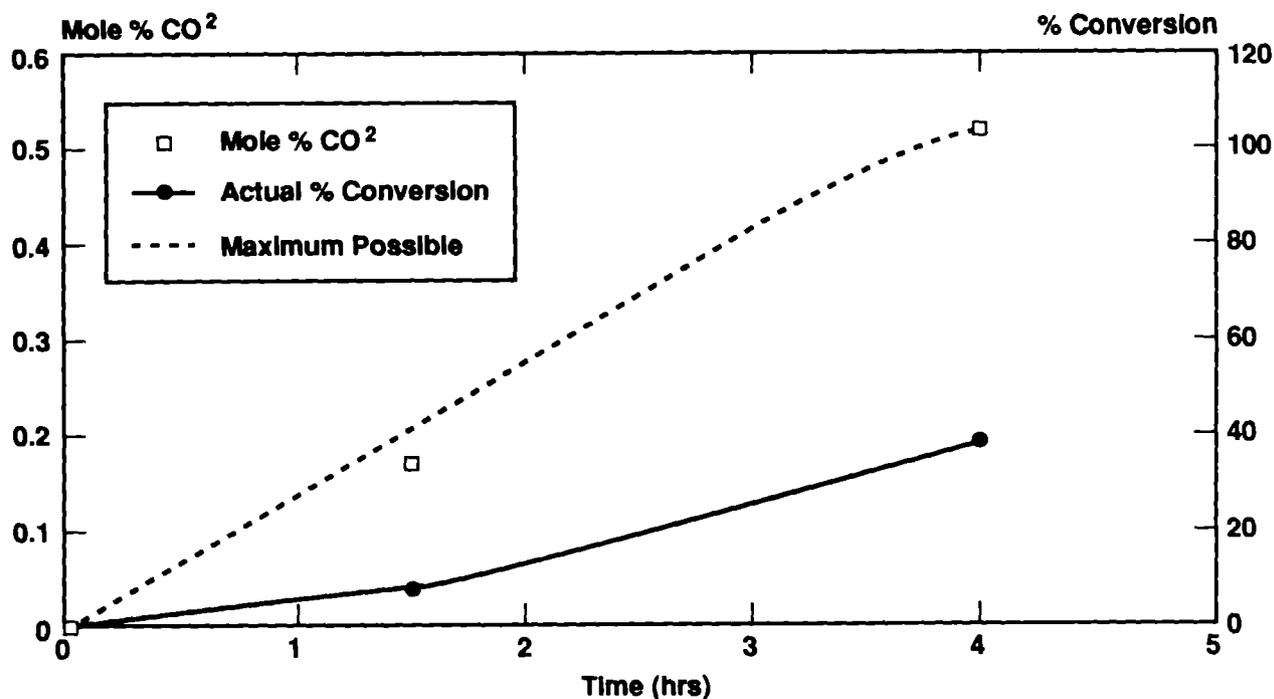


Figure 3. (a) Direct anodic oxidation of ethylene glycol in experiment without mediators. The cell current was 673 mA and the steady-state anolyte temperature was 36°C. The anolyte was 40 ml of 3.25 M HNO₃ and 0.22 M ethylene glycol. A gold rotating-cylinder anode (1.2 cm dia. × 1.78 cm) was used. The rotation speed was 1500 rpm.

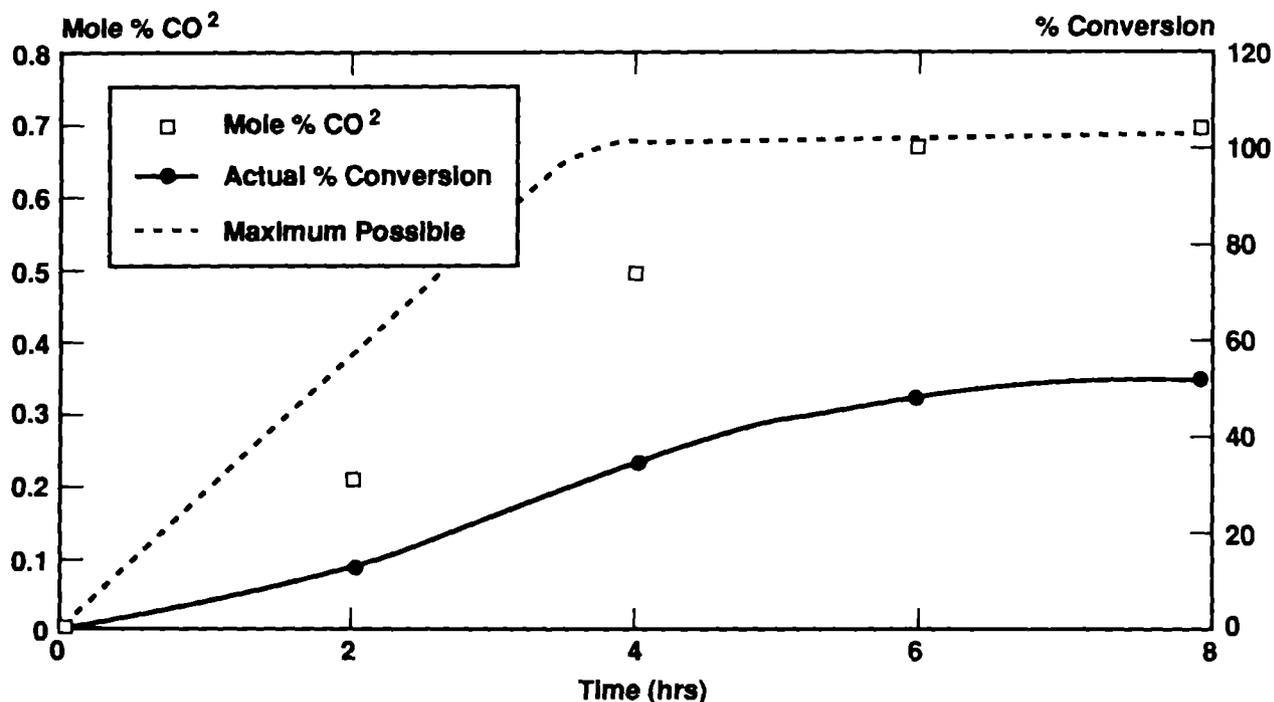


Figure 3. (b) This experiment was identical to (a), except a platinum rotating-cylinder anode (1.2 cm dia. × 1.78 cm) was used.

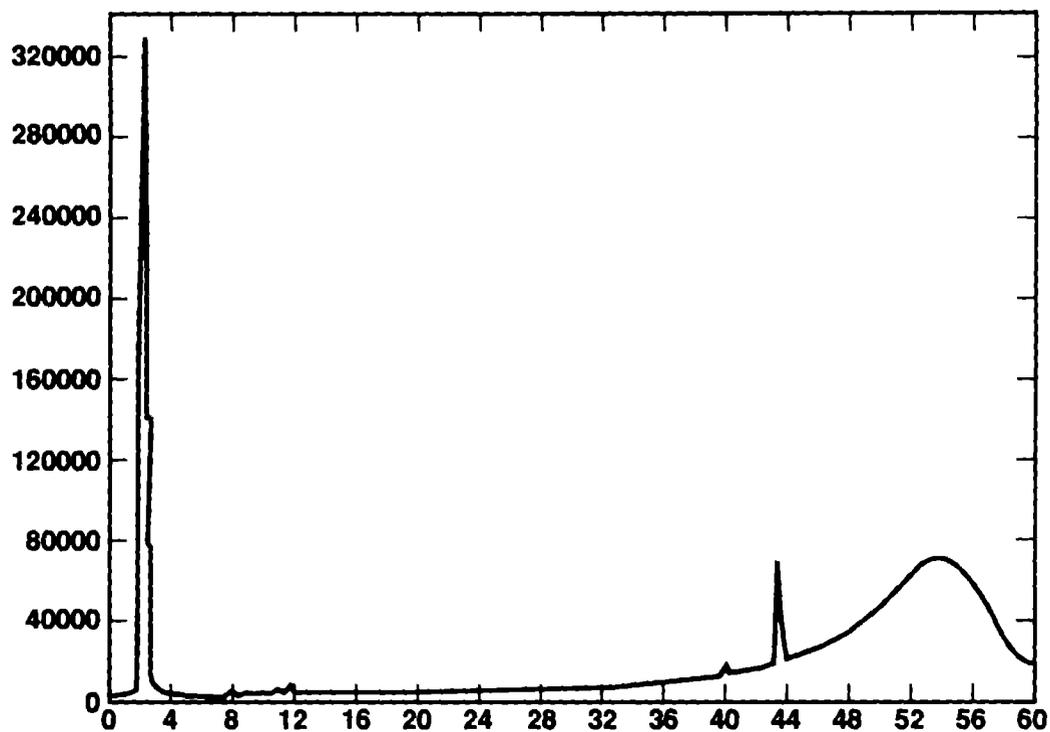


Figure 4. (a) Total ion chromatogram (TIC) of neat analyte showing species eluting from 0 to 60 minutes.

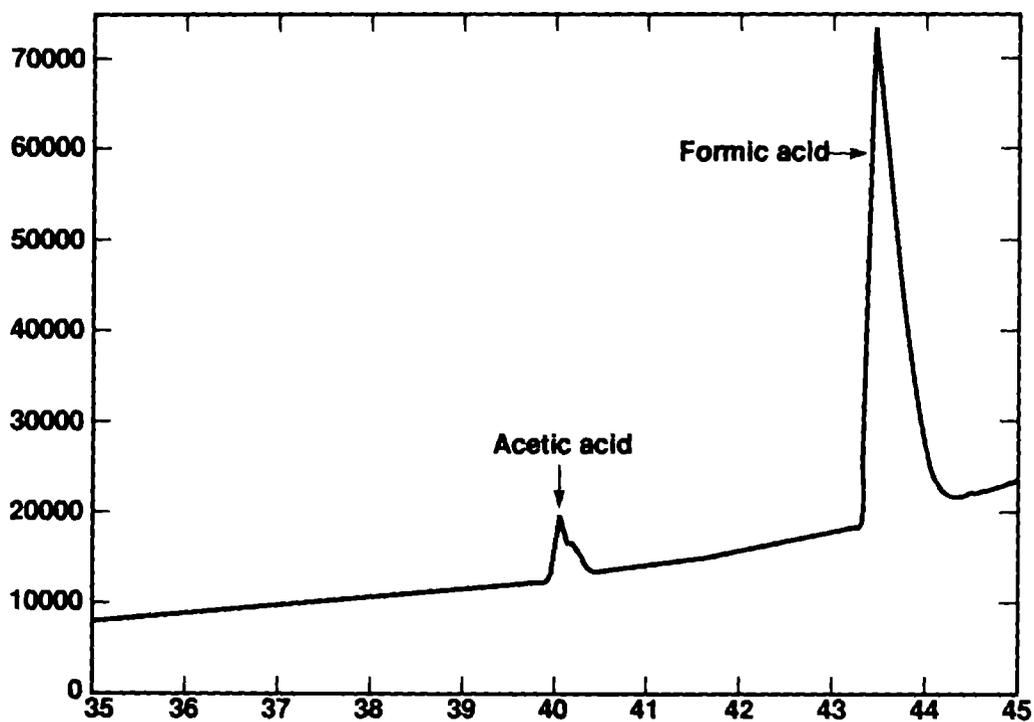


Figure 4. (b) Expanded TIC showing region from 35 to 45 minutes where formic and acetic acids elute.

5. The presence of Co(II) in the catholyte was found to suppress NO_x generation.
6. Fe(III) migration through Nafion cation exchange membranes was reduced by increasing

the concentrations of nitric acid in the anolyte and catholyte.

Acknowledgment

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References

1. J. C. Farmer, R. G. Hickman, F. T. Wang, P. R. Lewis, and L. J. Summers, "Electrochemical Treatment of Mixed and Hazardous Wastes: Oxidation of Ethylene Glycol by Ag(II)," U. Calif., Lawrence Livermore Laboratory, UCRL-JC-106947; *J. Electrochem. Soc.*, submitted for publication.
2. J. C. Farmer, F. T. Wang, R. A. Hawley-Fedder, P. R. Lewis, L. J. Summers, and L. Foils, "Electrochemical Treatment of Mixed and Hazardous Wastes: Oxidation of Benzene by Ag(II)," U. Calif., Lawrence Livermore Laboratory, UCRL-JC-107043; *J. Electrochem. Soc.*, submitted for publication.
3. J. C. Farmer, R. G. Hickman, F. T. Wang, and P. R. Lewis, "Mediated Electrochemical Oxidation of Ethylene Glycol," U. Calif., Lawrence Livermore Laboratory, UCRL-JC-105357 (1990); 179th Electrochem. Soc. Meeting, Washington, DC, May 5-10, 1991, Ext. Abs., Vol. 91-1, pp. 799-800, Electrochem. Soc., Pennington, NJ (1991).
4. J. C. Farmer, R. G. Hickman, F. T. Wang, P. R. Lewis, and L. J. Summers, "Initial Study of the Complete Mediated Electrochemical Oxidation of Ethylene Glycol," U. Calif., Lawrence Livermore Laboratory, UCRL-LR-106479 (1991).