1. Introduction

Microelectrode arrays and their potential applications have recently gained more attention in the electrochemical community. Electrodes of micrometer and submicrometer dimensions have become increasingly viable in the last decade as fabrication techniques improve. The manner in which these microelectrodes are produced make them ideal candidates for disposable sensors with identical characteristics. This work will focus on the design and applications of one particular type of electrode, the interdigitated array microelectrode (IDA).

The IDA electrodes have similar current responses to those of rotating ring-disk electrodes (RRDE). However, the geometry and experimental design of the IDA electrode is completely different compared to the RRDE. The much smaller and stationary IDAs have the capability to be used as sensors in many applications, including for use as portable detectors under field conditions. They can also be used to study and monitor electrochemical products at micrometer distances without substantial loss due to diffusion. The IDA electrodes have been modified by polymer films and used to study redox processes within these films. Other applications of modified IDA electrodes include using them to monitor diffusion in aqueous and gas phases.¹

In this research IDA electrodes have been used to study copper. A sensor for copper has the potential for both practical and academic applications, which include monitoring the concentration of copper in natural waters and studying corrosion
processes in the laboratory. Copper typically ranges in concentration from $10^{-8}$ to $10^{-6}$ M in natural waters.

Information about copper speciation is required to model accurately and predict its behavior in natural water systems. From an environmental science standpoint, such information is useful because the free ion form of copper is a trace nutrient in low concentrations, but it is toxic at higher concentrations. Total copper concentration, however, is not a comprehensive indicator of water quality because speciation directly affects the bioavailability of metals. The most bioavailable forms of copper are free copper (the aquated ion) and lipid-soluble complexes, whereas most organically complexed or particulate-bound copper species are not bioavailable. Natural processes, such as photolysis, can alter the bioavailability of copper. Because electrochemical methods of analysis in many instances can discriminate between differences in copper species, these techniques are ideal for studying photolysis reactions and products.

A spectroelectrochemical experimental apparatus was designed that would enable determination of values of rate constants of photochemical reactions for copper-organic complexes in an agarose gel matrix. Novel geometries of interdigitated arrays and spectroelectrochemical cells for these experiments have been developed.

Another important field of study is the corrosion of copper. Overall copper is very resistant to corrosion because of its noble properties and due to the formation of a cuprous oxide film. In spite of these factors, copper corrosion does occur and is a costly problem. Salinity greatly influences the rate of corrosion, but other factors
exist as well. Bacteria and their metabolites are becoming known for their biocorrosive effects, known as microbiologically influenced corrosion (MIC). Bacteria in aerobic and anaerobic environments can latch onto metal substrates and create films on these surfaces. These films contain the actual cellular material of the organisms plus their metabolites, and possibly other substances that have been incorporated into the structure as well (Fig. 1). Increases in rates of corrosion in harsh environments such as seawater and the occurrence of localized corrosion may be explained in part by MIC mechanisms. The field of biocorrosion is only beginning to uncover these processes in the laboratory and field.

The corrosion of copper in different media has been examined using interdigitated array electrodes. A novel experiment using IDA electrodes has been designed to determine the stability constants of copper corrosion products. For these experiments, copper was plated onto one lead of the IDA electrode. When this copper lead was anodized, the corrosion product was detected and measured at the other IDA lead. In the chloride system, where chloride ranged in concentration from 0.5 to 1.0 M, the stability constant for CuCl$_2^-$ was found to be $\log \beta_2 = (\text{CuCl}_2^-(\text{Cu}^+)(\text{Cl}^-)^2 = 5.88 \pm 0.03$. For the bromide system, where the bromide concentration ranged from 0.05 to 0.10 M, the stability constant for CuBr$_2^-$ was found to be $\log \beta_2 = (\text{CuBr}_2^-)/(\text{Cu}^+)(\text{Br}^-)^2 = 6.17 \pm 0.08$. These values fall within the range of values reported in the literature. The maleic acid system was also studied, as maleic acid is a common metabolite that might contribute to biocorrosion. The preliminary results from these experiments were also close to the literature values.
1.1. References


Figure 1.1. Schematic representation of a biofilm system. From Ref. 4.
2. Interdigitated Array Electrodes: Experimental Designs

Interdigitated array (IDA) electrodes have generated much interest as potential sensors due to their numerous advantages. They have a steady-state current response similar to that of a microelectrode, but the magnitude of their current is much larger. In principle, IDAs are similar to rotating ring-disk electrodes (RRDE), but they are much smaller and more versatile.

2.1. Introduction to Rotating Ring-Disk Electrodes

The rotating ring-disk electrodes (RRDE) are two-electrode systems in which a large disk electrode is surrounded by a ring electrode. A motor controls the rotation rate, and limiting currents increase as the rotation rate increases due to increased convective mass transport of electroactive species to the electrodes. Currents arise if the potential is appropriate to either reduce or oxidize a species. For example, suppose the current is monitored at the disk for a solution that has an oxidized species, Ox, which is reduced to form the species Red:

\[
\text{Ox} + ne^- \rightarrow \text{Red} \quad (2.1)
\]

where \(ne^-\) is the number of electrons required for the reaction. The current may also be measured at the surrounding ring. At the ring electrode, Red could be oxidized or further reduced to some other product. This is a useful experiment to study the processes of many types of reactions.
For the mass-transport limited case, the limiting current ($i_l$) at the disk is described by the Levich equation:\textsuperscript{1}

$$i_l = 0.620 n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C^-$$ \hspace{1cm} (2.2)

where $F$ is the Faraday constant, $A$ refers to the area of the electrode, $D$ is the diffusion coefficient, $\omega = 2\pi f$ is the angular rotation rate (radians per second), $\nu$ is the kinematic viscosity of the electrolyte, and $C^-$ is the bulk concentration of species.

An equation also exists for the current at the ring electrode when there is no current at the disk:\textsuperscript{1}

$$i_{R,l} = 0.620 n F \pi (r_3^3 - r_2^3)^{2/3} D^{2/3} \omega^{1/2} \nu^{-1/6} C^-$$ \hspace{1cm} (2.3)

where $r_3$ is the outer diameter of the ring, and $r_2$ is the inner diameter of the ring.

When $i_l$ vs. $\omega^{1/2}$ is plotted, the resulting Levich plot can yield important information about the system. From the slope of the Levich plot, which should be linear, the diffusion coefficient of electroactive species may be obtained. The line should also pass through the origin if the reaction is ideal and no other reactions are occurring.

\textbf{2.2 Introduction to Interdigitated Array Electrodes}

Each IDA electrode has two working electrodes, and its electrochemistry is similar to that of a rotating ring disk electrode (RRDE). As for the RRDE, one may set the potentials of the working electrodes such that Ox is reduced to Red, Red moves to the next electrode, and Red is oxidized back to Ox at the second electrode. The terminologies “collector” and “generator” electrodes are commonly
used because Red is generated at the first electrode and is subsequently collected at the next electrode where it is reduced back to Ox. This phenomenon is referred to as redox cycling. The IDA has many repetitions of these electrode pairs spaced micrometers apart, increasing the current response and the collection efficiency as well. Due to the close proximity of each working electrode to one another, steady-state conditions are reached under quiescent conditions, whereas the RRDE needs controlled convection to achieve steady-state responses. The close micrometer spacing of IDA electrodes gives rise to a steady-state response similar to that of microelectrodes. However, the overall size of an IDA is much larger than the typical microelectrode, giving rise to currents of a much larger magnitude, generating microamp instead of nanoamp currents typical of microelectrodes.

Thus it is possible to envision uses for IDA electrodes as sensors in cases where one wants to take advantage of a two-working-electrode system, but where it would be impractical to install a RRDE. Some uses to date include modifying electrodes for catecholamine detection in HPLC, and using IDAs to enhance detection limits of stripping voltammetry for reversible redox species. Some have taken advantage of the high collection efficiency of IDAs to study electroactive species generated at one electrode that have a short lifetime or a low yield and give inconclusive measurements with the RRDE. However, IDA electrodes at this point are largely used as research tools and not as commercially available sensors for routine analyses. A recent review of IDA electrodes by Niwa is available.
2.3. Interdigitated Array Electrode Equations

A sample depiction of an IDA electrode is given in Figure 2.1. Electrode dimensions such as number, width, spacing, and length of electroactive fingers all contribute to steady-state current ($I_{\text{lim,a,c}}$) responses of both the anode and the cathode, and can be described by:

$$|I_{\text{lim,a,c}}| = mnFC^*D[0.637\ln(2.55(1 + w_a/w_g)) - 0.19/(1 + w_a/w_g)^2]$$  (2.4)

where $w_a = w_c$ is the width of the anode and the cathode (also referred to as generator and collector), $w_g$ is the width of the gap between fingers, $m$ is the number of fingers, $b$ is the length of fingers, $C^*$ is the bulk concentration, and $D$ is the diffusion coefficient.\(^6\) This equation applies to the case of a reversible redox reaction with redox cycling. According to Eq. 2.4, the IDA electrodes therefore may be designed with a certain limiting current as the goal. Besides increasing the number and length of fingers, the gap between them can be decreased to boost the current response due to redox cycling. When the gap is reduced, more of the analyte diffuses directly to the next electrode without being lost. This “feedback effect” gives the resulting boost of current.\(^7\) IDA electrodes, depending on geometry, exhibit currents five to ten fold greater when both electrodes are connected in comparison with only one of the pair of electrodes. This current increase is known as redox cycling.

Other important characteristics of a given IDA are the time to reach steady-state\(^8\) (Eq. 2.5) and the average diffusion length between anode and cathode\(^5\) (Eq.\ldots\)
The time for the current to reach ninety-five percent of the steady state value, $t_{1.05}$, is given by:

$$t_{1.05} = 5.8 \frac{w^2}{d} e^{\left(\frac{3.3w_g}{w}\right)}$$

(2.5)

where $w = w_g + w_a$. The average diffusion length between anode and cathode, $d$, is given by:

$$d = 0.232w_a + w_g$$

(2.6)

Collection efficiency, $N_o$, also measures IDA response.\textsuperscript{9}

$$N_o = \left(\frac{i_{l,collector}}{i_{l,generator}}\right) \times 100\%$$

(2.7)

calculated from the ratio between the generator ($i_{l,generator}$) and the collector ($i_{l,collector}$) limiting currents. $N_o$ is greatly influenced by finger width and spacing because as the gap between electrodes decreases, there is less opportunity for analyte to diffuse into the bulk solution instead of to the next electrode. To compare, IDA electrodes have a much greater collection efficiency (~90%) than the RRDE (~25%).

Redox cycling at the IDA can be quantified. It is defined as the ratio of generator current when collector is connected to generator current when collector is at open circuit. The redox cycling value ($Rc$) can be calculated from the collection efficiency:\textsuperscript{9}

$$Rc = \frac{1}{1-N_o^2}$$

(2.8)

This equation is valid for electrodes whose generator and collector electrodes are of the same dimensions.
2.4. Instrumentation for Electrochemical Experiments

All electrochemical experiments were carried out on a PAR 400 LC Detector (EG&G PAR) controlled with a PC computer (486 or Pentium) using software developed in this laboratory. Most potentials were measured against the SCE reference electrode, except where noted. A few experiments used the Ag/AgCl reference electrode. The SCE and Ag wire were stored in saturated potassium chloride solutions when not in use. All solutions were deaerated with Ar gas, usually for 10-20 minutes. Measurements were taken at room temperature unless otherwise noted.

The limiting currents used in this study were obtained by use of a six point, three line procedure. In order to obtain the limiting current for a particular curve, one would mark six points on the curve: at the beginning and end of the foot of the curve; at the beginning and end of the rise of the curve; and at the beginning and end of the top plateau (Fig. 2.2). Three lines were calculated using the two points from each region. The limiting current was then the current difference between the lines from the bottom and top plateaus. Values for $E_{1/2}$, the halfwave potential, were also generated as part of this calculation.

It should be noted that experiments with the PAR 400 bipotentiostat could not be directly run at a particular scan rate. Instead, the operator inputs a step height and time to reach steady-state, $t_{ss}$, into the software. Therefore a $t_{ss}$ value of five seconds would cause the bipotentiostat to wait five seconds between each potential step before acquiring data.
2.5. IDA Sensors for Spectroelectrochemical Experiments

The IDA electrodes used for this research were custom designed and fabricated by the techniques of microlithography on a flat quartz substrate at the Center for Semiconductor Research at the Research Triangle Institute (Research Triangle Park, NC). For this project, eight electrodes per quartz slide were fashioned. The IDAs were designed to have the following dimensions: \( w_a = 5 \, \mu\text{m}, w_g = 2 \, \mu\text{m}, m = 142, \) and \( b = 2 \, \text{mm}. \) Platinum was deposited in a layer 10 to 15 nm thick on top of a 100 nm thick chromium layer that promoted adhesion of Pt to the quartz slide.

It should be noted that dimensions are limited by the fabrication techniques; as gap dimensions are reduced, the chance for shorts is increased. A short occurs when metal bridges the electrodes where an insulating gap should be. The short electrically connects two electrodes that by design should be entirely separate. The main cause for these shorts is the presence of dust particles settling between the leads during the fabrication process. These particles provide a surface for metal to be deposited in unintended places. A facility with the highest rated clean room environment possible, 100 particles per cubic meter or better if available, should therefore be used for fabrication.
2.5.1. IDA Fabrication

The IDA electrodes were fabricated using the following procedures. Quartz substrates were first degreased in acetone to remove organic contaminants. This was followed by a rinse in methanol and then in de-ionized water. The slides were dehydrated using a hot plate and then cooled to room temperature. A positive photoresist was spun onto the face of the slide and allowed to air-dry. The slides were then soft-baked on a hot plate at 115 °C. The resist was exposed to UV light, using the first mask for the metallization. The slides were hard-baked and then flood-exposed with UV light. The slides were then rinsed in a developer solution.

The slides were then taken into an e-beam evaporator for the deposition of Cr/Pt metallization. The evaporation consisted of about 50 nm Cr (to promote Pt adhesion), followed by about 10 to 15 nm of Pt. The evaporation of metals occurred over the whole quartz wafer surface. The metals from the unwanted areas, over the photoresist, were lifted off in acetone.

The slides were rinsed in methanol and D.I. water and blown dry. The slides were then loaded into a plasma-enhanced chemical vapor deposition (PECVD) chamber. A film of silicon nitride (Si$_3$N$_4$), about 300 nm thick, was deposited onto the slides. The deposition was carried out for about 60 min in two steps at a deposition rate of ~5 nm/min.

Following the Si$_3$N$_4$ deposition, the slides were taken from the plasma chamber at ~150 °C. The slides were coated with photoresist, air-dried and soft-baked. The slides were exposed using a second mask. This mask allowed silicon
nitride to insulate the leads of the IDA and counter electrodes from solution. The slides were hard-baked, and the silicon nitride was removed using a buffered HF (BHF) solution. This etch step required two min. Following the etch, the slides were rinsed thoroughly in D.I. water.

The IDAs fabricated as described above did have shorts, but an estimated 80% of electrodes with shorts were cleared by applying a potential with an AC current across the fingers. A multimeter was used to help diagnose shorts and to determine whether the clearing process was successful. A short was declared clear when the resistance between the two leads exceeded 20 MΩ.

2.5.2. Cell Design

Much effort was applied to cell design. In order to perform photoelectrochemical experiments, described below in more detail, cell design and electrode geometry needed to be compatible with a potentiostat and a light source for photolysis. Other challenging problems included ensuring water-tight electrical connections that were compatible with the thin layer cell design. In addition, experimental components such as counter, reference, and working electrodes had to fit into an optically transparent holder, which contained aqueous solution. Solutions and cell also were required to be free of oxygen.

It became apparent early, however, that the original cell was difficult to set up (Fig. 2.3). The IDA sides were fully immersed in analyte, thus requiring blocks of electrical contact leads to be insulated from solution. These blocks were clamped
down, but the entire process was cumbersome and often failed to provide perfect contact with the electrode leads. It is important to note that this design did have many desirable features: an ample reservoir of easily deaerated solution was available to the IDAs, and cell geometry allowed light to reach the cell.

A temporary cell held together by a ball-joint clamp was used for some experiments in solutions and in gels, as well. A ball-joint and Teflon washer were held tightly to the IDA slide with a clamp. The joint was cut to about an inch, which provided a cell volume of about 3 mL. A rubber septum with a hole in the center was used to close the cell while allowing insertion of the reference electrode and Ar line.

As indicated earlier, the original cell was of inadequate design. The present redesigned cell and IDA electrode were great improvements and function more predictably (Figs. 2.4-2.6). The IDA electrode dimensions remained the same, but the leads were brought up to the top of each slide to facilitate connections of electrode leads to the potentiostat. Calculations for the new lead lengths predicted an increase in resistance only for the two longest leads, which affects two IDAs. This was determined not to be a large problem since all measurements will be at steady-state, and a small shift in potential could be accommodated. An edge connector was used to connect the leads on the substrate to leads that interfaced with the potentiostat. The edge connector was used with minor modifications so it could be fitted to 28 gauge wire leads. It should be noted that after repeated insertions, the Pt for the lead connections eventually wore off the slide. The glassblower repaired this by sanding the edge of the slide with diamond paper to access Pt that had not been damaged.
An upright aluminum block fitted for temperature control served as the base of the cell, called a “sandwich” cell. The IDA electrode formed one side of the thin layer cell, with the organic-coated quartz slide forming the other side. A Teflon gasket fit between the two substrates. The cell was sandwiched together by pressure from an aluminum face plate, which was a hollow rectangle allowing light to pass through to the cell. Reference electrode contact was made through the solution inlet port. A pneumatic pump in series with the cell outlet pulled solution through the cell and into waste in a flow system design. Solution reservoirs were purged with argon before new solution was drawn into the cell. Electrical leads never contacted the solution, and electrode lead contact to the potentiostat was completely assured each time, reproducibly. Voltammograms for Ru (NH₃)₆³⁺ from this cell were similar to those from the other cell.

This cell design was also used for experiments with agarose gel, with the slight modification that tubing was not attached to the quartz faceplate. Warm agarose gel, still in its liquid state, was injected into one of the holes until the entire cell was filled with gel. A Ag/AgCl reference electrode was inserted through one of the holes and fed into the cell to make certain contact with the gel. The holes were then covered with small squares of Teflon tape in order to retard evaporation and shrinkage of the gel.
2.5.3. Characterization of the IDA Electrodes

The theoretical current response for these electrodes, using Eq. 2.4, would be 27 µA for 1 mM ruthenium hexaammine (Ru(NH$_3$)$_6^{3+}$) ($D_{\text{Ru(NH}_3\text{)}_6^{3+}} = 7.1 \times 10^{-6}$ cm$^2$/s). Laboratory results show a limiting current of 20-25 µA for these IDAs, which is in acceptable agreement with theory (Eq. 2.4). A typical voltammogram is shown in Fig. 2.7. The time to reach steady state is 1.0 s (Eq. 2.5), and the average diffusion length (Eq. 2.6) is 3.16 µm. Current for Ru(NH$_3$)$_6^{3+}$ solutions were generally about ten times larger than currents measured without redox cycling. These IDAs typically showed $N_0 \geq 95\%$ reflecting the small gap width between generator and collector fingers.

The limit of detection (LOD) for these electrodes was calculated using the slope of the calibration curve,

$$\text{LOD} = 3 \times \text{s.d.}_b / m \quad (2.9)$$

where s.d.$_b$ is the standard deviation of the blank, m is the slope of the calibration curve. These electrodes had a typical LOD of $1.9 \times 10^{-7}$ M for the anodic process of oxidizing Ru(II) to Ru(III). The reduction of residual oxygen prevents the cathodic LOD from approaching that of the anodic LOD. It should be noted that Ru(NH$_3$)$_6^{3+}$ represents an ideally reversible system, and other less ideal systems would not be expected to exhibit LODs as low as for this system.

During the course of the characterization experiments, it was noted that over time current response generally decreased. Rinsing with a variety of organic
solvents did not help, and cycling the potential did not correct the trend. Due to the fragility of IDA electrodes, no mechanically abrasive techniques can be used to clean the metal surfaces. In order to assess the problem, repeatability studies were conducted, again using Ru(NH$_3$)$_6^{3+}$. Current did decrease over time, from 5-15% rsd over four hours in the same solution. However, over 1 hour the decrease was very minor, about 1% rsd. Thus, by calibrating the IDA electrode before and after experiments, current response can be correlated with concentration of analyte.

The response of analyte in various concentrations of supporting electrolyte was also of interest, since freshwater systems are generally low in ionic strength. However, electrochemical experiments normally require 100-fold excess of supporting electrolyte to reduce voltage drop due to highly resistive solutions and minimize the effect of migration. Results with Ru(NH$_3$)$_6^{3+}$ indicate that current is constant over the range of 50- to 100-fold excess of electrolyte over the analyte concentration (Fig. 2.8).

### 2.6. IDAs for Corrosion Product Studies

These experiments did not have extraordinary requirements, so commercially available single electrodes (AAI-Abtech, Yardley, PA) that were more robust were used for corrosion studies. These were 100 nm thick platinum electrodes with 10 nm titanium to promote adhesion to the borosilicate substrate. The IDAs had the following dimensions: $w_a = w_c = w_g$ is 5 $\mu$m, $m = 50$, $b = 5$ mm. These were used as received and a typical jacketted cell was used for the experiments.
Because the gap and electrode widths are identical, the logarithm term falls out of Eq. 2.2 and the current response equation is greatly simplified. An example of theoretical current response, using Eq. 2.4, would be 17 µA for 1 mM ruthenium hexaammine. The time to reach steady state (Eq. 2.5) is calculated to be 4.25 s. The average diffusion length (Eq. 2.6) is 7.3 µm. The \( R_c \) (Eq. 2.8) value is 5.7. A sample voltammogram of \( \text{Ru(NH}_3\text{)}_6^{3+} \) is given in Fig. 2.9 and the limiting current value of 15.2 µA agrees well with the predicted current.

The limit of detection for these electrodes was also calculated. For 0.1 to 1 mM \( \text{Ru(NH}_3\text{)}_6^{3+} \) at 20.0 °C, the detection limit was calculated to be \( 6.5 \times 10^{-7} \) M for the cathodic current and \( 2.8 \times 10^{-7} \) M for the anodic current.

IDA electrodes cannot be polished to renew the electrode surface, so cleaning the electrode in acid is one way to mitigate the passivation of the electrode and to improve its reproducibility. The acid cycling routine used for the corrosion experiments entailed cycling both electrodes from -0.2 to +1.4 V five times in 1 M \( \text{H}_2\text{SO}_4 \). The potential was changed in a stepwise fashion in 100 mV increments with a 0.5 s pause between steps.
2.7. References


Figure 2.1. Representation of an IDA electrode. Note that fingers from one lead alternate with fingers from the other. Figure is not to scale; actual dimensions usually are less than 0.5 cm x 0.5 cm.
Figure 2.2. Method by which limiting current and $E_{1/2}$ are measured using the in-house program “FSQLT” by John J. O’Dea. An X designates the six points used to calculate the limiting current and the $E_{1/2}$ value.
Figure 2.3. Top view of original cell design. Electrical contact blocks were sealed to slide with Q-Dope (polystyrene). Polymer film refers to slide with immobilized complexes. Design and drawing by L.A. Mahoney.
Figure 2.4. New IDA electrode design. Leads from all eight IDA and counter electrodes run to the top of the slide to interface with an edge card connector. Substrate is 1 in. x 2 in. Dimensions of IDA electrodes remained unchanged.
Figure 2.5. Sandwich cell design. Gasket is designed to minimize interference with photolysis and to maximize complete solution replacement when solution is pumped into cell.
Figure 2.6. Diagram of entire sandwich cell design set up for experiments. Note that more than one solution is possible through use of a T-joint or other modifications.
Figure 2.7. Typical steady state voltammogram of 1 mM Ru(NH$_3$)$_6^{3+}$ in 0.1 M KCl. $N_o$ is 94.8%. Working electrode (WE) 1 is cycled from 0 V to -0.4 V (vs. SCE) and back in 5 mV steps, $t_{ss}= 0$ s, corresponding to 10 mV/s rate (-). WE 2 is held at 0 V (+).
Figure 2.8. Limiting current as a function of supporting electrolyte. Graph shows changes in absolute value of limiting current due to oxidation of Ru(II) to Ru(III) as a function of excess supporting electrolyte (KCl) at the IDA electrode. All solutions were $10^{-5}$ M Ru(NH$_3$)$_6^{3+}$ and KCl concentrations varied between zero to 100-fold. Results indicate that 50-fold supporting electrolyte is sufficient to compensate for migration.
Figure 2.9. Steady state voltammogram of 1 mM Ru(NH$_3$)$_6^{3+}$ in 0.1 M KCl at AAIAbtech IDA electrode. $N_0$ is 90.8%. Working electrode (WE) 1 is cycled from 0 V to -0.4 V (-), in 5 mV increments, $t_{ss}=5$ s. WE 2 is held at 0 V (+).
3. Photolysis Experiments

Using IDAs for photolysis studies should give experimentally determined values for formation and rate constants of reactions for surface-bound copper-organic complexes that will have practical applications for environmental scientists. Considerable work has been completed on adsorption and decomposition reactions on “clean” mineral surfaces.\(^1\) In many natural systems, however, organics rapidly coat particulates.\(^2,3\) In natural waters, nearly 90% of copper is complexed with organics, and, as a result, copper has a high affinity for sorption onto particles. Experimental studies of these sorbed complexes are difficult due to a number of problems. These include the heterogeneous nature of the particulate surface, the low concentrations of metals typically found in natural waters, the transient nature of reaction products (such as Cu(I)), the loss of sample integrity that results from sampling, isolation, and manipulation of the sample for analysis, and the lack of appropriate analytical techniques to quantify aqueous interfacial species. As described below, the unique geometry of the IDA electrode setup was designed to give new insight into the processes involved in photochemistry on a surface coated with an organic phase in contact with an aqueous phase.
3.1. Theory of Photolysis Experiments

The study of the photochemistry of surface-bound copper complexes was pursued through a novel set of experiments. A suitable experimental setup for photolysis studies with IDAs was the final outcome of this portion of the research.

Copper-amino acid complexes were used as the model complexes. Amino acids are well defined and are simple compared with other organic ligands found in natural waters. Bis-copper (CuL2) photolysis reactions have been studied in the solution phase and rates reported.4,5,6 An example of such a complex is Cu(Gly)₂ where L=glycine (Gly) (Fig. 3.1). The mechanism of photolysis is ligand to metal charge transfer, causing the reduction of Cu(II) to Cu(I), decomposition of the complex and release of Cu(I) into solution. Copper-amino acid complexes therefore are a good starting point for the experiments. The IDA electrodes should track the progress of photolysis reactions by detecting released Cu(I). By use of a sensor in a thin layer spectroelectrochemical cell, Cu(I) species released from amino acid complexes of Cu(II) could be detected and measured as a function of incident light intensity.

Kinetic rates were to be determined according to the following scheme:

\[
d[Cu(Gly)2]/dt = k[Cu(Gly)2][\text{light intensity}] \tag{2}
\]

where the concentration of Cu(Gly)₂ is followed over time by the IDA electrode as a function of light intensity for the photolysis reaction. If light intensity is constant, then Eq. 2 simplifies to a pseudo-first-order rate equation:
\[ \frac{d[Cu(Gly)2]}{dt} = k'[Cu(Gly)2] \]  

Integrating,

\[ \ln\left(\frac{(Cu(Gly)2)_0}{(Cu(Gly)2)_t}\right) = k't \]

where \((Cu(Gly)2)_0\) is the initial concentration, and \((Cu(Gly)2)_t\) is the concentration in time \(t\). By plotting \(\ln\left(\frac{(Cu(Gly)2)_0}{(Cu(Gly)2)_t}\right)\) vs. \(t\), the rate constant \(k'\) can be obtained from the slope. Thus, from knowing the concentration of the immobilized complex before irradiation, and by monitoring the decomposition product, Cu(I), using the IDA electrode, \(k'\) can be found experimentally. Because the only source of copper in the cell is the immobilized complex, total concentration of photolysed complex directly correlates with the amount of Cu(I) detected.

### 3.2. Development of “Artificial” Particle

Two scenarios were developed for the artificial particle that would mimic the coating on particulate surfaces in natural waters. The first was to coat a quartz slide with poly(methyl methacrylate) and immobilize the complex on the polymer surface. The second was to use an agarose gel matrix containing the copper complex.

#### 3.2.1. Poly(methyl methacrylate) Coating

The other side of the thin layer cell, where the copper-amino acid complex was to be immobilized, was developed and modified as part of this research. Both
spin coating and film casting devices were machined for applying immobilized complex to a quartz slide. Originally the organic coating was proposed to be a thin layer of poly(methyl methacrylate) (PMMA), but it became obvious as this coating was studied in more detail that PMMA would be unsuitable. PMMA is highly hydrophobic and water diffuses very slowly in this polymer, but copper-glycine complexes are water soluble complexes. Thus, once PMMA was impregnated with the complex, one would expect no possible diffusion of reaction product to the electrode through the aqueous solution between the polymer coated slide and the IDA electrode. Coating the polymer with the copper complex would have been equally futile, as there was no anchor for the complex to remain attached to the polymer surface. Additionally, this film easily peeled off the quartz substrate, so mechanical stability would have to be questioned as well for the PMMA coating.

3.2.2. Agarose Gel

Agarose gel was tested as an alternative membrane to PMMA. The lower melting point gels have excellent clarity, and provide a membrane permeable to aqueous solution, which is necessary for Cu(I) transport. High purity agarose gel (gelling temperature 29-33 °C) was purchased from Fluka and used as received. Gels were prepared in 60-mL bottles at 1% wt/vol concentrations. Gels were heated in the microwave until bubbling appeared, taken out and swirled, then heated again. This process was repeated until the gel was fully dissolved, usually no more than two minutes. The bottle was then transferred to a water bath to keep the liquid gel
hot, not boiling. Argon was bubbled into the warmed gel to keep it deoxygenated until ready for use.

Unfortunately, Cu(Gly)$_2$ (a deep blue complex) clearly diffuses from unmodified agarose gel in a matter of minutes (Fig. 3.2), rendering it unsuitable as the organic coating. This problem was solved by modifying the experiment so that the entire sandwich cell volume between the quartz slide and the IDA electrode was filled with agarose gel containing the copper complex. By placing a gasket over the IDA slide, then filling the volume with gel solution and placing a slide over the gasket, the resulting membrane thickness can be controlled. Since the agarose gel is actually 99% water, diffusion of photochemical product could occur within the gel and be detected by the IDA.

### 3.3. Electrochemistry of Photochemical Reactants and Products

Ultimately, the IDA electrodes were to be used to detect Cu(I), which is the product of the photochemical reaction of copper-amino acid complexes discussed above. However, Cu(I) is only stable with respect to Cu(II) in the presence of certain complexing media, such as chloride. An estimate of the amount of chloride needed to stabilize Cu(I) was given by Braun and Nobe, where $\frac{\text{Cu(II)}}{\text{Cu(I)}} \approx \left(10^{-5}/[\text{Cl}^-]^3\right)$. Therefore, to take advantage of unique IDA properties such as redox cycling, the Cu(I)/Cu(II) couple can be studied in chloride. Tests of copper in varying concentrations of chloride confirm Cu(I)/Cu(II) redox cycling at the IDA at sufficiently large concentration of chloride (Fig. 3.3). The IDA response for the Cu(I)/Cu(II)
couple in 1 M KCl shown in Fig. 3.3 corresponds to a collection efficiency of about 75%. Chloride concentrations of only 100-fold of copper give rise to redox cycling with these IDA electrodes. Rotating ring-disc experiments (RRDE) were performed to define the Cu(I)/Cu(II) couple response to chloride, and to confirm that results from IDA electrodes were not artificial. The RRDE results (Fig. 3.4) confirmed that for 1 mM copper solutions, the Cu(I)/Cu(II) couple was stabilized when 1000-fold excess chloride ion was present, as reported in experimental work by many others.\textsuperscript{7,8} Levich plots (Eq. 2.2) for these copper chloride complexes are shown in Figure 3.5. Using the slope, $D = 5.8 \times 10^{-6}$ cm$^2$ s$^{-1}$ was calculated, agreeing well with the value of $\sim 0.5 \times 10^{-5}$ cm$^2$ s$^{-1}$ reported by Orr et al. for CuCl$_2$, CuCl, and Cl$^-$.\textsuperscript{9}

The RRDE results also show that aqueous solutions of glycine and Cu(Gly)$_2$ solutions are electrochemically inactive in the potential range of the Cu(I)/Cu(II) couple (Fig. 3.6), and that even in the presence of 1 M KCl, the glycine complex of Cu(II) is preferred (Fig 3.7).

Due to the pH sensitivity of the glycine species, it was decided that a buffer should be present instead of simply adjusting the solution pH with NaOH. This was in an effort to ensure that any electrochemical products would not alter the pH at the IDA electrode surface. The desired pH of $\sim 8$ corresponded to that found in natural systems and the formation of the glycinate dianion. Phosphate buffer was initially tried, but due to the formation of a precipitate, probably Cu$_3$(PO$_4$)$_2$, this buffer was not suitable. Tris buffer, although a commonly used buffer in this pH range, was not a candidate due to its photochemical behavior.\textsuperscript{4} A carbonate/bicarbonate buffer ($\sim 1$ M, pH = 8) was used instead at sufficient buffer capacity for all the experiments.
likely to be performed. Since carbonate is present in seawater this buffer was
deemed a reasonable choice for these experiments.

The electrochemistry in the agarose gel was very similar, as expected, to the
behavior observed in aqueous solution. There was sufficient conductivity between
all electrodes to facilitate electrochemical experiments in the gel matrix. Of most
importance was the behavior of solutions of copper/chloride/carbonate buffer with
and without glycine added, since this would be the matrix for the photochemical
experiments. Comparing $E_{1/2}$ values showed that the Cu(II)/Cu(I) peak was shifted in
a negative direction about 70 mV when glycine was added in amounts of 100-fold
excess (Fig. 3.8). This potential difference indicated that indeed glycine was
complexing with Cu(II) in this medium. Thus, it would be possible to discriminate
between free Cu(I), the photolysis product, and Cu(I) bound with glycine.

3.4. Photochemical Experiments

For a description of the photoelectrochemical cell, please refer to section
2.4.2. The photolysis apparatus (Fig 3.9) was set up in a dark room. A high-
pressure mercury lamp (OSRAM HBO 200 W/2) was used as the source, and a
monochromator (Jarrell-Ash) selected the wavelength that impinged upon the cell.
Mirrors and lenses focused the light into a spot that roughly covered one IDA
electrode. In order to illuminate different electrodes, the cell holder was simply
translated in the x- or y-direction using precision micrometer stages.
3.4.1. Actinometry

Light intensity was determined by using ferrioxalate actinometry.\textsuperscript{10} There were several advantages using this actinometer for the sandwich cell setup. Stirring was not necessary, and oxygen did not have to be excluded. Additionally, quantum yields are accurately known. Unfortunately, ferrioxalate reacts with blue light as well as ultraviolet light, so one must work under darkroom conditions.

The line at 254 nm was initially tried, but due to self absorption this wavelength did not excite the actinometer. However, the line at 313 nm generated a strong response. This line was also suitable for study of photolysis of Cu(Gly)\textsubscript{2} that has been observed at about 310 nm from a Xe arc lamp.\textsuperscript{4}

According to the actinometry results, the irradiance the cell received was 1.22 ± 0.18 x 10\textsuperscript{-8} ein/min, or estimated irradiance of 2 x 10\textsuperscript{-3} einL\textsuperscript{-1}min\textsuperscript{-1}. This intensity is about 40% of intensity of sun at noon on a summer day. This compares with 1 x 10\textsuperscript{-4} einL\textsuperscript{-1}min\textsuperscript{-1} reported by Das et al.\textsuperscript{5} in their study of photolysis of Cu(II)-amino acids in aqueous solution.

3.4.2. Kinetic Experiments

For these experiments, the sandwich cell was filled with the Cu(Gly)\textsubscript{2}-containing gel. Chronoamperometry was performed to monitor the concentration of Cu(I) versus time of photolysis, since Cu(I) would only be generated from photochemical decomposition of Cu(Gly)\textsubscript{2}. One working electrode was set to oxidize
Cu(I) and the other working electrode was set to reduce Cu(II). The gel consisted of 3 x 10^{-5} M Cu(II), 3 x 10^{-3} M Gly, 2.5 M Cl\(^-\), and 1 M carbonate buffer (pH = 8). The concentration of Cu(II) was chosen so as not to exceed greatly the concentrations likely found in natural situations. This was well within the limit of detection for the electrode, as seen in the regular voltammogram of this solution (Fig 3.10).

Unfortunately, the experiment did not produce immediate results. In fact, no photochemical product was detected even after an entire weekend of photolysis. As it turned out, the half-life of the copper-glycine complex, 45 days\(^4\), was too long for the reaction to proceed far enough to exceed the limit of detection at these IDA electrodes. When this project was originally proposed, there was an expectation that the electrodes could be fabricated at such small dimensions to significantly decrease the limit of detection. If this had occurred, the long half-life would have been less of an obstacle. Our fabrication limit of a 2 µm gap between 5 µm leads widths apparently could not produce electrodes capable of low enough detection limits. Additionally, the software usually crashed every three to four hours making continuous data collection difficult.

β-alanine was considered as an alternative amine acid, as the half-life of copper-β-alanine is reported as 1.6 days\(^4\). However, the potential of the Cu(II)/Cu(I) couple in a cuprous solution of ten- and 100-fold β-alanine concentrations showed little shift compared to the halfwave potential without β-alanine added to the solution (Fig. 3.11). From the ring currents due to the oxidation of Cu(I) to Cu(II), E_{1/2} values are -0.10 V for both β-alanine solutions and ~-0.15 V without β-alanine. The lack of a significant shift of potential for the Cu(II)/Cu(I) peak upon addition of β-alanine
indicates that β-alanine would be a poor ligand choice for the
spectroelectrochemical experiments, since it would not be possible to discern the
Cu(I) generated from photolysis alone. The 100-fold β-alanine concentration above
was expected to be sufficiently in excess because Hayase and Zepp\textsuperscript{4} used a 50-fold
excess for their photolysis work.

3.5. Conclusions

A working spectroelectrochemical system for photolysis studies was
designed. This included redesigning the IDA electrode slide in order for it to
interface reliably with the potentiostat. Thermostatted spectroelectrochemical cells
were made for experiments in solution and gel matrices. However, a suitable
photoelectrochemical system was not found as part of this work. Future work would
include addressing the software reliability issue and expanding the complexes
beyond those included in this study.
3.6. References


Figure 3.1. Cu(Gly)$_2$ complex.
Figure 3.2. Absorbance of gel containing Cu(Gly)$_2$ after being in contact with water up to 15 minutes. The blue complex clearly diffused out of the film. $\lambda = 486$ nm (♦), 584 nm (□), 656 nm (▲).
Figure 3.3. Steady-state voltammogram of solution of 1 mM CuSO$_4$ and 0.75 M KCl. The IDA electrode is an AAI-Abtech electrode. W1 stepped from 0.4 V to -0.1 V and back (-) in 5 mV increments, $t_{ss}$ = 5 s. W2 held at 0.4 V (+). $N_0$ is 91%.
Figure 3.4. RRDE voltammogram of 1 mM CuSO₄ and 1 M KCl. Rotation rate is 250 rpm. W1 (Disk,+ ) stepped from 0.5 to -0.1 V, 2.5 mV step, tₜₜ = 5 s. W2 (Ring,-) held at 0.5 V. Nₒ is 24%.
Figure 3.5. Levich plot of 1 mM CuSO$_4$ and 1 M KCl from Pt/Pt RRDE experiments. The line for the cathodic limiting current (♦) is $y = 7.83x + 1.49$, $r^2 = 0.9991$. For the anodic limiting current (■) is $y = 1.80x + 0.62$, $r^2 = 0.9969$. 
Figure 3.6. RRDE voltammogram of solution of $10^{-4}$ M Cu(II) and $10^{-3}$ M glycine, $10^{-2}$ M KNO$_3$ as supporting electrolyte. No Cl$^-$ present in solution. Rotation rate is 1000 rpm. W1 (Disk,+) stepped from 0.5 to -0.1 V, 10 mV steps, $t_{ss}$ = 1 s. W2 (Ring,-) held at 0.5 V. Note the absence of Cu(II)/Cu(I) couple.
Figure 3.7. RRDE voltammogram of solution of $10^{-4}$ M Cu(II), $10^{-3}$ M glycine and 1 M KCl. Rotation rate is 1000 rpm. W1 (Disk,+) stepped from 0.5 to -0.1 V, 10 mV step height, $t_{ss} = 1$ s. W2 (Ring,-) held at 0.5 V. Note the absence of Cu(II)/Cu(I) couple.
Figure 3.8. Effects of adding glycine to agarose gel containing $3 \times 10^{-4}$ M Cu(II), 2.5 M Cl⁻ and carbonate buffer (1 M, pH = 8) at IDA electrode. $E_{1/2}$ is +0.01 V for Cu(II)/Cu(I) wave without glycine added (a,+). $E_{1/2}$ is shifted ~70 mV in the negative direction upon addition of 100-fold glycine (c,--). $E_{1/2}$ is only shifted ~10 mV in the negative direction upon addition of two-fold glycine (b,-). Only the forward direction of the voltammograms has been shown from 0.2 to -0.2 V, 2.5 mV increments, $t_{ss}=5$ s. Cathodic currents are due from reduction of Cu(II) to Cu(I) at the generator, and anodic currents are due to oxidation of Cu(I) to Cu(II) at the collector (0.4 V).
Figure 3.9. Photolysis experimental set-up (side view).
Figure 3.10. Voltammogram of gel consisting of $3 \times 10^{-5}$ M Cu(II), $3 \times 10^{-3}$ M Gly, 2.5 M Cl\(^-\), and 1 M carbonate buffer (pH = 8). W1 stepped from 0.2 V to -0.2 V and back (-), 2.5 mV step height, $t_{ss} = 5$ s. W2 held at 0.4 V (+). Note well-developed limiting current plateaus: $i_{lc} = 0.1519$ µA and $i_{la} = 0.1424$ µA.
Figure 3.11. RRDE voltammograms of solutions containing $10^{-4}$ M Cu(II), 2.5 M Cl$^-$, and 1 M carbonate buffer (pH = 8) with no additional $\beta$-alanine (c,$\cdash$), $10^{-3}$ M $\beta$-alanine (a,$\cdash$), and $10^{-2}$ M $\beta$-alanine (b,$\cdash$). Rotation rate is 2000 rpm. Cathodic currents are due to W1 (disk) stepped from 0.2 V to -0.3 V in 5 mV increments, $t_{ss}$ = 5 s, except $10^{-2}$ M $\beta$-alanine (+) that starts at 0.1 V. Anodic currents are measured for W2 (ring) held at 0.4 V. From the ring currents, where Cu(I) is oxidized to Cu(II), $E_{1/2}$ values are -0.10 V for both $\beta$-alanine solutions and ~-0.15 V without $\beta$-alanine. The small shift of potential, 50 mV, for the oxidation peak of Cu(I) upon addition of $\beta$-alanine indicates that $\beta$-alanine would not be an ideal ligand choice for the spectroelectrochemical experiments.
4. Determination of Stability Constants for Copper Corrosion Products Using Interdigitated Array Electrodes

The interdigitated array electrode (IDA) was proposed as an ideal device with which to evaluate stability constants of copper corrosion products. Because its two working electrodes cycle electrochemical products with great efficiency, we thought the concentration of electroactive corrosion products might be measured with great accuracy. Once the appropriate concentrations have been determined, simple calculations will yield the value of the equilibrium constant. This scheme only works if the Cu(I) is stabilized, either as the collector or generator species. Otherwise, Cu(II) species cannot be detected because during detection they would be fully reduced to Cu(0). Therefore, ligands were chosen based on their ability to stabilize Cu(I).

Although corrosion has been studied for many years, not all corrosive environments are well understood. In recent years, biocorrosion has garnered interest because of the apparent effects that bacteria have on corrosion, e.g. corrosion in clean artificial environments is different than in real environments (such as sea water)\(^1\). This process is known as microbiologically influenced corrosion (MIC). The field is wide open to study the mechanisms by which these bacteria influence corrosion. Metabolites such as organic acids can be produced by these organisms in greater, localized concentrations than those found under bulk conditions. Therefore, by studying the complexes between these organic acids and metals, one might gain insight into biocorrosive processes. Videla\(^1\) reported that
specific organic acids have been found as metabolites. These and their stability constant values when available are listed in Table 4.1. It is from this list that possible ligands to study biocorrosion were considered. In addition, the method was evaluated with the well characterized system of copper in chloride media, as well as in bromide solutions (Table 4.2).

4.1. Experimental Procedures

The platinum working electrodes used for these studies were IDAs manufactured by AAI-Abtech, Yardley, PA. The reference and counter electrodes were saturated calomel (SCE) and platinum wire electrodes, respectively. Experiments were performed in a jacketted cell that was thermostatted (25.0 °C unless noted otherwise) by a refrigerated circulator (Fisher Scientific Isotemp 1016). All chemicals were analytical reagent grade and used as received. Solutions were made with Milli-Q water (Milli-Q, Millipore Corp.). Argon bubbled through two gas washing bottles filled with ammonium vanadate solutions in order to, and all solutions were deaerated at least 20 minutes prior to use.

Several steps were necessary to evaluate equilibrium constants using IDAs. A calibration curve of limiting current vs. cuprous concentration was generated with Pt-Pt IDAs first. Solutions of appropriate concentrations were prepared using CuSO₄•5H₂O (Baker). Except for varying copper concentrations, each solution had the same matrix composition as the solution used in the actual corrosion experiment. Between each solution, the IDA was cleaned by acid cycling and
rinsed with copious amounts of Milli-Q water. Limiting currents for the collector, set at +0.40 V to ensure complete oxidation of Cu(I) to Cu(II), were used in the calibration curve.

The second part of the procedure was to deposit copper onto one set of fingers of the IDA. The plating solution was 0.37 M CuSO₄•5H₂O in 1.4 M H₂SO₄; this solution could be used many times before discarding. Copper was plated by applying a potential of -0.1 V to one lead for 33.33 s while the other lead was held at +0.40 V to prevent any copper from plating onto that lead. After plating the electrode was rinsed with water before further experiments were performed.

In order for each experiment to be repeated many times, the freshly prepared electrode needed to be completely covered with sufficient copper while still retaining the dimensions of the Pt substrate. Due to limitations of the potentiostat, exact current during deposition could not be monitored. Therefore to quantify the amount of copper deposited, chronoamperometry was performed to strip off all the deposited copper (Figure 4.1). This result was integrated to obtain the total charge due to copper oxidation. The total charge was 25,026 uC, which corresponds to 1.297 x 10⁻⁷ mol for a two-electron process. The area of the electrode is 0.0125 cm², giving a coverage of 1.0376 x 10⁻⁵ mol/cm². The radius of a copper atom is 1.27 Å, so if the atoms were touching one another, then we would expect 6.4516 x 10⁻¹⁶ cm²/Cu atom. Area divided by cm²/Cu atom yields 1.9375 x 10¹³ Cu atoms/monolayer. Multiplying moles by Avagadro’s number gives 7.8107 x 10¹⁵ atoms or 4030 layers of Cu, or about 1000 nm of copper on the electrode.
The last step and the crux of the experiment was to anodize selectively the copper lead and detect current from the corrosion product at the Pt collector electrode. These experiments were performed in solutions of chloride, bromide, or maleic acid, without any copper ions present in the bulk solution. Potential of the copper lead was chosen such that detected complex remained within the calibration curve values. The potential was also negative enough to afford many repetitions without stripping all copper off of the lead too fast. Typical anodization potentials were around -0.30 V vs. SCE.

Note that the calibration is a typical IDA experiment that takes advantage of redox cycling. The anodization is a different type of experiment, but redox cycling occurs in the anodization experiment too. Cu(I) that is produced at the generator is not cycled back to its precursor at the collector electrode; it is oxidized further to Cu(II). Then, as evidenced by the cathodic current for the generator that mirrors the anodic current magnitude in Fig. 4.3, Cu(II) is reduced to Cu(I) at the generator. Therefore, the same current to concentration relationship for the calibration curves exists for the actual anodization experiments. In other words, the calibration curves may be used in order to obtain concentration values from the measured currents without multiplying by any redox cycling values.

For the chloride experiments, total concentration of that anion was controlled by amounts of NaCl (Aldrich) and 1 mM HCl. Total chloride concentration was 0.50, 0.75, or 1.0 M. Experiments were performed at pH=3 to remove the possibility of interference by oxides or hydroxides.
Bromide solutions ranged in concentration from 0.010 to 0.10 M NaBr, and solutions were acidified by the addition of H$_2$SO$_4$ to a concentration of 1 mM.

Maleic acid (H$_2$Mal) solutions were made with C$_4$H$_4$O$_4$, and pH was adjusted with concentrated NaOH to minimize dilution. The pH meter (Corning pH meter 220) was always calibrated before each use.

4.2. Determination of Cuprous Chloride Equilibrium Constant

The predominant cuprous chloride species for the chloride concentrations between 0.5 and 1.0 M is CuCl$_2^-$. The overall equilibrium constant, $\beta_2$, to be determined for this species is defined as:

$$\beta_2 = \frac{(\text{CuCl}_2^-)}{(\text{Cu}^+)(\text{Cl}^-)^2} \quad (4.1)$$

The activity of each species is calculated from the concentration of each species using Bromley’s activity coefficient, described below. Chloride concentration is simply the analytical concentration. From the Nernst equation $[\text{Cu}^+]$ may be calculated:

$$E = E^0 + \frac{RT}{nF} \ln\left(\frac{[\text{Cu}^+]}{[\text{Cu}^0]}\right) \quad (4.2)$$

where $E$ is the potential set by the potentiostat, $RT/F = 0.02569$ V, and $E^0$ is the standard potential of the Cu$^+/Cu^0$ couple (0.273 V vs. SCE). The activity of Cu$^0$ is assumed to have the value of one. The missing piece of information then is $[\text{CuCl}_2^-]$, and this is obtained by measuring current due to oxidation of that species at the collector electrode and relating that current to concentration using the calibration curve.
Activity may be accounted for using Bromley’s method for calculating the activity coefficients:

\[
\log \gamma_i = -Az_i^2 I^{1/2} / (\rho^{1/2} + I^{1/2}) + (0.06 + 0.6B) z_i^2 I / [\rho + (1.5I/z_i^2)]^2 + Bl/\rho
\]  

(4.3)

where \(A\) is the Debye-Huckel constant (0.512 in aqueous solution), \(z_i\) is the charge on the ion, \(\rho\) is the solution density, \(B\) is the Bromley coefficient for the ion, and \(I\) (molarity) is the ionic strength. Bromley does not list a coefficient for \(\text{CuCl}_2^-\), so the assumption has been made that the coefficient is equal to that of \(\text{Cl}^-\) (Table 4.3).

Calibration curves used for \([\text{CuCl}_2^-]\) determination are given in Figure 2. Due to the length of time it took for each standard and the overall experiment, more calibration points were not measured. A sample stability constant determination is as follows: for 0.75 M \(\text{Cl}^-\) and copper working electrode at -0.30 V, an average limiting current of 0.5740 µA is obtained at the Pt collector electrode that is stepped from 0.1 to 0.4 V (Figure 4.3). Using the equation of the line for the calibration curve this current corresponds to 59.7 µM \(\text{CuCl}_2^-\). Assuming an activity coefficient of 0.67 for \(\text{CuCl}_2^-\), the activity of \(\text{CuCl}_2^-\) is 40.3 µM. Using the Cu(I) equilibrium value of \(2.057 \times 10^{-10}\) M, \(\log \beta_2\) is 5.89. This experiment was performed at different potentials, which are shown together in Fig. 4.4 for 0.75 M \(\text{Cl}^-\). Results of all chloride experiments are summarized in Table 4.4.

A closer look at the voltammogram presented in Fig. 4.3 is warranted. The copper working electrode (+) at first shows the expected negative current due to the anodization of Cu(0) to Cu(I). This current begins to change as the potential of the collector electrode changes. The positive current seen at the top right portion of the
voltammogram is due to the reduction of Cu(I) formed in the reproportionation reaction:

$$\text{Cu(II)} + \text{Cu(O)} \rightarrow 2 \text{Cu(I)}$$  \hspace{1cm} (4.4)

Because we assume equilibrium conditions, the Nernst equation applies and the amount of Cu(I) at the electrode surface remains constant. The Cu(II) is from the oxidation of Cu(I) at the Pt collector electrode, whose limiting current is seen at the bottom right of the voltammogram. The final feature that needs an explanation is the rapid decline of current at 0.1 V for the Pt collector. This is due to the oxidation of copper that plated onto the electrode during the rest between experiments. Because the rest potential must be the same for both electrodes, the rest potential was set at -0.4 V to ensure the generator electrode remained plated with copper between experiments.

Although the standard deviations are acceptable, a certain trend in the data is present. For these experiments, there was a general trend towards greater calculated log $\beta_2$ values at more negative Cu WE potentials. In order to determine whether residual oxygen was causing the behavior, a plot of [CuCl$_2^-$] vs. potential of copper working electrode was made for each solution. At more negative potentials, the slope veered away from the theoretical 59 mV reciprocal slope (Fig 4.5). When the values used only at potentials that correlated most closely to 59 mV were used, log $\beta_2 = 5.88$ std dev. 0.03, n=52 for all files. Residual oxygen is a reasonable explanation for this behavior because µM amounts could be present, corroding the Cu and thus causing an increase in the measured concentration of CuCl$_2^-$.
The above determinations assumed that the major and only contributing species to the current was CuCl$_2^-$.
This is not strictly true; for the range of chloride studied, CuCl$_{aq}$ is 0.2% to 0.5% of CuCl$_2^-$ using equilibrium values obtained by Orr et al.$^5$ To obtain more accurate equilibrium data and values, the CuCl$_{aq}$ complex should be considered. Taking into account both complexes would also enable this method to be used for less concentrated chloride solutions. Therefore a program was written based on the limiting currents measured at the Pt collector electrode versus the potential set at the copper working electrode. The equations (refer to Attachment 4.1) were based on previous work for a microdisk electrode published from this laboratory.$^5$ In order to get the best possible results, one must have a well defined curve shape, requiring many points at the most negative copper electrode potential region where the limiting current is essentially zero. Thus, one may obtain the full shape as the Pt limiting current increases as the copper working electrode potential is shifted in a positive direction. Investigation at this level of detail was not required for this system, the objective of which was to demonstrate the concept.

### 4.3. Determination of Cuprous Bromide Equilibrium Constant

Equilibrium constants values for copper bromide species from the literature are given in Table 4.2. The predominant cuprous bromide species for bromide concentrations between 0.05 and 0.10 M is CuBr$_2^-$.$^7$ This concentration range was chosen for study to make calculations and data analysis simpler. The overall equilibrium constant, $\beta_2$, to be determined is then defined as:
\[ \beta_2 = \frac{(\text{CuBr}_2^-)}{(\text{Cu}^+)(\text{Br})^2} \] (4.5)

Cuprous and bromide concentrations were determined in an analogous manner to the method for the chloride experiments outlined in section 4.2. Bromley’s activity coefficient is listed in Table 4.3. The cuprous bromide species was determined in the same manner as the cuprous chloride concentration, through use of a calibration curve to relate current from Cu(I) oxidation to concentration of CuBr$_2^-$.

Steady-state voltammograms for calibration curves were well-defined (Fig. 4.6). Taking all experimental results into account, \( \log \beta_2 = 6.42 \), std dev = 0.18 n=45 (Table 4.6). Refer to Figure 4.7 for an example of this experiment in 0.1 M NaBr.

Similar to the chloride results, this data set also had a general trend towards greater calculated \( \log \beta_2 \) values at more negative Cu WE potentials. When the values used only at potentials that correlated most closely to 59 mV reciprocal slope were used, \( \log \beta_2 = 6.17 \) (Table 4.7). These results are within an order of magnitude agreement with available literature values.

4.4. Determination of Copper-Maleic Acid Equilibrium Constants

Maleic acid was studied due to its reported Cu(II) and Cu(I) complexes (Table 4.1), making monitoring with IDAs possible because the monovalent state is stabilized. As seen in Figure 4.8, Cu(I) is stabilized as evidenced by the symmetrical near-mirror image plateau of the collector (held at 0.4 V) as Cu(II) is reduced at the generator electrode. The solid line is from the cyclic voltammogram of a Cu(II) solution without any maleic acid. The large rising cathodic current
peaking at about 0.1 V is due to the reduction of Cu(II) to Cu(0). Copper plates out because there is no species present to stabilize Cu(I). As the electrode potential is cycled back, oxidation occurs that results in the peak at ~0 V. As the maleic acid concentration is increased, Cu(I) is stabilized and plating occurs at more negative potentials. At a 1:1 Cu(II):maleic acid ratio (+), as the generator potential becomes more negative the collector current increases appreciably due to the presence of Cu(I). Once the potential reaches ~-0.15 V, the current rapidly increases due to copper plating out. As the potential is cycled back, the peaks at -0.15 V arise due to the generation of Cu(I) which is then oxidized to Cu(II) at the collector. These two peaks are the same height, because both are one-electron processes and $N_0$ is high. The final data set, at a 10:1 Cu(II):maleic acid ratio (o), was terminated at -0.2 V, before cycling back, due to evidence of Cu plating. In this case a limiting current plateau may be observed for both generator and collector electrodes, at 0.2 and -0.15 µA respectively, before plating occurs.

Since maleic acid is a weak acid, the relationship of its species versus pH is also necessary. The $pK_a$ values are 1.910 and 6.332. The distribution diagram was calculated using the MINEQL7 program (Fig. 4.9). Due to the probability of oxides and hydroxides forming at higher pH, pH=5 values were chosen to have sufficient Mal2- species.
4.4.1. Cu(II) Maleic acid complexes

The first maleic acid experiments were performed by anodizing the copper electrodes at positive enough potentials to generate Cu(II) ions. Because maleic acid stabilizes Cu(I), it is possible to detect CuMal complexes by a one-electron reduction process at the collector electrode.

The first solution chosen for study was 0.0255 M H₂Mal, adjusted to pH=5. However, the copper calibration curve was nonlinear. Therefore the concentration was increased one order of magnitude to 0.255 M H₂Mal, pH=5, to ensure enough complexing agent was available to complex all the copper ions formed by the electrolysis. This change resulted in linear calibration curves for the range studied.

Once calibration curves were obtained, plating and anodization of the copper working electrode was done similarly to the procedure outlined for the halide experiments. It was difficult to acquire reproducible results with this system, however. The calculated equilibrium values of $K_{\text{CuMal}} = 2$ were too low to be acceptable, as well.

The most likely explanation for these low values is precipitation of Cu(OH)₂. At the potential of the copper working electrode, Cu(II) concentration would be ~0.06 M, where precipitation is likely at pH=5.² This would decrease Cu(II) available for complexation with maleic species, providing a reasonable explanation for the apparent low concentration of CuMal complex recovered at the collector. Experimentally this scenario was tested by trying to recreate in the bulk solution the conditions that were calculated to exist at the copper working electrode.
Precipitation was observed when a solution of 0.255 M H₂Mal, pH = 5, was brought up to 0.03 M CuSO₄. Precipitation clearly occurred when the concentration of CuSO₄ added to the maleic acid solution (0.255 M, pH = 5) exceeded 0.30 M.

Anodizing the copper working electrode at more negative potentials to preclude precipitation is described below.

### 4.4.2. Cu(I) Maleic acid complexes

It is worthwhile to note that the NIST database for stability constants² listed only one complex for maleic acid and Cu(I) species, which was CuMal⁻ with $K_{\text{CuMal}^-} = 3.05$. Our reasoning in adjusting pH to 5 was to ensure that sufficient Mal₂⁻ was present. However other references³,⁴ report that all three forms of the acid complex with Cu(I). Stability constants for the three complexes from CuH₂Mal⁺ to CuMal⁻ have been reported (Table 4.1).

When the anodization potential of the copper working electrode is as negative as for the chloride and bromide experiments, calculated Cu(I) concentrations are very small and precipitation should not occur.⁹ Maleic acid concentrations were the same, 0.255 M, as for the previous experiments.

To ascertain whether the species formed by the anodization of Cu was Cu(I) or Cu(II) complex, the collector potential was initially set such that Cu(II) would be reduced to Cu(I), as noted in voltammograms used in the calibration curves. There was no current at this potential, so instead the collector was set to oxidize Cu(I) to Cu(II). Current was observed in this case. Thus the product is assumed to be a complex of Cu(I).
The experiment was performed at pH = 5. The calibration information may be viewed in Figure 4.10. Figure 4.11 shows a typical voltammogram for the response of the corrosion experiment in maleic acid solutions. In this case, the calculated value for K was much higher than the literature values, at log \( K_{\text{CuMal}} = 6.6 \). If all the current were due to the CuHMal complex, then log \( K_{\text{CuHMal}} = 5.4 \). The reciprocal slopes of log of complex concentration vs. potential for the least negative potentials (-0.25 V to -0.28 V) is 62 mV (Table 4.8).

The current measured at the collector might be due to a combination of cuprous-maleic acid complexes. At a pH value of 5, the two maleic acid species present in appreciable amounts are HMal\(^-\) and Mal\(^2-\), in amounts of 95% and 5% respectively (pK\(_{a,2}\) = 6.332 for maleic acid). Using the equilibrium values reported by Navon\(^3\) (Table 4.1), the CuHMal:CuMal\(^-\) ratio is 9:1 at a pH value of 5. In this case, making the assumption that 90% of the measured current is from CuHMal and 10% is from CuMal\(^-\), log \( K_{\text{CuMal}} = 4.8 \) and \( K_{\text{CuHMal}} = 4.5 \).

These values are a little larger than those previously reported by Navon, but more experiments would need to be performed in order to determine if these differences are significant. Interference with the electrode processes of interest is a possible cause of error in the results. One might argue that the pH is changing at the electrode surface, thus changing the ratio of species. However, at 0.255 M maleic acid, there should be a sufficient reservoir of acid present to buffer possible pH change resulting from any reactions at or near the electrode surface. There is also a possible reduction reaction in maleic acid solutions, but evidence for this was not seen at pH = 5. That reaction is the reduction of maleic acid to fumaric acid by
the addition of two protons and two electrons. The organic nature of maleic acid could also interfere with the electrode processes.

Future experiments that would help explain these results include changing the pH conditions and calculating resulting equilibrium values. Observing how these values change or remain constant as pH is varied should shed light on the actual identity or identities of the copper-maleic acid complexes.

4.5. Conclusions

A novel method to determine stability constants of cuprous corrosion products using IDA electrodes was studied. In the case of the halides Cl⁻ and Br⁻, equilibrium values were determined to be $\beta_2 = (\text{CuCl}_2^-)/(\text{Cu}^+)(\text{Cl}^-)^2 = 5.88 \pm 0.03$ and $\beta_2 = (\text{CuBr}_2^-)/(\text{Cu}^+)(\text{Br}^-)^2 = 6.17 \pm 0.08$, respectively. These values fall within the range of values reported in the literature. A system of equations that considers both $\text{CuCl}_2^-$ and $\text{CuCl}_{aq}$ species was solved for the copper chloride system. This could be used to calculate more accurate equilibrium values in the future. A similar system could be solved for the copper bromide case. Maleic acid was studied due to its significance in biocorrosion. Further experiments at different pH values need to be performed to obtain convincing results, but the initial results indicate that this method should also be applicable to organic acids.

This method of obtaining corrosion product stability constants with IDA electrodes is interesting and promising. It does need to be studied further to establish it as a routine method.
4.6. References


2. Smith and Martell. Critically Selected Stability Constant of Metal Complexes. NIST, v. 3.0, 1997


Table 4.1. Common organic acid metabolites that may contribute to corrosion. 

<table>
<thead>
<tr>
<th>Organic Acid</th>
<th>( \log K ) or ( \beta ) Cu(II) complexes a</th>
<th>( \log K ) or ( \beta ) Cu(I) complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric Acid</td>
<td>ML 2.22</td>
<td>N/A</td>
</tr>
<tr>
<td>Isocitric</td>
<td>ML 5.20</td>
<td>N/A</td>
</tr>
<tr>
<td>Cis-asconitic</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>( \alpha )-ketoglutaric</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Succinic</td>
<td>ML 2.7, 3.48</td>
<td>N/A</td>
</tr>
<tr>
<td>Maleic</td>
<td>ML 3.42, ML(_2) 5.2</td>
<td>ML 3.05(^a), 4.45(^b), 4.8(^d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MHL 4.31(^c), 4.08(^b), 4.5(^d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MH(_2)L 3.05(^c), 3.36(^b)</td>
</tr>
</tbody>
</table>
Table 4.2. Stability constants for chloride and bromide complexes. Values noted by a are from Orr et al.\textsuperscript{5} Values noted by b are from this work. All other values from reference 2.

<table>
<thead>
<tr>
<th>Copper Valence, Ligand</th>
<th>log $K_1$</th>
<th>log $\beta_2$</th>
<th>log $K_3$</th>
<th>$ML_3/(ML_2)(L)$</th>
<th>log $\beta_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(I), Cl\textsuperscript{-}</td>
<td>2.70, 2.93\textsuperscript{a}</td>
<td>5.19, 5.79, 6.06, 5.42, 5.54\textsuperscript{a}, 5.88\textsuperscript{b}</td>
<td>ML\textsubscript{3}/(ML\textsubscript{2})(L)</td>
<td>-0.67, -0.28, -0.12</td>
<td></td>
</tr>
<tr>
<td>Cu(II), Cl\textsuperscript{-}</td>
<td>-0.2 to 0.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(I), Br\textsuperscript{-}</td>
<td>3.53</td>
<td>6.28, 5.86, 6.17\textsuperscript{b}</td>
<td></td>
<td>7.45, 6.43</td>
<td></td>
</tr>
<tr>
<td>Cu(II), Br\textsuperscript{-}</td>
<td>-0.64 to -0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.3. Calculated activity coefficients using Bromley’s method.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Concentration (M)</th>
<th>Activity Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>1.0</td>
<td>0.556</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.75</td>
<td>0.67</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.50</td>
<td>0.69</td>
</tr>
<tr>
<td>Bromide</td>
<td>0.10</td>
<td>0.78</td>
</tr>
<tr>
<td>Bromide</td>
<td>0.075</td>
<td>0.78</td>
</tr>
<tr>
<td>Bromide</td>
<td>0.050</td>
<td>0.78</td>
</tr>
</tbody>
</table>
Table 4.4. Calculated stability constants for CuCl$_2^-$.

<table>
<thead>
<tr>
<th>[Cl$^{-}$]</th>
<th>Potential Range of Cu Working Electrode (V)</th>
<th>log $\beta_2 \pm$ s.d.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-0.36 to -0.30</td>
<td>6.02 ± 0.07</td>
<td>21</td>
</tr>
<tr>
<td>0.75</td>
<td>-0.36 to -0.25</td>
<td>5.92 ± 0.04</td>
<td>27</td>
</tr>
<tr>
<td>0.50</td>
<td>-0.36 to -0.25</td>
<td>5.95 ± 0.10</td>
<td>32</td>
</tr>
<tr>
<td>average of all data points</td>
<td></td>
<td>5.92 ± 0.15</td>
<td>80</td>
</tr>
</tbody>
</table>
Table 4.5. Calculated stability constants using only potentials that fall within Nernstian range for CuCl$_2^-$.

<table>
<thead>
<tr>
<th>[Cl$^-$]</th>
<th>Potential Range of Cu Working Electrode (V)</th>
<th>log $\beta_2 \pm$ s.d.</th>
<th>n</th>
<th>Reciprocal Slope (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-0.34 to -0.30</td>
<td>5.89 ± 0.02</td>
<td>15</td>
<td>58</td>
</tr>
<tr>
<td>0.75</td>
<td>-0.34 to -0.29</td>
<td>5.89 ± 0.02</td>
<td>18</td>
<td>60</td>
</tr>
<tr>
<td>0.50</td>
<td>-0.31 to -0.25</td>
<td>5.86 ± 0.02</td>
<td>18</td>
<td>62</td>
</tr>
<tr>
<td>average of all data points</td>
<td>5.88 ± 0.03</td>
<td>51</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.6. Calculated stability constants for CuBr$_2$.

<table>
<thead>
<tr>
<th>[Br$^-$]</th>
<th>Potential Range of Cu Working Electrode (V)</th>
<th>log $\beta_2 \pm$ s.d.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>-0.36 to -0.30</td>
<td>6.22 ± 0.14</td>
<td>12</td>
</tr>
<tr>
<td>0.075</td>
<td>-0.36 to -0.25</td>
<td>6.27 ± 0.04</td>
<td>12</td>
</tr>
<tr>
<td>0.050</td>
<td>-0.30 to -0.17</td>
<td>6.35 ± 0.20</td>
<td>21</td>
</tr>
<tr>
<td>average of all data points</td>
<td></td>
<td>6.31 ± 0.18</td>
<td>45</td>
</tr>
</tbody>
</table>
Table 4.7. Calculated stability constants using only potentials that fall within Nernstian range for CuBr$_2^-$.  

<table>
<thead>
<tr>
<th>[Br$^-$]</th>
<th>Potential Range of Cu Working Electrode (V)</th>
<th>log $\beta_2$ ± s.d.</th>
<th>n</th>
<th>Reciprocal Slope (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>-0.34 to -0.30</td>
<td>6.10 ± 0.03</td>
<td>6</td>
<td>67</td>
</tr>
<tr>
<td>0.075</td>
<td>-0.30 to -0.20</td>
<td>6.24 ± 0.02</td>
<td>6</td>
<td>63</td>
</tr>
<tr>
<td>0.050</td>
<td>-0.23 to -0.17</td>
<td>6.17 ± 0.09</td>
<td>9</td>
<td>56</td>
</tr>
<tr>
<td>average of all data points</td>
<td></td>
<td>6.17 ± 0.08</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.8. Calculated Cu(I) Maleic acid complexes at potential noted for copper working electrode. Total H₂Mal concentration of solutions is 0.255 M, pH = 5. Only the values for the potentials -0.25 and -0.28 should be considered due to the agreement of those values and the 62 mV reciprocal slope value.

<table>
<thead>
<tr>
<th>Cu WE (V)</th>
<th>log $K_{CuH₂Mal}⁺$</th>
<th>log $K_{CuHMal}$</th>
<th>log $K_{CuMal}⁻$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.25</td>
<td>8.0</td>
<td>5.4</td>
<td>6.6</td>
</tr>
<tr>
<td>-0.28</td>
<td>8.0</td>
<td>5.4</td>
<td>6.6</td>
</tr>
<tr>
<td>-0.30</td>
<td>8.3</td>
<td>5.8</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Reciprocal Slope (mV) 88
(-0.30 to -0.25 V)

Reciprocal Slope (mV) 62
(-0.28 to -0.25 V)
Figure 4.1. Stripping copper deposit off one IDA lead in 1 M KNO₃ solution. Integration results in total charge of 25026 µC.
Figure 4.2. Calibration curves of current due to oxidation of Cu(I) at collector electrode vs. Cu(II) concentration of standard solution. Equation of the lines for 1 M (◆), 0.75 M (▲), and 0.5 M (★) Cl⁻ are respectively: \( y = 7.26x + 0.031, r^2 = 0.9969; \) 
\( y = 9.92x - 0.018, r^2 =0.9928; \) 
\( y = 10.948x - 0.0092, r^2 =0.9997. \)
Figure 4.3. Voltammogram of 0.75 M Cl⁻ solution where copper working electrode \((+\)) is -0.30 V. This potential corresponds to a Cu(I) concentration of \(2.06 \times 10^{-10}\) M. Platinum collector (0.1 to 0.4 V, 10 mV steps, \(t_{ss} = 10\) s) where Cu(I) is oxidized has limiting current of 0.5740 µA \((-\)). The line at zero current is a software artifact, not an experimental result, that occurs because the voltammogram was terminated before the electrode was cycled back to the initial potential.
Figure 4.4. Voltammogram of 0.75 M Cl\(^{-}\) solution where copper working electrode (+) is at potential noted on figure. Platinum collector (-) where Cu(I) is oxidized, stepped in 10 mV increments, \(t_{ss} = 10\) s, from 0.1 to 0.45 V. The smallest currents (cathodic and anodic) occur at the most negative potentials of the copper working electrode, beginning with -0.36 V. Currents increase as potential of the copper working electrode become less negative.
Figure 4.5. Plot of log [CuCl$_2$] vs. potential of copper working electrode in 0.50 M Cl$^-$ solution. Reciprocal slope is 62 mV for points from -0.31 V to -0.25 V (-), which is the range for which the line is closest to the Nernstian value of 59 mV.
Figure 4.6. Calibration curves of current due to oxidation of Cu(I) at collector electrode vs. Cu(II) concentration of standard solution. Equation of the lines for 0.1 M (●), 0.075 M (▲), and 0.05 M (★) Br⁻ are respectively: $y = 9509.8x - 0.0089$, $r^2 = 0.9995$; $y = 9027.4x + 0.0095$, $r^2 = 0.9944$; $y = 10670.7x - 0.0014$, $r^2 = 0.9999$. 
Figure 4.7. Steady-state voltammogram of 0.1 M Br⁻ solution where copper working electrode (+) is -0.25 V. Platinum collector (-0.2 to 0.4 V, 10 mV steps, t_{ss} = 10 s) where Cu(I) is oxidized has limiting current of 0.1847 µA (-).
Figure 4.8. Cyclic voltammograms of 0.1 mM CuSO₄ solutions with different amounts of maleic acid. The pH was not adjusted, and 10 mM KNO₃ was added as supporting electrolyte. Maleic acid concentration: 0 M, pH = 3.2 (-), 10⁻⁴ M, pH = 3.6 (+), 10⁻³ M, pH = 2.7 (o). Working electrode 1 is stepped from 0.4 to -0.2 V in 5 mV increments, tₜₜ = 5 s. WE2 is held at 0.4 V. As the amount of H₂Mal increases, Cu(I) is becoming stabilized. Refer to text for discussion (Section 4.4).
Figure 4.9. Maleic acid distribution diagram as a function of pH, prepared using MINEQL+ program. The pKₐ values are 1.910 and 6.332. This work was done at the pH value of 5, where HMal⁻ and Mal²⁻ are 95% and 5%, respectively, of the total acid species present.
Figure 4.10. Calibration curve of Cu(I)-Maleic acid experiment. Current due to oxidation of Cu(I) at collector electrode vs. Cu(II) concentration of standard solution. All solutions are 0.255 M H$_2$Mal, pH adjusted to 5. Equation of the line is $y = 2.902x + 0.0106$, $r^2 = 0.9961$. 
Figure 4.11. Steady-state voltammogram of 0.255 M H$_2$Mal, pH = 5, where copper working electrode (+) is -0.28 V. Platinum collector (-0.1 to 0.4 V, 10 mV steps, $t_{ss}=10$ s) where Cu(I) is oxidized and has limiting current of 0.074 µA (-).
Appendix 4.1. Copper Anodization at the Interdigitated Electrode.
Copper Anodization at the Interdigitated Electrode

Reference:


Symbol Table

\( A \equiv \) electrode area
\( b \equiv \) length of IDE element, also a bias in observed currents
\( \beta_p \equiv \) formation constant of the \( p \)th complex
\( C \equiv \) bulk concentration of chloride ion
\( D \equiv \) diffusion coefficient
\( D_X \equiv \) diffusion coefficient of reacting species, \( X \)
\( E^0 = 0.273 \), standard potential
\( \delta \equiv \) diffusion layer thickness, \( \delta = \pi r/4 \) for microdisk electrode
\( \varepsilon(0; \sigma) \equiv \) residual errors with zero mean
\( F \equiv \) Faraday constant
\( f = F/RT \)
\( \gamma \equiv \) activity coefficient
\( i_{\text{lim}} \equiv \) limiting steady-state current
\( i_{\text{ss}} \equiv \) steady-state current
\( m \equiv \) ion valence, number of IDE fingers
\( N_0 \equiv \) collection efficiency
\( n \equiv \) number of electrons transferred
\( p \equiv \) ligand number, number of ligands per metal ion
\( R \equiv \) gas constant
\( T \equiv \) absolute temperature
\( [X]_S \equiv \) concentration of species \( X \) at the electrode surface
\( [X]_o \equiv \) concentration of species \( X \) in the bulk electrolyte
\( x \equiv \gamma_{\text{Cl}} [\text{Cl}^\text{−}]_s \), activity of chloride ion at the electrode surface
The general reaction for metal anodization in the presence of ligands is:

\[ M + pX^{m-} = MX_p^{(mp-n)-} + ne^- \]

where \( p \) is the number of ligands per metal ion.

The overall formation constant of the \( p \)th complex, \( \beta_p \), is given by:

\[ \beta_p = \left( \frac{MX_p^{(mp-n)-}}{(M^{n+})(X^{m-})} \right)^p \]

The steady-state current as a function of the concentration of reacting species \( X \) is:

\[ i_{ss} = \frac{(n/p)FAD_X(\partial C/\partial x)_S}{(n/p)FAD_X ([X]_S - [X]_o)}/\delta \]

The subscript \( S \) denotes evaluation at the electrode surface. The current is negative for an oxidation according to convention.

Under steady-state conditions the current at an interdigitated electrode as a function of the concentration of species \( X \) is:

\[ i_{ss} = -\left[ N_o mb(n/p)FAD \sum_p \left( \beta_p \left( \gamma_X^p/\gamma_{MX} \right) \right) p[X^{m-}]_S \right] \]

where all species are assumed to have the common diffusion coefficient, \( D \).

In the present case the initial bulk concentration of each product, \( [MX_p^{(mp-n)-}]_o \), is zero. Eliminating that term and using the overall formation constants and the Nernst equation gives:

\[ i_{ss} = -\left[ N_o mb(n/p)FAD \sum_p \beta_p \theta (\gamma_X^p/\gamma_{MX}) p[X^{m-}]_S \right] \]

where:

\[ \theta = e^{-nf(E-E^0)} \]

\[ f = F/RT = 38.93 \]

\[ E^0 = 0.273 \]

\( E^0 \) is known from an independent measurement.
The total current is expressed as the sum of contributions for the two cases, $p = 1$ and $p = 2$.

For $p = 1$:

$$i_1 = -(N_0 m b n F D) K_1 \theta \left( \gamma_{Cl^+} / \gamma_{CuCl} \right) \left[ Cl^- \right]_s$$

For $p = 2$:

$$i_2 = -(N_0 m b n F D) \beta_2 \theta \left( \gamma_{Cl^+}^2 / \gamma_{CuCl_{2}}^2 \right) \left[ Cl^- \right]_s^2$$

$i_1$ and $i_2$ are rendered dimensionless by dividing by the limiting current:

$$i_{\text{lim}} = -N_0 D m b n F C$$

This yields the dimensionless currents $\psi_1$ and $\psi_2$:

$$\psi_1 = K_1 \theta \left( \gamma_{Cl^+} / \gamma_{CuCl} \right) \left[ \left[ Cl^- \right]_s / C \right]$$

$$\psi_2 = \beta_2 \theta \left( \gamma_{Cl^+}^2 / \gamma_{CuCl_{2}}^2 \right) \left[ \left[ Cl^- \right]_s^2 / C \right]$$

where $C$ is taken to be the bulk concentration of chloride ion, $C = [Cl^-]_0$.

The total dimensionless current function is the sum of the individual current functions.

$$\psi = \psi_1 + \psi_2 = \theta / C \left( K_1 \left[ \gamma_{Cl^+} / \gamma_{CuCl} \right] \left[ Cl^- \right]_s + \beta_2 \left[ \gamma_{Cl^+}^2 / \gamma_{CuCl_{2}}^2 \right] \left[ Cl^- \right]_s^2 \right)$$

Let $x = \gamma_{Cl^-} \left[ Cl^- \right]_s$, the activity of $Cl^-$ at the surface of the electrode, then:

$$\psi = \left( \theta / C \right) \left( K_1 \left( 1 / \gamma_{CuCl} \right) x + \beta_2 \left( 1 / \gamma_{CuCl_{2}} \right) x^2 \right)$$

Assuming that the singly charged ionic species $Cl^-$ and $CuCl_{2}$ have the common activity coefficient, $\gamma$, and that $\gamma_{CuCl} = 1$, then the dimensionless current function simplifies to:

$$\psi = \left( \theta / C \gamma \right) \left( K_1 x + \beta_2 x^2 \right)$$
\[ \psi = (\theta x/C\gamma)(\beta_2 x + K_1\gamma) \]

where:

\[ \beta_2 = \frac{[\text{CuCl}_2]}{[\text{Cu}^+][\text{Cl}^-]^2} \]

The equation for mass balance of chloride ion is:

\[ [\text{Cl}^-]_0 = [\text{Cl}^-]_s + [\text{CuCl}]_s + 2[\text{CuCl}_2] \]

Multiplying by \( \gamma \) and using the definitions of the formation constants gives:

\[ \gamma C = x + K_1\theta \gamma x + 2\beta_2 \theta x^2 \]

\[ 2\beta_2 \theta x^2 + (1 + K_1 \theta \gamma) x - \gamma C = 0 \]

Recognizing this as a quadratic equation of the form \( ax^2 + bx + c = 0 \) and solving for \( x \) gives:

\[ x = \left(4\beta_2 \theta\right)^{-1}\left\{\left[(1 + K_1 \theta \gamma)^2 + 8\beta_2 \theta \gamma C\right]^{1/2} - (1 + K_1 \theta \gamma)\right\} \]

\[ x = \frac{-\left(1 + K_1 \theta \gamma\right) + \left[(1 + K_1 \theta \gamma)^2 + 8\beta_2 \theta \gamma C\right]^{1/2}}{4\beta_2 \theta} \]

Substituting this expression for \( x \) into the equation for dimensionless current gives:

\[ \psi = \left(\frac{\theta}{C\gamma}\right)\left(-\frac{1 + K_1 \theta \gamma}{4\beta_2 \theta}\right)\left[\beta_2\left(-\frac{(1 + K_1 \theta \gamma) + \left[(1 + K_1 \theta \gamma)^2 + 8\beta_2 \theta \gamma C\right]^{1/2}}{4\beta_2 \theta} + K_1\gamma\right)\right] \]

Terms \( \theta \) and \( \beta_2 \) cancel to give:

\[ \psi = \left(-\frac{(1 + K_1 \theta \gamma) + \left[(1 + K_1 \theta \gamma)^2 + 8\beta_2 \theta \gamma C\right]^{1/2}}{4\beta_2 C\gamma}\right)\left(-\frac{(1 + K_1 \theta \gamma) + \left[(1 + K_1 \theta \gamma)^2 + 8\beta_2 \theta \gamma C\right]^{1/2}}{4\theta} + K_1\gamma\right) \]
After minor rearrangement of terms the following solution for $\psi$ is obtained:

$$\psi = \left( \frac{-(1 + \theta K_1 \gamma) + \left[ (1 + \theta K_1 \gamma)^2 + 8\theta \beta_2 \gamma C \right]^{1/2}}{4\beta_2 C \gamma} \right) \left( \frac{-(1 + \theta K_1 \gamma) + \left[ (1 + \theta K_1 \gamma)^2 + 8\theta \beta_2 \gamma C \right]^{1/2}}{4\theta} \right) + K_1 \gamma$$

Since $\theta$ is a constant determined by an independent measurement of $E^0$, this equation clearly shows that the dimensionless current, $\psi$, is a function of exactly two quantities, $K_1\gamma$ and $\beta_2 \gamma C$. These two combinations of parameters are evaluated using non-linear least squares with experimental measurements of $E^0$ and $i_{ss}$ versus potential.

The dimensionless current, $\psi$, is related to the observable steady-state current, $i_{ss}$, by:

$$i_{ss} = a\psi(K_1\gamma, \beta_2 \gamma C) + b + \epsilon(0; \sigma)$$

where:

$$a = -N_d m b n F D C$$

$b$ is an experimental bias in the observed current.
Program Specification

Input:

1) pairs of potential and experimental steady-state current (steady-state voltammogram)
2) $E^0$, given by an independent measurement
3) estimate of $\log(K_1\gamma)$ and step size
4) estimate of $\log(\beta_2\gamma C)$ and step size

Output:

1) pairs of potential and model steady-state currents (model steady-state voltammogram)
2) optimal $\log(K_1\gamma)$
3) optimal $\log(\beta_2\gamma C)$