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ADDITIVE MONITORING AND INTERACTIONS
DURING COPPER ELECTROPROCESSING

by

Dale Wade Collins

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

2001
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Dale Wade Collins entitled ADDITIVE MONITORING AND INTERACTIONS DURING COPPER ELECTROPROCESSING and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

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ABSTRACT

The electrochemical deposition of copper has been a major focus of research for decades. Renewed interest in copper electroplating is not limited to the copper producers but is also a major concern of semiconductor manufacturers. The focus on copper electrochemistry by the semiconductor manufacturers has increased since IBM's announcement in 1997 that copper will be used for metallization in high speed/power semiconductors [1-3]. The desire to use copper instead of aluminum is simply a reflection on copper's superior conductivity (lower RC time constants) and resistance to electromigration (generally proportional to the melting point). This dissertation is the compilation of the research into analytical techniques for monitoring surface-active additives in common sulfuric acid/copper sulfate plating baths. Chronopotentiometric, DC and AC voltammetry were the major analytical techniques used in this research. Several interactions between the additives will also be presented along with their apparent decline in activity. The decline in activity is well known in the industry and is also detected by these methods as presented in chapters 4 and 5. Finally, a systemic approach for monitoring the additive Galactosal, which is commonly used in electrowinning, will be outlined. The monitoring system proposed herein would have to be adjusted for each electrowinning facility because each has a unique chemistry and cell configuration.
1. INTRODUCTION

The electrochemistry of copper has been extensively reviewed in the literature [4, 5]. Cupric reduction in a sulfuric acid electrolyte occurs via a two step process with the first electron transfer being the rate determining step at normal current densities [6-8]. The use of additives in copper electroprocessing was developed to improve deposit characteristics and increase current densities that would produce a quality deposit. Sulfuric acid based electrolytes are the most common for the metal producers because it is available as a by-product from the smelting process. Cyanide, chloride pyrophosphate as well as basic chemistries have found uses in differing industries or circumstances. Many other aspects of the copper electrodeposition have also been studied with differing results reported and will be discussed in chapter 2.

1.1 Copper Production

Copper use and production dates back 6,000 years or more [9]. Modern man's use of copper ranges from ornamental, to structural and electrical products. The art and science of producing copper has continuously improved for both the mining and refining process. With the decrease in ore grade, increase in environmental concerns, and ever-increasing demand for higher-purity copper, the need to improve copper production appears to be growing in the foreseeable future.

World wide copper mine production in 1998 was approximately 11.9 million tons per year with the United States producing 1.85 million tons per year [10-13]. Chile is the largest producer with an annual production of 3.66 million tons per year. The majority of
the copper, 73%, produced worldwide is produced via smelting with the final purity attained after electrorefining [11, 12]. Leaching followed by solvent extraction/electrowinning produces most of the remaining mine production copper. The United States annual copper consumption was nearly 3.01 million tons (apparent). As for any metal in these times, copper recycling is important with 14% of consumed copper coming from recycled sources.

In Arizona, copper production is extremely important with an estimated $10.4 billion dollars put into Arizona’s economy annually [10] and 82,000 residents jobs stemming directly or indirectly from the copper industry. The net value of the copper produced in Arizona is $2.82 billion dollars annually. Arizona accounts for 67% of the total copper production in the United States, 1.2 million tons.

1.2 Electrodeposition

Electrodeposition of copper is the primary method for obtaining high purity copper. It is well established that at appreciable current densities, the copper deposits plated from sulfuric acid are unacceptable [14-16]. The use of additives is common place in both electrorefining and electrowinning [17, 18]. Winand et al. elegantly illustrates the complex interactions of convection, additives and current density with one simple visual graph [19, 20]. Their graph, with the ratio of the current density to diffusion-limiting current verses inhibition intensity, simplifies the system and allows one to easily see that the overall deposition is controlled by multiple variables. Tremendous efforts have been
placed on finding additives and overall operating parameters to produce high quality copper.

The quantitative analysis and even the identification of the active components of an additive are difficult. Routine analytical tests are usually inadequate due to low sensitivity, extended testing time or interference from other additives. Several electrochemical techniques have been patented or published and are routinely used in monitoring the electrolyte quality of commercial electrorefining tank houses. The Reotrol process was developed by Asarco to measure thiourea in the electrolyte. Norddeutsche Affiniere developed a method to monitor glue and other additives known as CollaMat [21]. Several other electrochemical techniques have been used with varying success in the electrowinning or electrorefining of copper but tend to be limited in analysis capabilities or are difficult to automate [22-24].

Other industries that work with copper electrodeposition have developed methods to monitor the wide variety of additives. The most common technique is Cyclic Voltammetric Stripping (CVS). Additives in the electrolyte alter the deposition rate of copper. The copper stripping peak is more sensitive to these minor components [25, 26]. Differential Pulse Polarography [27] is another successful techniques which has a significant reduction in noise from charging current. One of the most promising possibilities, licensed and produced by Technic, is called the Real Time Analyzer (RTA) [28].
2. LITERATURE REVIEW

The deposition of copper through electrochemical means has been and is becoming even more of a technically important process. For over 130 years, copper electrowinning and electrorefining have been the crucial process in the production of pure copper (>99.9%). Recently the need to use copper metal lines in semiconductor manufacturing for higher current densities and lower RC time constants, has pushed the desire to control the deposition process to even greater heights. Because of the historical importance of electroprocessing of copper, significant work has been focused on the cathodic deposition of copper. A comprehensive review of the electrochemistry of copper can be found in Encyclopedia of Electrochemistry of the Elements, Volume 2 [5]. More recent reviews [18, 29] can also be found pertaining to copper production practices. The commercial drive for high purity copper with improved physical properties has driven research into the role of additives in controlling deposit structure and morphology. In addition to industrial copper plating being fundamentally a complex electrochemical system, the majority of the additives used in semiconductor and circuit board plating which are proprietary. Before reviewing the details of kinetics, complexation and additives, a brief review of the fundamental deposition process will be given.

2.1 Cathodic Deposition of Copper

Even with the electrochemistry of copper extensively researched and several major reviews published, certain aspects of copper deposition are ambiguous because of
unique features of copper. Several conflicting reports based on either bulk, microscopic, electrolyte or temperature differences confuses the information available about copper deposition. Fundamentally the two electron transfer for the direct reduction of cupric to metallic copper is unlikely to happen. Mattsson and Bockris initially proposed the two step model, Eq. 2.1 and Eq.2.2 [7].

\[
\text{Cu}^{2+} + e^- \xrightarrow{\text{slow}} \text{Cu}^+ \quad \text{Eq. 2.1}
\]

\[
\text{Cu}^+ + e^- \xrightarrow{\text{fast}} \text{Cu} \quad \text{Eq. 2.2}
\]

Their conclusions were based on comparison of the \(\alpha_c\) and \(\alpha_a\) (cathodic and anodic transfer coefficients) from theoretical and measured overpotential curves. They reported the \(\alpha_c\) and \(\alpha_a\) as 0.64+/−0.02 and 1.44+/−0.04, respectively. Upon comparison with experimental work and the asymmetry of the transfer coefficients, Mattson and Bockris suggested the rate-controlling step is surface diffusion at low current densities and charge transfer at high current densities. They further concluded at any appreciable current densities that Eq.2.1 was the slow step. Bockris and Enyo concurred with this assessment of the rate determining steps after further kinetic investigations of copper in several different electrolytes [6]. Others researchers have supported these findings [30, 31] [32] [33] [34] [35] [36] [37].

Typical values for the electrochemical information such as the exchange current density and reduction potentials for copper are shown in Table 2.1 and Table 2.2. One observation after examining the data in these tables, is the difference in the reported
formal potentials and some other fundamental information for copper. The variations tend to come from basic differences in the experimental conditions, i.e. bulk crystal deposits vs. amalgam, single crystal vs. polycrystalline substrate.

As with other metals, the electrodeposition of copper occurs in multiple steps. Despic and Popov have broken down the basic steps of metal electrodeposition as follows [38]:

1) Mass transfer of the electroactive species to the outer limit of the electrode double layer;

2) Electrosorption of the electroactive species;

3) Charge transfer from the cathode to the partially desolvated and uncomplexed ions, with the formation of adatoms on the cathode surface;

4) Lateral diffusion of adatoms on the metal surface until their incorporation into the crystal lattice.

Table 2.1 Electrochemical Data for Copper in Sulfuric Acid

<table>
<thead>
<tr>
<th>[Cu²⁺], M</th>
<th>[H₂SO₄], M</th>
<th>(jₐ) Anodic, mA/cm²</th>
<th>(jₐ) Cathodic, mA/cm²</th>
<th>ßₐnodic</th>
<th>ßₐcathodic</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>1.5</td>
<td>2.3</td>
<td>5.6</td>
<td>1.35±0.15</td>
<td>0.52</td>
<td>[30]</td>
</tr>
<tr>
<td>0.7</td>
<td>1.0</td>
<td>5.2</td>
<td>10.5</td>
<td>1.25</td>
<td>0.58</td>
<td>[30]</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>5.1</td>
<td>8.3</td>
<td>1.64±0.25</td>
<td>0.49</td>
<td>[7]</td>
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<tr>
<td>0.46</td>
<td>0.5</td>
<td>5.2</td>
<td>8.0</td>
<td>1.51±0.04</td>
<td>0.42±0.02</td>
<td>[6]</td>
</tr>
<tr>
<td>0.51</td>
<td>0.5</td>
<td>3.6</td>
<td>4.6</td>
<td>1.50±0.11</td>
<td>0.57</td>
<td>[5]</td>
</tr>
<tr>
<td>0.1</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>1.08</td>
<td>0.39</td>
<td>[5]</td>
</tr>
</tbody>
</table>
Substrate and slight variations in the electrolyte chemistry can alter the deposition process and/or deposit morphology by affecting one or more of the steps listed above. The substrate will have more influence on the initial deposition while additives and plating conditions such as current density exert more influence after several atomic layers. Other factors that can influence the mechanism of deposition are adsorption of ions and complexation of the cuprous or cupric species. A discussion on the role of chloride (and other halides) will be deferred to section 2.3.1.

Additives perform a dual role in the deposition of copper. They are diffusion barriers (includes adsorption site blocking) and/or complexing agents for copper. In addition, they can perform other obscure roles as well. The discussion on additives will be remanded until section 2.1.2. Before looking at joint interactions with copper and other components of the electrolyte, a fundamental review will be given for the simple sulfuric acid / copper sulfate electrolyte.

The concentration of the sulfuric acid affects the equilibrium potential of copper by complexing and changing the nature of electroactive species [39]. At low acid concentrations, adsorption of copper adatoms is enhanced. At higher concentration of a sulfuric acid results in a smaller number of free cupric and cuprous ions as more are complexed with the sulfate species in the electrolyte. As a result, the equilibrium potential becomes more negative. The adsorption of the cations such as copper on
surfaces in aqueous solutions, can be more adequately described as an ion exchange process [40-42]. With an increase in sulfate and bisulfate associated with higher acid concentrations, more surface sites become occupied with non-copper ions or adatoms. This results in a competitive ion exchange process at the cathode surface [43]. On Pt(111) Danilov has proposed the surface to be arranged as depicted in Figure 2.1 for 0.1 M CuSO₄ and 0.5 mM to 0.5 M H₂SO₄ electrolyte [39]. This proposed structure of the surface does change depending on the potential as expected when considering mechanisms related to the point of zero charge (PZC). The PZC is when the adsorbed positive charge and negative charge on the surface is zero. This potential is dependent on both the electrolyte and the solid surface.

Current density also plays a significant role not only on the deposition mechanism of copper but also the morphology of the metal deposit. At low current densities, it was found that the deposit follows the orientation of the substrate [44]. Ibl [15, 16] states copper deposition occurring in the mass transfer limiting current regime forms rough powdery deposits in CuSO₄/H₂SO₄ solutions. Therefore, the higher the current density the more likely rough deposits will occur. Ibl discusses smoothing of the current distribution only occurs when there is an activation overvoltage. Popov [14] observed dendritic copper forms at overpotentials greater than -550 mV in 0.1 M CuSO₄, 0.5 M H₂SO₄ at 25°C. Also, the grain size becomes progressively smaller as the current density increases [45], i.e. more active nucleation sites.
Table 2.2 Standard or Formal Potentials in Aqueous Solutions[5]

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>Standard or Formal Potential</th>
<th>Note</th>
<th>Ref:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁺ + e⁻ = Cu</td>
<td>0.522</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>Cu²⁺ + 2e⁻ = Cu</td>
<td>0.3475</td>
<td>Single Crystal</td>
<td>[48]</td>
</tr>
<tr>
<td>Cu²⁺ + 2e⁻ = Cu</td>
<td>0.3472</td>
<td>Single Crystal</td>
<td>[49]</td>
</tr>
<tr>
<td>Cu²⁺ + e⁻ = Cu⁺</td>
<td>0.167</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>Cu₂O + 2H⁺ + 2e⁻ = 2Cu + H₂O</td>
<td>0.471</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td>CuO₂⁻ + 4H⁺ + 2e⁻ = Cu₂O + H₂O</td>
<td>1.515</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td>2CuO + H₂ + 2e⁻ = Cu₂O + H₂O</td>
<td>0.669</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td>2Cu²⁺ + H₂O + 2e⁻ = Cu₂O + 2H⁺</td>
<td>0.203</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td>2CuO₂⁻ + 6H⁺ + 2e⁻ = Cu₂O + 3H₂O</td>
<td>2.566</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td>CuCl + e⁻ = Cu + Cl⁻</td>
<td>0.137</td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>Cu²⁺ + Cl⁻ + e⁻ = CuCl</td>
<td>0.538</td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>CuBr + e⁻ = Cu + Br⁻</td>
<td>0.033</td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>Cu²⁺ + Br⁻ + e⁻ = CuBr</td>
<td>0.640</td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>CuI + e⁻ = Cu + I⁻</td>
<td>-0.1852</td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>Cu²⁺ + I⁻ + e⁻ = CuI</td>
<td>0.86</td>
<td></td>
<td>[51]</td>
</tr>
</tbody>
</table>
2.1.1 Industrial Practices

Copper smelting followed by electrorefining has evolved both scientifically as well as industrially where the art and science are practiced with minimal cost. Not only has the process become more economically efficient, but also the environmental effects have diminished. Offgasses, water, energy and even several waste materials are recovered for use in other parts of the operation or as manufactured goods. Hydrometallurgical processing of copper via leaching followed by solvent extraction and electrowinning is relatively new and small in comparison. However, the hydrometallurgical route is accounting for an increasingly larger share of copper production because of better chemicals, process control, and lower production cost. With the current trend in copper pricing, more hydrometallurgical operations will be given greater consideration in the future.

Figure 2.1 Proposed Adlayers on a Pt(111) Surface in 0.1 M CuSO₄ and 0.5 mM to 0.5 M H₂SO₄ [39].
2.1.1.1 Electrorefining

The production of high purity copper (99.99% or greater) is mostly accomplished (approximately 73%) via smelting followed by electrorefining. Copper sulfides are generally processed in this fashion because of the availability of energy from combusting the sulfur content in the ore during the smelting process. Figure 2.2 is a flow chart depicting the fundamental steps involved in this method of production. Briefly, the ore is blasted, generally in an open pit mine. The ore is crushed and screened in stages until a fine ore of ~0.5 mm diameter is produced. The fine ore is sent to the froth flotation, which in turn separates the sulfide minerals from the gangue using differences in the hydrophobic nature of sulfides and gangue material (separation generally enhanced with chemical additives). The floating froth, which contains the sulfide minerals, is subsequently dried and sent to the smelter. Smelting involves the combustion of the sulfur content and reduction of the copper to form offgasses, a slag containing the majority of gangue material, and a matte phase containing most of the copper. The matte and slag have low solubility in one another and separate easily because of density differences. The matte is 'tapped' from the smelter and sent to the converter, which finishes the oxidation of the sulfur, reduction of the copper and slag formation of the iron. This molten copper is now approximately 99% copper [53]. The molten metal is casted as anodes that can be hung easily in an electrochemical cell.
Figure 2.2 Process flow for Cu smelting and electrowinning from Biswas and Davenport [53].
This is a very simplistic overview of the process. For more detail in the mining process and mineral processing stages see Wills [54]. For in depth discussion on the smelting and converting stages see Biswas and Davenport, [53].

Electrorefining of impure copper anodes is the next major step for production of high purity copper cathodes (99.99% copper less than 20 ppm impurities minus oxygen). Electrorefining first involves taking the impure copper anode and electrolytically dissolving the copper in a H₂SO₄/CuSO₄ electrolyte. Electrorefining operates on the principle that the potential of the electrochemical cell is controlled suitably to promote the dissolution of the copper and less noble metals at the anode while only reducing the copper at the cathode. Simply put, Eq. 2.3 a and b summarize the process.

\[
\begin{align*}
\text{Cu}^0 & \rightarrow \text{Cu}^{2+} + 2e^- \quad \text{Eq. 2.3a} \\
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu}^0 \quad \text{Eq. 2.3b}
\end{align*}
\]

Ideally the overall cell voltage would be 0.0 V. However, there are several types of energy or IR losses associated with the process. First, there are resistances from the equipment; i.e. contacts between anodes or cathodes and the bussbar. Second, polarization at the anode and cathode usually will increase the needed voltage to drive Eq. 2.3 a and b. Even without IR losses from the equipment and electrolytes, an additional small amount of energy is required to overcome kinetic and transport problems at the
atomic and molecular level. Typically an overvoltage around 0.3V is required to drive the reaction within the desired current densities of 200-300 Am$^2$ [29, 53].

The current is normally controlled and not the potential during the electrowinning process. A multitude of factors other than current density must also be controlled to obtain a marketable final cathode. For instance, the slimes, which contain the insoluble and undissolved species from the anode, can be mechanically entrapped in the cathode by excessive solution flow or agitation producing an impure cathode. Without proper flow control, the copper deposit will form dendrites that can short circuit, entrap electrolyte or change the physical properties that will damage the product. In order to keep production high, the current density of the facility is operated at the highest value which still produces acceptable cathodes.

The electrolytes used in copper ER have a wide chemical variation. Figure 2.3 through Figure 2.15 show the distribution of some of the major constituents, impurities and additives in the ER electrolyte from operations located around the world [18, 29]. Several facilities listed in the review papers are not included in this breakdown because of their unusual chemistry. These excluded facilities do recover copper but are not strictly copper mines and thus have unusual chemistries. Table 2.3 is a detail breakdown of the chemical composition for a common ER facility. There are distinct trends for the majority of the components for ER. Copper content is generally around 43 g/l, while the H$_2$SO$_4$ concentration, which has a slightly higher variation, is between 180 and 185 g/l. The chloride content is usually around 35-40 ppm, Figure 2.5, while the remainders of the
impurities given here have a much larger variation. Nickel, arsenic, iron, antimony, and bismuth vary depending on the ore and processing facility, Figure 2.6 through 2.10. The temperature of the electrolyte is generally between 60-66°C, Figure 2.11 and 2.12. The temperature tends to drop by the time it reaches the outlet of the cell. The temperature is kept elevated to help prevent anode passivation [55] and maintain higher solution concentrations to increase production.

Figure 2.3 Cu²⁺ Concentrations for ER Facilities Throughout the World.

Figure 2.4 H₂SO₄ Concentrations for ER Facilities Throughout the World.
Figure 2.5 Chloride Concentrations for ER Facilities Throughout the World.

Figure 2.6 Nickel Concentrations for ER Facilities Throughout the World.

Figure 2.7 Arsenic Concentrations for ER Facilities Throughout the World.

Figure 2.8 Iron Concentrations for ER Facilities Throughout the World.
Figure 2.9 Antimony Concentrations for ER Facilities Throughout the World.

Figure 2.10 Bismuth Concentrations for ER Facilities Throughout the World.

Figure 2.11 Inlet Temperature for ER Facilities Throughout the World.

Figure 2.12 Outlet Temperature for ER Facilities Throughout the World.
Figure 2.13 Glue Concentration for ER Facilities Throughout the World.

Figure 2.14 Thiourea Concentration for ER Facilities Throughout the World.

Figure 2.15 Avitone Concentration for ER Facilities Throughout the World.
Table 2.3 Typical Electrolyte Composition for Electrorefining.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration g/l, except where noted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>42.6</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>168</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1.66</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.119</td>
</tr>
<tr>
<td>Bismuth</td>
<td>0.173</td>
</tr>
<tr>
<td>Lead</td>
<td>0.007</td>
</tr>
<tr>
<td>Tellerium</td>
<td>0.001</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.073</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.33</td>
</tr>
<tr>
<td>Iron</td>
<td>0.16</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.009</td>
</tr>
<tr>
<td>Soluble Selenium</td>
<td>&lt;0.100 mg/l</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>236</td>
</tr>
</tbody>
</table>

2.1.1.2 Electrowinning

Electrowinning is part of the hydrometallurgical route in which the copper is processed in an aqueous form and accounts for most of the remaining copper mine production. Figure 2.16 is a flow chart for leaching, solvent extraction followed by electrowinning. The upgrade of the leach solution using solvent extraction and the electrowinning is often referred to as the SX/EW process. In this method, smelting and electrorefining are not used. Instead the copper ore is dissolved (leached) by either a dilute sulfuric acid or acid ferric sulfate solution depending on the copper containing...
minerals. The mine waste from the sulfide smelting process is also leached to recover any remaining copper. Certain other gangue minerals are also dissolved during the leaching process. In general, the crushed ore is placed on leaching pads and the leach solution is applied to the surface. The solution percolates through the heap liberating copper and other acid soluble constituents. Several typical leaching reactions for copper minerals are listed in Table 2.4.

The copper laden acid solution, known as pregnant leach solution (PLS), is sent to the solvent extraction (SX) plant after it is recovered from the leaching operation. The PLS is brought into contact with an organic phase that contains an extractant that is tailored to bind with cupric ion. The organic and aqueous phases are brought into contact with each other via a large mixer. The extractant, such as ketoxime or aldoxime, are designed to preferentially bind to the Cu^{2+} ion in the pH range of the PLS. Note that from the leaching reactions and other side reactions, acid is consumed and the pH increases. As indicated before, typical extractants will remove the copper from the aqueous phase as shown in Equation 2.4 [56].
Figure 2.16 Process flow for Cu solvent extraction and electrowinning from Biswas and Davenport [53].
Table 2.4 Common Leaching Reactions of Copper Minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Leaching Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native Cu</td>
<td>$\text{Cu} + 2\text{H}^+ + 1/2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Malachite</td>
<td>$\text{CuCO}_3 \cdot \text{Cu(OH)}_2 + 4\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{CO}_2 + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Brochantite</td>
<td>$\text{CuSO}_4 \cdot 3\text{Cu(OH)}_2 + 6\text{H}^+ \rightarrow 4\text{Cu}^{2+} + \text{SO}_4^{2-} + 6\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Antlerite</td>
<td>$\text{CuSO}_4 \cdot 2\text{Cu(OH)}_2 + 4\text{H}^+ \rightarrow 3\text{Cu}^{2+} + \text{SO}_4^{2-} + 4\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Atacamite</td>
<td>$3\text{CuO} \cdot \text{CuCl}_2 \cdot 3\text{H}_2\text{O} + 6\text{H}^+ \rightarrow 4\text{Cu}^{2+} + 2\text{Cl}^- + 6\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Azurite</td>
<td>$2\text{CuCO}_3 \cdot \text{Cu(OH)}_2 + 6\text{H}^+ \rightarrow 3\text{Cu}^{2+} + 2\text{CO}_2 + 4\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Chrysocolla</td>
<td>$\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{SiO}_2 + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Cuprite</td>
<td>$\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}^0 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Tenorite</td>
<td>$\text{CuO} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>$\text{Cu}_2\text{S} + 2\text{H}^+ + 1/2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{CuS} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Covellite</td>
<td>$\text{CuS} + 2\text{H}^+ + 2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>$\text{CuFeS}_2 + 16\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 17\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$</td>
</tr>
<tr>
<td>Bornite</td>
<td>$\text{Cu}_3\text{FeS}_4 + 36\text{Fe}^{3+} + 16\text{H}_2\text{O} \rightarrow 5\text{Cu}^{2+} + 37\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 32\text{H}^+$</td>
</tr>
</tbody>
</table>

\[
\frac{[2R - H]_{\text{org}} + [M^{2+} + \text{SO}_4^{2-}]_{\text{aq}}}{\text{Extraction}} \xrightarrow{\text{Stripping}} \frac{[R_2\text{M}]_{\text{org}} + [2\text{H}^+ + \text{SO}_4^{2-}]_{\text{aq}}}{\text{Eq. 2.4}}
\]

The technology for selectively binding $\text{Cu}^{2+}$ in one pH range and stripping the $\text{Cu}^{2+}$ from the organic at a different pH range is extremely crucial and has made significant advances. The preferred formulation of the extractant is typically a combination of several second-generation reagents. For example, LIX 984N, which is one of Henkel (now known as Cognis) Corporation MID most popular extractant is a mixture of two other reagents, LIX 84 and LIX 860. LIX 84 is a 5-nonylacetophenone
oxime with a small amount of 5-dodecylsalicylald oxime. LIX 860 is 5-dodecylsalicylald oxime and a small amount of 5-nonylactophenone oxime.

The organic/aqueous mixture is then allowed to separate in settling tanks where the loaded organic and the barren aqueous phase are removed from the top and bottom of the settler, respectively. The loaded organic is then mixed again with a different aqueous phase in which the pH is low enough to drive Eq. 2.4 in reverse. The stripped organic is reconditioned and recycled through the circuit while the loaded aqueous phase goes to the electrowinning cells. The electrolyte, PLS, extractant and other organic components are continuously regenerated and recycled back through the leaching-SX-EW process.

Copper electrowinning consist of reduction of Cu$^{2+}$ at the cathode and the oxidation of water at the anode. These reactions are given in Eq. 2.5 and 2.6

\[
\text{Cathode: } \text{CuSO}_4 + 2e^- \rightarrow \text{Cu}^0 + \text{SO}_4^{2-} \quad E^0 = 0.34V \quad \text{Eq. 2.5}
\]

\[
\text{Anode: } 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4e^- \quad E^0 = 1.23V \quad \text{Eq. 2.6}
\]

The anode is typically a Pb-Sn or Pb-Sn-Ca alloy [53]. Several new designs known as dimensional stable anodes (DSA) are being tested to reduce the overvoltage associated with the oxygen evolution and therefore, reduce the energy consumption [57].

The change in the acidity for the electrolyte during the EW process, is depicted by Eq.2.6. This increase in acid is used to strip Cu$^{2+}$ from the organic phase as shown in Eq.
2.4. As with electrowinning, the solutions used in electrowinning are recycled to optimize the overall process and minimize waste.

The majority of the SX/EW operations keep tight control on the acid and copper concentration not only to maintain the EW operating conditions but also to keep the SX circuit running properly. The cupric concentration for most facilities is around 35 g/l, Figure 2.17. The chloride content for EW electrolytes is about the same as for the ER operations at 40 ppm, Figure 2.18 and 2.5. As previously described, the acid will increase during the EW process from the oxidation of H2O as seen by comparing Fig. 2.19 and 2.20. The starting acid concentration is generally kept between 150 and 170 g/l H2SO4. The outlet increase is shown in Figure 2.20 with the histogram now skewed more towards the higher concentrations. Contamination of the electrolyte with iron is shown in Figure 2.23 and 2.24 for ferrous and ferric, respectively. The extraction of some iron is a side effect of the SX process that contaminates the electrolyte for EW. Cobalt is added at approximately 125 ppm to reduce the corrosion rate of the anode and minimize Pb contamination in the cathode. The typical levels used are shown in Figure 2.25. Manganese has been speculated as disrupting the SX/EW process and Figure 2.26 shows the concentrations found in industrial operations covered by the survey [18]. In addition to performing crucial roles in electrowinning, the additives used in EW must not interfere with the SX process and therefore guar is the typical additive used in EW facilities. Typical levels of guar are shown in Figure 2.27.
Figure 2.17 Copper concentrations for EW facilities throughout the world.

[Diagram showing histogram of copper concentrations in g/l with bars at 30, 35, 40, 45, 50, 55, 60, and 65 with corresponding frequency of facilities.]

Figure 2.18 Chloride concentrations for EW facilities throughout the world.

[Diagram showing histogram of chloride concentrations in ppm with bars at 0, 20, 40, 60, 80, and 100 with corresponding frequency of facilities.]

Figure 2.19 Inlet H₂SO₄ concentrations for EW facilities throughout the world.

[Diagram showing histogram of inlet H₂SO₄ concentrations in g/l with bars at 20, 60, 100, 140, 180, and 220 with corresponding frequency of facilities.]

Figure 2.20 Outlet H₂SO₄ concentrations for EW facilities throughout the world.

[Diagram showing histogram of outlet H₂SO₄ concentrations in g/l with bars at 80, 100, 120, 140, 160, 180, 200, and 220 with corresponding frequency of facilities.]
Figure 2.21 Inlet temperature for EW facilities throughout the world.

Figure 2.22 Outlet temperature for EW facilities throughout the world.

Figure 2.23 Ferrous concentrations for EW facilities throughout the world.

Figure 2.24 Ferric concentrations for EW facilities throughout the world.
Figure 2.25 Cobalt concentrations for EW facilities throughout the world.

Figure 2.26 Manganese concentrations for EW facilities throughout the world.

Figure 2.27 Guar Concentrations for EW Facilities Throughout the World.
2.1.1.3 General ER/EW Variables in Deposition

The deposition of copper from industrial electrolytes has many more variables to control than would first be predicted. Ettel [58] states the electrolyte composition such as the additive type, additive concentration, pH, and copper concentration are the most difficult to optimize. The type and desired concentration of a particular additive are already difficult to optimize, and then the rate of replacement of the additive adds even more variability to the process. Generally, the rate of disappearance is not well characterized and is know to be a function of many variables. For instance, the additive can be consumed by entering the deposit [59], being chemically decomposed in the electrolyte [60], or adsorbed on non-plating surfaces such as suspended particulates or cell walls [43, 58]. Other variables controlled during copper ER and EW are current density, temperature and flow or convection.

Winand et al [19, 20, 61, 62] summarized how the various aspects of the EW/ER operating parameters effect the deposit morphology. Figure 2.28 is a generalize plot of what type of copper deposit will result under various conditions. The ordinate in Figure 2.28 is expressed as a ratio of the current density to concentration of the plating species. Alternatively it can be expressed as the current density to the diffusion limiting current density. The abscissa is the inhibition intensity. Various types of deposits are further broken down and are displayed in Figure 2.29. The symbols used in both plots are defined as follows:

- Field-oriented isolated type ⇒ FI
• Basis-oriented reproduction ⇒ BR
• Twinning intermediate type ⇒ Z
• Field-oriented texture type ⇒ FT
• Unoriented dispersion type ⇒ UD

It should be noted these types of deposits are based on metallographic studies and not on theoretical nucleation-growth models. Either increasing the current density or changing anything that will alter the concentration of the plating metal at the surface of the cathode can move the position along the ordinate. For example, the ordinate can be shifted to lower values by increasing the metal concentration or by agitation. The inhibition intensity may be adjusted with additives.

Winand and Harlet [20] have also developed an equation to describe the surface concentration of organic additives under different boundary layer thickness, diffusion coefficient of organic, and current densities. This relationship was proposed to scale plating practice. For example, a set of conditions that give good deposition characteristics can be used to determine what needs to be adjusted to achieve similar results at a higher current density. However, for electrowinning and electrorefining some of the options are limited. For example, increasing stirring can lead to impurity problems as discussed by Biswas and Davenport and would often be avoided. [53].
Figure 2.28 General deposit characteristics for metals as a function of plating conditions. The symbols are $J =$ current density; $c_{Me^{2+}} =$ metal concentration; $J_d =$ diffusion limited current density. [20]
Figure 2.29 Metallographic analysis of electrodeposited metals with different plating parameters as defined by Winand et al. [20]
2.1.2 Review of Additives

The use of additives to obtain selected deposit properties is standard practice in all plating baths. The desired properties of the final product often dictate the type and quantities of additives used. As discussed in section 2.1.1, the control of the plating bath takes on a systems approach where each aspect works in conjunction with the others and the balance is sometimes hard to find. Additives are also used to increase the acceptable range of current densities for metal deposition. The more efficient the levelling and brightening of an additive, the higher the current density can be set and still obtain an acceptable deposit. Even with the accepted importance of additives, many debates surround their use and effects on the deposit.

Several key terms describing the role of the additives are difficult to define. Additives can generally be classified as brighteners, levelers, carriers, grain refiners or surfactants. Additives generally can be placed in one or more of these categories but can sometimes have synergistic properties. When used with other additives, the term levelers (smoothing additives) generally implies there is a geometric change of the surface which tends to redistribute the growth rates that will eliminate micro- and submicro-roughness. This can be further described as the ability of a plating bath with its additives to deposit thicker amounts of material in small recesses or at the bottom of the roughness and thinner amounts on the crest or protrusions [63].

Brightening is a crystallographic change where the growth rates at different crystal faces equalize [64]. Brightening by a plating bath and additives can also be defined as the
ability to produce fine deposits with grain sizes less than the wavelength of visible light and having oriented grain structure. Some believe that there may be no principle difference in brighteners and levelers. The thought on this is that brighteners do smoothing at a smaller scale. The concept of a bright deposit also refers to the reflectivity of the surface that several researchers have correlated with the grain size and texture [64]. In general, there is no analytical correspondence and deposits of different brightness can have the same size grains and apparent roughness. A small grain is necessary for a bright deposit, but is not sufficient to guarantee a bright deposit. The surface morphology must also be oriented with a tendency for the surface components being aligned in the same plane [63].

There are several factors that can be modified by additives to produce finer grain sizes. The most common is an increase in polarization at the cathode. This increased polarization will create more areas of supersaturation allowing more nuclei to form or more sites on the surface to become active. Polarization is directly related to the energy for the driving force for nucleation; \( \Delta G = -nFE \) where \( G \) is the Gibbs free energy increase, \( n \) number of electrons involved in the process, \( F \) is the Faraday constant and \( E \) is the potential increase needed to plate in the presence of additives. From classical nucleation, the Gibbs-Thompson equation describes the free energy change associated with nuclei growth and is shown in Eq. 2.7. \( \Delta G_n \) is the Gibbs free energy change to create the nuclei, \( \Delta G_v^* \) is the Gibbs free energy per unit volume change from the phase transition of the atom for the nuclei, \( r \) is the radius and \( \sigma \) is the surface tension [65].
Harrison [66] further developed an equation for the critical size of a nuclei as pertaining to electrochemical deposition onto a flat surface with a two dimensional hemispherical nucleus and is shown in Eq. 2.8a. The critical nucleus is also expressed for solidification and is shown in equation 2.8b.

\[ r^* = \frac{\sigma M}{zF\eta \rho} \]  
Eq. 2.8a

\[ r^* = \left( \frac{2\sigma_L V T_m}{L_v} \right) \frac{1}{\Delta T} \]  
Eq. 2.9b

The critical radius a nucleus must attain to grow is \( r^* \). \( F \) is the Faraday constant, \( z \) is the charge transferred, \( \sigma \) surface tension, and \( \rho \) is the density. For Eq. 2.8b, \( L_v \) is the latent heat of fusion per unit volume and \( T_m \) is the melting temperature. In traditional nucleation, the driving force is the undercooling, \( \Delta T \). In electrolplating, the driving force is the overpotential, \( \eta \), applied for the plating reaction. In each case, the critical radius decreases with an increase in the driving force. Since the initial stability of a nuclei is related to the shape of the forming nuclei and the surface tension associated with the solution, substrate and material being deposited, the increase in deposition potential will give an increase in the number of active sites. This increase in active sites forming more
nuclei will bring about impingement of the grains sooner. Thus the increase in nuclei and
impingement produce smaller grain sizes. The other major influence on crystal size is
from the additives or impurities forming additional heterogeneous nucleation sites. An
equation similar to the Gibbs-Thompson equation can be derived from a surface energy
balance stand point with the additional term called the shape factor, $S(\theta)$ [67]. This
additional term, shown in Eq. 2.9, has the values between 0 and 1 and describes the
decrease in difficulty to nucleate from a particular shape for a heterogeneous nucleation
site.

$$\Delta G^*_{\text{heterogeneous}} = S(\theta) \Delta G^*_{\text{homogeneous}}$$  \hspace{1cm} \text{Eq. 2.10}

A surfactant accumulates at the interface between a solid and a liquid and
modifies the surface tension [68]. A surfactant has a hydrophobic and a hydrophilic end,
which augments the wetting of the solid. Surfactants increase the wetting properties of
the bath by reducing its surface tension, which increases electrolyte contact in small
recesses. Any of the additives that perform this wetting increases are at least a surfactant
but could also function as any of the other classes of additives simultaneously.

2.1.2.1 Additive Models in Electroplating of Metals

Several models have been developed to explain how the additives promote or
depress a certain deposition quality. The general theory for brightening and smoothing is
based on an adsorption process in which the surface active substance (SAS) adsorb either
on the active sites on the substrate or specific crystallographic faces [64] [63]. Experimental results have shown that the SASs are adsorbed on the crest and inhibit the metal from plating at these locations. The metal adatom would then be forced to migrate over the surface into the recess areas until they find sites available for incorporation into the lattice.

The adsorption model can be further broken into a structure-sensitive and a current-sensitive model where in the additive is presumed to block the high points (geometrically and current density) from further metal deposition. There is very little difference between the current and the geometric model for how additives limit the amount of copper depositing at protrusions. This is because at any geometrical high spot, the electric field intensifies with the sharp radius of curvature. Upon further considerations, the model can be refined to be both an adsorption and diffusion process. This part of the model states diffusion of the additive, or one of its decomposition products limits the supply of the SAS to the surface of the cathode. Generally speaking, when the leveling is diffusion controlled, more additives reach the protrusions than the recesses. The additive is then strongly adsorbed onto the cathode and is either mechanically entrapped or electrochemically reduced at the surface. After the additive is reduced at the surface, it may be desorbed if the affinity for the surface has been lowered [63]. The incorporation of the additive or the degradation products of the additive into the deposit is known to occur for additives such as TU [59].
Radioisotopes were used to confirm that additive levels decrease during deposition and become entrapped in the metal and must be continuously added to keep optimal plating conditions [59].

Several non-diffusional models explaining additives role on electrodeposition are discussed by Oniciu and Muresan [63]. These include electrosorption based on structural properties of the surface, ion pairing of the additive and metal ion, complex formation, chemical film formation and interfacial tension. A single additive and its mechanism in the bath can be modeled using one or several of these concepts. This is an oversimplification of mechanisms for common additives found in plating baths since most additives are used in combination with each other. The interaction between the additives has been termed synergistic because the effect of the individual additive can be significantly different when used in conjunction with others [63].

2.1.2.2 List of Common Additives

There are only a few additives used in copper electrowinning and electrorefining. The more common additives are given in Table 2.5. The use of glue, thiourea and chloride are common for ER while the use of guar is less common for EW. Other additives studied for copper plating are more numerous and several are listed in Table 2.6. The plating baths for copper in the majority of other industries are proprietary formulations. The chemicals listed in Table 2.6 were mostly arrived at experimentally.
The true success of an additive for plating copper would most likely exclude it from having a significant number of publications because of the competitiveness.

Table 2.5 Common Additives Used in Electrowinning or Electrefining.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
<td>Electrowinning</td>
</tr>
<tr>
<td>Glue (animal protein)</td>
<td>Electrorefining</td>
</tr>
<tr>
<td>Chloride</td>
<td>Both</td>
</tr>
<tr>
<td>Guar (Galactasol)</td>
<td>Electrowinning</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Electrowinning</td>
</tr>
<tr>
<td>Lignin Sulfate</td>
<td>Electrorefining</td>
</tr>
</tbody>
</table>
Table 2.6 Additives used in copper electroplating reported in literature.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipropandisulonic Acid Disulfide Disodium Salt</td>
<td>[69]</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>[70]</td>
</tr>
<tr>
<td>Alkanethiols</td>
<td>[70]</td>
</tr>
<tr>
<td>Quaternary Ammonium Salts</td>
<td>[70]</td>
</tr>
<tr>
<td>Cetyltrimethylammonium Salts</td>
<td>[70]</td>
</tr>
<tr>
<td>4,5-Dithio-octan4e-1,8-Disulphonic Acid</td>
<td>[71]</td>
</tr>
<tr>
<td>3-Mercaptopropyl sulphonic Acid</td>
<td>[71]</td>
</tr>
<tr>
<td>Benzothiazoliane Derivative</td>
<td>[72]</td>
</tr>
<tr>
<td>Fuchsin</td>
<td>[73]</td>
</tr>
<tr>
<td>Methyl Violet</td>
<td>[73]</td>
</tr>
<tr>
<td>Phthalocyanine</td>
<td>[73]</td>
</tr>
<tr>
<td>Aminoguanidine</td>
<td>[73]</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>[73]</td>
</tr>
<tr>
<td>p-Toluene Solfonic Acid</td>
<td>[73]</td>
</tr>
<tr>
<td>Nonylphenal Ethoxylate</td>
<td>[73]</td>
</tr>
<tr>
<td>Ethyleneoxied-Propyleneoxide-Propylenoxide copolymer</td>
<td>[73]</td>
</tr>
<tr>
<td>Cysteine</td>
<td>[74]</td>
</tr>
<tr>
<td>Diguanidinium Disulphide</td>
<td>[74]</td>
</tr>
<tr>
<td>Safranine</td>
<td>[74]</td>
</tr>
<tr>
<td>Hydrolysed casein</td>
<td>[75]</td>
</tr>
<tr>
<td>Sulphonated wood fibers</td>
<td>[75]</td>
</tr>
<tr>
<td>Bindarene</td>
<td>[75]</td>
</tr>
<tr>
<td>Lignone</td>
<td>[75]</td>
</tr>
</tbody>
</table>

2.2 Fundamental Kinetic Aspects

In this section, a brief review of how copper grows electrochemically will be presented. For a more fundamental account of the growth process see Bockris et al. and Harrison [4, 66]. The growth rate of electrochemical systems can be controlled by the applied potential. As discussed before, the transition between a flat deposit and a
dendritic deposit or a powder can be controlled by the current densities. Ibl et al and Popov et al demonstrated copper deposits become powdery and dendritic above a critical overpotential [14-16]. Ibl reports this critical potential occurs very near the potential for the limiting current.

Large charge transfer polarization will make nucleation less difficult relative to the growth of existing crystallites. Therefore, metals with high charge transfer polarization like nickel deposit fine grains while low charge transfer metals like silver will deposit as course individual grains [58]. Copper with an intermediate charge transfer value normally forms as a course grain polycrystalline deposit. The charge transfer can be increased for the depositing metal by additives such as thiourea, glue and lignin derivatives.

Nucleation and growth of electrodeposition has been compared to classical approaches by Harrison and Thirsk [66]. The fundamental equations for either galvanostatic or potentiostatic methods of study are discussed within their work. The main point ascertained for copper deposition at appreciable current densities is that copper has been reported to grow 3 dimensionally (3D) or 2 dimensionally (2D) depending on the substrate and the quantities and type of additives used in the bath.

Several kinetic models have been developed to relate the current response to a potential step. Progressive nucleation is described by an equation such as Eq 2.10 in which the number of nuclei change with time.

\[ N = N_0[1 - \exp(-AT)] \]  

Eq. 2.11
No is the number of nucleation sites and A is the nucleation rate constant and t is the time. For small t, N=NoAt. Instantaneous nucleation is when the number of nucleation sites are fixed, i.e. N=No. After nucleation, growth of the copper can be describe by several models. The difference in the models of interest is that 2D growth is planar while 3D growth is hemispherical. Two different regimes also exist, diffusion control or kinetic control. For kinetic control, the rate determining step is the incorporation of the adatom into the lattice. Mass transfer of the ion to the surface establishes diffusion control.

The equations that have been developed based on kinetic control are given in Eq 2.11 to 2.14. Eq. 2.11 is for 2D growth with instantaneous nucleation.

\[
I_{\text{kinetic control \ instantaneous 2D}} = \left(\frac{2zF\pi MhN_0k^2}{\rho}\right)t \quad \text{Eq. 2.12}
\]

Eq. 2.12 is for progressive nucleation with 2D growth.

\[
I_{\text{kinetic control \ progressive 2D}} = \left(\frac{zF\pi MhA'N_0k^2}{\rho}\right)t^2 \quad \text{Eq. 2.13}
\]

Under kinetic control, instantaneous nucleation with 3D growth follows the relationship given in Eq. 2.13 while progressive nucleation with 3D growth follows Eq. 2.14.
The time dependence for the 2D progressive and the 3D instantaneous growth under kinetic control is of the same order which make distinguishing these types of growth using potentiostatic methods difficult.

The equations describing the current from diffusion control models are given in Eq. 2.15 and 2.16. The current for instantaneous nucleation followed by 3D growth is given in Eq. 2.15.

\[
I_{\text{kinetic control instantaneous 3D}} = \left( \frac{2zF\pi M^2 N_0 k^3}{\rho^2} \right) t^2
\]

Eq. 2.14

\[
I_{\text{kinetic control progressive 3D}} = \left( \frac{2zF\pi M^2 A' N_0 k^3}{3\rho^2} \right) t^3
\]

Eq. 2.15

With progressive nucleation followed by 3D growth, the current should follow Eq. 2.16

\[
I_{\text{diffusion control instantaneous 3D}} = \left( \frac{8\pi z FN_0 M^2 C^3 D^2}{\rho^2} \right) t^{\frac{1}{2}}
\]

Eq. 2.16

\[
I_{\text{diffusion control progressive 3D}} = \left( \frac{16\pi z FA' N_0 M^2 C^3 D^2}{3\rho^2} \right) t^{\frac{3}{2}}
\]

Eq. 2.17

In Eq. 2.11 to Eq. 2.16, \( A' \) is the nucleation rate constant, \( z \) is the atomic charge transferred, \( F \) is the Faraday constant, \( \rho \) is the density of the deposited metal, \( M \) is the molecular weight of the deposited metal, \( C \) is the metal ion concentration in solution, \( D \) is the diffusion coefficient of the metal ion, \( k \) is the reaction rate constant and \( t \) is the time. The 3D kinetic controlled equations have been modified to include spherical diffusion to the growing nucleus by Hills et al [76]. The nucleation rate constant becomes potential
dependent, Eq. 2.17, with the new form of the diffusion controlled equations given in 2.18 and 2.19 for instantaneous and progressive type nucleation, respectively. However, the time dependence has not changed and still remains $t^{1/2}$ and $t^{3/2}$ for instantaneous and progressive nucleation, respectively.

$$I_{\text{instantaneous}} = \frac{2Fl\pi N_0 M^2 (2DC)^{3/2}}{\rho^{1/2}} t^{1/2} \quad \text{Eq. 2.18}$$

$$I_{\text{progressive}} = \frac{2zF \pi A' N_0 M^2 (2DC)^{3/2}}{3\rho^{1/2}} t^{3/2} \quad \text{Eq. 2.19}$$

$$A = K \exp\left(-\frac{k\delta^3}{\eta^2}\right) \quad \text{Eq. 2.20}$$

In Eq. 2.19, $K$ and $k$ are constants while $\delta$ and $\eta$ are surface free energy and overpotential, respectively.

Another fundamental aspect of copper electrodeposition pertains to the initial copper layers formed on the substrate. It has been shown that under certain conditions, a layer of copper will deposit prior to application of the bulk deposition potential. This early deposition is called under potential deposition (UPD). The nature of the UPD layer is a function of multiple factors. The intuitive way of viewing the UPD layer is based on a bond counting method. Since bulk deposition of copper is based on the copper-copper bond of copper atoms in a face centered cubic (FCC) structure, a potential or free energy from the formation of these bonds can be assigned a standard reduction potential ($E^{\circ}_\text{Cu}$) of
approximately 0.344 vs. standard hydrogen electrode (SHE). However, the initial layer of copper is bonding directly to the substrate, for example Ti-Cu bond, and the structure of the layer is usually influenced by the substrate crystal structure. These and other interaction can lead to a layer of copper depositing below the bulk deposition value, \( E^0_{\text{Cu}} \). Multiple researchers have demonstrated copper forms UPD layers and have examined the UPD layer of copper on platinum [77-81]. However, the effect of UPD copper is limited in the bulk deposition region where most of the EW/ER occurs.

The epitaxy for copper deposit is generally a result of substrate interactions, such as UPD copper. As the deposition progresses, orientation becomes more dependent on the material being plated, bath composition and plating conditions [63]. Preferred orientation is a result of different crystal faces growing at different rates. The difference in deposition rates at specific faces is enhanced by preferential adsorption of foreign molecules such as impurities or additives. Additives and impurities can alter both the bulk deposition process and the UPD layer. The UPD layer can be disrupted or completely suppressed with additives under certain experimental conditions [77-79]. Even with the increased orientation and brightness from additives, Oniciu and Muresan [63] have stated there is no correlation between brightness and the degree of preferred orientation.
2.3 Electrochemical Studies of Additives

A tremendous number of papers have been published on the electrochemistry of copper. This review will be limited to the work related to copper electrowinning and electrorefining and their foundations. The effects of several additives will be presented followed by the work relating to the multiple additive effects.

2.3.1 Chloride

The exact role of chloride is highly debated in the literature. The one common aspect is that chloride has an effect on the deposition whether it is the only additive or in conjunction with other additives. Nila and Gonzales[82] correlated predominance area

![Figure 2.30 Predominance diagram for cupric with chloride and sulfate with H₂SO₄ = 0.73 M, Cu²⁺ = 10⁻² M at 25°C [82].](image)
and Pourbaix diagrams for the buffered Cu²⁺-Cl-H₂SO₄ system to experimental results. They concluded that fundamental thermodynamic properties could give insight into what is occurring at the surface of the cathode. Figure 2.30 is a predominance area diagram for cupric ion showing regions of stability for both chloride and sulfate complexes. The predominance diagram similar to Figure 2.30 for the cuprous ion is shown in Figure 2.31. The complexation of cuprous with chloride can occur as displayed by regions of stability shown in Figure 2.31 while a sulfate complex does not exist under these conditions. The distribution of Cu²⁺, Cu⁺, Cl⁻ and SO₄²⁻ plotted as the Cl⁻ concentration against the redox potential is depicted in Figure 2.32. Notice that Cu⁺ does not appear except when complexed with Cl⁻. The typical Pourbaix diagram (Eh vs. pH) is shown in Figure 2.33. Notice the caption on Figure 2.32 and 2.33 are at different concentrations than the electrolyte for EW or ER operations. What should be taken into account is that the potential and concentration in the stagnant layer and surface of the cathode are not the same as the bulk. For example, chloride is known to adsorb onto the surface and will therefore be more concentrated than in the bulk of the solution.
Figure 2.31 Predominance diagram for cuprous, chloride and sulfate system with $H_2SO_4 = 0.73$ M and $Cu = 10^{-5}$ M at 25°C [82].

Figure 2.32 Predominance Diagram for Cupric/Cuprous Complexes with Chloride at Different Chloride Concentrations and potentials; $pSO_4^- = 0.14$, $H_2SO_4 = 0.73$ at 25°C [82].
Figure 2.33 Predominance diagram for copper complexes with acid and chloride with Cu"=10^{-2}, NH₄Cl=1 M at 25°C [82].
Chloride has been reported as changing several different aspects of the deposition of copper. From a standard electrochemical perspective, chloride has been reported as both a polarizer and depolarizer. Sun and O'Keefe have reported that 40 ppm chloride acts as a depolarizer in a typical electrorefining solution [83]. Wang and O'Keefe further reported that chloride at less than 5 ppm acts as a polarizer with the formation of CuCl. At chloride concentrations higher than 20 ppm, they suggest additional complexations can be influencing the interaction of chloride, which acts as a depolarizer at these concentrations. With slightly higher copper and sulfuric acid concentrations, Yao similarly report that chloride acts as a polarizer at concentrations less than 15 ppm and a depolarizer above 15 ppm [84]. Similar results have been found to support the conclusions that chloride act as a polarizer until a critical concentration is attained and then becomes a depolarizer [85-88]. Franklin et al have explained the role of chloride as forming a CuCl film [89]. They also contend this copper chloride film increases current efficiency by shifting the hydrogen evolution to higher overpotentials.

Several studies have looked at the influence of chloride on the initial deposition of copper on platinum, gold, 316 stainless steel and HOPG [83, 86, 90 - 92]. Most of these investigations are with multiple additives. Chloride was found to have an additional role for the UPD of copper onto Pt single crystals depending on the crystallographic face. The UPD peaks on the Pt(111) crystal were split further apart while a diminution of the
anodic/cathodic peak from 80 to 40 mV vs. SCE was found for the Pt(100) surface. Minimal effect was seen on the Pt(110) surface.

2.3.2 Thiourea

The effect of thiourea on the early stages of deposition has been studied on several different substrates. Bhatt et al [78] evaluated the inhibition of under potentially deposited copper on single crystal Pt. They determined that the thiourea depressed and eventually eliminate the UPD peaks seen on Pt(111), (100) and (110). Not only were peaks removed, but also new peaks appear closer to the bulk deposition potential of copper. Significantly more hysteresis (125 mV) was found between the cathodic and anodic peak. The model developed by Bhatt et al has a copper layer attached on an adsorbed additive layer at the cathode. The copper layer appears to have similarities to UPD copper. However, extrapolation of this work to industrial scale is limited because of low copper concentration (0.13 M and 0.5 M) and low temperature (23°C) used in this work.

Sun and O'Keefe studied the effect of thiourea on the nucleation of copper on stainless steel cathodes [83]. Their work includes the effects of chloride with thiourea using typical electrowinning conditions (40 g/l Cu^{2+}, 180 g/l H_{2}SO_{4} at 40°C). The study used both SEM and current transients from potential step experiments to evaluate the nucleation mechanism. The typical copper nucleation with glue and chloride occurs via progress nucleation followed by growth of the 3-D centers under diffusion control. Based
on the change in the time dependents of current upon addition of 0.5 ppm thiourea, the nucleation mechanism changed to instantaneous.

Thiourea influences the deposition of copper on Au(111) in an extremely different fashion than what was found for stainless steel. Instead of shifting the nucleation from progressive to instantaneous [83], it shifts the copper nucleation from a mixed behavior to purely instantaneous [93]. However, the conditions are also different with the Cu$^{2+}$ and H$_2$SO$_4$ concentrations being significantly lower, 6.3x10$^{-1}$ M vs. 1x10$^{-3}$ and 1.84 M vs. 5x10$^{-2}$ M respectively. The significant conclusion of this work is based on the strong bond between gold and TU, which interrupts the UPD layer of copper [94]. This disruption increases the number of available nucleation sites. Even low concentrations (10$^{-7}$ M TU) markedly increase the number of nuclei. The review work at Pt and Au substrates demonstrates the same additive can have drastically different effects on different substrates.

2.3.3 Glue

Glue, or animal protein is generally used in ER facilities. Figure 2.13 is a histogram of the levels of glue used in typical ER electrolytes. There is some difficulty in quantifying and identifying the active leveling component in glue because of the very nature of the product. The glue used industrially is from rendering plants. Most suppliers can maintain the quality of their product but have a difficult time with establishing an industrial standard. For example, the moisture and chloride content can be variable
because of the difference in the feedstock for the rendering process. Some glue has been found to contain chloride contamination from the CaCl$_2$ rendering process, see section 4.3. Glue is generally used in conjunction with other additives such as chloride and thiourea. However, a basic understanding of the influence glue will be presented. Figure 2.34 is the simplified structural unit for glue. [95]

\[
\begin{align*}
&\{ \text{CH}_3 \}, \{ \text{O} \text{CH}_2 \text{CH}_2 \}, \{ \text{H} \}, \{ \text{O} \text{H} \text{H} \}, \\
&\{ \text{C} = \text{C} \text{N} \}, \{ \text{C} = \text{C} \text{N} \}, \{ \text{C} = \text{C} \text{N} \}, \{ \text{C} = \text{C} \text{N} \}, \{ \text{C} = \text{C} \text{N} \}, \\
&\{ \text{O} \text{H} \text{H} \}, \{ \text{H} \}, \{ \text{O} \text{H} \text{H} \}, \{ \text{CH}_3 \}.
\end{align*}
\]

Figure 2.34 A Simplified Structural Unit of Glue [95].
The active component of glue (animal glue or collagen proteins) is not the original molecule, which tend to have a molecular weight in the hundreds of thousands. Instead, the glue goes through several types of reactions in the hot H₂SO₄. For instance, hydrolysis of the proteins would be common place. Denaturing is also a common process for proteins in which the proteins unfold. Saban et al. performed size exclusion chromatography to determine the active component of the glue and found a molecular weight of approximately 10,000 to be the most active [96]. This can only be a rough estimated because the standards that were used were in their original tightly formed clusters while the glue had already been exposed to a solution containing 150g/l H₂SO₄, 46 g/l Cu²⁺ as CuSO₄ for 40 to 80 minutes. Saban et al described the degradation rate constant with Eq. 2.20 in an electrolyte similar to that used in EW and ER with a temperature range of 42 to 70 C and a glue concentration between 100 to 3000 mg/L.

\[ k' = 1.5 \times 10^7 \exp \left( \frac{-9951}{T} \right) \text{min}^{-1} \]  
Eq. 2.21

The degradation rate was also zero order with respect to initial concentration of the protein and first order with respect to acid concentration.

Wu Hu et al. [97] reported scanning electron microscopy results of how glue influences the growth of copper on copper. Initially, copper favors epitaxial (incomplete) growth in the presence of glue. As the deposit continues, a (111) texture develops. Eventually side growth and nodule formation occurs. Results in this work are sketchy because no adjustment of glue concentration was made during long term experiments and
results with and without chloride were interspersed without a systematic approach for joint interactions.

The literature tends to claim glue acts as a leveler while it polarizes the system [24, 60, 83, 87, 98, 99]. However, most experiments that attempted to controlled the contamination of chloride had difficulty reproducing the polarizing effect [24, 60, 99]. The need to have chloride present in the system to produce any polarizing effects from glue is presented in section 4.3.

2.3.4 Guar Gum

The use of guar gum by electrowinning facilities has become common with nearly 62% of the facilities employing on the average 240 g/tonne of copper processed [18]. The basic structure of guar is shown in Figure 2.35. The use of a hydroxy modified guar gum is common. The modified guar gum has improved handling and preparation characteristics. Henkel Inc, MID supplies this under the trade name Galactasol. The use of guar in mining originally was as a depressant for froth flotation. For example, guar is used in copper mining to depress talc during the froth flotation of sulfide minerals but was later determined to have a beneficial role in electrodeposition of copper. Guar was found to extend the upper end of acceptable current densities for EW of copper.
The studies on the effects of guar on the deposits are very limited. From literature it is reported that guar is a brightener [100]. Henkel has shown in their sales literature a significant decrease in the grain size of copper deposits when compared to the deposits that used animal protein (glue) [101]. Previous patents claim the use of guar gum improves the quality of electroplated metals[102]. There is no work on the how guar differs in its interaction with copper deposition from glue, i.e. leveling mechanism, brightening or polarization.

![Typical structural unit of guar gum](image)

Figure 2.35 Typical structural unit of guar gum [95]
2.3.5 Multiple Additive Investigations

Most works reported in the literature from industrial research, have all used several additives simultaneously in the electrolyte. Several reports have specifically examined multiple additive effects on copper electrodeposition. The majority of these studies have looked at only two additives at a time. The effects of halides in conjunction with glue were previously examined and showed that polarization occurred for chloride, bromide and iodide [87] with the glue. However, the work also showed polarization when the glue was used without any halide added to the system. The different amounts of polarization vs. the halide concentration from [87] is shown in Figure 2.36.

AC impedance with glue, thiourea and NaCl was studied in 0.71 M CuSO$_4$ and 1.80 M H$_2$SO$_4$ electrolytes by Fabricius and Sundholm [85]. They found NaCl had a depolarizing effect, except at low concentrations and overpotentials where a polarizing effect was found. At low thiourea concentrations (<1 ppm), no significant effect on the cell impedance was found. However at low overpotentials (<100 mV), thiourea had a slight depolarizing effect.
Figure 2.36 Cathode polarization for various halide concentrations with 25 ppm glue in 125 g/l CuSO₄ and 100 g/l H₂SO₄ at 200 Am⁻² from [87].
Wang and O’Keefe [98] investigated the combined effect of 40 ppm Cl⁻, 2 ppm total glue, 5 ppm thiourea and 5 ppm Avitone in 0.57 M Cu²⁺ and 1.65 M H₂SO₄ at 40°C. The major conclusion was that glue eliminated the nodulation problem created by the chloride and thiourea at high current densities (up to 200 Am⁻²). The drawback for this work was no additive replenishment occurred during the tests that were up to 3 hours. O’Keefe’s group have reported other results from multiple additive studies [83]. For example, in other studies nodulation of the copper did occur at 350 A/m² with the electrolyte of 40 g/l Cu²⁺ and 180 g/l H₂SO₄ with high thiourea (10 ppm) and 5 ppm Cl⁻. Additionally, the current response from a potential step to −600 mV vs. mercurous sulfate reference electrode was shown to have an extended induction time. This induction time is described as the region where nucleation is occurring. Also, an uneven nodular texture to the surface was found using scanning electron microscopy. The extended induction time was said to arise from an incomplete or disrupted organic layer on the surface at these conditions [98].

de Maere and Winand [61] tested 10 combinations of thiourea, glue and Cl⁻. They claimed that thiourea was the most important additive. Other combination of additives could be used to bring the deposit quality back after one additive is changed. From the reference conditions, a good deposit can be obtained when the Cl⁻ is increased from 35 to 50 ppm by doubling the thiourea and glue concentration. The amount of sulfur in the deposit increased with the concentration of thiourea but was also a function of Cl⁻ and
glue levels in the electrolyte. In conclusion, the optimal additive levels of a system are complex and difficult to determine.

2.4 In situ monitoring of electrolyte additives

The majority of in situ methods for monitoring additive levels in electroplating solutions are centered on electrochemical techniques. The major emphasis of electrochemical techniques is logical because the process being monitored is mostly electrochemical. However, the use of other techniques should not be discounted. All appropriate tools used in analytical chemistry should be examined for sensitivity, ease of automation, and time for analysis. Several industrial techniques are successfully used but may be improved upon and are discussed below. Several non electrochemical techniques are also discussed.

2.4.1 Reatrol Process

Goffman and Thomas [75, 103] have several patents assigned to Asarco which describe the use of Differential Pulse Polarography (DPP) with a Static Dropping Mercury Electrode (SDME). The potential sensing method is called the Reatrol process and is used to monitor the levels of thiourea in copper electrorefining. The major claim for automated analysis and control of thiourea is the location and the methodology in controlling the concentration and not the analytical technique. Goffman and Thomas assert in their patent that the monitoring should be done with the effluent stream and not
the inlet. The methodology includes claiming there should be trace quantities of TU remaining in the effluent. The mixing and replenishing of additives are two of the major reasons for having a continuous flow of electrolyte during electrorefining. The implementation of a monitoring device at the effluent is a logical extension of the need to supply additives to the deposit at all locations in the cell.

The analytical method to determine the TU levels was not new and Goffman and Thomas [75] even refer their readers to application notes from EG&G for experimental details [104]. The patents also claim that a mercurous sulfate reference electrode should be used in place of the mercurous chloride reference electrode suggested by EG&G. This is no doubt a result of trying to control the chloride contamination in the electrolyte and maybe avoid high temperature degradation of the SCE. The determination of thiourea using the DPP and SDME is described in more detail in several application notes by EG&G [104-109]. DPP is similar to traditional voltammetry in that the potential is scanned through a potential region and the response current is measured. However, DPP will alternatively step the voltage to the desired value and wait a predetermined time and then measure the current. This stepping and waiting allows the charging current to decay sufficiently which minimizes background noise. Furthermore, Reatrol has good sensitivity and reproducibility because of fresh surfaces created by the dropping mercury electrode and the strong affinity of thiourea to mercury [110]. However, DPP has also been used to quantify other additives in electroprocessing but tends to be limited to electroactive species.
2.4.2 CollaMat Process

The quantitative CollaMat system is based on the US Patent 4,834,842 and assigned to Norddeutsche Affinerie. The inventors Lagner et al have implemented a simple polarization technique in a sample stream from the bath. The system uses at least three electrodes and no true reference electrode. As claimed in the patent, the working electrode is a Pt wire. The system can be described as follows.

1. There is a continuous flow of a sample stream from the plating bath.
2. The WE surface is fresh at the start of each measurement. This is done by feeding wire into the flow cell at the start of each test.
3. A constant current is applied and the rate of change of the polarization (dV/dt) is measured.
4. The measured dV/dt is then compared to a calibration plot to determine the concentration of the additive or readout on an arbitrary scale. The additives are adjusted to obtain the predetermined optimum concentration on either the standardized or arbitrary scale.

The CollaMat process uses the change in the rate of polarization (slope of the time vs. potential curve) resulting from the increase in concentration of the inhibiting specie or species. Therefore, any additive or increase in concentration of an additive that polarizes the working electrode can be monitored with CollaMat. The flexibility of the CollaMat monitoring system also has certain limitations. One such limitation occurs when other
additives or impurities are present which increases the rate of polarization and cannot be separated. It is known that thiourea temperature, \([H_2SO_4]\) and \([Cu^{2+}]\) all will have an effect on \(dV/dt\).

2.4.3 Real Time Analyzer

The use of AC voltammetry and DC voltammetry has been combined in a patented analysis system [111] licensed to Technic, Inc. and is called the Real Time Analyzer (RTA). [28] The RTA system is an automated, on-line, \textit{real-time} in situ system that monitors the bath quality and can be used to automatically replenish the chemicals predetermined levels by a control system. As in AC Cyclic Voltammetry, the RTA uses the increase spectral detail of the second harmonic (see section 2.5.3) combined with the DC component to determine levels for major and minor components. The RTA system can analyze electroactive as well as electroinactive components. The second harmonic component from AC voltammetry used by RTA is sensitive to changes in the capacitance components, which are associated with adsorption and desorption process as well as Faradaic process. The details of AC voltammetry will be presented in section 2.5.3. The strengths of this technique are also its current limitations. Because of the increase spectral detail, each bath type with the proprietary additives has to be evaluated independently.
2.4.4 CVS Process

Cyclic voltammetric stripping (CVS) was first patented in 1979 by Tench and Ogden [112]. It has been successfully implemented when monitoring the overall quality of the plating bath. CVS is a derivation of anodic stripping voltammetry (ASV), which is generally used to detect trace amounts of metals [113], and cyclic voltammetry. Similar to cyclic voltammetry, the potential for CVS is swept from a starting voltage to a cathodic potential and then the direction is reversed and the final potential is once again in the anodic region for the metal. It was found that the stripping peak was more sensitive to additive levels and bath quality than the plating peak for CVS. The high sensitivity ($10^{-10}$ to $10^{-11}$ M) for a metal using ASV is accomplished by first reducing and preconcentrating the metal as a Hg amalgam. Similarly, CVS increased sensitivity is from integrating the total effect on the deposition step and examining the rapidly stripping anodic peak. For ASV, Eq. 2.21 relates the bulk concentration of the electrolyte to the stripping current peak ($i_p$) for a HMDE by Eq. 2.21.

$$i_p = AD_m^2 C_m^* [(2.69 \times 10^4) n^2 v^2 - \frac{(0.725 \times 10^5) n D_m^2}{r_0}]$$

Eq. 2.22

For Eq. 2.21, $r_0$ is the radius of Hg drop, $D_m$ is the diffusion coefficient, $C_m^*$ is the bulk metal concentration, $A$ is the surface area of the Hg drop, $n$ is the number of electrons in process and $v$ is the sweep rate. Since the quantity of the metal concentrated in the amalgam is in a small volume, the fast scan through the stripping peak results in a significant increase in the peak current over the plating portion. Similarly, the copper
plate during the cathodic portion of CVS concentrates the metal at the surface and will result in a large peak upon the anodic sweep. Since the additive generally decelerates or accelerates the deposition of copper, the ratio of the stripping peak of copper with additives and without are used to determine the concentration of the additive.

External standards were initially used to calculate the concentration via CVS. Tench and Ogden [114] have since shown that the concentration (or additive effectiveness in the electrolyte) can be monitored without using external standards. This is done by comparing the peak obtained in the electrolyte with the additive with a sufficiently high rotation speed to keep a steady flux of the additive to the surface, and without rotation. Tench and Ogden claim that the slow diffusion of the additive to the stagnant electrode yields a zero effective concentration of the additive at the surface of the electrode.

2.4.5 Other Electrochemical Techniques

Glue degradation and quantification can also be monitored by impedance spectroscopy. Fabricius and Sundholm [85] showed that using the imaginary part of the impedance one is able to monitor the levels of glue. A chronopotentiometric method of monitoring levels of glue has been developed that requires limited equipment by Blechta et al [60, 115]. Additional chronopotentiometric studies for glue and thiourea have been reported using slightly different procedures to minimize the effects of other electrolyte components [23, 116]. Ultrafiltration, solution pretreatment with peroxide, dilution and
heating have all been used to separate other bath components and/or increase the sensitivity of the signal. Linear sweep voltammetry has also been studied with limited success for \textit{in situ} monitoring [99].

Cyclic voltammetry has been put forth as a method to monitor additives by numerous researchers [24, 117-121]. Several ER facilities have attempted to monitor the levels of additives in this manner but have discontinued the practice. Several of the reasons were lack of sensitivity at the desired additive levels, dependence on operator interpretation and the inability to automate the process [60, 115]. A slightly different CV approach was presented by Dakkouri et al. in which the UPD peaks of copper on Pt(111) were monitored [122]. They found the copper UPD peaks are heavily influenced by organic additives. Future work to scale this method to ER/EW solutions has not been reported.

2.4.6 Non-Electrochemical Techniques

The use of surface sensitive optical methods for monitoring additives is promising since the additives tend to concentrate at the active surface. Raman spectroscopy may be suitable for monitoring additive levels in copper sulfate electrolytes. Plieth [121] show that light scattering from a laser can give information on surface roughness, nucleation process and general morphology. Surface Enhanced Raman Spectroscopy (SERS) has been used to study the adsorption process [123] and should be capable of monitoring additives in electroplating. High performance size exclusion liquid chromatography was
previously used to evaluate glue hydrolysis in various bath conditions and this technique could be successful in monitoring bath quality. The major drawback is the expense of the equipment. Very little work towards automated bath analysis has been done in this area at this time for EW/ER

2.5 Electrochemical Techniques

2.5.1 Chronopotentiometry

Chronopotentiometry is an electrochemical technique in which the current steps from open circuit to a desire current, which is maintained through the cell. The voltage required to deliver this set current is monitored and recorded versus time. Such a graph, V vs. t, is called a chronopotentiogram (CP). The voltage across the cell during electrolysis is controlled by the Redox potential, as described in its simplest form by the Nernst Equation. The Nernst Equation is shown in Eq. 2.22.

\[ E = E^0 + 0.0591 \log(C_o/C_R) \]  

Eq. 2.23

In Eq. 2.22, \( E^0 \) is the formal potential, \( E \) is the measured potential, \( C_o \) and \( C_R \) are the surface concentration of the oxidized and reduced species, respectively.

At sufficient currents, the surface concentration will be depleted. The potential initially changes slowly when the surface concentration decreases from the passage of current as described by Equation 2.22. Replenishment of the species reacting at this
voltage is generally limited by diffusion. Eventually, there is insufficient concentration at the surface to maintain the impressed current and the voltage will then increase until another reaction can supply the current or the instrumentation reaches the voltage limit of the equipment.

Sand's originally noted that in an unstirred solution under linear diffusion control, the potential slowly increased until there was a rapid change in potential [113]. Again, this rapid change is a result of the insufficient diffusion of the species involved in the Faradaic reaction to the surface. The time that this rapid change occurs is given by Eq. 2.23. \( \tau \) is called the transition time, \( n \) is the number of electrons transferred in the reaction, \( A \) is the surface area of the electrode, \( D_o \) is the diffusion coefficient of the metal ion and \( C_o \) is the bulk concentration of the metal ion.

\[
\frac{1}{\tau^2} = \frac{nFAD_o^2}{4C_o \pi^2}
\]

Eq. 2.24

2.5.2 Linear Sweep and Cyclic Voltammetry

Voltammetry is the study of the current response to a potential. Two typical potential profiles applied are linear sweep or cyclic. For linear sweep voltammetry (LSV), the potential is swept from a starting voltage to a final voltage at a predetermined sweep rate (mV/sec). Similarly, cyclic voltammetry (CV) has a starting potential with a sweep rate. The additional step in CV is to reverse the sweep direction once the potential reaches the end point for LSV, hence a cycle.
The current response for the sweeping voltage depends on the $[M^{n+}]$ concentration, diffusion coefficients, and the reversibility of the EC reaction. The various mathematical solutions for the current are given in [113]. For a typical reversible EC reaction, the relationship for the peak current ($i_p$) is:

$$i_p = \left(2.69 \times 10^4\right) n^\frac{1}{2} A D_0^\frac{1}{2} \nu^\frac{1}{2} C_0^*$$  

Eq. 2.25

In Eq. 2.24, $A$ is the area of the electrode, $D_0$ is the diffusion coefficient, $C_0^*$ is the bulk concentration and $\nu$ is the sweep rate. The difference between the peak voltage ($E_p$) for the anodic and the cathodic in a cyclic voltammogram can be used to estimate the reversibility of the system. The peak separation for an ideal reversible EC process should be $2.3RT/nF$ ($59/n$ mV @ 25°C). The shape of the current peak is also a function of the transfer coefficient ($\alpha$).

2.5.3 AC Voltammetry

AC Voltammetry or Polarography is an electrochemical technique where the perturbation of the system is a slow sweeping potential, referred as the DC component, that is similar to cyclic voltammetry with an AC signal superimposed on the DC component. Figure 2.36 is a graphical representation of the applied waveform during typical AC voltammetry. The DC sweeping signal is generally varied slowly so that the AC and DC diffusional components are uncoupled [113]. The DC response sets the surface concentrations that resemble the bulk as viewed by the much faster varying AC
component. Instrumentally, this superposition is generally accomplished by an adder type potentiostat [113].

Any explanation of AC voltammetry requires a basic definition of cell impedance. The physical processes contributing to the cell impedance were divided into several categories by Smith [[124] and are:

- Ionic migration,
- Charging of the double layer,
- Faradaic processes, such as electrochemical reactions, or adsorption processes.

Alternating current flowing from the Faradaic component can only occur when both oxidized and reduced forms of the electro active species are present. A better understanding of the AC current requires using a simple model of the electrochemical interface such as the Randles circuit [125]. In this model, the electrode/electrolyte interface acts as a set of typical electronic components as shown in Figure 2.37. The solution resistance (electrolyte resistance) is $R_e$ and the double layer capacitance is $C_d$. The Faradaic impedance component can be broken into two parts, the charge transfer resistance, $R_{ct}$, and the Warburg impedance [113].
The Warburg impedance is a diffusional type resistance, which can be solved under different boundary conditions. For instance the complete circuit impedance can be described by Eq. 2.25 using the boundary condition that the diffusion layer is of infinite thickness [125].

\[
\text{Re}(Z) = R_e + R_\alpha (1 + \frac{\lambda}{2\omega}) - R_\alpha^2 \lambda^2 C_{dl} \]

\[
\text{Im}(Z) = \frac{R_\alpha \lambda}{\sqrt{2\omega}} \tag{2.26}
\]

The frequency dependence can be seen by the $2\omega$ terms which are defined as the angular frequency of the sinusoidal perturbation ($2\pi$*frequency). The diffusional aspect for this solution is in the $\lambda$ term. $\lambda$ is given in Eq. 2.26 with $k_f$ and $k_b$ being the electrochemical
rate constants and $D_O$ and $D_R$ are the diffusion coefficients for the oxidized and reduced species, respectively.

$$\lambda = \frac{k_f}{\sqrt{D_o}} + \frac{k_b}{\sqrt{D_R}}$$  \hspace{1cm} \text{Eq. 2.27}

For more analysis of modeling the interface, the reader is referred to several types of works such as impedance spectroscopy [125-130] and AC voltammetry [124, 125, 131-136].

The double layer charging current limits the frequency for fundamental AC voltammetry. The double layer charging current increases proportionately with frequency while the Faradaic component normally increases with the square root or less of the frequency [124, 137]. Eventually the current response will be totally from the double layer as the cell basically shorts through $C_{dl}$ of Figure 2.37. The detection of electroactive species with AC voltammetry tends to be limited to approximately $10^{-4}$ M because of the increased fraction of current from the double layer.

Several methods have been devised to minimize or separate the charging current from the Faradaic current. One such method is called phase sensitive detection for AC voltammetry [124, 138-140]. Phase sensitive AC Voltammetry is based on the fact that the charging current is generally around $90^\circ$ out of phase from the applied alternating voltage while the Faradaic current is $45^\circ$ or less out of phase. The ohmic resistance tends to cause the charging current to be slightly off from the $90^\circ$ phase angle [124].

Phase selective detection can be accomplished by software (Fourier Analysis [141-144]) or by using a lock in amplifier [134, 145]. The lock in amplifier has several
key features that enhance AC voltammetry [146, 147]. In the case of AC voltammetry, the lock in amp can be envisioned as multiplying the current output from the cell (converted to a voltage) by the complex conjugate of the perturbation signal. The applied voltage signal which is used as the multiplier, can be phase shifted by the lock in amplifier in order to multiply the output signal by the perturbation signal of a desired phase angle. Therefore, any signal that is in phase will be amplified by superposition of the two waves. The lock in amplifier can determine the total magnitude and phase of the current (angular relation to the perturbation signal) or isolate and monitor the current at a particular phase angle and frequency. For more details on the lock in amplifiers see references [148, 149].

2.5.3.1 Fundamental Frequency

The term fundamental in AC voltammetry refers to the frequency of the perturbation. The fundamental response is the classical response used in phase sensitive voltammetry. The Faradaic response has commonly been used to measure kinetic parameters. The Faradaic current response to a small amplitude AC signal has been derived by several researchers and for a more in depth analysis see [124, 150]. The solution for the Faradaic current of an electrochemical reaction depends on the degree of reversibility of the system. Generally, the sinusoidal applied voltage is small to maintain \(i - \eta\) linearity. The solution is given in Eq. 2.27 assuming linearity and a completely reversible system.
2.5.3.2 Higher Harmonics

The impedance of a Faradaic process and double layer charging are not perfectly linear. Current flowing as a result of a sinusoidal applied voltage, such as in AC voltammetry, will contain nonlinear contributions. These nonlinear elements are more commonly known as higher harmonics combined with a DC rectification component. The nonlinearity of the Faradaic component is usually greater than the double layer charging [124]. Therefore, the measurement of higher order current components has been studied to reduce charging current effects on electrochemical systems. Similar to Eq. 2.27 boundary conditions, the solution for the second harmonic is given in Eq. 2.28.

\[
I(\omega t) = \frac{n^2 F^2 AC_o(\omega D_0)^2}{4RT\cosh^2(j/2)} \frac{\Delta E}{\sin(\omega t + \frac{\pi}{4})} \quad \text{Eq. 2.28}
\]

\[
I(2\omega t) = \frac{2^2 n^2 F^3 AC_o(\omega D_0)^2}{16R^2T^2\cosh^3(j/2)} \frac{\Delta E^2 \sinh(j/2)}{\sin(2\omega t - \frac{\pi}{4})} \quad \text{Eq. 2.29}
\]
Table 2.7 is a list of the terms for the solutions associated with the different components of the Faradaic current amplitude. Note that for small perturbations (ΔE ≤ 8/n mV) the solutions would only require p=0. With larger perturbations, p would be 1, 2 or larger which results in higher harmonics.

The major problem with AC voltammetry is the complexity in the math. Microcomputers have helped in tractability of the math but dissecting the terms from experimental data and giving them physical meanings is still extremely complex. Not only are there contributions to the current response that change with degree of reversibility or secondary reactions, but there are adsorption processes that interfere and have become an area of study in and of itself.

2.5.4 Tensammetric Response

A derivative of the AC voltammetry of surfactants has been given the name tensammetry. Multiple papers have been published on the use of AC voltammetry to determine trace quantities of surfactants [151-156] Bersier and Bersier have discussed whether tensammetry is a useful tool or laboratory toy. They concluded tensammetry was an ideal method for trace analysis of a surfactant in dilute aqueous solutions. The main advantage with the tensammetric approach similar to 2nd harmonic AC voltammetry, is the detection of the non-Faradaic responses. The previous focus has been on dilute surfactants on Hg electrodes in weak electrolytes. Investigations have been conducted of mixture of surfactants, alcohols and surfactants at water treatment facility [157-160]. No
work was found regarding tensammetry in concentrated solutions similar to conditions found in Cu electrowinning and electrorefining
Table 2.7 Contributions to the current amplitudes from higher order components [124]

See Note

<table>
<thead>
<tr>
<th>Current</th>
<th>( P=0 )</th>
<th>( p=1 )</th>
<th>( p=2 )</th>
<th>( p=3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_{dc} )</td>
<td>( \frac{K}{(1 + e^{i})(\pi t)^2} )</td>
<td>0</td>
<td>( \frac{-K\delta^2 \sinh(j/2)}{16(\pi t)^2 \cosh^3(j/2)} )</td>
<td>0</td>
</tr>
<tr>
<td>( I(\text{wt}) )</td>
<td>0</td>
<td>( \frac{K\delta^2 w^2}{4 \cosh^3(j/2)} )</td>
<td>0</td>
<td>( \frac{K\delta^2 w^2 [2 \cosh^2(j/2) - 3]}{64 \cosh^4(j/2)} )</td>
</tr>
<tr>
<td>( I(2\text{wt}) )</td>
<td>0</td>
<td>0</td>
<td>( \frac{2^{\frac{3}{2}} K\delta^2 w^2 \sinh(j/2)}{16 \cosh^3(j/2)} )</td>
<td>0</td>
</tr>
<tr>
<td>( I(3\text{wt}) )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>( \frac{3^{\frac{3}{2}} K\delta^2 w^2 [3 - 2 \cosh^2(j/2)]}{192 \cosh^4(j/2)} )</td>
</tr>
</tbody>
</table>

Note: \( \delta = nF\Delta E/RT; K = nFAC_0 D_0^{1/2} \)
3. EXPERIMENTAL

3.1 Rotating Disk Electrode

The rotating disc electrode (RDE) employed in this research was a Pine Instruments Model AFMDI1980PTHT high temperature Pt disk electrode. The Pt disk had a diameter of 5 mm and was designed to withstand temperatures up to 80°C. The surface was used as received except for thoroughly rinsing in isopropyl alcohol, followed by 50% wt. nitric acid and then DI water. The electrode had previously been used for copper diffusion experiments and therefore has been exposed to repeated plating and stripping of copper in 0.63 M CuSO₄ with 1.63 M H₂SO₄. A Pine Instruments Analytical Rotator was used to control the rotational speed up to 1,000 rpm. A jacketed reactor with 750 grams of the electrolyte was used in each test. The temperature was controlled to ± 0.5°C. The reference and auxiliary electrode were mercurous sulfate electrode (MSE) and high purity copper rod (99.99 less oxygen), respectively.

The moving contact on the rotator introduced considerable noise in the signal. Figure 3.1 shows the degree of noise introduced during the preliminary experiment. To reduce this noise, the contact on the rotator was continuously polished during each test with 1000 grit sandpaper. Figure 3.2 displays the reduction of noise but also shows that there is still some noise introduced from the rotator which limits the resolution of this work.
Figure 3.1 Chronopotentiogram using a Pt RDE in synthetic electrolyte prior to polishing. Experimental conditions are 40 g/l Cu$^{2+}$, 10 ppm Glue, 160 g/l H$_2$SO$_4$ at 65°C, 300 rpm, and 5,100 A/m$^2$.

Figure 3.2 Chronopotentiogram using a Pt RDE in Synthetic Electrolyte with polishing of the contact during test. Experimental conditions are 40 g/l Cu$^{2+}$, 10 ppm glue with 40 minute hydrolysis, 160 g/l H$_2$SO$_4$, 65°C, 300 rpm, and 5,100 A/m$^2$. 
3.2 Stationary Microelectrode

The working electrode (WE) used for the experiments requiring a small surface area was a 1 mm diameter Pt wire mounted Pyrex glass and fire polished. The Pt wire was purchased from Aldrich (7440-06-4) and had a purity of 99.9%. The diameter of the wire was 1.0 mm which gave a cross sectional surface area of $7.85 \times 10^{-7}$ m$^2$. The surface of the electrode was roughened with 600 grit sand paper. Several electrodes were produced in this manner. The reproducibility of the experiments for each electrode was accomplished by cycling the electrode in standard electrolyte at 65°C between plating and stripping copper at least 50 times. The cyclic voltammetry parameters used for this preconditioning step were 1.0 V to -0.5 V vs. MSE at 65°C with a sweep rate of 25 mV sec$^{-1}$. Prior to use, the electrode was thoroughly rinsed with DI H$_2$O, then isopropyl alcohol. The electrode was then rinsed again with DI H$_2$O and placed in a 50% HNO$_3$ solution for five minutes. The final rinse with copious amounts of DI water was done and the electrode glass sides were wiped with a Chem Wipe to remove water droplets.

3.3 Flow Cell

A flow cell was built to explore the possibility to create a continuous monitoring system instead of a batch process. The flow cell is shown in Figure 3.3. The reference electrode generally used was the same MSE as all the other experiments except it was placed in the Tygon tubing upstream of the working electrode. A “plug” identical to the one used in the Luggin probe was also used to isolate the electrode. Several tests were performed using a copper wire reference. One key feature of this cell is the counter
electrode (CE) is the entire base plate. The surface of the base plate, i.e. counter electrode, was wet sanded with 600 grit sand paper and DI H₂O. The Pt working electrode is same type of Pt wire described in section 3.2, except it is pressed into a PTFE block instead sealed in Pyrex glass. A Master Flex peristaltic pump (Model No. 07550-60) with a small tubing pump head was used to deliver the flow through the cell. The pump/head combination had the ability to deliver flow rates from 0.006 to 77 mL min⁻¹. The flow rate was manually calibrated for each test condition to approximately 15 ml/min.

### 3.4 Chronopotentiometry

Chronopotentiometry experiments were used to evaluate the cathodic polarization increase associated with the addition of galactosal, chloride and glue. The increase in polarization to quantify the additives in the electrolyte has been discussed in the literature, see section 2.4.2. The techniques was carried out in a three electrode configuration using either a EG&G Model 273 Potentiostat/Galvanostat or a Cypress Systems 5100. The reference electrode was a saturated mercurous sulfate electrode (MSE). The auxiliary electrode was a high purity copper rod (>99.99% Cu less oxygen) approximately 15 cm long and 0.64 cm in diameter.

The synthetic electrolyte refers to a solution prepared in the lab from Reagent Grade 1.63 M sulfuric acid and 0.63 M cupric sulfate pentahydrate. These concentrations were chosen to simulate the average acid/copper content of electrowinning/electrorefining, see section 2.1.2. A closed glass cell with 750 g of the electrolyte was
Figure 3.3 Flow cell with assembled cell shown on the left and cell top. While on the right is separated cell showing the Teflon top and Cu plate base. Cell volume was fixed by placing a gasket between the two pieces. Typical gasket used was 0.024" spacer.
placed in a hot water bath and heated to 65 ±0.2°C. The reference electrode was placed in
a Luggin probe filled with the synthetic electrolyte and then all three electrodes place into
the cell. The cell and electrodes were allowed to come to thermal equilibrium for twenty
minutes. Stepping the voltage to 0.8 V vs. MSE and holding for approximately one
minute anodically cleaned the surface of the electrode prior to each experiment. The
electrolyte was than vigorously stirred with an overhead stirrer and then allowed stand for
5 minutes to become quiescent.

The test began with a 300 A m⁻² cathodic current step for 5 minutes or more
(typically 8.3 minutes). At the end of this pulse, an anodic current of 6,100 Acm⁻² was
immediately applied for equivalent amount of time. The potential was recorded during
the complete anodic and cathodic pulses.

3.5 AC Voltammetry

The AC voltammetry was performed using a EG&G Princeton Applied Research
(PAR) Model 273 potentiostat coupled with a PAR 5210 lock-in amplifier and a Wavetek
Model 19 signal generator. The AC signal was generated from a Wavetek Model 20
function generator and applied to the front panel external input (ext. input) on the
potentiostat. The function generator controlled the magnitude of the AC signal with a
power knob (analog) and two attenuating circuits. This appears to severely limit the
stability of the AC signal and did cause problems in the amplitude of the peaks in the AC
voltammograms. The front panel AC signal was superimposed onto the DC ramp of the
Model 273 by an adder type circuit built into the Model 273.
The current through the cell was converted to a voltage by the potentiostat. The current range of the current to voltage (I-V) converter was set for maximum gain for the larger of either the DC or the AC current component. The range was ordinarily set at ±2 volts full scale for ± 10 μA for the I-V converter. This signal was in turn fed into the Model 5210 lock in amplifier.

The output of the lock-in amplifier was read directly from the front panel of the lock in amplifier using a National Instruments Lab-PC-1200/AI data acquisition card. The Lab-PC-1200/AI card used to collect the output was capable of gathering data at 100 kS/sec at 12 bit resolution. The board gain was generally set to 1 with a range of ± 5 V except for total magnitude-phase data collection. The gain in these experiments was maximized first at the potentiostat and then at the lock-in amplifier to minimize amplification of stray voltages. The Model 273 direct current CV scan was controlled programmatically by the serial connection and the PC computer using LabVIEW 4.0 for Windows 95. The equipment setup is shown in Figure 3.4. The Labview VIs used to collect and process data are attached as Appendix A.
Figure 3.4 Electronic Wiring and Hardware Configuration.
3.5.1 Galactasol Preparation

The Galactasol was first prepared as a 1,000 ppm stock solution by heating approximately 750 ml of DI H₂O to 65°C. Next, two grams of the powder organic was added slowly while vigorously stirring. The solution was then poured into a 2 liter volumetric flask and cooled to room temperature. After thoroughly rinsing the beaker and pouring it into the volumetric flask, the flask was topped off. Some organic most likely remained in the beaker. However, the majority was recovered and the process was found to give consistent concentration for the solutions.

Prior to the addition of any of the organic, the electrolyte was preheated in a hot water bath to 65°C. The organic was allowed to degrade in the electrolyte at 65°C for a predetermined time as needed for each experiment. A Luggin probe filled with the base electrolyte and a Hg/HgSO₄ reference electrode was placed approximately 1 cm from the WE. The auxiliary electrode (AE) was a 1.0 cm in diameter copper rod. Approximately 16 cm² of the AE was exposed to the electrolyte. An impeller was placed in the electrolyte to stir the system prior to each measurement. The same program that controlled the Model 273 and collected the data controlled the stirring duration.

The steps involved in preconditioning the electrode are as follows:

1. Stirred at 200 rpm for 2 minutes.

2. System was allowed to become quiescent for 1 minute.

3. An anodic pulse of 1.15 V vs. MSE with the desired AC signal superimposed was applied for 30 seconds (anodic cleaning of surface).
4. The prescribed cyclic voltammetry scan was started immediately.

3.5.2 Fundamental Harmonic

As stated previously, the current through the cell was converted to a voltage signal that was used as the input for the lock-in amplifier. The reference signal for the lock-in amplifier was the TTL signal supplied directly from the Wavetek Model 20 function generator. The output of the lock-in amplifier was set to report the magnitude of the AC signal at 60° and 150° phase angles unless otherwise indicated.

3.5.3 2nd Harmonic

The 2nd harmonic signal was collected in exactly the same manner as the fundamental, 3.5.1, except the 2F function was enabled on the Model 5210. This in essence had the lock-in amplifier report the magnitude of the AC component of current at the set phase angles that occurred at twice the excitation frequency. The magnitude and frequency of the perturbation signal are changed and indicated for each test that is reported.

3.6 Capillary Electrode (Increased Sensitivity for Glue)

The electrode was constructed from Pt wire (99.9%) with a diameter of 1.0 mm. The Pt wire was encased in a glass capillary tube by heating the Pyrex type glass and elongated the entire tube to reduce the inside diameter until it sealed around the wire.
The wire was polished prior to encasing in the glass tube. The remaining tube past the end of the Pt wire was cut and polished to leave approximately a 1.0 mm channel.

3.7 AFM

The morphology, location and density of the deposits and additives were studied with atomic force microscopy (AFM). AFM images were collected using a NanoScope III (Digital Instruments, Santa Barbara CA). Highly oriented pyrolytic graphite, mica and polycrystalline copper were used as substrates. The majority of the images were collected using the Tapping Mode of the NanoScope III. In Tapping Mode, the probing tip of the instrument is driven to resonance by a small piezoelectric crystal. This probe is a cantilever etched from a single crystal silicon wafer. A differential optical detector with a laser-mirror setup that works like an optical lever arm was used to measure the amount of vertical displacement of the probe. The vertical displacement is determined by focusing the laser on the end of the cantilever. The oscillation of the reflected beam is measured by the detector and mirror arrangement. The surface of the substrate is brought up until a predetermined amount of dampening of the signal from the probe occurs. Fixed at this root mean square dampening, the sample is then rasterred under the tip at a constant height. In contact mode, the probe is dragged across the surface in similar manner as a record needle on a phonograph.
3.8 Electrolyte Solutions

A synthetic electrolyte was used during most of this work. The solution contained 1.63 M H₂SO₄ and 0.63 M Cu²⁺ added as CuSO₄·5H₂O. The solution was prepared in 1 liter volumes using only Reagent Grade chemicals and DI water from a Millipore RO system. The industrial electrolytes were collected from the various cell houses. They were always stored at roughly 50°C to minimize precipitation of the CuSO₄ from the system. It was found that the synthetic electrolyte could be processed by heating to ~90°C for 1.5 hours and to remove any noticeable glue, thiourea or guar. The heating (decomposing of the industrial electrolyte) was done on a temperature controlled hot pad designed to heat 6 inch wafers. The temperature control was within a few degrees and could be programmed to shut off after the prescribed time.
4. RESULTS

Chapter 4 contains the results with a brief discussion to explain some of the information ascertained from the results. Initially, the results will be centered on the research using CP for glue, TU and Cl\(^-\). During this portion of chapter 4 the results are generally discussed in the amount of polarization for the reduction of Cu\(^{2+}\). However, some of the results relate to the other information found on the chronopotentiograms such as the time to remove the deposited Cu.

The later half of the chapter will report and discuss the use of 2\(^{nd}\) harmonic phase sensitive AC voltammetry as a quantitative tool. The emphasis in this section will be the detection of guar (added as Galactasol\(\text{TM}\)) and the dissection of the voltammograms by examining each component of the electrolyte with DC voltammetry, fundamental phase sensitive AC voltammetry and 2\(^{nd}\) harmonic phase sensitive AC voltammetry. Only a brief analysis of the voltammograms will be presented in chapter 4. Chapter 5 will have further analysis and conclusion for the information reported in this chapter.

4.1 Glue Results

In this study, the effects of the additives on the plating of copper at constant currents were examined. These constant current studies, known also as chronopotentiometry, were unusual because of the high concentrations of the copper and sulfuric acid in the electrolyte. The conventional method for discussing CP results entails examining the transition time from the Sands Equation:
\[
\frac{1}{\tau^2} = \frac{1}{nFAD_0^2\pi^2C_0} \quad \text{Eq. 4.1}
\]

Also, information on the diffusion of Cu that changes upon the addition of glue, TU and Cl\(^-\) could be evaluated with Eq. 4.1. The conditions selected for the chronopotentiometric test are typical for copper electrorefining. The current density was set at 300 Am\(^-2\) with the Cu\(^{2+}\) concentration set at 40 g/l. To estimate the transition time using Eq. 4.1, \(n\) was set equal to 2 while the diffusion coefficient was set at \(1.2 \times 10^{-5} \text{cm}^2\text{sec}^{-1}\). The estimated time until copper diffusion would not be able to support the impressed current was calculated as \(\tau = 156\) secs. The predicted value of \(\tau\) was considered to be large for the Sands equation and thus minimal information for this work can be obtained from this approach.

In fact no evidence of a sharp potential changes were found in the 40 g/l Cu\(^{2+}\) / 160 g/l H\(_2\)SO\(_4\) chronopotentiograms using typical planar electrodes. The typical CP, shown in Figure 4.1, has no sharp increases associated with the reaction switching from Cu reduction to another reaction.

There are several reasons why no characteristic \(\tau\) for the system was found experimentally. One reason is that the lengthy transition time allows sufficient radial diffusion to the surface, which would increase \(\tau\). Second, the plating process has density gradients forming at the surface that would create more convection at the WE. Even with the WE inverted there are still significant density gradients that form small vortices which were seen while plating and dissolving copper for extended periods. The results of the convection and radial diffusion would be to lengthen any transition time. The convection
from the density gradients and inherent vibrations from working in the water-circulating bath resulted in no observable transition times for these electrolytes. This indicates the Cu^{2+} reaction was continually proceeding during the course of the CP experiments, albeit with differing amounts of polarization. However, several features are apparent in typical CPs for this work. These features were shifts in potential not associated with typical transition time events. An example of the complete set of data collected during each CP test is shown in Figure 4.2. As discussed in the experimental section, the current is reversed from cathodic to anodic at 8.33 minutes to prepare the working electrode for further experimentation. The cathodic current density of 300 Am^{-2} did not display any transition time but small amounts of polarization were evident with different combinations of additives. Again, no transition time is seen in the first 8.33 minutes of Figure 4.1. The switch to 600 Am^{-2} anodic created the first sharp potential increase. The second larger increase occurs when all the Cu has been oxidized and the galvanostat searches for the next anodic reaction, oxygen evolution.

The small increase in polarization from the addition of 10 ppm glue as predicted from the work of Blechta et al [60] is shown in Figure 4.1. Since the polarization is related to the amount of glue found at the surface, a RDE was used to see if increase transport to the WE improves the polarization signal. The use of a RDE was found to only slightly change the chronopotentiograms. Figure 4.3 is a CP using a Pt RDE at similar conditions to Figure 4.1. The only difference is the applied current is increased to keep the same current density for the RDE which has a much larger area than the previous
Figure 4.1 Chronopotentiograms using a 1.0 mm Pt wire embedded in epoxy. Experimental conditions were 40 g/l Cu$^{2+}$, 160 g/l H$_2$SO$_4$, 65°C and 300 A/m$^2$.

Figure 4.2 Chronopotentiogram using a 1.0 mm Pt wire embedded in epoxy. Experimental conditions were 40 g/l Cu$^{2+}$, 160 g/l H$_2$SO$_4$, 65°C and 300 A/m$^2$ cathodic and 600 A/m$^2$ anodic.
WE. There was a problem with stability for the Pt RDE at elevated temperatures. The first RDE slowly had the electrolyte seep between the PTFE and the Pt disk and eventually failed completely while the second produced the RDE results presented in this work. Upon addition of glue, only a small polarization occurred for any of the experiments. The 1 ppm and blank experimental results had significant fluctuations, which were enough to make 1 ppm indistinguishable from the base synthetic electrolyte without glue as depicted in Figure 4.3. At 10 ppm glue, there was a small increase in polarization of only 9 mV. This is in contrast to the 70 mV increase that was reported by Blechta et al [60]. The cathodic polarization with 10 ppm glue correlates to a decrease in the active surface area of the working electrode. A simplistic site-blocking model can be envisioned as the adsorption of the glue (or additive) on the protrusions or active sites on the working electrode, which decreases the available surface area for deposition. Figure 4.4 illustrates the long chain organic molecules adsorbing on the surface of the working electrode. The model for electroinactive species effecting the deposition was discussed in section 2.5 with other models which are further reviewed by Loshkarev [64]. The Tafel equation, Eq. 4.2 can be used if one assumes that only the surface area changes with the addition of glue to the electrolyte.

\[ \eta = a + b \log i \]  

Eq. 4.2

The constants a and b can be easily canceled out but are defined as \( a = \frac{(RT/\alpha nF) \ln i_0} \) and \( b = \frac{(RT/2.303\alpha nF)} \). In Eq. 4.2, R is the ideal gas constant, T is temp, n is number of
Figure 4.3 CPs for Synthetic Electrolyte with 0, 1, and 10 ppm Glue using RDE @ 330 rpm

Figure 4.4 Proposed surface adsorption of additives such as glue during metal deposition at protrusions. Model from (*).
electrons involved in reaction, F is Faraday’s constant and \( \alpha \) is a constant describing the
symmetry of the activation energy barrier. Using the Tafel equation, one can envision the
surface coverage increasing as the polarization increases with constant current. The
percentage of the surface covered that would account for the increase in current would be
23\%.

The polarization shift had previously been suggested as a signal that could be used
to quantify glue in copper/sulfuric acid plating baths [60, 115]. As shown in Figures 4.1
and 4.3, the polarization does not appear to be a sufficient analytical signal for monitoring
 glue in the synthetic electrolyte. However, an interesting feature was observed when the
electrode current was switched and will be present in section 4.5.

4.1.1 Chloride Activation of Glue

The small inconsistent polarization caused by the addition of glue was the
fundamental reason for further exploring glues behavior in the synthetic electrolyte. The
observed modest polarization seemed to contradict many of the previous studies found in
the literature. From trial and error and observations that some glue samples would
degradate and activate the next aliquot of glue added, it was determined that \( \text{Cl}^- \) and/or a
 glue decomposition products had a significant effect on whether the glue was effective at
polarizing the Cu deposition. It was speculated that the \( \text{Cl}^- \) content of some of the glue
 batches were higher than other batches and proved to be very troublesome to identify with
inconsistent glue sample properties.
Figure 4.5 - CPs for Synthetic Electrolyte without Glue, with glue and with Glue and Cl⁻ together using the Microelectrode
The CPs for the base electrolyte with glue, and with glue and Cl\(^-\) are shown in Figure 4.5. The addition of glue alone had almost no effect while a large cathodic polarization of approximately 115 mV occurred when 40 ppm Cl\(^-\) was added to the electrolyte. It has been previously reported that Cl\(^-\) can also cathodically polarize the plating of Cu, see 2.3.1. Tests without the glue and different levels of Cl\(^-\) in the electrolyte were conducted to confirm this increase in polarization. As shown in Figure 4.6a, 40 ppm of Cl\(^-\) was found to slowly increase the polarization up to 2 minutes. The general fluctuations, as shown in Figure 4.6b, obscured the results for times greater than 2 minute. The copper deposit becomes rough without additives, such as glue, in the electrolyte and was found to cause significant fluctuations as the rough deposit protrudes into the electrolyte.

4.1.1.1 Chloride Contamination in the Glue

The discrepancy with the magnitude of the polarization with and without Cl\(^-\) indicated a possibility of contamination of the electrolyte with Cl\(^-\) from the glue in our experiments. Some of the previous studies reported larger polarization from the addition of glue but the magnitude of which tended to vary between studies. However, there were experimental differences found in most of the studies reported in the literature. For example, the results reported by Blechta [60, 115] were in industrial electrolytes that undoubtedly contained Cl\(^-\). Furthermore, Conrad et al. [24] discussed how the electrolyte
Figure 4.6 CPs for Synthetic Electrolyte and the Synthetic electrolyte with Cl⁻ using the Channel Microelectrode: (a) Initial Polarization (b) Extended Polarization
needed to have the decomposition products to produce quality Cu deposits. Since sporadic polarization was found from reported test and for some test in this work, a systematic look at where chloride could possibly enter the system was undertaken. Possible sources of chloride are given in Table 4.1. After brief examination of the reagent grade chemicals, it was conjectured that the majority of chloride contamination was from the glue.

Table 4.1 Estimated Chloride Content of Components

<table>
<thead>
<tr>
<th>Component</th>
<th>$[\text{Cl}]$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$·5H$_2$O</td>
<td>5-6</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Galactasol</td>
<td>3</td>
</tr>
<tr>
<td>Glue</td>
<td>100-1500</td>
</tr>
</tbody>
</table>

Accelerated hydrolysis and decomposition tests were performed to evaluate any chloride contamination and any effect of the glue decomposition products on the polarization of Cu plating from these electrolytes. A recycled electrolyte was prepared by heating the electrolyte which contained the glue for extended periods of time at elevated temperature, see section experimental procedure. Figure 4.7 shows that the recycled electrolyte CP is very similar to the base electrolyte CP. However, the recycled electrolyte did show significant differences in subsequent CP experiments with additional glue. The degree of polarization caused by the addition of glue was sporadic for the recycled electrolyte. It was found that only the glue originally used produced unusual
Figure 4.7 CPs for the synthetic electrolyte showing Cl⁻ contamination from previous additions of glue. The experimental conditions are 65°C, 1.63 M H₂SO₄, 0.63 M CuSO₄ and 1,275 Am⁻². The WE was Pt RDE while the CE was a Cu Rod. Recycled electrolyte prepared by heating electrolyte with glue for 2 hrs. at ~90°C.
polarization effects when put through the thermal recycling process, Figure 4.8. Upon testing a different glue (original company stopped selling the first type), no such variation in the polarization occurred. Through comparison with the industrial and the synthetic electrolyte, it was found that chloride must be present to achieve any appreciable polarization. This was deduced by adding the elements from Table 2.3 until a similar increase in polarization occurred. Chloride with glue was the only combination of elements that are known to be in the industrial electrolyte to yield a similar increase. Therefore, it was concluded that the original glue samples contained various amounts of chloride from the rendering process.

4.1.1.2 Flow injection analysis of chloride solutions

Pretreatment of the Pt working electrode is crucial for obtaining consistent electrochemical data. The problem of surface contamination between experiments could possible contribute to the fluctuations seen during the chloride contamination analysis. To provide insight into the effect surface contamination or handling damage of the WE had on the results, several flow cell tests were conducted. The flow cell was constructed so the feed solution could be altered during a chronopotentiometric test, thus changes would only be from the differences in the electrolyte. In Figure 4.9, the first 2 minutes shows the polarization of the WE by 10 ppm glue. At 2 minutes the feed for the cell was switched to an electrolyte which also contained 40 ppm chloride with the glue. The hydrolysis times for the glue in the electrolyte without and with Cl\textsuperscript{-} were identical, 15
Figure 4.8 CPs for the synthetic electrolyte showing Cl⁻ contamination from previous additions of glue. The experimental conditions are 65°C, 1.63 M H₂SO₄, 0.63 M CuSO₄ and 1,275 Am². The WE was Pt RDE while the CE was a Cu Rod. Recycled electrolyte prepared by heating electrolyte with glue for 2 hrs. at ~90°C. The a, b, c and blank are separate experiments.
Figure 4.9 CP for the synthetic electrolyte showing electrolyte without 40 ppm Cl\textsuperscript{-} before 2 minutes and with 40 ppm Cl\textsuperscript{-} after 2 minutes. Experimental were 1.63 M H\textsubscript{2}SO\textsubscript{4}, 0.63 M CuSO\textsubscript{4} and 1,275 Am\textsuperscript{-2}. The WE was Pt while the CE was a Cu plate.
minutes at start of the test. With this method, no decomposition products or anything from the EC reactions at the cathode or anode were allowed back into the electrolyte. Therefore, only the chloride content is responsible for the polarization increase seen in Figure 4.9 after 2 minutes. The spike in the potential at 2 minutes was from an air bubble passing through the cell. The 30 mV potential shift was smaller than what was previously reported in this work. The small potential shift was most likely from the shearing forces the cathode was exposed to by the solution flow. The cell was designed to impinge the electrolyte directly onto the Pt WE as seen in Figure 3.3.

4.1.2 Industrial Electrolytes

Table 2.3 is the weekly chemical analysis of the industrial electrolyte used in this portion of the research. This is not a complete analysis of all the elements in the electrolyte. Instead this is a combination of the most abundant and some select elements that have been reported as creating problems in the refining process. The industrial electrolyte was preconditioned as described in 3.8 to remove any effect of glue left in the electrolyte from the refinery. The thermal decomposition of the electrolyte was found to be sufficient to destroy the glue. Andersen et al proposed this method [99] and was confirmed here to work except for the few complications discussed in section 4.1.1.1 when the Cl' content of the electrolyte was low.

The electrolyte from a local refinery was tested within 2 hours of taking the sample from the cell house. The industrial electrolyte, prior to the thermal pretreatment,
exhibited polarization that was not found in the synthetic electrolyte. That is to say, the as received electrolyte still had active glue. Even after 2 weeks at a 50°C holding temperature, there was still polarization as shown in Figure 4.10. After treating the electrolyte by heating to 90°C for more than 2 hours, no residual polarization was seen as shown in Figure 4.11. To confirm that the effect of glue can be removed by heating the electrolyte, an aliquot of glue was placed in the industrial electrolyte. After a CP was obtained for the solution, which showed polarization from the glue, the electrolyte was thermally treated and the original baseline was reestablished.

The set of CPs for the industrial electrolyte with 0, 1 and 10 ppm glue with 15 minutes hydrolysis is shown in Figure 4.12. Calibration plots were developed from the slope of the CP. It was determined that the total amount of polarization from the glue in these tests was fairly consistent for any glue concentration if the tests were allowed to run long enough. The rate of polarization was found to be dependent on the glue concentration and plots of ΔV verses glue concentration were constructed. For glue concentrations between 0 and 10, the best correlation was found with Δt to be between t=0.1 and 1.0. Other Δt values where test but had lower correlation coefficients. The calibration plot with Δt set between t=0.1 and 1.0 verses glue concentration is shown in Figure 4.13 with a correlation coefficient greater than 0.94.
Figure 4.10 CPs for the industrial electrolyte after 2 weeks storage at 50°C. Experimental conditions were stationary Pt WE and 300 Am⁻².

Figure 4.11 CPs for the industrial electrolyte after 2 hours at ~90°C. Experimental conditions were Pt RDE at 300 rpm and 300 Am⁻². Also shown is the synthetic electrolyte with 40 ppm Cl⁻ with same conditions.
Figure 4.12 CP for the Industrial Electrolyte with 0, 1, and 10 ppm Glue. Experimental conditions 1.63 M H₂SO₄, 0.63 CuSO₄, 65°C. The WE was Pt RDE at 300 rpm with a Cu rod for the CE.

Figure 4.13 - Calibration plot for the potential shift between t=0.1 and 1 minutes vs. glue concentration for the industrial electrolyte previously subjected to the thermal pretreatment.
4.2 Thiourea Results

The majority of the previous work concerning additives has been limited to changing the levels of Cl\(^-\), glue or thiourea one at a time. Several researchers have shown the influence of two additives but very little has been done with all three [83, 85, 98, 161, 162]. In this work, several set concentrations were used to explore the interactions of glue, Cl\(^-\) and thiourea. Thiourea addition to the synthetic electrolyte caused a slight inhibition followed by a slow depolarization, Figure 4.14 a and b. Wang and O'Keefe also reported the initial increase in polarization by thiourea at concentrations between 5 and 10 ppm [98]. Sun and O'Keefe implied that thiourea promotes instantaneous nucleation on stainless steel [83]. The switch from 3 D nucleation to instantaneous nucleation should result in an increase in polarization as was found here on a Pt surface.

Chloride with thiourea was also examined. Figures 4.15 a and b are CPs showing the initial and extended polarization from the different combinations of Cl\(^-\) with thiourea and just Cl\(^-\). Chloride at 40 ppm was found to slowly increase the polarization compared to the electrolyte without, as shown in Figure 4.15. For times greater than 2 minutes, the general fluctuations tended to obscure the results between the base line synthetic electrolyte and the synthetic electrolyte with 40 ppm Cl\(^-\) as seen Figure 4.15 b. The initial polarization and subsequent depolarization seen for thiourea in Figure 4.14 a and b, were also present when thiourea and Cl\(^-\) where combined. The depolarization was noticeably more pronounced with Cl\(^-\) as seen by comparing Figure 4.14 a with 4.15 b. The initial ~5 mV polarization for copper deposition from thiourea alone increased to nearly 20 mV with both thiourea and Cl\(^-\) in the electrolyte. For times greater than 1 minute, the thiourea with 40 ppm Cl\(^-\) showed a continuous depolarization.
Figure 4.14 CPs for Synthetic Electrolyte with Thiourea using a Channel Microelectrode: (a) Initial Polarization (b) Extended Polarization
Figure 4.15 CPs for Synthetic Electrolyte with Cl\(^-\) and TU using the Channel Microelectrode: (a) Initial Polarization (b) Extended Polarization
4.3 Combined Polarization of Glue, Cl\(^-\), and Thiourea

As previously shown in Figure 4.1, glue in the synthetic electrolyte had a minimal effect on the polarization. This small polarization is shown again in Figure 4.16, where the results for the 10 ppm glue are not significantly different from the blank. However, with the addition of 40 ppm Cl\(^-\), a substantial polarization immediately occurs for the first minute of copper deposition. The resulting polarization of over 100 mV with the simple adsorption blocking model would suggest that the majority of the surface is covered or inactive. The use of all three additives in the synthetic electrolyte is also shown in Figure 4.16. The addition of TU with glue and Cl\(^-\) initially increases the polarization within the first few seconds followed by a region of slight depolarization. After about 30 seconds, polarization increases noticeably for about 3 minutes. The potential after about 3.5 minutes levels out at approximately -610 mV and remains relatively constant for the remainder of the experiment. An additional 80 mV of polarization resulted from the presence of thiourea in the synthetic electrolyte over that for the electrolyte, which only contained Cl\(^-\) and glue. The slope in the initial region of polarization (i.e. ~1 minute) was found to be sensitive to the presence of thiourea and glue as shown in Figure 4.17. Figure 4.17 has two lines that were used to estimate the slope of the rapidly increasing regions of the CPs for the electrolyte, which only differ in the thiourea content. The slope for the CP without thiourea was -105 mV/min while for the electrolyte with 5 ppm thiourea was -116 mV/min. The sensitivity of the slope and the delay of the rapidly increasing region
Figure 4.16 CPs for Synthetic Electrolyte with Glue, Cl\textsuperscript{-} and Thiourea using the Microelectrode

Figure 4.17 CPs for Synthetic Electrolyte with Glue, Cl\textsuperscript{-} and Thiourea showing slope of rapidly increasing polarization region.
when thiourea was present would suggest that the CollaMat method might need modifying depending on the levels of thiourea in the electrolyte.

As with any EC study, the results are extremely dependent on having a reproducible electrode. Total reproducibility was difficult in this work. The combined effect of TU, Cl\(^-\) and glue were examined with two different microelectrodes that were prepared slightly different. One Pt wire WE was mounted in epoxy and the second was mounted in a glass tube which produced a flatter surface. The first method was prone to small fluctuations in the mounting of the Pt wire (swelling of the epoxy from extended exposure to the electrolyte) in which the wire was sometimes recessed a small amount into the surface. This effect was found to enhance the sensitivity of the electrode to low concentrations of the additives. Figure 4.18 is similar to Figure 4.19 except the surface of the electrode was flush with the retaining walls. Upon comparing the graphs it can be seen that the trends are similar but there are key differences. For instance, the baseline for the electrolyte plus Cl\(^-\) is much flatter. The onset of the rapidly increasing portions of the CP is also delayed for the glue with Cl\(^-\) and the glue, TU and Cl\(^-\) chronopotentiograms.

4.4 Nickel vs. total sulfate polarization effects

Previous studies have indicated that Ni\(^{2+}\) will polarize the system [99]. However, the sulfate concentration was also increased when the nickel was added as a sulfate. To minimize the effect of [SO\(_4^{2-}\)] the total sulfate concentration ([SO\(_4^{2-}\)]\(_{\text{total}}\)) was fixed at 2.5
Figure 4.18 - CPs for Synthetic Electrolyte with Glue, and Cl\textsuperscript{-} for a Pt Electrode Mounted in Epoxide. Surface of Pt Recessed from swelling.

Figure 4.19 - CPs for Synthetic Electrolyte with Glue, and Cl\textsuperscript{-} for a Pt Electrode Mounted in Pyrex. Surface of Pt flush with side walls.
M. The $[\text{SO}_4^{2-}]_{\text{total}}$ was adjusted using Na$_2$SO$_4$. Figure 4.20 is the graph for the base electrolyte and the SO$_4^{2-}$ adjusted baseline with and without Ni$^{2+}$. The CP without Ni$^{2+}$ at 2.5 M $[\text{SO}_4^{2-}]_{\text{total}}$ displayed the same type trends as previously found with the Pt RDE in Figure 4.3. Initially there is a slight depolarization and then a fairly constant potential is maintained, $\sim$372 mV vs. MSE.

Comparisons were made with the electrolyte containing 40 ppm Cl$^{-}$ at the higher sulfate level and are shown in Figure 4.21. With the $[\text{SO}_4^{2-}]_{\text{total}}$ at 2.5 M, the amount of polarization increased from only a 1 or 2 mV for the lower SO$_4^{2-}$ to a fairly consistent 5 mV, see Figure 4.21. The effect of thiourea and glue with 40 ppm Cl$^{-}$ were also tested and are shown in Figure 4.22 and Figure 4.23 with 5 g/l Ni$^{2+}$. The high sulfate electrolyte with thiourea and 40 ppm Cl$^{-}$ depolarized the system until it was nearly identical to the base electrolyte, as shown in Figure 4.22 and 4.23. The combined polarization of glue with thiourea, Cl$^{-}$ and glue indicates Ni$^{2+}$ had a minimal effect on the polarization of copper deposition as deduced by comparing Figures 4.22 and 4.23.
Figure 4.20 Chronopotentiograms for the Cathodic step with a Pt RDE in Synthetic Electrolyte. Experimental conditions: 40 g/l Cu\(^{2+}\), 160 g/l H\(_2\)SO\(_4\), 65°C, 2.5 M [SO\(_4\)]\(_{total}\), 300 rpm and 300 Am\(^{-2}\).

Figure 4.21 Chronopotentiograms for the Cathodic step with a Pt RDE in Synthetic Electrolyte. Experimental conditions: 40 g/l Cu\(^{2+}\), 160 g/l H\(_2\)SO\(_4\), 65°C, 2.5 M [SO\(_4\)]\(_{total}\), 300 rpm and 300 Am\(^{-2}\).
Figure 4.22 Chronopotentiograms for the Cathodic step with a Pt RDE in Synthetic Electrolyte. Experimental conditions: 40 g/l Cu$^{2+}$, 160 g/l H$_2$SO$_4$, 65°C, 2.5 M [SO$_4$]$^{2-}$, 0 g/l Ni$^{2+}$, 300 rpm, and 300 Am$^{-2}$.

Figure 4.23 Chronopotentiograms for the Cathodic step with a Pt RDE in Synthetic Electrolyte. Experimental conditions: 40 g/l Cu$^{2+}$, 160 g/l H$_2$SO$_4$, 65°C, 2.5 M [SO$_4$]$^{2-}$, 5 g/l Ni$^{2+}$, 300 rpm, and 300 Am$^{-2}$.
4.5 Stripping Analysis

As discussed previously, the initial polarization results were not sufficient for monitoring levels of glue found in ER/EW facilities. This conclusion was originally postulated based on data collected without Cl⁻ in the electrolytes. Less than 10 mV of overpotential resulted from the addition of 10 ppm, and normal operating levels for ER/EW are less than 3 ppm, which implies less than 1 mV/ppm glue for the signal. Instrumental noise was generally in the 1-5 mV range and would interfere with the measurement. However, there was additional information collected that presented the possibility to monitor the levels of glue in a different manner.

The current reversal was originally executed to prepare the WE for the next experimental run. From examining the CP with both the cathodic and anodic portion, it was ascertained that the time to remove the copper was not constant. The stripping time was determined by the rapid increase in the potential associated with the onset of oxygen evolution. The time (or quantity of Cu deposited) was found to be related to the glue levels in the electrolyte.

4.5.1 Synthetic Electrolytes

In order to increase productivity, the computer controlled galvanostat was set up to automatically strip the plated copper after each chronopotentiometric experiment. It was noted that there was a trend in the length of time it took to strip the copper and the
quantity of glue in the electrolyte during the plating. As shown previously, Figure 4.2 is the complete chronopotentiogram with the current reversal to remove the plated copper. The first sharp rise in Figure 4.2 is from simply switching from plating at 300 Am\(^{-2}\) to stripping at \(-6.12 \times 10^{-7}\) Am\(^{-2}\). The second sharp rise occurs when all the copper has been removed and the galvanostat increases the potential until another reaction occurs such as oxygen evolution in this case. The rapid rise in potential was sometimes interrupted with a small plateau or ledge before the surface was completely free of metallic copper or other substance that would oxidize in this potential region. The onset of the oxygen evolution tended to be variable as part of the electrode became devoid of copper, which caused current density to increase in the remaining Cu plated regions. The increase current density brings upon a shift in the potential to higher values. This shift is the ledge or plateau for different experiments and is shown in Figure 4.24. Therefore, the time to anodically remove all the copper was taken as the time at which the potential reaches 0.375 V vs. MSE and is called the stripping time throughout this work.

4.5.1.1 Decrease in stripping time with increasing levels of glue

Figure 4.25 shows CPs for the synthetic electrolyte where the time it took for the Cu to be stripped from the surface was found to be inversely proportional to the glue concentration. A plot of the time it took the voltage to reach 375 mV vs. glue concentration is shown in Figure 4.26. A correlation coefficient of 0.87 for a curve fitted to 2nd order polynomial was obtained for the bench top test with synthetic electrolyte
Figure 4.24 CPs for the Synthetic Electrolyte with 10 ppm glue showing inconsistent onset of oxygen evolution. Scan 1 and Scan 2 were conducted under similar conditions.
Figure 4.25 Extended CPs for Synthetic Electrolyte with 0, 1 and 10 ppm.

Figure 4.26 Calibration Plot; Time to 375 mV vs. Glue Concentrations for the Synthetic Electrolyte
without Cl\(^-\). The good correlation between stripping time and glue concentration inspired further research with other electrolytes. The possibility of improvement through optimization of the experimental procedure further encouraged research with industrial electrolytes and will be presented in 4.5.2.

4.5.1.2 Increase in stripping time with glue after the addition of thiourea

The use of a single additive such as glue is generally not done in ER/EW or any other electroplating process. Figures 2.5, 2.13, and 2.14 indicate that the majority of ER operations use TU and Cl\(^-\) in conjunction with glue. TU was found to shift the stripping times to larger values, Figure 4.27. Logically, this would be expected from a quality standpoint. If the time to strip the Cu from the WE decreases, the deposit has less copper to remove during the anodic step. From inspection of the WE and electrolyte, it was concluded that glue alone did not produce quality deposits. Not only was the Cu coverage on the WE sporadic and dull, but there were also small amounts of solid Cu left in the electrolyte at the end of the test. This indicates some of the metallic Cu fell off either during the anodic or cathodic portion and would again decrease the time to strip.

4.5.2 Industrial Electrolytes

A set of CPs for the industrial electrolyte illustrating the stripping time for several levels of glue is shown in Figure 4.28. The time shift behavior for the industrial electrolyte is not as well behaved. Plotting the time shift vs. glue concentration for the electrolyte is shown in Figure 4.29. The time shift is now directly related to the
Figure 4.27 Anodic portion of the CPs for Synthetic Electrolyte with Glue, Cl⁻ and TU using the microelectrode.
Figure 4.28 Extended CPs for the Industrial Electrolyte with 0, 1, and 10 ppm Glue.

Figure 4.29 Calibration Plot; Time to 375 mV vs. Glue Concentration for the Industrial Electrolyte

\[ y = -0.0007x^2 + 0.0248x + 15.049 \]

\[ R^2 = 0.378 \]
concentration of glue in the electrolyte, whereas for the synthetic electrolyte it was inversely related, Figures 4.26. Upon further experimentation with the synthetic electrolyte, it was found that Cl\(^-\) and TU had a tremendous effect on the deposition of Cu, see 4.2. It can be concluded from the small slope shown in Figure 4.29 that the addition of other elements can influence the time to strip and therefore this method to monitor glue is insufficient.

4.6 Glue Adsorption

The adsorption of glue onto copper was explored using Tapping Mode AFM. With Tapping Mode AFM, the tip-sample interactions are minimized and it was predicted the interaction would not dislodge all of the proposed adsorbed glue. The adsorption of glue without any charge being passed (i.e. no copper deposition) was examined for several aqueous solutions. The only difference in the aqueous solutions studied was the Cl\(^-\) concentration; solution A was nearly free of chloride (< 1 ppm) and solution B contained 40 ppm Cl\(^-\). Both solutions contained 0.1 M H\(_2\)SO\(_4\) and 10 ppm glue.

The substrate used for the adsorption test were Cu plated Si (Si). Several test were conducted on the electron beam deposited Cu while the others used were electrochemically plated samples from SemiTool. The initial seed layer required for plating Si wafers was accomplished using a sputtering technique. The Cu deposits on the Si samples were smoother with a surface roughness of 10-15 nm RMS. Alternatively, Cu substrates were obtained that were plated using electron beam sputtering. The electron beam deposited samples were significantly smoother with an RMS of 5 nm. However,
the electron beam coated samples had excess surface contamination that could not be removed without the plated Cu flaking off the Si substrate. Results where similar for the electron beam and electrodeposited Cu, albeit larger features for the electrodeposited samples, with better reproducibility for the SemiTool samples. The surface oxide on the Cu was removed by rinsing with a 1.0 M H₂SO₄ prior to placing approximately 250 μl of solution A or B onto the surface. The lower acid content of A and B was to minimize the etching of the Cu which would roughen the Cu surface. Some surface roughening was found but the nodular surface features were still prevalent as shown for the blank in Figure 4.30. The image shown in Figure 4.30 was of the Cu surface after rinsing with the acid.

It is postulated that the glue in the Cu electrolytes does not effectively adsorb onto the surface unless the surface has Cl⁻ also adsorbed on it. To test this, Cu substrates were exposed to solution A and B and then examined with the AFM for glue adsorption. Figure 4.31 is an AFM image of the same Cu covered Si substrate that has been exposed to solution A. The image is very similar to the blank, Figure 4.30. Figure 4.32 is the AFM image of the surface of the sample exposed to solution B. There is now a distinct difference with spots of something adsorbed onto the surface. They were approximately 50 to 125 nm across and 18 to 50 nm high. Initially the surface objects appear to be similar to details seen in Figure 4.31: such as the nodular texture of the electrochemically deposited Cu. However, at higher magnification it became evident that the surface is distinctly different for the sample exposed to solution A and solution B. The blank and
the sample exposed to solution A are similar as shown in Figure 4.33 and 4.34, respectively. Again the Cu substrate exposed to solution A and B showed a marked difference with large globular objects on the surface of the Cu surface exposed to the solution containing both glue and Cl⁻. As seen from the poor quality of the image shown in Figure 4.35, it was difficult to obtain an image for the samples that were used with solution A. The difficulty is from the nature of the objects adsorbed on the surface. They tend to deform and apparently foul the tip of the probe that produced low quality images at higher magnification. Figure 4.34 and Figure 4.35 used the same probe tip and Figure 4.34 was imaged first. This precludes the features in Figure 4.35 being artifacts from debris on the tip. The adsorbed objects seen in Figure 4.35 where even more distinctive from the sample dipped in solution B with a scan size of 250 nm by 250 nm, Figure 4.36. The fraction of the surface covered with glue was inconsistent for the samples. The difference of whether the glue settled on the surface verses truly adsorbing was difficult to distinguish. If the sample was prepare by placing a drop on the surface and after about a minute tipping the sample to allow the liquid to flow off, then both A and B solutions left glue on the surface. However, when the samples were gently rinsed with DI H₂O, only samples exposed to solution B showed any appreciable adsorption of glue.
Figure 4.30 Tapping Mode AFM image of Cu surface after cleaning with 1.0 M H$_2$SO$_4$.

Figure 4.31 Tapping Mode AFM image of Cu surface after cleaning with 1.0 M H$_2$SO$_4$ and putting 250 ml of Solution A on the surface for 60 seconds. Surface was gently rinsed with DI H$_2$O.
Figure 4.32 Tapping Mode AFM image of Cu surface after cleaning with 1.0 M H₂SO₄ and putting 250 ml of Solution B on the surface for 60 seconds. Surface was gently rinsed with DI H₂O.
Figure 4.33 Tapping Mode AFM image of Cu surface after cleaning with 1.0 M H₂SO₄.

Figure 4.34 Tapping Mode AFM image of Cu surface after cleaning with 1.0 M H₂SO₄ and putting 250 ml of Solution A on the surface for 60 seconds. Surface was gently rinsed with DI H₂O.
Figure 4.35 Tapping Mode AFM image of Cu surface after cleaning with 1.0 M H₂SO₄ and putting 250 ml of Solution B on the surface for 60 seconds. Surface was gently rinsed with DI H₂O.

Figure 4.36 Tapping Mode AFM image of Cu surface after cleaning with 1.0 M H₂SO₄ and putting 250 ml of Solution A on the surface for 60 seconds. Surface was gently rinsed with DI H₂O.
4.7 Guar Results

The detection of guar in copper plating solutions was difficult. The original hypothesis that sufficient polarization occurs with the addition of guar to Cu electrolyte was tested by preparing a portable monitoring system using the method proposed by Blechta [60,115]. A simple galvanostat controlled via a PC was built and tested. Because of the unusual preliminary test results with glue in the electrolyte, a set of experiments were performed with purchased potentiostat/galvanostat. These results were expanded and discussed in sections 4.1 to 4.6. The experiments to determine the levels of guar were more complex and difficult and will be discussed in this section.

4.7.1 DC Techniques

Multiple techniques were used to find an efficient analytical tool that can be put directly into ER/EW facilities to monitor additive levels. The CP technique compared both the polarization and stripping times vs. guar and proved to be futile. The cathodic portion of the CP with 5 ppm guar is shown in Figure 4.37. Only a relatively small potential shift of 10 mV was observed with the addition of guar. The dashed line in Figure 4.37 is the baseline for the same industrial electrolyte used in previous sections. The tests were performed with the industrial electrolyte described in Table 2.3, with an RDE at 300 rpm. The electrolyte was preconditioned as described previously for the glue
and TU experiments in the experimental section and 4.2. Other rotation speeds up to 1,000 rpm and lower current densities were tested with similar results.

The 10 mV cathodic potential shift upon the addition of 5 ppm guar to the industrial electrolyte would be insufficient to monitor guar levels in the harsh environment of commercial EW facility. Even with high quality potentiostat, the 10 mV potential shift was insufficient compared to the noise levels experienced during this research. The time to strip method described for glue in section 4.5 was explored as an analytical tool. No significant difference was detected using several electrolyte combinations. For example, the lack of time shift for the industrial electrolyte is shown in Figure 4.38.

Cyclic voltammetry was also used to evaluate levels of guar in the synthetic electrolyte. The cyclic voltammograms for the synthetic electrolyte is shown in Figure 4.39. There were several features of interest in these voltammograms, which are labeled peak #1, #2 and #3 in Figure 4.39. To explore these features, the scan range in the copper cathodic region was lowered. The main feature that needed to be determined was the peak labeled #1 at 62 mV vs. MSE. This peak was apparent in some scans and not others. It was determined (see Section 4.7.3) to only appear when the WE was anodically pretreated above about 950 mV vs. MSE or when the anodic turning/starting point of the sweep was greater than the approximately 1000 mV in an electrolyte containing H₂SO₄. Figure 4.39 displays that the peak was repeated on successive sweeps with the anodic turning point at 1200 mV. Upon further examination, the peak at 62 mV that was present
Figure 4.37 CPs for the industrial electrolyte with no guar and with 5 ppm guar at 65°C after 25 minutes and a Pt RDE with a rotation speed of 300 rpm.

Figure 4.38 CPs for the industrial electrolyte with no guar and with 5 ppm guar at 65°C after 25 minutes and a Pt RDE with a rotation speed of 300 rpm.
Figure 4.39 DC cyclic voltammograms for 0.63 M CuSO₄ and 1.63 M H₂SO₄. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the synthetic electrolyte.
had nothing to do with the guar or copper in solution. Impurities or reduction of platinum oxide or hydride are possible and will be reviewed further in section 5.3.

4.7.2 AC Voltammetry Results

Fundamental AC voltammetry was used to evaluate the levels of guar in the synthetic electrolyte. The fundamental harmonic was initially tested in an attempt to minimize the complexity of the analysis and equipment. The voltammograms for the synthetic electrolyte with and without guar using typical conditions are shown in Figure 4.40 and 4.41. Notice in Figure 4.41 that there was no significant difference in the voltammogram upon the addition of guar.

According to several publications [131, 138, 140, 163, 164], 2nd Harmonic (typically denoted as 2F) AC voltammetry combined with phase sensitive detection would provide information on non Faradaic processes such as adsorption of organics on the surface of electrodes. Figure 4.42a is the 2F AC voltammogram for the 160 g/l H$_2$SO$_4$, 40 g/l CuSO$_4$ and 40 ppm Cl$^-$ synthetic electrolyte used in most of this study. Figure 4.42b has 5 ppm guar added to the electrolyte. The addition of guar to the synthetic electrolyte was found to depress several peaks in the voltammogram, such as the peak labeled in Figure 4.42a and b. Therefore, a series of tests were conducted to clarify which peaks are responsive to the levels of guar and to optimize the detection process.

The first parameter adjusted was the frequency of the AC signal. The sweep rate for the triangular wave was set at 20 mV/sec, while the AC amplitude was fixed at 25 mV
Figure 4.40 Fundamental AC Voltammograms for Synthetic Electrolyte with 40 ppm Cl\textsuperscript{-}, at 65°C without Galactosol was added to the electrolyte 40 minutes prior to start of the experiment. The AC amplitude was 70 mV RMS @ 10 KHz.

Figure 4.41 Fundamental AC Voltammograms for Synthetic Electrolyte with 40 ppm Cl\textsuperscript{-}, at 65°C with 5 ppm Galactosol. The Galactosol was added to the electrolyte 40 minutes prior to start of the experiment. The AC amplitude was 70 mV RMS @ 10 KHz.
Figure 4.42 2nd Harmonic AC voltammograms for 0.63 M CuSO₄ and 1.63 M H₂SO₄ with 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
RMS. The range of the triangular DC wave was from 0.75 mV anodic to -0.5 mV cathodic. This was established to maximize the AC current for the fine structure of the voltammograms and still maintain a large sweep range without over ranging the potentiostat, lock in amp, or data acquisition card. Excessive preconditioning was used to insure reasonable stability. The preconditioning cycle was a 5-minute stirring cycle with a 3-blade impeller set at approximately 200 rpm. A 2-minute rest followed immediately with the cell left at open circuit. An anodic cleaning at 1.15 mV DC (anodic) with the AC signal superimposed was applied for 1 minute. At the end of the one minute anodic cleaning of the Pt surface, the experiment begins with the DC signal immediately stepping to the starting point for the triangular wave front, 0.75 mV vs. MSE. The AC portion of the signal was generally superimposed during the anodic cleaning portion of the experiment. Data collection usually started during the rest period but sometimes started during the stirring cycle to monitor the open circuit potential.

Frequencies from 50 Hz to 15 KHz were tested are shown in Figures 4.43a and b for the 2F current response at a 60° phase shift while the quadrature component (150°) is displayed in Figures 4.44a and b. The peaks in the AC voltammogram were all assigned according to their occurrence from the start of the experiment. They were further broken down into two groups, based on their current phase relationship, 60° or 150°. There were 31 peaks originally assigned and labeled in the 2F AC voltammograms and are shown Figures 4.45a and 4.45b. The peaks that showed promise for a quantitative signal for guar from the 60° current component were 11, 12, 13, 14, and 15. The peaks found to the
Figure 4.43a 2nd Harmonic AC voltammograms for 60° current component in 0.63 M CuSO₄ and 1.63 M H₂SO₄ with 40 ppm Cl⁻. Experimental conditions were 65°C, 25 mV/sec, Pt WE, Cu CE and a MSE reference in a Luggin Probe filled with the synthetic electrolyte.
Figure 4.43b 2\textsuperscript{nd} Harmonic AC voltammograms for 60\degree current component in 0.63 M CuSO\textsubscript{4} and 1.63 M H\textsubscript{2}SO\textsubscript{4} with 40 ppm Cl\textsuperscript{-}. Experimental conditions were 65\degree C, 25 mV/sec, Pt WE, Cu CE and a MSE reference in a Luggin Probe filled with the synthetic electrolyte.
Figure 4.44a 2nd Harmonic AC voltammograms for 150° current component in 0.63 M CuSO₄ and 1.63 M H₂SO₄ with 40 ppm Cl⁻. Experimental conditions were 65°C, 25 mV/sec, Pt WE, Cu CE and a MSE reference in a Luggin Probe filled with the synthetic electrolyte.
Figure 4.44b 2nd Harmonic AC voltammograms for 150° current component in 0.63 M CuSO₄ and 1.63 M H₂SO₄ with 40 ppm Cl⁻. Experimental conditions were 65°C, 25 mV/sec, Pt WE, Cu CE and a MSE reference in a Luggin Probe filled with the synthetic electrolyte.
Figure 4.45 2nd Harmonic AC voltammograms for 0.63 M CuSO$_4$ and 1.63 M H$_2$SO$_4$. Experimental conditions were 65°C, 20 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte. The AC signal was 25 mV RMS at 500 Hz.
sensitive to guar for the 150° current component were 11, 12, 13, and 14. These peaks were compared and peaks 15 and 16 from the 60° component and 13 and 14 form the 150° component were chosen for their large responses, Figure 4.46. The position and number of peaks were found to change as the frequency changed and sometimes the peaks became intermixed. Table 4.2 summarizes the frequencies and the two peaks with the most response from each test.

The magnitudes of several peaks sensitive to levels of guar were larger at higher frequencies. However, upon comparing the difference in the magnitude of the response for the added guar as shown in Figure 4.45a and b, it became evident that the highest frequencies were not the best choice for the detection of guar. The most sensitive 4 peaks were selected from 50 to 15,000 Hz and are listed in Table 4.2. The peaks in Table 4.2 refer to the peaks labeled in Figure 4.45a and b. Note as the frequency increases the peaks change significantly in the voltammograms. For example, some peaks diminished while others increase. Figure 4.46 shows the most prospective peaks based on the initial scans that were 4.43a through 4.44b. Two sets of peaks became the most logical choices out of four prospective sets of peaks for monitoring guar levels and are shown in Figure 4.46. The largest peak difference between the electrolyte without guar and with guar is from the 150° current component that occurred at approximately 197 mV vs. MSE for the applied triangular wave.
Figure 4.46 Total current changed for each frequency from the addition of 5 ppm guar after 20 minutes in solution. The electrolyte was 160 g/l H₂SO₄, 40 g/l Cu^{2+} and 40 ppm Cl⁻ at 65°C.
The largest peak difference for the 60° current component occurred at 225 mV vs. MSE for the applied triangular wave. Henceforth, when referring to the position of the peak it will be the voltage of the DC triangular wave for the AC voltammograms. This would be equivalent to the voltage applied for the typical DC cyclic voltammetry. The superimposed AC excitation voltage does not control where the peak occurs but influences the peak height and width, at a constant frequency.

The sweeping nature of the triangular wave can be plotted in a more traditional manner where the ordinate is simply the triangular wave voltage. Similar to CV, the potential sweeps back across the graph without introducing two zero points on the abscissa as previously shown in Figures 4.41 through 4.45. Such plots for the 60° and 150° current component are shown in Figures 4.47a and b, respectively. However, the

<table>
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<th>Frequency Hz</th>
<th>60° Current Component Peak Number Figure 4.45a</th>
<th>150° Current Component Peak Number Figure 4.45b</th>
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<td>12,13</td>
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<tr>
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Figure 4.47 2\textsuperscript{nd} Harmonic AC voltammograms for 0.63 M CuSO\textsubscript{4} and 1.63 M H\textsubscript{2}SO\textsubscript{4}. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte. The AC signal was 70 mV RMS at 10 KHz. (a) is the 60° current component while (b) is the 150° current component.
more unconditional manner will be kept to help clarify what are the cathodic and anodic peaks and to eliminate overlap. The problem with distinguishing the cathodic from the anodic portions for the copper AC voltammograms is that the sign of the peak does not denote the direction of current flow. The sign of the current for the peaks in the AC voltammograms denotes whether it is in phase with the lock in circuitry. The inability of the sign on the current to distinguish the anodic and cathodic portion for DC signal can be seen by examining Figure 4.47 where the peaks between -250 and -500 mV vs. MSE are both positive. The peaks associated with Cu deposition and stripping are labeled for the 60° and 150° current component in Figure 4.47a and b. In fact, by definition both anodic and cathodic current must flow to have an AC current.

The next parameter examined was the amplitude of the AC voltage added to the triangular waveform. The peak current difference between the electrolyte with guar and without guar continued to increase overall the AC amplitudes (RMS) tested. Although the signal increased, the scatter in the data became more pronounced. Figure 4.48 is the plot of the magnitude of the quantitative signal as the AC amplitude increases for three different sets of data for the 60° and 150° components combined. As mentioned previously, the scatter becomes more problematic above approximately 80 mV RMS.

A simple way of analyzing the data would be to plot the AC amplitude vs. the standard deviation. For the limited data set, there was a distinctive trend when the standard deviation was minimized. Figure 4.49 is the plot of the standard deviation vs. AC amplitude fitted to a second order polynomial. A minimum deviation was obtained
Figure 4.48 Total peak depression for both the 60° and 150° current components selected for monitoring guar in the synthetic electrolyte.

Figure 4.49 The minimum standard deviation for the total depression from both the 60° and 150° current peaks at different AC amplitudes.

\[
y = 0.0004x^2 - 0.0577x + 7.9328 \\
R^2 = 0.8378 \\
\text{minimum} = 72.1 \text{ mV}
\]
from the second derivative of the equation for the fitted line, Figure 4.49 at 72.1 mV RMS. A value of 70 mV ± 0.1 mV RMS was established as the AC perturbation signal for the remainder of the test.

The effect of sweep rate on the quantitative analysis of guar was minimal. The standard deviation for the peak height was fairly constant from 1 mV/sec to 100 mV/sec, Figure 4.50. The standard deviation for the sample set was between 20-30 Am⁻². The standard deviation is still relatively high and further work on reproducibility is needed and will be discussed in Chapter 5.

4.7.2.1 2F AC Voltammetry Peak Selection

The selection of the peak was done based on the previously described procedure for the synthetic electrolyte. Based on these results, the peak labeled #1 in Figure 4.42 was used for the signal to monitor guar. Based on the previous discussion, the experimental conditions were 70 mV RMS for the AC amplitude, 25 mV/sec for the sweep rate and a scan range of 750 to -500 mV vs. MSE. Additionally, the depression of peak #1 and peak #2 with the addition of guar can be combined to monitor the guar level. As will be discussed in section 4.7.3.3, impurities in the electrolyte and the concentration of the major constituents can influence the peak. The use of standards to develop a calibration curve for monitoring guar with the depression of peak #1 requires an electrolyte with a matrix similar to the EW bath chemistry. Unfortunately, several things plague the industrial use of this 2F AC voltammetry technique. Several problems and
Figure 4.50 Standard deviation of the $150^\circ$ current component for the selected peak vs the sweep rate. Standard deviation from a sample set of 7 trials at each sweep rate.
options for alleviating the problems of obtaining a standard electrolyte matrix are discussed in section 4.7.3.3 and 4.7.4.

4.7.3 Contribution of Different Components of the Electrolyte to the Voltammograms

The synthetic electrolyte, 1.63 M H₂SO₄ + 0.63 M CuSO₄, was broken down into the base components and DC, AC fundamental and AC 2F voltammetry were performed with different combinations of EW additives. In this chapter, the basic differences of the additives on the voltammograms for the individual components will be discussed. The summation of all the plots development into the final 2nd harmonic AC voltammogram will be discussed Chapter 5.

4.7.3.1 DC Components in Phase Sensitive Voltammograms

The DC voltammogram for DI H₂O showed relatively little information, Figure 4.51. However, there is a small cathodic peak near -62 mV vs. MSE for both with and without chloride voltammograms, 6 and 8 A/m², respectively. The addition of 40 ppm chloride not only slightly diminished the cathodic peak, but also shifted the entire voltammogram up by 5-50 A/m².

The DC cyclic voltammogram for H₂SO₄ with and without 40 ppm chloride showed little difference, Figure 4.52. There is a noticeable cathodic peak at -62 mV vs. MSE, which is roughly the same potential as the peak found in Figure 4.51. Upon the addition of 5 ppm guar, the cathodic peak was depressed roughly 20 and 60 Am⁻² for the
Figure 4.51 DC cyclic voltammograms for DI H₂O with and without chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
voltammograms with and without chloride, respectively. The peak for the voltammogram with guar and without chloride was not only depressed but was also shifted about 12 mV more cathodic, Figure 4.53.

The DC plating of copper in a 0.65 M CuSO₄ electrolyte shows minimal difference in the cathodic peak for the electrolyte with and without 40 ppm chloride, Figure 4.54. The cathodic peak for each is located just slightly past -500 mV, which is where the sweep direction is reversed. Note the copper cathodic peak is not a complete peak that is typically seen in cyclic voltammetry. Instead, the voltage range covered in these scans has been reduced and the peak current is located near the reversal of the voltage sweep. The stripping peak for copper at 98 mV vs. MSE had an 8% increase, -2580 to -2790 Am⁻², upon the addition of the 40 ppm chloride. The addition of guar increased the plating peak for the electrolyte without chloride by 3.8%, Figure 4.55. There was a minimal effect (~1.5% increase) on the cathodic peak. The anodic peak with the guar became nearly indistinguishable between with and without 40 ppm chloride, 2835 Am⁻². The anodic peak increase for the electrolyte with chloride was only about 1.7%, while the increase for the electrolyte without chloride increased by nearly 10%. The anodic peak was also shifted 25 mV more anodic with the addition of guar for both electrolytes. An additional anodic peak was found for the electrolytes without the chloride at 200 mV vs. MSE and can be seen by comparing Figure 4.56 with 4.57.

The DC voltammogram for the electrolyte containing the CuSO₄ and H₂SO₄, Figure 4.58, were very similar if the previous voltammograms were superimposed with
Figure 4.52 DC cyclic voltammograms for 1.63 M H₂SO₄ with and without chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.53 DC cyclic voltammograms for 1.63 M H₂SO₄ with and without chloride and 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.54 DC cyclic voltammograms for 0.63 M CuSO\textsubscript{4} with and without chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.55 DC cyclic voltammograms for 0.63 M CuSO\textsubscript{4} with and without chloride and 5 ppm Galactasol at 40 minutes oxidation. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.56 DC cyclic voltammograms for 0.63 M CuSO₄ with and without chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.57 DC cyclic voltammograms for 0.63 M CuSO₄ with and without chloride and 5 ppm Galactosol at 40 minutes oxidation. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
several key differences. The small cathodic peak in Figure 4.58 is similar to the one seen in Figure 4.52 and 4.53. The cathodic peak for copper is still at the same location, -500 mV vs. MSE, but is approximately 27% larger with the addition of H₂SO₄. The background current is also 3 times as large when compared to Figure 4.54. The addition of guar to the synthetic electrolyte caused a small depression for the cathodic peak as seen by comparing Figure 4.59 with Figure 4.58, which is the opposite of what is found for electrolyte containing only CuSO₄. The copper anodic peak was also shifted ~140 mV more cathodic. The peak value also increased by roughly 50% for both with and without chloride electrolytes when compared to the electrolyte that only contained CuSO₄.

4.7.3.2 AC Fundamental Harmonic Components in Phase Sensitive Voltammograms

The fundamental phase sensitive detection voltammogram for DI H₂O with and without 40 ppm Cl⁻ are shown in Figures 4.60 and 4.61. No peaks were found for this electrolyte. The base current shown in Figure 4.60 and 4.61 are not from a cathodic current but rather the background current. To further explain currents in AC voltammetry, one should understand that negative and positive current is not related to an anodic or cathodic process. The sign of the current relates to the phase in relation to the sensing circuit on the lockin amplifier. A positive current at 150° phase angle for the lockin amplifier is a quantification of the AC current that is at 150° from the perturbation signal.
Figure 4.58 DC cyclic voltammograms for 0.63 M CuSO₄ and 1.63 M H₂SO₄ with and without chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.59 DC cyclic voltammograms for 0.63 M CuSO₄ and 1.63 M H₂SO₄ with 5 ppm guar and with or without 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.60 Fundamental AC cyclic voltammograms for the DI H₂O. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.61 Fundamental AC cyclic voltammograms for the DI H₂O with 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE, a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
The fundamental phase sensitive voltammograms for \( \text{H}_2\text{SO}_4 \) without and with 40 ppm chloride are shown in Figures 4.62 and 4.63, respectively. The difference in the voltammograms is the smoothing of the voltammogram from the addition of 40 ppm chloride. It is difficult to quantitate peaks and compare because the peaks are irregular and some disappear completely upon the addition of Cl\(^-\). The addition of 5 ppm guar to the electrolyte without chloride only smoothed out the central peak at -500 mV vs. MSE for the 150° current component, Figure 4.64. The addition of 40 ppm chloride with guar had a similar effect on the voltammogram as it did for the electrolyte without guar, Figure 4.65 and 4.63 respectively.

The fundamental AC voltammograms for electrolyte with only CuSO\(_4\) are shown in Figures 4.66 through 4.69. The addition of chloride to the CuSO\(_4\) electrolyte only slightly depressed the background current for the 150° current component; the 60° current component had a slight increase in the complete voltammogram. The addition of guar had a more complex effect on the voltammogram for \( \text{H}_2\text{SO}_4 \) electrolytes with and without chloride. Without chloride, the addition of guar decreased the 150° current component throughout the voltage range, see Figures 4.66 and 4.68. The magnitude of the depression was not constant across the voltammogram. On the other hand, the addition of guar to the electrolytes with chloride showed a general increase in current across the voltammogram, as seen in Figures 4.67 and 4.69, respectively.

The fundamental phase sensitive voltammograms for the electrolyte with both CuSO\(_4\) and \( \text{H}_2\text{SO}_4 \) are even more complex then either of the voltammograms from their
Figure 4.62 Fundamental AC voltammograms for the 1.63 M H₂SO₄. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the synthetic electrolyte.

Figure 4.63 Fundamental AC voltammograms for the 1.63 M H₂SO₄ with 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.64 Fundamental AC voltammograms for the 1.63 M H₂SO₄ with 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.65 Fundamental AC voltammograms for the 1.63 M H₂SO₄ with 40 ppm chloride and 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.66 Fundamental AC voltammograms for the 0.63 M CuSO$_4$.
Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.67 Fundamental AC voltammograms for the 0.63 M CuSO$_4$ with 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.68 Fundamental AC cyclic voltammograms for the 0.63 M CuSO$_4$ with 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.69 Fundamental AC voltammograms for the 0.63 M CuSO$_4$ with 40 ppm chloride and 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
respective components. First of all, chloride at 40 ppm had a significant effect on the voltammogram without guar, Figures 4.70 and 4.71. The two central peaks increased 27% and 6% upon the addition of 40 ppm chloride. The true peak height is hard to define because there does not appear to be a baseline to eliminate the background. Other minor peaks in the more anodic regions, 0.0→0.74 are more troublesome and will be discussed in Chapter 5 when the 2nd harmonic voltammogram is analyzed.

The addition of guar to the CuSO₄ and H₂SO₄ electrolyte had only a small effect. The two central peaks of 150° current component increased slightly with the addition of guar as shown in Figure 4.72. The voltammogram electrolyte with chloride, Figure 4.73, also was only slightly affected by the addition of guar. The peak at 125 mV vs. MSE on the reverse sweep was depressed slightly, 16%, when guar was present at 5 ppm.

4.7.3.3 AC 2nd Harmonic Results Components in Phase Sensitive Voltammograms

The 2nd harmonic voltammograms will be briefly discussed here. The majority of the analysis will be deferred to Chapter 5 where the direct correlation to the DC, AC fundamental and AC 2nd harmonic (2F) will be presented. In this section, general differences will be presented for the various voltammograms. Figure 4.74 and 4.75 are the 2F voltammograms for just DI H₂O. Again, there is only a very small background current.

The H₂SO₄ 2F voltammogram has a tremendous amount of information, Figures 4.76 through 4.77. The addition of 40 ppm chloride to the H₂SO₄ electrolyte significantly
Figure 4.70 Fundamental AC voltammograms for 0.63 M CuSO₄ and 1.63 M H₂SO₄. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.71 Fundamental AC voltammograms for 0.63 M CuSO₄ and 1.63 M H₂SO₄ with 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.72 Fundamental AC voltammograms for 0.63 M CuSO₄ and 1.63 M H₂SO₄ and 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.73 Fundamental AC voltammograms for 0.63 M CuSO₄ and 1.63 M H₂SO₄ with 40 ppm chloride and 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.74 2\textsuperscript{nd} Harmonic AC voltammograms for DI H\textsubscript{2}O. Experimental conditions were 65\textdegree{}C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.75 2\textsuperscript{nd} Harmonic AC voltammograms for DI H\textsubscript{2}O with 40 ppm chloride. Experimental conditions were 65\textdegree{}C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.76 2nd Harmonic AC Voltammogram for 1.63 M H₂SO₄. Experimental conditions were 65°C, 25 mV/sec, Pt WE, were 65°C, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.77 2nd Harmonic AC voltammograms for the 1.63 M H₂SO₄ with 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
altered the voltammogram as can be seen by comparing Figures 4.76 with 4.78 and Figures 4.77 and 4.79. The two central peaks at about -300 mV vs. MSE for the forward and reverse sweep of the 60° current component decreased slightly with the addition of 40 ppm chloride. Most of the other peaks for the 60° current component were either completely or almost completely suppressed upon the addition of chloride. Similarly, the voltammogram for the electrolyte with H₂SO₄ and guar showed the same behavior, as shown in Figure 4.76 for just H₂SO₄ and Figure 4.77 for H₂SO₄ and 40 ppm Cl⁻.

The addition of guar to the H₂SO₄ electrolyte significantly depressed the 150° current peak at 200 mV vs. MSE during the sweep reversal portion of the voltammogram, Figure 4.78. Guar also slightly depressed all the peaks for both the 150° and 60° current component. The same general depression of the peaks was found when comparing voltammograms with H₂SO₄ and chloride with the addition of guar as shown in Figure 4.79. The significant reduction in the peak at 200 mV vs. MSE was not seen for the electrolyte with chloride because the peak does not exist with the Cl⁻ containing electrolytes, Figure 4.77 and 4.79.

The AC 2F voltammograms for CuSO₄ electrolytes are shown in Figures 4.80 through 4.83. The nonlinear component from the plating of copper is extremely small as indicated by the slight depression in the 60° and 150° current component in voltammograms shown in Figures 4.80 and 4.81. The perturbation in the -100 mV range for 60° and 150° current component of Figure 4.80 and 4.81 were not significantly
Figure 4.78 2nd Harmonic AC Voltammogram for 1.63 M H$_2$SO$_4$ with 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.79 2nd Harmonic AC voltammograms for the 1.63 M H$_2$SO$_4$ with 5 ppm guar and 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.80 2nd Harmonic AC voltammograms for 0.63 M CuSO$_4$. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the synthetic electrolyte.

Figure 4.81 2nd Harmonic AC voltammograms for the 0.63 M CuSO$_4$ with 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.82 2nd Harmonic AC cyclic voltammograms for the 0.63 M CuSO$_4$ with 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the synthetic electrolyte.

Figure 4.83 2nd Harmonic AC voltammograms for the 0.63 M CuSO$_4$ with 40 ppm chloride and 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the synthetic electrolyte.
changed with the addition of chloride. In fact, the variation of replicates showed similar changes.

The addition of guar to the electrolyte did alter the linear behavior of the current slightly, which resulted in a small peak at \(-200\,\text{mV}\) for the forward scan of the voltammograms shown Figures 4.82 and 4.83. There was a 2F response again when the sweep direction was changed at \(-500\,\text{mV}\). The major interest in Figure 4.82 and 4.83 were the significant increases in the peak at \(-200\,\text{mV}\) on the reverse sweep when guar was in the CuSO\(_4\) electrolyte. The increase in the peak at \(-200\,\text{mV}\) was more pronounced when 40 ppm chloride was present, i.e. 15 to 20% for the 60° and 150° current component, respectively.

The AC 2F voltammograms for the synthetic electrolyte (0.63 M CuSO\(_4\) + 1.63 M H\(_2\)SO\(_4\)) are shown in Figures 4.84 through 4.87. Again, the comparison to the DC, fundamental, and other 2F voltammograms will be discussed in Chapter 5. The basic comparison of the voltammograms with chloride and without was an increase in the peaks centered near the \(-500\,\text{mV}\) turning point. The peaks at \(+200\,\text{mV}\) for both directions showed an inversion of the peaks for the 60° and 150° current components. This inversion of the peaks was also present when guar was added to the electrolyte as shown in Figure 4.86 without Cl\(^-\) and Figure 4.87 with 40 ppm Cl\(^-\). The voltammogram for the electrolyte without chloride had a general increase in all the peaks when guar was added except for the peak at \(-300\,\text{mV}\) on the reverse sweep of the 150° current component. However, with chloride present in the electrolyte, the most depressed peak
was the 200 mV peak as deduced from comparing Figure 4.85 with 4.87. peak at 
~200 mV during the sweep reversal. This peak was not affected by guar.
Figure 4.84 2nd Harmonic AC voltammograms for 0.63 M CuSO$_4$ and 1.63 M H$_2$SO$_4$. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.85 2nd Harmonic AC voltammograms for 0.63 M CuSO$_4$ and 1.63 M H$_2$SO$_4$ with 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
Figure 4.86 2nd Harmonic AC voltammograms for 0.63 M CuSO$_4$ and 1.63 M H$_2$SO$_4$ and 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.87 2nd Harmonic AC voltammograms for 0.63 M CuSO$_4$ and 1.63 M H$_2$SO$_4$, 40 ppm chloride and 5 ppm guar. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in a Luggin Probe filled with the Synthetic Electrolyte.
4.7.3.4 Contributions of Mn, Co, and Fe to the final spectra

The electrolytes used in EW contain more than just Cu\(^{2+}\), H\(_2\)SO\(_4\), Cl\(^-\) and guar. Several of the more common elements and concentration distributions for commercial facilities were discussed in 2.1.1.2. Preliminary tests were conducted to insure that Fe\(^{3+}\), Co\(^{2+}\) and Mn\(^{2+}\) did not completely interfere with the detection of guar. Figure 4.88 and 4.89 are the 2F AC voltammogram for different combinations of the solutions with Co\(^{2+}\), Fe\(^{3+}\) and Mn\(^{2+}\). Figure 4.88 is for a phase angle of 60° while 4.89 is for 150° phase angle. As seen when comparing two peaks between -200 and -250 on the reverse sweep, the other elements depress the signal slightly. However, the addition of guar still depresses the peak used for in this work for monitoring guar. The effects of matrix and other additives all influence the detection of guar and will require standards to be made in an electrolyte that is similar in composition.

4.7.4 Removal of trace organics to obtain baseline solutions for calibration

Removing the organics in the industrial EW solutions was attempted to obtain a standard blank with the matrix of the electrolyte being monitored. The synthetic electrolyte was originally doped with 10 ppm guar. Activated carbon, alumina and nonfunctional resins were used to try and remove the guar and obtain the original voltammograms by using a reverse flow column procedure. In all cases the voltammograms changed so that they could not be used for the standard matrix during a calibration.
Figure 4.88 2nd Harmonic AC voltammograms for 0.63 M CuSO₄, 1.78 g/l Fe³⁺ and 1.63 M H₂SO₄ with 40 ppm Cl⁻ at different levels of Co and Mn. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE and a MSE reference in Luggin Probe filled with the Synthetic Electrolyte.

Figure 4.89 2nd Harmonic AC expanded view voltammograms for the 0.63 M CuSO₄, 1.78 g/l Fe³⁺ and 1.63 M H₂SO₄ with 40 ppm chloride at different levels of Co and Mn.
4.7.4.1 Thermal Decomposition

As in 4.1.2, the use of heat can decompose the guar and obtain the same baseline as the electrolyte without guar. The time to obtain the same baseline was reported to be nearly 15 hours at 50°C. However, at 90°C the time to decompose the guar was reduced to roughly 3 hours. The thermal treatment of the electrolyte at the EW facility would therefore produce a matrix matched solution for the standards.

4.8 Potential Step

The potential step data for the nucleation studies are grouped based on the chemistry of the electrolyte. Figure 4.90, 4.91 and 4.92 are the current vs. time curves for the electrolyte containing the synthetic electrolyte, with the addition of 40 ppm Cl⁻, and with 5 ppm galactosol and 40 ppm Cl⁻. The start of the potential step is designated at t=0 in these figures. The initial decay in the current is a result of the capacitive charging of the interface. For -350 to -352 mV vs. MSE, the capacitive current was the only current present. For the electrolytes without galactosol, the current increased after the capacitive decay and an induction time. The induction time is where copper nuclei are being generated as described in the literature. [83, 165, 166] The synthetic electrolyte with chloride, Figure 4.91, displayed a noticeable depolarization for copper plating with a 20% or more increase in the current for the -353, -354, -355 and -356 mV potential steps when compared to the synthetic electrolyte without chloride, Figure 4.90. With the
addition of guar, the current was decrease by 10 to 25% over the same potential range, Figure 4.92.
Figure 4.91 Potential step current response for a Pt electrode in the synthetic electrolyte with 40 ppm Cl⁻.

Figure 4.92 Potential step current response for a Pt electrode in the synthetic electrolyte with 40 ppm Cl⁻ and 5 ppm galactosol.
Figure 4.90 Current response for a potential step with a Pt electrode in the synthetic electrolyte.
5. DISCUSSION

The analysis and major points from the data were presented in Chapter 4 and will be summarize in this chapter. The unusual behavior of glue in the electrolyte with and without other additives initially will be presented. Subsequently, the results from other additives in a typical ER electrolyte will be discussed. The AC voltammetry for guar will be summarized from both a fundamental and observational point of view. Finally, a brief review of the problems associated with the implementation of a 2F AC voltammetric additive control system will be provided.

5.1 Glue Interaction during Copper Plating and Stripping

The use of gelatin or animal glue in electrorefining has been studied with various levels of success. The deposit characteristics from an electrolyte containing glue are well known. However, the mechanisms controlled by the additives used in obtaining quality deposits are vague. The major focus of this research was to develop a monitoring system that would be used in situ during Cu electroprocessing. In the context used in this work, in situ implies the ability to determine the quantity of an additive (glue or guar) directly without removing a sample from the cell house. In order to achieve this, a portable system with a probe that contains the working electrode, auxiliary electrode and reference electrodes rugged enough to be inserted into the electrolyte in the cell house was selected. The electrochemical techniques evaluated as monitoring methods also provided information regarding the mechanism of the additive glue with other Cl⁻ and thiourea present.
5.1.1 The Effect of Glue on Copper Stripping

The stripping technique presented in 4.5 proved to be effective for monitoring glue in electrolytes containing only H₂SO₄ and CuSO₄. Even in these simple solutions, the results were somewhat perplexing. The degree of polarization previously reported for Cu deposition in the presence of glue was not found in the synthetic electrolyte without Cl⁻. An alternative approach using the time needed to strip Cu from the WE at 600 Am⁻² after plating for a set amount of charge was successful above 1 ppm as shown in Figure 4.26. However, the sensitivity is poor and there appears to be a lot of scatter in the data. To effectively monitor levels of glue, the procedure needs refining. The interference's caused by thiourea, Cl⁻ and other impurities or additives limits the usefulness of this method. Further research into this analytical procedure was suspended when it was determined the polarization of the WE became significantly larger when Cl⁻ was present.

Several interesting features help develop an understanding of what glue does during copper deposition. The decrease in time it took to strip the copper, which had been plated during 500 seconds at a constant current of 300 Am⁻² appeared to be the opposite of what was intuitively expected. It was observed that after the plating and stripping of Cu in solutions containing glue, there where small Cu particulates at the bottom of the cell. Apparently some of the metallic Cu became detached from the electrode surface prior to being oxidized. The perplexing part was that the glue has been reported to increase the deposit quality and not decrease the quality at low concentrations. Yet in these typical solutions of sulfuric acid and copper sulfate it apparently was detrimental,
i.e. some of the Cu fell off the WE and was found at the bottom of the cell. If an improvement in deposit quality were to occur, then the stripping time would have increased for the samples with small amounts of glue. No such increase occurred.

A simple beaker test confirmed that glue only needed to be present during the plating phase of the typical chronopotentiometric test. The beaker test results and the observation of increased Cu at the bottom of the EC cell after the test for samples with glue leads to the conclusion that glue produces poorer quality deposits under these conditions. This contradicts why glue is used as a leveler in the first place. However with the addition of Cl\textsuperscript{-} and TU, the stripping method became more unreliable. In fact, for the industrial electrolyte the slope of the function relating time to strip the Cu to glue concentration was now positive. The positive slope is what would be predicted if glue in the electrolyte were to produce a better deposit. The draw back of using the time to strip Cu for the industrial electrolyte was the low correlation coefficient and small slope. The correlation coefficient could possible be increased with optimization of the technique, but the slope would most likely not be changed significantly.

The chronopotentiometric techniques described previously are similar to the technique developed by Tench and Ogden [112] for measuring brighteners and suppressors. Their technique is called Cyclic Voltammetric Stripping (CVS) and was developed to monitor additives in the circuit board manufacturing industry. CVS is similar to typical cyclic voltammetry but emphasis is placed on the stripping peak area. The combined effects of all additives in the bath have a crucial influence on the
deposition rate of Cu on the forward sweep of the voltammogram. The area of the peak for the stripping is then more distinguishable (better signal to noise) and is related to the polarization effects of the additives from the time Cu plating begins. The individual polarizations at each potential during the CV scan can be summed up as simple short chronoamperometrograms. Similarly, a constant current equivalent can be envisioned for CVS in which only the first 5 to 20 seconds of the chronopotentiogram are represented by a typical CVS scan.

5.1.2 Polarization

As previously discussed in Chapter 2.3.3 glue is predicted to adsorb on the surface of the cathode at protrusions and possibly other active sites. A rough estimate of the fraction of the active surface sites covered by the glue can be described using the polarization increase form the chronopotentiometric studies. The amount of polarization increase can be related to the surface area using a current density-overpotential relationship such as the Tafel or Butler-Volmer equation. The assumptions needed to use such a model is the fundamental reaction is not altered upon the addition of additives such as glue. Instead, the available reaction sites or surface area decreases when glue adsorbs on the surface. This adsorption increases the polarization, which is measured during a chronopotentiometric experiment. The exchange current density is related to the standard heterogeneous rate constant as described by equation 5.1.
\[ i = nF \alpha C^{*} \left( 1 - \alpha \right) C^{*n} \]  \hspace{1cm} \text{Eq. 5.1}

The selection of the current density-overpotential relationship was made based on the amount of polarization. The Tafel equation relates the observed current density with the overpotential when the back reaction is less than 1% of the forward reaction i.e. \((i_{\text{anodic}} < 0.01 \times i_{\text{cathodic}})\). With the assumptions discussed above the Tafel equation is the simplified form of the Butler-Volmer equation for these CP experiments.

The need for chloride to enable glue to act as a polarizing agent (suppressor) is similar to what is common in circuit board manufacturing with polyethylene glycol. [167] Others have seen an effect of chloride on the ability of glue and thiourea [83, 84, 88, 91, 98, 161] but minimal work was found on electrolytes extremely low in chloride content.

5.1.3 Calibration curves

In summary, the adsorption of glue in the current density region used for electrorefining was found to be substantially lower than previously reported as indicated by 15 mV or less cathodic polarization at 300 Am\(^{-2}\) [60, 115] [99] [23]. The previous publications, which reported higher levels of cathodic polarization appear to be contaminated by Cl\(^-\) or used industrial electrolytes. Industrial electrolytes certainly contain more Cl\(^-\) than the synthetic electrolyte used in this work. Even with extreme care used in preparing the synthetic electrolyte in this work, a small contamination of Cl\(^-\) was present from the Reagant Grade chemicals, which was typically less than 3 ppm. In addition, the glue was reported to contain between 100 and 1500 ppm Cl\(^-\). The
quantitative analysis of additives used in Cu electrorefining has many difficulties. For example, detecting low concentrations of the additive in high acid/copper levels with a multitude of other impurities is difficult. Besides the sensitivity issues, complex interactions of every component in the electrolyte further complicates the measurements. Several of the interactions of Cl\(^{-}\), TU and glue on the deposition of copper were found using CP and are listed below.

1. Polarization from glue in the absence of Cl\(^{-}\) was minimal.
2. The initial polarization by thiourea occurred with or without Cl\(^{-}\) and/or glue.
3. Depolarization caused by low levels of thiourea during the first few seconds was present in all electrolyte combinations containing thiourea.
4. The continuous slow depolarization by thiourea was not present when Cl\(^{-}\) and glue were both in the electrolyte. Instead, the combination of thiourea, Cl\(^{-}\) and glue showed a significant polarization increase after about 30 seconds.

5.2 In Situ Guar Monitoring

Chronopotentiometric methods, which showed limited success for evaluating levels of glue, had similar difficulties for guar. In addition to the low polarization (< 10 mV in the synthetic electrolyte) the increase in activity (larger cathodic polarization) from the addition of Cl\(^{-}\) was not present for guar like it was for glue. Figure 4.37 showed that a total of 12 mV for 5 ppm guar in an industrial electrolyte was achieved. However, 5 ppm
is between 5 and 10 times higher than typically used in industry as shown in Figure 2.27. The time to strip Cu was completely insensitive to guar levels in the electrolyte.

As previously discussed AC voltammetry was selected as an approach for an in situ method because of the sensitivity of the method to electroinactive species as well as Faradaic process. The noise from background plant operations would be minimal because the lockin amplifier uses the frequency dependence of the signal, which is typically used to minimize noise in DC signals for other analytical methods such as Atomic Adsorption Spectroscopy.

The 2nd harmonic current response for monitoring guar was successful in all solutions tested. Evaluating the calibration curves shown in Figure 5.1, 5.2 and 5.3 illustrates the major accomplishments. The first two calibration curves are for a electrolyte that was unstirred during the measurement. The sensitivity of the method to low concentrations apparently limits the use of the method for either the peaks at the two different phase angles, 60° in Figure 5.1 and 150° in Figure 5.2. However, with gently agitation (~100 rpm with a 3 bladed impeller) the method became very sensitive at low concentrations and appears to taper off after about 5 ppm at this agitation rate. Mass transport, either through the concentration gradient after the anodic preclean or the bulk transport from agitation after preclean, control the amount of guar on the surface of the working electrode. The surface guar concentration is what controlled the amount of depression of the second harmonic peak selected in section 4.7.2. Since no Faradaic current was detected in this region and there was a corresponding depression of the same
Figure 5.1 Calibration curve for Galactasol using 2nd Harmonic AC voltammetry in an unstirred cell. Current response is for the 60° component.

Figure 5.2 Calibration curve for Galactasol using 2nd Harmonic AC voltammetry in an unstirred cell. Current response is for the 150° component.
Figure 5.3 Calibration curve for Galactasol using 2$^{nd}$ Harmonic AC voltammetry with stirring at ~100 rpm for an impeller. Response is for the 150° current component.

\[ y = -19.19x^2 + 113.82x + 522.12 \]
\[ r^2 = 0.999 \]
region for the fundamental current response, it was concluded that guar/Galactosol
adsorption on the surface decreases the dielectric constant. With aqueous electrolytes
having dielectric constants in the range of 50-80 and organic compounds having dielectric
constants of generally less than 10, the displacement of water molecules in the charge
separation region would definitely lower the capacitance. The lower capacitance would
thus result in lower amount of charge accumulating on the surface since the $q$ transported
onto the surface of any capacitor is proportional the capacitance. The lower charge
transport would result in a decrease in the fundamental and the 2$^{nd}$ harmonic current
response that is seen when guar is added to the electrolyte.

The information obtained from the AC and DC voltammetric studies will be
further discussed in this section. Because of the details of a 2F AC voltammogram
encompasses much more than typical voltammetry, a systematic discussion of the 2F
voltammograms will be presented in 5.3.1. Several key features will be discussed and
include the Faradaic vs. the non-Faradaic nature of the peaks in the voltammogram.
Another component to note is the Cl$^-$ effect around the peak of interest for monitoring
guar in the 2F AC voltammogram.

5.2.1 Voltammogram Analysis

The DC, AC and 2F AC voltammograms were initially discussed in Chapter 4.7.
In section 4.7.3, the voltammograms from the various components of the synthetic
electrolyte were presented with a brief discussion relating the differences in the
voltammograms with the addition of guar and Cl\(^-\). In this section, the contributions of the individual components of the synthetic electrolyte to the \(2F\) AC voltammogram will be presented. The first thing is to separate the peaks in regions where Cu deposition occurs vs. the peaks where no deposition is occurring. Figure 4.58 is the DC voltammogram for the synthetic electrolyte without and with Cl\(^-\). The cathodic current for depositing Cu was from -362 mV on the forward sweep and -345 mV on the reverse sweep. The switch from cathodic to anodic current varied slightly for the electrolyte with and without guar and the average potential was therefore selected. The stripping or anodic Cu peak starts at the same potential, -345 mV, where the plating peak stops. This is only a rough estimation without accounting for the background charging currents in each case. However, this is sufficient to set the outside boundaries where plating and stripping of Cu occurs. The stripping of Cu continues as the voltage increases until no metallic Cu remains on the surface of the Pt WE. The Cu was generally completely oxidized by -125 mV on the reverse sweep.

The Faradaic regions on a \(2^{nd}\) harmonic AC voltammogram for Cu are graphically labeled in Figure 5.4. This does not in any way imply that all the peaks are related to Cu reduction and oxidation. On the contrary, the nonfaradaic currents from the H\(_2\)SO\(_4\) are significant and will be discussed in more detail in the sections that follow.

Figure 5.5 is a typical \(2F\) AC voltammogram for the synthetic electrolyte with 40 ppm Cl\(^-\) while Table 5.1 summarizes the peaks from the figure for each of the current components. Upon close examination of Figures 4.58 and 4.59, a small cathodic peak is
Figure 5.4 AC and DC Cyclic Voltammograms with the 1.15 V vs. MSE anodic pretreatment. The experimental conditions were 0.63 M Cu²⁺, 1.63 M H₂SO₄, Pt WE, Cu CE, 65°C, and 25 mV/sec.
Figure 5.5 2<sup>nd</sup> Harmonic AC voltammogram for the Synthetic Electrolyte with 40 ppm Cl<sup>-</sup>. Peaks labeled A and B are the 60° and 150° current components. Experimental conditions are 25 mV/sec, 70 mV rms.
Table 5.1 Typical Peaks from a 2F AC Voltammogram containing Synthetic Electrolyte with 40 ppm Cl\textsuperscript{-}.

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Location V vs. MSE @65\degree C</th>
<th>Location V vs. NHE</th>
<th>Peak Height Am\textsuperscript{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>0.175</td>
<td>0.792</td>
<td>108</td>
</tr>
<tr>
<td>2A</td>
<td>0.086</td>
<td>0.703</td>
<td>26.6</td>
</tr>
<tr>
<td>3A</td>
<td>-0.225</td>
<td>0.392</td>
<td>118</td>
</tr>
<tr>
<td>4A</td>
<td>-0.347</td>
<td>0.270</td>
<td>72.6</td>
</tr>
<tr>
<td>5A</td>
<td>-0.382</td>
<td>0.235</td>
<td>-58.0</td>
</tr>
<tr>
<td>6A</td>
<td>-0.461</td>
<td>0.156</td>
<td>383</td>
</tr>
<tr>
<td>7A</td>
<td>-0.479</td>
<td>0.138</td>
<td>-101</td>
</tr>
<tr>
<td>8A</td>
<td>-0.397</td>
<td>0.220</td>
<td>600</td>
</tr>
<tr>
<td>9A</td>
<td>-0.300</td>
<td>0.317</td>
<td>-181</td>
</tr>
<tr>
<td>10A</td>
<td>-0.172</td>
<td>0.445</td>
<td>99.0</td>
</tr>
<tr>
<td>11A</td>
<td>0.257</td>
<td>0.874</td>
<td>-612</td>
</tr>
<tr>
<td>12A</td>
<td>0.440</td>
<td>1.057</td>
<td>87.6</td>
</tr>
<tr>
<td>1B</td>
<td>0.133</td>
<td>0.750</td>
<td>-268</td>
</tr>
<tr>
<td>2B</td>
<td>-0.215</td>
<td>0.402</td>
<td>171</td>
</tr>
<tr>
<td>3B</td>
<td>-0.375</td>
<td>0.242</td>
<td>212</td>
</tr>
<tr>
<td>4B</td>
<td>-0.429</td>
<td>0.188</td>
<td>374</td>
</tr>
<tr>
<td>5B</td>
<td>-0.475</td>
<td>0.142</td>
<td>-377</td>
</tr>
<tr>
<td>6B</td>
<td>-0.348</td>
<td>0.269</td>
<td>772</td>
</tr>
<tr>
<td>7B</td>
<td>-0.165</td>
<td>0.452</td>
<td>214</td>
</tr>
<tr>
<td>8B</td>
<td>0.235</td>
<td>0.852</td>
<td>-612</td>
</tr>
<tr>
<td>9B</td>
<td>0.386</td>
<td>1.003</td>
<td>-53.0</td>
</tr>
</tbody>
</table>
present in the voltammogram at approximately -80 mV vs. MSE. From comparing
Figures 4.52, 4.54 and 4.58 it was concluded that the cathodic peak at ~80 mV was
dependent on the acid content and preconditioning step. Several possibilities exist for the
source of this cathodic peak and will be discussed in the next section. However, this peak
is needed to explain the difference in the peak number 1A with 1B and 11A with 8B for
the 60 and 150° current component for the 2F AC voltammogram in Figure 5.5.

The reducible species at the Pt WE surface from the preconditioning step has a
dramatic effect on the peak of interest for monitoring guar. Prior to reduction of the layer
on the Pt WE, minimal process occur that contributes to the 2F AC peaks numbered 1A
and 1B in Figure 5.5. Upon comparing the corresponding peaks from the forward
(increasingly more cathodic) and reverse (increasingly more anodic), 1A with 11A and
1B with 8B, it was concluded the surface became more active after the Pt film from the
pretreatment was reduced. The reduction of the anodically precleanned surface also
established a more reproducible surface for the WE electrode. Once the oxide was
removed from the Pt WE, the amount of guar on the surface was than completely
dependent on the diffusion of the guar to the surface. From Ficks first law Eq. 5.2, the
flux is proportional to the concentration gradient, \( \frac{dC_{guar}}{dx} \).

\[
j_{guar} = D_{guar} \frac{\partial C_{guar}}{\partial x_{guar}} \quad \text{Eq. 5.2}
\]

\( j_{guar} \) is the flux to the surface of the WE in planar form and \( D_{guar} \) is the diffusion
coefficient of guar in the electrolyte for Eq. 5.1. To increase sensitivity to solutions with
lower concentrations of guar, stirring of the electrolyte was also used to add a convective
term. The increase in sensitivity can be seen by comparing the calibration curve from an unstirred test shown in Figure 5.2 and for the gently stirred vessel shown in Figure 5.3. The stirring was done using a 3 blade impeller at 100 rpm. A flow cell test was also conducted. These tests were unsuccessful because the flow cell design had high shear at the surface of the WE. The nature of the peaks used to monitor guar will be further analyzed in section 5.3.

The nonfaradaic contributions to the 2F AC voltammogram for the regions where Cu is either plated or stripped is significant. To begin with, the 2F contributions for 0.63 M CuSO₄ and 1.63 M H₂SO₄ are shown in Figures 4.78 and 4.80, respectively. A better visual presentation for the contributions from each of the components in the bath is shown in Figure 5.6. The bold vertical lines in Figure 5.6c are the boundaries for Cu plating and Cu stripping. The corresponding 2F peaks for Cu plating should be found between the regions that are marked plating and stripping in Figure 5.6c. However, the 2F voltammogram labeled as Figure 5.6a shows that the peaks for copper plating are limited to the very edge of stripping the Cu. To further illustrate the nonfaradaic component of the AC 2F voltammogram, Figure 5.6b has significant peaks with only H₂SO₄ present that are similar to the final voltammogram in Figure 5.6c. This suggests that the acid is the major species in the electrolyte contributing to the peaks in the Faradaic region. Upon the addition of Cu to the acid, the voltammogram significantly alters with additional peaks about 0.300 V vs. MSE. These peaks are highly sensitive to Cl⁻ as well and were shown in Figures 4.78 and 4.79. These peaks were also the most
Figure 5.6 2nd Harmonic AC voltammograms for a) 0.63 M CuSO$_4$, b) 1.63 M H$_2$SO$_4$ and c) both. Each solutions also contained 40 ppm chloride. Experimental conditions were 65°C, 25 mV/sec, Pt WE, graphite CE with an MSE reference.
responsive to the addition of guar. The proposed interaction is that the Cu-Cl complex at the surface is contributing to the peak 11A and 8B in Figure 5.6. As shown in Figures 4.77 and 4.78, the effect of Cl⁻ on just the electrolyte with H₂SO₄ is substantial in the region above 0 V vs. MSE on the stripping side but is not the same as when the Cu is introduced into the system. The Cu-Cl complexation is commonly known to alter the deposition and stripping of Cu, see section 4.7.3.1 and Figure 4.56 and 4.57.

5.2.1.2 Platinum Oxy/hydroxide Reduction

Various authors [39, 178] have reported the formation of platinum oxides at anodic potentials greater than 0.8 V vs. NHE in H₂SO₄ solutions. It is clearly evident in Figure 4.58 that a platinum oxide or hydroxide peak is reduced at -80 mV vs. MSE. It should be pointed out that the oxidized form of the Pt metal is difficult to ascertain from the literature. There have been reports published on the formation of oxides, hydroxides and a mixture of oxyhydroxides [168-172] [173, 174] [175, 176]. In these reported studies the experimental methods for determination of the oxidized phase of Pt required at a minimum removal of the WE from the electrolyte. Some of the methods also required placing the sample in a vacuum. In all cases, the surface of the Pt can not be guaranteed to be the same as what was formed in the H₂SO₄ electrolyte.

Figure 5.7 through 5.10 are the DC cyclic voltammogram for the synthetic electrolyte with different sweep ranges. The typical CV is shown in Figure 5.9a while b shows the applied anodic pretreatment of 1.15 vs MSE from about 0.4 to 1.4 minutes
with current response vs. time. The resulting from the anodic current clearly decays and is from double layer charging and formation of an oxyhydroxide film as well as small amounts of oxygen evolution. At the start of the typical CV, no anodic current flows during the early stages of the first sweep from 0.75 to -0.5 V vs. MSE as shown in Figure 5.9a. The cathodic peak at ~80 mV is clearly shown in the first sweep. On the subsequent sweeps, a much smaller cathodic peak was found and is shown in Figure 5.9a. The peak is shifted almost +170 mV. It was expected to have the peak diminished because the oxide formation would only result from the CV scan and not the anodic pretreatment, as was the case for the first sweep. However, the shift in peak potential was not expected. This implies that the surface layer produced at the higher and extended duration of the anodic preclean was more stable.

The sweep range of the CV had a dramatic impact on the small cathodic peak for Pt oxyhydroxide reduction for the second-fourth sweeps and relatively no affect on the peak at -80 mV vs. MSE for the first sweep. The scan range was varied form a starting potential of 0.75 to 1.20 V vs. MSE and the resulting peak position for the 1st and 2nd sweep are shown in Figures 5.7 through 5.10. It becomes clearly evident that the current peak position is dependent on the anodic potential and times at that potential the Pt WE are exposed to during the CV. With the sweep range at 1.20 V, the 2nd-4th sweeps are nearly identical to the peak resulting form the 1st sweep which was held at 1.15 V vs. MSE for 1 minute prior to the start of the CV experiment and is shown in Figure 5.10.
Figure 5.7 Cyclic Voltammograms with the 0.75 V vs. MSE anodic pretreatment
a) is a typical CV with the first and second sweep, b) is the applied
voltage and current density vs. the time from the start of the experiment.
Figure 5.8 Cyclic Voltammograms with the 0.95 V vs. MSE anodic pretreatment
a) is a typical CV with the first and second sweep, b) is the applied voltage and current density vs. the time from the start of the experiment.
Figure 5.9 Cyclic Voltammograms with the 1.15 V vs. MSE anodic pretreatment
a) is a typical CV with the first and second sweep, b) is the applied voltage and current density vs. the time from the start of the experiment.
Figure 5.10 Cyclic Voltammograms with the 1.15 V vs. MSE anodic pretreatment
a) is a typical CV with the first and second sweep, b) is the applied voltage and current density vs. the time from the start of the experiment.
Also note that the current decay during the first minute, shown in Figures 5.9b to 5.10b, decreases but does not fall to zero. This current decay suggests that the layer is still growing after the first minute or gas evolution is slow. It also helps explain why the peak is not as great for the 2nd and greater sweeps shown in Figure 5.9.

The cathodic peak at ~80mV was not found in the CV for the CuSO₄ only electrolyte. As seen in Figures 4.54 and 4.55 the platinum oxyhydroxide reduction peak is not evident. However, the cathodic peak position would be pH dependent for both an oxide and a hydroxide film on the Pt surface. Eq. 5.3 for an oxide and Eq 5.4 for the hydroxide can describe the electrochemical dissolution of the Pt in acid electrolyte.

\[
PtO + 2H^+ + 2e^- \rightarrow Pt + H_2O \quad \text{Eq. 5.3}
\]

\[
Pt(OH)_2 + 2H^+ + 2e^- \rightarrow Pt + 2H_2O \quad \text{Eq. 5.4}
\]

Irrespective of the standard potential for either reaction, the reduction peak locations would follow a similar Nernst relationship such as:

\[
E = E^0 - \frac{RT}{2F} \ln \frac{1}{[H^+]^2} \quad \text{Eq. 5.5}
\]

The shifting of the peak of the second sweep compared to the first sweep of the CV is already shown in Figures 5.7 to 5.10. With T the temperature at 338 K, the potential would shift -72 mV per pH unit increase. The pH of the 0.63 M CuSO₄ was 3.5 while the 1.63 M H₂SO₄ / 0.63 M CuSO₄ electrolyte was below 0. With a change of over 3.5 pH units, the peak potential would move over 250 mV in the anodic direction. As shown in
Figure 4.55 the peak potential for the reduction of the Pt film is now in the range where Cu\textsuperscript{2+} reduction is occurring. Therefore, the reduction of the Pt oxyhydroxide is now only a small artifact for the onset of Cu\textsuperscript{2+} reduction.

5.2.1.3 Chloride and the Oxidation of Pt

The addition of Cl\textsuperscript{-} to the synthetic electrolyte was found to impact the Pt oxidation/reduction during typical cyclic voltammograms. Figure 5.11 and 5.12 are typical CVs for the synthetic electrolyte with and without 40 ppm Cl\textsuperscript{-}. The addition of Cl\textsuperscript{-} lowers the cathodic peak current for the peak associated with Pt oxyhydroxide reduction by 65 A/m\textsuperscript{2} and moves the position of the peak 70 mV more anodic. The Cl\textsuperscript{-} also suppresses the cathodic peak at roughly 110 mV vs. MSE for the 2\textsuperscript{nd} and higher sweeps compared to Cl\textsuperscript{-} free synthetic electrolyte as shown in Figures 5.11 and 5.12. Also for the electrolyte with 40 ppm Cl\textsuperscript{-} a wavy or 2 broad peaks at 20 and 25 mV for the 2\textsuperscript{nd} and higher scans became apparent in Figure 5.11.

The addition of Cl\textsuperscript{-} to the electrolyte, which only contained 1.63 M H\textsubscript{2}SO\textsubscript{4}, had a different behavior. The cathodic peak for the reduction of the Pt film was not substantially effected by the addition of Cl\textsuperscript{-} as shown in Figure 5.13 and 5.14. Only a slight decrease and anodic shift for the 2\textsuperscript{nd} to 4\textsuperscript{th} scans were detected, 10 A/m\textsuperscript{2} and 25 mV respectively.
Figure 5.11 Cyclic Voltammograms with the 1.15 V vs. MSE anodic pretreatment a) is a typical CV style and b) is the applied voltage and current density vs. the time from the start of the experiment. The experimental conditions were 0.63 M Cu$^{2+}$, 0.01 M H$_2$SO$_4$, Pt WE, Cu CE, 65° C, and 25 mV/sec.
Figure 5.12 Cyclic Voltammograms with the 1.15 V vs. MSE anodic pretreatment 
a) is a typical CV style and b) is the applied voltage and current density 
vs. the time from the start of the experiment. The experimental conditions 
were 0.63 M Cu^{2+}, 1.63 M H_2SO_4, Pt We, Cu CE, 65°C, and 25 mV/sec.
5.3 Voltammetry and the 2nd Harmonic Current Response with Guar

The 2nd harmonic response of the synthetic electrolyte with and without Cl\textsuperscript{−} and/or guar is complex. The different components of the DC, AC and 2nd harmonic AC voltammogram based on the components of the electrolyte were presented in 4.7.3. In this section, the final 2nd harmonic AC voltammogram for the electrolyte containing 40 g/l Cu\textsuperscript{2+}, 160 g/l H\textsubscript{2}SO\textsubscript{4} and 40 ppm Cl\textsuperscript{−} will be discussed in terms of practicality as a quantitative peak for guar. To begin with, the DC voltammogram for the synthetic electrolyte with different additives was relatively simple. These voltammograms contained only the Pt oxyhydroxide (5.2) surface reduction and copper reduction and subsequent oxidation, see Figures 4.51-4.59. The fundamental response was more complex but fewer complexities than the 2nd harmonic response. Figures 4.60 to 4.73 are the fundamental AC response for the stepwise introduction of different components of the synthetic electrolyte. What became evident in Figure 4.62 through 4.65 was the bisulfate and sulfate anions strongly impacted the voltammogram with the successive replacement of sulfate by bisulfate by most likely H\textsuperscript{+} on the surface as the potential became more cathodic. When the acid only AC voltammograms peak current values (over 10,000 A/m\textsuperscript{2}) were compared to the copper sulfate only solutions (just over 1,000 A/m\textsuperscript{2}), Figure 4.62 vs. 4.66, the majority of the AC response was from surface changes not associated with Faradaic processes. Subsequent comparison of the fundamental AC voltammogram of copper and acid with both the copper only and acid only voltammograms, strongly
Figure 5.13 Cyclic Voltammograms with the 1.15 V vs. MSE anodic pretreatment. a) is a typical CV style and b) is the applied voltage and current density vs. the time from the start of the experiment. The experimental conditions were 1.63 M H₂SO₄, Pt We, Cu CE, 65°C, and 25 mV/sec.
Figure 5.14 Cyclic Voltammograms with the 1.15 V vs. MSE anodic pretreatment
a) is a typical CV style and b) is the applied voltage and current density
vs. the time from the start of the experiment. The experimental conditions
were 1.63 M H₂SO₄, 40 ppm Cl⁻, Pt WE, Cu CE, 65°C, and 25 mV/sec.
indicates the copper acid combinations is mostly dependent on the acid. The major
difference is the peaks become more distinctive. However, the addition of Cl\(^-\) to the
electrolyte is substantially different for the acid and copper only compared to the
acid/copper combination. With acid only, the smaller more anodic peaks become
flattened as the charged Cl\(^-\) is most likely adsorbed on the surface. For the copper only,
the effect is more subtle with only a slight decrease in the baseline current between 0.75
and 0.00 V vs. MSE. With both copper and acid present, the addition of Cl\(^-\) distinctively
changes the peaks in the more cathodic region of the voltammogram. With these
statements in mind, the 2\(^{\text{nd}}\) Harmonic AC voltammograms may be qualitatively
explained.

5.3.1 Voltammogram Buildup

As discussed in 5.3, the acid only has substantially more components in the
voltammogram than the copper sulfate only voltammogram, Figure 4.76 and 4.80. In
fact, the copper sulfate has almost no second harmonic response. This is the opposite of
the DC response where the Faradaic copper reduction/oxidation was the dominant
process. Now that the acid is the more distinctive feature of the 2\(^{\text{nd}}\) harmonic AC
voltammogram, the need to think about the adsorption/desorption and other capacitive
process must be used in describing what is happening at the surface. From a capacitor
type approach, the things that can be changing to give a second harmonic must be
nonlinear. In dilute solutions this 2\(^{\text{nd}}\) harmonic is well characterized but is said to
disappear, as the electrolyte becomes more ionic [177]. However, there are distinctive
higher harmonics when working away from the ideal linear polarization typically used in AC voltammetry (i.e. 70mV RMS vs. <5 mV RMS).

Now consider the voltammogram shown in Figure 4.84, there is a distinctive change in the peaks when comparing this to the acid or copper only voltammogram. Most notable are the peaks prior to sweep reversal at −0.5 V vs. MSE. More important for the quantitative measurement of guar is the peak located between 0.0 to 0.5 V vs. MSE on the positive sweep portion of the voltammogram. The acid only 2\textsuperscript{nd} harmonic AC voltammogram, Figure 4.78 compared to 4.84, dominates this region of the voltammogram for the synthetic electrolyte. However with the addition of Cl\textsuperscript{−}, there is a considerable change in the acid/copper voltammogram compared to the acid only voltammogram. The acid only voltammogram shows the peak in this region is suppressed almost completely by the addition of Cl\textsuperscript{−}. However, the peak between 0.00 and 0.5 in the anodically sweeping portion is inverted when Cl\textsuperscript{−} is added to the acid/copper solution. It was found that 1 ppm started to depress this peak and completely inverted it without much change after 6 ppm Cl\textsuperscript{−}. Mechanistically, a complex with the sulfate/chloride and copper must be affecting this peak. Since the peak is small during the cathodically sweeping portion of the scan, the process is most likely inhibited by the oxy/hydroxy Pt surface. In fact, with repeated cycles of this voltammogram the first portion of the voltammogram from 0.5 to −0.25 V vs. MSE becomes similar to the anodically sweeping portion, as seen by looking at peak A in Figure 5.15. With the addition of guar, this peak is suppressed.
Figure 5.15 2\textsuperscript{nd} Harmonic Current Response for Synthetic Electrolyte Containing 40 ppm Cl\textsuperscript{-}. A pretreatment of 60 seconds at 1.15 V with a 70 mV RMS sinusoidal signal superimposed was applied prior to first scan. Peak A is the complimentary peak for the peak used for Guar measurement (i.e. on the Cathodic sweep).
The addition of guar to the 2nd harmonic voltammogram for copper sulfate increased the current response but minimized the more central peaks of the acid only voltammograms, Figure 4.78 and Figure 4.82. With the addition of Cl\(^-\), the response for copper sulfate only increased while the acid response was further suppressed, Figure 4.79 and 4.83. Now combining these observations it is concluded the mechanism that is causing the 2nd harmonic response is extremely complex with acid, sulfate, copper and Cl\(^-\) having overlapping effects. None the less, these interactions with guar can be used to quantitatively measure the concentration of guar in the electrolyte.

5.4 Nucleation of Copper with the addition of Galactosol (Guar)

The potential step study of the nucleation mechanism of copper on Pt showed little difference with the addition of galactasol. The current vs. time relationship can be used to characterize the nucleation mechanism as described in section 2.2. It must be emphasized that a change in the time dependence can suggest there is a change in nucleation and growth mechanism of the process. As with most nucleation models, there are limitations. In particular, these experiments are limited by impingement of the nuclei, surface condition of the WE, and in particular to the hardware used to collect the data. To minimize the problems of impingement, only the first portion of the increase region post induction will be used.

The time dependence of the current was found to correlate to \(t^{2/3}\) or \(t^2\). However, by comparing the correlation coefficient for the first part of the experiment, it was found
that there was significant difference in the correlation coefficient for both time
dependence and no improvement in either correlation coefficient if the time was
decreased. Significant noise was found in the potential step experiments. Even after
shielding, the noise in the first portion of the potential step experiments was a problem.
The main noise was from the method the data was collected. Since the Model 273
potentiostat was programmed via serial communication, it was found to be too slow and
noisy to use the autoranging current capability. Instead a single range was selected that
would not interfere with the data acquisition card. Optimally for the potentiostat, a lower
current setting would have been used. However, the data card had problems responding
to the spike from charging of the double layer at the beginning of the experiment. The
remaining noise is not bit level but is rather close with a range of 6-10 bits at the scale
used to eliminate recovery problems of the data acquisition card.

The duration of the experiment for each electrolyte was chosen separately. For
instance, the synthetic electrolyte with chloride had copper plating at a lower potential
than electrolytes without chloride and the current rose more rapidly. The comparison of
the different electrolyte's slope and correlation coefficient ($R^2$) for $t^{32}$ are shown in Table
5.2 and for $t^2$ in Table 5.3.
Table 5.2 Slope and Correlation Coefficients for Potential Step Experiments with time plotted as $t^{3/2}$.

<table>
<thead>
<tr>
<th>Potential mV vs. MSE</th>
<th>Electrolyte</th>
<th>Slope</th>
<th>Correlation Coefficient ($R^2$)</th>
<th>Duration, Secs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-355</td>
<td>SE*</td>
<td>0.110</td>
<td>0.860</td>
<td>1</td>
</tr>
<tr>
<td>-356</td>
<td>SE*</td>
<td>0.376</td>
<td>0.982</td>
<td>1</td>
</tr>
<tr>
<td>-354</td>
<td>SE* + 40 Cl$^-$</td>
<td>0.203</td>
<td>0.935</td>
<td>0.375</td>
</tr>
<tr>
<td>-355</td>
<td>SE* + 40 Cl$^-$</td>
<td>1.691</td>
<td>0.934</td>
<td>0.375</td>
</tr>
<tr>
<td>-356</td>
<td>SE* + 40 Cl$^-$</td>
<td>14.170</td>
<td>0.977</td>
<td>0.375</td>
</tr>
<tr>
<td>-354</td>
<td>SE* + 40 Cl$^-$ + 5 guar</td>
<td>0.013</td>
<td>0.974</td>
<td>1</td>
</tr>
<tr>
<td>-355</td>
<td>SE* + 40 Cl$^-$ + 5 guar</td>
<td>0.103</td>
<td>0.850</td>
<td>1</td>
</tr>
<tr>
<td>-356</td>
<td>SE* + 40 Cl$^-$ + 5 guar</td>
<td>0.523</td>
<td>0.953</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 5.3 Slope and Correlation Coefficients for Potential Step Experiments with time plotted as $t^2$.

<table>
<thead>
<tr>
<th>Potential mV vs. MSE</th>
<th>Electrolyte</th>
<th>Slope</th>
<th>Correlation Coefficient ($R^2$)</th>
<th>Duration, Secs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-355</td>
<td>SE*</td>
<td>0.109</td>
<td>0.859</td>
<td>1</td>
</tr>
<tr>
<td>-356</td>
<td>SE*</td>
<td>0.373</td>
<td>0.982</td>
<td>1</td>
</tr>
<tr>
<td>-354</td>
<td>SE* + 40 Cl$^-$</td>
<td>0.203</td>
<td>0.945</td>
<td>0.375</td>
</tr>
<tr>
<td>-355</td>
<td>SE* + 40 Cl$^-$</td>
<td>1.697</td>
<td>0.978</td>
<td>0.375</td>
</tr>
<tr>
<td>-356</td>
<td>SE* + 40 Cl$^-$</td>
<td>7.724</td>
<td>0.996</td>
<td>0.375</td>
</tr>
<tr>
<td>-354</td>
<td>SE* + 40 Cl$^-$ + 5 guar</td>
<td>0.030</td>
<td>0.980</td>
<td>1</td>
</tr>
<tr>
<td>-355</td>
<td>SE* + 40 Cl$^-$ + 5 guar</td>
<td>0.103</td>
<td>0.861</td>
<td>1</td>
</tr>
<tr>
<td>-356</td>
<td>SE* + 40 Cl$^-$ + 5 guar</td>
<td>0.525</td>
<td>0.993</td>
<td>1</td>
</tr>
</tbody>
</table>

No significant difference was found between the correlation coefficients for $t^2$ and $t^{3/2}$ as seen from comparing their values in Table 5.2 and 5.3. The role of chloride in the nucleation of Cu on SS316 was previously found not to influence the mechanisms. [83]
Similar results were found here with an increase in current and a i.e. depolarization by the addition of chloride but did not a change in the mechanism. Galactosol was also found not to influence the mechanism of copper nucleation and growth on platinum with low over potential..

From a visual inspection of the graphs, Figure 5.16 through 5.18, $t^{3/2}$ appears to have a better fit based on curvature for all of the electrolytes studied. This was not supported by the two different correlation coefficients. Similarly Sun and O'Keefe [83] reported the same time dependence for copper, copper and chloride and with glue. However, the conditions were extremely different than what were reported here. An improvement in the correlation and or distinction between $t^{3/2}$ and $t^2$ was not found through a range of time scales. The times chosen were selected because any decrease in the time range would not result in improvement in $R^2$ for either time dependence. From a mechanistic perspective, $t^{3/2}$ indicates a diffusion controlled 3D progressive mechanism, equation 2.16. If $t^2$ were accepted as the dependence one of the two kinetic control models given in section 2.2 would be indicated [83]. The data collected in this work does not conclusively support either model but does indicate that no mechanistic change occurred with the addition of guar or chloride.
Figure 5.16 Potential step current response for the synthetic electrolyte at -355, -356, -357 mV vs. MSE at 65°C plotted as a function of $t^{3/2}$. 
Figure 5.17 Potential step current response for the synthetic electrolyte with 40 ppm Cl\(^-\) at -355, -356, -357 mV vs. MSE at 65°C plotted as a function of \(t^{1/2}\).
Figure 5.18 Potential step current response for the synthetic electrolyte with 40 ppm Cl\(^-\) and 5 ppm Guar at -355, -356, -357 mV vs. MSE at 65°C plotted as a function of \(t^{3/2}\).
Figure 5.19 Potential step current response for the synthetic electrolyte -355, -356, -357 mV vs. MSE at 65°C plotted as a function of $t^2$. 

\[ y = 0.3758x + 1.9231 \quad R^2 = 0.982 \]

\[ y = 0.1097x + 1.5512 \quad R^2 = 0.8601 \]

\[ y = 0.0293x + 1.3345 \quad R^2 = 0.2655 \]
Figure 5.20 Potential step current response for the synthetic electrolyte with 40 ppm Cl\textsuperscript{−} at -355, -356, -357 mV vs. MSE at 65°C plotted as a function of t\textsuperscript{2}. }

\[ y = 14.173x + 3.8956 \quad R^2 = 0.9766 \]
\[ y = 1.6909x + 3.0517 \quad R^2 = 0.9342 \]
\[ y = 0.2032x + 1.9386 \quad R^2 = 0.9454 \]
Figure 5.21 Potential step current response for the synthetic electrolyte with 40 ppm Cl\(^-\) and 5 ppm Guar at -355, -356, -357 mV vs. MSE at 65°C plotted as a function of \(t^{1/2}\).
6. CONCLUSIONS

The role of glue, thiourea and chloride in copper electorefining is of considerable importance. Without these additives, the efficient production of high purity copper efficiently would not be attainable. The emphasis of this work was to examine the methods for effectively monitoring these additives in the electrolyte. The work has proven useful in a more fundamental sense. First, the actions of the additives are very much interrelated. At times, the effect was synergistic. For instance, the significant increase in the polarization with glue, thiourea and chloride present was extremely different when the three worked in conjunction. One can envision that the thiourea enhanced the nucleation of copper [83] while chloride enabled the glue to adsorb onto the protruding nuclei created by the thiourea which would in turn inhibit (level) the deposit. Each additive could and most likely had other effects on the growing deposit. However, a base assumption would be there should be some sort of ratio of the additives to maintain a good deposit.

Guar or galactosol is used instead of glue in electrowinning because of multitude of upstream process issues. The galactosol has several effects on the deposition of copper. [101] [100] Methods to monitor this additive have just recently been reported [95] but may suffer several disadvantages. The main disadvantage is that any component in the electrolyte that can inhibit copper and has a different transport rate to the surface of the measuring electrode will alter the reading. The use of 2nd harmonic AC voltammetry allows one to select different peaks that may not be affected by dragout of chemicals.
from, i.e. the SX facility upstream from EW. However, this main advantage is also major set back since each facility will have a different chemistry that would most likely entail recalibration, reoptimization, and even selection of different peaks all together.

The main points of this work are summarized below.

• Chronopotentiometry is not effective for determining guar levels.
• Simple striping time analysis is not suitable for commercial electrolytes.
• The polarization from glue in the absence of chloride was minimal.
• The initial polarization by thiourea occurred with or without chloride and/or glue.
• Fundamental AC Voltammetry with Phase Sensitive Detection was capable of detecting low levels of glue.
• Optimization for each electrolyte used in industry is required.
• 2F AC voltammetry (tensammetry) is capable of monitoring Galactasol at the desired levels.
• The peak of interest for determining Galactasol is dependent on the total electrolyte makeup.
• Reproducibility is greatly dependent on the Pt WE and the preconditioning steps.
• Solution flow enhances the sensitivity of AC voltammetry to Galactasol.

The following points can summarize future work needing to be examined;

• Assembly and field testing of a portable system.
• Optimization of the pretreatment for WE.
- Surface Enhanced Raman Spectroscopy to determine role the surface active species have on the reduction of copper.
- Studies Co, Mn and Fe effect on on the 2F AC Voltammetric peaks.
- Possibility of a mathematical model for the system?
7. APPENDIX

This section contains the diagrams for the Labview Programs that were used to collect and partially analyze the data collected for the AC voltammetry and potential step experiments. This code is designed to use RS-232 control of the Model 273 potentiostat/galvanostat combined with a data acquisition card that has at least 3 analog inputs and 8 bit digital outputs. Because of the flexibility of the Labview platform, this code could easily be ported to platforms other than Windows 95 and any National Instrument data acquisition card. Unlike C or Basic, this code is not lines of code but icons representing subroutines and icons representing specific operations. The following printouts are the programs and subroutines that were created for this work. Other subroutines not printed here are standard in the Labview programming package.

7.1 AC voltammetry with auto control of stirring and conditioning

The program listed here will setup the potentiostat and run the AC voltammetry experiments including stirring, pretreatment, rest and data collection. This program does not allow changes to the potential from the front panel but can be changed in the subroutines. The data is stored from the Model 273 in a circular buffer and then streamed to a file in a spreadsheet compatible format. The program was constructed in Laview version 4.0 and run with a PC based system with an Pentium 166 MMX processor. The
program is capable of running on 16 Mbytes of RAM but was found to perform without delays using 32 Mbytes.
Default settings: 4800 Baud, 7 bits, 1 stop bit, no parity, XON/XOFF on

**Readings**

**Error Code**

- 0

**COM Port**

- 1

**baud rate**

- 4800

**data bits**

- 7

**Stop bits**

- 1 bit 0

**parity**

- no parity 0

**buffer size**

- 1024

**flow control etc.**

- input XON/XOFF
- input HW Handshake
- input alt HW HShk
- output XON/XOFF
- output HW Handshak
- output alt HW HShk

**XOFF byte**

- 13

**XON byte**

- 11

**parity error byte**

- 0
EXTERNAL SIGNAL TO BE ADDED TURNED ON

COM Port

KEY 46

Readings

750

Error Code
DELAY FOR 273

KEY 9; KEY 14; KEY 29; KEY 38; KEY 33; KEY 14; KEY 29; KEY 38

E/I APPLIED SET FOR 273

KEY 15; KEY 3; KEY 6; KEY 3; KEY 12; KEY 38
### Readings

<table>
<thead>
<tr>
<th>Current Range</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 No Filter</td>
</tr>
<tr>
<td>1</td>
<td>1 Low Pass</td>
</tr>
<tr>
<td>2</td>
<td>Potentiostat/Galvanostat</td>
</tr>
<tr>
<td>3</td>
<td>Measure Only</td>
</tr>
<tr>
<td>4</td>
<td>1 Galvanostat</td>
</tr>
<tr>
<td>5</td>
<td>2 Potentiostat</td>
</tr>
<tr>
<td>6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>COM Port</th>
<th>Single or Continuous</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>CONTINUOUS</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Error Code</th>
<th>0</th>
</tr>
</thead>
</table>

### Flow Control etc.

- Baud rate: 4800
- Data bits: 7
- Stop bits: 1
- Parity: 0
- Buffer size: 1024

### Communication Settings

- Input XON/XOFF
- Input HW Handshake
- Input alt HW HShk
- Output XON/XOFF
- Output HW Handshake
- Output alt HW HShk

### Parity Error

- XOFF byte: 13
- XON byte: 11
- Parity error byte: 0
SERIAL PORT INITIALIZE

- Buffer size
- Flow control etc.
- Baud rate
- Data bits
- Stop bits
- Parity

1 [0..9]

50
SELECT POTENTIOSTAT/GALVANOSTAT

SET MODE
HIGH STABILITY OR HIGH SPEED
<table>
<thead>
<tr>
<th>Command</th>
<th>273 COMMAND</th>
</tr>
</thead>
<tbody>
<tr>
<td>COM Port</td>
<td>1</td>
</tr>
<tr>
<td>Error Code</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Baud Rate</th>
<th>4800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Bits</td>
<td>7</td>
</tr>
<tr>
<td>Stop Bits</td>
<td>1</td>
</tr>
<tr>
<td>Parity</td>
<td>0</td>
</tr>
<tr>
<td>Buffer Size</td>
<td>1024</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow Control etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input XON/XOFF</td>
</tr>
<tr>
<td>Input HW Handshake</td>
</tr>
<tr>
<td>Input alt HW HShk</td>
</tr>
<tr>
<td>Output XON/XOFF</td>
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<tr>
<td>XOFF byte</td>
</tr>
<tr>
<td>XON byte</td>
</tr>
<tr>
<td>Parity error byte</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>
COM Port

273 Command

Error Code
7.2 Program to control Potential Step Experiments

The potential step program was set up to run sequential potential step experiments. Once the starting value was entered on the front panel, the program will run from the starting potential and increment the potential by one mV until the numbers of cycles are completed. Each potential will be saved as a spreadsheet file that is named at the start of program execution and a suffix automatically incremented to distinguish which potential the data collected at. The program allows for a preconditioning step of the WE as well as solution stirring. A rest period is also completely selectable by the operator. A prestep potential is also available to minimize the charging current from the WE pretreatment. Again the data is stored in a buffer and then streamed to the hard drive as a spreadsheet.
7.3 Program for Analysis of Labview Data

The program listed below will take any Labview saved data for the potential step or AC voltammetry experiments and display it in graphical format as well as give pertinent information about any peaks in the voltammogram. There are cursors set up to place at the start of each scan and then the other cursors are locked to the appropriate data. As the cursor is slid to the peaks, both the peak position and peak size is outputted to the screen.
On each loop iteration, read the requested number of scans (each one less in the file), then plot the results. On the next iteration, display the number of channels supported.

Read the scan rate (first number of each line in the file) and set a scale value of the chart before starting the loop.
8. REFERENCES


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126. Bai, L. and B.E. Conway, *AC impedance of faradaic reactions involving electrosorbed intermediates: Examination of conditions leading to pseudoinductive behavior represented in three-dimensional impedance...*


