PASSIVATION OF COPPER IN ALKALINE CHLORIDE SOLUTIONS

by

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We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

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ABSTRACT

Using polarization and impedance studies, the breakdown of passive films on copper in buffered alkaline sodium chloride was found to be caused by a loss of pH control at the metal surface. The loss of pH control was still observed when there was sufficient buffer species present to neutralize the total protons generated from the aqueous corrosion of copper. This indicates that the loss of pH control is a localized phenomenon. At the onset of passive film breakdown film defects were detected with the use of impedance modeling. The production of protons that accompany the local corrosion of copper to form HCuO₂⁻ ions at these defect sites consumes all the conjugate base buffer species at the defects. The ensuing drop in local pH has a detrimental effect on the remaining oxide layer. The local acidic condition causes the precipitation of CuCl and hence prevents re-passivation.

Impedance modeling was successful in determining the thickness of the passive film in-situ. The passive film thickness was determined to be in the range of 7.0Å to 108.8Å, which is in line with published values from ex-situ XPS studies. The impedance modeling was also successful in identifying film defects at the onset of passive film breakdown.
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ACKNOWLEDGEMENTS

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1 INTRODUCTION

The corrosion resistance of copper in alkaline solutions is dependent upon the formation of an electrochemically generated film of oxide or hydrated oxide. This film promotes passivity by acting as a diffusion barrier between the metal surface and the environment, thus impeding the corrosion kinetics. The quality of the protection provided by a passive film depends on its physical characteristics. A desirable passive film is stable, adherent, and relatively defect free. Under certain conditions a passive film is prone to breakdown and undergoes dissolution, thereby accelerating the corrosion rate of the metal substrate.

The anodic behavior of copper in alkaline solutions has been the subject of numerous studies.$^{1-17}$ It is well established that the corrosion resistance of copper is dependent on the presence of a cuprous and cupric oxide (hydroxide) passive film. A review of recent publications has shown that the stability of the passive layer in alkaline solutions may be decreased by complexing agents and enhanced by buffer species.

Copper is widely used and readily available in very pure form. As such, the passivation of copper in alkaline solutions represents a model situation for the study of passivation in general. Examining the mechanisms of passive film formation, growth, and breakdown on copper in alkaline solutions may lead to practical solutions in preventing corrosion of metals and alloys that result from the breakdown of passive films.
2 LITERATURE REVIEW

2.1 THERMODYNAMICS

Thermodynamic studies on the stability of metals in aqueous solutions was pioneered by Pourbaix via the construction of potential (E) - pH diagrams based on thermodynamic free energy data. These diagrams are useful in predicting the predominant stable species at a given E and pH. As such, it is easy to predict as a first approximation whether the metal will be immune, corrode, or passivate under certain conditions. Given the thermodynamic data listed in Table 2.1, the E-pH diagram for copper in water as prepared by Pourbaix is shown in Figure 2.1. This diagram shows that Cu\textsubscript{2}O and CuO are predominant in the pH ranges that are slightly acidic to slightly alkaline. Aqueous H\textsubscript{2}CuO\textsubscript{2}\textsuperscript{-} ions can co-exist with Cu\textsubscript{2}O and CuO at a slightly alkaline pH. A simple diagram depicting the regions of immunity, corrosion, and passivation is shown in Figure 2.2. It is important to note that E-pH diagrams are only a guide to predicting passivation. The thermodynamic diagrams do not take into account kinetics or possible differences in local solution chemistry at the metal surface.
<table>
<thead>
<tr>
<th>SPECIES</th>
<th>$\Delta G^0$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Cu}_2\text{O}$</td>
<td>-146.4</td>
</tr>
<tr>
<td>CuO</td>
<td>-127.2</td>
</tr>
<tr>
<td>$\text{Cu}^+$</td>
<td>50.2</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}$</td>
<td>65.0</td>
</tr>
<tr>
<td>H$\text{CuO}_2^-$</td>
<td>-257.0</td>
</tr>
<tr>
<td>$\text{CuO}_2^{2-}$</td>
<td>-182.0</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-228.6</td>
</tr>
</tbody>
</table>
Figure 2.1 E-pH Diagram for Copper in Water at 25 °C (V = V_HRE, Standard Hydrogen Reference Electrode)\textsuperscript{18}.
Figure 2.2 E-pH Diagram for Copper Showing Regions of Corrosion, Passivation, and Immunity at 25°C.
2.2 PASSIVE FILM CHARACTERISTICS

It is generally agreed that the passive film on copper consists of a duplex structure of Cu$_2$O and CuO or Cu(OH)$_2$. According to Sato a less protective Cu$_2$O exists adjacent to the metal which is encapsulated with a more protective CuO or Cu(OH)$_2$ barrier layer as shown in Figure 2.3$^{19}$. Numerous potentiostatic studies have shown the presence of two passive states corresponding to the anodic formation of Cu$_2$O and CuO or Cu(OH)$_2$.$^{1,6,8,10-14,16,20-23}$ For example, the polarization curve of copper in a pH 11 solution buffered with borate (shown in Figure 2.4) shows an anodic peak of -0.26Vsse (silver/silver chloride/saturated potassium chloride reference electrode) corresponding to Cu$_2$O formation and an anodic peak at -0.03 Vsse corresponding to Cu(OH)$_2$ formation$^6$. Voltametric studies have shown that a thin layer of Cu$_2$O forms initially. This is followed by growth of a thicker Cu$_2$O layer and then followed by growth of the CuO-Cu(OH)$_2$ layers.$^{5,11}$

![Figure 2.3 Illustration of a Passive Film on Copper$^{19}$.](image)
Figure 2.4 Polarization Curve of Copper at pH 11 Buffered with Borate.
Shirkhanzadeh et al describe the initial stages of passivation in terms of nucleation and growth processes. Discrete nuclei of Cu(I) species form on the surface, followed by the growth and coalescence of the Cu(I) surface nuclei to produce the initial Cu$_2$O monolayers$^{15}$. In-situ spectroelectrochemical studies by Pyun et al have shown that hydroxides of Cu(I) and Cu(II) are first formed by anodic oxidation and then transformed to oxides upon aging$^2$. Studies by Marchiano et al revealed that at least three different Cu(I) species are formed during Cu$_2$O formation. The first is a soluble Cu(OH)$_2$ species, followed by aging to Cu(OH), followed by further aging to Cu$_2$O$^3$. Laz et al determined that growth of the CuO oxide occurs via electrodissolution of and diffusion of Cu species through the passivating layer$^{20}$. This mechanism was also confirmed by Drogowska et al$^4$. In addition, they found that the duplex film exhibits logarithmic growth kinetics$^{20}$.

Photopotential studies on the passive film have shown that the Cu$_2$O behaves like a p-type semiconductor (with the presence of electron-holes in the lattice) and CuO behaves like an n-type semiconductor (with excess electrons in the lattice). As such, CuO has a higher electrical conductivity than Cu$_2$O$^{20,25}$.

X-ray photoelectron spectroscopy (XPS) studies of anodically formed oxides in an alkaline medium (Kautek et al) showed the presence of the dual Cu$_2$O and Cu(OH)$_2$ layers of a combined thickness of 40 Å to 60 Å$^{23}$. XPS studies on air formed oxides on copper (Chawla et al) have shown a dual oxide structure in the range of 24 Å thick$^{26}$.

Gravimetric, optical interference, and electrometric studies on air formed oxides have
shown that a visible discoloration is observed once the film thickness exceeds a range of 190 Å to 380 Å\textsuperscript{36}.

2.3 EFFECT OF HALIDES

Numerous studies have shown that the presence halides adversely affects the passive film. Thermodynamic calculations conducted by Tromans et al have shown that soluble copper chloride complexes can prevent passivation. The E-pH diagram depicting the predominant species in the presence of copper, chlorine, and water is shown in Figure 2.5\textsuperscript{27}. This diagram clearly shows that the formation of soluble CuCl\textsubscript{2} complexes and non protecting CuCl decreases the stability region of Cu\textsubscript{2}O and CuO.
Figure 2.5 Cu-Cl-H$_2$O Equilibria at 25°C in the Presence of 0.67 Activity of Cl$^-$ Ions. Situation Equivalent to 1M NaCl$^{27}$. 
Drogowska et al found that the presence of sodium chloride in an alkaline solution has an adverse effect on the passive film by increasing the solubility of the passive film and promotes dissolution. Formation of the more soluble cuprous chloride (CuCl) or cupric chloride (CuCl\(_2\cdot3\text{Cu(OH)}_2\)) suggests that the copper oxide/solution interface becomes acidic during dissolution as shown in Figure 2.5\(^{10,27}\). Nishikata et al found that a concentration of greater than 0.5M chloride ions caused pitting corrosion in an alkaline pH 11 solution. This pitting corrosion was attributed to a decrease in the stability of the passive film\(^{6}\). Elser et al found that the formation of sub-monolayer halide complexes prior to the formation of Cu\(_2\)O and CuO has a detrimental effect on passivity. In addition, fluoride complexes were found to have the most detrimental effect on passivity. This is followed by chloride complexes, bromide complexes, and then iodide complexes\(^{17}\).

Pitting investigations by Souto et al showed that pit initiation on copper begins via a random nucleation on the Cu surface in the presence of NaClO\(_4\)\(^{14}\). It was also found that chloride ions hinder the performance of inhibitors\(^{4}\).

\[ \text{SO}_4^{2-} \text{ is an aggressive ion to copper. In the presence of an inhibitor, adsorption of the sulfate ions on the surface of the copper competes with the adsorption of the inhibitor}^{12}. \text{ Souto et al discovered that the presence of Na}_2\text{SO}_4 \text{ causes defects in the passive film, and hence, promotes dissolution of copper through the passive layer}^{13}. \text{ Potentiodynamic studies by Al-Kharafi et al found that sulfate} \]
ions were less aggressive than chloride ions. Thermodynamic calculations conducted by Tromans et al showed that the presence of ammonia decreases the stability region of CuO via the formation of a Cu(NH₃)₆²⁺ ion. Studies conducted by Kinoshita et al showed that copper is more susceptible to pitting in the presence of NO₃⁻ ions.

2.5 EFFECT OF BUFFER SPECIES

Studies involving bicarbonate buffers have been contradictory. Most studies have found that HCO₃⁻ enhances passivation whereas others have shown that HCO₃⁻ is detrimental to passivation. Milosev et al found that the presence of a HCO₃⁻ buffer has an inhibitor effect on copper and resists attack of aggressive anions via a competition mechanism. Studies by Drogowska et al found that concentrations of greater than 0.05M NaHCO₃ improve the resistance of copper to localized corrosion. Similarly Sanchez et al found that passivation is enhanced via the formation of copper carbonates in which the structure is dependent upon the HCO₃⁻ concentration. Tromans et al found that a higher concentration of a buffer species promote resistance to passive film breakdown by neutralizing surface protons generated by the film forming process. Studies have also indicated that Na₂CO₃ enhances the passive film better than NaHCO₃. In addition, high fluid velocities at the copper surface enhances passivation. On the contrary, studies conducted by Adeloju et al found that the initial formation of copper carbonates competes with the formation of Cu₂O and, as a result, has a detrimental effect.
on passivation\textsuperscript{7,21}. Studies by Nishikata et al have found that the stability of the passive layer is lowered by the presence of carbonate ions\textsuperscript{6}.

There is general agreement that the presence of phosphate or borate buffers enhances passivation. Drogowska et al found that a high phosphate to chloride ratio results in the formation of a thin protective layer whereas a high chloride to phosphate ratio results in the precipitation of a thick porous deposit on the surface\textsuperscript{29}. Laz et al found that phosphate ions enhance passivation via the formation of a protective copper phosphate species on the surface\textsuperscript{20}. Studies conducted by Al-Kharafi et al found that phosphate ions promote resistance of copper to aggressive anions such as sulfates, chlorides, and iodides\textsuperscript{9}. De Chialvo et al found that borate buffers inhibit the formation of CuCl during pit growth\textsuperscript{8}. 
Although there have been many studies conducted on copper in alkaline solutions, very few studies have been devoted to examining the mechanism of passive film formation, growth, and breakdown. This thesis is directed toward applying a combination of traditional and novel electrochemical techniques to determine the mechanisms of passive film breakdown. Polarization studies conducted in solutions of different buffer concentrations and under different fluid flow rates (via a rotating disk electrode) will provide clues on how changes in surface pH affect passive film breakdown. In addition, the use of AC impedance spectroscopy will allow the characteristics of the passive film to be modeled. As such, the film characteristics during film formation, growth, and breakdown can be determined in-situ. There have been no publications to date on the use of AC impedance spectroscopy to examine passivation of copper in alkaline solutions.
4 EXPERIMENTAL

4.1 SOLUTION PREPARATION

All test solutions were prepared from reagent grade chemicals and distilled water. Alkaline 1M sodium chloride test solutions were prepared in 1L batches by adding 58.45 grams of sodium chloride and the required buffer agent into a beaker and bringing the total volume to 1L with distilled water. For solutions buffered with sodium carbonate and sodium bicarbonate a molar ratio of 1.45 sodium carbonate to sodium bicarbonate was added to bring the pH to near 10.5. For example, for a desired 0.01M buffer concentration, 0.7316 grams of sodium carbonate monohydrate (molecular weight of Na₂CO₃.H₂O of 124.00 g/mole) and 0.3444 grams of sodium bicarbonate (molecular weight of NaHCO₃ of 84.01 g/mole) would be added. For the solutions buffered with sodium tetraborate, 3.8142 grams of Na₂B₄O₇ (molecular weight 381.42 g/mole) would bring the solution to a 0.01M buffer concentration.

The pH measurements were conducted via a two point calibrated Corning Model 125 pH meter with a combination glass pH electrode. Measured pH values of the prepared solutions were generally up to 0.3 pH value below 10.5 for solutions buffered with sodium carbonate and sodium bicarbonate, and up to 1.8 pH value below 10.5 for solutions buffered with sodium tetraborate. Further pH adjustments were made with small
incremental additions of 1M sodium hydroxide until a stable reading of pH 10.5 ± 0.05 was achieved. A list of the test solutions used in this research is shown in Table 4.1.

Table 4.1 List of Test Solutions

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>NaCl (M)</th>
<th>Na₂CO₃ (M)</th>
<th>NaHCO₃ (M)</th>
<th>Na₂B₄O₇ (M)</th>
<th>Total Buffer Concentration (M)</th>
<th>pH</th>
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<td>1</td>
<td>1</td>
<td>0.0059</td>
<td>0.0041</td>
<td>0.010</td>
<td></td>
<td>10.5</td>
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<td>0.0204</td>
<td>0.050</td>
<td></td>
<td>10.5</td>
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<td>0.0592</td>
<td>0.0408</td>
<td>0.100</td>
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<td>4</td>
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<td>0.2959</td>
<td>0.2041</td>
<td>0.500</td>
<td></td>
<td>10.5</td>
</tr>
<tr>
<td>5</td>
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<td></td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td>10.5</td>
</tr>
<tr>
<td>6</td>
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<td>0.010</td>
<td></td>
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</tr>
<tr>
<td>7</td>
<td>1</td>
<td></td>
<td>0.050</td>
<td>0.050</td>
<td></td>
<td>10.5</td>
</tr>
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</table>

4.2 SAMPLE PREPARATION

Rotating disk electrode test specimens were prepared by machining copper blocks of greater than 99.96% purity to 11.3 mm diameter and 2 mm thickness disks. Each disk was subsequently mechanically polished to a 600 grit finish to ensure consistency of the surface finish. Prior to each test a disk was partially inserted into a recessed Teflon disk holder supplied with the EG&G model 616 rotating disk electrode. The Teflon disk holder was then turned over, rested on a flat Teflon block and pressed until the disk was perfectly flush with the rim. The spring loaded contact was connected to the back of the test specimen and the sample holder was connected to the main body of the rotating disk electrode as shown in Figure 4.1.
A = DISK
B = DISK HOLDER
C = O-RINGS
D = MAIN BODY
E = SPRING
F = CONTACT STUD
G = SPINDLE
H = SPINDLE COVER

Figure 4.1 Assembly of the Rotating Disk Electrode Specimen
4.3 ELECTROCHEMICAL CELL SET-UP

The 750 mL Teflon electrochemical cell consisted of five pre-drilled inlets for the rotating disk electrode, two platinum mesh counter electrodes, a saturated calomel reference electrode (sce), and a nitrogen purge tube. The test set-up is shown in Figure 4.2.

Figure 4.2 Electrochemical Cell Set-Up
4.4 POLARIZATION SCAN TECHNIQUES

Polarization scans were conducted with the Solartron 1280 potentiostat, which was connected to an MS-DOS personal computer via a GPIB-488 interface. Software was written in Microsoft Quickbasic to control the Solartron 1280 and to acquire data from the experiments. Prior to each test, the rotation speed of the electrode was set from the front control panel. Nitrogen purging was conducted for 30 minutes to remove dissolved oxygen from the cell. The working electrode was then polarized at a potential of -0.9 V vs. SCE for 30 minutes to reduce the air-formed oxide. The potential was then swept from -0.9 V vs. SCE to +0.9 V vs. SCE at a scan rate of 1 mV per second. The control software is listed in Appendix I.

4.5 AC IMPEDANCE SCAN TECHNIQUES

AC impedance scans were conducted with the combination of the Solartron 1280 potentiostat and the Solartron 1250 frequency response analyzer. The Solartron 1280 was used to polarize the test specimen to the desired test potential, whereas the Solartron 1250 was used to apply an external ±10 mV sinusoidal potential over a frequency sweep such that the impedance could be measured. Both instruments were connected to an MS-DOS personal computer via a GPIB 488 interface and software was written in Microsoft Quickbasic to control the impedance experiments and to acquire the impedance data. Prior to each test, the rotation speed of the electrode was set from
the front control panel. Nitrogen purging was conducted for 30 minutes to remove dissolved oxygen from the cell. The working electrode was then polarized at a potential of -0.9 V SCE for 30 minutes to reduce the air formed oxide. The potential was then stepped to -0.4 V SCE and held at this potential for 5 minutes to allow the cell to stabilize. A ±10 mV sinusoidal potential was then superimposed over the polarization potential and impedance measurements were made over a frequency sweep from 65535 Hz to 0.1 Hz. Impedance scans were conducted at a range of polarization potentials from -0.4 V SCE to 0.5 V SCE at 0.1 V increments. A control software program for the impedance experiments is listed in Appendix II.

4.6 ROTATION SPEEDS

All polarization and AC impedance experiments were conducted at both 50 RPM and 5000 RPM. These rotation speeds were selected because the diffusion layer thickness is proportional to the inverse square root of rotation speed$^{34}$, and as such, the diffusion layer thickness would be changed by a factor of 10.
5 RESULTS

5.1 POLARIZATION STUDIES

The general polarization curve of copper in a sodium chloride media buffered to an alkaline pH is characterized by several distinct regions as shown schematically in Figure 5.1. At the beginning of the potential sweep below the corrosion potential ($E_{corr}$) (Region I), species in the aqueous solution are reduced. Protons are reduced to hydrogen gas and trace oxygen (not removed from nitrogen purging) is reduced to water. The electrochemical reactions for the reduction of protons and oxygen are as follows:

$$2H^+ + 2e^- \rightarrow H_2$$  \hspace{1cm} 5.1

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$  \hspace{1cm} 5.2

Region II directly above $E_{corr}$ is where copper actively corrodes as per the following reaction:

$$Cu \rightarrow Cu^+ + e^-$$  \hspace{1cm} 5.3
Following the active corrosion regime, a fairly noticeable active-passive transition occurs (Region III). This has been observed in all polarization scans in this work under the specified conditions. After Region III, passivation occurs (Region IV). This is characterized by a sudden decrease in current (or corrosion rate) and is due to the formation of a thin, adherent oxide which acts as a diffusion barrier between the copper metal and the solution. The passive region contains a small peak (IV). From a review of published findings, it is determined that the transition peak (III) corresponds to the formation of Cu₂O and peak (IV) corresponds to the anodic formation of CuO or Cu(OH)₂. Possible passivation reactions are as follows, where Equation 5.4 represents peak III, and 5.5 and 5.6 correspond to peak IV.

\[
\begin{align*}
2\text{Cu} + \text{H}_2\text{O} &\rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^- & \text{5.4} \\
\text{Cu} + \text{H}_2\text{O} &\rightarrow \text{CuO} + 2\text{H}^+ + 2\text{e}^- & \text{5.5} \\
\text{Cu} + 2\text{H}_2\text{O} &\rightarrow \text{Cu(OH)}_2 + 2\text{H}^+ + 2\text{e}^- & \text{5.6}
\end{align*}
\]

With increasing potential, the pitting potential (Eₚᵣᵢ₉) is reached. This is characterized by a sudden increase in current which is representative of passive film breakdown. Eₚᵣᵢ₉ is an important value in this study because it relates to the ability of the passive film to resist breakdown. A higher Eₚᵣᵢ₉ value represents a higher resistance to film breakdown, whereas a lower Eₚᵣᵢ₉ value represents a lower resistance to film breakdown. The transpassive
regime at the high potentials (Region V) characterized by a diffusion controlled mechanism represents the formation of a non-protective precipitate or film.

Figure 5.1 Typical Polarization Curve for Copper in 1M NaCl in a Buffered Alkaline Solution.

The polarization behavior of copper in a 1M sodium chloride media buffered to an alkaline pH was studied under several conditions. The effects of buffer type, concentration, and rotation speed with a rotating disk electrode were studied. The results are shown in the following sections.
5.1.1 POLARIZATION BEHAVIOR - EFFECT OF BUFFER TYPE

The effects of buffer type are shown on the polarization curves in Figures 5.2 to 5.5. Polarization experiments were conducted in 1M sodium chloride with identical concentrations of either a sodium bicarbonate/carbonate buffer or a sodium tetraborate buffer at identical rotation speeds. Each polarization curve of copper in a 1M sodium chloride solution buffered with either sodium bicarbonate/carbonate or sodium tetraborate exhibited some form of passivation. Under identical test conditions, there was very little difference in the shape of the polarization curve between the sodium bicarbonate/carbonate buffer and the sodium tetraborate buffer. Other than the fact that the sodium bicarbonate/carbonate buffered solution continually had a higher corrosion potential than the sodium tetraborate buffered solutions, there was very little difference in the pitting potentials or the passive current densities. The higher corrosion potential for the solutions buffered with sodium bicarbonate/carbonate may be attributed to a small amount of carbon dioxide formation via Equation 5.7. Data of the corrosion potentials, pitting potentials, and the passive current densities are summarized in Table 5.1. The polarization data was reproducible as repeated experiments yielded near identical results.

\[ \text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]  

5.7
Figure 5.2 Polarization Curve of Copper in 1M NaCl, Rotating at 50 RPM, Buffered to pH 10.5 with (1) 0.01M Sodium Bicarbonate/Carbonate, and (2) 0.01M Sodium Borate at 23°C.
Figure 5.3 Polarization Curve of Copper in 1M NaCl, Rotating at 5000 RPM, Buffered to pH 10.5 with (1) 0.01M Sodium Bicarbonate/Carbonate, and (2) 0.01M Sodium Borate at 23°C.
Figure 5.4 Polarization Curve of Copper in 1M NaCl, Rotating at 50 RPM, Buffered to pH 10.5 with (1) 0.05M Sodium Bicarbonate/Carbonate, and (2) 0.05M Sodium Borate at 23°C
Figure 5.5 Polarization Curve of Copper in 1M NaCl, Rotating at 5000 RPM,
Buffered to pH 10.5 with (1) 0.05M Sodium Bicarbonate/Carbonate, and (2) 0.05M Sodium Borate at 23°C
Table 5.1 Summary of Polarization Data for Different Buffer Types

<table>
<thead>
<tr>
<th>Buffer Type</th>
<th>Rotation (RPM)</th>
<th>Corrosion Potential (Vsce)</th>
<th>Pitting Potential (Vsce)</th>
<th>Passive Current Density (A/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>-0.38</td>
<td>0.09</td>
<td>1.6 x 10⁻¹</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>-0.50</td>
<td>0.05</td>
<td>1.8 x 10⁻¹</td>
</tr>
<tr>
<td>0.01M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>-0.40</td>
<td>0.11</td>
<td>9.3 x 10⁻¹</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>-0.51</td>
<td>0.18</td>
<td>1.8 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>-0.33</td>
<td>0.12</td>
<td>1.4 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Borate</td>
<td>50</td>
<td>-0.51</td>
<td>0.18</td>
<td>1.1 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>-0.41</td>
<td>0.58</td>
<td>3.6 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Borate</td>
<td>5000</td>
<td>-0.42</td>
<td>0.50</td>
<td>7.5 x 10⁻¹</td>
</tr>
</tbody>
</table>

Note: passive current densities are taken at -0.1 Vsce

5.1.2 POLARIZATION BEHAVIOR - EFFECT OF BUFFER CONCENTRATION

The effects of buffer concentration on the passivation of copper in 1M sodium chloride buffered to pH 10.5 are shown clearly in Figures 5.6 to 5.9. Figure 5.6 shows the differences in polarization behavior between 0.01M, 0.05M, 0.1M, and 0.5M sodium bicarbonate/carbonate buffered solutions at a pH of 10.5 and a rotation speed of 50 RPM. Figure 5.7 shows the difference between 0.01M, 0.05M, 0.1M, and 0.5M sodium bicarbonate/carbonate buffered solutions at 5000 RPM. Figure 5.8 shows the difference between 0.001M, 0.01M, and 0.05M sodium borate solutions running at 50 RPM.
Figure 5.9 shows the difference between 0.001M, 0.01M, and 0.05M sodium borate buffered solutions running at 5000 RPM.

Figure 5.6 Polarization Curve of Copper in 1M NaCl, Rotating at 50 RPM, Buffered to pH 10.5 with (1) 0.01M Sodium Bicarbonate/Carbonate, (2) 0.05M Sodium Bicarbonate/Carbonate, (3) 0.1M Sodium Bicarbonate/Carbonate, and (4) 0.5M Sodium Bicarbonate/Carbonate at 23°C
Figure 5.7 Polarization Curve of Copper in 1M NaCl, Rotating at 5000 RPM, Buffered to pH 10.5 with (1) 0.01M Sodium Bicarbonate/Carbonate, (2) 0.05M Sodium Bicarbonate/Carbonate, (3) 0.1M Sodium Bicarbonate/Carbonate, and (4) 0.5M Sodium Bicarbonate/Carbonate at 23°C
Figure 5.8  Polarization Curve of Copper in 1M NaCl, Rotating at 50 RPM, Buffered to pH 10.5 with (1) 0.001M Sodium Borate, (2) 0.01M Sodium Borate, and (3) 0.05M Sodium Borate at 23°C
Figure 5.9 Polarization Curve of Copper in 1M NaCl, Rotating at 5000 RPM, Buffered to pH 10.5 with (1) 0.001M Sodium Borate, (2) 0.01M Sodium Borate, and (3) 0.05M Sodium Borate at 23°C
During each polarization test, the copper specimen remained bright and shiny until there was breakdown of the passive film. Following the passive film breakdown a non-adherent blue-green precipitate formed. This precipitate continually spalled off the surface of the rotating copper disk. A sample of this precipitate was analyzed on the EDX and was shown to contain 40.12 atomic percent chlorine and 59.88 atomic percent copper. As such, it is fair to assume that the majority of this precipitate is cuprous chloride (CuCl). In each of the graphs shown in Figures 5.6 to 5.9 there is a clear and repeatable increase in pitting potential with increasing buffer concentration. At the higher buffer concentrations of 0.5M sodium bicarbonate/carbonate no passive film breakdown was observed and the specimen remained shiny throughout the test. The corrosion potentials, pitting potentials, and passive current densities for each test are summarized in Table 5.2.
Table 5.2 Summary of Polarization Data For Increasing Buffer Concentration

<table>
<thead>
<tr>
<th>Buffer Type</th>
<th>Rotation (RPM)</th>
<th>Corrosion Potential (Vsce)</th>
<th>Pitting Potential (Vsce)</th>
<th>Passive Current Density (A/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>-0.38</td>
<td>0.09</td>
<td>1.6 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>-0.33</td>
<td>0.12</td>
<td>1.4 x 10⁻¹</td>
</tr>
<tr>
<td>0.1M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>-0.33</td>
<td>0.33</td>
<td>1.8 x 10⁻¹</td>
</tr>
<tr>
<td>0.5M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>-0.43</td>
<td>no pitting</td>
<td>1.8</td>
</tr>
<tr>
<td>0.01M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>-0.40</td>
<td>0.11</td>
<td>9.3 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>-0.41</td>
<td>0.58</td>
<td>3.6 x 10⁻¹</td>
</tr>
<tr>
<td>0.1M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>-0.36</td>
<td>0.65</td>
<td>7.6 x 10⁻¹</td>
</tr>
<tr>
<td>0.5M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>-0.45</td>
<td>no pitting</td>
<td>8.1</td>
</tr>
<tr>
<td>0.001M Sodium Borate</td>
<td>50</td>
<td>-0.39</td>
<td>-0.08</td>
<td>1.9 x 10⁻¹</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>-0.50</td>
<td>0.05</td>
<td>1.8 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Borate</td>
<td>50</td>
<td>-0.51</td>
<td>0.18</td>
<td>1.1 x 10⁻¹</td>
</tr>
<tr>
<td>0.001M Sodium Borate</td>
<td>5000</td>
<td>-0.31</td>
<td>-0.08</td>
<td>3.6</td>
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<td>0.01M Sodium Borate</td>
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</tr>
<tr>
<td>0.05M Sodium Borate</td>
<td>5000</td>
<td>-0.42</td>
<td>0.50</td>
<td>7.5 x 10⁻¹</td>
</tr>
</tbody>
</table>

Note: passive current densities are taken at -0.1 Vsce
5.1.3 POLARIZATION BEHAVIOR - EFFECT OF ROTATION SPEED

The effects of rotation speed on the passivation of copper in alkaline buffered 1M sodium chloride are shown in Figures 5.10 to 5.15. Figure 5.10 shows the polarization curves of the 0.01 sodium bicarbonate/carbonate buffered solution at pH 10.5 at rotation speeds of 50 RPM and 5000 RPM. Figure 5.11 shows the polarization curves for the 0.05M bicarbonate/carbonate buffered solution at 50 RPM and 5000 RPM. Figure 5.12 shows the polarization curves for the 0.1M bicarbonate/carbonate buffered solution at 50 RPM and 5000 RPM. Figure 5.13 shows the polarization curves for 0.5M bicarbonate/carbonate buffered solutions at 50 RPM and 5000 RPM. Figure 5.14 shows the polarization curves for the 0.01M sodium borate buffered solution at 50 RPM and 5000 RPM. Figure 5.15 shows the polarization curves for the 0.05M sodium borate buffered solution at 50 RPM and 5000 RPM.
Figure 5.10 Polarization Curve of Copper in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Bicarbonate/Carbonate Rotating at (1) 50RPM, and (2) 5000RPM at 23°C
Figure 5.11 Polarization Curve of Copper in 1M NaCl Buffered to pH 10.5 with 0.05M Sodium Bicarbonate/Carbonate Rotating at (1) 50RPM, and (2) 5000RPM at 23°C
Figure 5.12 Polarization Curve of Copper in 1M NaCl Buffered to pH 10.5 with 0.1M Sodium Bicarbonate/Carbonate Rotating at (1) 50RPM, and (2) 5000RPM at 23°C
Figure 5.13  Polarization Curve of Copper in 1M NaCl Buffered to pH 10.5 with 0.5M Sodium Bicarbonate/Carbonate Rotating at (1) 50RPM, and (2) 5000RPM at 23°C
Figure 5.14 Polarization Curve of Copper in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Borate Rotating at (1) 50RPM, and (2) 5000RPM at 23°C
From the polarization curves that compare the effects of rotation speed on the passivation behavior of copper in buffered alkaline 1M sodium chloride, there is clearly an increase in pitting potential at the higher rotation speeds. The increase in pitting potential with increasing rotation speed is greater at the higher buffer concentrations. This indicates that the diffusion of the buffer species to the surface of the copper in alkaline 1M sodium chloride plays an important role in the prevention of passive film breakdown. In addition, the passive current density increases with increasing rotation speed, which shows that
passivation follows a diffusion controlled mechanism. The corrosion potentials, pitting potentials, and passive current densities (data from Table 5.2) are re-arranged in Table 5.3 to show the effects of rotation speed. A plot of pitting potential as a function of buffer concentration is shown in Figure 5.16 (note that tests performed in the 0.5M bicarbonate/carbonate buffered solution exhibited no passive film breakdown).

Table 5.3 Summary of Polarization Data Showing Effects of Rotation Speed

<table>
<thead>
<tr>
<th>Buffer Type</th>
<th>Rotation (RPM)</th>
<th>Corrosion Potential (Vsce)</th>
<th>Pitting Potential (Vsce)</th>
<th>Passive Current Density (A/m²)</th>
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<td>-0.33</td>
<td>0.12</td>
<td>1.4 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>-0.41</td>
<td>0.58</td>
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<tr>
<td>0.1M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>-0.33</td>
<td>0.33</td>
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<td>no pitting</td>
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<td>0.05M Sodium Borate</td>
<td>5000</td>
<td>-0.42</td>
<td>0.50</td>
<td>7.5 x 10⁻¹</td>
</tr>
</tbody>
</table>

Note: passive current densities are taken at -0.1 Vsce
Figure 5.16: Plot of Pitting Potential Versus Buffer Concentration For All Experiments Conducted.
5.2 AC IMPEDANCE SPECTROSCOPY STUDIES

AC Impedance Spectroscopy (ACIS) is a relatively new electrochemical technique used to examine the electrochemical and physical properties of electrochemical systems. This technique was first used by Randles and Somerton in 1952\textsuperscript{30}. In this thesis ACIS is used as a tool to study the physical characteristics of the passive film in-situ. A passive film in-situ inherently has a certain amount of capacitance and resistance depending on its physical characteristics. Thus, the passive film impedes current flow in a similar fashion to an electrical circuit consisting of capacitors and resistors. With ACIS the capacitive and resistive components of the passive film can be determined by measuring the electrical impedance of the cell over a frequency sweep. A small amplitude (± 10mV) sinusoidal potential perturbation superimposed over the polarization potential is applied such that an impedance measurement can be obtained without (or negligibly) affecting the equilibrium condition of the passive film. As such, the passive film can be characterized by modeling the passive film with an electrical equivalent circuit as shown in Figure 5.17.
The passive film is capable of charging and discharging with an applied AC potential, and thus has a certain amount of capacitance (known as the passive film capacitance, $C_{\text{film}}$). In addition, the passive film has a certain resistance to current flow (represented by the passive film resistance, $R_{\text{film}}$). Finally the electrolyte has a certain resistance (represented by the solution resistance, $R_{\text{solution}}$). To understand the basics of ACIS it is necessary to discuss the theory of impedance for capacitors and resistors, the modeling of electrochemical cells with electrical equivalent circuits, and the use of these models to characterize the electrochemical and physical parameters of an electrochemical cell.
5.2.1 THEORY OF IMPEDANCE FOR CAPACITORS AND RESISTORS

Capacitors and resistors are physically different from one another and thus behave differently when an AC potential is applied. The theory of impedance of capacitors, resistors, and capacitor-resistor combinations will be described in order to clarify the subsequent presentation of the experimental AC impedance data.

5.2.1.1 IMPEDANCE OF CAPACITORS

A capacitor consists of two parallel conducting plates separated by an insulating material, known as a dielectric (Shown in Figure 5.18).

![Figure 5.18 A Capacitor](image-url)
When a DC voltage is applied across a capacitor, the plates become charged (Figure 5.19) and thus prevent the passage of current. Hence, a capacitor has an infinite impedance when a DC voltage is applied. However, when the polarity of the charged plates alternate (e.g. when a sinusoidal voltage is applied) the capacitor discharges, thereby allowing current to pass (illustrated in Figure 5.20). In general, a capacitor has two important characteristics due to the charge-discharge effect when a sinusoidal voltage is applied. The first is frequency dependent impedance, and the second is a time lag between the resulting current and the applied voltage.

Figure 5.19 Charged Capacitor
5.2.1.1.1 FREQUENCY DEPENDENT IMPEDANCE OF CAPACITORS

As the frequency of the applied voltage across a capacitor is increased (i.e. as the polarity of the charged plates alternate at a faster rate), the capacitor discharges and then charges at a faster rate. Therefore, the higher the frequency of the applied voltage, the more current is allowed to pass resulting in a lower impedance. Equations 5.8 describes the relationship between the magnitudes of impedance for a capacitor and the frequency of the applied voltage.

\[ Z_{\text{capacitor}} = \frac{1}{\omega \cdot C} \]  

Equation 5.8
Where:

\[ Z_{\text{cap}} = \text{Magnitude of Impedance For a Capacitor (Ohms)} \]

\[ \omega = \text{Angular Frequency} = 2 \times \pi \times \text{Frequency (Hz)} \]

\[ C = \text{Capacitance (Farads)} \]

**5.2.1.1.2 TIME LAG BETWEEN CURRENT AND VOLTAGE**

The charge-discharge effect of a capacitor is not instantaneous, but occurs over a short period of time. Thus, when a sinusoidal voltage is applied across a capacitor, the resulting current lags the applied voltage by a certain amount of time. Therefore, the resulting current is out of phase with respect to the applied voltage according to Equations 5.9 and 5.10 respectively.

\[ V(t) = V_0 \sin(\omega t) \quad 5.9 \]

\[ I(t) = I_0 \sin(\omega t + \theta) \quad 5.10 \]
Where:

\[ V(t) = \text{Applied Voltage} \]

\[ I(t) = \text{Measured Current} \]

\[ V_o = \text{Peak Voltage} \]

\[ I_o = \text{Peak Current} \]

\[ \omega = \text{Angular Frequency} \]

\[ t = \text{Time} \]

\[ \theta = \text{Phase Angle (time lag)} \]

For a capacitor the phase angle is always 90° or \( \pi/2 \) radians. In other words, when a sinusoidal voltage is applied across a capacitor the resulting current is always out of phase by 90° or \( \pi/2 \) radians. This is illustrated graphically in Figure 5.21.

Figure 5.21 Applied Voltage and Resulting Current for a Capacitor
5.2.1.2 IMPEDANCE OF RESISTORS

Resistors are simpler components compared to capacitors because the impedance response of a resistor is independent of frequency (or time). The impedance of a resistor is equal to the resistance. In addition, the measured current and applied voltage are in phase for a resistor. In other words, there is no time lag between the measured current and the applied voltage ($\theta = 0$).

5.2.2 IMPEDANCE OF THE PASSIVE FILM CIRCUIT MODEL

The basic electrical equivalent circuit used to model a passive film is called a Randles Circuit as shown in Figure 5.22 (and is equivalent to the situation in Figure 5.17).

![Randles Circuit](image)

Figure 5.22 Randles Circuit used to Model a Passive Film
Since the Randles Circuit is composed of both capacitance and resistance, the impedance response of this circuit ought to be somewhere in between the impedance response of a purely resistive circuit and a purely capacitive circuit. Therefore, the impedance of the Randles Circuit will be dependent on the applied voltage, and the phase angle will be somewhere in between 0° and 90°.

5.2.3 VECTOR REPRESENTATION OF IMPEDANCE

Impedance is essentially a vector quantity consisting of the magnitude of impedance (a scalar quantity) and a direction (phase angle). This representation of impedance is called polar form. Impedance can also be represented by two component vectors consisting of a real component of impedance and an imaginary component of impedance, called rectangular form (see Figure 5.23).
The real component of impedance represents the "in phase" resistance of the circuit, and the imaginary component of impedance represents the "out of phase" reactance of the circuit. A purely resistive circuit would have only resistance (real component of impedance) and no reactance (imaginary component of impedance), whereas a purely capacitive circuit would have only reactance and no resistance. Equations 5.11, 5.12, and 5.13 describe the relationship between polar form and rectangular form.
\[ |Z| \angle \theta = Z' + jZ'' \]
\[ |Z| = \sqrt{Z'^2 + Z''^2} \]
\[ \theta = \arctan \left( \frac{Z''}{Z'} \right) \]

Where:

- \(|Z|\) = Magnitude of Impedance
- \(\theta\) = Phase Angle
- \(Z'\) = Real Component of Impedance (Resistance)
- \(Z''\) = Imaginary Component of Impedance (Reactance)
- \(j = \sqrt{-1}\)

### 5.2.4 Calculation of Impedance for a Randles Circuit

With the electrical circuit model of the passive film (Randles Circuit) as shown in Figure 5.22, the passive film is represented by a parallel combination of a capacitor \(C_{\text{film}}\) and a resistor \(R_{\text{film}}\). As such, the impedance of this parallel circuit is calculated by the parallel circuit rule as follows:
\[ Z_{\text{film}} = \frac{1}{\left( \frac{1}{Z_{\text{resistor}}} + \frac{1}{Z_{\text{capacitor}}} \right)} \quad 5.14 \]

\[ Z_{\text{film}} = \frac{1}{\left( \frac{1}{R_{\text{film}}} + j\omega C_{\text{film}} \right)} \quad 5.15 \]

Where:

- \( Z_{\text{film}} \) = Impedance of the Passive Film

By multiplying both the numerator and the denominator of Equation 5.15 by \( \left( \frac{1}{R_{\text{film}}} - (j\omega C_{\text{film}}) \right) \), the impedance of the passive film \( (Z_{\text{film}}) \) can be rearranged to rectangular form as shown by Equation 5.16.

\[ Z_{\text{film}} = \frac{1}{R_{\text{film}} C_{\text{film}}^2 \left( \omega^2 + \frac{1}{R_{\text{film}}^2 C_{\text{film}}^2} \right)} - j \frac{\omega}{C_{\text{film}} \left( \omega^2 + \frac{1}{R_{\text{film}}^2 C_{\text{film}}^2} \right)} \quad 5.16 \]

By adding the series solution resistance \( (R_{\text{solution}}) \) to the passive film impedance, the impedance of the Randles Cell model \( (Z_{\text{cell}}) \) becomes (in rectangular form):
This cell impedance can be converted to polar form to allow for plotting simplicity without the need to deal with complex numbers. The cell impedance in polar form (magnitude $|Z_{CELL}|$ and phase angle $\theta$) is calculated as follows:

\[
Z_{CELL} = R_{solution} + \frac{1}{R_{film}C_{film}^2 \left( \omega^2 + \frac{1}{R_{film}^2 C_{film}^2} \right)} - j \frac{\omega}{C_{film} \left( \omega^2 + \frac{1}{R_{film}^2 C_{film}^2} \right)} \tag{5.17}
\]

\[
|Z_{CELL}| = \sqrt{\left( R_{solution} + \frac{1}{R_{film} C_{film}^2 \left( \omega^2 + \frac{1}{R_{film}^2 C_{film}^2} \right)} \right)^2 + \left( \frac{\omega}{C_{film} \left( \omega^2 + \frac{1}{R_{film}^2 C_{film}^2} \right)} \right)^2} \tag{5.18}
\]

\[
\theta = \text{ARCTAN} \left( \frac{\omega}{C_{film} \left( \omega^2 + \frac{1}{R_{film}^2 C_{film}^2} \right)} \right) \tag{5.19}
\]
Note that in electrochemistry (as opposed to electrical engineering) the sign of the phase angle is reversed so that the phase lag can be plotted on the positive axis for simplicity.

\[
\frac{\omega}{C_{\text{film}} \left( \omega^2 + \frac{1}{R_{\text{film}}^2 C_{\text{film}}^2} \right)}
\]

\[\therefore \theta = \arctan \left( \frac{R_{\text{solution}} + \frac{1}{R_{\text{film}} C_{\text{film}}^2 \left( \omega^2 + \frac{1}{R_{\text{film}}^2 C_{\text{film}}^2} \right)}}{\omega} \right)\]

\[5.20\]

5.2.5 PLOTTING IMPEDANCE DATA

Impedance data is plotted on what is called a Bode Plot. This is a dual y-axis plot of log magnitude of impedance and phase angle versus log frequency. A typical Bode plot is shown in Figure 5.24.
The typical Bode plot of the basic model of a passive film consists of two impedance plateaus and one phase angle peak. The first impedance plateau is seen at a low frequency and is equivalent to the sum of the film resistance ($R_{film}$) and the solution resistance ($R_{solution}$). This plateau is seen because the impedance of the passive film capacitance is very high at low frequencies (since $|Z_{film\ \text{capacitor}}| = \frac{1}{\omega C_{film}}$), thus the current only passes through $R_{film}$ and $R_{solution}$. The second impedance plateau is seen at a high frequency and is equal to $R_{solution}$. This is seen because at the high frequencies, the impedance of $C_{film}$ is very small and as such shunts $R_{film}$. At intermediate frequencies, a phase angle peak is seen because the impedance of $C_{film}$ is significant.
5.2.6 AC IMPEDANCE DATA DURING PASSIVE FILM FORMATION AND BREAKDOWN

Impedance data were obtained at increasing electrochemical potentials such that the physical characteristics of the passive film could be modeled in-situ during film formation and breakdown. These impedance scans were conducted at 0.1 Volt increments from -0.4 Vsce to 0.5 Vsce in a 1M sodium chloride solution, buffered to pH 10.5 with a 0.01M sodium borate buffer at both 50 RPM and 5000 RPM. The Bode plots for the impedance scans conducted in 1M sodium chloride, buffered to pH 10.5 with 0.01M sodium borate at 50 RPM are shown in Figures 5.25 to 5.34.

Figure 5.25 Bode Plot for Copper at -0.4 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.
Figure 5.26  Bode Plot for Copper at -0.3 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.

Figure 5.27  Bode Plot for Copper at -0.2 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.
Figure 5.28 Bode Plot for Copper at -0.1 V_{sce} in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.

Figure 5.29 Bode Plot for Copper at 0 V_{sce} in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.
Figure 5.30  Bode Plot for Copper at 0.1 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.

Figure 5.31  Bode Plot for Copper at 0.2 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.
Figure 5.32 Bode Plot for Copper at 0.3 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.

Figure 5.33 Bode Plot for Copper at 0.4 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.
Figure 5.34 Bode Plot for Copper at 0.5 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM.

The Bode plots shown in Figures 5.25 to 5.34 are used to characterize the passive film characteristics during formation and breakdown. During passive film formation (from -0.4 Vsce to -0.1 Vsce) there is a distinct difference between the low frequency and the high frequency impedance. This indicates that a passive film is present on the surface of the copper as the difference between the low frequency impedance and the high frequency impedance represents the passive film resistance. In addition, the phase angle shows a distinct peak. The frequency in which the phase angle peak occurs increases with increasing potential in the passive region. In this potential range the sample remained bright and shiny. At a potential of 0 Vsce there is a noticeable drop in the low frequency impedance concurrent with a splitting of the phase angle peak to form a lower frequency
peak and a higher frequency peak. This occurs at the onset of the passive film breakdown as the polarization curve shown in Figure 5.14 indicate that the pitting potential is 0.03 V SCE under the tested conditions. At 0.1 V SCE a single phase angle peak is present at the higher frequency. This is concurrent with the rapid formation of a blue-green precipitate determined to be cuprous chloride from previous EDX analysis. At 0.2 V SCE and above, the passive film resistance drops to a negligible value and the phase angle peak disappears. In this potential range heavy corrosion is observed along with spalling of the blue-green precipitate from the surface of the copper. Passive film resistance, solution resistance, and phase angle peak data from these Bode plots are summarized in Table 5.4. With a conductance of 77.5 mmho/cm for 1M sodium chloride, a surface area of 1 cm$^2$, and a reference electrode distance of approximately 1 cm from the working electrode, the solution resistance is calculated to be 12.9 ohms. This is close to the measured solution resistance obtained from the impedance experiments. The slight increase in solution resistance at the higher potentials represents changes in local solution chemistry (possibly due to CuCl formation).
Table 5.4 Summary of Impedance Data for Copper in 1M Sodium Chloride
 Buffered to pH 10.5 with 0.01M Sodium Borate rotating at 50 RPM

<table>
<thead>
<tr>
<th>Buffer Type</th>
<th>Rotation (RPM)</th>
<th>Potential (Vsce)</th>
<th>Passive Film Resistance (Ohms)</th>
<th>Solution Resistance (Ohms)</th>
<th>Frequency of Phase Angle Peak (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>-0.4</td>
<td>1874</td>
<td>12</td>
<td>14.7</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>-0.3</td>
<td>1585</td>
<td>12</td>
<td>18.9</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>-0.2</td>
<td>3511</td>
<td>12</td>
<td>297.6</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>-0.1</td>
<td>2565</td>
<td>12</td>
<td>619.7</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>0.0</td>
<td>285</td>
<td>14</td>
<td>29.8, 17569.3</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>0.1</td>
<td>1000</td>
<td>15</td>
<td>5925.5</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>0.2</td>
<td>24</td>
<td>17</td>
<td>no peak</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>0.3</td>
<td>18</td>
<td>14</td>
<td>no peak</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>0.4</td>
<td>22</td>
<td>16</td>
<td>no peak</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>0.5</td>
<td>24</td>
<td>20</td>
<td>no peak</td>
</tr>
</tbody>
</table>

The results of the impedance scans taken between -0.4 Vsce to 0.5 Vsce, at 5000 RPM in 1M sodium chloride, buffered to pH 10.5 with 0.01M sodium borate are shown in Figures 5.35 to 5.44.
Figure 5.35 Bode Plot for Copper at -0.4 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.

Figure 5.36 Bode Plot for Copper at -0.3 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.
Figure 5.37  Bode Plot for Copper at -0.2 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.

Figure 5.38  Bode Plot for Copper at -0.1 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.
Figure 5.39 Bode Plot for Copper at 0 V\text{SCE} in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.

Figure 5.40 Bode Plot for Copper at 0.1 V\text{SCE} in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.
Figure 5.41 Bode Plot for Copper at 0.2 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.

Figure 5.42 Bode Plot for Copper at 0.3 Vsce in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.
Figure 5.43  Bode Plot for Copper at 0.4 V_{sce} in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.

Figure 5.44  Bode Plot for Copper at 0.5 V_{sce} in 1M NaCl buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM.
For the impedance results conducted at the higher rotation speeds (5000 RPM) there is a distinct difference between the impedance at the low frequencies and the impedance at the high frequencies during the stages of passive film formation (from -0.4 Vsce to 0.1 Vsce). This observed effect is consistent with the polarization scans (Figure 5.14) which indicate that the pitting potential is 0.17 Vsce. The frequency in which the phase angle peak occurs increases with increasing potential in the passive region up to a potential of -0.1 Vsce. At 0 Vsce and 0.1 Vsce there is a decrease in the frequency in which the phase angle peak occurs although the film still remains passive. This suggests that there is a change in the film characteristics resulting from changes in film capacitance. In this potential range of -0.4 Vsce to 0.1 Vsce the sample remained bright and shiny. At 0.2 Vsce there is a distinct drop in the low frequency impedance, accompanied by a sudden increase in the frequency of the phase angle peak. This is concurrent with the observed breakdown of passivation which is accompanied with the sudden generation of a blue-green cuprous chloride precipitate. At potentials between 0.3 Vsce and 0.5 Vsce the low frequency impedance remains low. In addition, a splitting of the phase angle is noted and is concurrent with the observed generation of a cuprous chloride precipitate. The impedance data from the high rotation speed tests are summarized in Table 5.5. Again the increase in solution resistance at potentials from 0.3 Vsce to 0.5 Vsce represents changes in local solution chemistry possibly due to CuCl formation.
Table 5.5 Summary of Impedance Data for Copper in 1M Sodium Chloride

Buffered to pH 10.5 with 0.01M Sodium Borate rotating at 5000 RPM

<table>
<thead>
<tr>
<th>Buffer Type</th>
<th>Rotation (RPM)</th>
<th>Potential (Vsce)</th>
<th>Passive Film Resistance (Ohms)</th>
<th>Solution Resistance (Ohms)</th>
<th>Frequency of Phase Angle Peak (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>-0.4</td>
<td>2117</td>
<td>17</td>
<td>13.8</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>-0.3</td>
<td>1000</td>
<td>9</td>
<td>36</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>-0.2</td>
<td>3511</td>
<td>9</td>
<td>183.3</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>-0.1</td>
<td>3511</td>
<td>9</td>
<td>233.6</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>0.0</td>
<td>6579</td>
<td>9</td>
<td>120.1</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>0.1</td>
<td>4806</td>
<td>9</td>
<td>33.6</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>0.2</td>
<td>81</td>
<td>9</td>
<td>2553.2</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>0.3</td>
<td>208</td>
<td>14</td>
<td>3.8, 16237.8</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>0.4</td>
<td>731</td>
<td>32</td>
<td>3.1, &gt;100000</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>0.5</td>
<td>534</td>
<td>43</td>
<td>2.0, &gt;100000</td>
</tr>
</tbody>
</table>
6 DISCUSSION

6.1 POLARIZATION BEHAVIOR

The increase in pitting potential with increasing buffer concentration and rotation speed clearly indicates that mass transport of the buffer species to the copper surface resists passive film breakdown. The mass transport of the conjugate base buffer species through the diffusion layer to copper surface can be calculated with the steady state diffusion equation derived from Fick's Law\(^1\) shown in Equation 6.1. This equation ignores electrical migration effects, which are negligible with a 1M sodium chloride supporting electrolyte.

\[
J_{[B]} = \frac{D_{[B]}([B]_b - [B]_s)}{\delta}
\]

6.1

Where:

\(J_{[B]}\) = Flux of the Conjugate Base from the Bulk to the Surface (moles/m\(^2\) sec)

\(D_{[B]}\) = Diffusion Coefficient (m\(^2\)/s)

\([B]_b\) = Concentration of the Conjugate Base in the Bulk (moles/m\(^3\))

\([B]_s\) = Concentration of the Conjugate Base at the Surface (moles/m\(^3\)) = 0 (if consumed)

\(\delta\) = Diffusion Layer Thickness (m)
For a sodium bicarbonate/carbonate buffer, at any given pH the concentration of the conjugate base (carbonate ion) and the conjugate acid (bicarbonate ion) can be calculated by solving Equations 6.2 and 6.3.

\[ \log \left( \frac{[CO_3^{2-}]}{[HCO_3^{-}]} \right) = -10.34 + pH \quad 6.2^{18} \]

\[ [CO_3^{2-}] + [HCO_3^{-}] = \text{Total Buffer Concentration} \quad 6.3 \]

Using Equations 6.2 and 6.3 the carbonate and bicarbonate ion concentrations for all solutions containing a sodium bicarbonate/carbonate buffer were calculated and are summarized in Table 6.1.

Table 6.1 Summary of Calculated Bicarbonate and Carbonate Concentrations

<table>
<thead>
<tr>
<th>Total Buffer Concentration (M)</th>
<th>pH</th>
<th>[HCO_3^-]</th>
<th>[CO_3^{2-}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>10.5</td>
<td>0.0041</td>
<td>0.0059</td>
</tr>
<tr>
<td>0.05</td>
<td>10.5</td>
<td>0.0204</td>
<td>0.0296</td>
</tr>
<tr>
<td>0.1</td>
<td>10.5</td>
<td>0.0409</td>
<td>0.0591</td>
</tr>
<tr>
<td>0.5</td>
<td>10.5</td>
<td>0.2045</td>
<td>0.2955</td>
</tr>
</tbody>
</table>

*1M = 1000 moles/m³
Sodium tetraborate buffer behaves slightly differently in that the tetraborate ion $[\text{B}_4\text{O}_7^{2-}]$ is not predominant at low concentrations. Instead at low concentrations, the $[\text{B}_4\text{O}_7^{2-}]$ ion will dissociate to $[\text{H}_3\text{BO}_3]$, $[\text{H}_2\text{BO}_3^-]$, and $[\text{HBO}_3^{2-}]$ depending on the pH. The actual concentrations of $[\text{H}_3\text{BO}_3]$, $[\text{H}_2\text{BO}_3^-]$, and $[\text{HBO}_3^{2-}]$ for any given pH can be determined by solving the following three equations and three unknowns:

\[
\log \left( \frac{[\text{H}_3\text{BO}_3^{-}]}{[\text{H}_2\text{BO}_3^{-}]} \right) = -9.21 + pH \quad 6.4^{18}
\]

\[
\log \left( \frac{[\text{HBO}_3^{2-}]}{[\text{H}_2\text{BO}_3^{-}]} \right) = -12.70 + pH \quad 6.5^{18}
\]

\[
[\text{H}_3\text{BO}_3] + [\text{H}_2\text{BO}_3^{-}] + [\text{HBO}_3^{2-}] = 4 \cdot [\text{B}_4\text{O}_7^{2-}]_{\text{added}} \quad 6.6
\]

Using Equations 6.4 to 6.6 the $[\text{H}_3\text{BO}_3]$, $[\text{H}_2\text{BO}_3^-]$, and $[\text{HBO}_3^{2-}]$ concentrations are calculated for the various concentrations tested in this work. The calculated results are summarized in Table 6.2. Since $[\text{H}_2\text{BO}_3^-]$ has the highest concentration at pH 10.5, it is considered to be the conjugate base.
Table 6.2 Summary of Calculated Borate Concentrations

<table>
<thead>
<tr>
<th>Concentration of $[\text{Na}_2\text{B}_4\text{O}_7]$ added (M)</th>
<th>pH</th>
<th>$[\text{H}_3\text{BO}_3]$ (M)*</th>
<th>$[\text{H}_2\text{BO}_3^-]$ (M)*</th>
<th>$[\text{HBO}_3^{2-}]$ (M)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>10.5</td>
<td>0.000194</td>
<td>0.003782</td>
<td>0.000024</td>
</tr>
<tr>
<td>0.01</td>
<td>10.5</td>
<td>0.001940</td>
<td>0.037822</td>
<td>0.000239</td>
</tr>
<tr>
<td>0.05</td>
<td>10.5</td>
<td>0.009699</td>
<td>0.189108</td>
<td>0.001193</td>
</tr>
</tbody>
</table>

* 1M = 1000 moles/m³

The diffusion layer thickness determined by rotating electrode experiments depends on the flow conditions (laminar or turbulent). The flow conditions are determined by the Reynolds Number which is calculated as follows:

$$\text{Re} = \frac{U I}{\nu}$$

Where:

$\text{Re} = \text{Reynolds Number}$

$U = \text{Maximum Radial Velocity (m/s)}$

$I = \text{Distance = Radius of the Disk Electrode (m)}$

$\nu = \text{Kinematic Viscosity of the Electrolyte (m}^2/\text{s})$

As a first approximation, a Reynolds Number less than 500,000 indicates laminar flow, whereas a Reynolds Number greater than 500,000 indicates turbulent flow for flat plate conditions$^{31}$. 
The maximum radial velocity can be calculated via the following equation:\(^\text{32}\):

\[ U = \sqrt{2\omega r} \quad 6.8 \]

Where:

\( \omega \) = Angular Velocity (rad/s)
\( r \) = Radius of the Disk Electrode (m)

For a maximum rotation speed of 5000 RPM, a radius of 0.00565 m, and a kinematic viscosity of 1.056 \( \times \) 10\(^{-6}\) m\(^2\)/s for 1M NaCl\(^33\), the Reynolds Number is calculated to be 22,384. This suggests that the flow is laminar for all rotating disk conditions tested in this thesis.

Under laminar flow conditions the thickness of the diffusion layer (as determined by the diffusion of the conjugate base species to the surface of the copper) is determined by the modified Levich Equation\(^34\) (Equation 6.9):

\[ \delta = 1.805 \cdot [0.8934 + 0.316 \cdot \left( \frac{D}{v} \right)^{0.36} \] \( \cdot \omega^{-1/2} \cdot \nu^{1/6} \cdot D^{1/2} \quad 6.9 \]
Where:

\[
\delta = \text{Diffusion Layer Thickness (m)}
\]

\[
D = \text{Diffusion Coefficient of Conjugate Base (m}^2/\text{s})
\]

\[
\nu = \text{Kinematic Viscosity of the Electrolyte (m}^2/\text{s})
\]

\[
\omega = \text{Angular Velocity (rad/s)}
\]

Using the diffusion and viscosity data shown in Table 6.3, the diffusion layer thickness is calculated (using Equation 6.9) for the sodium bicarbonate/carbonate buffer solutions and the sodium borate buffered solutions at 50 RPM and 5000 RPM. The results are summarized in Table 6.4.

Table 6.3 Summary of Diffusion and Viscosity Data

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion Coefficient of ([\text{CO}_3^{2-}]) (m²/s)¹⁵</td>
<td>0.923 \times 10⁻⁹</td>
</tr>
<tr>
<td>Diffusion Coefficient of ([\text{H}_2\text{BO}_3⁻])* (m²/s)¹</td>
<td>1 \times 10⁻⁹</td>
</tr>
<tr>
<td>Kinematic Viscosity of 1M \text{NaCl} (m²/s)³³</td>
<td>1.056 \times 10⁻⁶</td>
</tr>
</tbody>
</table>

* based on typical values for ions³⁷
Table 6.4 Calculated Diffusion Thicknesses

<table>
<thead>
<tr>
<th>Buffer Type</th>
<th>Rotation (RPM)</th>
<th>Diffusion Layer Thickness (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>2.22 x 10^{-6}</td>
</tr>
<tr>
<td>Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>2.22 x 10^{-7}</td>
</tr>
<tr>
<td>Sodium Borate</td>
<td>50</td>
<td>2.31 x 10^{-6}</td>
</tr>
<tr>
<td>Sodium Borate</td>
<td>5000</td>
<td>2.31 x 10^{-7}</td>
</tr>
</tbody>
</table>

Substituting the conjugate base data given in Tables 6.1 and 6.2 and the diffusion layer thickness data given in Table 6.4, into Equation 6.1, the influx of the conjugate base to the surface of the copper is calculated for all conditions tested in this thesis (assuming that [B], approaches zero). The results are summarized in Table 6.5.
Table 6.5 Flux of Conjugate Base to Copper Surface

<table>
<thead>
<tr>
<th>Buffer Type</th>
<th>Rotation (RPM)</th>
<th>Conjugate Base</th>
<th>Flux (moles/m²sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>[CO₃²⁻]</td>
<td>2.46 x 10⁻³</td>
</tr>
<tr>
<td>0.05M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>[CO₃²⁻]</td>
<td>1.23 x 10⁻²</td>
</tr>
<tr>
<td>0.1M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>[CO₃²⁻]</td>
<td>2.46 x 10⁻²</td>
</tr>
<tr>
<td>0.5M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>[CO₃²⁻]</td>
<td>1.23 x 10⁻¹</td>
</tr>
<tr>
<td>0.01M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>[CO₃²⁻]</td>
<td>2.46 x 10⁻²</td>
</tr>
<tr>
<td>0.05M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>[CO₃²⁻]</td>
<td>1.23 x 10⁻¹</td>
</tr>
<tr>
<td>0.1M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>[CO₃²⁻]</td>
<td>2.46 x 10⁻¹</td>
</tr>
<tr>
<td>0.5M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>[CO₃²⁻]</td>
<td>1.23</td>
</tr>
<tr>
<td>0.001M Sodium Borate</td>
<td>50</td>
<td>[H₂BO₃⁻]</td>
<td>1.63 x 10⁻³</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>[H₂BO₃⁻]</td>
<td>1.63 x 10⁻²</td>
</tr>
<tr>
<td>0.05M Sodium Borate</td>
<td>50</td>
<td>[H₂BO₃⁻]</td>
<td>8.17 x 10⁻²</td>
</tr>
<tr>
<td>0.001M Sodium Borate</td>
<td>5000</td>
<td>[H₂BO₃⁻]</td>
<td>1.63 x 10⁻²</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>[H₂BO₃⁻]</td>
<td>1.63 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Borate</td>
<td>5000</td>
<td>[H₂BO₃⁻]</td>
<td>8.17 x 10⁻¹</td>
</tr>
</tbody>
</table>

The flux of H⁺ ions formed by the passivation reactions (Equations 5.4 to 5.6) can be calculated from the passive current density using the following equation¹:
\[ J_{H^+} = \frac{i_p}{F} \]  

6.10

Where:

\( J_{H^+} \) = Flux of protons (moles/m\(^2\) sec)

\( i_p \) = Passive Current Density (A/m\(^2\))

\( F \) = Faraday’s Constant = 96500 A.sec/eq.mole

Using Equation 6.10, the flux of hydrogen ions formed during the passivation is calculated for all tests conducted in this thesis. The calculated flux of hydrogen ions are summarized in Table 6.6 (the flux of the conjugate base species are included for comparison).
Table 6.6 Flux of Hydrogen Ions Produced During Passivation

<table>
<thead>
<tr>
<th>Buffer Type</th>
<th>Rotation (RPM)</th>
<th>Passive Current Density (A/m²)</th>
<th>H⁺ Flux (moles/m²sec)</th>
<th>Conjugate Base Flux (moles/m²sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>1.6 x 10⁻¹</td>
<td>1.7 x 10⁻⁶</td>
<td>2.46 x 10⁻³</td>
</tr>
<tr>
<td>0.05M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>1.4 x 10⁻¹</td>
<td>1.5 x 10⁻⁶</td>
<td>1.23 x 10⁻²</td>
</tr>
<tr>
<td>0.1M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>1.8 x 10⁻¹</td>
<td>1.9 x 10⁻⁶</td>
<td>2.46 x 10⁻²</td>
</tr>
<tr>
<td>0.5M Sodium Bicarbonate/Carbonate</td>
<td>50</td>
<td>1.8</td>
<td>1.9 x 10⁻³</td>
<td>1.23 x 10⁻¹</td>
</tr>
<tr>
<td>0.01M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>9.3 x 10⁻¹</td>
<td>9.6 x 10⁻⁶</td>
<td>2.46 x 10⁻²</td>
</tr>
<tr>
<td>0.05M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>3.6 x 10⁻¹</td>
<td>3.7 x 10⁻⁶</td>
<td>1.23 x 10⁻¹</td>
</tr>
<tr>
<td>0.1M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>7.6 x 10⁻¹</td>
<td>7.9 x 10⁻⁶</td>
<td>2.46 x 10⁻¹</td>
</tr>
<tr>
<td>0.5M Sodium Bicarbonate/Carbonate</td>
<td>5000</td>
<td>8.1</td>
<td>8.4 x 10⁻³</td>
<td>1.23</td>
</tr>
<tr>
<td>0.001M Sodium Borate</td>
<td>50</td>
<td>1.9 x 10⁻¹</td>
<td>2.0 x 10⁻⁶</td>
<td>1.63 x 10⁻³</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>50</td>
<td>1.8 x 10⁻¹</td>
<td>1.9 x 10⁻⁶</td>
<td>1.63 x 10⁻²</td>
</tr>
<tr>
<td>0.05M Sodium Borate</td>
<td>50</td>
<td>1.1 x 10⁻¹</td>
<td>1.1 x 10⁻⁶</td>
<td>8.17 x 10⁻²</td>
</tr>
<tr>
<td>0.001M Sodium Borate</td>
<td>5000</td>
<td>3.6</td>
<td>3.7 x 10⁻⁵</td>
<td>1.63 x 10⁻²</td>
</tr>
<tr>
<td>0.01M Sodium Borate</td>
<td>5000</td>
<td>1.8 x 10⁻¹</td>
<td>1.9 x 10⁻⁶</td>
<td>1.63 x 10⁻¹</td>
</tr>
<tr>
<td>0.05M Sodium Borate</td>
<td>5000</td>
<td>7.5 x 10⁻¹</td>
<td>7.8 x 10⁻⁵</td>
<td>8.17 x 10⁻²</td>
</tr>
</tbody>
</table>

As shown in Table 6.6 the influx of the conjugate base species is much greater than the out-flux of hydrogen ions generated during the passivation of copper. As such, it is unlikely that the small amount of protons generated during copper passivation (Equations
5.4 to 5.6) is the cause of the observed loss of pH control which accompanies passive film breakdown. Instead the breakdown of passivation must be caused by the localized generation of protons (decreasing the local pH) likely initiating at one or more defect sites in the passive film. According to Pourbaix, the HCuO$_2^-$ ion can co-exist with the passive CuO or Cu(OH)$_2$ species\textsuperscript{18}. As such, the occurrence of Equation 6.11 at a defect site will result in a large local current density (since there is no local passivation) and thus result in a large local generation of protons that will consume any conjugate base species in the vicinity.

$$
\text{Cu} + 2\text{H}_2\text{O} = \text{HCuO}_2^- + 3\text{H}^+ + 2e^- \quad 6.11
$$

With a drop in the surface pH, cuprous chloride will precipitate via Equation 6.12. Published literature has shown that once CuCl is formed re-passivation can no longer take place as it becomes impossible to form a passive barrier layer over the CuCl film\textsuperscript{17}. As such, the formation of CuCl interferes with passivation regardless of the diffusion of the conjugate base species to the surface.

$$
\text{Cu} + \text{Cl}^- = \text{CuCl} + e^- \quad 6.12
$$
6.2 AC IMPEDANCE - MODELLING OF THE PASSIVE FILM

The physical parameters of the passive film can be characterized by equating the measured impedance (shown on the Bodes Plots in Figures 5.25 to 5.44) of the cell to the impedance of the electrical circuit model (Figure 5.22), and then mathematically deconvoluting the individual circuit components of the model. The electrical parameters of the passive film such as passive film resistance and capacitance are used to estimate the physical characteristics of the passive film in-situ.

The film resistance and the solution resistance are determined simply from the plateaus of impedance versus frequency plot. Since the impedance of the film capacitor is inversely proportional to the applied frequency (Equation 5.8), the impedance of the film capacitor is very large at low frequencies and very small at high frequencies. As such, at low frequencies current only passes through the film resistor \( R_{\text{film}} \) and the solution resistor \( R_{\text{solution}} \) as shown in Figure 6.1. At the high frequencies the passive film resistor is shunted, only allowing current to pass through the solution resistor (Figure 6.2). Therefore, the film resistance is equivalent to the impedance at the low frequencies minus the impedance at the high frequencies and the solution resistance is equal to the impedance at the high frequencies.
Figure 6.1 Current Path Through Circuit Model at Low Frequencies

Figure 6.2 Current Path Through Circuit Model at High Frequencies
The film capacitance is determined from the frequency at which the phase angle peaks. This is determined by differentiating the phase angle equation (Equation 6.13) with respect to frequency and equating this value to zero. The derivation is as follows:

\[
\frac{d\theta}{d\omega} = 0 \quad 6.13
\]

Where:

\[
\theta = \arctan \left( \frac{\omega}{C_{film} \left( \omega^2 + \frac{1}{R_{film}^2 C_{film}^2} \right)} \right)
\]

(From Equation 5.20)

Application of the chain rule to Equation 6.14 yields the following:

\[
\frac{d}{dx} \arctan(x) = \frac{1}{1 + x^2} \quad 6.14
\]

\[
\frac{d\theta}{d\omega} = R_{solution} \omega^2 C_{film}^2 R_{film}^2 - R_{film} - R_{solution} = 0 \quad 6.15
\]
By rearranging Equation 6.15:

\[ \omega_{\theta\text{max}} = \frac{\sqrt{R_{\text{film}} + R_{\text{solution}}}}{\sqrt{R_{\text{film}}^2 C_{\text{film}}^2 R_{\text{solution}}}} \]  

Therefore:

\[ C_{\text{film}} = \frac{R_{\text{film}} + R_{\text{solution}}}{R_{\text{film}} \omega_{\theta\text{max}}^2 R_{\text{solution}}} \]  

Where:

- \( C_{\text{film}} \) = Film Capacitance (Farads)
- \( R_{\text{film}} \) = Film Resistance (Ohms)
- \( R_{\text{solution}} \) = Solution Resistance (Ohms)
- \( \omega_{\theta\text{max}} \) = Angular Frequency at the Phase Angle Peak (Hz)

For a parallel plate electronic capacitor, the relationship between the capacitance and dielectric thickness is determined by Equation 6.18:

\[ C = \frac{K A}{4 \pi d} \]
Where:

\[ C = \text{Capacitance (Electrostatic Units)} \]

1 Farad = \(9 \times 10^{11}\) Electrostatic Units

\[ K = \text{Dielectric Constant} \]

\[ A = \text{Surface Area of the Conducting Plate (cm}^2\text{)} \]

\[ d = \text{Thickness of the Dielectric (cm)} \]

Once the capacitance of the passive film is known, the in-situ passive film thickness can be estimated from the following equation:

\[
\begin{align*}
\frac{d}{A} &= \frac{K}{4\pi} \frac{1}{C_{\text{film}}} \\
6.19
\end{align*}
\]

Where:

\[ C_{\text{film}} = \text{Capacitance (Electrostatic Units) determined by Equation 6.17} \]

1 Farad = \(9 \times 10^{11}\) Electrostatic Units

\[ K = \text{Dielectric Constant}^{19,33} = 11 - 18 \text{ for Cu}_2\text{O and 18.1 for CuO} \]

\[ A = \text{Surface Area of the Rotating Disk Electrode = 1 cm}^2\]

\[ d = \text{Thickness of the Passive Film (cm)} \]
6.2.1 ANALYSIS OF IMPEDANCE RESULTS

Using the impedance results, the thickness of passive films are calculated on the assumption that a Cu$_2$O/CuO duplex film is present on the surface of the test specimens and that the dielectric constant for the passive layer is 18. In the 1M sodium chloride solution buffered to pH 10.5 with 0.01M sodium borate rotating at 50 RPM the film thickness values at -0.4 Vsce and -0.3 Vsce are calculated to be 2.2 Å and 2.6 Å respectively using the impedance data (Table 5.4). According to the polarization curve shown in Figure 5.14, these two potentials correspond to the active region and as such the thin film detected from the impedance scans may correspond to the electrical double layer. The double layer thickness is estimated to be 2.88 Å, based on the assumption that the thickness of the electrical double layer is approximately equal to the radius of a solvated cuprous cation (a cuprous cation surrounded by water molecules$^{33}$). Using a dielectric constant for the electrical double layer of approximately 78.54 (estimated with dielectric constant for water$^{33}$), the modeled thickness of the double layer is calculated to be 9.6 Å and 11.3 Å at -0.4 Vsc and -0.3 Vsc respectively. Since these values are greater than the expected thickness of the electrical double layer, the impedance response at these potentials are likely caused by a composite effect of the electrical double layer and an adsorbed surface film (or possibly the electrical double layer and the diffusion layer). At -0.2 Vsc and -0.1 Vsc the film thickness increases substantially to 61.2 Å and 108.8 Å respectively. This is consistent with the passivation observed on the polarization plot. At 0 Vsc the passive film resistance drops by nearly ten fold and the phase angle splits into
two peaks (one at a low frequency and one at a high frequency). The splitting of the phase angle peak is caused by a dual impedance effect that is likely caused by the presence of large defect sites in the passive film. The impedance response of both the non defect sites and the defect sites results in two phase angle peaks. A possible circuit model for a passive film with large defect sites is shown in Figure 6.3. This model consists of two parallel Randles Circuits, with which the effect of the thin non-defective (and possibly non-protective) film is represented by the film capacitance and the film resistance positioned in a series array with the thick defective film capacitance and the defective film resistance.

![Circuit Model for a Passive Film with Large Defect Sites](image.png)

**Figure 6.3. Circuit Model for a Passive Film with Large Defect Sites**

Since the defective portion of the film is much thicker than the non defective portion $C_{\text{film}}$ would be much greater than $C_{\text{defect}}$. As such, the impedance of $C_{\text{film}}$ would be significant at low frequencies and the impedance of $C_{\text{defect}}$ would be significant at high
frequencies (since $|Z_{\text{capacitor}}| = \frac{1}{\omega C}$). A typical Bode plot for this type of circuit (shown in Figure 6.4) consists of three impedance plateaus and two phase angle peaks.

**Figure 6.4 Typical Bode Plot of Circuit Model of Passive Film with Large Defects**

The first impedance plateau which occurs at a low frequency is equivalent to the sum of the non defective film resistance $R_{\text{film}}$, the defective film resistance $R_{\text{defect}}$, and the solution resistance $R_{\text{solution}}$. This impedance plateau is seen because the impedance of both $C_{\text{defect}}$ and $C_{\text{film}}$ are very high at low frequencies, thus current only passes through $R_{\text{film}}$, $R_{\text{defect}}$, and $R_{\text{solution}}$. As the frequency increases, the impedance of the $C_{\text{film}}$ decreases, and
thus shunts the $R_{film}$ (note that the frequency is still low enough such that the impedance of the defective film capacitor is very high). At this point the second impedance plateau equivalent to the sum of $R_{defect}$ and $R_{solution}$ occurs. In addition, the first phase angle peak occurs because of the reactance effect of $C_{film}$. As the frequency increases even higher, the impedance of $C_{defect}$ decreases and, thus shunts the $R_{defect}$. At this point the third impedance plateau, equivalent to the solution resistance occurs. This effect is seen because the impedance of $C_{defect}$ is very low at very high frequencies, and thus the $R_{defect}$ is shunted. In addition, the second phase angle peak occurs because of the reactance of $C_{defect}$.

Deconvoluting the circuit components of the large film defect model requires simplification of the double parallel circuit into simple Randles circuits such that the defect capacitance and the film capacitance can be determined. The following steps describe the deconvolution of the circuit components of the large defect film model.

Step 1: Determine $R_{film}$, $R_{defect}$, and $R_{solution}$ from the impedance plateaus of the impedance versus frequency plot (Figure 6.4).

Step 2: Since $C_{film}$ is much larger than $C_{defect}$, the impedance of $C_{defect}$ is much higher than the impedance of $C_{film}$ at low frequencies. As such, the double parallel circuit can be simplified to a simple Randles circuit for low frequencies as shown in Figure 6.5.
Figure 6.5 Simplified Large Defect Model for Low Frequencies

Step 3: Using the low frequency simplified circuit, and the frequency at which the first phase angle peak occurs, the defect capacitance can be calculated using Equation 6.20.

\[ C_{film} = \frac{R_{film} + (R_{defect} + R_{solution})}{\sqrt{\frac{R_{film}^{2} \omega^{2}}{\text{max}} (R_{defect} + R_{solution})}} \]

Step 4: At the higher frequencies the impedance of the \( C_{film} \) becomes very small, therefore the double parallel circuit can be simplified to a simple Randles circuit as shown in Figure 6.6.
Step 5: Using the high frequency simplified circuit, and the frequency in which the second phase angle peak occurs, the film capacitance can be calculated using Equation 6.21.

\[ C_{\text{defect}} = \sqrt{\frac{R_{\text{defect}} + R_{\text{solution}}}{R_{\text{defect}}^2 \omega_{\text{max}}^2 R_{\text{solution}}}} \]  

6.21

From the impedance plateaus of the Bode plot taken at 0 Vsce (Figure 5.29), the non-defective film resistance \((R_{\text{film}})\) is 258 ohms, the defective film resistance \((R_{\text{defect}})\) is estimated to be 13 ohms, and the solution resistance \((R_{\text{solution}})\) is 14 ohms. The frequency \((\omega = 2\pi f)\) of the first phase angle peak \((f_{\text{at max}})\) occurs at 29.8 Hz and the second phase angle peak \((f_{\text{at max}})\) occurs at 17569.3 Hz. The non-defective film capacitance \((C_{\text{film}})\) and the defective film capacitance \((C_{\text{defect}})\) are calculated to be \(6.73 \times 10^{-5}\) Farads and \(9.68 \times 10^{-7}\) Farads respectively. As such the calculated effective thickness for the non
defective film is calculated to be 2.4 Å and the effective thickness of the defective film is 165.4 Å. Again since the thickness of the non-defect region is so small, it likely corresponds to a composite effect of the electrical double layer (a local site of active corrosion) and a thin adsorbed film. The lower resistance of the defective film (13 ohms) as compared to the non-defective film (258 ohms) reinforces the fact that the defective film is very porous. This also corresponds to the pitting potential of 0.03 Vsce as determined from the polarization curve (Figure 5.14).

At 0.1 Vsce a single phase angle peak occurs at a high frequency of 5925.5 Hz. This corresponds to a film thickness of 718.8 Å. This thick porous film is likely composed of CuCl, which was observed at this potential. At potentials at and above 0.2 Vsce, the phase angle peak disappears and the impedance drops to the level of the solution resistance. This indicates that no film or precipitate is present and the copper surface is rapidly corroding.

The impedance results for the tests conducted in 1M sodium chloride solution buffered to pH 10.5 with 0.01M sodium borate rotating at 50 RPM are summarized in Table 6.7.
Table 6.7 Summary of Impedance Results for Tests Conducted in 1M NaCl
Buffered to pH 10.5 with 0.01M Na₂B₄O₇ Rotating at 50 RPM

<table>
<thead>
<tr>
<th>Potential (Vsce)</th>
<th>Frequency at Phase Angle Peak (Hz)</th>
<th>R_{film} (Ohms)</th>
<th>R_{defect} (Ohms)</th>
<th>R_{solution} (Ohms)</th>
<th>Film Thickness (Å)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.4</td>
<td>14.7</td>
<td>1862</td>
<td>0</td>
<td>12</td>
<td>2.2₁, 9.6₂</td>
<td>thin film &amp; electrical double layer</td>
</tr>
<tr>
<td>-0.3</td>
<td>18.9</td>
<td>1573</td>
<td>0</td>
<td>12</td>
<td>2.6₁, 11.3₂</td>
<td>thin film &amp; electrical double layer</td>
</tr>
<tr>
<td>-0.2</td>
<td>297.6</td>
<td>3499</td>
<td>0</td>
<td>12</td>
<td>61.2</td>
<td>passive film present</td>
</tr>
<tr>
<td>-0.1</td>
<td>619.7</td>
<td>2553</td>
<td>0</td>
<td>12</td>
<td>108.8</td>
<td>passive film present</td>
</tr>
<tr>
<td>0.0</td>
<td>29.8 &amp; 17569.3</td>
<td>258</td>
<td>13</td>
<td>14</td>
<td>2.4 &amp; 165.4</td>
<td>passive film with large defects, onset of film breakdown</td>
</tr>
<tr>
<td>0.1</td>
<td>5925.5</td>
<td>985</td>
<td>0</td>
<td>15</td>
<td>718.8</td>
<td>thick non-protective CuCl</td>
</tr>
<tr>
<td>0.2</td>
<td>no peak</td>
<td>7</td>
<td>0</td>
<td>17</td>
<td>0</td>
<td>no film, high corrosion rate</td>
</tr>
<tr>
<td>0.3</td>
<td>no peak</td>
<td>4</td>
<td>0</td>
<td>14</td>
<td>0</td>
<td>no film, high corrosion rate</td>
</tr>
<tr>
<td>0.4</td>
<td>no peak</td>
<td>6</td>
<td>0</td>
<td>16</td>
<td>0</td>
<td>no film, high corrosion rate</td>
</tr>
<tr>
<td>0.5</td>
<td>no peak</td>
<td>4</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>no film, high corrosion rate</td>
</tr>
</tbody>
</table>

Footnote *1: Using the dielectric constant of copper oxide
Footnote *2: Using the dielectric constant of the electrical double layer

In the 1M sodium chloride solution buffered to pH 10.5 with 0.01M sodium borate rotating at 5000 RPM the film thickness values at -0.4 Vsce and -0.3 Vsce are calculated to be 2.6 Å and 3.4 Å respectively using the impedance data shown in Table 5.5 and the dielectric constant for copper oxide. Using the dielectric constant for the electrical double layer, these thickness values are calculated to be 11.3 Å and 14.8 Å respectively. Again this indicates that the impedance response at -0.4 Vsce and -0.3 Vsce is likely due to a composite effect of the electrical double layer and a thin adsorbed film. The polarization curve shown in Figure 5.14 shows that these two potentials are in the active region. In the passive region from potentials -0.2 Vsce to -0.1 Vsce, the passive film grows to 32.7 Å
and then to 41.6 Å. Still in the passive region from 0 Vsce to 0.1 Vsce the passive film thickness begins to decrease from 29.3 Å to 7.0 Å. The passive film resistance remains high at 6570 ohms and 4997ohms respectively. At 0.2 Vsce (30mV above the pitting potential as shown on the polarization curve in Figure 5.14) there is a large drop in the passive film resistance to 72 ohms followed by an increase in the film thickness to 61.6 Å. A large drop in passive film resistance in combination with an increase in film thickness indicates that the film is porous. Since only a single phase angle peak is present, the defect sites in this porous film must be small. From 0.3 Vsce to 0.5 Vsce the phase angle splits to a very low frequency peak and a very high frequency peak. This is consistent with the precipitation of a very defective cuprous chloride film. At 0.3 Vsce, 0.4 Vsce, and 0.5 Vsce the thickness values of the thin surface film are calculated to be 0.2 Å, 0.6 Å, and 0.4 Å respectively (assuming a dielectric constant for copper oxide). Using a dielectric constant for the electrical double layer, these thickness values are calculated to be 0.9 Å, 2.6 Å, and 1.7 Å respectively. Since these values are close to the estimated thickness of the electrical double layer (2.88 Å), it is fair to assume that the non-defective region of the model represents the electrical double layer at these potentials. The thickness of the thick defective CuCl portion of the film at 0.3 Vsce, 0.4 Vsce, and 0.5 Vsce are 115.7 Å, 1860.0 Å, and 2777.4 Å respectively.

The impedance results for the tests conducted in 1M sodium chloride solution buffered to pH 10.5 with 0.01M sodium borate rotating at 5000 RPM are summarized in Table 6.8.
Table 6.8 Summary of Impedance Results for Tests Conducted in 1M NaCl
Buffered to pH 10.5 with 0.01M Na$_2$B$_4$O$_7$, Rotating at 5000 RPM

<table>
<thead>
<tr>
<th>Potential (V SCE)</th>
<th>Frequency at Phase Angle Peak (Hz)</th>
<th>$R_{film}$ (Ohms)</th>
<th>$R_{defect}$ (Ohms)</th>
<th>$R_{solution}$ (Ohms)</th>
<th>Film Thickness ($\text{Å}$)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.4</td>
<td>13.8</td>
<td>2100</td>
<td>0</td>
<td>17</td>
<td>2.6$^{*1}$, 11.3$^{*2}$</td>
<td>thin film &amp; electrical double layer</td>
</tr>
<tr>
<td>-0.3</td>
<td>36.0</td>
<td>991</td>
<td>0</td>
<td>9</td>
<td>3.4$^{*1}$, 14.8$^{*2}$</td>
<td>thin film &amp; electrical double layer</td>
</tr>
<tr>
<td>-0.2</td>
<td>183.3</td>
<td>3502</td>
<td>0</td>
<td>9</td>
<td>32.7</td>
<td>passive film present</td>
</tr>
<tr>
<td>-0.1</td>
<td>233.6</td>
<td>3502</td>
<td>0</td>
<td>9</td>
<td>41.6</td>
<td>passive film present</td>
</tr>
<tr>
<td>0.0</td>
<td>120.1</td>
<td>6570</td>
<td>0</td>
<td>9</td>
<td>29.3</td>
<td>passive film present</td>
</tr>
<tr>
<td>0.1</td>
<td>33.6</td>
<td>4797</td>
<td>0</td>
<td>9</td>
<td>7.0</td>
<td>thin passive film present</td>
</tr>
<tr>
<td>0.2</td>
<td>2553.2</td>
<td>72</td>
<td>0</td>
<td>9</td>
<td>61.6</td>
<td>passive film with small defects, onset of film breakdown</td>
</tr>
<tr>
<td>0.3</td>
<td>3.8 &amp; 16237.8</td>
<td>185</td>
<td>9</td>
<td>14</td>
<td>0.9$^{*2}$, 115.7$^{*3}$</td>
<td>thick porous CuCl film</td>
</tr>
<tr>
<td>0.4</td>
<td>3.1 &amp; 100000</td>
<td>674</td>
<td>25</td>
<td>32</td>
<td>2.6$^{*2}$, 1860.0$^{*3}$</td>
<td>thick porous CuCl film</td>
</tr>
<tr>
<td>0.5</td>
<td>2.0 &amp; 100000</td>
<td>453</td>
<td>38</td>
<td>43</td>
<td>1.7$^{*2}$, 2777.4$^{*3}$</td>
<td>thick porous CuCl film</td>
</tr>
</tbody>
</table>

Footnote $*1$: Using the dielectric constant of copper oxide  
Footnote $*2$: Using the dielectric constant of the electrical double layer  
Footnote $*3$: Thickness of the porous cuprous chloride film using a dielectric constant of 18

6.3 CORRELATION OF FILM THICKNESS WITH PUBLISHED LITERATURE

Using the impedance modeling technique derived in this thesis, the passive film thickness ranged from 7.0 Å to 108.8 Å under the conditions tested. These values are very close to documented XPS studies conducted by Kautek et al who found that the thickness of a copper oxide anodically formed in an alkaline solution under specific conditions ranged from 40 Å to 60 Å$^{23}$. Similar studies conducted by Chawla et al found that the thickness of an air formed oxide on copper is approximately 24 Å. The calculated...
film thickness values are also below the first optical interference thickness of approximately 190 Å. As such, this suggests that the method of using impedance data to determine passive film thickness is approximately correct.

6.4 LIMITATIONS OF IMPEDANCE SPECTROSCOPY

It is rare that an electrochemical cell can be represented exactly by an ordinary ideal electrical circuit. Thus the usefulness of AC impedance spectroscopy relies on the accuracy with which the electrical circuit models the electrochemical cell. In most cases, fairly accurate models can be used to determine the simplified characteristics of the passive film. Interpretation also relies on the accuracy of the dielectric constant which may not be readily available in published literature (particularly for passive films which are hydrated oxides). Comparisons of modeled data with measured impedance data shown in Appendix III shows that the models used in this study are fairly accurate.

6.5 MECHANISM OF PASSIVE FORMATION, GROWTH, AND BREAKDOWN

Based on the results of the polarization and impedance studies, the process of film formation, growth, and breakdown on copper in buffered alkaline solutions is summarized. In the region of active corrosion a composite of the electrical double layer and a thin non-protective film in the range of 2.2 Å to 3.4 Å are present on the surface of the copper. In the passive region, a film in the range of 7.0 Å to 108.8 Å thick forms on the surface
consisting of a protective Cu$_2$O/CuO duplex structure. The formation of defects in the passive film initiates the breakdown of the film. At the non-protected sites, copper corrodes forming HCuO$_2^-$ ions and H$^+$ ions. The generation of protons results in a drop in the local pH, and therefore causing further breakdown of the passive film. The low pH results in the precipitation of a non-protective cuprous chloride on the surface of the copper. This cuprous chloride prevents re-passivation as a protective barrier layer cannot be formed.
7 CONCLUSIONS

Studies on the behavior of copper in buffered alkaline sodium chloride solutions were consistent with the following conclusions.

(1) Passive film breakdown on copper in buffered alkaline sodium chloride is a result of a loss of pH control at the surface of the metal.

(2) The initial loss of pH control that causes passive film breakdown is still observed when there is sufficient conjugate base influx to neutralize the total hydrogen ions generated from the corrosion process. As such, the loss of pH control must be a localized phenomenon.

(3) The initiation of passive film breakdown occurs when there are defects present in the passive film.

(4) Copper corrodes in these defect sites forming \( \text{HCuO}_2^- \) ions and \( \text{H}^+ \) ions. The protons generated in this defect site results in a drop in local pH.

(5) In order to prevent the initiation of passive film breakdown, an excess buffer concentration is required to neutralize the drop in local pH.

(6) There is little difference between the sodium bicarbonate/carbonate buffer and the sodium tetraborate buffer in preventing passive film breakdown of copper in alkaline sodium chloride solutions. Sodium bicarbonate/carbonate buffer solutions produce a higher corrosion potential that is possibly due to carbon dioxide formation.
(7) The loss of pH control results in the precipitation of a solid cuprous chloride.

(8) Cuprous chloride prevents re-passivation regardless of the influx of the buffer species.

(9) The passive film thickness can be accurately determined from AC impedance studies by determining the frequency at which the phase angle peaks.

(10) Film defects can be detected with AC impedance studies by virtue of a phase angle shift and a drop in film resistance.
8 RECOMMENDATIONS FOR FUTURE WORK

Using the techniques described in this thesis, it is recommended that the following work be conducted in the future.

(1) Using XPS studies to determine the thickness of anodically formed passive films and AC impedance studies to determine film capacitance, the dielectric constant for these passive films can be determined for different metals and alloys.

(2) Further work is suggested on using the polarization and AC impedance techniques described in this thesis to examine the passivation behavior of different metals and alloys.
9 REFERENCES


APPENDIX I: MICROSOFT QUICKBASIC PROGRAM FOR CONTROLLING ELECTROCHEMICAL DEVICES FOR POLARIZATION EXPERIMENTS

'1286 POLARIZATION PROGRAM BY NORMAN CHOW
DECLARE SUB PAUSE (DELAY!)
DECLARE SUB STATUSBYTE (SP%, BIT%())
DIM BIT%(7)

CLS

'INITIALIZE BOARD AND DEVICE
OPEN "GPIBO" FOR OUTPUT AS #1
OPEN "GPIBO" FOR INPUT AS #2
OPEN "C:\DATA\TEST.DAT" FOR APPEND AS #3
PRINT #1, "ABORT"
PRINT #1, "RESET"
PRINT #1, "REMOTE"
PRINT #1, "OUTPUT 12, BK4" 'INITIALIZE
PAUSE (2)

'GENERAL PARAMETERS
PRINT #1, "OUTPUT 12, BY1" 'STANDBY CE/OC
PRINT #1, "OUTPUT 12; RR5" '1K STANDARD RESISTOR
PRINT #1, "OUTPUT 12; IL5" 'CURRENT LIMIT 200mA
PRINT #1, "OUTPUT 12; EB1" 'ERROR BEEP OFF
PRINT #1, "OUTPUT 12; PV.9" 'POLARIZATION VOLTAGE .9V
PRINT #1, "OUTPUT 12; GDO" 'DVM DIGITS 5X9s
PRINT #1, "OUTPUT 12; TR1" 'RECYCLE
PRINT #1, "OUTPUT 12; OL1" 'LIMIT

'SWEEP PARAMETERS
PRINT #1, "OUTPUT 12; VA.9" 'V1=.9V
PRINT #1, "OUTPUT 12; TA1800" 'T1=1800SEC
PRINT #1, "OUTPUT 12; VB-.9" 'V2=-.9V
'PRINT #1, "OUTPUT 12; TB10" 'T2=10SEC
'PRINT #1, "OUTPUT 12; VC.1" 'V3=.1V
'PRINT #1, "OUTPUT 12; TC10" 'T3=10SEC
'PRINT #1, "OUTPUT 12; VD.5" 'V4=.5V
'PRINT #1, "OUTPUT 12; TD10" 'T4=10SEC
PRINT #1, "OUTPUT 12; DL1" 'DELAY=1SEC
PRINT #1, "OUTPUT 12; SM1" 'SEGMENTS 1

'-------------------------------
'ECI SCREEN DISPLAY
PRINT #1, "OUTPUT 12; UL3" 'LEFT WINDOW RE
PRINT #1, "OUTPUT 12; UR5" 'RIGHT WINDOW POLARIZATION
'-------------------------------
'BEGIN
PAUSE (2)
PRINT #1, "OUTPUT 12; RU1;" 'DVM RUN ON
INPUT "PRESS [ENTER] TO POLARIZE SAMPLE", DUMMY
PRINT #1, "OUTPUT 12, RU0;" 'DVM RUN OFF
PAUSE (1)
PRINT #1, "OUTPUT 12; PW1;" 'STANDBY TO ON
PRINT #1, "OUTPUT 12; RU1;" 'DVM RUN ON
PAUSE (2)
INPUT "PRESS [ENTER] TO SWEEP", DUMMY
CLS
PRINT "CELL ON"
'PAUSE (1800)
PRINT #1, "OUTPUT 12, RU0;" 'DVM RUN OFF
PRINT #1, "OUTPUT 12; TR3;" 'TRIGGER SYNC
PRINT #1, "OUTPUT 12; GP1;" 'GPIB LONG ON
PAUSE (1)
PRINT #1, "OUTPUT 12; RU1;" 'DVM RUN ON
CLS
PRINT "SWEEPING"
PAUSE (5)
PRINT #1, "OUTPUT 12; SW1;" 'RAMP SWEEP
PAUSE (5) 'FOR 5 SECOND DELAY
FLAG = 0
FLAG3 = 0
CLS
SCREEN 9
VIEW (80, 48)-(600, 272)
WINDOW (-5, -1)-(5, 1)
AREA = .01 * .01
LOCATE 23, 32
PRINT "CURRENT DENSITY (A/m", CHR$(253); ")"
LOCATE 6, 3
PRINT "P"
LOCATE 7, 3
PRINT "O"
PRINT ".3"
LOCATE 21, 29
PRINT ".2"
LOCATE 21, 36
PRINT ".1"
LOCATE 21, 43
PRINT "0"
LOCATE 21, 50
PRINT "1"
LOCATE 21, 56
PRINT "2"
LOCATE 21, 63
PRINT "3"
LOCATE 21, 69
PRINT "4"
LOCATE 21, 76
PRINT "5"
LOCATE 20, 7
PRINT ".1.0"
LOCATE 16, 7
PRINT ".0.5"
LOCATE 12, 7
PRINT " 0.0"
LOCATE 8, 7
PRINT " 0.5"
LOCATE 4, 7
PRINT " 1.0"
LINE (-5, -1)-(5, -1)
LINE (-5, 1)-(5, 1)
LINE (5, -1)-(5, 1)
LINE (-5, 1)-(5, 1)
FOR I = -5 TO 5
LINE (I, -1)-(I, -.94)
NEXT I
FOR K = 2 TO 9
XLOG = LOG(K) / LOG(10)
LINE (I + XLOG, -1)-(I + XLOG, -.97)
NEXT K
NEXT I
FOR J = -1 TO 1 STEP .1
LINE (-5, J)-(-4.9, J)
NEXT J
AREA = .01 * .01
PRINT #1, "ENTER 12"

112
INPUT #2, POLS, I$
POL = VAL(POLS)
I = VAL(I$
POL1 = POL
VOLT1 = -POL1
CURR1 = \log(\frac{\text{ABS}(I)}{\text{AREA}})) / \log(10)

READDATA:
FLAG = FLAG + 1
PRINT #1, "ENTER 12"
INPUT #2, POLS, I$
POL = VAL(POLS)
I = VAL(I$
IF FLAG = 10 THEN 'SAVE 1 OUT OF 10 DATA POINTS
IF POL < .25 AND ABS(I) > .0001 AND FLAG3 = 0 THEN PRINT #1, "OUTPUT 12;
RR2;": FLAG3 = 1
WRITE #3, POL, I
FLAG = 0
VOLT2 = -POL
CURR2 = \log(\frac{\text{ABS}(I)}{\text{AREA}})) / \log(10)
COLOR 5, 0
LINE (CURR1, VOLT1)-(CURR2, VOLT2), 11
VOLT1 = VOLT2
CURR1 = CURR2
END IF
'SERIAL POLL
PRINT #1, "SPOLL 12"
INPUT #2, SP%
CALL STATUSBYTE(SP%, BIT%())
IF BIT%(2) <> 1 THEN GOTO READDATA
PRINT #1, "OUTPUT 12; PW0;" 'ON TO STANDBY
CLOSE (3)

'AUTOSCALE LOG PLOT
SCREEN 0
CLS
OPEN "C:\DATA\TEST.DAT" FOR INPUT AS #4
AREA = .01 * .01
VMAX = -1000
VMIN = 1000
IMAX = -1000
IMIN = 1000
DO UNTIL EOF(4)
INPUT #4, V, I
VOLT = -V
CURR = LOG(ABS(I / (AREA))) / LOG(10)
IF VOLT < VMIN THEN VMIN = VOLT
IF VOLT > VMAX THEN VMAX = VOLT
IF CURR < IMIN THEN IMIN = CURR
IF CURR > IMAX THEN IMAX = CURR
LOOP
CLOSE (4)
VMIN = INT(VMIN * 10) / 10
VMAX = INT((VMAX * 10) + .5) / 10
VSCALE:
IF INT(((VMAX - VMIN) * 10) / 4) * 4 <> INT((VMAX - VMIN) * 10) THEN VMIN = INT((VMIN * 10) - 1) / 10
IF INT(((VMAX - VMIN) * 10) / 4) * 4 <> INT((VMAX - VMIN) * 10) THEN VMAX = INT((VMAX * 10) + 1.5) / 10
IF INT(((VMAX - VMIN) * 10) / 4) * 4 <> (VMAX - VMIN) * 10 THEN GOTO VSCALE
IMIN = INT(IMIN)
IMAX = INT(IMAX + 1)
OPEN "C:\DATA\TEST.DAT" FOR INPUT AS #4
CLS
SCREEN 9
VIEW (80, 48)-(600, 272)
WINDOW (IMIN, VMIN)-(IMAX, VMAX)
FLAG2 = 0
LOCATE 23, 32
PRINT "CURRENT DENSITY (A/m")
LOCATE 6, 3
PRINT "P"
LOCATE 7, 3
PRINT "O"
LOCATE 8, 3
PRINT "T"
LOCATE 9, 3
PRINT "E"
LOCATE 10, 3
PRINT "N"
LOCATE 11, 3
PRINT "T"
LOCATE 12, 3
PRINT "I"
LOCATE 13, 3
PRINT "A"
LOCATE 14, 3
PRINT "L"
LOCATE 16, 1
PRINT "(Vsce)"
FOR I = IMTN TO IMAX
LOCATE 22, ((65 / (IMAX - IMTN)) * (I - IMTN)) + 9
PRINT "10"
LOCATE 21, ((65 / (IMAX - IMTN)) * (I - IMTN)) + 10
PRINT I
NEXT I
LOCATE 20, 7
PRINT VMIN
LOCATE 16, 7
PRINT VMIN + (VMAX - VMIN) / 4
LOCATE 12, 7
PRINT VMIN + (VMAX - VMIN) / 2
LOCATE 8, 7
PRINT VMIN + (3 * (VMAX - VMIN) / 4)
LOCATE 4, 7
PRINT VMAX
LINE (IMTN, VMIN)-(IMAX, VMIN)
LINE (IMTN, VMAX)-(IMAX, VMAX)
LINE (IMAX, VMIN)-(IMAX, VMAX)
LINE (IMTN, VMAX)-(IMIN, VMIN)
FOR I = IMIN TO IMAX
LINE (I, VMIN)-(I, VMIN + .06)
FOR K = 2 TO 9
XLOG = LOG(K) / LOG(10)
LINE (I + XLOG, VMIN)-(I + XLOG, VMIN + .03)
NEXT K
NEXT I
FOR J = VMIN TO VMAX STEP .1
LINE (IMIN, J)-(IMIN + .1, J)
NEXT J
INPUT #4, V, I
VOLT1 = -V
CURR1 = LOG(ABS(I / (AREA))) / LOG(10)
DO UNTIL EOF(4)
INPUT #4, V, I
VOLT2 = -V
CURR2 = LOG(ABS(I / (AREA))) / LOG(10)
COLOR 5, 0
IF VOLT2 < VOLT1 AND 2 * INT(FLAG2 / 2) = FLAG2 THEN FLAG2 = FLAG2 + 1
IF VOLT1 < VOLT2 AND 2 * INT(FLAG2 / 2) <> FLAG2 THEN FLAG2 = FLAG2 + 1
LINE (CURR1, VOLT1)-(CURR2, VOLT2), FLAG2 + 11
VOLT1 = VOLT2
CURR1 = CURR2
LOOP
CLOSE (4)
END'

SUB PAUSE (DELAY!)
CONST SECONDSINDAY = 24& * 60& * 60&
LOOPFINISH = TIMER + DELAY
IF LOOPFINISH > SECONDSINDAY THEN
LOOPFINISH = LOOPFINISH - SECONDSINDAY
DO WHILE TIMER > LOOPFINISH
LOOP
END IF
'IF PAUSE DOES NOT OCCUR AROUND MIDNIGHT:
DO WHILE TIMER < LOOPFINISH
IF TIMER < 1 AND LOOPFINISH > 86399 THEN GOTO 123
LOOP
123
END SUB'

SUB STATUSBYTE (SP%, BIT%())
X% = SP%
FOR I% = 0 TO 7
Y% = X% MOD 2
BIT%(I%) = Y%
X% = FIX(X% / 2)
NEXT I%
END SUB'
APPENDIX II: MICROSOFT QUICKBASIC PROGRAM FOR CONTROLLING
ELECTROCHEMICAL DEVICES FOR AC IMPEDANCE EXPERIMENTS

'1286/1250 AC IMPEDANCE PROGRAM BY NORMAN CHOW
DECLARE SUB PAUSE (DELAY!)
DECLARE SUB STATUSBYTE (SP%, BIT%)
DIM BIT%(7)

CLS

'INITIALIZE BOARD AND DEVICE
OPEN "GPIBO" FOR OUTPUT AS #1
OPEN "GPIBO" FOR INPUT AS #2
OPEN "C:\DATA\AC\FILENAME.DAT" FOR APPEND AS #3

PRINT #1, "ABORT"
PRINT #1, "RESET"
PRINT #1, "REMOTE"

'RESET 1250
PRINT #1, "OUTPUT 6; TT2" 'INITIALIZE
PAUSE (.5)
PRINT #1, "OUTPUT 6; SM" 'SCROLL MINI STATUS
PAUSE (.5)
PRINT #1, "OUTPUT 6; SO0201" 'SOURCE VOLTS/AMPS
PAUSE (.5)
PRINT #1, "OUTPUT 6; AU3" 'Ch 1 SHORT
PAUSE (.5)
PRINT #1, "OUTPUT 6; AU4" 'Ch 2 SHORT
PAUSE (.5)
PRINT #1, "OUTPUT 6; IP1, 1" 'INPUT CHANEL 1 FROM REAR
PAUSE (.5)
PRINT #1, "OUTPUT 6; IP2, 1" 'INPUT CHANEL 2 FROM REAR
PAUSE (.5)

'RESET 1286
PRINT #1, "OUTPUT 12; BK4" 'INITIALIZE
PAUSE (.5)
PRINT #1, "OUTPUT 12; PW0" 'STANDBY
PAUSE (.5)
PRINT #1, "OUTPUT 12; P00" 'P STAT
PAUSE (.5)
PRINT #1, "OUTPUT 12; RR3" '10 OHM STANDARD
RESISTOR*********************
SRESIS = 10 'STANDARD
RESISTOR*********************
PAUSE (.5)
PRINT #1, "OUTPUT 12; IL6" 'CURRENT LIMIT 2 AMPS
PAUSE (.5)
PRINT #1, "OUTPUT 12; OL2" 'OVERLOAD WARNING
PAUSE (.5)
PRINT #1, "OUTPUT 12; BY1" 'CE /OC ON STANDBY
PAUSE (.5)
PRINT #1, "OUTPUT 12; PV.9" 'POLARIZATION VOLTAGE -0.9
VOLTS********************
PAUSE (.5)
PRINT #1, "OUTPUT 12; PI1" 'POL I/P x 0.01
PAUSE (.5)
PRINT #1, "OUTPUT 12; DG2" 'DIGITS 4x9 60 Hz
PAUSE (.5)
PRINT #1, "OUTPUT 12; TR1" 'TRIGGER RECYCLE
PAUSE (.5)
PRINT #1, "OUTPUT 12; DC1" 'DRIFT CORR. OFF
PAUSE (.5)
PRINT #1, "OUTPUT 12; PX9" 'PAR1 = POL
PAUSE (.5)
PRINT #1, "OUTPUT 12; PY5" 'PAR2 = I
PAUSE (.5)
PRINT #1, "OUTPUT 12; RH1" 'DATA OUTPUT HEADING OFF
PAUSE (.5)
PRINT #1, "OUTPUT 12; VX1" 'V x 10***************
PAUSE (.5)
PRINT #1, "OUTPUT 12; IX1" 'I X 10***************
PAUSE (.5)
PRINT #1, "OUTPUT 12; FI1" 'LP FILTER ON*************
PAUSE (.5)

'DVM DISPLAY
PRINT #1, "OUTPUT 12; GP0" 'GPIB OFF
PRINT #1, "OUTPUT 12; TR1" 'DVM RECYCLE
PRINT #1, "OUTPUT 12; RU1" 'DVM ON

'SETUP 1250
PRINT #1, "OUTPUT 6; OP3,1" 'FILE ALL
PAUSE (.5)
PRINT #1, "OUTPUT 6; FC" 'CLEAR FILE
PAUSE (.5)
PRINT #1, "OUTPUT 6; FS31" 'FILE SIZE 31 BLOCKS
PAUSE (.5)
PRINT #1, "OUTPUT 6; AM1" 'GENERATOR AMPLITUDE 1/100 VOLTS
VOLT********************
PAUSE (.5)
PRINT #1, "OUTPUT 6; MI.1" 'MINIMUM FREQUENCY .1
Hz***********************
PAUSE (.5)
PRINT #1, "OUTPUT 6; MA65535" 'MAX. FREQUENCY 65535
Hz***********************
PAUSE (.5)
PRINT #1, "OUTPUT 6; GS30" '30 DATA
POINT************************************
PAUSE (.5)
PRINT #1, "OUTPUT 6; IS210" 'INTEGRATION TIME 210 SECONDS
PAUSE (5)

'-------------------------------------------------------------------------------
'TURN CELL (1286) ON
RUNNO = 0 'SET 1ST RUNNO TO 0
PRINT #1, "OUTPUT 12; ON0" 'POL V/I POTENTIAL
POLARIZATION*********************
PRINT #1, "OUTPUT 12; OL1" 'OVERLOAD LIMIT
PRINT #1, "OUTPUT 12; VTO" 'AUTO V REJECT
PRINT #1, "OUTPUT 12; BR1" 'BIAS REJECT MEASURE THEN ON
PRINT #1, "OUTPUT 12; IL6" 'CURRENT LIMIT 2 AMPS
PRINT #1, "OUTPUT 12; PW1" 'CELL ON
PAUSE (300) 'INITIAL POLARIZATION TIME
*****************************************************************************

-------------------------------------------------------------------------------

RERUN:
IF RUNNO = 0 THEN
PRINT #1, "OUTPUT 12; PV.4" 'POLARIZE TO -.4Vsce
PAUSE (300)
END IF
IF RUNNO = 1 THEN
PRINT #1, "OUTPUT 12; PV.3" 'POLARIZE TO -.3Vsce
PAUSE (300)
END IF
IF RUNNO = 2 THEN
PRINT #1, "OUTPUT 12; PV.2" 'POLARIZE TO -.2Vsce
PAUSE (300)
IF RUNNO = 3 THEN
PRINT #1, "OUTPUT 12; PV.1" 'POLARIZE TO -.1Vsce
PAUSE (300)
END IF
IF RUNNO = 4 THEN
PRINT #1, "OUTPUT 12; PV0" 'POLARIZE TO 0Vsce
PAUSE (300)
ENDIF
IF RUNNO = 5 THEN
PRINT #1, "OUTPUT 12; PV-.1" 'POLARIZE TO .1Vsce
PAUSE (300)
IF RUNNO = 6 THEN
PRINT #1, "OUTPUT 12; PV-.2" 'POLARIZE TO .2Vsce
PAUSE (300)
IF RUNNO = 7 THEN
PRINT #1, "OUTPUT 12; PV-.3" 'POLARIZE TO .3Vsce
PAUSE (300)
ENDIF
IF RUNNO = 8 THEN
PRINT #1, "OUTPUT 12; PV-.4" 'POLARIZE TO .4Vsce
PAUSE (300)
ENDIF
IF RUNNO = 9 THEN
PRINT #1, "OUTPUT 12; PV-.5" 'POLARIZE TO .5Vsce
PAUSE (300)
ENDIF
'-----------------------------------------------
'RUN 1250
PRINT #1, "OUTPUT 6; OP2,1" 'GPIB FILE ALL
PAUSE (.5)
PRINT #1, "OUTPUT 6; SC2" 'LOG SCAN DOWN
PAUSE (.5)
PRINT #1, "OUTPUT 6; RE" 'ANALYZER RECYLE
PAUSE (.5)
PRINT #1, "OUTPUT 6; RG" 'START GENERATOR
PAUSE (.5)
'-----------------------------------------------
'DOWNLOAD DATA
'GRAPH
CLS
SCREEN 9

120
WIDTH 80, 43
COLOR 11, 0
LOCATE 3, 32
PRINT FILENMS$
LOCATE 4, 32
PRINT DATES$; " "; TIMES$
COLOR 11, 0

'X-AXIS LABELLING FREQUENCY
'
XMIN = -1
XMAX = 5
L = XMAX - XMIN
STP = 18.5 / L
I = 0
FOR XLABEL = XMIN TO XMAX STEP 3
LOCATE 41, 18 + INT((2.4 * I * STP) + .5)
PRINT "10"
LOCATE 40, 19 + INT((2.4 * I * STP) + .5)
XLABS = STR$(XLABEL)
PRINT XLABS
I = I + 3
NEXT

'left y-axis, impedance
'
YMIN = 1 'MINIMUM
IMPEDANCE****************************************
YMAX = 6 'MAXIMUM
IMPEDANCE****************************************
L = YMAX - YMIN
STP = 14 / L
I = 0
FOR YLABEL = YMIN TO YMAX
YLABS = STR$(YLABEL)
IF YLABEL = YMAX THEN
LOCATE 40 - INT((2.4 * I * STP) + .5), 14
PRINT "10"
LOCATE 39 - INT((2.4 * I * STP) + .5), 15
PRINT YLABS
ELSE
LOCATE 39 - INT((2.4 * I * STP) + .5), 14
PRINT "10"
END
LOCATE 38 - INT((2.4 * I * STP) + .5), 15
PRINT YLAB$
END IF
I = I + 1
NEXT

'right y-axis labelling, phase angle

TMIN = 0 'MINIMUM PHASE
ANGLE*****************************
TMAX = 90 'MAXIMUM PHASE
ANGLE*****************************
COLOR 9, 0
L = (TMAX - TMIN) / 15
STP = 14 / L
I = 0
FOR YLABEL = TMIN TO TMAX STEP 15
LOCATE 39 - INT((2.4 * I * STP) + .5), 64
YLAB$ = STR$(YLABEL)
PRINT YLAB$
I = I + 1
NEXT
COLOR 11, 0

LOCATE 42, 33
PRINT "Frequency, (Hz)"
Y1$ = "IMPEDENCE"
Y2$ = "PHASE ANGLE"
FOR I = 1 TO LEN(Y1$)
LOCATE 14 + I, 9
PRINT MID$(Y1$, I, 1)
NEXT I
LOCATE 16 + LEN(Y1$), 6
PRINT "("; CHR$(234); "cm"; CHR$(253); ")"
COLOR 9, 0
FOR J = 1 TO LEN(Y2$)
LOCATE 14 + J, 70
PRINT MID$(Y2$, J, 1)
NEXT J
LOCATE 16 + LEN(Y2$), 68
PRINT "(DEG)"
LOCATE 42, 1
COLOR 11, 0
'plot ticks

WINDOW (XMIN, YMIN)-(XMAX, YMAX)
LINE (XMIN, YMIN)-(XMIN, YMAX)
LINE (XMIN, YMAX)-(XMAX, YMAX)
LINE (XMIN, YMIN)-(XMAX, YMIN)
COLOR 9, 0
LINE (XMAX, YMAX)-(XMAX, YMIN)
COLOR 11, 0
INCX = (XMAX - XMIN) / 100
INCY = (YMAX - YMIN) / 100
FOR XTICK = XMIN TO XMAX
  LINE (XTICK, YMIN)-(XTICK, YMIN + 3 * INCY)
  LINE (XTICK, YMAX)-(XTICK, YMAX - 3 * INCY)
NEXT
FOR XTICK = XMIN TO XMAX STEP 3
  LINE (XTICK, YMIN)-(XTICK, YMIN + 5 * INCY)
  LINE (XTICK, YMAX)-(XTICK, YMAX - 5 * INCY)
NEXT

FOR YTICK = YMIN TO YMAX
  LINE (XMIN, YTICK)-(XMIN + 5 * INCX, YTICK)
FOR I = 2 TO 9
  YLOG = YTICK + 1 + LOG(I / 10) / 2.3
  LINE (XMIN, YLOG)-(XMIN + 3 * INCX, YLOG)
NEXT

'READDATA
PRINT #1, "ENTER 6"
INPUT #2, FREQ, REA, IMG
REA = REA * SRESIS
IMG = IMG * SRESIS
WRITE #3, FREQ, REA, IMG
FREQ1 = LOG(FREQ) / LOG(10)
TIMP1 = LOG((REA^2 + IMG^2)^.5) / LOG(10)
PHAS1 = (ATN(-IMG / REA)) * (180 / 3.1415)
FLAG2 = 0
READDATA2:
FLAG1 = FLAG1 + 1
IF FLAG2 = 0 AND FREQ < 10 THEN
PRINT #1, "OUTPUT 12; F11" 'LOW PASS FILTER ON
FLAG2 = 1
END IF
PRINT #1, "ENTER 6"
INPUT #2, FREQ, REA, IMG
REA = REA * SRESIS
IMG = IMG * SRESIS
WRITE #3, FREQ, REA, IMG
FREQ2 = LOG(FREQ) / LOG(10)
TIMP2 = LOG((REA^2 + IMG^2) .5) / LOG(10)
PHAS2 = (ATN(-IMG / REA)) * (180 / 3.1415)
WINDOW (XMIN, YMIN)-(XMAX, YMAX)
LINE (FREQ1 - INCX, TIMP1 - INCY)-(FREQ1 + INCX, TIMP1 + INCY), 11
LINE (FREQ1 - INCX, TIMP1 + INCY)-(FREQ1 + INCX, TIMP1 - INCY), 11
TIMP1 = TIMP2
'REIGHT AXIS TICKS
COLOR 9, 0
WINDOW (XMIN, TMIN)-(XMAX, TMAX)
INCT = (TMAX - TMIN) / 100
FOR YTICK = TMIN TO TMAX STEP 15
LINE (XMAX, YTICK)-(XMAX - 5 * INCX, YTICK)
NEXT
'PLOT THE PHASE ANGLE VERSUS THE FREQUENCY
LINE (FREQ1 - INCX, PHAS1 - INCT)-(FREQ1 + INCX, PHAS1 + INCT), 9, B
FREQ1 = FREQ2
PHAS1 = PHAS2
'SERIAL POLL
PRINT #1, "SPOLL 6"
INPUT #2, SP%
CALL STATUSBYTE(SP%, BIT%())
IF BIT%(2) <> 1 THEN GOTO READDATA2

PAR$ = "C:\PJSCREEN /UON /PT /AC /M16 /CD /RN"
SHELL PAR$
'CALL INT86OLD(5, INARY%, OUTARY%)
'END PLOT
CLOSE (3)
PRINT #1, "OUTPUT 12; PW0" 'ON TO STANDBY
PAUSE (.5)
PRINT #1, "OUTPUT 6; SG" 'GENERATOR STOP
PRINT #1, "OUTPUT 6; BK" 'BREAK

RUNNO = RUNNO + 1
PAUSE (60) ' PAUSE TIME BETWEEN RUNS
IF RUNNO < 10 THEN
  FILENMS = "C:\DATA\POL.00" +
  LTRIM$(STR$(RUNNO))************ **************
ELSEIF RUNNO > 9 AND RUNNO < 100 THEN
  FILENMS = "C:\DATA\POL.0" +
  LTRIM$(STR$(RUNNO))***********************
ELSE
  FILENMS = "C:\DATA\POL." +
  LTRIM$(STR$(RUNNO))***********************
END IF
OPEN FILENMS FOR APPEND AS #3
IF RUNNO < 9 THEN GOTO RERUN:
ELSE

SUB PAUSE (DELAY!)
CONST SECONDSINDAY = 24& * 60& * 60&
LOOPFINISH = TIMER + DELAY
IF LOOPFINISH > SECONDSINDAY THEN
  LOOPFINISH = LOOPFINISH - SECONDSINDAY
DO WHILE TIMER > LOOPFINISH
  LOOP
END IF
'IF PAUSE DOES NOT OCCUR AROUND MIDNIGHT:
DO WHILE TIMER < LOOPFINISH
IF TIMER < 1 AND LOOPFINISH > 86399 THEN GOTO 123
LOOP
123
END SUB'*******************************

SUB STATUSBYTE (SP%, BIT%())
X% = SP%
FOR 1% = 0 TO 7
  Y% = X% MOD 2
BIT%(I%) = Y%
X% = FIX(X% / 2)
NEXT I%

END SUB'************************************
APPENDIX III: COMPARISON OF MEASURED IMPEDANCE DATA WITH MODELED IMPEDANCE RESULTS

Figure A1. Measured Versus Model Impedance for Copper at -0.4 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM

Figure A2. Measured Versus Model Impedance for Copper at -0.3 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM
Figure A3. Measured Versus Model Impedance for Copper at -0.2 Vsce in 1M NaCl
Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM

Figure A4. Measured Versus Model Impedance for Copper at -0.1 Vsce in 1M NaCl
Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM
Figure A5. Measured Versus Model Impedance for Copper at 0.0 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM

Figure A6. Measured Versus Model Impedance for Copper at 0.1 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM
Figure A7. Measured Versus Model Impedance for Copper at 0.2 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM

Figure A8. Measured Versus Model Impedance for Copper at 0.3 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM
Figure A9. Measured Versus Model Impedance for Copper at 0.4 Vsce in 1M NaCl
Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM

Figure A10. Measured Versus Model Impedance for Copper at 0.5 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 50 RPM
Figure A11. Measured Versus Model Impedance for Copper at -0.4 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM

Figure A12. Measured Versus Model Impedance for Copper at -0.3 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM
Figure A13. Measured Versus Model Impedance for Copper at -0.2 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM

Figure A14. Measured Versus Model Impedance for Copper at -0.1 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM
Figure A15. Measured Versus Model Impedance for Copper at 0.0 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM

Figure A16. Measured Versus Model Impedance for Copper at 0.1 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM
Figure A17. Measured Versus Model Impedance for Copper at 0.2 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM

Figure A18. Measured Versus Model Impedance for Copper at 0.3 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM
Figure A19. Measured Versus Model Impedance for Copper at 0.4 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM

Figure A20. Measured Versus Model Impedance for Copper at 0.5 Vsce in 1M NaCl Buffered to pH 10.5 with 0.01M Sodium Tetraborate Rotating at 5000 RPM