FUNDAMENTAL STUDIES OF THE ANODIC BEHAVIOR OF THIOUREA
IN COPPER ELECTROREFINING

by

ZHIMIN ZHENG

B.Sc. The Xian University of Architecture and Technology, 1983
M.Sc. The University of Alaska Fairbanks, 1995

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to the required standard

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Department of Metals and Materials Engineering

The University of British Columbia
Vancouver, Canada

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ABSTRACT

The behavior of thiourea in the anodic process of copper electrorefining was investigated using various advanced electrochemical techniques with a view to establishing an accurate method to determine its effect on the anode process in certain highly concentrated copper sulfate-sulfuric acid electrolytes. It was found that thiourea acted as an inhibitor hindering the anodic dissolution of copper. Combination measurements of chronoamperometry and rotating disk electrode were sensitive to the addition of trace concentration of thiourea and were able to quantify the characteristics of the inhibition effect on the anodic dissolution process.

The various techniques used – linear sweep voltammetry, chronoamperometry combined with the use of the rotating disk electrode, chronopotentiometry measurements and AC impedance provided results which exhibited excellent agreement. Together the measurements provided detailed information about the inhibition effect on the interfaces of the copper electrodes. An interaction mechanism was proposed to describe the inhibition.

The effects of cupric ions, protons, and thiourea were determined. The influence of formamidine disulfide, one of decomposition products of thiourea, on the anodic dissolution of copper was also investigated. The chronopotentiometry technique demonstrated the most promise as an experimental method as it provided a simple measurement of copper passivation at various concentrations of thiourea.
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<tr>
<td>(A)</td>
<td>Electrode surface area, cm(^2)</td>
</tr>
<tr>
<td>(C)</td>
<td>Capacitance, F</td>
</tr>
<tr>
<td>(C_b)</td>
<td>Bulk concentration of species, molarity</td>
</tr>
<tr>
<td>(C_d)</td>
<td>Double layer capacitance, F</td>
</tr>
<tr>
<td>(C_f)</td>
<td>Capacitance of coatings, F</td>
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<tr>
<td>(C_{M^{z+}}^{0})</td>
<td>Bulk concentration of metal ion (M^{z+}), molarity</td>
</tr>
<tr>
<td>(C_{po})</td>
<td>Capacitance of the pore of coatings, F</td>
</tr>
<tr>
<td>(C_s)</td>
<td>Species concentration at electrode surface, molarity</td>
</tr>
<tr>
<td>(D_{Cu^{2+}})</td>
<td>Diffusion coefficient of cupric ions, cm(^2) sec(^{-1})</td>
</tr>
<tr>
<td>(D_{M^{z+}})</td>
<td>Diffusion coefficient of the metal ion (M^{z+}), cm(^2) sec(^{-1})</td>
</tr>
<tr>
<td>(E)</td>
<td>Alternating voltage, V</td>
</tr>
<tr>
<td>(\Delta E)</td>
<td>Magnitude of voltage perturbation, V</td>
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<tr>
<td>(E_0^{M+/M})</td>
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</tr>
<tr>
<td>(e^-)</td>
<td>Electron</td>
</tr>
<tr>
<td>(F)</td>
<td>Faradaic constant, C</td>
</tr>
<tr>
<td>(f^-)</td>
<td>Frequency, Hz</td>
</tr>
<tr>
<td>(\Delta G_{298}^0)</td>
<td>Standard Gibbs free energy change in a chemical process, J/mol</td>
</tr>
<tr>
<td>(\Delta H)</td>
<td>Enthalpy change in a chemical process, J/mol</td>
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<tr>
<td>(I)</td>
<td>Current, A</td>
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<tr>
<td>(i_a)</td>
<td>Anodic current density, A/cm(^2)</td>
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<tr>
<td>(i_{cor-a})</td>
<td>Anodic current densities at interface of metal-electrolyte without coating, A/cm(^2)</td>
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<tr>
<td>(i_{cor-c})</td>
<td>Cathodic current densities at interface of metal-electrolyte without coating, A/cm(^2)</td>
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<tr>
<td>(i_{cor,coat})</td>
<td>Sum of corrosion current density in the presence of inhibitor, A/cm(^2)</td>
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<td>(i_{met,cor-a})</td>
<td>Anodic current densities measured at interfaces of metal-electrolyte, A/cm(^2)</td>
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<tr>
<td>(i_{met,cor-c})</td>
<td>Cathodic current densities at interfaces of metal-electrolyte, A/cm(^2)</td>
</tr>
<tr>
<td>(i_{peak})</td>
<td>Peak current density, A/cm(^2)</td>
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<tr>
<td>(i_{sol,cor-a})</td>
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<tr>
<td>(i_{sol,cor-c})</td>
<td>Cathodic current densities at interfaces of coating film-electrolyte, A/cm(^2)</td>
</tr>
<tr>
<td>(j)</td>
<td>Imaginary number, (\sqrt{-1})</td>
</tr>
</tbody>
</table>
\( K_{\text{CuSO}_4} \) Stoichiometric dissociation coefficient of copper sulfate
\( K_{\text{H}_2\text{SO}_4} \) Stoichiometric dissociation coefficient of bisulfate
\( k_{\text{Cu}^{2+}} \) Reaction rate coefficient for copper dissolution, cm sec\(^{-1}\)
\( L \) Inductance, F\(^{-1}\)
\( l_{\text{eff}} \) Effective diffusion thickness, cm
\( n \) Electrons per molecule oxidized
\( P_{\text{CPE}} \) Fractional element in CPE circuit.
\( Q_{\text{CuSO}_4} \) Equilibrium constant of copper sulfate
\( Q_{\text{H}_2\text{SO}_4} \) Equilibrium constant of bisulfate
\( q \) General infinite diffusion coefficient, \( \Omega \text{ cm}^2 \text{ sec}^{-p} \)
\( q_{\text{eh}} \) Charge in a capacitor, C
\( R_{c_\text{t}} \) Resistance of coatings, \( \Omega \)
\( R_{\text{po}} \) Resistance of pore, \( \Omega \)
\( R_{\text{e}} \) Resistance of electrolyte solution, \( \Omega \)
\( R_{p}^0 \) Resistance obtained in the absence of thiourea, \( \Omega \)
\( R_{p}^\text{in} \) Resistance obtained in the presence of thiourea, \( \Omega \)
\( R_1 \) Polarization resistance, \( \Omega \)
\( R_2 \) Diffusion resistance, \( \Omega \)
\( R_3 \) Slimes layer resistance, \( \Omega \)
\( T \) Absolute temperature, K
\( T_{\text{CPE}} \) Frequency independent parameter, \( \Omega^{-1} \text{ cm}^2 \text{ sec}^{-p} \)
\( t \) Time, sec
\( U(t) \) Permeability of slimes, cm sec\(^{-1}\)
\( v_{\text{sw}} \) Potential sweep rate, mV/sec
\( W \) General finite diffusion impedance, \( \Omega \)
\( Y \) Admittance vector, \( \Omega \)
\( Y' \) Real part of admittance, \( \Omega^{-1} \)
\( Y'' \) Imaginary part of admittance, \( \Omega^{-1} \)
\( Z \) Impedance vector, \( \Omega \)
$Z'$  Real part of impedance, $\Omega$

$Z''$  Imaginary part of impedance, $\Omega$

$Z_C$  Impedance vector of capacitor, $\Omega$

$Z_D$  Diffusion impedance, $\Omega$

$Z_{parallel}$  Impedance vector of parallel combination of resistor with capacitor, $\Omega$

$Z_R$  Impedance vector of resistor, $\Omega$

$Z_w$  Impedance vector of Warburg, $\Omega$

$\beta$  Formation constant

$\delta$  Thickness of diffusion layers, cm

$\delta_{pre}$  Thickness of the surface films, cm

$\delta(t)$  Thickness of the slimes layer, cm

$\epsilon_c$  Dielectric constant of coatings

$\epsilon_0$  Permittivity of coatings, $C^2 N^{-1} m^{-2}$

$\epsilon_s$  Porosity of the surface films

$\epsilon(t)$  Porosity of the slimes layer

$\eta_a$  Activation potential, V

$\eta_c$  Concentration overpotential, V

$\eta_r$  Potential drop of the slimes layer, V

$\theta$  Surface coverage

$\nu$  Kinematic viscosity of electrolyte solution, $cm^2 sec^{-1}$

$\sigma_w$  Warburg coefficient, $\Omega^{-1} cm^{-2} sec^{0.5}$

$\nu_{hr}$  Heterogeneous reaction rate, mol $cm^{-3} sec^{-1}$

$\psi$  Phase shift between two sinusoidal, degrees, radians

$\omega$  Angular frequency, rad sec$^{-1}$

$\omega_{max}$  Maximum frequency at which AC impedance was analyzed, rad sec$^{-1}$

$\omega_{rde}$  Angular velocity of rotating disk electrode, rad sec$^{-1}$

$\sigma$  Amount of generated slimes, kg/t Cu,
ACKNOWLEDGEMENTS

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Chapter 1 Introduction

Electrolytic copper is widely used in various industries around the world. The majority of electrolytic copper is produced by the copper electrorefining process in which impure copper is refined through dissolution from an impure copper anode and deposition on the cathode.

Thiourea as an addition agent is added in the copper refining process to improve the quality of copper cathode. Previous studies, which will be referred to in detail later, have explored the effect of thiourea on the cathodic process. In these studies it was found that a certain amount of thiourea depresses the cathodic potential and levels the sharp discharge spots, leading to improved morphological and compositional quality of the copper cathode.

The influence of thiourea on the anodic process of copper electrorefining has been seldom reported. In these reports it was found that over half of the added thiourea reports to the anode slimes. Investigations on copper in dilute acidic solutions showed conflicting results. Some indicated that thiourea acts as an accelerator to enhance the dissolution rate of copper. Others demonstrated that thiourea acts as an inhibitor to depress the dissolution rate of copper.

In copper electrorefining plants impure copper is dissolved in highly concentrated solutions. The ratio of thiourea to major species concentrations is one to one million. There is a distinct gap between the theoretical studies and industrial operating conditions.

Cyclic voltammetry technique has employed extensively to investigate the effect of thiourea on both the copper anodic and cathodic processes. It shows some disadvantages: (1) experiments on the cathodic process show significant effect of thiourea compared with that of the anodic process at a certain high concentration of thiourea; (2) the effect of thiourea cannot be identified for both processes at low concentrations of thiourea; (3) the technique is not sensitive for quantifying the effect of thiourea on the anodic process.

The purpose of the present work was to investigate the effect of thiourea on the anodic process of copper electrorefining in highly concentrated copper sulfate-sulfuric acid solution and at various concentrations of thiourea. Of particular interest was the quantitative characterization
of the effect of thiourea on the anodic process by using simple and rapid electrochemical techniques.

In addition, it is considered that anode processes such as passivation may be influenced by the presence of thiourea in solution. In spite of numerous studies on copper passivation, the relationship between passivation and addition of thiourea has seldom been reported. In the present investigation various electrochemical techniques were employed to investigate this relationship.

Knowledge of the solution chemistry of copper sulfate-sulfuric acid in the presence of thiourea is essential for the investigation of the behavior of thiourea in copper electrorefining. A mathematical model was introduced to predict the speciation in highly concentrated copper sulfate-sulfuric acid solution.

Steady state and transient state electrochemical techniques were employed to determine the effect of thiourea on the anodic and cathodic dissolution processes of copper. The influence of thiourea, combined with changing concentration of major species of copper sulfate-sulfuric acid, on the dissolution process was investigated as well.

The in-situ electrochemical technique, AC impedance measurement, was used to investigate the effect of thiourea on the copper electrode interface. Of particular interest was the identification of the properties of interfaces with respect to anode slimes formation in the absence and presence of thiourea.

Physical models were selected and employed to make a connection between the obtained AC impedance spectra and the physical, chemical or electrochemical properties of the interfaces.

The intention of the present study was to ensure that the experimental results would provide useful guidance to industrial operations using thiourea. A comprehensive array of electrochemical techniques was used to characterize the behavior of thiourea at low concentrations.
Chapter 2 Literature Review

The copper electrorefining process has been used since its development by Elkington in England in 1865. In this process an impure copper anode is purified by anodic dissolution and deposition on a cathode. Most of impurities and precious metals contained in the anode report in the anode slimes. Additives are added to the electrolyte to improve the quality of cathode copper. The essential copper electrorefining process involves dissolution of copper, transport of copper ions through the anode slimes, and deposition of copper at the cathode.

2.1 Copper Electrorefining Process

Copper industrial practices normally are classified by two main processes. Copper flotation concentrates are treated by smelting, converting, and anode electrorefining. Oxide and secondary sulfide ores are treated by leaching and solvent extraction-electrowinning (SX-EW). Electrorefined copper accounts for approximately 80% of all copper production in the world. The first patents on electrolytic refining of copper were those of James Elkington, published in England in 1865 to 1870. The first electrolytic copper refinery in the United States, built in Newark, New Jersey, by the Balbach Smelting and Refining Company[1], was operated from 1883 to 1918. The present annual production of refined copper is over 9 million tonnes[2]. In the process of copper electrorefining, copper in the anode dissolves into a copper sulfate-sulfuric acid refining solution and the copper metal is plated on cathodes. In the electrorefining process the impurities predominately report to the anode slimes which accumulate on the surface of the anode and after a period of times the slimes fall to the bottom of the refining cell. Some impurities such as arsenic, antimony, bismuth, nickel and iron partially dissolve into the bulk solution. Precious metals (gold, silver, PGM’s) and selenium and tellurium report to the slimes.

Copper electrorefining has been improved through the introduction of new materials handling and sensing techniques. One of the innovations is in the area of uniform weight anode casting. This technique is important for improving cathode purity[3]. The second is the treatment of starter sheet straightening by which the cathodic current efficiencies and quality are significant improved. Thirdly, infrared inspection of anodes and cathodes from overhead cranes for the detection of shorts or open circuits has improved current efficiencies and lowered labor costs.
Electrochemical improvements have also been introduced into the copper electrorefining process. Current density for direct current operation reaches an average value of 231 A/m², while for periodic reverse current (PRC), an average 338 A/m² has been reported[3]. A combination of glue, thiourea, Avitone and chloride as addition agents has shown a marked improvement on the cathode quality at Noranda’s CCR refinery in Montreal East[4]. Filtration of tankhouse electrolyte, especially for the stripper sections, is accepted as a simple way to improve cathode quality at minor cost. By this method most of small particles of anode slimes which can serve as nucleation points for nodule formation are removed from the stripper system[5]. The REATROL method of addition agents monitoring, developed by ASARCO, is used to control thiourea levels in electrorefining baths. Thiourea promotes cathode smoothness and reduces nodule formation. Nodule formation is one of the chief causes of shorting in copper electrolysis. Thus the method has resulted in a marked improvement in current efficiencies, and the quality of copper cathode[6]. Table 2-1 shows the production capacity and additives application for major copper electrorefiners.

2.2 Fundamental Research of Copper Dissolution

The common view of pure copper anodic dissolution is that the metal copper is oxidized directly to cupric ions according to the reaction:

\[
Cu^0 = Cu^{2+} + 2e^- \quad (2-1)
\]

However, many fundamental researches [7-11] have confirmed that the copper oxidation process involves two simple electrochemical reactions. Excellent review papers by Bertocci and Turner[7] and Newman[8] illustrated the copper dissolution process and presented a well-developed model for the relationship between the anodic current density and overpotential.

Mattson and Bockris[9] were the first to indicate that the reaction occurs by the two single electron steps with one being the rate-determining step. In a sulfate medium, the reactions occur as follows:

\[
Cu = Cu^{+} + e^- \quad (2-2)
\]

\[
Cu^{+} = Cu^{2+} + e^- \quad (2-3)
\]
Table 2-1. Comparison of capacity and additives between major producers worldwide[10].

<table>
<thead>
<tr>
<th>Refinery</th>
<th>Cathode Capacity (t/yr)</th>
<th>Current Density (A/m²)</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inco Limited CCCR, Canada</td>
<td>170,000</td>
<td>183</td>
<td>Glue, Tembind, Cl</td>
</tr>
<tr>
<td>Falconbridge Ltd. Kidd Creek, Canada</td>
<td>103,000</td>
<td>250</td>
<td>Glue, Thiourea, Cl</td>
</tr>
<tr>
<td>Noranda CCR Refinery, Canada</td>
<td>350,000</td>
<td>260</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Corp.-del Cobre de Chile, Chuiquicamate</td>
<td>653,000</td>
<td>220-230</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Corporacion del Cobre de Chile, Potrerillos</td>
<td>134000</td>
<td>234</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Empress Nacional de Mineria, Chile</td>
<td>210,000</td>
<td>335*</td>
<td>Glue, Thiourea, Avitone</td>
</tr>
<tr>
<td>Shenyang Smelter, China</td>
<td>60,000</td>
<td>280-330*</td>
<td>Glue, Thiourea, Cl, Cheese</td>
</tr>
<tr>
<td>Mansfelder Kupfer &amp; Messing GmbH, Germany</td>
<td>60,000</td>
<td>245-270</td>
<td>Glue, Thiourea, Cl</td>
</tr>
<tr>
<td>National Iranian Cu Industries Co, Iran</td>
<td>158,000</td>
<td>220</td>
<td>Glue, Thiourea, Cl, Magnafl</td>
</tr>
<tr>
<td>Hibi Kyodo Smelting Co. Ltd, Japan</td>
<td>161,000</td>
<td>294-305*</td>
<td>Glue, Thiourea, Cl</td>
</tr>
<tr>
<td>Kosaka Smelting &amp; Refining Co, Japan</td>
<td>60,000</td>
<td>223</td>
<td>Glue, Thiourea, Cl</td>
</tr>
<tr>
<td>Mitsubishi Materials Corp, Japan</td>
<td>190,000</td>
<td>226</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Nippon Mining and Metals Co, Hitachi, Japan</td>
<td>132,000</td>
<td>185</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Nippon Min. and Met. Co, Saganoseki, Japan</td>
<td>198,000</td>
<td>258-260</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Onahama Seling and Refining Co, Japan</td>
<td>294,000</td>
<td>222-230</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Sumitomo Met. Min. Co., Nishibara, Japan</td>
<td>126,000</td>
<td>220</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Sumitomo Metal Mining Co. Ltd, Toyo, Japan</td>
<td>84,000</td>
<td>270</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Minero Peru, Peru</td>
<td>150,000</td>
<td>213</td>
<td>Glue, Thiourea, Cl</td>
</tr>
<tr>
<td>Phillipine Assoc. Smelting &amp; Refining, Leyte</td>
<td>172,500</td>
<td>300*</td>
<td>Glue, Thiourea, Cl</td>
</tr>
<tr>
<td>Palabora Mining Co. South Africa</td>
<td>140,000</td>
<td>277</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Rio Tinto Metals SA, Spain</td>
<td>140,000</td>
<td>343*</td>
<td>Glue, Thiourea, Cl</td>
</tr>
<tr>
<td>Asarco Inc, Texas, USA</td>
<td>500,000</td>
<td>227.8</td>
<td>NA</td>
</tr>
<tr>
<td>Copper Range Co, Michigan, USA</td>
<td>70,000</td>
<td>273</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Cyprus Miami Mining Corp, Arizona, USA</td>
<td>190,000</td>
<td>280-320</td>
<td>Glue, Thiourea, Avitone</td>
</tr>
<tr>
<td>Kennecott Utah Copper Refinery, Utah, USA</td>
<td>281,000</td>
<td>240</td>
<td>Glue, Thiourea, Cl</td>
</tr>
<tr>
<td>Phelps Dodge Refining Corp, Texas, USA</td>
<td>410,716</td>
<td>270</td>
<td>Glue, Thiourea, Avitone, Cl</td>
</tr>
<tr>
<td>Copper Division of Southwire Corp, USA</td>
<td>123,000</td>
<td>305</td>
<td>Glue, Thiourea, Cl</td>
</tr>
<tr>
<td>Zambia Cons. Cu Mines Ltd, Kitwe, Zambia</td>
<td>220,000</td>
<td>226-318*</td>
<td>Glue, Tembind, Borresper, Cl</td>
</tr>
<tr>
<td>Zambia Cons. Cu Mines Ltd, Mufulira, Zambia</td>
<td>266,000</td>
<td>206-303</td>
<td>Glue, Thiourea, Orzan, Cl</td>
</tr>
</tbody>
</table>

* Using periodic reversal of current in some or all cells.
The mechanism of the copper dissolution reaction has been explained in detail by other researchers. Bockris et al.[11,12] proposed that the rate-determining step is controlled by charge transfer or surface diffusion at low current densities and by charge transfer alone at high current densities. Slaiman and Lorenz[13] used a double-pulse galvanostatic method to illustrate that at low current densities the overpotential causing the slowness of second step reaction contains charge transfer diffusion components. The preference appeared to be related to the experimental conditions. The mechanism of the reaction also was investigated by Jardy et al.[14] using a quartz crystal microbalance and rotating disk electrode system. Their results showed that the dissolution valence is a function of current density and that the mechanism for copper dissolution in 0.1 M Na₂SO₄ acidified to pH 1.5 is:

\[ \text{Cu} = \text{Cu}^+ + e^- \]  \hspace{1cm} (2-4)

At current densities less than $10^6$ A/cm²

\[ \text{Cu}^+_{(ads)} = \text{Cu}^+_{(sol)} \]  \hspace{1cm} (2-5)

\[ \text{Cu}^+_{(sol)} = \text{Cu}^{2+}_{(sol)} + e^- \]  \hspace{1cm} (2-6)

At current densities greater than $10^2$ A/cm²

\[ \text{Cu}^+_{(ads)} = \text{Cu}^{2+}_{(sol)} + e^- \]  \hspace{1cm} (2-7)

Although the mechanism of copper dissolution is declared clearly in the theory, significant efforts have been made to understand the kinetics of copper dissolution. The Tafel slope, which predicts an anodic dissolution behavior, has been verified to a degree by Bockris et al.[15,16] who reported an average value of 40 mV (they revealed a range of average values from 28 to 50 mV). Turner and Johnson[17] presented the value of 43 ± 4 mV. Brown and Thirsk[18] observed the value of 45 ± 5 mV. The data acquisition region in all of the above cases was limited to a potential span of less than 60 mV (+30 mV to +90 mV), which is unusually narrow for Tafel slope behavior.

The present literature survey shows that the apparent valency of copper during dissolution is a function of the current density[19]. It was found that at low current densities the apparent valency of copper is less than 2. Matisson and Bockris[9] explained that the apparent valency of
copper in cupric solutions should tend to be less than 2, if the overpotential for Reaction (2-2) is larger than that for Reaction (2-3). Under these conditions, the concentration of cuprous ion at the electrode is greater than in the bulk, so that more cuprous ion is produced at the electrode than is oxidized to cupric ion. At high dissolution rates, the diffusion of cuprous ion becomes negligible and the apparent valency is very close to 2.

However, another kind of explanation was given by Molodov et al.[20] At high current densities, cuprous ions can be generated so quickly that they react with each other – Reaction (2-8). This provides yet another possible chemical or electrochemical route for copper dissolution.

\[ 2Cu^{+}_{(sol)} = Cu^{2+}_{(sol)} + Cu^{0} \]  \hspace{1cm} (2-8)

It is obvious that the complexity of the dissolution mechanism of pure copper leads to some inherent difficulties when discussing the passivation of impure copper anodes.

2.3 Investigation of Copper Anode Passivation

One of the major challenges to researchers and copper refiners is to understand fully the mechanism of copper anode passivation (Generally, anode passivation refers to the virtual stoppage of the active dissolution of a copper anode). Anode passivation results in a high energy consumption, low production capacity, and poor cathode quality[21]. The minimization of anode passivation could ultimately improve worldwide copper quality and decrease production costs.

Compared to the dissolution of pure copper, the dissolution of impure copper anodes is far more complicated. There are two interfaces existing near an impure copper anode surface during the anode dissolution. One is between the anode surface and the adjacent slimes, and the other between the slimes and the bulk solution. It is sure that when the process of anode slimes formation or deformation changes, these interfaces as well as the slimes layer itself strongly influence the kinetics of the impure copper anode dissolution.

A number of factors influencing the anode passivation have been catalogued including insoluble precipitation, slimes and impurities, additives, and electrolysis operating conditions. Anode passivation was studied extensively by Abe and Goto[22,23,24] in 1980’s. They focused on the role of the electrolyte temperature, sulfuric acid concentration, and oxygen levels in impure copper anode matrices. Sedzmir and Gumovska[25] investigated the effect on an impure
copper anode dissolution process of electrolysis variables such as current density, the solution flow rate, solution composition, and temperature. The mechanism of slimes formation, in the presence of arsenic, sulfur, antimony, bismuth, nickel, silver, tin and other impurities was studied using different methods by Noguchi et al.[26,27,28,29,30]. Chen and Dutrizac examined the influence of silver and nickel in impure copper anodes on the formation of anode slimes[31,32], as well as the behavior of some other impurities in the dissolution process[33,34,35]. Numerous investigations have also been conducted on the behavior of impurities in copper electrolytes, formation characteristics of impurities in anodes and characteristics of anode slimes. Cooper[36] authored an excellent survey of recent work.

Noguchi et al.[30] described in fair detail the behavior of anode impurities in copper electrorefining. The relationship between passivation and factors related to the anode impurities and slimes formation, is given as the following diagram:

---

**Figure 2-1. Factors relating to anode passivation.**

Many hypotheses have been reported on the process of anode passivation, but there is much disagreement concerning the mechanism of passivation. Several major mechanisms have been postulated and are discussed below.
2.3.1 Insoluble precipitation on the copper anode surface

The main cause of anode passivation is attributed to a decrease of the anode active area induced by the precipitation of copper sulfate. Among the theories, Abe[37] elucidated that the anode slimes layer (compounds containing impurity elements in cast anodes) is generated and adheres to an impure copper anode surface. With continuing dissolution of the anode, the slimes layer creates a resistance to the migration of copper ions passing through the slimes layer, thus the removal rate of copper ions declines, and the copper ions accumulate near the anode inside the slimes layer. When the concentration of CuSO₄ becomes saturated, a non-conductive film of CuSO₄·5H₂O forms and adheres on the anode surface, finally leading to passivation.

Abe et al.[38] further confirmed that the copper anode passivation resulted from precipitation of copper sulfate on anode surfaces. Through experiments they demonstrated three points of evidence to confirm the formation of copper sulfate. The precipitation is found on an anode surface when the anode is removed from the electrolyte immediately following passivation. Crystalline cupric sulfate is present on the anode surface when filter paper (used as an artificial diffusion barrier to simulate a slimes layer) is removed after passivation. When a passivated anode is kept on open-circuit in the electrolyte, the cupric sulfate re-dissolves and the anode then shows the same typical potential-time passivation curve.

It is worth pointing out that when Abe et al. carried out their experiments the concentration of copper sulfate was kept at more than 0.68 M and the temperature was approximately 60 °C. In this case there is no way of identifying whether the precipitated copper sulfate was generated before moving the electrode out of solutions or during removal since the test solutions can dry quickly on the electrode when it is taken out from test solutions.

These findings coincide with the discussion presented by Kortum[39] on film formation and growth. An oxide coating on metals is predominantly an ion-conducting film which forms only after an increase in voltage caused by the formation of a non-conducting film. It is believed that the non-conducting film is CuSO₄·5H₂O precipitated from a boundary layer with saturated cupric ions. The appearance of the copper sulfate film results in an increase in potential, which is favorable for the formation of Cu₂O.

Using potentiostatic and voltammetry techniques, Garneau et al.[40] made a pure copper sample passivated in an impurity free-electrolyte. Then, they determined the passivation layer on
the copper sample surface to be copper sulfate by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

Besides copper sulfate precipitation, cuprous oxide is regarded as a main contributor to the copper anode passivation. The occurrence of cuprous oxide makes an anode slimes layer considerably thicker and denser. Therefore the diffusion of copper ions from an anode is seriously inhibited. Abe and Goto[41,42] employed SEM measurements to identify the cuprous oxide phase appearing on the surface of copper anodes when the anode experienced passivation under-the chronopotentiometry control. The results indicated that most of the Cu$_2$O contained in a crude copper anode is dissolved into the electrolytic solution, while perhaps 3~5 % reports to the anode slimes. Jin and Ghali[43] demonstrated similar results to Goto’s after they conducted chronopotentiometric measurements to perform copper anode passivation followed by SEM and XPS examinations.

A series of studies by Chen and Dutrizac[44,45,31,32,34] and more recent studies by Kuxmann and Meyer[46] with their synthesized anodes of Cu-Ag-Se confirmed the formation of cuprous oxide. They proposed following mechanism to describe the formation of cuprous oxide and other compounds:

\[
\text{Cu}_2\text{Se} + m\text{Ag} + \text{H}_2\text{O} = \text{Ag}_2\text{Se} + (m-2)\text{Ag} + \text{Cu}_2\text{O} + 2\text{H}^+ + 2e^- \quad (2-9)
\]

\[
\text{Cu}_2\text{Se} + x\text{H}_2\text{O} = 2\text{Cu}_2\text{Se}_x + x\text{Cu}_2\text{O} + 2x\text{H}^+ + 2xe^- \quad (2-10)
\]

\[
\text{Cu}_2\text{Se} + \text{H}_2\text{O} = 2\text{Cu}_3\text{Se}_2 + \text{Cu}_2\text{O} + 2\text{H}^+ + 2e^- \quad (2-11)
\]

Brugger et al.[47] examined the microstructure of cuprous oxide formed during copper electrolysis. SEM examinations of passivated anodes revealed that a homogenous cuprous oxide layer adheres to the passivated anode surface. In addition, they pointed out that the cuprous oxide particles initially existed in the copper anode quickly dissolve during the active dissolution of copper anodes, and no evidence shows the existed copper oxide adhering on the surface of copper anode and promoting anode passivation.
2.3.2 Impurity behavior in copper anode process

Under normal industrial electrowinning operating conditions, pure copper will not passivate. Many researchers have believed that the ultimate cause of passivation is the impurities contained within impure copper anodes and electrolyte solutions. Impurities in the anode are the result of the original ore or scrap feed. As the anode dissolves, some impurities report to the slimes, others to the electrolyte. Impurities in the electrolyte become concentrated over time in the closed electrolyte system.

A number of researchers have studied anode impurities by using specially alloyed copper samples and a few impure copper anodes from different copper refineries to understand the relationship between impurities and copper passivation. The alloyed copper usually contains one or two metallic impurity elements and oxygen. Minotas et al.[21] used voltammetry technique on alloys of Cu-Sb, Cu-As, and Cu-O to investigate the copper passivation. They found that susceptibility to passivation decreases in the order of Cu-Sb > pure Cu > Cu-As. No explanation was given for the phenomena. They also concluded that the anodic behavior of these alloys is affected by the presence of dissolved oxygen. The dissolved oxygen acts as an oxidizing agent for cuprous ions and can further react with the cuprous oxide layer by forming a cupric oxide which in turn dissolves in the highly acid medium. Thus, oxygen appears to delay the passivation process.

Noguchi et al.[26-30] used copper samples alloyed individually with S, Se, Pb, Ag, Bi, Sn, Ni, and Sb in the range of 2,000 to 50,000 ppm. Using voltammetry technique, they found that anodes with sulfur (2,000ppm), arsenic (30,000ppm), bismuth (40,000ppm), and silver (30,000ppm) passivate quickly, while samples with nickel, tin, lead, and selenium do not passivate. However, the impurity loadings in the samples that did passivate are much higher than normally found in using impure copper anodes. Gumowska and Sedzimir[48] investigated copper alloyed with lead and oxygen using a chronopotentiometry technique. They concluded that a lead content up to 2 wt% (20,000ppm) does not influence passivation. Oxygen, on the other hand, was found to promote passivation.

It is apparent that the results using specialty alloys are contradictory. Alloys with single elements also eliminate the possibility of interactions between impurities and may not have a microstructure similar to commercial copper anodes. Therefore, impure copper anode samples
have been studied as well. The behavior of various impurities during the copper dissolution is shown in Table 2-2. The inter-relationships of the amount of generated slimes, the amount of impurities and degree of passivation are summarized in Table 2-3.

Although most of the previous studies have focused on the influence of impurities on anode passivation, there are some publications illustrating how the electrolyte chemistry can affect the passivation process. It is believed that electrolyte composition and temperature play a critical role in passivation. Numerous researchers have shown that passivation is aggravated by increasing the copper and acid concentrations, or decreasing the temperature[38,49,51,52]. Noguchi et al. showed that time to passivation decreased with increasing Sb$^{3+}$, As$^{3+}$, Bi$^{3+}$ and dissolved O$_2$ in the electrolyte[28].

Specific experiments were designed by Abe and Goto[23] to study the effect of sulfuric acid on the copper oxidation process. The results showed that when the sulfuric acid concentration increases, the changes in the diffusion coefficient of copper ion and viscosity of a typical solution both tend to be favorable for increasing the anode passivation. Increasing the concentration of sulfuric acid also results in a thicker and denser slimes layer. It is believed that reactions between sulfuric acid and some slimes compounds occur and lead to the formation of finer particles.

While all of the above-mentioned information is critical in understanding the complex issues involved in anode passivation, none fully elucidates the cause of passivation in impure commercial copper anodes. Even though numerous authors[22-24,27-30,40,52] have reported observations of passive films, such as CuSO$_4\cdot5$H$_2$O, Cu$_2$O and CuO, no completely satisfactory passivation mechanism has been proposed.
Table 2-2. Behavior of impurities during copper electrorefining [30].

<table>
<thead>
<tr>
<th>Behavior on dissolution, Element</th>
<th>Existence form in anode</th>
<th>Dissolution state in electrolyte</th>
<th>Type of compound in slime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>solid solution</td>
<td>element/compound</td>
<td></td>
</tr>
<tr>
<td>1. Anodically dissolved</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Soluble in electrolyte--------Ni</td>
<td>αNi</td>
<td>Ni(II)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>As(III)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>Sb(III)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bi</td>
<td>Bi(III)</td>
<td></td>
</tr>
<tr>
<td>B. Precipitated by electrolyte</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrolysis-----------------------As</td>
<td>αAs</td>
<td>As(III)</td>
<td>Cu₂As</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>Sb(III)</td>
<td>Sb₂O₃</td>
</tr>
<tr>
<td></td>
<td>Bi</td>
<td>Bi(III)</td>
<td>Bi₂O₃</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>Pb(II)</td>
<td>PbO</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>Ag(I)</td>
<td>Ag</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>Sn(II)</td>
<td>SnO₂·nH₂O</td>
</tr>
<tr>
<td>Formation of insoluble sulfate---Pb</td>
<td>αNi</td>
<td>[Pb]</td>
<td>PbSO₄</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>[Pb]</td>
<td>NiSO₄</td>
</tr>
<tr>
<td></td>
<td>Bi</td>
<td>[Bi]</td>
<td>Bi₂(SO₄)₃</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>[Bi]</td>
<td>Ag₂SO₄</td>
</tr>
<tr>
<td>2. Soluble in electrolyte--------O</td>
<td>[Cu₂O]</td>
<td>Cu(II)</td>
<td></td>
</tr>
<tr>
<td>3. Insoluble in electrolyte</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metallic impurities-------------Ag</td>
<td>[Ag]</td>
<td></td>
<td>Ag</td>
</tr>
<tr>
<td>Nonmetallic impurities----------Se</td>
<td>[Cu₂Se]</td>
<td></td>
<td>Cu₂Se</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>[Cu₂S]</td>
<td>Cu₂S</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>NiO</td>
<td>NiO</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>[Cu₂As]</td>
<td>Cu₂As</td>
</tr>
<tr>
<td></td>
<td>Bi</td>
<td>[Bi₂O₃]</td>
<td>Cu₂S</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>[Sb₂O₃]</td>
<td>Bi₂O₃</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>(SnO₂)</td>
<td>Sb₂O₃</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>[PbO]</td>
<td>SnO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PbO</td>
</tr>
</tbody>
</table>
Table 2-3. Influence of impurities on amount of slimes and passivation[30].

<table>
<thead>
<tr>
<th>Element</th>
<th>Existence Form in Anode</th>
<th>Type of compound in Slimes</th>
<th>Influence on Amount of Slimes</th>
<th>Influence on Passivation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solid</td>
<td>Element</td>
<td>Low Oxygen</td>
<td>High Oxygen</td>
</tr>
<tr>
<td>S</td>
<td>[CuS]</td>
<td>CuS</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Se</td>
<td>[CuSe]</td>
<td>CuSe</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Ag</td>
<td>[Ag]</td>
<td>Ag, AgSO₂</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Pb</td>
<td>[Pb]</td>
<td>PbO, PbSO₄</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>As</td>
<td>[Cu₂As₃, As₂O₃]</td>
<td>Cu₂As₃</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>Bi</td>
<td>[Bi]</td>
<td>Bi⁺⁺⁺ Bi₂O₃, Bi₂(OH)₃</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Sb</td>
<td>[Sb₂O₃]</td>
<td>Sb₂O₃</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Ni</td>
<td>[NiO]</td>
<td>NiO, NiSO₄</td>
<td>N</td>
<td>/</td>
</tr>
<tr>
<td>Sn</td>
<td>[SnO₂]</td>
<td>SnO₂, SnH₂O</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>

+: Increase, number of (+) shows the degree of effect; -: Decrease; N: No effect; /: No measurement.
2.3.3 Additives behavior in copper electrorefining process

Protein colloid (glue), thiourea, Avitone, and chloride ion are the most common additives used in electrorefining copper. The role of additives in industrial copper electrorefining is vital for achieving production of high quality cathodic copper. By virtue of their leveling abilities in plating processes, additives minimize nodular growth and allow a higher current density operation that would not normally be possible in their absence. The higher current density translates into increased production and profits for refineries.

The exact role of additives in metal electrorefining is poorly understood. Historically, the use of additives in copper electrorefining has been more of an art than a science. Trial and error was, and still is, the primary method in determining which additives and in what proportions are ideal for producing high quality, smooth copper cathodes. In the last two decades a number of researchers have take a more scientific approach to studying their behavior and the leveling mechanisms [53,54,55,56,57,58,59]. This includes studying the effects of additives on cathode polarization and morphology.

**Leveling function of thiourea**

Numerous publications have emphasized the influence of thiourea on the electrolytic deposition of copper, since thiourea has been used as a grain-refining agent for decades. The behavior of thiourea in the copper deposition process was investigated by Ke et al. [60] using an electrode with single crystal spheres. X-ray examination of the deposit showed that in the absence of thiourea the growth of copper is only on the (111) faces of the crystal. In contrast, a finer grained deposit appears over the entire sphere when thiourea is present in the solution. On the other hand, radiotracer measurement of thiourea labeled with S-35 indicated that thiourea was strongly but fairly uniformly adsorbed on these spheres. This adsorption was believed to be responsible for the modification of the crystal structure and grain growth of the deposit.

Knuutila et al. [61] pointed out that a low concentration of thiourea has a depolarizing effect on the deposition of copper. The depolarization enhances the formation of a fine grain size copper deposit on the cathode surface. A high concentration of thiourea, however, inhibited
strongly the growth of single nuclei. The influence of the thiourea on the quality of copper cathode is described briefly in the paper.

Afifi et al.[62] studied the behavior of thiourea in copper cathodic process. The measurements in a solution with a higher concentration of thiourea reveal a rapid increase of cathodic deposition with an increase of current density. A lower concentration of thiourea induces a beneficial effect on the surface roughness of the deposits. A very fine crystalline morphology was only observed in the deposit plated from a solution with a lower content of thiourea. In contrast, a higher concentration of thiourea leads to nodular growth.

There is a disadvantage to adding a large amount of thiourea during copper electrolysis, because of the sulfur contamination of the cathodes. Schab[63] determined the value of sulfur in the cathodes in laboratory experiments. Radiotracer measurements showed that the sulfur content in the cathode increases with the amount of thiourea added, and the amounts of sulfur coming from thiourea were approximately 50% of the total sulfur content in the cathode. Thiourea contamination on the cathode was interpreted to be principally the decomposition of thiourea complex with copper on the cathode. Szymaszek et al.[64] confirmed this hypothesis through polarographic studies and pointed out that at low thiourea concentrations the cathode is covered with a copper complex having a low ligand number. Predominant is a complex of Cu⁺ with formamidine disulfide – [Cu(CSN₂H₄)₂⁺], whereas at high concentrations, the dominant complex is [Cu₃(CSN₂H₄)₄]²⁺.

Two main mechanisms of thiourea action on copper deposition have been summarized by Farndon et al.[65]. In the first, the thiourea is supposed to be hydrolyzed or reduced:

\[
\text{H}_2\text{NCSNH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{NCONH}_2 + \text{H}_2\text{S} \tag{2-12}
\]

\[
\text{H}_2\text{NCSNH}_2 + 2\text{H}^+ + 2\text{e} \rightarrow \text{NH}_2\text{CN} + \text{H}_2\text{S} \tag{2-13}
\]

The H₂S thus produced reacts with copper to produce the sulfide. The solubility product of CuS is low and precipitates at the cathode surface. This is consistent with the fact that the copper deposit contains a small amount of CuS, which is detected by using a radiotracer to examine the labeled S-35 and C-14[66]. The second mechanism involves the reduction of Cu²⁺ in the electrolyte and the formation of complexes on the cathode.

In solution:
\[2\text{Cu}^{2+} + 2\text{H}_2\text{NCSNH}_2 \rightarrow 2\text{Cu}^+ + [-\text{SC(=NH)NH}_2]_2 + 2\text{H}^+ \quad (2-14)\]

At the cathode:

\[
\text{Cu}^+ + n\text{H}_2\text{NCSNH}_2 \rightarrow \text{Cu}^+(\text{H}_2\text{NCSNH}_2)_n \quad (2-15)
\]

\[
\text{Cu}^+(\text{H}_2\text{NCSNH}_2)_n + e \rightarrow \text{Cu} + n\text{H}_2\text{NCSNH}_2 \quad (2-16)
\]

The authors believed that at low concentrations of thiourea, the complex on the electrode surface is \(\text{CuSCNH}_2(=\text{NH})\), whereas for the solution containing a higher concentration of thiourea, the complexes correspond to \(\text{Cu}^+(\text{H}_2\text{NCSNH}_2)_n\), where \(n = 4, 6\).

**Inhibitor of metals**

The use of thiourea as an inhibitor for preventing metal corrosion has been widely investigated. It is commonly known that thiourea has both inhibition and acceleration characteristics for iron and carbon steel corrosion in acid media. On the other hand, its nitrogen-substituted derivatives, such as ethylene thiourea and tetramethyl thiourea, have always been found to have a good inhibitor effectiveness for preventing iron corrosion[67].

The inhibitive action of thiourea on the corrosive behavior of ARMCO iron was investigated by Brinic et al.[68] in de-aerated 0.5 M \(\text{H}_2\text{SO}_4\) solution at 30 °C by means of electrochemical impedance spectroscopy. The obtained results showed that the inhibition of thiourea has a maximum value increasing concentration up to a critical level. The authors stated that within the critical concentration of thiourea, the thiourea is more likely to be present as a molecular species adsorbing vertically on the electrode surface. The adsorption of thiourea molecules occurs through the Fe-S interaction by replacement of the adsorbed water from the iron surface:

\[
(\text{NH}_2)_2\text{CS}_{(aq)} + x\text{H}_2\text{O}_{(ad)} \leftrightarrow (\text{NH}_2)_2\text{CS}_{(ad)} + x\text{H}_2\text{O}_{(aq)} \quad (2-17)
\]

where \(x\) is the number of water molecules replaced by one molecule of thiourea. When thiourea blocks the active site, the iron dissolution is decreased significantly.

Another peculiar characteristic of thiourea, viz the change in its inhibitor effectiveness with concentration, has been investigated extensively[69,70,71]. These experimental data confirm that starting at a lower concentration the inhibitor’s effectiveness increases, reaching a maximum value after which it decreases monotonically.
Piliai and Narayan[72] have given their interpretation of the maximum inhibition by investigating the anodic dissolution of iron in acid solution in the presence of thiourea. At a lower concentration of thiourea, the anodic dissolution is hindered by the adsorption of thiourea. With increasing thiourea concentration, the adsorption of thiourea molecules increases, leading to the further inhibition of iron dissolution. Meanwhile, thiourea (denoted as TU in following equations) can undergo protonation in acid solution according to the following reaction:

\[
\text{TU} + \text{H}_3\text{O}^+ = [\text{TU}^+\text{H}] + \text{H}_2\text{O}
\]  

(2-18)

The protonated thiourea (presented as [TU]'H) is considered to take part and catalyze the iron dissolution process:

\[
2\text{Fe} + ([\text{TU}]'\text{H})_{\text{ads}} + \text{H}^+ \rightarrow 2\text{Fe}^{2+} + \text{H}_2\text{S} + [\text{TU}]^{2+}_{\text{ads}} + 4\text{e}^-
\]  

(2-19)

where ([TU]'H)_{ads} and [TU]^{2+}_{ads} are the species adsorbed on the surface of iron.

The authors pointed out that when the added thiourea is less than a critical concentration, both non-protonated and protonated species in solution increase with bulk thiourea concentration according to the protonation equilibrium (Eq. (2-18)). With the increase in thiourea concentration, the surface excesses of both non-protonated and protonated species increase. Both of them tend to be adsorbed on the electrode surface, but the content of thiourea molecules is always greater than that of the protonated thiourea in the solution. The non-protonated thiourea can attain its saturation coverage prior to that of protonated thiourea, leading to a decrease in iron dissolution.

However, beyond the critical concentration of thiourea, thiourea molecules can be assumed to attain their saturation coverage. Further increase in thiourea concentration does not result in an increase in the adsorption of its molecules. On the other hand, the quantity of protonated thiourea can continue to increase leading to accelerating iron corrosion by Eq. (2-19) at a higher concentration of thiourea.

Kolevatova[73] investigated the inhibition of thiourea on the copper corrosion in acid solutions. He found that the corrosion rate of copper is considerably depressed in the presence of thiourea, whereas temperature has the opposite effect on the corrosion rate. An increase of 30 °C doubles the corrosion rate. Rest potential measurements show the potential shifting positively in
the presence of thiourea. Thiourea is detected from films formed on the copper surface. This is regarded as a major factor in the decrease in the corrosion rate.

**Thiourea deportment in copper electrefining**

Since the 1960's the radiotracer technique has been employed in copper electrolysis to investigate thiourea behavior on copper cathodes[63,63,64,74,75]. Meanwhile, some researchers noted that thiourea appears active not only in the cathodes, but also on both electrolyte solutions and anodes. In order to determine the consumption of thiourea in the copper refining process, many efforts have been made to investigate the deportment of thiourea in the process.

The required amount of thiourea in the copper electrolysis was investigated by Schab et al.[63]. Tests were run 380 hours at 65 °C in the electrolyte (40 g/L Cu²⁺, 190 g/L H₂SO₄, current density 300 A/m²) with thiourea added continuously. The sulfur balance showed that approximately 62 % of the thiourea added to the electrolyte is transferred to the anode slimes and to the cathodes. The anode slimes consume about 40 % of the total amount added, and cathode deposit contains 22 % of the added thiourea. About 30 % of the thiourea is missing in the electrolysis system. In addition, it was observed that the distribution of thiourea into the anode slimes and cathode deposit is affected not only by the concentration of thiourea in the electrolyte but also by the impurity contents in the copper anode. When an impure copper anode was used as a working electrode, the thiourea concentration of the electrolyte was lower than that when electrolytic copper was used as the working electrode.

The distribution of thiourea among the electrolyte, cathodic deposit and anode slimes was determined by Kaltenboeck[76] using S³⁵-labeled thiourea. It was found that the content of S³⁵-labeled thiourea in the cathode increases with increasing current density from 250 to 450 A/m². But the content of the labeled did not exceed 5.4 ppm, even at the maximum current density of 450 A/m². The thiourea reporting to the anode slimes was about 52~59% of the total original amount added.

Data on the quantity of thiourea consumed on a copper anode in the electrolyte (0.63 M Cu²⁺, 1.94 M H₂SO₄, current density 500 A/m²) were obtained in laboratory experiments by Kolevatova et al.[77]. Their data indicated that thiourea is consumed to a considerable extent in both the cathode and the anode processes during copper electrolysis. Approximately 83% of the
original amount of thiourea reported to the anode slimes, and the remainder to the cathode. Consumption of thiourea rose with an increase in the initial concentration of thiourea, and the consumption increases sharply with a rise in temperature. The thiourea content declined in the solution to about 90% of the original amount within 4 hours at 20 °C. At 50 °C the decline increased to 50% of the original amount within the same period of time. It was found that by adding an appropriate amount of thiourea the anode dissolution is enhanced and the roughness of the corroding surface becomes more pronounced.

Lieber[78] made a theoretical estimation of the required amount of thiourea. He attempted to calculate the value based on the speed of diffusion of the thiourea molecules in the cathode diffusion layer. The calculated values were found to be much higher than these encountered in industrial practice.

Behavior of thiourea in copper sulfate-sulfuric acid solutions

In a concentrated acidic solution (CuSO₄, H₂SO₄), Javet and Hintermann[79,80] reported that thiourea slowly forms a complex with Cu⁺, which decomposes slowly:

\[ \text{Cu}^+ + \text{TU} \rightarrow \text{(CuTU)}^+ \rightarrow \text{degradation products} \quad (2-20) \]

where \( k_1 \) and \( k_2 \) are kinetic constants whose values decrease when the thiourea concentration decreases (at 100mg/L TU, \( k_1 = 7.9 \times 10^{-4} \text{ sec}^{-1} \) and \( k_2 = 1.5 \times 10^{-5} \text{ sec}^{-1} \); while at 40 mg/L TU, \( k_1 = 6.3 \times 10^{-4} \text{ sec}^{-1} \) and \( k_2 = 8.4 \times 10^{-6} \text{ sec}^{-1} \)).

Baub and Schiﬀner[81] observed the decomposition of thiourea in weakly acidic copper sulfate solutions (pH from 1.5 to 3.8, 0.5 M CuSO₄ 20 °C), when an amount of thiourea was added to the solution, the pH value of the solution decreased as a function of time. Infra-red spectra analysis indicated that there is a Cu(I)-thiourea complex which precipitates out of the solution after the thiourea is added to the solution. However, the complex did not have any simple formula. The following reaction was hypothesized:

\[ 2(\text{NH}_2)_2\text{CS} + 2\text{Cu}^{2+} = \text{Cu}^+ + 2\text{H}^+ \quad (2-21) \]
The thiourea is oxidized by cupric ions leading to the release of protons and hence a decrease in pH. The newly generated Cu$^+$ is complexed by thiourea to precipitate out of the solution.

According to Gupta[82] thiourea may be oxidized in successive stages to form a number of products. The first of the products is formamidine disulfide, which is formed easily in acidic solutions by the action of oxidants such as hydrogen peroxide at room temperature.

$$2\text{CS(NH}_2\text{)}_2 = [(\text{NH}_2\text{)}_2\text{-C-S-S-C-(NH}_2\text{)}_2]^{2+} + 2\text{e}^- \quad (2-22)$$

This reaction is followed by slower reactions, in which products are formed having sulfur in higher oxidation states such as sulfate ions.

Krewska et al.[83] illustrated that when in contact with Cu$^{2+}$, thiourea is oxidized, leading to generating formamidine disulfide. The reaction of Cu$^{2+}$ with thiourea (TU) can be given as:

$$\text{Cu}^{2+} + (n+1)\text{TU} = [\text{Cu(TU)}_n]^+ + 1/2 [(\text{NH}_2\text{)}_2\text{-C-S-S-C-(NH}_2\text{)}_2]^{2+} \quad (2-23)$$

Furthermore, thiourea forms more stable complexes with Cu$^+$ and the reaction takes place according to the equation:

$$\text{Cu}^+ + n\text{TU} = [\text{Cu(TU)}_n]^+ \quad (2-24)$$

The values of the formation constants are: \(\log \beta_1 = 10.2; \log \beta_2 = 13; \log \beta_3 = 15.9; \log \beta_4 = 18.1\), respectively, for Cu(TU)$^+\), Cu(TU)$_2^+$, Cu(TU)$_3^+$, Cu(TU)$_4^+\).

Ratajczak[84] showed in polarographic studies that complexes of varying compositions can be formed from \([\text{Cu}_2(\text{TU})(\text{CSSC})]^2+\) up to Cu(TU)$_n^+$ in copper sulfate solutions. These complexes are formed at a very large excess of free thiourea. Within some Cu:TU ratios, formamidine disulfide can act as a ligand and forms a mixed complex \([\text{Cu(CSSC)}_n(\text{TU})_m]^+\).

**Oxidation of thiourea**

Kuzeci and Kammel[85] examined the oxidation of thiourea at a carbon paste electrode in acidic aqueous solution (49 g/L H$_2$SO$_4$) at 25 °C. The cyclic voltammograms of thiourea at the carbon paste electrode in the absence of Cu$^{2+}$ showed two oxidation peaks and one reduction peak (Figure 2-2 a). The author stated that the first oxidation peak corresponds to the reaction:
\[ 2\text{CS(NH}_2\text{)}_2 = (\text{NH})(\text{NH}_2\text{)}\text{C-S-S-C(NH}_2\text{)}(\text{NH}) + 2\text{H}^+ + 2e^- \] \hspace{1cm} (2-25)

The second oxidation peak is attributed to the formation of thiourea oxides. However, the reduction peak indicates that the formamidine disulfide \((\text{NH})(\text{NH}_2\text{)}\text{C-S-S-C(NH}_2\text{)}(\text{NH})\) is reduced to thiourea. The large peak separation of this redox couple indicates the irreversibility of the reaction. In the presence of cupric ions at 0.32 g/L and presence of sulfuric acid at 49 g/L (Figure 2-2 b), two additional oxidation peaks are observed. The first one responds to the dissolution of copper deposited during cathodic sweep, and the second one is attributed to the formation of \(\text{Cu(TU)}n^+\). The third one is accounted for by the oxidation of thiourea.

It should be noted that at high anodic potential the oxidation of thiourea and formamidine disulfide may occur spontaneously. Oxidation of thiourea and formamidine disulfide yields a mixture of sulfoxides and sulfonic acids. Separation and identification of these products are not simple[86].

![Figure 2-2. Cyclic voltammograms corresponding to the presence of 0.76 g/L thiourea at room temperature in (a) 49 g/L \(\text{H}_2\text{SO}_4\), (b) 0.32 g/L \(\text{Cu}^{2+}\) and 49 g/L \(\text{H}_2\text{SO}_4\). (FDS – formamidine disulfide).](image)

Krzewska et al.[86] performed chemical and electrochemical oxidation of thiourea in 1 M \(\text{HClO}_4\) solution. The current vs. potential plot of the oxidation of thiourea on the platinum and graphite electrodes shows one peak current at a potential of 1.4 \(V_{\text{SHE}}\). Spectrophotometric measurements shown the absorption spectrum of formamidine disulfide at 200nm. The authors proposed a mechanism involving the electrochemical oxidation of thiourea – the oxidation of thiourea proceeding via a slow one-electron transfer reaction producing a radical \((\text{NH}_2)_2\text{-C-S}^+\)
which rapidly dimerizes to formamidine disulfide. In the presence of Cu²⁺, the absorption spectrum of [Cutuₓ]⁺ at 340 nm was determined in the solution (Cu²⁺ = 32 g/L and HClO₄ = 100 g/L) mixed with thiourea aqueous solutions. A mechanism for the oxidation of thiourea with Cu²⁺ was proposed corresponding to Eq. (2-23).

The electrochemical oxidation of thiourea was also studied by Yan et al.[87] using in-situ Fourier transform infrared (FTIR) spectroscopy. Tests were conducted at different potentials to oxidize thiourea in NaCl or NaCl + HCl solutions. The in-situ FTIR spectroscopy confirmed the mechanism of a two-step oxidation of thiourea in chloride solutions. The first step is the formation of formamidine disulfide at a potential of 0.5 Vₜₐₜ and the second step the further oxidation of formamidine disulfide to HSO₄⁻ and SO₄²⁻ at a potential > 1.3 Vₜₐₜ.

Kirchnerova and Purdy[88] studied the oxidation process of thiourea on a platinum electrode at constant potentials of 0.7 and 1.2 V (SHE) in a HNO₃ solution at 25 °C. The results are listed in Table 2-4.

Table 2-4. Results of the oxidation of thiourea on platinum electrode.

<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>Potential (V)</th>
<th>Thiourea (mmol/50mL)</th>
<th>Apparent No. of electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 M HNO₃</td>
<td>0.7</td>
<td>0.01</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>0.01</td>
<td>2.01</td>
</tr>
</tbody>
</table>

Based on these tests, a mechanism for the oxidation of thiourea was proposed: in nitric acid solution the first step involves a one-electron transfer at 0.7 V at a platinum electrode. The oxidation product is a short-lived radical ion [(NH₂)₂-C-S]⁺ which rapidly dimerizes to formamidine disulfide. A further oxidation step takes place at 1.2 V, the oxidation product appearing to be the diprotonated sulfonic acid [(NH₂)₂-C-S-O₂⁻] which reacts with thiourea (when present in sufficient concentration) to form formamidine disulfide.

Employing a platinum wire gauze as a working electrode to oxidize thiourea in hydrochloric acid solutions at 40 °C, Reddy and Krishnan[89] stated that thiourea oxidation involves two steps. One thiourea molecule is oxidized to form a free radical during the charge transfer process.
which is the rate-determining step. Then the two free radicals combine to form formamidine disulfide.

\[
\text{CS(NH}_2\text{)}_2 = \left[ \text{NH}_2\right] C - S' + H^* + e^-
\]

\[
2\left[ \text{NH}_2\right] C - S = \text{N} \rightleftharpoons \text{C - S - S - C} \left[ \text{NH}_2\right]
\]

By using infrared spectroscopy they found that the oxidation product of thiourea is formamidine disulfide.

**Thiourea behavior in copper anodic dissolution**

Although thiourea is mainly used to improve the physical properties of copper cathodes in the electorefining of copper, it does affect the copper anode dissolution process. Stankovic[90] investigated the effect of thiourea on anodic copper dissolution and cathodic deposition in a solution containing 0.7 M CuSO$_4$ and 1.5 M H$_2$SO$_4$. The results obtained indicated that thiourea has an inhibiting effect on the kinetics of copper dissolution. The anodic transfer coefficient becomes smaller compared to that without thiourea. The adsorption of thiourea at the electrode surface is interpreted as a main factor inhibiting the copper dissolution.

The effect of thiourea on the chemical and electrochemical dissolution of copper were studied systematically by Buketov and Makarov[91] in a solution of 0.6 M CuSO$_4$ and 1.5 M H$_2$SO$_4$ at 55 °C. They found that the presence of thiourea in the solution during electrolysis induced the formation of a passivation film at the electrode surface. The examination of slimes showed that the slimes are composed partly of metal sulfides. A change in the cuprous ions concentration in the electrolyte was also detected during the electrolysis. It is believed that the complex formation follows the reaction:

\[
2\text{Cu}^+ + 5\text{CS(NH}_2\text{)}_2 + \text{SO}_4^{2-} + \text{H}_2\text{O} = \{\text{Cu}_2[\text{CS(NH}_2\text{)}_2]_8\cdot\text{H}_2\text{O}\}\text{SO}_4
\]

Nevertheless, Fu and Lian[92] argued that thiourea molecules formed a natural complex with the cuprous ions and sulfate radicals according to the reaction:

\[
2\text{Cu}^+ + 8\text{CS(NH}_2\text{)}_2 + \text{SO}_4^{2-} = \{\text{Cu}_2[\text{CS(NH}_2\text{)}_2]_8\}\text{SO}_4
\]
Takada et al.[93] studied the effect of thiourea on the passivation of various copper anodes in 0.5 M H$_2$SO$_4$ at 25 °C and concluded that the thiourea promotes copper dissolution during anodic polarization. Thiourea, however, acts as an inhibitor of the anodic reaction in galvanostatic electrolysis promoting passivation.

In the solution containing 0.6 M CuSO$_4$, 1.6 M H$_2$SO$_4$ and 0.11 M NiSO$_4$ at 65 °C, Jin and Ghali[43] investigated the influence of the additives on the passivation of pure copper and impure copper electrodes in galvanostatic electrolysis. They found that during the dissolution of the pure copper electrode the time to passivation increases with an increase in the thiourea content when the thiourea concentration is below a certain amount. After that, the time to passivation decreases with the increasing thiourea content. The cuprous ions were believed to be the principal cause of the anode passivation in the absence of thiourea. The resulting formation of a slime layer of copper powder and copper oxides hinders the diffusion of cupric ions from the electrode surface to the bulk solution. The formation gives rise to the precipitation of solid copper sulfate which in turn promotes the increase of the copper powder and the copper oxides. Since thiourea can complex cuprous ions, at a low concentration of thiourea, the dominant reaction is the complexation of thiourea with cuprous ions, which decreases the formation rate of the slimes layer to a certain extent. Thus the time to passivation is proportional to the content of thiourea. At a higher concentration of thiourea, the adsorption of thiourea or the complexes becomes so important that the active surface of the copper anode is reduced remarkably. Therefore, the time to passivation is inversely proportional to the thiourea content.

Shivrin et al.[94] studied the effect of the thiourea and its derivatives on the kinetics of the copper anodic process. The anodic dissolution tests were conducted in a solution of 8×10$^{-3}$ M CuSO$_4$ and 0.52 M H$_2$SO$_4$. The derivatives studied were cyanamide, urea, dicyanamide, dicyandiamide, and guanidine. Based on the test results the author illustrated the role of thiourea and its derivatives in the kinetics of the anodic process, and presented a mechanism for the inhibition involving the adsorption of these substances and the complexes of the substances and copper ions.

Korshin et al.[95] examined the interaction of thiourea with a copper electrode in sulfuric acid. The adsorption of thiourea on the electrode was observed. A measurement using radioactive indicator C$^{14}$ further confirmed the adsorption occurrence. The adsorbed substance was found to be polythioureas.
Buketov and Makarov[96] conducted tests of anodic copper dissolution in 0.6 M CuSO₄ and 1.5 M H₂SO₄ at 55 °C. By determining the changes in the ratio of cuprous to cupric ions with varying thiourea concentration in the electrolytes, they argued that the anode surface films are physically adsorbed reaction products and complex compound of cuprous ions with thiourea.

Hiskey and Cheng[97] illustrated that the time to passivation is a function of thiourea concentration. For small additions, 1-5 ppm, thiourea improves the passivation behavior, but for large additions, greater than 15 ppm, the passivation time decreased. They believed that at higher concentrations of thiourea the adsorption of thiourea and its oxidized products dominates the passivation process.

**Stability of thiourea in copper electrolysis system**

Using radiotracer S-35 labeled thiourea in an electrolyte containing 0.7 M Cu²⁺ and 1.74 M H₂SO₄ at 50 °C, Kaltenboeck and Woebking[76] found an occurrence of the decomposition of thiourea in the electrolyte without any applied current. They believed that the decomposition was caused by the formation of unstable sulfate-thiourea complexes. When adding chloride ion into the electrolyte, they found that the thiourea content was stable during a five-hour test. The stabilization of thiourea in the electrolyte was interpreted as the formation of more stable chloride-thiourea complexes.

Goto et al.[98,99] investigated the stability of thiourea in various solutions at 80 °C without applied external current. Their observations indicated that thiourea is stable in pure water and 2 M H₂SO₄ aqueous solution. Consequently the concentration of thiourea appears as a constant. The presence of pure copper in the electrolyte (0.75 M Cu²⁺, 2 M g/L H₂SO₄, 0.85 mM Cl⁻, at 80 °C) made thiourea more stable than in the electrolyte without the pure copper immersed. In the later case the thiourea content decreased up to approximately 60 % of the original amount within 1 hour; furthermore, thiourea completely disappears in the electrolyte within 90 hours (Table 2-5).

Goto et al.[98] also pointed out that during copper electrolysis the thiourea concentration in the electrolytes decreases, and the rate of diminution is proportional to the current density. Within five hours the percentage decrease is 22 % at a current density of 200 A/m², and 30 % at a current density of 500 A/m².
Table 2-5. Percentage decrease of thiourea in 250 mL of electrolyte with copper plates of different surface areas at 80 °C[98].

<table>
<thead>
<tr>
<th>Surface area of copper plate</th>
<th>Percentage decrease in thiourea %</th>
<th>*Ratio of volume to area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 min.</td>
<td>30 min.</td>
</tr>
<tr>
<td>8 x 5 cm²</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td>1 x 5</td>
<td>52</td>
<td>55</td>
</tr>
<tr>
<td>1 x 2.5</td>
<td>57</td>
<td>56</td>
</tr>
<tr>
<td>1 x 0.5</td>
<td>56</td>
<td>63</td>
</tr>
</tbody>
</table>

*Our calculation for the ratio of electrolyte volume vs. surface area of copper plate.

Based on the above literature review the following conclusions can be drawn for the characteristics of thiourea:

- Thiourea is an active agent in the acidic solutions and has redox and complex formation abilities. Thiourea can reduce cupric ions to form cuprous ions and formamidine disulfide in copper sulfate solutions. It can be oxidized at high anodic potential forming formamidine disulfide in acidic solutions.
- Thiourea complexed strongly with cuprous ions and the formed complex decomposes slowly (in days).
- Thiourea shows a strong inhibiting effect on the corrosion of metals in acidic solutions.
- Thiourea functions as a leveling regent to influence sharply on the structure of the copper deposit in copper electrorefining.
- More than 50 % of the added thiourea reports to the anode slimes, while 20 % reports to the cathodes.
- The thiourea content in highly concentrated copper sulfate-sulfuric acid solutions at high temperature, can decrease rapidly.

Unfortunately in the above literature review most publications refer either to very simple cases in which thiourea is present in very dilute aqueous solutions or to very complicated cases where thiourea is present in solutions containing multiple electrolytes and additives. In addition,
most publications focus on the influence of thiourea on the cathodic process of copper refining with only a few dealing with the influence on the anodic process. Furthermore, no attention coupling of the stability of thiourea in the highly concentrated copper sulfate-sulfuric acid solutions has been shown in those publications.

2.4 Characterization of Slimes Layer

An understanding of the slimes chemistry and morphology is imperative because the slimes layer can inhibit diffusion of cupric ions from an anode surface to the bulk. The inhibition leads to anode passivation. Chen and Durizac [31-35,100,101] determined the phases present in the slimes layer by using SEM-EDX. The important phases detected are \((\text{Cu,Ag})_2\text{Se}\) rings, euhedral NiO crystals, \(\text{PbSO}_4\), silicates, kupferglimmer, and various complex oxides. Most of these phases are formed during prior pyrometallurgical processing. During dissolution they are released from the anode. Several phases, however, are formed or transformed during the electrorefining process. Selenium occurs predominantly as a metal deficient copper selenide \((\text{Cu}_{2-x}\text{Se})\) along the grain boundaries of the copper matrix. Scott[102] and Chen and Durizac[34,101] found out that silver ions react rapidly with the selenides causing a transformation from \(\text{Cu}_2\text{Se}\) to \(\text{Ag}_2\text{Se}\) during electrorefining. Hiskey et al.[103] claimed the reaction of silver ions with the selenides causes a 20% increase in the volume of the selenide phase. This would help to explain why Abe and Goto[104] noted that an anode with high silver exhibits a thicker and denser slimes layer than other anodes.

Abe, Burrows, and Ettel[38], who carried out chronopotentiometric measurements for impure copper anodes, demonstrated that the time to passivation decreases with increasing amounts of slimes on impure copper anodes.

Petkova[105] performed a sedimentation study to determine the particle sizes of anode slimes. He found that the particle sizes vary from 0-30 microns in diameter with most being between 10-30 microns.

Copper electrorefining tests were carried out in small and large laboratory scale electrolysis cells by Claessens et al.[106] Twenty-four impure copper anodes were used in the tests. By determining the composition of the anodes and formed slimes, they developed empirical
equations showing the rate of slimes formation as a function of the individual impurities present in anodes.

Abe and Goto[107] attempted to determine the pore size of the slimes layer. Millipore filter papers having pore diameters in the range 0.22 to 8 μm, were firmly attached on the surface of pure copper anodes and used as “aged slimes”. Combining the results of both the electrolys of these anodes with aged slimes and actual crude copper anodes, a relationship between the amount of anode slimes formed and the porosity of the slimes was obtained:

\[ \log \sigma = 0.725 - 1.645 \log(P.S.) \]  \hspace{1cm} (2-30)

where \( \sigma \) is the amount of generated slimes and \( P.S. \) is the size of slimes porosity. Although Eq. 2-33 does not show much theoretical meaning about the anode passivation, the authors believed that the equation provides a relative index of the porosity of slimes when comparing different kinds of crude copper anodes. For example, they found that a copper anode with high oxygen level easily undergoes passivation with a slimes formation value of 17 kg/t Cu. When an anode has a low oxygen level, the slimes formation value is 5.8 kg/t Cu. They thought that the latter must be less passive than the former. Computing the slimes porosity for both copper anodes, they obtained values of 0.49 and 0.91 μm for the copper anode containing high and low levels of oxygen, respectively. The test showed that at the same polarization condition, the time to passivation for the former is 6 min. and 12 min. for the latter.

Gu et al.[108] collected the information about the formation of copper anode slimes by using a laser-based visualization technique and a digital image camera combined with current/time monitoring and polarization experiments. The pattern of slimes formation shows that the slimes phase generation is a highly non-uniform process. The growth propagation pattern is related closely to temperature, current density and anode composition. They found that the higher the current density and the lower the temperature, the more the slimes formation.

Cheng et al.[109] characterized the slimes layers by using chronopotentiometry technique and SEM-EDX measurement. They obtained data on the compositional changes and phases present in different regions.
Table 2-6. General SEM-EDS results for impure copper anode[109].

<table>
<thead>
<tr>
<th>Region</th>
<th>Slimes layer</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>I: Active Dissolution</td>
<td>Cu-Se rings</td>
<td>thin slimes layer</td>
</tr>
<tr>
<td></td>
<td>Cu-Se-Ag inclusions</td>
<td>unreacted areas</td>
</tr>
<tr>
<td></td>
<td>copper sulfate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>silver powder</td>
<td></td>
</tr>
<tr>
<td>II: Pre-passivation</td>
<td>Cu-Se rings</td>
<td>moderate slimes layer</td>
</tr>
<tr>
<td></td>
<td>Cu-Se-Ag inclusions</td>
<td></td>
</tr>
<tr>
<td></td>
<td>copper sulfate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>silver powder</td>
<td></td>
</tr>
<tr>
<td></td>
<td>copper oxide</td>
<td></td>
</tr>
<tr>
<td>IV: Post-passivation</td>
<td>Cu-Se rings</td>
<td>thick slimes layer</td>
</tr>
<tr>
<td></td>
<td>Cu-Se-Ag inclusions</td>
<td></td>
</tr>
<tr>
<td></td>
<td>copper sulfate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>copper oxide</td>
<td></td>
</tr>
</tbody>
</table>

The above-cited publications demonstrate the composition and microstructure of the anode slimes layer by using SEM-EDS techniques, with the slimes layers samples examined out of the electrolysis cell. Major problems induced by using these methods are as follows: the microstructure of the slimes layer could be significantly destroyed or altered; the interface of the slimes layer vs. the bulk disappears completely; and some phases could be changed during SEM-EDS measurement due to high vacuum and temperature at certain location in the samples.

2.5 Mathematical Models

The development of mathematical models of electrode reactions has been reviewed extensively in the literature by Newman et al.[110,111,112]. However, most of the modeling
studies have focused on cathodic processes. Some of them were developed to deal with the dissolution and deposition of metals from dilute solutions.

The electrodes covering slimes can be regarded as porous electrodes. Many theories of porous electrode have been developed. Chizmadzhev and Chirkov[113] gave a very complete review of porous electrodes. Table 2-6 shows the major rate processes and associated parameters in porous electrodes. A pioneering theoretical analysis was given by Newman and Tobias[111]. Dunning et al.[114] expanded this theory and gave their experimental results.

Table 2-7. Electrochemical reaction parameters in porous electrodes

<table>
<thead>
<tr>
<th>Reaction Related Variables</th>
<th>Associated Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Transfer</td>
<td>Diffusion Coefficient</td>
</tr>
<tr>
<td></td>
<td>Mass Transfer Coefficient</td>
</tr>
<tr>
<td>Electrode Kinetics</td>
<td>Exchange Current Density</td>
</tr>
<tr>
<td></td>
<td>Reaction Order</td>
</tr>
<tr>
<td>Electric Conduction</td>
<td>Electric Conductivity in Solid</td>
</tr>
<tr>
<td></td>
<td>Ionic Conductivity in Solution</td>
</tr>
<tr>
<td>Double-layer Charging</td>
<td>Double Layer Capacitance</td>
</tr>
<tr>
<td>Micro-structure</td>
<td>Porosity</td>
</tr>
<tr>
<td></td>
<td>Pore Size Distribution</td>
</tr>
</tbody>
</table>

The following is a list of assumptions generally employed in the development of mathematical models for porous electrodes.

(1) Infinitely dilute solution theory is applied. According to Rousar et al.[115], in concentrated electrolytes the theory of transport in dilute solution should be abandoned because independent diffusion of each species cannot be assumed. They proposed the concept of phenomenological transport coefficients to circumvent this difficulty. Nevertheless, transport based on dilute solution theory, employing empirical diffusion data at high solute concentrations if necessary, avoids excessive mathematical complexity.

(2) The pore and particle geometry is disregarded. This allows the analysis of matrix and solution current densities on a macroscopic scale.
(3) No provision is made for non-isothermal operation.

(4) Capacitive effects of double-layer charging are ignored. Since the anode life will be several days this assumption is certainly valid.

(5) The pore dimensions are unimportant relative to the electrode dimension. This may be reasonable because the pore size will be at least one order of magnitude smaller than the minimum electrode dimension.

(6) No provision is made for edge of entrance effects. Obviously, the case of anodic dissolution of copper in highly concentrated copper sulfate-sulfuric acid does not match the above assumption for the model.

Alkire and Place[116] modeled the anodization of a copper-coated porous stainless steel electrode for various ratios of mass transfer to charge transfer resistance. In order to decouple time from the mass balance equation, a pseudo steady-state condition is assumed: for a small time increment the concentrations of species at any position are assumed to be constant. These concentrations are then adjusted by performing an unsteady state mass balance on an elemental slice of the electrode over a length of time equal to the time increment.

Several assumptions would likely not be applied in impure copper anode dissolution:

(1) The matrix of coated film is infinitely conductive.

(2) There is no convection in the electrode.

(3) The anodic reaction does not produce a porous product layer so ionic diffusion and migration through a product layer are not considered.

Newman and Tobias[111] derived a relatively simple, but more general, one-dimensional model of a particulate electrode reacting anodically. They aimed to assess how variations in current distribution in the electrode are affected by (a) the electrical conductivity ratio of solid phase (particulate matrix) to electrolyte, and (b) the rate of mass transfer of species from within the electrode to the bulk solution. When the concentration of species within the electrode was the same as in the bulk solution, they explained that the overall anodic process could be thought of as being entirely set by the rate of the Faradaic process, or “activation controlled”. They investigated two limiting conditions by using the linear and Tafel polarization equations, corresponding to low and high current densities, respectively. Their results may be summarized as follows:
(1) When the electrical conductivity of the solid phase is low compared to the solution phase, most of the reaction occurs near the current distributor.

(2) When the solid phase electrical conductivity is very high, most of the reaction occurs near the particulate electrode-solution interface.

(3) When the electrical conductivity of the two phases is roughly equal, the reaction tends to occur at both of the above interfaces. However, as the electrical conductivity of both phases increases, while remaining equal, the reaction becomes uniformly distributed throughout the electrode.

A number of review papers present various simple models and critically discuss the relative importance of the electrochemical reactions under different conditions[110,113,117,118,119]. Among these models Inami et al.[119] have built a fairly simple mathematical model to characterize the slimes layer generated on a nickel sulfide anode. They assumed that:

(1) The anode potential consists of the electrode equilibrium potential ($E_{M+/M}^0$), the polarization (activation) potential ($\eta_a$), the concentration overpotential ($\eta_c$), and the voltage drop of the slimes layer ($\eta_t$):

$$E_{\text{anode}} = E_{M+/M}^0 + \eta_a + \eta_c + \eta_t \quad (2-31)$$

(2) Among the factors, the electrode and activation potentials were treated as constants. The concentration and the potential drop of slimes layer change with the electrolysis time. According to Ohm’s law, the potential drop of the slimes layer can be expressed by:

$$\eta(t)_R = \delta(t)R(t)i_a \quad (2-32)$$

where $i_a$ is anodic current density ($A/cm^2$), $\delta(t)$ the thickness of the slimes layer (cm), $R(t)$ the ohmic resistance of the slimes layer ($\Omega cm$).

(3) The relationship between the slimes layer and solution resistance was derived by Koh and Fortini[120]

$$R_s/R(t) = \frac{\varepsilon(t)}{1 + n[1 - \varepsilon(t)]^n} \quad (2-33)$$

where $R_s$ is the ohmic resistance of electrolyte solution ($\Omega cm$), $R(t)$ the ohmic resistance of the slimes layer ($\Omega cm$), $\varepsilon(t)$ is the porosity of the slimes layer, $n$ is a constant.
(4) The potential drop of the slimes can be rewritten as:

\[
\eta(t) = \frac{\delta(t)iR_v\{1 + n[1 - \varepsilon(t)]^2\}}{\varepsilon(t)} \tag{2-34}
\]

(5) The concentration overpotential appears to depend on the porosity and permeability of the slimes layer.

\[
\eta(t)_c \propto \log\{1 + A_i\delta(t)/[U(t)]^2\varepsilon(t)\} \tag{2-35}
\]

where \(\delta(t)\) is the thickness of the slimes layer, \(A\) is a constant.

(6) The potential of anode can be rewritten as the follows:

\[
E_{(\text{anode})} = E_{M+M}^0 + \eta_a + B\log\{1 + A_i\delta(t)/[U(t)]^2\varepsilon(t)\} + \frac{\delta(t)iR_v\{1 + n[1 - \varepsilon(t)]^2\}}{\varepsilon(t)} \tag{2-36}
\]

where \(B\) is a constant. \(U(t)\) is the permeability of slimes.

As we can see there are many physical parameters about the slimes incorporated in the model. Unlike nickel anode slimes, copper anode slimes are very fragile. It is impossible to measure the real permeability of slimes using conventional methods.

2.6 Summary

Given the large number of questions arising from the above literature review on copper anode passivation and the characteristics of thiourea in the copper electorefining, it is necessary to make some comments and to define more precisely the goal of the investigation to be conducted.

- The copper anodic dissolution process under industrial operating conditions is far more complex than in a simple laboratory experiment using dilute electrolyte solutions. To deal with copper anode passivation occurring during the anodic dissolution process, a number of researchers have carried out fairly extensive investigations on the process. Numerous factors are regarded as having unfavorable effects on the process: (a) Impurities in the copper anode exhibit a variety of physical and chemical behaviors, making it almost impossible to identify the exact role played in the process. (b) The formation and accumulation of anode slimes lead to significant differences in the electrolyte solution.
properties near the anode surface compared with the bulk solution. (c) Additives introduced into the copper refining process not only play a role in the cathodic process, but are also involved in the anodic process such as reporting to the slimes.

- Many conflicting data on thiourea behavior in copper sulfate-sulfuric acid solutions have been found with most investigations seeing carried out in dilute solutions.
- The stability of thiourea under the conditions of copper refining industrial practice has been overlooked. No publications show that any efforts have been made to identify the stability of thiourea in experimental designs.
- The mechanism of the anodic dissolution of the copper anode in the presence of thiourea is poorly understood.
- The role of thiourea with respect to copper anode passivation is not well understood.
- The solution chemistry of copper sulfate-sulfuric acid in the presence of thiourea is essential for the investigation of thiourea behavior in copper electrorefining. Publications in this area are lacking.
- Methods for characterizing anode slimes ex-situ have a number of problems. In-situ methods have not been noted in the published literature.
- Characterization of the behavior of anode slimes, especially in the presence of thiourea, has not been reported.

Objectives of the current investigation are:
- To establish the mechanism of influence of thiourea on the dissolution of the copper anode and to identify the relationship between thiourea and anode passivation.
- To determine the dominant factors in combination with thiourea affecting the dissolution of the copper anode.
- To characterize the behavior of anode slimes in the presence of thiourea.

2.7 References


Chapter 3 Experimental Techniques

In order to simplify the system of anodic dissolution of copper, most of the experiments were carried out in solutions containing only copper sulfate and sulfuric acid. No impurity ions were introduced to the solutions, except additives. An electrolytic grade copper and a commercial copper anode were chosen as samples and machined as designed working electrodes. All experiments were carried out in small batch electrochemical cells with a conventional three-electrode arrangement. In order to obtain highly sensitive results in this research, different electrochemical techniques were employed. Some experiments were conducted under single electrochemical technique control, others were run under combination controls with several techniques.

3.1 Analyses of Chemical Solutions and Copper Samples

Chemicals and solutions

The electrolyte solutions of copper sulfate-sulfuric acid were prepared using reagent-grade copper sulfate pentahydrate (> 99% wt%, Fisher Science) and deionized water. The reagent-grade sulfuric acid (96-98% wt% BDH Chemicals) was then added to the solutions. The conductivity of deionized water was $4.56 \times 10^{-8} \, \Omega^{-1} \text{cm}^{-1}$. A typical electrolyte solution, used for all experiments in the investigation, contained $42 \, \text{g/L} \, \text{Cu}^{2+}$ and $160 \, \text{g/L} \, \text{H}_2\text{SO}_4$, except as otherwise noted. Sufficient volumes of solutions were made to be used for every single set of experiments. An inert gas, 99.99% nitrogen, was used for deaeration of the solutions in the electrochemical cells.

Copper samples

The copper samples used as working electrodes came from two sources. Electrolytic grade copper rod (99.999 wt%) was supplied by Goodfellow Inc. The electrolytic grade copper is simply called “pure copper” in the thesis. Commercial copper anode (98 wt%) came from BHP Copper. The commercial copper anode (simply called “impure copper”) was received as a full size commercial anode from BHP Copper. For this work, a piece was taken from the bottom of
the anode. Two thin pieces of samples were taken, 2 and 8 cm above the bottom of the anode, for chemical analysis. The compositions of the samples are listed in Table 3-1.

Table 3-1. Analysis of the pure and impure copper samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Se ppm</th>
<th>Bi ppm</th>
<th>Sb ppm</th>
<th>As ppm</th>
<th>Pb ppm</th>
<th>S ppm</th>
<th>Ni ppm</th>
<th>Sn ppm</th>
<th>Ag ppm</th>
<th>Au ppm</th>
<th>O ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure*</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0</td>
<td>0.01</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Part I</td>
<td>443</td>
<td>56</td>
<td>54</td>
<td>958</td>
<td>113</td>
<td>23</td>
<td>186</td>
<td>43</td>
<td>347</td>
<td>15.4</td>
<td>737</td>
</tr>
<tr>
<td>Part II*</td>
<td>386</td>
<td>53</td>
<td>51</td>
<td>934</td>
<td>102</td>
<td>29</td>
<td>183</td>
<td>43</td>
<td>332</td>
<td>14.3</td>
<td>867</td>
</tr>
</tbody>
</table>

Note: Pure* is the pure copper sample, Part I* and Part II* are the samples taken from two different places on the piece of commercial copper anode.

3.2 Electrochemical Cell

Electrochemical cells

A 120-mL EG&G electrochemical cell and 500-mL reaction beaker-glass jacketed cell (VWR Canlab) were adopted as experimental cells. The EG&G cell was used to study the anodic and cathodic behavior of copper rotating disc electrodes. For each experiment 100 mL of the stock solution was added into it. The jacketed cell was employed to investigate the anodic behavior of copper stationary electrodes and was filled with 200 mL of test solution for each test. Schematics of the three-electrode electrochemical cells are presented in Figure 3-1 and Figure 3-2.

A Plexiglas cover was used to hold the electrodes in a fixed position and to avoid loss of water due to electrolyte evaporation at 65 °C. The cover had holes through which the electrical connections to the electrodes were made. Prior to each experiment the solutions in the cells were sparged with the pure nitrogen for 20 minutes. During each experiment, nitrogen was continually introduced to the space above the solution to keep the atmosphere inert for the electrolysis system (Figure 3-3).
Electrodes

The three electrodes installed in both electrochemical cells were the working electrode, reference electrode and counter electrode. The machined copper samples were employed as working electrodes. During experimental measurements the working electrodes experienced anodic dissolution or cathodic deposition. Electrolytic grade copper foil was used as a counter electrode to close the circuit for electronic flow through a working electrode. A saturated mercury-mercurous sulfate electrode was used as a reference electrode to aid electrochemical measurements.

The working electrodes were made of the pure and the impure copper. Both copper materials were machined to be cylinders with a diameter of 0.5 cm. Some of the cylinders were screwed in at one end with copper wire covered with high density PVC. Then the assemblies were mounted in epoxy leaving a 0.1963 cm² working surface exposed. These are called copper stationary electrodes. Others were directly mounted in epoxy exposing a 0.1963 cm² working surface. These were then machined as standard rotating disc electrodes (RDE) with 1.2 cm as the outer diameter and 5 cm high. The surface area of all copper cylinders was carefully polished before the cylinders were mounted in epoxy. No leakage of test solution into the electrodes has been observed during experiments.

The copper stationary electrode was used in the jacketed cell and subjected to voltammetry, chronopotentiometry, and AC impedance measurements. The copper RDE was employed in the EG&G electrochemical cell and subjected to the potential step measurements. Before each experiment was carried out, the faces of the stationary and RDE electrodes were mechanically polished down to a 6-μm finish and rinsed with deionized water. Then the electrodes were immediately transferred to the electrochemical cells. The schematic diagrams of the stationary and RDE electrodes are shown in Figure 3-4.

The counter electrode was made of electrolytic grade copper foil (BHP Copper) with dimensions 4 cm in length, 3.5 cm high. The counter electrode area was big enough to minimize its effect on the cell impedance.

The saturated mercury-mercurous sulfate (MSE) was immersed into a silicon centrifuge tube fully filled with test solutions. An Amber latex rubber tubing filled with test solutions served as a salt bridge connecting MSE and a modified Luggin capillary. The end of the Luggin
Figure 3-1. Assembly of the EG&G cell and three-electrode system with a rotating disk electrode with a face down exposed surface.

Figure 3-2. Assembly of the EG&G cell and three-electrode system with a stationary working electrode with a vertical exposed surface.
Figure 3-3. Schematic diagrams of nitrogen sparging tube.
Figure 3-4. Schematic diagrams of (a) rotating disk electrode and (b) stationary electrode.
capillary with a hole 0.05 cm in diameter was placed in parallel with a working electrode. The distance between them was approximately 0.5 mm. The potential of the reference assembly was measured with respect to a laboratory standard MSE in a saturated K$_2$SO$_4$ solution at the beginning and end of each day. No appreciable change in the potential difference between the two MSE reference electrodes was observed over the course of the experiment (usually 2±1 mV).

Since the mercury-mercurous sulfate reference electrode was immersed in the typical electrolyte solution containing Cu$^{2+}$ 42g/L, H$_2$SO$_4$ 160g/L, there must be a liquid junction potential (E$_{LJP}$) existing between the test solution and saturated K$_2$SO$_4$. Correction for E$_{LJP}$ was evaluated from the Henderson formula[1], using the molar concentrations of the ionic species and the limiting (infinite dilution) ionic diffusion coefficients of H$^+$, K$^+$, Hg$^+$, HSO$_4^-$, and SO$_4^{2-}$ ions. The calculated E$_{LJP}$ was 8 mV.

The MSE potential was calibrated as 0.64 V. All potentials measured as V$_{MSE}$ were referenced to the SHE via the conversion V$_{SHE}$ = V$_{MSE}$ + 0.64 V.

**Temperature control**

The electrochemical cells previously described were connected with a water bath. This bath had a volume of 9 liters. Heat was provided by a 500-watt immersion heater. Water in the bath was pumped out to pass through the jacket of an electrochemical cell and recycled back to the bath. A bath temperature was controlled automatically. A thermistor probe was used to monitor the bath temperature. This experimental setup allowed temperature control within ± 0.5 °C of the set point.

### 3.3 Experimental Equipment

Two different experimental setups in two laboratories were used to carry out all experiments in the investigation. The setup of the EG&G Potentiostat/Galvanostat was adopted for conducting conventional electrochemical measurements, such as the voltammetry, chronopotentiometry, and potential step measurements. The setup of the Solartron Electrochemical Interface combined with a Frequency Response Analyzer was employed for carrying out in-situ electrochemical measurements – AC impedance measurements. Figure 3-5 is the schematic representation of the two experimental setups.
Figure 3-5. Schematic illustration of experimental setup. A is the setup of conventional electrochemical measurement. B is the setup of in-situ electrochemical measurement.
M273A Potentiostat/Galvanostat

The M273A Potentiostat/Galvanostat is a utility that contains a power amplifier, differential electrometer, IR compensation circuit, and computer interface. Using this instrument, one can perform potential or current control measurements and obtain highly reproducible data. Exquisite shielding and grounding circuit design allows for minimizing the internal electronic noise, giving high sensitivity and quiet output signal. Four-terminal current-to-voltage converter circuit is designed for accurate, rapid measurements, preventing the degradation of current from cell-cable resistance, capacitance, and inductance. During the test, the device was controlled by SoftCorr II software. The SoftCorr II software automates all of the subtasks involved in running an experiment. Under control of custom menu selections, it automatically commands the Potentiostat/Galvanostat, acquires the data, and plots the data on the display screen. Data from an experiment can be stored and recalled at any time.

Solartron electrochemical interface and frequency response analyzer

The 1286 Electrochemical Interface is similar to the M273A Potentiostat/Galvanostat. It can control and measure the DC characteristics of many electrochemical cells. The Solartron 1250 Series Frequency Response Analyser (FRA) is a sine wave generator. With specified designation, it can significantly reject any harmonic responses and reduce random noise. By combination of the 1286 Electrochemical Interface and FRA, the system can record the response of an electrochemical cell to a small potential or current perturbation applied over a predetermined frequency range. "CorrWare" and "ZPlot" are the PC software which maximizes the performance of both the Interface and the FRA for a variety of in-situ experimental measurements.

3.4 Electrochemical Techniques

Copper dissolution and passivation are electrochemical processes of interest in the present investigation. The investigation of the copper dissolution and passivation was carried out by using various electrochemical techniques to elucidate the mechanisms and reactions involved. A number of important electrochemical techniques have been discussed thoroughly by Bard and
Faulkner[2] and by others[3-6]. There are four techniques frequently used in electrochemical investigations. They are the potential-sweep method, controlled potential transient, controlled current transient, and AC impedance.

**Potential-sweep method**

The potential-sweep method (or voltammetry) utilizes a potential sweep applied between the working and reference electrodes to observe changes in current as a function of voltage. Based on the potential sweep application, there are two common voltammetry techniques which are linear sweep voltammetry (LSV) and cyclic voltammetry (CV). For LSV the potential is increased at a constant rate from an initial to a final voltage. The CV is like the LSV in the use of a constant sweep rate, however, as the name implies, the potential is cycled between two values. The cycling process can be repeated numerous times. This usually serves to determine how reactions are affected within the swept potential ranges. The reacting species and reaction mechanisms may be identified. Information concerning adsorption phenomena and electro-active intermediates may be obtained.

**Controlled potential transient**

Controlled Potential Transient – Potential Step. The potential between the working and reference electrodes is controlled in a desired manner. At time $t_0$, an applied voltage is instantaneously stepped from one value $V_1$ to another $V_2$. The resulting current is then measured as a function of time. This usually serves for the determination of exchange current density. The IR drop between the working and reference electrodes must be small or be appropriately compensated.

**Controlled current transient**

Controlled Current Transient – Chronopotentiometry. The electrochemical cell current is controlled in a constant manner for the duration of the test, and the potential between the working and reference electrodes is measured as a function of time. In industrial copper electorefining, copper anode dissolution is mostly controlled by the employed constant current densities. In the laboratory investigation, the dissolution can be realized by using the same
method. The advantage of this technique is that the boundary conditions are based on the known currents or fluxes. A disadvantage is that double-layer charging occurs throughout the experiment. The charging current is not easily resolved from the faradic response since the electrode potential is varying throughout the experiment. In addition, stepwise reactions are difficult to identify.

**AC impedance**

During an AC impedance experiment, a sinusoidal potential perturbation is applied between the working and reference electrodes. The corresponding AC current, having the same frequency but different phase and amplitude, is measured. After recording the AC potential and current, a complex impedance can be calculated. By separating and studying real and imaginary parts of complex impedances over a range of frequencies, it is possible to analyze the reaction mechanism and surface film characteristics.

One of the advantages of the AC impedance technique is that corrosion processes can be studied on short time scales. A single experiment can provide information on processes which exhibit a wide range of relaxation times. High frequency measurements can be used to determine kinetic electron transfer rates, while data from low frequency measurements can be used to determine the effects of mass transfer[4].

Another advantage in AC measurements is the use of smaller perturbations at the corroding interface such that measurements remain at or near the corrosion potential. This measurement technique is non-destructive, whereas in DC techniques, the system is often polarized to a potential far away from the corrosion potential. The reactions at a polarized electrode may also involve film formation and/or adsorption effects which are not easily detected in DC techniques. The AC impedance technique will be one of the best choices to determine these effects[5].

Three important criteria must be met when evaluating corrosion rates from impedance data. The first is linearity. If the impedance response is independent of amplitude of the input function, linear equivalent circuits can be used to model the electrode/solution interface. This condition holds with small amplitude excitation signals of 10 mV peak-to-peak or less. The second condition is causality. The impedance response of the electrochemical cell must be a direct result of the excitation signal applied to the interface. The third criterion states that the system must be
stable over the measurement time period. The last criterion is often difficult to obtain in corroding systems, especially when films form on the electrode surface and when the polarization resistance does not remain constant.

Since most voltage/current response in electrochemical cells is non-linear, impedance measurements must be obtained near the open circuit potential and at low current densities. A sufficiently wide frequency range must be investigated to ensure detection of all relaxation phenomena at the interface. Diffusional mass transfer and film growth may limit the overall reaction rate at the lower limit, 0.1 mHz. At high frequencies, the time scale is short and diffusional mass transfer effects may be negligible compared to those from electron transfer. In addition, the solution contribution to the impedance defines the upper limit in most systems, usually greater than 10 kHz[6].

3.5 References


Chapter 4 Chemistry of Copper Sulfate-Sulfuric Acid System

The thermodynamics of copper sulfate and sulfuric acid solutions have been studied extensively by many researchers. The importance of species distribution in mixed and highly concentrated electrolyte solutions has been realized by hydrometallurgists and electrochemical engineers. In this investigation it is essential to determine the distribution of dominant species in copper sulfate-sulfuric acid solutions, to understand the copper dissolution and passivation processes.

4.1 Solution Chemistry of Copper Sulfate-Sulfuric Acid

Chemical equilibrium

In copper electrorefining, the electrolyte solutions consist mainly of copper sulfate-sulfuric acid. It is common in copper refining to calculate the concentrations of cupric ion and sulfate ion without considering the ion pair and bisulfate dissociation. Studies on the composition of copper sulfate-sulfuric acid solutions[1,2,3,4] reveal that the dominant species in the solutions are Cu²⁺, SO₄²⁻, H⁺, HSO₄⁻, and CuSO₄. It is believed that the following chemical equilibria exist when copper sulfate and sulfuric acid are present in an electrolyte solution[5,6,7,8].

Copper sulfate ion pair dissociation:

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-} \quad (4-1)$$

Bisulfate dissociation:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2+} \quad (4-2)$$

Thermodynamic data

It is important to understand the species stability when studying the copper dissolution in copper sulfate-sulfuric acid solution. Constructing an Eh-pH diagram of Cu-H₂SO₄-H₂O is one of methods by which one can identify the stable conditions of species in copper sulfate-sulfuric acid
solutions. As many researchers have pointed out, the phases of \( \text{Cu}_2\text{O} \) and \( \text{CuO} \) occur in surface films under anode passivation conditions[9,10,11,12]. Hence, these two phases have been selected and presented in the diagrams. The acid phases are stable in copper refining. The sulfur phases of \( \text{H}_2\text{S} \) and \( \text{HS}^- \), and \( \text{S}^{2-} \) are not presented in the diagram. In order to simplify the construction of the diagrams \( \text{Cu}_2\text{S} \) and \( \text{CuS} \) are not presented.

The thermodynamic data of the species selected for presentation in the diagram are available at ambient temperature[13] but not at elevated temperatures. Thus the data with respect to elevated temperature need to be calculated. Peters and Dreisinger[14] have given a comprehensive summary on computing thermodynamic data of species in various solutions of hydrometallurgical processes. The methods were used to determine values for the species in copper sulfate-sulfuric acid solution. Table 4-1 shows the Gibbs free energy data corresponding to 25, 60, 65, and 70 °C (Appendix I).

Table 4-1. Summary of Gibbs free energy for species at temperatures of 25 to 70 °C. (The data are expressed in J/mol).

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta G_{298}^0 ) **</th>
<th>( \Delta G_{333}^0 )</th>
<th>( \Delta G_{338}^0 )</th>
<th>( \Delta G_{343}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}^+ )</td>
<td>0</td>
<td>-1206</td>
<td>-1387</td>
<td>-1569</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} \text{aq} )</td>
<td>65700</td>
<td>70142</td>
<td>70662</td>
<td>71190</td>
</tr>
<tr>
<td>( \text{Cu}_2\text{O} )</td>
<td>-148100</td>
<td>-151456</td>
<td>-151958</td>
<td>-152465</td>
</tr>
<tr>
<td>( \text{CuO} )</td>
<td>-134000</td>
<td>-135575</td>
<td>-135816</td>
<td>-136059</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4^{-} \text{aq} )</td>
<td>-756010</td>
<td>-758600</td>
<td>-758784</td>
<td>-758909</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-} \text{aq} )</td>
<td>-744630</td>
<td>-742598</td>
<td>-742120</td>
<td>-741581</td>
</tr>
<tr>
<td>( \text{CuSO}_4\cdot5\text{H}_2\text{O} )</td>
<td>-1906389</td>
<td>-1857723</td>
<td>-1856736</td>
<td>-1843754</td>
</tr>
<tr>
<td>( \text{O}_2 \text{g} )</td>
<td>0</td>
<td>-3923</td>
<td>-4496</td>
<td>-5071</td>
</tr>
<tr>
<td>( \text{H}^+ \text{aq} )</td>
<td>0</td>
<td>539</td>
<td>575</td>
<td>599</td>
</tr>
<tr>
<td>( \text{H}_2 \text{g} )</td>
<td>0</td>
<td>-4611</td>
<td>-5282</td>
<td>-5955</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} \text{aq} )</td>
<td>-237180</td>
<td>-239764</td>
<td>-240158</td>
<td>-240558</td>
</tr>
</tbody>
</table>

** The values were obtained from Handbook of Chemistry and Physics[15].
Activity coefficients

The activities and activity coefficients of the above species are essential for constructing the Eh-pH diagrams, because species stability is a function of concentration. There are three different concentration scales – mole fraction, molality and molarity. Molarity is most commonly used in hydrometallurgy. Therefore, the molarity of these species should be converted to activity in this section.

In an aqueous solution containing a single electrolyte, one can simply calculate single ion activity coefficients. However, it is impossible to measure single activity coefficients for all species in solutions containing mixed electrolytes.

A number of models have been developed to evaluate single activity coefficients and mean activity coefficients with respect to species like cations, anions and molecules in different kinds of electrolyte solutions. In addition, there are many models proposed to estimate parameters such as water activity, temperature effect, and species hydration degree. These parameters have to be used to modify models used for predicting activity coefficients with respect to single electrolyte solutions. No published paper shows how one can evaluate the activity coefficients corresponding to solutions containing multi-electrolytes with using one single model.

The theories of Bates[16], Stokes-Robinson[17], and Meissner[18,19] take into account of the water activity, temperature effect, and species hydration degree. Thus their models and computing procedures were chosen for use in the present investigation. The activity coefficients of cupric ion, proton, and sulfate ion, and mean activity coefficients were predicted by using these chosen methods (Appendix I). Table 4-2 shows the results of the evaluations.
Table 4-2. The estimated values of activity coefficient and mean activity of species in copper sulfate-sulfuric acid electrolyte at 25, 60, 65, and 70 °C.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Cu$^{2+}$</th>
<th>H$^+$</th>
<th>SO$_4^{2-}$</th>
<th>CuSO$_4$</th>
<th>HSO$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Activity Coefficient</td>
<td>Activity Coefficient</td>
<td>Activity Coefficient</td>
<td>Mean Activity Coefficient</td>
<td>Mean Activity Coefficient</td>
</tr>
<tr>
<td>25</td>
<td>0.9686</td>
<td>0.4466</td>
<td>0.1534</td>
<td>0.3855</td>
<td>0.2617</td>
</tr>
<tr>
<td>60</td>
<td>0.895</td>
<td>0.424</td>
<td>0.1471</td>
<td>0.3628</td>
<td>0.2497</td>
</tr>
<tr>
<td>65</td>
<td>0.8837</td>
<td>0.4201</td>
<td>0.1459</td>
<td>0.3590</td>
<td>0.2476</td>
</tr>
<tr>
<td>70</td>
<td>0.8726</td>
<td>0.4163</td>
<td>0.1445</td>
<td>0.3551</td>
<td>0.2453</td>
</tr>
</tbody>
</table>

Species Distribution

The species distribution at temperatures of 25 and 65 °C was calculated considering the ion pair, CuSO$_4$, and bisulfate dissociation. The mass balance and the chemical equilibrium with temperature correction were modeled as follows:

There are three mass balance equations

\[ 2C_1 = [H^+] + [HSO_4^-] \] \hspace{1cm} (4-3)

\[ C_1 + C_2 = [HSO_4^-] + [SO_4^{2-}] + [CuSO_4] \] \hspace{1cm} (4-4)

\[ C_2 = [Cu^{2+}] + [CuSO_4] \] \hspace{1cm} (4-5)

where \( C_1 \) and \( C_2 \) are the proton and CuSO$_4$ concentrations, respectively.

There are two equilibrium constants:

\[ Q_{CuSO_4} = \frac{[Cu^{2+}][SO_4^{2-}]}{[CuSO_4]} \] \hspace{1cm} (4-6)

\[ Q_{HSO_4} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \] \hspace{1cm} (4-7)
Three equations relate to equilibrium constants and real ionic strength

\[
\log Q_{\text{CuSO}_4} = \log K_{\text{CuSO}_4} - \frac{4.05\sqrt{I}}{1 + 1.618\sqrt{I}} + 0.052 \quad (4-8)
\]

\[
\log Q_{\text{HSO}_4^{-}} = \log K_{\text{HSO}_4^{-}} + \frac{2.032\sqrt{I}}{1 + 1.10\sqrt{I}} \quad (4-9)
\]

\[
I = \frac{1}{2} \sum C_i Z_i^2 = 2[Cu^{2+}] + \frac{1}{2}[H^+] + \frac{1}{2}[\text{HSO}_4^{-}] + 2[\text{SO}_4^{2-}] \quad (4-10)
\]

where \( K_{\text{CuSO}_4} \) is the stoichiometric dissociation coefficient of copper sulfate and \( K_{\text{HSO}_4^{-}} \) is the stoichiometric dissociation coefficient of bisulfate.

Many researchers have reported the effect of temperature variation on the stoichiometric dissociation coefficient. The constant for copper sulfate with temperature correction can be written[8]:

\[
\log K_{\text{CuSO}_4}^T = \log K_{298} - \frac{\Delta H}{2.303R} \left( \frac{1}{T} - \frac{1}{298} \right) \quad (4-11)
\]

The constant for bisulfate was given by Marshall and Jones[20]

\[
\log K_{\text{HSO}_4^{-}}^T = 56.889 - 19.886\log T - \frac{2307.9}{T} - 0.00647T \quad (4-12)
\]

Newton's method with a Jacobian matrix routing was employed to solve equation (4-3 to 4-12). The initial individual ion concentrations were chosen based on assuming cupric-sulfate and sulfuric acid completely ionized. For these assumed values of concentration, the system of equations was solved by a numerical iterative method to obtain a full set of species concentration values. With the new concentration values, the second calculation was carried out to reevaluate and compare with the previous assumption. If the absolute difference between the present and the previous values of the concentration is less than a predefined acceptable error (say, <10^-5), the speciation calculations are complete (Appendix II).
Table 4-3. Evaluated concentrations of species in the typical electrolyte solution at 25 and 65 °C.

<table>
<thead>
<tr>
<th>Species</th>
<th>Cu²⁺</th>
<th>CuSO₄⁻</th>
<th>H⁺</th>
<th>HSO₄⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>0.077</td>
<td>0.0012</td>
<td>105.147</td>
<td>0.2541</td>
<td>1.735</td>
</tr>
<tr>
<td>65°C</td>
<td>0.274</td>
<td>0.0038</td>
<td>104.716</td>
<td>0.2356</td>
<td>1.727</td>
</tr>
</tbody>
</table>

The values of species activity in Table 4-3 were calculated by multiplying the evaluated concentrations with the relative activity coefficients or mean activity coefficients shown in Table 4-2.

**Eh-pH diagram for Cu-H₂SO₄·H₂O**

The CSIRO Thermochemistry program is one of the popular software programs for developing Eh-pH diagrams. It contains a large and accurate thermodynamic database. It allows one to input thermodynamic data and activities of the interested species with respect to any temperatures to modify its database, and lets one construct the diagrams corresponding to a particular temperature.

In the current investigation the Eh-pH diagram for the Cu-H₂O system at 25 °C and 65 °C were constructed and shown in Fig.4-1 and Fig.4-2. The calculated data listed in Table 4-3 were used for constructing these diagrams. It is interesting to see that the stable area of cupric ion shrinks with the increase in temperature. The abscissa equilibrium value (pH) of the area decreases from 3.38 down to 2.01 and the ordinate equilibrium value (Voltage) of the area moves upward from 0.32 to 0.35 when the temperature changes from 25 °C to 65 °C. Both equilibrium line 3 (cupric ions/cupric oxide) and line 4 (cupric ions/cuprous oxide) in Fig.4-2 move up toward the left hand-side of the figure comparing with Fig.4-1. This indicates that the tendency of the formation of cuprous oxide and cupric oxide in the low pH range (2 to 4) is enhanced by the increase in temperature. According to Fig.4-2, it is possible that Cu₂O and CuO can be formed when the pH reaches about 2. This agrees well with the observations in which many researchers claimed that the phases of Cu₂O and CuO were to be present in the anode surface films[9,21,22,23].
Figure 4-1. Eh-pH diagram for Cu-H$_2$SO$_4$-H$_2$O at 25 °C and 1 atm. (Activity: [Cu$^{2+}$] = 0.0012, [H$^+$] = 0.775, and [HSO$_4^-$] = 0.4016. At point (F) pH = 3.38 and Eh = 0.41 V. At point (G) pH = 2.14 and Eh = 0.32 V)

Figure 4-2. Eh-pH diagram for Cu-H$_2$O at 65 °C and 1 atm. (Activity:[Cu$^{2+}$] = 0.0038 M, [H$^+$] = 0.727 M, and [HSO$_4^-$] = 0.394 M. At point (F) pH = 2.01 and Eh = 0.441 V. At point (G) pH = 1.74 and Eh = 0.35 V)
4.2 Electrolyte Physico-chemical Properties

The physicochemical properties of the copper sulfate-sulfuric acid electrolyte solution have been reported extensively due to the wide usage of this system in studies on copper deposition. Direct experimental measurements and modeling computations have been adopted by many researchers. However, there are many conflicts found in these reports due to the use of different instruments and building various models[24,25,26,27,28]. In this work, most physicochemical parameters were measured directly in the laboratory. Price and Davenport[29] offered fairly comprehensive predictive methods for calculating viscosity, special conductivity, and density. Their computation values agree well with their measured data. In addition, it should be noted that they have taken account of more highly concentrated copper sulfate and sulfuric acid solutions. Thus the Price and Davenport's method was chosen to evaluate these parameters in this investigation.

Viscosity

Viscosity of the solution was measured using Cannon-Fenske routine viscometer for transparent liquids. The viscometer is immersed in a constant temperature water bath at 65 °C and calibrated using deionized water. Six viscosity measurements were carried out and the mean measured value was 0.007537 g cm$^{-1}$ sec$^{-1}$. The value of viscosity was also calculated using Price's and Davenport's equation, which is 0.007325 g cm$^{-1}$ sec$^{-1}$.

Specific conductivity

The specific conductivity of the typical electrolyte solution was evaluated from Price and Davenport's equation[29]. The correlation was reported to be accurate to ± 10 % for the conditions given as 165–225 g/L acid, 30–60 g/L copper and 50–70 °C. The calculated value of the specific conductivity was 0.6086 Ω$^{-1}$cm$^{-1}$.

Density

The density of the solution was measured using a 25-mL Bingham-Type pycnometer. The pycnometer was calibrated measuring the density of deionized water. Measurements were made
at a temperature of 65 °C. Five density measurements were made and the mean density value obtained was 1.162 g/cm$^3$. This measured value was compared with that evaluated from Price and Davenport's equation[29]. The calculated value was 1.166 g/cm$^3$.

### 4.3 Electrolyte Solution Chemistry of Copper-Sulfuric Acid-Thiourea

The addition of thiourea to the copper sulfate-sulfuric acid solution is critical for controlling the quality of the cathode deposit. Thiourea behaves as a leveling and grain refining agent to minimize nodular growth. In most instances there is a definite, desirable concentration range for thiourea, with either a deficiency or excess yielding undesirable results[30]. The situation is further complicated by the fact that the critical thiourea concentration is often in the range of 5 ppm or less and interactions among the various species in solution can cause modifications to the active amount present in solution[31]. The true concentration can deviate from the physical amount added to the electrolyte because of hydrolysis, incorporation into the deposits, deposition in anode slimes, chemical reaction with the electrolyte, and other dissolved species or electrochemical alteration at either electrode.

The chemistry of thiourea in copper sulfate and sulfuric acid aqueous solution has been summarized in Chapter 2. Clearly, there are some conflicts among those reports. Martell et al.[32] published a bibliography of complexation of thiourea with copper ions, proton, and other metal ions. Chemical equilibria and equilibrium constants were collected and listed. The authors claimed that the equilibrium constants were measured at the specified conditions of temperature and ionic strength. The selected values were those considered to be the most reliable of those available in the literature. In some cases the value was the median of several values whereas in other cases it was the average of two or more values.

Since the solution chemistry of thiourea is essential for understanding the electrochemical behavior of thiourea in copper electrorefining, an attempt has been made to estimate the distribution of thiourea and the relative species in concentrated copper sulfate-sulfuric acid electrolyte solutions. The calculations were based on the following conditions:

- Chemical equilibrium at 25 °C
- Solution containing 0.66 M Cu$^{2+}$ and 1.63 M H$_2$SO$_4$
- No Cu$^+$ present in the solution
• Ignoring the dissociation of HSO₄⁻
• No change in proton concentration
• Complexes between thiourea and cupric ion are
  • ML₁/M.L
  • ML₂/M.L²
  • ML₃/M.L³
  • ML₄/M.L⁴

where M denotes cupric ion and L denotes thiourea.

There are four chemical equilibria

\[ \log \left[ \frac{[(CuTU)^{2+}]}{[Cu^{2+}][TU]} \right] = 0.8 \quad (4-13) \]

\[ \log \left[ \frac{[(CuTU₂)^{2+}]}{[Cu^{2+}][TU]²} \right] = 0.9 \quad (4-14) \]

\[ \log \left[ \frac{[(CuTU₃)^{2+}]}{[Cu^{2+}][TU]³} \right] = 1.0 \quad (4-15) \]

\[ \log \left[ \frac{[(CuTU₄)^{2+}]}{[Cu^{2+}][TU]⁴} \right] = 1.1 \quad (4-16) \]

where TU is symbol of thiourea.

There are two mass balance equations

\[ [Cu^{2+}] + [(CuTU)^{2+}] + [(CuTU₂)^{2+}] + [(CuTU₃)^{2+}] + [(CuTU₄)^{2+}] = 1.26 \times 10^{-3} \quad (4-17) \]

\[ [TU] + [(CuTU)^{2+}] + [(CuTU₂)^{2+}] + [(CuTU₃)^{2+}] + [(CuTU₄)^{2+}] = 3.95 \times 10^{-4} \quad (4-18) \]

The value (0.00126 M) in Eq. (4-17) is the copper concentration obtained from the previous numerical computation when considering the dissociation of the copper sulfate ion pair and bisulfate. The value of 3.95×10⁻⁴ M in Eq. (4-18) corresponds to the solution containing 30 mg/L
thiourea. The above equations were solved simultaneously using previous numerical methods. The evaluated values corresponding to 5 mg/L and 30 mg/L thiourea are listed in Table 4-4 (see Appendix II).

Table 4-4. The evaluated concentration of species in solution containing 42g/L Cu$^{2+}$ and 160 g/L H$_2$SO$_4$ at 25 °C.

<table>
<thead>
<tr>
<th>Initial presented TU in solution</th>
<th>[Cu$^{2+}$] mg/L</th>
<th>([CuTU]$^{2+}$) mg/L</th>
<th>([CuTU$_2$]$^{2+}$) mg/L</th>
<th>([CuTU$_3$]$^{2+}$) mg/L</th>
<th>[TU] mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mg/L</td>
<td>7.68×10^{-2}</td>
<td>6.75×10^{-5}</td>
<td>1.58×10^{-8}</td>
<td>8.94×10^{-12}</td>
<td>2.53×10^{-15}</td>
</tr>
<tr>
<td>30 mg/L</td>
<td>7.64×10^{-2}</td>
<td>4.57×10^{-4}</td>
<td>6.22×10^{-7}</td>
<td>1.57×10^{-9}</td>
<td>1.29×10^{-12}</td>
</tr>
</tbody>
</table>

It is clear that the copper ion concentration is slightly decreased with the increase in the initial thiourea concentration. However, the magnitude of changes in copper concentration is very small at the temperature. The amount of the complexes is dependent on the initial thiourea concentration. Since the chemical equilibrium constants of thiourea species at elevated temperature are lacked of, the speciation of thiourea and copper ions could not evaluated in this thesis. Data in Table 4-4 indicate that normal chemical analysis and electrochemical measurements face a challenge when investigating the behavior of thiourea in the environment of highly concentrated copper sulfate-sulfuric acid electrolyte solutions.

4.4 References


Chapter 5 Behavior of Thiourea in Anodic Dissolution of Copper – I

This section focuses mainly on finding out whether voltammetry is sensitive enough to provide evidence of thiourea inhibition on the rate of anodic dissolution of copper. Since the dissolution of the impure copper is more complicated than that of the pure copper due to slimes generation during the dissolution of the impure copper, the pure copper was tested first in order to get more information under relatively simple conditions.

Like most other studies on the anodic dissolution of metals, the linear sweep voltammetry was adopted as the basic electrochemical method to investigate the dissolution process. The electrode potential is varied linearly with a constant rate between two points (usually between the open circuit potential to a more positive anodic potential), and the resulting current vs. voltage curve is recorded. In the simplest case, the measured current is proportional to the rate of an electrochemical reaction. Therefore, using linear sweep voltammetry, we can observe the dissolution rate of the copper electrode by simultaneously measuring the current and potential on the electrode.

Most copper refineries have employed constant current to dissolve copper anodes. Based on this fact, chronopotentiometry was used to obtain information about thiourea inhibition on the anodic dissolution of the pure and the impure copper electrodes. During experiments a pre-selected constant current was applied to the copper electrodes. The resulting potential on these electrodes was recorded vs. time.

5.1 Voltammetric Behavior of Anodic Dissolution of Copper

5.1.1 Experimental technique

The stationary electrodes of the pure copper and impure copper electrodes were employed as working electrodes in the study of the anodic dissolution. The electrochemical cell was the VWR jacketed reactor in which 200 ml of a typical copper sulfate-sulfuric acid solution was placed.
Nitrogen was sparged into the solution in the cell for 20 minutes. After that the polished copper stationary electrodes were immersed in the cell and nitrogen was sparged continually into the bottom of the cell for an additional 5 minutes.

The thiourea aqueous solutions were prepared prior to a set of experiments and were used within 24 hours of preparation. Five minutes prior to the start of each test, the thiourea solution was added to the electrochemical cell. The solution was stirred using a magnetic stirrer in order to keep thiourea well mixed with the solution. All measurements were carried out under the static conditions.

The M273A Potentiostat/Galvanostat combined with the linear sweep voltammetry program was used to control the anodic dissolution. For the pure copper electrode at a fixed thiourea concentration, three to five replications were conducted to ensure that accurate and dependable values were generated.

5.1.2 Results and discussion

The preliminary experiments for studying the anodic dissolution of the pure copper were conducted in the potential range between 0.27 to 1.5 V\textsubscript{SHE} in a typical electrolyte solution containing 42g/L Cu\textsuperscript{2+}, 160g/L H\textsubscript{2}SO\textsubscript{4}.

A voltammogram of the pure copper polarized at a sweep rate of 50 mV/s is shown in Figure 5-1. Distinctive behaviors make it convenient to partition this curve into four regions. In region I (0.27 to 0.69 V), the current rises linearly to a peak current \(i_p\). The linear segment in the region I indicates an active dissolution of copper. A sharp decrease in current is observed across region II (0.69 to 0.82 V) in which the current decreases rapidly and reaches a minimum value, \(i_{min}\). It is reported that at the moment of peak current occurrence, copper sulfate salt precipitates out on the electrode surface resulting a drop in current density. The precipitated copper sulfate salt functions as a barrier contributing to the decrease of the anodic current density[1,2]. The current starts to rise again in region III (0.82 to 1.05 V) and levels off in region IV (E > 1.05 V). The rising current in region III was interpreted as a result of the increased rate of chemical dissolution of the copper sulfate salt[3]. The current plateau observed in region IV is maintained as a constant value until the end of the test. The current is called of limiting current, \(i_L\). It is believed that the electrode is fully passivated at the limiting current.
Based on the above information on the anodic dissolution in the wide range of positive potential, further experiments were carried out under active dissolution (Region I) and the passive dissolution (Region IV) conditions to investigate the behavior of the pure copper. The effect of thiourea on the behavior with respect to both active and passive dissolution was also investigated.

![Voltammogram of the pure copper electrode polarized in a typical electrolyte solution at a sweep rate of 50 mV/s.](image)

5.1.2.1 Active dissolution process of pure copper

Active dissolution behavior of the pure copper electrode, with varying concentrations of thiourea from 0 to 30 mg/L, was studied using linear sweep voltammetry at a sweep rate of 0.5 mV/s over the potential range 0.27 to 0.55 V\textsubscript{SHE}. The plot of current density-potential is shown in Figure 5-2. Observation indicates that within the potential range of 0.31 to 0.55 V\textsubscript{SHE}, anodic current density increases linearly with potential in the absence or the presence of thiourea. Curves of current density vs. potential with respect to the absence and presence of thiourea are all parallel. The top one corresponds to the pure copper dissolution in the absence of thiourea, while the bottom one corresponds to the dissolution in the presence of 30 mg/L thiourea. By comparing the current density at a fixed potential point, one can find that the current density decreases in proportion to the thiourea addition.
During the active dissolution the net rate of the copper dissolution near the surface of the pure copper electrode can be expressed using a local current:

$$
\nu_{\text{net}} = \frac{i}{nFA}
$$

(5-1)

where $\nu_{\text{net}}$ is the net rate, $i$ the local current, $n$ electrons per molecule oxidized, $F$ the Faradaic constant, and $A$ the surface area. According to Eq. 5-1 the dissolution rate of the pure copper is proportional to the anodic current density. Therefore, one can draw a conclusion that the dissolution rate decreases with increasing concentration of thiourea.

There are several possibilities for explaining how a small amount of thiourea causes the anodic current density decrease. During the dissolution of the pure copper, ions are continuously generated on the surface of the pure copper, and copper ions move with a limited speed from the surface to the bulk. The concentration of copper ions near the surface, $C_s$, is always higher than that away from the electrode, $C_b$. The relation between the concentration difference, $C_s - C_b$, and the local current density, $i$, can be expressed as follows:

$$
i = nFk(C_s - C_b)
$$

(5-2)

where $k$ is the mass transport coefficient, which can be expressed as:
\[ k = \frac{D_{Cu^{2+}}}{\delta} \]  

(5-3)

where \( D_{Cu^{2+}} \) is the diffusion coefficient of copper ions and \( \delta \) the thickness of the Nernst diffusion layer. If the difference in concentration of \( C_s - C_b \) and the boundary layer thickness are kept constant, decreasing the diffusion coefficient can cause the current density to decrease. It is very unlikely that the diffusion coefficient of copper ions depends on the change in thiourea concentration.

If the difference in concentration and the diffusion coefficient are kept constant, increasing the diffusion layer thickness could cause the decrease in the current density. Can thiourea change the diffusion layer thickness? Abe et al. [4] measured the thickness of the diffusion layer, and reported value of 0.3 cm in an ordinary electrolyte system. If all of the thiourea at 30 mg/L were to accumulate on the surface through adsorption or precipitation on the surface through complexation with other species, it could not seriously change the thickness of the diffusion layer. Based on the calculation in Chapter 4, the total concentration of complexes of thiourea with cupric ion is only \( 7.2 \times 10^4 \) ppm. This low concentration could not cause any significant increase in the diffusion layer thickness.

Organic substances usually have a much lower dielectric constant than water molecules. Thiourea has been widely used as an inhibitor to prevent metal corrosion and in most cases thiourea has been found adsorbed on the metal surfaces. Thus adsorption of thiourea on the pure copper surface would be favored as the reason for reduced anodic dissolution. Thus, the adsorption of thiourea on the surface could directly cause the dissolution rate to decrease. The active surface sites of the pure copper could be blocked partially by thiourea, and thiourea could have a direct effect on the properties of the electrical double layer at the surface of the pure copper electrode, reducing the dissolution rate. Figure 5-3 shows a proposed schematic diagram of the surface of a copper electrode with respect to thiourea adsorption.

![Figure 5-3. The schematic diagram of a copper electrode surface covered by thiourea.](image-url)
Once a metal covered by a coating substance is immersed in solution under corrosion conditions, the measured current density on the metal coated is equal to the sum of the anodic and cathodic current densities at the interfaces of the coating film-electrolyte and the metal-electrolyte[5].

\[ i_{\text{cor,coat}} = i_{\text{met,cor-a}} + i_{\text{sol,cor-a}} + i_{\text{met,cor-c}} + i_{\text{sol,cor-c}} \]  

(5-4)

where \(i_{\text{cor,coat}}\) is the sum of corrosion current density in the presence of inhibitor, \(i_{\text{met,cor-a}}\) and \(i_{\text{sol,cor-a}}\) are the anodic current densities measured at interfaces of metal-electrolyte and coating film-electrolyte, respectively. \(i_{\text{met,cor-c}}\) and \(i_{\text{sol,cor-c}}\) are the cathodic current densities measured at interfaces of metal-electrolyte and coating film-electrolyte respectively.

Assuming that the metal surface is not completely covered by the coating substance, the inhibition efficiency is denoted as \(\theta\). Equation 5-4 then becomes:

\[ i_{\text{cor,coat}} = (1 - \theta) i_{\text{cor-a}} + i_{\text{sol,cor-a}} + (1 - \theta) i_{\text{cor-c}} + i_{\text{sol,cor-c}} \]  

(5-5)

where \(i_{\text{cor-a}}\) and \(i_{\text{cor-c}}\) are the anodic and cathodic current densities measured at the metal-electrolyte interface without coating, respectively.

In the present investigation, for the pure copper electrode the applied anodic polarization potentials were far from the corrosion potential, and the cathodic current density can be ignored according to Eq. 5-5. In addition, since thiourea is not a conductor, the current density measured on the interface of the surface film-electrolyte can be ignored. Thus, Equation 5-5 can be simplified as follows:

\[ i_{\text{cor,coat}} = (1 - \theta) i_{\text{cor}} \]  

(5-6)

\[ \theta = 1 - \frac{i_{\text{cor,coat}}}{i_{\text{cor}}} \]  

(5-7)

where \(i_{\text{cor}}\) is the anodic current density measured on the working electrode in the absence of thiourea at a pre-selected potential. \(i_{\text{cor,coat}}\) denotes the anodic current density measured in the presence of thiourea at the pre-selected potential. \(\theta\) is the inhibition efficiency of thiourea, which reflects the degree of working electrode surface blocked by adsorbed thiourea. The lower the

---

1 Inhibition of thiourea on anodic dissolution of copper could result from physical, chemical adsorptions of thiourea and its complexes with other dominant species in the experimental system. All these possible behaviors of thiourea were defined as the inhibition efficiency.
current density of $i_{cor,coat}$, the higher the inhibition efficiency. One can see that the $i_{cor,coat}$ is proportional to the concentration of thiourea. Thus, it is certain that thiourea functions as an inhibitor to hinder the dissolution rate of the pure copper in the active dissolution region.

The values of the inhibition efficiency, corresponding to the data in Figure 5-2 in the potential range 0.28 to 0.53 V$_{SHE}$, are listed in Table 5-1.

Table 5-1. Calculated inhibition efficiency (%) corresponding to the active dissolution of the pure copper electrode at constant potentials in the range 0.28 to 0.53 V$_{SHE}$.

<table>
<thead>
<tr>
<th>Anode potential V$_{SHE}$</th>
<th>Thiourea concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5] mg/L</td>
</tr>
<tr>
<td>0.28</td>
<td>11.43±1.95</td>
</tr>
<tr>
<td>0.30</td>
<td>8.23±0.59</td>
</tr>
<tr>
<td>0.34</td>
<td>5.46±0.87</td>
</tr>
<tr>
<td>0.40</td>
<td>5.38±0.93</td>
</tr>
<tr>
<td>0.45</td>
<td>2.09±0.81</td>
</tr>
<tr>
<td>0.50</td>
<td>3.27±0.93</td>
</tr>
<tr>
<td>0.53</td>
<td>4.16±0.78</td>
</tr>
</tbody>
</table>

From the data in Table 5-1 it is obvious that the coverage is reciprocal to the potential increase. There are two possibilities to explain this observation. At a low potential the dissolution rate of the pure copper is low, and thiourea can easily approach the surface of the pure copper and adsorb on the surface. With increase in the potential, the dissolution rate increases and the migration and diffusion are accelerated. In this case the movement of copper ions influences thiourea adsorption and leads to a decrease in inhibition efficiency. Thiourea could interact with copper ions to form complexes. The diffusion of such complexes away from the surface could cause the inhibition efficiency to decrease with increased anodic potential.

In addition, each linear sweep voltammetry experiment was conducted at sweep rate of 0.5 mV/s and required approximately 9 minutes for the potential scan in the range 0.28 to 0.53 V.
During this time thiourea may undergo decomposition or complexation, leading to a decrease in the inhibition efficiency.

5.1.2.2 Passive dissolution process of pure copper

A number of the LSV measurements, with varying sweep rates from 1 to 100 mV/s, were conducted in a potential range 0.27 to 1.5 V\textsubscript{SHE} and in the absence of thiourea. When the sweep rate was set at 50 mV/s, the voltammogram showed that there was a window indicating a current plateau starting at 1.1 V\textsubscript{SHE}. The current plateau was independent of the potential and reproducible (Figure 5-4).

![Voltammograms](image)

Figure 5-4. Voltammograms of the pure copper electrode polarized at various sweep rates of 5 mV/s to 100 mV/s.

Some researchers\cite{6,7,8} investigated copper passivation during copper dissolution in cupric sulfate-sulfuric acid solutions at high anodic potentials. X-ray photoelectron spectroscopy examination of a film formed in the current plateau region revealed that a considerable amount of CuSO\textsubscript{4}·5H\textsubscript{2}O and Cu\textsubscript{2}O was present in the film. It was suggested that after a copper electrode reaches a maximum dissolution rate, the saturation concentration of copper ions in the diffusion layer is reached rapidly. At this point the precipitation of copper sulfate salt on the electrode
surface occurs. The formation of cuprous oxide is the result of the continuous dissolution of copper in a saturated solution of copper sulfate. The reaction can be given as follows:

$$2Cu^+ + H_2O \rightarrow Cu_2O + 2H^+ \quad (5-8)$$

The limiting current was also found to increase with temperature and to decrease with increasing copper sulfate concentration.

Since the surface films of copper sulfate salt and copper oxide formed on the surface of the pure copper during the passive dissolution, the mass transport coefficient should be modified based on Eq. 5-3:

$$k = \frac{D_{Cu^+}}{\delta + \frac{\delta_{pre}}{\varepsilon_s}} \quad (5-9)$$

where $\delta_{pre}$ is the thickness of the surface films and $\varepsilon_s$ the porosity of the surface films. According to Eq. 5-9, if the formation of the surface films and the chemical dissolution of the surface films reach a balance, the thickness of the surface films should be constant and the porosity of the films should be constant as well. Thus, the current density could be independent of anodic potential.

What will be the limiting current in the presence of thiourea within the passivation potential range? A set of experiments was conducted to determine the effect of thiourea on the limiting current during passivation. The measurements were conducted at 50 mV/s with varying concentrations of thiourea 0 to 20 mg/L. The resulting values of the limiting current are shown in Table 5-2.

The data in Table 5-2 do not show a significant difference in the limiting current density. Even though the concentration of thiourea increased to 20 mg/L, which is far more concentrated than in industrial practice (<5 mg/L), the value of limiting current density with respect to a thiourea-free electrolyte is almost same as that in the presence of thiourea. Under the mass transfer control condition the thiourea adsorption has less influence on the dissolution rate compared with the effect of the formation of other surface films such as copper sulfate and copper oxides. On the other hand, under the passive dissolution of the pure copper it took more than 30 minutes to finish a test. It is possible for thiourea to undergo decomposition or interact
with other species, or even to be oxidized. The literature review has indicated that thiourea can be oxidized at high potential and can decompose.

Table 5-2. Values of current plateau obtained from the anodic polarization curves for the pure copper electrode in the typical electrolyte solution without and with added thiourea.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>0</th>
<th>1</th>
<th>5</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>limiting current density A/cm²</td>
<td>0.435±0.002</td>
<td>0.434±0.001</td>
<td>0.452±0.003</td>
<td>0.452±0.006</td>
</tr>
</tbody>
</table>

In order to find other windows by which the thiourea effect of thiourea on copper dissolution could be easily identified, a set of experiments was conducted by changing the sweep rate from 1 mV/s to 100 mV/s. The effect of sweep rate on the plot of current vs. potential was determined. Thiourea concentration was maintained at 5 mg/L. Other experimental conditions were controlled the same as those in the previous tests. The observation in Figure 5-5 shows that the current density values corresponding to the presence of thiourea in the active dissolution region are almost same as those in absence of thiourea. However, the peak current values with respect to the presence of thiourea are smaller than in the absence of thiourea.

![Voltammograms](image)

Figure 5-5. Voltammograms of the pure copper electrode polarized in the presence of 5 mg/L thiourea with varying sweep rate 1 mV/s to 100 mV/s.
For the above experiments, the peak current densities could be regarded as results of semi-infinite linear diffusion. Therefore, the peak current density can be expressed by the following equation [9]:

\[
i_{\text{peak}} = 0.4463 \frac{(nF)^{\frac{3}{2}}}{(RT)^{2}} \left( C_s - C_0 \right) D_{\text{Cu}}^{\frac{1}{2}} v_{\text{sw}}^{\frac{1}{2}}
\]

where \( i_{\text{peak}} \) is the peak current density; \( n, F, R, \) and \( T \) are the common expressions; and \( v_{\text{sw}} \) is the sweep rate.

According to Eq.5-10 the concentration gradient is the only parameter that can be changed, if we compare the peak current density at different concentrations of thiourea at the same sweep rate. To determine the influence of thiourea on the peak current density of the pure copper electrode, two series of LSV measurements were carried out. The electrode was polarized in the typical electrolyte solution in the absence of thiourea and in the presence of 5 mg/L thiourea, respectively (Figure 5-6).

![Figure 5-6](image)

**Figure 5-6.** Plot of peak current density vs. the square root of sweep rate corresponding to the pure copper polarized in the absence of thiourea and in the presence of 5 mg/L thiourea.

The peak current densities vary linearly with respect to the square root of the sweep rate. This indicates that the pure copper dissolution occurs under diffusion control. Although the curves corresponding to the absence and presence of thiourea are parallel, the value in the curve
for a thiourea-free solution is higher than that in the presence of thiourea. Obviously, thiourea does change the concentration profile on the surface of the copper and results in the decrease in the maximum reaction rate. The adsorption of thiourea on the active sites of the anode surface should be the main factors contributing to the decrease in the peak current in the presence of thiourea.

5.1.2.3 Dissolution of impure copper

Anodic dissolution behavior of the impure copper was studied by using the stationary electrode of the impure copper electrode as a working electrode in the present investigation. The experimental setup was the same as that applied for the stationary electrode of the pure copper. The preliminary tests were carried out in the potential range between 0.27 to 1.5 V$_{\text{SHE}}$ at a sweep rate of 50 mV/s in the typical electrolyte solution containing 42g/L Cu$^{2+}$, 160g/L H$_2$SO$_4$. The obtained voltammogram is similar as that of the pure copper stationary electrode. Four regions were observed, viz active dissolution region, onset of passivation region, chemical dissolution of precipitation region, and limited current region. The peak current density corresponding to the commercial copper anode is smaller than that of the pure copper.

Anode slimes were generated throughout the dissolution of the impure copper. Thus, when the dissolution rate reaches the maximum value there is a certain amount of slimes formation on the surface of the electrode. In contrast there are no slimes when the dissolution rate of the pure copper reaches the maximum value. Based on Eq. 5-10, when the slimes layer is generated on the surface of the electrode, the mass transport coefficient must decrease. This results in the peak current with respect to impure copper being lower than that of pure copper.

The experiments were conducted in varying concentrations of thiourea from 0 to 30 mg/L at sweep rate of 0.5 mV/s over the potential range from 0.30 to 0.45 V$_{\text{SHE}}$. The evaluated values of the inhibition efficiency were listed in Table 5-3. Data in Table 5-3 show the same trends as for the pure copper. At a certain thiourea concentration, the inhibition efficiency decreases with increasing potential. At a fixed potential the coverage is dependent on the increase in the thiourea concentration.
Table 5-3. Evaluated inhibition efficiency (%) corresponding to the active dissolution of the impure copper in various of thiourea concentrations at a potential range of 0.30 and 0.45 $V_{SHE}$.

<table>
<thead>
<tr>
<th>Anode potential $V_{SHE}$</th>
<th>Thiourea concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$[TU]$ 5 mg/L</td>
</tr>
<tr>
<td>0.30</td>
<td>12.23±1.05</td>
</tr>
<tr>
<td>0.34</td>
<td>8.43±0.98</td>
</tr>
<tr>
<td>0.40</td>
<td>5.30±0.68</td>
</tr>
<tr>
<td>0.45</td>
<td>3.46±0.70</td>
</tr>
</tbody>
</table>

The effect of sweep rate on the voltammogram obtained at a thiourea concentration of 5 mg/L was determined as well. Other experimental conditions were controlled in same way as those for the pure copper. The data are displayed in Figure 5-7. It is clear that the voltammogram is similar to the one in Figure 5-5. However, the peak currents are lower than those for the pure copper electrode. It is believed that thiourea’s function is similar in the dissolution processes of the pure and impure copper.

![Voltammograms](image)

Figure 5-7. Voltammograms of the impure copper polarized in the presence of 5 mg/L thiourea with varying sweep rate 2 mV/s to 50 mV/s.
It is worth pointing out that the results of the LSV for the pure copper in region from II to IV are difficult to replicate, especially for the impure copper in these regions. Since the copper sulfate precipitates are generated on the surface of the pure copper in these regions, they disturb the mass transfer on the surface when they grow and undergo chemical dissolution. For the pure copper it is possible to get fairly reproducible results, if we accept a certain degree of measurement noise. However, by using the same method as that for pure copper to study behavior of the impure copper, it is impossible to obtain reproducible results due to combined effect of anode slimes formation, thiourea adsorption and copper sulfate precipitation.

Meanwhile the data in Table 5-1 show that the inhibition efficiency increases with the change in concentration of thiourea at a fixed potential. The maximum degree of inhibition efficiency is approximately 40%. This value is much lower compared with that of copper dissolution in the presence of benzotriazole (BTA)[10] and iron dissolution in the presence of thiourea[11]. In these cases the inhibitor, BTA, was reported to adsorb strongly on the metal surfaces and to complex rapidly with the metal ions which were adsorbed on the electrode surface, leading to higher inhibition efficiency (>70%). From this comparison we can conclude that the lower inhibition efficiency may result from a week adsorption of thiourea.

Summarizing the above experimental results, we can make conclude that the LSV measurement is not a satisfying technique to investigate the influence of thiourea on the dissolution of both pure and impure copper. The results show poor reproducibility. The data, used to characterize the thiourea effect on copper dissolution, are obtained over a long period of time. Within the duration we cannot be sure how much thiourea decomposes or complexes with other species. Unlike the adsorption of common corrosion inhibitors on surfaces of metal, the thiourea adsorption on the rough surface of the copper working electrode is poorly understood in the LSV measurements. Therefore, the effect of thiourea on active dissolution of the pure and impure copper was not investigated further with the linear sweep voltammetry.

5.2 Chronopotentiometric Behavior of Anodic Dissolution of Copper

In the previous experiments, the investigations were carried out under controlled potential. This is totally different from the practice used in the copper electrorefining. In copper electrorefining most producers dissolve impure copper anode under the controlled current.
Usually, the current density is maintained as a constant, which could vary from 200 to 300 A/m$^2$ depending on different refineries. Thus, in this section, chronopotentiometry (constant current density) was employed to study the passivation processes of copper electrodes. This method was reported to be sensitive enough to accurately determine multiple element effects in copper anodes[3,12].

One of the differences between this laboratory study and industrial electrorefining is the current density employed. In industrial electrorefining, current densities at the anode range between 176 and 400 A/m$^2$ with typical values between 200 and 300 A/m$^2$. To accelerate passivation into a manageable time frame, 800, 1910, and 3820 A/m$^2$ were utilized. Since the majority of studies in this investigation utilized a current density at one order of magnitude larger than that in industrial practice, usually anode passivation will occur. The time to passivation is commonly used as a predictor of anode passivation.

In the present investigation the pure copper and the impure copper electrodes were dissolved by chronopotentiometry at pre-selected current densities. In order to easily identify the effect of thiourea on the dissolution process of these copper electrodes, various current densities were employed based on time frame of passivation occurring within two or three hours. In this case the experiments did not become time consuming. Meanwhile, the penetration of electrolyte into the copper working electrode could be prevented.

5.2.1 Experimental technique

The stationary electrodes of the pure copper and the impure copper anode were employed as working electrodes on which the anodic dissolution was conducted. The electrochemical cell was the VWR jacketed reactor in which 200 ml of a typical copper sulfate-sulfuric acid solution was added. The nitrogen was sparged to the solution in the cell for 20 minutes. After that the copper stationary polished electrodes were immersed in the cell and nitrogen was continually sparged for an additional 5 minutes.

After the electrodes were immersed in the electrolyte at open potential for five minutes, constant currents densities were then applied to the electrodes using an EG&G model 273A Potentiostat/Galvanostat combined with a chronopotentiometry program. The constant current densities varying from 800 A/m$^2$ and 3820 A/m$^2$ were selected based on previous work by a
number of researchers[3,13,14] who illustrated that this current density results in enough sensitivity to observe the effect of anode composition on passivation in an acceptable time frame. All experiments were run under static conditions.

For each electrode at a pre-selected current density, five replications were conducted to ensure that accurate and dependable values were generated. In the present investigation, the effect of thiourea, dominant species' concentration, and current density on both the pure and impure copper electrodes were examined. The thiourea solution was prepared as in the previous experiment in this section.

5.2.2 Results and discussion

5.2.2.1 Pure copper electrode

Chronopotentiometric measurements, in the absence and presence of thiourea, were conducted using pure copper as the working electrode in order to elucidate the passivation phenomena. The chronopotentiometry was performed at pre-selected current densities of 800, 1910 and 3820 A/m² in the typical electrolyte solution containing 42g/L Cu²⁺, 160g/L H₂SO₄ with the absence of thiourea. Each test was carried out for 2 hours. Three replications were conducted with respect to each current density. The chronopotentiograms corresponding to these pre-selected current densities were shown in Figure 5-8.

![Figure 5-8. Chronopotentiograms of pure copper electrode at 65 °C in typical electrolyte solution.](image-url)
It is obvious that anodic potential increased slightly with time in the time frame. There is no passivation occurring within the time frame of the test. The top line is with respect to 3820 A/m$^2$ and the bottom line with respect to 800 A/m$^2$. These lines are almost in parallel, but between these lines there is approximately a 60 mV potential difference. Theoretically, the anodic potential is a composite with the electrode potential, overpotential of activation, and potential drop of the electrolyte solution. Therefore, we are sure the overpotential of activation and potential drop of the solution should be the major contributors to the potential difference of 60 mV.

5.2.2.2 *Impure copper electrode*

Chronopotentiometric measurements, in the absence of thiourea, were conducted using the impure copper electrode as the working electrode in order to elucidate the passivation phenomena. The chronopotentiometry was performed at preset current densities of 800, 1910 and 3820 A/m$^2$ in the typical electrolyte solution containing 42g/L Cu$^{2+}$, 160g/L H$_2$SO$_4$ with the absence of thiourea. Chronopotentiograms, responding to the impure copper at less and equal to 800 A/m$^2$, show the anodic potential varying linearly with time. However, with respect to 1910 and 3820 A/m$^2$ chronopotentiograms show that the anodic potential rises dramatically to 7 V$_{SHE}$ at different times (Figure 5-9).

![Figure 5-9. Chronopotentiograms of the impure copper at constant current densities of 800, 1910 and 3820 A/m$^2$.](image)
Replications for the impure copper at each current density were carried out for five times. The time to passivation exhibited corresponding to 1910 A/m\(^2\) shows reproducibility within 20 seconds. However, the time to passivation corresponding to 3820 A/m\(^2\) is not identical. The range is approximately 80 seconds.

Gu et al.[14] pointed out that anode slimes generation is a highly non-uniform process, and the slimes formation rate is dependent on current density. The higher the current density, the more rougher the slimes phase. Therefore, in our case the slimes phase with respect to 3820 A/m\(^2\) should be much rougher than the one with respect to 1910 A/m\(^2\). That could be a major factor which disturbs the reproducibility of time to passivation at the high current density.

Figure 5-10 shows a typical chronopotentiogram for a commercial copper anode at 3820 A/m\(^2\). Distinctive behaviors make it convenient to partition this curve into four regions. In region I (0 to 250 seconds), the voltage rises linearly to a value beyond which a potential oscillations will occur. In this region, the working electrodes go through the active dissolution process. In region II, minor potential oscillations appeared within 30 to 50 seconds prior to passivation. The amplitude of these oscillations gradually increases with time. This is called the pre-passivation region. In region III, the passivation onset region, a sharp increase in potential exhibits more than a fifteen-fold increase in potential at a very short time. In region IV, the passivation region, continuous potential oscillation occurred and its magnitude is higher than 7 volts in this region.

![Figure 5-10. Typical chronopotentiogram of the commercial copper anode at 3820 A/m\(^2\) and 65 \(^\circ\)C in typical electrolyte solution.](image)
The persistent oscillation is strong and irregular. The time to passivation, \( t_p \), was denoted to be a function of working electrode tending to experience passivation. This is a period of time after which, at constant applied current density, a sudden increase in the anode potential occurs. In general, the smaller the current density, the longer the passivation time.

Sedzimir and Gumowska\[15\] developed a model to illustrate the dependence of passivation time on the anode current density with respect to their impure copper samples. In the model they made an assumption, viz, that the transport of copper ions in the vicinity of the anode surface is determined solely by diffusion. Then, the passivation time was proposed to possess a linear dependence on the logarithm of \( (1-i_p/i_A) \), where \( i_A \) is the anode current density and \( i_p \) is the maximum current density permissible avoiding passivation. The latter depends linearly on the cupric ion concentration (when the sulfate ion concentration is constant). The logarithm of \( i_p/(C_s - C_b) \) is reciprocal to the absolute temperature of the electrolyte solution, where \( C_s \) is saturated concentration of cupric ion, and \( C_b \) is the bulk cupric ion concentration.

According to this model, their anode sample would passivate immediately within 1 second in a solution containing 0.63 M Cu\(^{2+}\) and 1.73 M \( \text{H}_2\text{SO}_4 \) when an anode current density of 1320 A/m\(^2\) was employed. Comparing the result with the present investigation at 1910 A/m\(^2\), the passivation time is more than 4000 seconds, which is totally different. Sedzimir and Gumowska only took account of the role of cupric ion diffusion from the anode surface to the bulk in their model. The formation of anode slimes and some factors induced by slimes, which could affect the kinetics of anodic dissolution, have not been taken into account. It is inappropriate to use this simple model to describe the complicated passivation of impure copper.

It should be mentioned that before we carried out the experiments, two factors were considered. One is to preset the time frame of the tests. The other is to choose a current density of 1910 A/m\(^2\) as a standard parameter. According to Goto et al.[16] the thiourea consumption is proportional to the current density, they found that within 5 hours the thiourea content in solutions decreased 20 % to 30 % at the current density of 200 A/m\(^2\) and 500 A/m\(^2\), respectively. Therefore, presetting the time frame within two hours should limit thiourea decomposition. In addition, the value of 3820 A/m\(^2\) is 7 times as high as that for 500 A/m\(^2\) which Goto used. At the current density, the thiourea concentration in the test solution should decrease down to a certain level, which is what we want to eliminate. The value of 800 A/m\(^2\) at which the impure copper does not experience passivation in the absence of thiourea is low (Figure 5-9). The current
density of 1910 A/m$^2$ is in middle of these values, at which we expect that the thiourea content would not decrease sharply within two hours and we can still get fairly reproducible data.

5.2.2.3 The effect of thiourea

The effect of thiourea on the dissolution of pure and impure copper was investigated by using the chronopotentiometric technique. In both cases, the experimental electrolyte solution is composed of 42g/L Cu$^{2+}$, 160g/L H$_2$SO$_4$, and varying concentrations of thiourea 0.5, 1, 2, 3, 4, 5, 10, 20, and 30 mg/L. Three minutes prior to starting the chronopotentiometric measurements, thiourea aqueous solution was added to the cell. The anodic current density in the measurements was controlled identically at 1910 A/m$^2$.

To illustrate the effect of thiourea on the pure and impure copper dissolution, the passivation times corresponding to a variety of thiourea concentrations are selected and listed in Table 5-4 and demonstrated in Figure 5-11, respectively.

Table 5-4. Passivation of the pure copper in the presence of thiourea.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>Passivation time ($t_p$) sec.</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>None</td>
<td>No passivation within 2 hrs</td>
</tr>
<tr>
<td>1.0</td>
<td>None</td>
<td>No passivation within 2 hrs</td>
</tr>
<tr>
<td>2.0</td>
<td>None</td>
<td>No passivation within 2 hrs</td>
</tr>
<tr>
<td>3.0</td>
<td>None</td>
<td>No passivation within 2 hrs</td>
</tr>
<tr>
<td>4.0</td>
<td>None</td>
<td>No passivation within 2 hrs</td>
</tr>
<tr>
<td>5.0</td>
<td>None</td>
<td>No passivation within 2 hrs</td>
</tr>
<tr>
<td>10.0</td>
<td>6543±20</td>
<td>Passivated</td>
</tr>
<tr>
<td>20.0</td>
<td>5501±14</td>
<td>Passivated</td>
</tr>
<tr>
<td>30.0</td>
<td>4713±9</td>
<td>Passivated</td>
</tr>
</tbody>
</table>

Data in Table 5-4 show that at the concentration range of 0.5 mg/L to 5 mg/L thiourea does not show passivation within a time frame of two hours. However, when the concentration is higher than 5 mg/L, thiourea has a negative effect on the dissolution of the pure copper within a time frame of two hours. The higher the thiourea concentration the shorter the passivation time.
Although there are no passivation occurrences at less than 10 mg/L of thiourea in the two-hour experiment, this does not mean that the pure copper would not experience passivation. It could be passivated beyond the time frame at any time. In this section, it is not necessary to conduct the test over two hours due to the decomposition of thiourea at high anodic current density.

Figure 5-11 depicts that the passivation time decreases with increasing thiourea concentration. At the thiourea-free condition, the passivation time of the impure copper is approximately 4700 seconds. In the presence of 0.5 mg/L thiourea, the passivation time is approximately 4100 seconds. However, the passivation time drops down to 2100 seconds when the addition of thiourea reaches 30 mg/L. This observation indicates that the anodic dissolution of the impure copper is hindered by thiourea present in the electrolyte solution. Even at 0.5 mg/L which is a very low level of thiourea concentration compared with the level in copper refining operations, the inhibition of thiourea on the anodic dissolution still can be observed.

![Graph](image)

Figure 5-11. Passivation time corresponding to thiourea concentration under the chronopotentiometric measurements for the impure copper.
In addition, the observation shows that the passivation time does not decrease linearly with increasing concentration of thiourea. The passivation time decreases rapidly within a thiourea concentration of 0.5 to 3 mg/L.

It is worth mentioning that five replications of the chronopotentiometric measurements were carried out at each level of thiourea concentrations, and the value of passivation time showed reproducibility within 50 seconds. The error of average for the passivation time is 1.5 %. Sedzimir and Gumowska[15] used chronopotentiometry to measure the passivation time of their impure copper at 850 A/m². The replications were more than 12 times. The reported error of the average for passivation time was 2 %.

Replications, corresponding to anodic current density of 3890 A/m² and any level of thiourea concentration, were not reproducible. The values of passivation time changed from 100 seconds to 150 seconds. The estimated error of average is over 17 %, which is not acceptable.

5.3 Passivation Mechanism for Pure Copper and Impure Copper Anode

Within the time frame of two hours, the pure copper demonstrate undergoes active anodic dissolution no matter how high the applied anodic current density. However, controlled at the same current density as the pure copper, the impure copper experiences passivation. In fact, during the dissolution of the impure copper two distinct events occur. First, surface film – anode slimes begin to be generated on the surface. The slimes gradually occupy and reduce the active area of the surface, and cause an increase in the current density in those areas which are unoccupied. Consequently, increasing current density in the active area raises the copper ion concentration in the electrolyte within the pores of the slimes. Secondly, the slimes become a barrier hindering copper ions from diffusing from the surface to the bulk solution, this causes extensive increase in the concentration of copper ions at the surface. When the copper ion reaches its saturated concentration, copper sulfate (pentahydrate or other kinds of salts) will precipitate, and grow on the surface and in the pores of the growing slimes. At this point, the surface is covered with slimes and copper sulfate.

Meanwhile, among the precipitated copper sulfate, the formation of copper oxide occurs. The slimes, copper sulfate, and copper oxide films continue to grow with time, causing the
increase in anodic potential. Eventually, this leads to the formation of a non-conducting or weakly conducting surface film and the dissolution of copper stops completely. At this point the passivation is complete. The formation rate of these non-conducting films is obviously dependent on the applied anodic current density and the components existing in the impure copper anodes. Thus, the dependence causes the passivation time to be proportional to the applied anodic current density.

During the dissolution of impure copper thiourea will immediately adsorb on the surface of the impure copper surface when thiourea is added to the electrolyte. The adsorption film of thiourea acts as barrier film which blocks the active area of the surface. This will accelerate the growth of the films of copper sulfate and copper oxide on the surface and eventually lead to passivation. The higher the concentration of thiourea, the higher the formation rate of surface films, and the shorter the passivation time.

Through chronopotentiometric measurements, the effect of thiourea on the anodic dissolution of the pure and impure copper is quantitatively described by comparing the passivation time with respect to different concentrations of thiourea. This agrees well with the results obtained by using linear sweep voltammetry.

On the other hand, there is a disadvantage in determining the effect of thiourea on the dissolution of copper electrodes. Because thiourea is expected to be unstable and to undergo decomposition and complexation with copper ions and proton ions, it is necessary to look for more efficient methods to characterize the behavior of thiourea in the process of copper dissolution.

5.4 References


Chapter 6 Behavior of Thiourea in the Anodic Dissolution of Copper – II

The previous linear sweep voltammetric and chronopotentiometric measurements (Chapter 5) demonstrate that thiourea can hinder the anodic dissolution rate of pure copper and impure copper electrodes. However, the procedure of thiourea addition in the laboratory experiments is quite different from that in industrial copper electrefining. In industrial practice, thiourea aqueous solutions are added directly to the electrochemical cells continuously.

In contrast, all of the studies discussed in Chapter 5 were conducted adding thiourea aqueous solution to the electrochemical cell eight minutes prior to the start of each experiment. Even though the cell was kept on open potential before starting an electrochemical measurement, within the time of open potential, there was the possibility that the active thiourea concentration decreased with time. Since a low concentration of thiourea was added in the highly concentrated copper sulfate-sulfuric acid solution, thiourea might have interacted with copper ions or sulfuric acid.

In the preceding experiments (Chapter 5), the concentration of thiourea in the test solution was controlled from 5 mg/L to 30 mg/L. However, the test solution consisted of highly concentrated copper sulfate-sulfuric acid solution in which the dominant species are cupric ions, protons, and bisulfate ions. The concentrations of cupric ions and sulfuric acid are approximately 40,000 mg/L and 300,000 mg/L, respectively. These values are more than a thousand times the maximum concentration of thiourea used in the previous tests.

Obviously, it is a challenge to study effect of thiourea on the copper dissolution process in the presence of a trace level of thiourea. There are two possibilities by which the effect of thiourea can be determined. The first is to specify the experimental conditions by using a highly concentrated thiourea-copper sulfate-sulfuric acid solution or by diluting the concentration of copper sulfate-sulfuric acid to the level of milligrams per liter, whereby the effect of thiourea on copper dissolution is emphasized. However, using the above experimental conditions means significantly changing the composition of the electrolyte used in the industrial operation. Under these conditions the experimental results would not represent industrial practice. The second approach is to make use of sensitive electrochemical measurements to determine the effect of thiourea on the copper dissolution process without changing significantly the solution.
composition. The objective of this chapter is to find an electrochemical method which is sensitive to the presence of thiourea in a highly concentrated copper sulfate-sulfuric acid solution.

6.1 Stability of Thiourea

It is important to understand the behavior of thiourea in the concentrated electrolyte solution without the occurrence of any electrochemical reaction. A study of the stability of thiourea, in a specified electrolyte contained 0.5 M CuSO₄, was conducted at 23°C and 65°C. The initial solution pH was adjusted within the range 1.8 to 3.3 using sulfuric acid. For each test 100 mL of electrolyte was added in the VWR jacketed cell. The solution pH was monitored throughout test by using an Accumet pH Meter 50 (Fisher Scientific).

At room temperature 23°C, one test solution's initial pH was adjusted to 3.3 and the other was 1.91. At 65°C, one pH was 3.19 and the other 1.85. Before starting a test, a known amount of thiourea aqueous solution was added to the test solution, and the concentration of thiourea in the test solution was 0.76 g/L. The added thiourea was mixed quickly with the solution by magnetic stirring. After thiourea addition the pH of the solution was recorded every 30 seconds, and after 5 minutes of the test the pH was recorded every 5 or 10 minutes. Figure 6-1 shows a plot of solution pH versus time.

![Figure 6-1. Plots of solution pH vs. time corresponding to the presence of 0.76 g/L thiourea at various temperatures and initial pH.](image-url)
The test with respect to the initial pH of 1.85 showed that the pH decreased slightly as a function of time within the first few minutes and then tended to be constant. Even though the test temperature was quite different, the two lines are almost in parallel. However, for the test with initial pH over 3, the pH decreased rapidly as a function of time. Especially, at 65 °C the pH dropped faster than at 23 °C. This indicates that at higher temperature thiourea reacts faster than at lower temperature.

It should be mentioned that when the test at the initial pH of 3.19 was conducted at 65 °C, while thiourea was added to the solution, the solution color became cloudy. Consequently, the solution color changed from dark blue to dark green within 7 minutes. Similarly, the color changed gradually over 40 minutes when the test was carried out at 23 °C. In contrast to the above tests, as thiourea was added to the solution, the tests with an initial pH of 1.85 showed that clouding substances appeared and then immediately disappeared. The solution color was unchanged over one hour and the color still appeared as dark blue. Varying temperature from 23 °C to 65 °C did not result in any difference in the observations.

The test solution in the absence of thiourea appears dark blue caused by the cupric ions. Thus, when thiourea was mixed with the test solution corresponding to a high initial pH, the solution color change indicated that some substances were generated. Raub et al.[1] observed a similar phenomenon when they studied the effect of thiourea on the deposition of copper in a copper sulfate solution which originally contained no cuprous ions. They examined the suspended solid substance using infrared spectroscopy, and pointed out that the substance consisted of complexes of Cu(TU)\(^{+}\). They postulated that cuprous ions were generated according to the following reaction.

\[
2Cu^{2+} + 2(HHfN > C = S) \Leftrightarrow 2Cu^{+} + (H_{N}H \geq C - S - S - C \leq NH) + 2H^{+} \quad (6-1)
\]

According to Eq. 6-1 continuously adding thiourea will shift the reaction direction to the right hand side, if the concentration of cupric ions is constant. Therefore, the concentration of cuprous and proton ions will increase. In the previous tests, the pH dropped as a function of time indicating that protons were generated continuously. In addition, the solution color changed from blue to green indicating that the occurrence of cuprous ions. These two facts are perfectly consistent with the illustrations using Eq. 6-1.

The above experimental results demonstrate that thiourea can interact quickly with copper ions in concentrated copper sulfate solution, and thiourea appears more reactive at 65 °C than at
low temperature. Changing the solution concentration of thiourea or of the dominant species such as copper ions and protons could not prevent the occurrence of the interaction between thiourea and these ions.

6.2 Behavior of Thiourea in the Anodic Dissolution Process

Based on the above results, the addition of thiourea prior to starting the tests, was replaced by the continuous injection of thiourea for the duration of the tests. During a test a known amount of thiourea aqueous solution was injected into a certain amount of a test solution at a pre-selected time. Before adding thiourea, the test solution contained no thiourea. The anodic currents before and after injecting thiourea were interpreted as the effect of thiourea on the rate of anodic dissolution of copper.

One of the challenges of the continuous addition of thiourea is the problem of the effective mixing thiourea with the test solutions. The rotating disk electrode (RDE) has advantages for overcoming this problem. A copper RDE was used as the working electrode immersed in a test solution. During a test, a motor accurately controls the rotation speed of the RDE. Thus, a well defined hydrodynamic field formed around the RDE. After careful injection, thiourea is rapidly mixed with the test solution in the electrochemical cell.

6.2.1 Experimental technique

The rotating disk electrodes of the pure copper and the impure copper were employed as working electrodes on which the anodic dissolution takes place. Rotation speed was controlled by a Model 636 Electrode Rotator (EG&G). The electrochemical cell was the EG&G cell to which 100 ml of a typical copper sulfate-sulfuric acid solution was added. Nitrogen was sparged into the solution in the cell for 20 minutes. The copper RDE was polished and immersed in the cell and nitrogen was continually sparged into the bottom of the cell for an additional 5 minutes. The thiourea aqueous solutions were prepared prior to a set of experiments and were used within 24 hours of the preparation.

Before starting a test the cell was kept on open circuit potential for 5 minutes. Then, a potential step with a magnitude of ΔE was applied to the RDE. During the test the rotation speed was kept constant and the resulting current vs. time plots were recorded.
The M273A Potentiostat/Galvanostat combined with the chronoamperometry (potential step) program were used to control the anodic dissolution. With respect to the anodic dissolution of the pure and impure copper RDE at a fixed thiourea concentration, three to five replications were conducted to ensure that accurate and dependable values were generated.

In this section all experiments were designed to maintain the copper electrodes in active dissolution. The passivated dissolution of copper was not discussed in this section. In order to run lab tests with a working electrode potential similar to that in industrial operations, a potential step jumping from $E_{op}$ (0.275 $V_{SHE}$) to 0.34 $V_{SHE}$ was chosen for both the pure and impure copper RDE. Thus, the anodic current changes can be regarded as a manifestation of the influence of thiourea on the rate of copper dissolution in the presence of thiourea.

### 6.2.2.1 Determination of experimental parameters

Preliminary tests were carried out for determining the appropriate rotation speed. It was found that within the range of 300 to 3600 rpm the anodic current is independent of rotation speed. Thus, a speed of 2400 rpm was chosen as the standard speed for the tests employing pure copper RDE. For impure copper RDE a speed of 400 rpm was chosen. Microscopy examination showed that the slime layer generated on the anode surface remained on the anode surface at this speed.

In addition, preliminary potential step measurements showed that after about 250 seconds the current reached a constant value. Therefore, a 250-second period was chosen as a typical point at which thiourea was injected into the electrochemical cell. The amount of thiourea solution injected was less than 0.5 mL. After the injection, tests were kept running for over 250 seconds. The anodic current-time behavior before and after injecting thiourea was recorded.

Figure 6-2 shows a typical diagram of potential step test corresponding to thiourea injection. Figure 6-2(a) shows the potential-time control procedure while Figure 6-2(b) depicts the anodic current-time behavior before and after thiourea injection. The observation in the latter shows that the initial anodic current rapidly decreased following thiourea injection. Before injecting thiourea, the initial current reaches a constant level. At the moment of the injection, the initial current decreases rapidly down to a certain level then reaches another constant value. These observations suggest two possibilities. Firstly, the initial current drop may result from thiourea participating in the process of anodic dissolution. Secondly, physical disturbance of the liquid.
injection may cause the change in value of the initial current, even though a small amount of thiourea was injected.

![Graph showing current density over time with thiourea injection](image)

Figure 6-2. A typical plot corresponding to Cu RDE potential step test at 0.34 V\text{SHE} in the typical electrolyte solution with injection of 20mg/L thiourea at rotation speed of 2400 rpm, at 65\degree C.

In order to identify the physically disturbing effect of injecting the solution on the initial current, two identical tests were carried out under the potential control condition similar as the previous test shown in Figure 6-2. In contrast to Figure 6-2, the tests demonstrated that when a 0.5 mL electrolyte with thiourea-free was injected to the cell, the anodic current density remained essentially unchanged near 0.15 A/cm\textsuperscript{2} for a test period of 500 seconds. This confirms that the rapid decrease in the current is related to the presence of thiourea and is not due to the physical disturbance of the test solution by the injection process.

6.2.2.2 Dissolution of pure copper in the presence of thiourea

The dissolution behavior of the pure copper RDE, with the injection of thiourea varying from 5 mg/L to 30mg/L, was studied using the potential step at a potential jump from open potential, E\text{op}, to 0.34 V\text{SHE}. Plots of current density vs. time, corresponding to the injection of various concentrations of thiourea, are shown in Figure 6-3. All curves exhibit the initial current density drop following thiourea injection. Obviously, the depressed current density is dependent
on the concentration of thiourea. The higher the thiourea concentration the lower the value of the depressed current density. In addition, it is clear that the initial anodic current rapidly decreases within about 5 seconds following thiourea injection no matter how much thiourea was added. This provides additional confirmation of the fact that anodic current density decrease is due mainly to the addition of thiourea. Furthermore, this behavior is consistent with the polarization behavior of the linear sweep voltammetry and chronopotentiometry.

Figure 6-3. Plots of anodic current density vs. time at varying concentrations of thiourea for pure copper dissolution at potential 0.34 V_

As reported in chapter 5, the concept of the inhibition efficiency was introduced to illustrate the inhibition effect of thiourea on the copper dissolution. According to Eq. 5-1 the inhibition efficiency of thiourea related to curves in Figure 6-3 was calculated and listed in Table 6-1. It is clear that the inhibition efficiency is dependent on the concentration of thiourea. The higher the concentration of thiourea the higher the inhibition efficiency.

Table 6-1. Calculated inhibition efficiency vs. varying concentration of thiourea corresponding to the active dissolution of the pure copper electrode at a constant potential of 0.34 V_

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>21.06±0.03</td>
<td>31.03±0.05</td>
<td>40.13±0.04</td>
<td>49.38±0.05</td>
</tr>
</tbody>
</table>
6.2.2.3 Dissolution of pure copper in varying concentrations of solution species

In numerous publications[2,3,4] the authors have interpreted their results on the inhibiting effect of thiourea by various reaction mechanisms including adsorption of thiourea molecules and of related complexes on the metal surface. For highly concentrated copper sulfate-sulfuric acid solutions, few authors however, have proposed a mechanism of interaction of thiourea with copper ions and evidence to confirm those complexations. None of the papers explains how the products generated by the interaction behave during the active dissolution of the copper. In this section the effect of thiourea on the anodic dissolution of copper was studied at various concentrations of copper ions and protons.

Two series of tests were conducted. Firstly, potential step measurements, with varying cupric ion concentration, were conducted at a constant concentration of sulfuric acid and thiourea. Secondly, with varying sulfuric acid concentration potential step measurements were carried out at a constant concentration of cupric ions and thiourea. The anodic current densities before and after the injection of thiourea were recorded and used for the computation of inhibition efficiency.

Relationship between the inhibition efficiency and concentration of cupric ion in the presence of a certain amount of thiourea

The behavior of copper dissolution, with varying cupric ion concentration from 5 g/L to 42 g/L, was investigated using the potential step method in a solution containing 160 g/L H₂SO₄ with the injection of 20 mg/L thiourea. A marked decrease in the initial anodic current following thiourea injection was observed. The evaluated inhibition efficiency corresponding to the different concentrations of cupric ions is listed in Table 6-2. It is obvious that the inhibition efficiency decreases slightly with the increase in the concentration of cupric ions.

Table 6-2. Inhibition efficiency vs. varying concentration of cupric ions in response to the active dissolution of the pure copper electrode in the presence of 20 mg/L thiourea.

<table>
<thead>
<tr>
<th>[Cu²⁺] g/L</th>
<th>5</th>
<th>10</th>
<th>21</th>
<th>42</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ %</td>
<td>46.30±0.07</td>
<td>46.05±0.06</td>
<td>45.59±0.04</td>
<td>40.13±0.05</td>
</tr>
</tbody>
</table>
Numerous authors have proposed[5,6,7,8] that several interactions of thiourea with copper ions can take place when thiourea is present in copper sulfate solutions. One of the reactions can be written as:

\[ Cu^{2+} + (n + 1)(H_2N > C = S) \Leftrightarrow [Cu(H_2N > C = S)_n]^+ + \frac{1}{2}(H_2N > C - S - C \leq NH) \quad (6-2) \]

Based on the preceding experimental observations and Eq.(6-2), thiourea can behave in two ways when it is injected into the electrochemical cell. Following the injection, some of the thiourea molecules would be adsorbed on the surface of copper electrode. Meanwhile others would interact with cupric ions simultaneously to form cuprous complexes and formamidine disulfide. The adsorbed thiourea molecules could block the active sites on the surface, causing the anodic current density to decrease.

If the adsorption of thiourea molecules dominates the active dissolution of copper, the value of inhibition efficiency would be dependent on the concentration of thiourea in the solution. According to Eq. (6-2) increasing the concentration of copper ions will increase the concentration of the products. This should result in decreasing the concentration of thiourea. Thus, the more concentrated is the cupric ion, the higher the consumption of thiourea due to the interaction between thiourea and cupric ions. Consequently, less active sites on the surface are blocked causing the inhibition efficiency to decrease.

According to the calculations in Chapter 4, the concentration of free thiourea is much higher than its concentration in the complexes. For example, when 30 mg/L thiourea is present in the solution containing 42 g/L Cu\(^{2+}\) and 160 g/L H\(_2\)SO\(_4\), the concentration of complexes is approximately 2 mg/L. If 20 mg/L thiourea is added to the electrolyte solution, it is believed that there is small amount of thiourea which interacts with cupric ions. Therefore, when the copper ion concentration varies from 5 to 40 g/L and 20 mg/L thiourea is injected into the solutions, the thiourea concentration in the solution should decrease with increasing copper ion concentration. However, the decrease in thiourea concentration should not be significant. This explains why the inhibition efficiency decreases slightly with increase in cupric ions (Table 6-2).
Relationship between the inhibition efficiency and concentration of sulfuric acid in the presence of a certain amount of thiourea

The behavior of copper dissolution, with varying sulfuric acid concentrations from 160 g/L to 184 g/L, was studied using the potential step method in solution containing 42 g/L Cu^{2+} with the injection of 20 mg/L thiourea. A marked decrease in the initial anodic current following thiourea injection was observed. The evaluated inhibition efficiency corresponding to the different concentrations of sulfuric acid is listed in Table 6-3. Clearly, the inhibition efficiency shows a similar trend to the results listed in Table 6-2. The inhibition efficiency decreases slightly with the increase in concentration of sulfuric acid.

Table 6-3. Inhibition efficiency vs. varying concentration of sulfuric acid in response to the active dissolution of the pure copper electrode in the presence of 20 mg/L thiourea.

<table>
<thead>
<tr>
<th>[H_2SO_4] g/L</th>
<th>160</th>
<th>168</th>
<th>176</th>
<th>184</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ %</td>
<td>40.13±0.02</td>
<td>39.12±0.01</td>
<td>36.25±0.01</td>
<td>35.35±0.01</td>
</tr>
</tbody>
</table>

Some researchers\[9,10\] have proposed that cupric ions can be reduced by thiourea, with the reaction products being protons, FDS, and cuprous ions (Eq. (6-1)). Based on this equation, increasing the concentration of sulfuric acid will increase the proton concentration resulting in a higher concentration of the reactants. This shift should make more thiourea available to cover the copper surface, if the acid level is raised at a constant cupric ion concentration. In contrast to the prediction, the inhibition efficiency actually decreases with increase in the concentration of sulfuric acid (Table 6-3). This behavior may be due to the protonation of thiourea molecules, which can be written as:

\[
\begin{aligned}
\text{H}_2\text{N}^+ + \text{Cu}^{2+} &\Rightarrow \text{Cu^{+}} + \text{H}_2\text{O} \\
\text{H}_2\text{N}^+ + \text{Cu}^{2+} &\Rightarrow \text{Cu^{+}} + \text{H}_2\text{O}
\end{aligned}
\]

According to Eq. (6-3), thiourea can exist as free molecules and a protonated species when present in copper sulfate-sulfuric acid solutions. The concentrations of the protonated species should be determined by the equilibrium constant for the protonation. Increasing the concentration of sulfuric acid should result in a decrease in thiourea concentration in the
solution. Consequently, decreasing the thiourea concentration should lead to a decrease in the inhibition efficiency.

Two series of experiments were carried out to confirm the above supposition. One set of experiments was conducted with thiourea concentrations from 4 mg/L to 30 mg/L. The electrolyte solution contained 42 g/L Cu\(^{2+}\) and 1 g/L \(\text{H}_2\text{SO}_4\). A second set of experiments was conducted under the same conditions, but the sulfuric acid concentration was 160 g/L instead of 1 g/L. The dependence of the inhibition efficiency on the concentration of sulfuric acid is shown in Figure 6-4. It is clear that the coverage corresponding to the lower concentration of sulfuric acid is significantly higher than that in the concentrated sulfuric acid solutions. The results are in good agreement with those in Table 6-3, providing additional confirmation that increasing thiourea protonation leads to a depression in the inhibition efficiency.

![Figure 6-4](image)

Figure 6-4. Comparison of dependence of the inhibition efficiency on the concentration of thiourea in the presence of low and high concentrations of sulfuric acid.

Since the above tests were carried out in a solution of highly concentrated cupric ions, the cupric ions present should impact the concentration of thiourea in the solutions. To eliminate the possibility of cupric ions interacting with thiourea, a series of experiments, with a solution containing 160 g/L of sulfuric acid and 97.3 g/L \(\text{Na}_2\text{SO}_4\), was carried at concentrations of thiourea varying from 5 mg/L to 30 mg/L. The calculated inhibition efficiency is listed in Table 6-4.

The data in Table 6-4 show that the inhibition efficiency is dependent on the concentration of thiourea. Comparing the inhibition efficiency in Table 6-1 with the values in Table 6-4, the latter are higher than the former. This indicates that without cupric ions, more thiourea can
adsorb on the surface of the copper electrode, leading to higher inhibition efficiency. In addition, the results of Table 6-4 confirm indirectly that cupric ions interact with thiourea, and the interaction causes the inhibition efficiency of thiourea on the rate of anodic dissolution to decrease.

Table 6-4. Inhibition efficiency vs. varying concentrations of thiourea in response to the active dissolution of the pure copper electrode in the solution containing only 160 g/L H₂SO₄.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ %</td>
<td>27.63±0.01</td>
<td>41.35±0.03</td>
<td>51.09±0.06</td>
<td>57.77±0.06</td>
</tr>
</tbody>
</table>

In order to address the interaction between copper ions and thiourea, a series of experiments with the test solution containing 42 g/L Cu²⁺ and 231.9 g/L Na₂SO₄, was carried at concentrations of thiourea varying from 5 mg/L to 30 mg/L. The calculated inhibition efficiency is given in Table 6-5.

Table 6-5. Inhibition efficiency vs. varying concentration of thiourea in response to the active dissolution of the pure copper in a solution containing only 42 g/L Cu²⁺ and pH = 3.95.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ %</td>
<td>27.61±0.01</td>
<td>47.82±0.03</td>
<td>59.16±0.06</td>
<td>64.35±0.07</td>
</tr>
</tbody>
</table>

The table shows that the inhibition efficiency is also dependent on thiourea concentration. Comparing the inhibition efficiency in Table 6-1 with that in Table 6-5, one notes that the former is lower than the latter. This indicates that without the appearance of protons, more non-protonated thiourea can adsorb on the surface of copper electrode, leading to higher inhibition efficiency. In addition, the results of Table 6-5 confirm indirectly that the protons do interact with thiourea, and the interaction decreases the inhibition efficiency of thiourea on the rate of anodic dissolution.
6.2.2.4 Effect of formamidine disulfide on the anodic dissolution of pure copper

Although the interaction of copper(II) with thiourea have been studied by numerous researchers[5-9,11,12,13], the behavior of formamidine disulfide (FDS), corresponding to the anodic dissolution of copper in a highly concentrated copper sulfate-sulfuric acid solution has not been reported. Previous studies (section 6.2.2.2) have shown that thiourea interacts with copper(II) and the interaction leads to the formation of formamidine disulfide. Thus the behavior of FDS in worth investigating to further understand the behavior of thiourea in the anodic dissolution process.

Chemical reagent FDS (97%) from Alfa AESAR was employed in the present investigation. The stock solutions of FDS were prepared from solid FDS dissolved in deionized water at room temperature. The solutions were used for tests within one day and then discarded. The mixed solution of thiourea and FDS was prepared by mixing the solutions of thiourea and of FDS in a desired procedure.

Behavior of active dissolution of pure copper in the presence of formamidine disulfide

The potential control in the potential step experiments was identical to that used in the previous tests. The injection of FDS was similar to the procedure for injecting thiourea. Preliminary tests were conducted to investigate the behavior of the anodic dissolution of the pure copper in the presence of formamidine disulfide. In Figure 6-5 the large figure shows anodic current-time behavior before and after FDS injection. The inset shows the potential-time control. Point A indicates the time of FDS injection, point B the current measurement at 30 seconds after the injection, while point C displays the current measurement at 250 seconds after the injection.

Figure 6-5 shows that the initial anodic current decreases and reaches a minimum value within about 30 seconds following FDS injection. After that time, the current slightly increases until the end of test. Although the curve in Figure 6-5 shows a similar trend of current density drop to that for thiourea injection (Figure 6-2), two different phenomena in Figure 6-5 have to been pointed out. First the magnitude of initial current density decrease following FDS injection is smaller than that in the case of thiourea injection. Secondly, the current density following FDS injection increases slightly with time until the end of test, instead of remaining constant. This behavior indicates that FDS stability is dependent on time. Thus, the behavior of FDS in copper dissolution, with varying concentrations of FDS from 5 mg/L to 20 mg/L, was studied using
potential step measurement. Figure 6-6 demonstrates the dependence of the inhibition efficiency, evaluated at different times after FDS injection, on varying concentration of FDS.

Figure 6-5. A typical plot corresponding to RDE potential step test with injection of 10 mg/L formamidine disulfide (FDS).

Figure 6-6. Dependence of the inhibition efficiency evaluated at different times on varying concentrations of FDS in the active dissolution of the pure copper.

These observations demonstrate that the inhibition efficiency evaluated either at 30 seconds or 250 seconds is dependent on the concentration of FDS. In addition, the coverage evaluated at
30 seconds is higher than that at 250 seconds. The difference may result from the decomposition of FDS or interactions between FDS and some species in the copper sulfate-sulfuric acid solution. Meanwhile, the results indicate that the combination experiment of the potential step and RDE of pure copper is sensitive to demonstrate a very low current drop due to the injection of FDS. Furthermore, comparing the values in Table 6-1 and Figure 6-6 it is obvious that the inhibition efficiency with respect to FDS addition is smaller than that with thiourea injection. This indicates that the inhibition efficiency of FDS is weaker than that of thiourea.

**Behavior of pure copper in the addition of mixed solution of thiourea and FDS**

The anodic dissolution behavior of the pure copper, with injection of mixed solutions of thiourea and FDS, was studied using the potential step measurement. During these tests, the thiourea concentration varied from 5 mg/L to 30 mg/L, and the concentration of FDS was maintained at a constant value of 10 mg/L. After a 250-second potential jump period, the mixed solution was injected into the electrochemical cell. The anodic currents, before and after injection of the mixed solutions were recorded and used to calculate the inhibition efficiency. The relation of inhibition efficiency to thiourea concentration in a mixed solution is shown in Figure 6-7. The observation exhibits the dependence of the inhibition efficiency on the concentration of thiourea.

![Figure 6-7](image)

Figure 6-7. Inhibition efficiency vs. varying concentration of thiourea corresponding to the pure copper RDE at a constant FDS concentration of 10 mg/L.
In order to identify the effect of thiourea and FDS on the rate of the active dissolution of the pure copper, the inhibition efficiency data corresponding to the addition of thiourea by itself, FDS by itself, and mixed solutions of thiourea and FDS, are given in Table 6-6.

Table 6-6. Comparison of the inhibition efficiency corresponding to the addition of thiourea, FDS, and mixed solutions of thiourea and FDS.

<table>
<thead>
<tr>
<th>TU or FDS mg/L</th>
<th>Inhibition efficiency (%)</th>
<th>TU only</th>
<th>FDS only*</th>
<th>Mixed ([TU]_var+[FDS]_cons)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>21.06±0.03</td>
<td>1.98±0.01</td>
<td>21.1±0.03</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>31.03±0.05</td>
<td>2.6±0.1</td>
<td>32.37±0.03</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>40.13±0.04</td>
<td>4.31±0.02</td>
<td>43.23±0.06</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>49.38±0.05</td>
<td>6.86±0.02</td>
<td>49.57±0.08</td>
<td></td>
</tr>
</tbody>
</table>

Note: * Inhibition efficiency evaluated at 30s after injection of FDS by itself.

** Inhibition efficiency evaluated responding to injection of mixed solution of TU and FDS. [TU]_var denotes the concentration varying from 5 to 30 mg/L. [FDS]_cons denotes a constant concentration of 10 mg/L.

TU only and FDS only denote the addition of thiourea by itself and FDS by itself, respectively.

Generally, the evaluated inhibition efficiency is significant dependent on the concentration of thiourea or FDS. Thus the rate of copper dissolution is depressed by increasing the concentrations of the additives. The effect of FDS inhibition on the anodic dissolution rate is much less than that of thiourea and the mixed additives. The rank of inhibition effect is the mixed > thiourea > FDS. Theoretically, in the presence of thiourea and FDS, the evaluated inhibition efficiency should have been somewhat higher than that of thiourea by itself due to combined inhibition contributed by thiourea and FDS. However, the difference in the inhibition efficiency, corresponding to the injection of thiourea/FDS and thiourea by itself, is quite small.

To determine whether there is an interaction between thiourea and FDS when they are mixed, one series of tests, with simultaneous injection of thiourea and FDS separately, was carried out. The experimental conditions of the tests were similar to those in the previous
experiments. The thiourea concentration varied from 5 mg/L to 30 mg/L, while the concentration of FDS was 10 mg/L. At 250 seconds after the start of the potential step, the aqueous solutions of thiourea and FDS were injected separately into the electrochemical cell at the same time. The inhibition efficiency with respect to the addition of the separate solutions is given in Table 6-7.

Table 6-7. Dependence of the inhibition efficiency on the procedures of additives addition corresponding to the pure copper dissolution.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>[FDS] mg/L</th>
<th>Inhibition efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TU and FDS added separately</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>26.54±0.03</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>36.05±0.04</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>47.33±0.07</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>52.84±0.09</td>
</tr>
</tbody>
</table>

The data in Table 6-7 show that the inhibition efficiency with respect to the separate injection of thiourea and FDS is dependent on the concentration of thiourea and the values are higher than those for the injection of mixed solutions of thiourea and FDS. Two possible reasons could explain this observation. First there is an interaction between FDS and thiourea. When thiourea and FDS injected separately into the electrochemical cell most of thiourea and FDS could adsorb rapidly on the surface of copper electrode, and a small amount may participate in the interaction. However, when thiourea and FDS are mixed together and then injected into the electrochemical cell, some of them could interact before being added to the cell. Therefore, the adsorbed thiourea and FDS contents would be less than in the former case.

Secondly, when thiourea and FDS are injected separately into the electrochemical cell, both are mixed rapidly with the electrolyte solution. The possibility of interaction between them should be smaller than that in the mixed solutions. In the presence of FDS, the interaction of thiourea with cupric ions to form FDS should be hindered to a certain level. Thus, more thiourea should be adsorbed on the surface than when the mixed solutions of thiourea and FDS are injected into the cell.
6.2.2.5 Effect of sulfite on anodic dissolution of pure copper

The inhibition effects of thiourea and FDS on the anodic dissolution of the pure copper were further investigated by adding a mild reducing reactant. According to Eq. (6-2), FDS is one of products of the oxidation of thiourea. At an initial constant concentration of thiourea, an attempt was made to change the concentration of FDS so that the equilibrium between thiourea and FDS could be shifted. Consequently, the inhibition efficiency should be changed as a function of the change in the FDS concentration. Tests were carried out in solutions containing 0.1 M SO$_3^{2-}$ in the presence of either thiourea or FDS. The simultaneous addition of a mixed solution of thiourea and FDS was performed as well.

**Behavior of thiourea/FDS in the solutions containing SO$_3^{2-}$ and SO$_3^{2-}$ free**

It is well known that SO$_3^{2-}$ is a strong reductant. When SO$_3^{2-}$ is added to a typical electrolyte containing 42g/L Cu$^{2+}$, 160g/L H$_2$SO$_4$, there are two dominant reactions:

$$2\text{Cu}^{2+} + \text{SO}_3^{2-} + \text{H}_2\text{O} = 2\text{Cu}^{+} + \text{SO}_4^{2-} + 2\text{H}^+$$  \hspace{1cm} (6-4)

$$2\text{H}^+ + \text{SO}_3^{2-} = \text{SO}_2 \uparrow + \text{H}_2\text{O}$$  \hspace{1cm} (6-5)

If FDS is added to the system at the same time, the following reaction may take place

$$(\text{HN} =) \text{H}_2\text{NCSSCNH}_3^{+} (= \text{NH}) + \text{SO}_3^{2-} + \text{H}_2\text{O} = 2(\text{H}_2\text{N})_2\text{CS} + \text{SO}_4^{2-} + 2\text{H}^+$$  \hspace{1cm} (6-6)

Suppose the above reactions occur simultaneously and the rates of SO$_3^{2-}$ consumption are equal in the reactions of Eq. (6-4), Eq. (6-5), and Eq. (6-6). Then, according to the reaction of Eq. (6-6), the generated TU can reach concentrations from $[\text{TU}] = (5/150.22 \times 76.12) = 2.5\text{mg/L}$ to $[\text{TU}] = (20/150.22 \times 76.12) = 10.1\text{mg/L}$ when the initial concentrations of FDS are 5mg/L and 20mg/L. If most of the newly generated thiourea could block the surface of copper, the inhibition efficiency will increase significantly.

To confirm the above assumption, potential step tests with the injection of FDS from 5 mg/L to 20 mg/L were conducted at a potential jump from the open potential ($E_{\text{op}}$) to 0.34 V$_{\text{SHE}}$ in the solution containing 42g/L Cu$^{2+}$, 160g/L H$_2$SO$_4$, and 12.6g/L Na$_2$SO$_3$ (equal to 0.1M SO$_3^{2-}$). The dependence of the inhibition efficiency on the concentration of FDS in the presence of
SO$_3^{2-}$ is given in Table 6-8. The data corresponding to the absence of SO$_3^{2-}$ are listed in the table as well.

Table 6-8. Inhibition efficiency vs. varying the concentration of FDS in the absence and presence of SO$_3^{2-}$.

<table>
<thead>
<tr>
<th>[FDS] mg/L</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ %</td>
<td>1.37±0.01</td>
<td>1.57±0.01</td>
<td>1.71±0.01</td>
<td>1.94±0.01</td>
</tr>
<tr>
<td>0.1M SO$_3^{2-}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>θ %</td>
<td>1.98±0.01</td>
<td>2.60±0.01</td>
<td>4.31±0.01</td>
<td>6.86±0.01</td>
</tr>
<tr>
<td>SO$_3^{2-}$ free</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data in Table 6-8 show that the inhibition efficiency corresponding to the addition of SO$_3^{2-}$ is smaller than that in the absence of SO$_3^{2-}$, which is in contrast to the assumption. The reason may be due to the inert behavior of FDS in reacting with SO$_3^{2-}$ or to a low reaction rate in Eq. 6-6. Furthermore, it is possible that the partial FDS complexes with cuprous ion lead to a decrease in the concentration of FDS with less FDS adsorbing on the surface of copper.

It should be pointed out that cuprous ion concentration could be changed based on the reactions Eq. (6-4, 6-5, and 6-6) when SO$_3^{2-}$ is added to the typical electrolyte solution. Theoretically, by adding 0.1M of SO$_3^{2-}$ to the solution, the concentration of cuprous ion could reach a maximum value of (0.1/3*2*63.55) = 4.237 g/L, which is as 13 times as that in the equilibrium condition at 65 °C [14]. This value is not real because the real value would depend on the reaction kinetics and equilibria of the species interactions. Nevertheless, the generation of cuprous ions cannot be ignored. When FDS or thiourea is present in the solution containing SO$_3^{2-}$, the complexation between the cuprous ion with FDS could lead to the decrease in the concentration of FDS or thiourea and cause a decrease in the inhibition efficiency directly.

In order to confirm the preceding prediction, a series of experiments with injection of thiourea from 4 mg/L to 30 mg/L was conducted. The potential step was controlled from $E_{op}$ to 0.34 V$_{SHE}$. The test solution contained 42g/L Cu$^{2+}$, 160g/L H$_2$SO$_4$ and 12.6g/L Na$_2$SO$_3$ (equal to 0.1M SO$_3^{2-}$). The dependence of the inhibition efficiency on the concentration of thiourea in the presence of SO$_3^{2-}$ is given in Table 6-9. The data corresponding to the absence of SO$_3^{2-}$ are listed in the table as well. It is clear that the inhibition efficiency corresponding to the absence of SO$_3^{2-}$
is much higher than that in the presence of $SO_3^{2-}$. This confirms that the above prediction is reasonable.

Table 6-9. Inhibition efficiency vs. varying the concentration of thiourea in the absence and presence of $SO_3^{2-}$.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>4</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta %$</td>
<td>$0.1M SO_3^{2-}$</td>
<td>$18.15\pm0.02$</td>
<td>$30.85\pm0.02$</td>
<td>$44.55\pm0.07$</td>
</tr>
<tr>
<td>$\theta %$</td>
<td>$SO_3^{2-}$ free</td>
<td>$28.22\pm0.03$</td>
<td>$37.17\pm0.04$</td>
<td>$48.26\pm0.04$</td>
</tr>
</tbody>
</table>

It is clear that the inhibiting efficiency of FDS is far smaller than that of thiourea comparing the data in Tables 6-8 and 6-1. Therefore, the effect of $SO_3^{2-}$ can be ignored in any further investigation.

**Sensitivity of combination measurement with the potential step and the RDE**

In the preceding experiments, the thiourea concentration in solution ranged from 5 mg/L to 30 mg/L, which values are higher than those employed in the industrial operation (maximum 5 mg/L). Even though the preceding results have demonstrated that the experimental method has high a sensitivity with respect to the addition of thiourea in the test solutions, this method has not been tested to determine the effect of thiourea at a low concentration level on the rate of copper dissolution.

A series of anodic dissolution measurements, with varying thiourea concentrations in the range 0.5 to 4 mg/L, was conducted in a solution containing 42g/L Cu$^{2+}$, 160g/L $H_2SO_4$ at 65 °C. The instrument and dissolution control conditions were same as the described previously. The results are shown in Figure 6-8. The observations show a similar trend of thiourea inhibition on the rate of anodic dissolution to that in the presence of higher thiourea concentrations. The higher the concentration of thiourea the lower the rate of anodic dissolution of copper.

Based on Figure 6-8, the inhibition efficiency corresponding to different thiourea concentrations was evaluated with the data being reported in Table 6-10. At 0.5 mg/L thiourea the evaluated inhibition efficiency was 1.2 %. This effect could not be determined using cyclic
voltammetry. In addition, comparing the inhibition efficiency at 4 mg/L and 0.5 mg/L thiourea, the ratio of the inhibition efficiency is $16.73/1.23 = 13.6$. Even the former’s concentration is 8 times higher than the latter, but the former’s inhibition efficiency is over eight times the latter’s. This indicates that thiourea plays a very important role in the anodic dissolution of copper.

![Plot of anodic current density vs. time with respect to thiourea injection for the pure copper dissolution.](image)

Figure 6-8. Plots of anodic current density vs. time with respect to thiourea injection for the pure copper dissolution.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>1.23±0.01</td>
<td>6.43±0.01</td>
<td>9.49±0.01</td>
<td>12.74±0.02</td>
<td>16.73±0.02</td>
</tr>
</tbody>
</table>

Table 6-10. Calculated inhibition efficiency vs. varying low concentration of thiourea corresponding to the active dissolution of the pure copper electrode.

6.2.2.6 Electrochemical behavior of impure copper anode in the anodic dissolution processes

Like the preceding measurements of the electrochemical behavior of the RDE of pure copper, the behavior of impure copper was investigated using the potential step combined with the rotating disk electrode. A series of tests was conducted with a RDE of the impure copper
employed as a working electrode in the electrolysis system. During the tests thiourea was injected into the electrochemical cell and the resulting anodic current before and after the injection of thiourea was recorded. The combined effect of thiourea and FDS on the dissolution of impure copper RDE was also investigated by using same methods as were employed for the pure copper RDE.

**Potential step tests at the potential of active dissolution of impure copper anode**

Potential step tests were conducted in typical electrolyte solutions. After being kept at open circuit potential for 5 minutes, RDE of impure copper anode was stepped from $E_{op}$ to 0.34 $V_{SHE}$. After a period of 250 seconds thiourea, FDS, or mixed solution of thiourea and FDS were injected into the electrochemical cell. The resulting anodic currents were recorded and extracted for calculating the inhibition efficiency. Considering the generation of anode slimes during the impure copper dissolution, the rotation speed was lowered down to 400 rpm to avoid slime separating off from the electrode surface.

**Effect of addition of thiourea on the dissolution rate of the impure copper**

Preliminary tests, with injection of thiourea at concentrations from 5 mg/L to 30mg/L, were conducted in a solution containing 42 g/L Cu$^{2+}$ and 160 g/L H$_2$SO$_4$ at potential jump from rest potential to 0.34 $V_{SHE}$. Plots of anodic potential vs. time are shown in Figure 6-9.

![Figure 6-9. Plots of anodic current density vs. time at varying concentrations of thiourea for impure copper dissolution.](image-url)
Unlike the pure copper electrode, the initial anodic current of the impure copper electrode decreases markedly following the injection of thiourea, taking 80 to 100 seconds to reach a constant value. The duration between the initial current decreasing and constant current occurring is specially defined as a pre-inhibition time. Since anode slime is generated simultaneously during the dissolution of the impure copper electrode, it takes time for the thiourea to pass through the anode slimes layer. This diffusion causes the pre-inhibition time for the impure copper anode to be longer than that for the pure copper.

Dependence of inhibition efficiency on the concentration of thiourea is shown in Table 6-11. It is clear that the inhibition efficiency is proportion to the concentration of thiourea.

Table 6-11. Inhibition efficiency vs. varying concentration of thiourea in response to active dissolution of the impure copper.

<table>
<thead>
<tr>
<th>[TU] g/L</th>
<th>5</th>
<th>10</th>
<th>21</th>
<th>42</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ %</td>
<td>22.62±0.03</td>
<td>35.11±0.04</td>
<td>43.25±0.05</td>
<td>52.18±0.07</td>
</tr>
</tbody>
</table>

**Relationship between inhibition efficiency and concentration of cupric ions in the presence of a certain amount of thiourea**

The dissolution behavior of the impure copper, with varying cupric concentrations from 5 g/L to 42 g/L, was studied in a solution containing 160 g/L H₂SO₄ with injection of 20 mg/L thiourea. The dependence of the inhibition efficiency on the concentration of cupric ion in the presence of a certain amount of thiourea is listed in Table 6-12.

Table 6-12. Inhibition efficiency vs. varying the concentration of cupric ions in response to the active dissolution of the impure copper RDE in the presence of 20 mg/L thiourea.

<table>
<thead>
<tr>
<th>[Cu²⁺] g/L</th>
<th>5</th>
<th>10</th>
<th>21</th>
<th>42</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ %</td>
<td>46.34±0.06</td>
<td>44.13±0.04</td>
<td>43.45±0.05</td>
<td>43.25±0.03</td>
</tr>
</tbody>
</table>

The data of Table 6-12 show that the coverage efficiency decreases slightly with the increase in the concentration of the cupric ion, which is consistent with the results with respect to the pure copper.
copper. It provides further confirmation that cupric ions interact with thiourea, the interaction causing the concentration of thiourea to decrease leading to inhibition efficiency depression.

Comparing the values of inhibition efficiency in Table 6-1 with those in Table 6-11, the values in Table 6-1 are slightly smaller than those in Table 6-11. The difference may result from the different surface states of the pure and impure copper electrodes. When both electrodes experienced anodic active dissolution, the surface of the pure copper electrode was clean with no surface film. However, on the surface of the impure copper electrode anode slimes were generated continuously. With slimes growth, these slimes could cover some parts of the surface area of the impure copper. When thiourea is present, thiourea adsorbs on the surface of the impure copper. Thus the generated slime and thiourea adsorption serve to block the more active sites on the impure copper surface. Thus, the calculated inhibition efficiency should be higher in the case of the impure copper electrode.

**Behavior of impure copper with the addition of thiourea and FDS**

Two sets of tests were conducted to investigate the influence of both thiourea and FDS on the dissolution of the impure copper RDE. Potential step and RDE were employed for these tests. Injection of a mixed solution of thiourea and FDS comprised one set of tests, and the simultaneous injection of solutions of thiourea and FDS separately comprised the other. The dependence of inhibition efficiency on the method of addition of thiourea and FDS is shown in Table 6-13.

Table 6-13. Dependence of the inhibition efficiency on the addition of separate and mixed solution of thiourea and FDS.

<table>
<thead>
<tr>
<th>[TU]</th>
<th>[FDS]</th>
<th>$\theta_{[TU/FDS]_{sep}}$</th>
<th>$\theta_{[TU/FDS]_{mix}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L</td>
<td>mg/l</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>11.06±0.01</td>
<td>4.16±0.01</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>24.92±0.03</td>
<td>12.68±0.02</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>36.18±0.05</td>
<td>32.13±0.04</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>48.11±0.07</td>
<td>45.68±0.06</td>
</tr>
</tbody>
</table>
Inhibition efficiency in Table 6-13 shows a trend similar to that for the pure copper. The inhibition efficiency with respect to the injection of thiourea and FDS separately is dependent on the concentration of thiourea, with the values of inhibition efficiency being higher in the separate addition than in the addition of mixed solutions of thiourea and FDS.

The sensitivity of the combination measurement for the dissolution of the impure copper with the injection of thiourea has been tested. A series of anodic dissolution measurements, with varying thiourea concentrations from 0.5 to 4 mg/L, was conducted in a solution containing 42 g/L Cu^{2+}, 160 g/L H_{2}SO_{4} at 65 °C. The instrument and dissolution control conditions were the same as in the previous sections. A similar trend of thiourea inhibition on the rate of impure copper dissolution was noted in the presence of higher thiourea concentrations. The higher the concentration of thiourea the lower the rate of anodic copper dissolution.

Figure 6-10. Plots of anodic current density vs. time with respect to thiourea injection for the impure copper dissolution.

Based on Figure 6-10, the inhibition efficiency corresponding to different thiourea concentrations was evaluated and listed in Table 6-14. The evaluated inhibition efficiency is proportional to the increase in the concentration of thiourea. For a solution contains 0.5 mg/L thiourea the inhibition efficiency was 0.67 %. The value is so low that its significance is questionable. Thus, the effect of thiourea at this level could be ignored. In addition, the inhibition efficiency with respect to 4 mg/L thiourea equals 17%, which is higher than the value measured by cyclic voltammetry (inhibition efficiency 8 % corresponding to 5 mg/L). This demonstrates
that the combination measurement has higher sensitivity for responding to the presence of thiourea than does cyclic voltammetry.

Table 6-14. Calculated inhibition efficiency vs. varying low concentration of thiourea corresponding to the active dissolution of the impure copper electrode.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ (%)</td>
<td>0.67±0.00</td>
<td>3.64±0.00</td>
<td>6.25±0.01</td>
<td>11.21±0.01</td>
<td>17.03±0.02</td>
</tr>
</tbody>
</table>

Summary

Sensitivity to the effect of thiourea on copper dissolution is improved significantly by using a combination of the potential step and RDE. A strong inhibition of thiourea on the rate of active copper dissolution was observed. There is evidence that thiourea experiences several processes when it is present in concentrated copper sulfate-sulfuric acid solutions. These processes include adsorption on the surface of the working electrode, interaction of thiourea with cupric ions, of thiourea with formamidine disulfide, and protonation of thiourea. Experimental results indicate that these interactions have a positive effect in reducing the influence of thiourea on the rate of anodic dissolution. These interactions result in a depression of the inhibition efficiency. The proposed mechanism for the inhibition of thiourea on the active dissolution of copper working electrodes involves the adsorption of thiourea on the surface of the copper electrodes. This adsorption of thiourea leads to a reduction in the rate of copper dissolution. In addition, the interactions of thiourea with cupric ions, protons, and formamidine disulfide result in a certain reduction in the inhibition efficiency.

6.3 Behavior of Thiourea on Cathodic Deposition Process

The inhibition of thiourea on the dissolution of the copper anode has been investigated systematically in the preceding experiments. One might ask whether a similar influence exists during copper deposition on the cathode. The characterization of metal deposition processes has been studied extensively in current years[15,16,17,18]. One of the main concerns among the investigators is the determination of the additive concentration in the electrolyte[19]. Some
researchers believed that to obtain a good copper morphology, a polarizing effect in the adsorption of additives is necessary. This has been related to an increase in the rate of nucleation that occurs when the exchange current decreases and the overpotential increases[20,21,22,23]. There is considerable literature on the effect of additives on the morphology of electrodeposited copper[20,24,25,26,]. It is believed that the deposition kinetic parameters are strongly affected by small quantities of additives[23,27].

Using cyclic voltammetry, Wang et al.[20] demonstrated that as the concentration of thiourea increased the cathodic potential became more negative. At a cathodic potential < - 0.2 V (vs. open potential), a current plateau occurred which was independent of cathodic potentials. The formation of the current plateau was attributed to the adsorption of thiourea-copper ion complexes.

Souto[28] studied the inhibition effect of thiourea on the reduction of Cd(II) ions at the mercury electrode in a 1 M KF solution and gave an interpretation in which thiourea is adsorbed on the surface and disturbed the transfer of electrons across the double layer.

Afifi et al.[3] showed the relationship between the cathodic current efficiency and thiourea concentration in electrolyte solutions, and pointed out that there was a large decrease in cathodic current efficiency when the thiourea concentration was as low as 5 mg/L. At higher concentrations, thiourea increased the current efficiency.

Krzewska et al.[29] demonstrated that at temperatures < 40 °C, thiourea has a catalytic effect on the rate of copper deposition when its concentration varied from 0.5 to 2 mg/L, and when its concentration was over 2 mg/L thiourea significantly inhibited the rate of copper deposition. However, over 40 °C these effects became insignificant in comparison to the measurement error.

Winand et al.[19] found that at low thiourea concentrations (< 1 mg/L) the cathodic current density is proportional to the increase in thiourea content, and the current density varied inversely with thiourea concentration when it is over 2 mg/L.

Although the behavior of thiourea adsorbing on the copper cathode has been investigated extensively, the published experimental results are so complicated leading to many conflicting explanations about the thiourea adsorption behavior according to the literature review. Obviously, correct interpretation of the thiourea adsorption on the deposition of copper is essential in understanding the adsorption behavior of thiourea during the dissolution of copper.
The experiments in this section were designed to determine the characteristics of thiourea adsorption and interpret the adsorption by referring to changes in kinetic parameters related to the mass transfer and diffusion in the double layer.

6.3.1 Experimental technique

Cyclic voltammetry experiments were conducted using the same equipment and setup as in previous tests. The working electrode (stationary or rotating disk electrode) served as a cathode. A platinum gauze was employed as the anode (counter electrode). A Hg/Hg₂SO₄ (saturated K₂SO₄) served as the reference electrode. The M273A Potentiostat/Galvanostat combined with the cyclic voltammetry program was used to control the deposition and dissolution of copper.

The voltammetric measurements were carried out in a solution containing 42 g/L Cu²⁺ and 160 g/L H₂SO₄ at 65 °C. The potential sweep was driven in a cathodic direction from open potential to a pre-selected maximum potential then reversing to the starting potential. Various sweep rates were tested but 0.5 mV/s gave the most consistent results. Initial experimentation involved establishing reference curves for copper deposition in the absence of thiourea and then for various concentrations of thiourea. The sweep cycle was repeated several times until a reproducible curve was observed. Thus, the cathodic current was recorded and could be used for data interpretation.

It should be pointed out that in many publications on the cathodic process of copper deposition researchers have seldom mentioned the stability of thiourea in highly concentrated copper sulfate-sulfuric acid solution at elevated temperature. In order to eliminate the change in the concentration of thiourea during the experiments, a rotating disk electrode of pure copper in conjunction with the potential step combined with thiourea injection was employed in this investigation.

The rotating disk electrode of the pure copper was employed as working electrodes on which copper deposition takes place. The instrument setup was similar to that in Section 6.2. Before starting a test, the cell was kept at open circuit potential for 5 minutes. Then, a potential step with magnitude ΔE was applied to the RDE of copper. During the test the rotation speed was kept constant and the resulting current recorded as a function of time.

The M273A Potentiostat/Galvanostat combined with the chronoamperometry program was used to control the deposition. With respect to the copper deposition of the pure RDE at a fixed
thiourea concentration, three to five replications were conducted to ensure that accurate and dependable values were generated.

6.3.2 Results and discussion

Cyclic voltammetric measurements

Two distinctive cyclic voltammetric measurements were carried out in order to identify the effect of thiourea on the copper deposition process. The results are shown in Figure 6-11. It is clear that without thiourea the cathodic current density is linearly dependent on the cathodic potential. However, in the presence of 20 mg/L thiourea, there is a current plateau occurrence in the middle part of swept cathodic potential resembling a limiting current or cathodic passivation. On the forward cathodic sweep direction of the curve, the plateau is essentially eliminated and the current density begins to be dependent on the potential. The value of the plateau current density is approximately 41.2 mA/cm² over the potential range of 0.02 to 0.15 V$_{\text{SHE}}$. This indicates that thiourea inhibits the rate of copper deposition.

A series of cyclic voltammetric measurements, with varying concentration of thiourea from 5 to 30 mg/L at 65 °C, was conducted in an attempt to understand the behavior of thiourea in the process of copper deposition. The results, shown in Figure 6-12, demonstrate a strong inhibiting action of thiourea on the rate of copper deposition as the thiourea concentration increases. It is interesting that the cathodic current density becomes independent of cathodic potential when the concentration of thiourea is raised.

![Figure 6-11. Voltammograms of cathodic deposition of copper in the absence and presence of thiourea of 20 mg/L at 65 °C, solution containing 40 g/L Cu$^{+2}$, 160 g/L H$_2$SO$_4$.](image-url)
Figure 6-12. Plots of cathodic current density vs. potential corresponding to the cathodic deposition of copper in varying thiourea concentrations from 5 to 30 mg/L.

Since the procedure of thiourea addition in the copper deposition experiments was conducted before starting each test, obviously, the cyclic voltammetry could not eliminate the problem which was caused by thiourea consumption before starting the experimental measurements. Thus, the combination of potential step measurement and RDE was employed to investigate the behavior of copper deposition in the presence of thiourea.

Experiments of the potential step combined RDE were conducted using the same solution concentration and temperature as were employed in the voltammetry experiments. Prior to the potential step measurements, the cyclic sweep voltammetry was repeated 3 times until a steady state curve was obtained. Then the system was switched to potential step measurement, and the RDE was stepped from $E_{op}$ (0.275 V$_{SHE}$) down to a cathodic potential of -0.57 V$_{mse}$ (0.07 V$_{SHE}$). This potential was chosen because plateaus of cathodic current always appeared in the potential region during the running of the cyclic voltammetric experiments. After a period of 250 seconds, a known volume of thiourea was injected into the cell. The resulting current vs. time behavior, before and after injecting thiourea, was recorded and employed to calculate the inhibition efficiency corresponding to various concentrations of thiourea.

Figure 6-13 shows a typical diagram for the potential step test. During this test thiourea was injected into the electrochemical cell after 900 seconds. The initial cathodic current decreases
sharply following thiourea injection. Before injecting thiourea, the initial current density increased linearly with time. At the moment of the injection, the initial current decreased rapidly to a certain level then became constant. There are two possible explanations for this observation. First the initial current drop may result from thiourea participating in the copper deposition process. Secondly, physical disturbance of the thiourea injection may cause the change in value of the initial current, even though a small amount.

![Figure 6-13](image)

Figure 6-13. Potential step measurement corresponding to injecting thiourea of 20 mg/L for copper deposition.

An experiment was carried out to identify the physically disturbing effect of injecting the solution on the initial current under identical potentiostatic conditions. Instead of injecting thiourea aqueous solution to the cell, the electrolyte solution with thiourea-free was injected to the cell. The resulting cathodic current density increased linearly as a function of time throughout the test. This result confirms that thiourea injection causes the rate of copper deposition to decrease with thiourea having an inhibiting effect on the process of copper deposition.

The behavior of copper deposition with varying thiourea concentrations of 5 to 30 mg/L, was studied using the potential step measurement under the identical potential jump as in the previous tests. The resulting cathodic current density before and after the injection of thiourea was recorded and the inhibition efficiency was calculated using the same method as in the previous sections corresponding to the anodic dissolution of copper. The results are given in
Table 6-15. The inhibition efficiency with respect to anodic dissolution in the presence of thiourea is shown in Table 6-15 as well.

Table 6-15. Comparison of inhibition efficiency corresponding to anodic and cathodic processes at varying concentration of thiourea.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>inhibition efficiency for anodic dissolution</td>
<td>21.06±0.03</td>
<td>31.03±0.05</td>
<td>40.13±0.04</td>
<td>49.38±0.05</td>
</tr>
<tr>
<td>inhibition efficiency for cathodic deposition</td>
<td>73.44±0.06</td>
<td>79.25±0.06</td>
<td>83.36±0.07</td>
<td>84.83±0.05</td>
</tr>
</tbody>
</table>

It is obvious that thiourea not only inhibits the anodic dissolution process but also inhibits the cathodic deposition process. The inhibition of cathodic process could result from the adsorption of substances on the copper surface. These substances could be thiourea and products generated from thiourea interacting with copper ions. Since the copper deposition process involves a two-step reduction of copper ions, complexes of thiourea with cuprous ions could also influence the process of copper deposition. In addition, the occurrence of the plateau (Figure 6-12) and the current drop (Figure 6-13) demonstrate directly the inhibiting effect of thiourea on the rate of copper deposition.

According to Figure 6-12 the plateau of cathodic current density is independent of potential within the range 0 to 0.12 V_{SHE}. This could be considered as a limiting current density assuming that the concentration of the depositing cupric ions at the cathode electrode surface is negligible. Therefore, the reaction rate coefficient of cupric ions corresponding to the plateau can be estimated as follows:

$$i_{pt} = 2FkC_b$$  \hspace{1cm} (6-7)

where $i_{pt}$ is the current density of the plateau; $k$ the reaction rate coefficient; $C_b$ the bulk concentration of cupric ion; and $F$ Faraday constant. Thus, the estimated $k$ equals to $5.02 \times 10^{-3}$ cm/s when $i_{pt} = 0.0042$ A/cm², $C_b = 0.0043$ mol/dm³.

In addition, the reaction rate coefficient can be calculated knowing the well-defined hydrodynamics of the rotating disk electrode.
where $k_{cu^{2+}}$ is the reaction rate coefficient, $D_{cu^{2+}}$ the diffusion coefficient, and $\delta$ the thickness of the diffusion layer. $D_{cu^{2+}}$ values reported in literature are different, the average value of $1.1*10^{-5}$ was chosen for the calculation[30,31]. $\delta$ can be estimated from the following equation:

$$\delta = 1.61D_{Cu^{2+}}^{\frac{1}{3}}v^{\frac{1}{6}}\omega_{rde}^{-\frac{1}{2}}\quad(6-9)$$

where $\omega_{rde}$ is the angular velocity (167.47 rad/s), $D_{Cu^{2+}}$ diffusion coefficient of cupric ion ($1.1*10^{-5}$ cm$^2$/s), and $\nu$ kinematic viscosity of the electrolyte (0.00649 cm$^2$/s). Thus the calculated thickness equals to $1.2*10^{-3}$ cm. With the estimated value of $\delta$, a new reaction rate coefficient value $k_1$, equals to $9.21*10^{-3}$ cm/s. The value indicates that thiourea can cause a decrease of 45 % in the reaction rate coefficient. It is therefore not surprising that even low concentrations of thiourea can yield substantial changes in the morphology and growth of the cathode.

Wang et al.[20] and Szymaszek et al.[9] studied the copper deposition at low and high concentrations of thiourea and proposed the mechanisms of thiourea effect on the deposition (Figure 6-14 and 15). They pointed out that thiourea interacts with copper ions and forms the cuprous formamidime disulfide, Cu(FDS)$^+$, and thiourea complexes with cuprous ions, to form complexes Cu(TU)$^+$. At low concentrations of thiourea, Cu(FDS)$^+$ is considered to be more predominant than Cu(TU)$^+$. As the concentration of thiourea increases, Cu(TU)$^+$ should predominate.
Figure 6-14. Mechanism of deposition of copper with respect to low concentrations of thiourea[32].

Fig.6-14 shows that Cu(FDS)\(^+\) formed is apparently reduced to thiourea and copper relatively easily, allowing the thiourea produced to react chemically with cupric ions forming more FDS as:

\[
(Cu(H_2N \geq C - S - S - C \leq NH)) + e^- \Leftrightarrow Cu^0 + (H_2N \geq C - S - S - C \leq NH) \quad (6-10)
\]

\[
(H_2N \geq C - S - S - C \leq NH) + 2H^+ + 2e^- \Leftrightarrow 2(H_2N > C = S) \quad (6-11)
\]

\[
2Cu^{2+} + 2(H_2N > C = S) \Leftrightarrow 2Cu^+ + (H_2N \geq C - S - S - C \leq NH) + 2H^+ \quad (6-1)
\]

\[
2Cu^+ + 2(H_2N \geq C - S - S - C \leq NH) \Leftrightarrow 2(Cu(H_2N \geq C - S - S - C \leq NH))^+ \quad (6-12)
\]
Figure 6-15. Mechanism of deposition of copper with respect to a high concentration of thiourea[32].

According to the theories of Wang et al.[20] and Szymaszek et al.[9], the reactions of Eq. (6-1, 6-11, and 6-12) are more likely to happen at low concentrations of thiourea. Cu(FDS)$^+$ is the main complex present on the cathodic surface along with cupric ions. Cu$^+$ ions can be deposited easily compared to the deposition from Cu$^{2+}$ ions. This may be evidence for the catalytic effect associated with low concentrations of thiourea. By contrast at high concentrations of thiourea, more thiourea exists as Cu(TU)$^+$ or Cu(TU)$^{2+}$ from which it is more difficult to reduce cupric ions to copper. These complexes contribute mainly to the inhibition of the rate of copper deposition.

Obviously, the behavior of thiourea in the cathodic process is much more complicated than that at the anode. Not only cuprous and cupric ions discharge on the cathode, but also products of thiourea interact with other species. The behavior of copper deposition at low levels of thiourea was studied by using the combination measurement – potential step and RDE. Thiourea concentration varied from 0.5 to 4 mg/L. The results are shown in Figure 6-16. The observation demonstrates that at concentrations less than 1 mg/L, thiourea behaves as a catalytic reagent to accelerate the cathodic process. Thiourea above 1 mg/L inhibits the rate of cathodic deposition.
This is in fairly good agreement with the published literature among where it is widely written that low concentrations thiourea decrease cathodic polarization[1933,34] and higher concentrations hinder the rate of deposition.

![Figure 6-16. Plots of cathodic current density-time corresponding to copper deposition by injecting thiourea at concentrations varied from 0.5 to 4 mg/L.](image)

Calculated inhibition efficiency based on the data in Figure 6-16 is reported in Table 6-16. It is clear that the inhibition efficiency is dependent on the concentration of thiourea except for thiourea < 1 mg/L, and that the thiourea functions as an inhibitor to hinder the rate of copper deposition.

Table 6-16. Calculated inhibition efficiency vs. varying low concentrations of thiourea corresponding to copper deposition.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ %</td>
<td>22.03±0.02</td>
<td>46.16±0.05</td>
<td>54.01±0.05</td>
<td>64.05±0.06</td>
</tr>
</tbody>
</table>
6.4 Probable Mechanism of Inhibition of Thiourea on Copper Anodic Dissolution and Copper Deposition

Based on the observations in Figure 6-16, when thiourea (> 1 mg/L) is present in the concentrated copper sulfate-sulfuric acid solution, the cathodic current density decreases rapidly within about few seconds. If the complexes of thiourea with copper ions cause the current density to decrease, the reactions (Figure 6-15) should be fast enough to take place. In fact Wang et al.[20] and Szymaszek et al.[9] did not show evidence to confirm these reactions. On the other hand, if thiourea molecules adsorb directly on the cathode surface, they would rapidly block the active sites on the cathode surface and cause the cathodic current density to decrease. The observation in Figure 6-16 seems to confirm this prediction.

It is interesting that in Figure 6-16 the curve with respect to thiourea concentration of 0.5 mg/L is quite different from the other curves. Before the addition of thiourea, the trend of the curve is similar to that of the others. After the injection of thiourea, within a few seconds the cathodic current density decreases to certain of level then starts to increase as a function of time. It takes approximately 100 seconds to reach a constant level which is higher than the initial current level for a thiourea-free solution. It is believed that decrease of the cathodic current following thiourea injection is caused by the adsorption of thiourea on the surface of the cathode with the adsorbed thiourea blocking the active sites in the surface thereby depressing the rate of copper deposition.

Two possibilities could account for the increase of the cathodic current density with time. Firstly, supposing the formation rates Cu(FDS)$^+$ and Cu(TU)$^+$ or Cu(TU)$^{2+}$ are equal, then part of the added thiourea could be consumed due to formation of the above complexes. Since the discharge rates of these complexes are low and the dominant species of copper ions continually interact with thiourea, the thiourea content in solution decreases with time. Thus, some part of blocked surface should be unblocked due to thiourea consumption. This would result in an increase in the current density. In addition, the curves, corresponding to a higher level of thiourea concentration, show that after reaching the minimum value, the current density increases slightly as a function of time. This indicates that the thiourea inhibiting effect on the rate of copper deposition becomes smaller with time.

Secondly, the concentration of Cu(FDS)$^+$ could be higher than that of the other complexes of thiourea with copper. However, it is believed that the major part of Cu(FDS)$^+$ does not come
from Reaction 6-1, because the preceding section has shown no evidence supporting the reaction to generate Cu(FDS)$^+$ and protons. Nevertheless, reaction of Eq. (6-1) could not be the reaction which produces a larger amount of Cu(FDS)$^+$ due to highly concentrated sulfuric acid. However, the reaction of Eq. 6-2 could be a dominant reaction through which a certain amount of Cu(FDS)$^+$ could be generated. If the discharge possibility of Cu(FDS)$^+$ is higher than that of the complexes Cu(TU)$^+$ and Cu(TU)$^{2+}$. Cu(FDS)$^+$ could accelerate the rate of copper deposition.

Sykut[35] studied the catalytic effect of thiourea on the electrochemical reduction of Zn (II) ions at mercury electrode in various supporting electrolytes and explained the observed adsorption as the formation of a Hg-S-Zn(II) complex that caused acceleration of the electron transfer across the diffusion double layer. Sykut’s theory could be a possible explanation for the catalytic effect of thiourea on the rate of copper deposition. However, it is hard to explain why the catalytic effect disappears at high levels of thiourea concentration.

A small amount of thiourea (≥ 5 mg/L) was reported to be enough to block the active sites of the cathode surface. Ke et al.[36] determined the behavior of thiourea in copper deposition process by using radiotracer measurement of thiourea labeled with S$^{35}$. They demonstrated that thiourea is strongly and fairly uniformly adsorbed on the (111) faces of the copper crystal.

Comparing the values of inhibition efficiency with respect to anodic dissolution and cathodic deposition in the presence of thiourea, the inhibition efficiency for anodic dissolution is smaller than that for cathodic deposition. Since in the anodic dissolution process there is only one electrochemical reaction occurring – viz, the oxidation of metallic copper, when the reaction active sites are blocked mainly by thiourea adsorption, the dissolution rate could be significantly hindered. However, in the cathodic process, there are several electrochemical reactions taking place, in which Cu(TU)$^+$. Cu(TU)$^{2+}$ and Cu(FDS) are involved. These species need to diffuse to the surface of the cathode and the discharged on the active sites on the surface. Since their discharge rates are different, the species with a slow discharge rate have to occupy the active sites for a longer time than those with a fast discharge rate. This could cause the active sites to decrease after a certain period of time. Because thiourea is the other source for blocking the active sites on the surface, the inhibition efficiency on the cathode should be higher than that on the anode, when the thiourea concentration is the same in both processes.
6.5 References


Chapter 7 Behavior of Thiourea in the Anodic Dissolution of Copper – III

7.1 Introduction

The application of alternating currents has been a tool in electrochemistry for more than 100 years[1]. In the early 1900s, Warburg described diffusional mass transport as due to sine wave currents leading to the concept of the Warburg impedance. However, at this time it was not well understood that charge transfer processes contributed to the overall electrode impedance. In that period impedance measurements had been applied for many years to measure the differential double layer capacity at polarized electrodes. The work of Randles[2] which presents his equivalent circuit combining the elements of charge transfer, double layer capacitance, diffusion, and solution conductivity, is generally recognized as being the foundation of the well-known AC impedance method for the investigation of electrode processes. However, aside from the work of Grahame[3], the potentialities of AC impedance techniques for the study of electrode kinetics were not recognized until much later[4] and especially after the excellent review by Sluyters-Rehbach and Sluyters[5].

To date, the use of AC techniques has proven useful in the investigation of many electrochemical systems, including batteries[6], solid electrolytes[7,8,9], electroplating operations and corroding metals[10,11,12,13,14,15] The aim is generally to describe the properties of the system in terms of impedance parameters in an equivalent circuit, which can then be interpreted in terms of physico-chemical phenomena.

In addition to the works of Sluyters-Rehbach and Sluyters[5] there are a number of excellent reviews on applications and fundamental of AC impedance techniques[16,17,18,19]. Many of the topics covered in these reviews are beyond the scope of this discussion.

The electronic theory of sinusoidal currents and voltages is based on relatively simple laws. An alternating voltage can be expressed as:

\[ E = \Delta E \sin(\omega t) \]  
\( (7-1) \)
where \( E \) and \( \Delta E \) are the voltage and the magnitude of voltage perturbation, \( \omega \) an angular frequency and \( t \) is a time.

When the alternating voltage is applied to the following electrical circuit elements: resistor, capacitor, and inductor, a resultant current can be determined as in Ohm’s law \( (E = iR) \). For a resistance, \( R \), the current is given by

\[
\Delta i = \frac{\Delta E}{R} \sin(\omega t) \tag{7-2}
\]

for a capacitance, \( C \)

\[
\Delta i = \frac{\Delta E}{C} \sin(\omega t + \psi) \tag{7-3}
\]

for an inductance, \( L \)

\[
\Delta i = \frac{\Delta E}{\omega L} \sin(\omega t - \psi) \tag{7-4}
\]

For any combination of the above circuit elements, the relation between a sine wave voltage and current can be described by two quantities – the ratio of the amplitudes, \( \Delta E/\Delta i \) and a phase shift, \( \psi \), between current and voltage. An impedance, \( Z \), is defined as a vector of magnitude \( Z = \Delta E/\Delta i \) and a phase angle, \( \psi \). Alternatively, an impedance vector may be defined by specifying the magnitudes of its real, \( Z' \), and imaginary, \( Z'' \), components, as defined by equations:

\[
Z' = \Re(Z) = \frac{\Delta E}{\Delta i} \cos(\psi) \tag{7-5}
\]

\[
Z'' = \Im(Z) = \frac{\Delta E}{\Delta i} \sin(\psi) \tag{7-6}
\]

In complex notation

\[
Z = Z' + jZ'' \tag{7-7}
\]

Where \( j = \sqrt{-1} \)

The admittance, \( Y \), is defined as the inverse of the impedance:

\[
\frac{1}{Z} = Y = Y' + jY'' \tag{7-8}
\]
The goal of AC impedance is to measure the impedance $Z$ as $Z'$ and $Z''$ and then to use simple circuit analogues to model the response. If the amplitude of the voltage excitation is kept low, for example, < 10 mV, the measured response may often be assumed to be composed of a linear array of resistor, capacitors, and inductors. Then, the electrode response can, in principle, be modeled in terms of such an array. The most frequently used four basic circuit elements can be written as shown in Table 7-1.

Table 7-1. Symbols of AC impedance basic circuit elements and related math functions presentation

<table>
<thead>
<tr>
<th>Element</th>
<th>Math function</th>
<th>Impedance</th>
<th>Real Part</th>
<th>Image Part</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>$R$</td>
<td>$Z = R$</td>
<td>$Z' = R$</td>
<td>$Z'' = 0$</td>
<td></td>
</tr>
<tr>
<td>Capacitor</td>
<td>$C$</td>
<td>$Z = \sqrt{}(j\omega C)$</td>
<td>$Z' = 0$</td>
<td>$Z'' = \frac{1}{j\omega C}$</td>
<td></td>
</tr>
<tr>
<td>Inductor</td>
<td>$L$</td>
<td>$Z = j\omega L$</td>
<td>$Z' = 0$</td>
<td>$Z'' = j\omega L$</td>
<td></td>
</tr>
<tr>
<td>Constant Phase Element</td>
<td>CPE</td>
<td>$Z_{CPE} = \frac{1}{(T(j\omega P)}$</td>
<td></td>
<td></td>
<td>$\rightarrow$</td>
</tr>
</tbody>
</table>

where $\omega = 2\pi f$ (rad/sec), and $f$ is frequency in unit of Hz.

The presentation of complex impedance data can be classified in two ways: a Nyquist diagram (commonly called complex plane plot) and a Bode plot. The Nyquist diagram consists of a set of points, each representing the magnitude and direction of the impedance vector at a particular frequency. A typical example of a Nyquist diagram is shown in Figure 7-1. An alternative method of plotting the circuit in Figure 7-1 is by means of Bode plot. The Bode plot presents the relationships of logarithm impedance modulus, $Z$, vs. logarithm frequency, $f$, and phase angle, $\psi$, vs. logarithm frequency, which are show in Figures 7-2 and 7-3, respectively.
Figure 7-1. Nyquist diagram corresponding to a dummy cell. Inert shows the components of the dummy cell.

Figure 7-2. Bode plot of absolute magnitude of impedance vs. logarithm frequency for the dummy cell.
Information on circuit elements is easy to identify in the Nyquist diagram (Figure 7-1). An ideal semicircle depicts the circuit composed of a resistor in parallel with a capacitor. Two ideal semicircles standing one by one represents an entire parallel circuit in series with another entire parallel circuit. The Bode diagram (Figure 7-2 and 7-3) is a more straightforward display of the values of resistors and capacitors. As shown in Figure 7-1 certain circuit elements exhibit characteristics in the Bode plots (Figure 7-2 and 7-3). The impedance module at different frequency range symbolizes the different resistance. A capacitance, with respect to the smaller semicircle can be evaluated from the peak in the phase angle plot according to:

$$\omega_{\text{max}} = \frac{1}{C_1 R_2 \sqrt{1 + \frac{R_2^2}{R_1}}}$$  \hspace{1cm} (7-9)$$

There has been some argument in the literature as to the best method of displaying AC impedance data. In the present investigation, it is straightforward to display the data in all the above diagrams with commercial software. However, it was found that the AC impedance of the present electrochemical cell system did not demonstrate a simple equivalent circuit like that in Figure 7-1, since there was some impedance that could not be simplified as a pure resistor or capacitor. Thus, the Nyquist diagram was chosen as a key tool to display the AC impedance data in the present investigation.
Ideally, a planer electrode may be represented by the equivalent circuits shown in Figure 7-4. In fact during impure copper anode dissolution, especially in the presence of thiourea, the existence of surface adsorption, slimes layer formation, and surface roughness could complicate the frequency response. Figure 7-4 also shows the Nyquist diagrams for the idealized planer electrode systems, represented by the simple equivalent circuits in combining with algebraic manipulations. It must be noted that AC measurement response, with respect to the behavior of impure copper in presence of thiourea, is no longer so simple.

For the simple nature case – double layer charging and solution resistance (Figure 7-4 (a)), the impedance data in the related Nyquist diagram can be computed as:

\[ Z = Z_R + Z_C = R_s + \frac{1}{j\omega C_d} \]  

(7-10)

When double layer charging, charge transfer resistance, and solution resistance occur (Figure 7-4 (b)), the impedance data should be estimated as follows:

\[ Z = Z_R + Z_{parallel} = R_s + \frac{R_{ct}}{1 + j\omega R_{ct} C_d} = R_s + \frac{R_{ct}}{1 + \omega^2 R_{ct}^2 C_d^2} - \frac{j\omega C_d R_{ct}^2}{1 + \omega^2 R_{ct}^2 C_d^2} \]  

(7-11)

Re-arranging the above equation:

\[ Z = Z' + jZ'' \]  

(7-12)

where \( Z' = R_s + \frac{R_{ct}}{1 + \omega^2 R_{ct}^2 C_d^2} \)  

(7-13)

and \( Z'' = -\frac{\omega C_d R_{ct}^2}{1 + \omega^2 R_{ct}^2 C_d^2} \)  

(7-14)
Figure 7-4. Schematics of AC impedance of idealized planer electrode systems[20,21].
When Warburg impedance is present (Figure 7-4 (c)), the impedance can be described as follows:

\[ Z = Z_N + Z_{C,R} = R_s + \frac{R_d + Z_\omega}{1 + j\omega R_d C_d + j\omega Z_\omega C_d} \tag{7-15} \]

The Warburg impedance symbolized semi-infinite diffusion can be defined as follows[7,8,12]:

\[ Z_w = \sigma_w (j\omega)^{-0.5} \tag{7-16} \]

where \( \sigma_w \) is the Warburg coefficient.

The electrochemical system in this section employed either pure copper or impure copper anode electrode. Most tests presented in this section were conducted using electrochemical impedance spectroscopy (EIS). Some AC impedance measurements were conducted in the absence of thiourea during the anodic dissolution, others were carried out in the presence of thiourea.

According to the preceding investigations in DC measurement (Chapter 5 and 6), the impure copper working electrode was polarized to a potential far removed from the open circuit potential. The dissolution of impure copper in those tests, in the presence of thiourea at the polarized potential, involved Faradaic reaction, slimes layer formation, and thiourea adsorption stages.

When the anodic dissolution process of impure copper is studied by AC impedance measurements, the measurement system also involves these electrochemical steps. Faradaic reactions, anode slimes formation, mass transfer and diffusion, and these could take place on the surface of the electrode and anode slimes. Using the EIS to characterize these steps is very complicated. Although a few papers discussed the anodic dissolution of metals combining the formation of adherent surface films by using the EIS, numerous papers have been published interpreting the impedance spectra for the corrosion of metals coated with thin films[22,23,24,25,26,27]. The most important applications of the EIS in modern electrochemistry have been made in investigations of the reactions between a polymer coating and a corrosive environment and of the corrosion reactions at the metal/coating interface. The current study takes advantage of the technique and theories which have been used in the evaluation of corrosion protection by polymer coatings to characterize copper dissolution and anode slimes.
The object of AC impedance is to model the dissolution process in terms of circuit elements such as shown in Table 7-1, and from that model to be able to draw conclusions about the dissolution process in the absence and presence of thiourea.

In the present investigation it is essential to understand the effect of thiourea on the anodic dissolution process. It is possible to take advantage of AC impedance to study the simplified anodic dissolution process in the absence and presence of thiourea. One of the advantages of AC measurements is the use of smaller perturbations at a corroding interface. Measurements remain near the open circuit potential or corrosion potential, and the effects of Faradaic and slimes formation do not dominate the rate processes at these potentials. Thus, by eliminating the effects of Faradaic reaction and slimes formation, the anodic dissolution process can be simplified.

Another advantage of AC measurement is that the copper anodic dissolution process can be investigated over a wide range of frequencies by which the kinetic electron transfer rates may be determined at high frequency measurements, and the effects of mass transfer may be determined at low frequency.

In the absence of DC current, application of an AC voltage at low frequencies generates sinusoidal concentration gradients whose amplitudes decrease exponentially from the electrode surface towards the bulk electrolyte[28,29]. These concentration gradients cause a characteristic AC energy absorption. As the AC frequency is increased, ionic diffusion cannot keep up with the change in direction and so energy absorption disappears to be replaced by a phase angle characteristic of a capacitor that represents processes in the vicinity of the electrical double layer.

Significant efforts were made for combining chronopotentiometry and AC impedance measurements throughout which the effect of presence of thiourea on anodic dissolution of impure copper anode could be easily identified. Especially, the characterization of an “aged” anode slimes, generated by anodically dissolved impure copper anode in the absence and presence of thiourea for a period of time, would provide more detailed information on the behavior of thiourea in the anodic dissolution of impure copper.

7.2 Experimental Procedure

A three-electrode electrochemical cell was employed in the present investigation. These electrodes were a stationary copper anode (working electrode), a mercury-sulfate electrode
(reference), and a pure copper foil (counter electrode). The electrolyte contained 42g/L Cu²⁺, and 160g/L H₂SO₄. The temperature was controlled at 65 °C ± 0.2 °C.

The electrochemical instrumentation employed was a 1286 Solartron Electrochemical Interface (SEI) and 1250 Solartron Frequency Response Analyzer (FRA). The SEI controlled the potential on the stationary copper electrode referring to the reference electrode. The FRA generated a sinusoidal waveform in the frequency range between 0.01 mHz and 65.5 KHz. The SEI and FRA were connected to a personal computer in which a “ZPlot” software was installed. These three devices worked simultaneously, and during AC measurements the “ZPlot” program controlled the whole system. The AC impedance data were demonstrated and studied by means of “ZView” software.

Nitrogen was sparged to the solution from the bottom of the cell for 20 minutes before starting each test. Once a stationary copper electrode was immersed in the deaerated test solution, the electrochemical cell was kept at open potential for 8 minutes. During each test nitrogen was introduced into the space above the solution level to keep an inert atmosphere in the cell. The impedance spectra were recorded either at open potential (rest potential) or at a more positive anodic potential. The thiourea aqueous solution was added 5 minutes prior to the start of each test. Stirring was applied to ensure the mixing of the thiourea with the test solution.

### 7.3 Results and Discussion

#### 7.3.1 Determination of experimental parameters

AC impedance is strongly dependent on surface conditions and frequency scanning ranges. A series of preliminary tests was carried out to find the frequency range in which AC impedance could demonstrate the behavior of copper dissolution. The sensitivity of AC impedance, with respect to the thickness of the slimes layer, was examined. The stability of the slimes layer was determined throughout these tests as well.

**Frequency range**

The FRA generates a frequency range is between 0.0000628 rad/sec and 411340 rad/sec, which is a very wide range of frequency. In fact, the range used in the EIS measurements is
limited more by the electrochemical aspects of the system than by instrumentation. Measurements at very low frequencies take a long time, during which the interface of solid/solution or slime layers can change dramatically. If a measurement is taken at 0.0000628 rad/sec, the time frame is greater than one day, and the changes in the interface or slime layers during the measurement at the frequency could make the result meaningless. At high frequency, the changes in capacitance and inductance combine with nonuniformity of current distribution at the electrode surface, to make the results unreliable.

The preliminary EIS tests focused on scanning a sufficiently wide range of frequencies (from 408200 to 0.00628 rad/sec) at variable potentials (from the open potential to 0.64 V_{SHE}). The impedance spectra, corresponding to a pure copper working electrode at frequencies > 237380 or < 0.0628 rad/sec, showed very complicated phenomena, which are far beyond the explanation by the current theory of the EIS. For an impure copper working electrode, the impedance spectra at >31400 or < 0.0628 rad/sec were also much complicated. Therefore, the frequency ranges of 0.0628 rad/sec to 237380 rad/sec and 0.0628 rad/sec to 31400 rad/sec were chosen for measuring the pure copper and impure copper working electrodes respectively. The potential biases were controlled at a certain of point in a potential range from the open potential to 0.34 V_{SHE}.

**Characteristic of impedance with respect to different aged copper electrodes**

The investigation was designed to generate a certain amount of slimes adhering to the surface of an impure copper electrode. The impure copper electrode, with adhered slimes generated by means of the chronopotentiometric method, was defined as an aged copper electrode. The EIS was employed to characterize quantitatively the physical and electrochemical properties of the whole system. Generating slimes under different polarization conditions may impact the quantities and properties of anode slimes. When considering the possibility of excessive time consumption and electrode material consumption in the present investigation, two different methods were adopted to conduct AC impedance measurements. The two methods involved passing either a low or high anodic current density for a certain period of time.

Experiments at either 800 A/m^2 or 1910 A/m^2 were performed by controlling a constant current density to dissolve an impure copper stationary electrode. After reaching the pre-selected time, the dissolution under the DC current control was ended. Immediately the AC impedance measurement was carried out. The duration for switching the measurement programs from the
DC current control to the AC control was approximately 10 seconds. Typical Nyquist diagrams with respect to the two current densities are shown in Figure 7-5.

![Figure 7-5](image)

Figure 7-5. Effect of aged electrode with different applied anodic current densities on the impedance spectra within two hours.

AC impedance spectra of impure copper aged at low current density were significantly different than those obtained at high current density. The former shows one capacitance feature at high and intermediate frequencies, and followed by a diffusion impedance feature at low frequencies. Unlike the former, the latter show two capacitance features within the high and intermediate frequencies, and a diffusion impedance feature at low frequencies. Obviously, the AC impedance spectra corresponding to impure copper aged at high current density can provide more information than that aged at low current density. In addition, the previous chronopotentiometric experiments in Chapter 5 show a benefit in carrying out the experiments in a convenient time frame. Especially when thiourea is present in the test solution, the decomposition of thiourea can be limited within a certain low level by conducting a small time frame test. Therefore, investigations in the following sections were focused on a high current density of 1910 A/m².

**Stability of anode slimes**

During anodic dissolution of the impure copper electrode, slimes are generated. Since most tests in the present study focused on the EIS measurements for an aged copper anodes, the
stability of the generated slimes which adhere to the electrode surface is crucial for getting accurate and reproducible data using the AC impedance technique. Therefore, two sets of experiments were conducted. One was the dissolution of an impure copper RDE by controlling a constant current density followed by the dissolution with a constant potential control. The other was the dissolution by controlling a constant current density followed by a fixed frequency impedance measurement at DC biases of 0.3 and 0.34 V<sub>SHE</sub>. The results are displayed in Figures 7-6 to 7-8.

![Figure 7-6](image1.png)

**Figure 7-6.** Plot of voltage vs. time corresponding to the dissolution of commercial copper working electrode at 0.15A/cm<sup>2</sup> for 1800 sec.

![Figure 7-7](image2.png)

**Figure 7-7.** Anodic current vs. time with respect to constant potential dissolution of commercial copper RDE at 0.34 V<sub>SHE</sub>, and rotating speed of 200 rpm.
Figure 7-8. Relationship between absolute impedance and frequency corresponding to galvanostatic dissolution followed by EIS measurement at three different DC biases.

The values of recorded voltage and recorded anodic current density, in Figures 7-6 and 7-7, are quite stable. These values are virtually constant. No significant changes in magnitudes of voltage were observed in the test shown in Figure 7-7, even though the generated slime was surrounded by a strong electrohydrodynamic condition (a RDE combining a constant potential control). Figure 7-8 shows constant values of absolute impedance were obtained in AC impedance measurements corresponding to different anodic potentials. These observations indicate that under these test conditions, the generated slimes are quite stable and adherent to the working electrode.

7.3.2 AC impedance behavior of pure copper electrode

7.3.2.1 Impedance behavior of pure copper in the absence of thiourea

The dissolution behavior of pure copper, at anodic potentials varying from 0.275 V_{SHE} to 0.36 V_{SHE}, was studied by the EIS in the solution without thiourea. The AC signal applied between the reference and working electrode had a peak-to-peak amplitude of 1 mV. The amplitude of the perturbing AC signal at < 5 mV was found to have a negligible effect. The frequency range used was between 237380 rad/sec and 0.0628 rad/sec.
Figure 7-9 demonstrates the effect of anodic potential on the impedance of the pure copper electrode dissolved in the absence of thiourea. It is clear that when the electrode is polarized anodically (from 0.2835 to 0.3 V_{SHE}), both real and imaginary parts of the impedance become smaller. The impedance data cannot be described correctly by a simple equivalent circuit of types discussed previously, because all AC spectra appear as depressed semicircles instead of ideal semicircles (It is common that a semicircle be like these in Figure 7-9 is called a capacitive loop). The depression of the semicircle may result from three sources. First there is non-uniform current distribution caused by the geometry of the cell or by screening the part of the working electrode with the Luggin capillary. Secondly, the structure of copper electrode surface changes due to mass dissolving off or plating out. Thirdly, formation of adsorbed intermediates occurs.

For the pure copper electrode in the above case, it is likely that the roughness of surface results in the occurrence of the depressed semicircle. Before immersion in the cell, the pure copper electrode was polished down to 6 μm. At this moment surface sites were uniform. After AC impedance measurements, the surface was found to be rough and the sites became heterogeneous.

Theoretically, homogeneous dissolution of pure copper could be modeled by an equivalent circuit which contains solution resistance in series with a in parallel combination of double layer...
capacitance and polarization resistance. Since curves in Figure 7-9 demonstrate depressed semicircles, a distributed element, constant phase angle element (CPE), was introduced to model the obtained AC impedance data.

In publications it is common that a distributed element, constant phase angle element (CPE), has been used to model depressed semicircles[7]. In principle, the impedance expression of the CPE can be described by the following equation.

\[
Z_{CPE} = \frac{1}{T_{CPE}(j\omega)^{P_{CPE}}}
\]  

(7-17)

where \( T_{CPE} \) is the frequency independent parameter, \( j \) the imaginary number, \( \omega \) the frequency, \( P_{CPE} \) the fractional element in CPE circuit.

The CPE is defined by two values, \( T_{CPE} \) and \( P_{CPE} \). If \( P_{CPE} \) equals 1 then the equation is identical to that of a capacitor. If \( P_{CPE} \) equals 0.5, the equation is the so-called Warburg impedance[7,10,11]. When \( P_{CPE} \) equals -1, the equation is identical to an inductor.

An equivalent circuit with respect to the pure copper dissolution was proposed which was similar as that in Figure 7-4 (b). The CPE was introduced to the circuit to modify the double layer capacitor since the surface became rough during the dissolution of impure copper. The proposed equivalent circuit used to fit the obtained AC impedance data consisted of \( R_s \) (solution resistance) in the series with the parallel combination of CPE and \( R_p \) (Polarization resistance).

![Circuit Diagram](image)

Figure 7-10. Schematic diagram for the physical model of pure copper dissolution in the absence of thiourea.
At the high frequency range, the interception of the Nyquist diagram with the real axis is equal to the value of solution resistance. After subtracting the solution resistance the parameters of $T_{\text{CPE}}$, $P_{\text{CPE}}$, and $R_p$ corresponding to each set of the data in Figure 7-9, were evaluated using a non-linear least squares fit procedure. Estimated parameters from the curve fitting are shown in Table 7-2. The estimated data show that the increase in anodic potential caused an increase in $T_{\text{CPE}}$ and decrease in $R_p$. The exponent $P_{\text{CPE}}$ is in the range of 0 to 1, but it decreases with increase in the anodic potential.

Table 7-2. Estimated parameters corresponding to the pure copper dissolution in the absence of thiourea.

<table>
<thead>
<tr>
<th>Polarization potential $V_{\text{SHE}}$</th>
<th>$T_{\text{CPE}}$ $\Omega^{-1} \text{cm}^2 \text{s}^{0.6 \times 10^{-6}}$</th>
<th>$P_{\text{CPE}}$</th>
<th>$R_p$ $\Omega \text{ cm}^2$</th>
<th>Estimated $D_{\text{Cu}}^{2+}$ $\text{cm}^2 \text{s}^{0.5 \times 10^{-6}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.275</td>
<td>0.049±0.001</td>
<td>0.611±0.01</td>
<td>1.01±0.037</td>
<td>1.007</td>
</tr>
<tr>
<td>0.280</td>
<td>0.052±0.002</td>
<td>0.586±0.008</td>
<td>0.92±0.027</td>
<td>1.081</td>
</tr>
<tr>
<td>0.285</td>
<td>0.064±0.001</td>
<td>0.569±0.004</td>
<td>0.801±0.032</td>
<td>1.738</td>
</tr>
<tr>
<td>0.290</td>
<td>0.199±0.008</td>
<td>0.456±0.004</td>
<td>0.625±0.027</td>
<td>12.53</td>
</tr>
<tr>
<td>0.295</td>
<td>0.226±0.007</td>
<td>0.448±0.012</td>
<td>0.356±0.014</td>
<td>15.14</td>
</tr>
</tbody>
</table>

The diffusion coefficient of metal ion $M^{2+}$ was estimated according to the expression of the general infinite diffusion impedance suggested by MacDonald[30].

\[
Z_D = q(j\omega)^{-P_{\text{CPE}}} \tag{7-18}
\]

where $Z_D$ is the diffusion impedance and $q = 1/ T_{\text{CPE}}$, the general infinite diffusion coefficient.

When $P_{\text{CPE}} = 0.5$, the Warburg coefficient, $\sigma_w$, can be obtained from $q$ by the following:

\[
\sigma_w = \frac{RT}{(nF)^2} \frac{\delta}{C_M^{-1}, D_M^{-1}} \left( \frac{D_M^{2+}}{\delta^2} \right)^{0.5} = \frac{RT}{(nF)^2} \frac{1}{C_M^{0}, D_M^{0.5}} \tag{7-19}
\]

When $P_{\text{CPE}}$ is different than 0.5 the $q$ is given by the following equation:
\[ q = \frac{RT}{(nF)^2} \frac{\delta}{C_{M^{z+}}^0 D_{M^{z+}}} \left( \frac{D_{M^{z+}}}{\delta^2} \right)^\nu = \frac{RT}{(nF)^2} \frac{\delta^{1-2\nu}}{C_{M^{z+}}^0 D_{M^{z+}}^{1-\nu}} \]  

(7-20)

where \( C_{M^{z+}}^0 \) is bulk concentration of metal ion \( M^{z+} \) and \( D_{M^{z+}} \) the diffusion coefficient of the metal ion.

Since the value of the CPE exponent, \( \nu_{\text{CPE}} \), varies within the range of 0.4 to 0.6, the dissolution processes at different potentials are in diffusion control. The diffusion coefficient of cupric ion, \( D_{M^{z+}} \), was evaluated according to Eq. (7-19). The magnitude of the estimated diffusion coefficient is one order of magnitude difference. This probably resulted from two facts. First, the Nyquist diagram of the pure copper electrode failed to exhibit either a pure finite diffusion impedance or Warburg impedance, as required to apply the frequency transition method[31,32]. Secondly, the value of the diffusion layer thickness, which was used in the present calculation, was not the real one. Considering the geometry of the electrochemical cell and of the electrode, the thickness of this layer may be different in different places on the surface of the electrode. The thickness of the layer at the electrodes is usually set within the range 10^{-3} to 10^{-2} cm[33]. When conducting the calculation of the diffusion coefficient in Table 7-3, the thickness was chosen to be 10^{-2} cm. In the present investigation, the system is in a static state, the average thickness of the diffusion layer is probably higher than the value used in this section. The estimated data were found to be well fitted by the transfer function of the proposed equivalent circuit within the fitting error of 5%. Figure 7-11 is a typical curve fitting result compared with the experimental.

![Figure 7-11. Nyquist diagram for the simulation of impedance of pure copper at 0.275 V_{SHE}.](image)
An understanding of the effect of thiourea on the anodic dissolution process is essential in the present investigation. It is possible to take advantage of AC impedance to study a simplified anodic dissolution process in the absence and presence of thiourea. One of the advantages in AC measurements is the use of smaller perturbations at the corroding interface. Measurements remain near the open potential or corrosion potential, and the effects of Faradaic and slimes formation do not dominate the rate processes at these potentials. Thus, by eliminating the effects of Faradaic reaction and slimes formation, the anodic dissolution process can be simplified.

Theoretically, AC impedance studies in the presence of a net Faradaic current are analogous to the impedance studies in the absence of a net DC bias provided the electrochemical processes under investigation behave linearly. If conditions at the electrode/electrolyte interface change due to the presence of current, they will be reflected in the AC impedance spectrum. For example, nonlinearities in the response of the system can produce a net rectification current and a rectified voltage. The presence of these nonlinearities and their effects on the related electrochemical processes have been studied using Faradaic Rectification Techniques[34]. However, in the present investigation, the formation of anode slimes takes place in the dissolution process of impure copper in the presence of a net Faradaic current. On the other hand, in highly reversible systems where diffusion controls the dissolution process, AC studies in the presence of a DC current can provide a better insight as to the extent to which concentration gradients become established in the anode boundary layer. Also, information on the effects produced by the presence of addition agents can be derived from AC studies.

### 7.3.2.2 Impedance behavior of pure copper in the presence of thiourea

The dissolution behavior of the pure copper, at varying concentration of thiourea from 1 mg/L to 5 mg/L, was studied at the open potential. The resulting impedances are shown in Figure 7-12.

The observations in Figure 7-12 demonstrate the effect of thiourea on the impedance of the pure copper electrode dissolution. Obviously the real part impedance corresponding to the right-hand sides (low frequency) depends on the concentration of thiourea. When the thiourea concentration increases (from 1 mg/L to 5 mg/L), the impedance value decreases. For each AC spectrum, a linear part appears in the high frequency range followed by a depressed semicircle in
the low frequency range. In contrast, the AC spectra with respect to the thiourea-free condition do not show such characteristics.

Figure 7-12. The effect of thiourea on the impedance of pure copper dissolution.

Sluyters-Rehbach and Suyters[35] have given a comprehensive explanation about a finite diffusion-controlled electrochemical reaction at high frequencies. MacDonald[30] proposed a similar idea to illustrate the straight line which appeared at high frequencies. Based on their theories, the equivalent circuit with respect to the observation in Figure 7-12 is proposed, which is composed of a solution resistance in series with finite diffusion impedance and in series with a parallel combination of CPE and polarization resistance (Figure 7-13).

Figure 7-13. Schematic diagram for the physical model of pure copper dissolution in the presence of thiourea.

The finite diffusion impedance is defined by three parameters which are $R_w$, $T_w$, and $P_w$. It can be written as follows:
where \( R_w \) is a resistance, \( T_w \) the frequency independent parameter, and \( P_w \) the fractional element in the finite diffusion circuit.

Curve fitting is carried out by using the ZView software attached nonlinear least square program. The best fitted parameters are listed in Table 7-3.

Table 7-3. Best fitted parameters corresponding to the pure copper dissolution in the presence of thiourea.

<table>
<thead>
<tr>
<th>Thiourea conc., mg/L</th>
<th>( R_w ) ( \Omega \text{ cm}^2 )</th>
<th>( T_w ) ( \Omega^1 \text{ cm}^2 \cdot \Omega^1 \text{ cm}^2 \cdot \mu \times 10^6 )</th>
<th>( P_w ) ( \Omega^1 \text{ cm}^2 \cdot \Omega^1 \text{ cm}^2 \cdot \mu \times 10^6 )</th>
<th>( r_{\text{corr}} ) ( \Omega^1 \text{ cm}^2 \cdot \Omega^1 \text{ cm}^2 \cdot \mu \times 10^6 )</th>
<th>( P_{\text{corr}} ) ( \Omega^1 \text{ cm}^2 \cdot \Omega^1 \text{ cm}^2 \cdot \mu \times 10^6 )</th>
<th>( R_p ) ( \Omega \text{ cm}^2 )</th>
<th>Inhibition efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.765±0.002</td>
<td>0.761±0.024</td>
<td>0.354±0.011</td>
<td>0.737±0.004</td>
<td>0.571±0.03</td>
<td>1.056±0.056</td>
<td>4.33</td>
</tr>
<tr>
<td>2.0</td>
<td>0.865±0.001</td>
<td>0.785±0.015</td>
<td>0.457±0.039</td>
<td>0.613±0.005</td>
<td>0.685±0.018</td>
<td>1.174±0.078</td>
<td>13.95</td>
</tr>
<tr>
<td>3.0</td>
<td>0.879±0.001</td>
<td>0.801±0.023</td>
<td>0.447±0.021</td>
<td>0.585±0.003</td>
<td>0.789±0.011</td>
<td>1.834±0.093</td>
<td>44.94</td>
</tr>
<tr>
<td>5.0</td>
<td>0.926±0.009</td>
<td>0.827±0.037</td>
<td>0.453±0.043</td>
<td>0.508±0.005</td>
<td>0.824±0.009</td>
<td>4.631±0.141</td>
<td>78.19</td>
</tr>
</tbody>
</table>

According to Ohm's law, the dissolution rate – anodic current density can be expressed to be reciprocal to the charge transfer resistance. The low resistance means a high dissolution rate, vice versa, the high resistance indicates a low dissolution rate. In Table 7-3 the parameter of polarization resistance (or charge transfer resistance), \( R_p \), predicts a trend which exhibits a noticeable dependence on thiourea concentration. The higher the concentration of thiourea, the higher the resistance would be. These resistance values represent evidence supporting the conclusion that thiourea inhibits the rate of copper dissolution. The conclusion was drawn from the previous steady state and transient state electrochemical same measurements (seen Chapter 5 and Chapter 6).

Inhibition efficiency, which is the characteristic of thiourea inhibition in copper dissolution, is calculated using the value of polarization resistance according to the following equation:

\[
\text{Inhibition efficiency} = 1 - \frac{R_p^0}{R_p^{\mu}} \quad \text{(7-22)}
\]
where $R_p^0$ is the resistance obtained in the absence of thiourea (the value is 1.01 \(\Omega\)cm\(^2\) Table 7-2), and $R_p^{**}$ is the resistance obtained in the presence of thiourea.

The calculated values of surface coverage (Table 7-3), which show a consistent trend with increase in thiourea concentration, are higher than those obtained in the previous DC steady and transient state experiments. The main difference between the DC and AC experiments is the potential level. In DC measurements, the potential is controlled far from the rest potential. In contrast, the AC measurements were conducted at the rest potential. The data in Table 5-1 (Chapter 5) demonstrate that inhibition efficiency decreases with increases in the electrode potential. These AC impedance results above provide further confirmation about thiourea inhibition of the copper dissolution process.

![Figure 7-14. Nyquist diagram for the simulation of AC impedance for the pure copper in the absence of thiourea.](image)

### 7.3.3 AC impedance behavior of impure copper anode electrode

The previous experimental results show that the anodic slimes, copper sulfate, and copper oxide films can grow with time during impure copper dissolution (Section 5.2, Chapter 5). Compared with pure copper dissolution, these phenomena make it more difficult to detect the effect of thiourea on the dissolution since the formation of surface film is a function of time. In addition, AC impedance measurements should be conducted in a range of frequency (from high
to low) in which the frequency scanning at low level of frequency can take a longer time to be completed, but at high level the scanning takes a very short time. There is a possibility that at high frequency the surface film profile measured is not the same as that measured at low frequency, since the surface film would be expected to grow with time.

A specific procedure was used to eliminate the effect of surface film change on AC measurement of impure copper anodic dissolution. The chronopotentiometry mentioned in Chapter 5 was introduced to this section of the investigation. By anodic dissolution over a period of time at a pre-selected constant anodic current density, the impure copper electrode would generate amount of anodic slimes which covers the electrode surface. Within different time frames, the amount of the slimes will be different. Normally, the longer the dissolution time, the larger the amount of slimes that will be generated. Following the chronopotentiometric measurements, AC impedance measurements were subsequently conducted at the rest potential.

The previous chronopotentiometric measurements showed four regions from active to passivated dissolution (Section 5.2, Chapter 5). Termination of chronopotentiometry was chosen either in Region I, the active dissolution, or Region IV, full passivation dissolution. It is believed that during active dissolution the dissolution rate is stable and the slimes layer growth is stable. Region II, pre-onset passivation, was not chosen as the termination due to potential oscillations occurring. It is believed that the surface is significantly covered by the anode slimes, sulfate and oxide film in Region II. At this moment the dissolution and formation of the films of copper sulfate and copper oxide caused oscillation occurrence. Within Region III, the surface films are not in a stable state. In Region IV, the anode surface is completely covered with a non-conducting or weakly conducting film. This causes the anode to stop dissolving and the surface films stop growing. Thus, the surface films should be in a stable state.

7.3.3.1 Impedance behavior of impure copper anode in the absence of thiourea

The impure copper electrode was dissolved in a 42 g/L Cu$^{2+}$ and 160 g/L H$_2$SO$_4$ solution by using chronopotentiometry. Time frames were chosen based on terminating the impure copper electrode before entering the pre-onset passivation and after entering the full passivation regions. A constant anodic current was controlled at 1910 A/m$^2$. Under these conditions, a certain amount of anode slimes can be generated, and these slimes have characteristics with respect to active and passivation dissolution. Before carrying out AC measurements the impure copper electrode can
be described as the Cu$_0$/slimes (either active or passive) system. At the rest potential AC impedance measurements were then conducted. Table 7-4 provides DC and AC measurement conditions corresponding to the absence of thiourea.

Table 7-4. Summary of chronopotentiometry and AC impedance measurement conditions for impure copper dissolved in the electrolyte free of thiourea.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>Current density A/m$^2$</th>
<th>Passivation</th>
<th>Time sec.</th>
<th>Frequency range rad/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1910</td>
<td>No</td>
<td>4750</td>
<td>0.0628</td>
</tr>
<tr>
<td>0</td>
<td>1910</td>
<td>Yes</td>
<td>4860</td>
<td>0.0628</td>
</tr>
</tbody>
</table>

**AC impedance measurements carried out before passivation with electrolyte solution without thiourea**

For combination measurement the experimental setup and the procedure of chronopotentiometry were similar to that referred to in Section 5.2.1, Chapter 5. Three to five replications were conducted to ensure that accurate and dependable data were generated. For all tests the slimes layers showed good stability for AC impedance measurement, no slimes falling off the surface of the electrode. Chronopotentiograms and AC spectra were highly reproducible under the identical test conditions. Thiourea aqueous solution was not added to the electrochemical cell.

Figure 7-15 represents a typical Nyquist diagram for the impure copper electrode in the absence of thiourea. There are two depressed semicircles in the high and intermediate frequency regions. In addition one straight line was observed which was approximately in 45° in the low frequency range. The line could be contributed by a Warburg impedance.
Figure 7-15. A typical Nyquist diagram of impure copper electrode after aging for 79 minutes in the absence of thiourea.

Since the impure copper dissolution process involves formation of anode slimes, the generated anode slimes could be homogeneous in covering the anode surface or heterogeneous. Assuming slimes formation progresses homogeneously, the anode surface would be uniformly covered by the slimes. The physical microstructure of the anode and anode slimes under active dissolution of copper can be described by the diagram in Figure 7-16.
Figure 7-16. Physical microstructure of the anode and anode slimes corresponding to anodic active dissolution of commercial copper.

Most authors agree that the simple equivalent circuit in Figure 7-17 can be used for the analysis of impedance data for polymer coated metals exposed to corrosive media[36,37]. With existing coatings the equivalent circuit must simultaneously take account of the polarization resistance ($R_p$) and the pore resistance ($R_{po}$) of the surface film. A double layer capacitance ($C_d$) is in parallel with the polarization resistance. The coating capacitance ($C_{po}$) is in parallel with the pore resistance which reflects the protective properties of the coating.

However, the above equivalent circuit cannot demonstrate the straight line occurring in the low frequency range in Figure 7-15. It is necessary to add a Warburg impedance to the equivalent circuit. Furthermore, the double layer capacitor should be replaced by a general CPE to account for the depressed semicircle. The modified equivalent circuit is shown as follows:
Figure 7-17. Primary proposed equivalent circuit corresponding to the physical microstructure of the anode and anode slimes for the impure copper experiencing active dissolution.

Figure 7-18. Modified equivalent circuit with respect to the physical microstructure of the anode and anode slimes for the impure copper experiencing active dissolution.

Using the complex non-linear least squares fitting program, it was found that the equivalent circuit of Figure 7-18 could not be fitted well within an error < 10%. The reason may be that curve fitting in this case was limited in the frequency range 31400 to 0.068 rad/sec, which is smaller than that corresponding to polymer coatings (628000 to 0.00628 rad/sec). Armstrong et al.[38] proposed a method to interpret the AC impedance data of passivated metal. By developing a model of interface impedance in serials connected together, the impedance spectra
were fairly well fitted. Alkire et al. [39] used a similar model to investigate the effect of benzotriazole on the copper dissolution process, and obtained reproducible results. Based on the data in Figure 7-15, the impure copper electrode can be described as the system containing solution phase, copper-slimes layer interface, slimes layer, slimes layer-solution interface. Therefore, another equivalent circuit is proposed and depicted in Figure 7-19.

\[ \text{Figure 7-19. Proposed equivalent circuit with respect to the physical microstructure of the anode and anode slimes for the impure copper experiencing active dissolution.} \]

In the above circuit, the components are defined as:

- \( R_s \) – the solution resistance
- \( \text{CPE}_1 \) – the double layer capacitance associated with non-homogeneity due to formation of slimes layer which attaches to the electrode surface
- \( R_1 \) – polarization resistance
- \( \text{CPE}_2 \) – semi-infinite diffusion capacitance associated with ionic diffusion across the slime layers
- \( R_2 \) – diffusion resistance
- \( W \) – general finite diffusion impedance.

The best fitted values of these components for the equivalent circuit are shown in Table 7-4. The data show that the Warburg exponent is near \( 45^\circ \) which symbolizes Warburg diffusion of cupric ions. Further analysis of the calculated values will be discussed in the next section. By using the estimated values a simulation was carried out with the ZView simulation software program, and the simulated result is shown in Figure 7-20.
Figure 7-20. Nyquist diagram for the simulation of AC impedance of impure copper in active dissolution in the absence of thiourea.

**AC impedance measurements carried out after passivation – electrolyte solution containing no thiourea**

A typical Nyquist diagram of passivated impure copper is given in Figure 7-21. The impedance shows two overlapping capacitive features and a low-frequency inductive feature. Previous chronopotentiometric measurements showed that the recorded potential on the passivated impure copper is ten times greater than that corresponding to a non-passivated anode (Section 5.2, Chapter 5). Under this condition, a significant amount of copper sulfate could precipitate, and copper oxides could form. These phenomena lead to a denser slimes film on the surface of the impure copper. Therefore, the denser film should impact the copper ion diffusion, and the denser film could cause the diffusion control of copper ions at the pre-selected low frequencies to be absent. Attempts were made to measure the impedance at a lower frequency than 0.0628 rad/sec, but the impedance spectra were chaotic and not reproducible.
Figure 7-21. Nyquist diagram of impure copper electrode after experiencing passivation in the absence of thiourea.

Based on the observation, an equivalent circuit is proposed and displayed in Figure 7-22. The first part of the circuit represents the polarization of the impure copper, and the second the formed slimes layer. $R_3$ and $L$ were caused by the denser slimes layer formation. The inductance feature was reported to arise from a number of sources[40,41,42,43], for example, some type of adsorption process. There is no uniform agreement as to the cause of this inductive type of behavior. Thus, this inductance could be employed to represent the physical properties of the slimes layer.

Figure 7-22. Proposed equivalent circuit with respect to the physical microstructure of the anode and anode slimes for the impure copper experiencing passivated dissolution.
The best fitting values of the components for the circuit are presented in Table 7-5. Analysis of CPE\textsubscript{i} component shows that polarization resistance with respect to the passivated electrode ($R_1=1.134\Omega\ \text{cm}^2$) is approximately three times higher than that of the active electrode ($R_1=0.425\ \Omega\ \text{cm}^2$). This value indicates that the dissolution rate of the passivated electrode was strongly hindered by passivation.

Table 7-5. Summary of parameters for AC impedance of impure copper experiencing non-passivated and passivated dissolution.

<table>
<thead>
<tr>
<th>Passivation</th>
<th>$\tau_{\text{CPE,1}}\ \Omega^4\ \text{cm}^{-2}\ \text{s}^{-1}\times10^{-6}$</th>
<th>$\rho_{\text{CPE,1}}\ \Omega\ \text{cm}^2$</th>
<th>$\tau_{\text{CPE,2}}\ \Omega^4\ \text{cm}^{-2}\ \text{s}^{-1}\times10^{-6}$</th>
<th>$\rho_{\text{CPE,2}}\ \Omega\ \text{cm}^2$</th>
<th>$\tau_{\nu}\ \Omega^4\ \text{cm}^{-2}\ \text{s}^{-1}\times10^{-6}$</th>
<th>$\rho_{\nu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>0.167±0.006</td>
<td>0.965±0.013</td>
<td>0.425±0.012</td>
<td>0.018±0.000</td>
<td>0.805±0.019</td>
<td>0.5±0.006</td>
</tr>
<tr>
<td>Yes</td>
<td>0.142±0.002</td>
<td>0.672±0.006</td>
<td>1.134±0.067</td>
<td>0.009±0.000</td>
<td>0.997±0.021</td>
<td>0.454±0.002</td>
</tr>
</tbody>
</table>

Analysis of the two CPE components of Table 7-5 shows that $\tau_{\text{CPE}}$ value decreases from CPE\textsubscript{i} to CPE\textsubscript{2}. Mansfeld\[44\] interpreted the decrease in capacitance as the result of an increase in surface film thickness. Since $\tau_{\text{CPE,1}}$ and $\tau_{\text{CPE,2}}$ represent capacitance of Cu/slimes interface and of slimes, respectively, the lower value of $\tau_{\text{CPE}}$ indicates a larger thickness of film. Using the best fitted data a Nyquist diagram was of the simulation conducted. The good agreement between experimental results and the simulated data is demonstrated in Figure 7-23.

![Nyquist Diagram](image)

Figure 7-23. A typical Nyquist diagram of the simulation of impure copper experiencing passivation dissolution in the absence of thiourea.
7.3.3.2 Impedance behavior of impure copper anode in the presence of thiourea

Previous steady state and transition state experiments have shown the effect of thiourea on the impure copper dissolution through adsorption on the surface of the electrode. The adsorbed thiourea blocks the active sites on the electrode surface leading to a decrease in the rate of copper dissolution.

Typical experiments were conducted to study the effect of thiourea on the dissolution process by AC impedance measurements under the active and passivated dissolution conditions. Thiourea was added 5 minutes prior to each test. All of the experimental conditions are listed in Table 7-6.

Table 7-6. Summary of DC and AC measurements for the impure copper dissolved in electrolyte solution containing thiourea

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>DC Control</th>
<th>AC Control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current density A/m²</td>
<td>Passivation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1910</td>
<td>No</td>
</tr>
<tr>
<td>20</td>
<td>1910</td>
<td>Yes</td>
</tr>
</tbody>
</table>

AC impedance measurements carried out before passivation with electrolyte solution containing thiourea

A typical Nyquist diagram of impure copper the presence of thiourea is given in Figure 7-24. There are significant differences between this plot and that obtained in the absence of thiourea (Figure 7-15). The impedance shows two overlapping capacitive features and a low-frequency inductive feature. Preceding chronopotentiometric measurement showed that the time to passivation decreased to 2280 seconds from 4750 seconds that in the absence of thiourea. Under this condition, the significant blockage by adsorption of thiourea on the surface of the impure copper electrode causes the impure copper to enter the passivation stage quickly.
Figure 7-24. A typical Nyquist diagram of impure copper electrode prior to passivation in the presence of thiourea.

Although the impure copper electrode experienced the generation of a slimes layer and adsorption of thiourea, an equivalent circuit for the AC impedance in Figure 7-22 could be used to interpret the data for the impure copper in the presence of thiourea. The values of the components for this circuit are reported in Table 7-7. Analysis of these data will be discussed in the next section. With the estimated values a simulation was carried out. The simulation result is presented in Figure 7-25.

Figure 7-25. Nyquist diagram for impure copper without passivation in the presence of thiourea.
AC impedance measurements carried out after passivation appearing – electrolyte solution with thiourea

The impedance of the impure copper experiencing passivation in the presence of thiourea was measured and is presented in Figure 7-26. There is a difference between this plot and that obtained for the active dissolution (Figure 7-11). Two slightly overlapping capacitive features were observed. An inductive feature was obtained at low frequencies.

Figure 7-26. Nyquist diagram of impure copper after experienced passivation in the presence of thiourea.

The equivalent circuit of Figure 7-22 was used to interpret this impedance data. The results are given in Table 7-7.

Table 7-7. Estimated parameters for impure copper in the presence of thiourea under active and passive dissolution.

<table>
<thead>
<tr>
<th>Passivation</th>
<th>$T_{\text{CPE-1}}$</th>
<th>$P_{\text{CPE-1}}$</th>
<th>$R_1$</th>
<th>$T_{\text{CPE-2}}$</th>
<th>$P_{\text{CPE-2}}$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>0.638±0.021</td>
<td>0.94±0.034</td>
<td>0.512±0.019</td>
<td>0.458±0.009</td>
<td>0.97±0.026</td>
<td>1.762±0.098</td>
<td>3.11±0.079</td>
<td>5.88±0.087</td>
</tr>
<tr>
<td>Yes</td>
<td>0.009±0.00</td>
<td>0.613±0.01</td>
<td>0.485±0.007</td>
<td>0.031±0.00</td>
<td>0.717±0.018</td>
<td>3.68±0.085</td>
<td>14.53±0.52</td>
<td>3.76±0.04</td>
</tr>
</tbody>
</table>

Comparing the values of $T_{\text{CPE-1}}$ and $T_{\text{CPE-2}}$ in both experiments, it was found that the values in the presence of thiourea are at least one order of magnitude lower than those in the absence of
thiourea. The values of $R_2$ and $R_3$ in the presence of thiourea are higher than those in the absence of thiourea. Hukovic et al.[45], Spinelli et al.[46], and Harrington et al.[47] demonstrated that the interface capacitance of Armco iron decreased with an increase in the concentration of thiourea in different acidic media. It was also found that the polarization resistance of the Armco iron increased with an increase in thiourea concentration. These authors drew the conclusion that the observations were due to the adsorption of thiourea on the surface of the Armco iron. The present results are in good agreement with those of the above-cited authors. This leads to a further confirmation of thiourea absorption on the surface of the copper electrode.

It should be noted that the results of AC impedance, with respect to the impure copper electrode in the absence of thiourea, are not comparable with those in the presence of thiourea. Since the time frames are different, the amount of anode slimes should be quite different. These differences could be reflected in the AC impedance. The simulation data and the results of the test corresponding to the presence of thiourea are shown in Figure 7-27.

![Figure 7-27. Nyquist diagram of the simulation of impure copper electrode experienced passivation dissolution in the presence of thiourea.](image)

**AC impedance of impure copper at low concentrations of thiourea**

Since the thiourea addition in industrial copper electrorefining is less than 5 mg/L, the behavior of the impedance of impure copper in the concentration range 1 to 5 mg/L thiourea was investigated. The time frame for aging the impure copper was pre-selected at 38 minutes at which time the thicknesses of the anode slimes for each test would be expected to be similar. After going through the time frame, the electrochemical measurements were switched from DC
control to AC control. Figure 7-28 shows the Nyquist diagram corresponding to different thiourea concentrations.

![Nyquist diagram](image)

Figure 7-28. Nyquist diagram of impure copper in the varying concentrations of thiourea.

The curves show the same shapes as the impure copper without passivation at a high concentration of thiourea (20 mg/L). Distinct inductor features appeared on each curve. Both the real and imaginary parts of the impedance decrease with an increase in the concentration of thiourea. The curve near the axis of real part of impedance, with respect to impure copper examined directly by AC impedance measurement in the absence of thiourea, did not show an inductive feature. This behavior is different with that obtained in the presence of thiourea. Curve fitting was conducted using the equivalent circuit of Figure 7-22. Best fitted parameters are shown in Table 7-8.
Table 7-8. Best fitted parameters corresponding to the impure copper dissolution in the presence of low concentrations of thiourea.

<table>
<thead>
<tr>
<th>[TU] mg/L</th>
<th>$T_{CPE-1}$ $\Omega^2$ cm$^2$ s$^{-1}$ x 10$^{-6}$</th>
<th>$R_1$ $\Omega$ cm$^2$</th>
<th>$T_{CPE-2}$ $\Omega^2$ cm$^2$ s$^{-1}$ x 10$^{-6}$</th>
<th>$P_{CPE-2}$</th>
<th>$R_2$ $\Omega$ cm$^2$</th>
<th>$R_3$ $\Omega$ cm$^2$</th>
<th>$L$ H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.721±0.079</td>
<td>0.964±0.044</td>
<td>0.404±0.02</td>
<td>1.231±0.047</td>
<td>0.963±0.028</td>
<td>1.316±0.038</td>
<td>3.89±0.09</td>
</tr>
<tr>
<td>2.0</td>
<td>1.632±0.061</td>
<td>0.974±0.039</td>
<td>0.417±0.007</td>
<td>0.93±0.032</td>
<td>0.971±0.038</td>
<td>1.47±0.045</td>
<td>2.06±0.1</td>
</tr>
<tr>
<td>3.0</td>
<td>1.429±0.067</td>
<td>0.953±0.036</td>
<td>0.457±0.018</td>
<td>0.841±0.026</td>
<td>0.967±0.046</td>
<td>1.57±0.039</td>
<td>3.06±0.1</td>
</tr>
<tr>
<td>5.0</td>
<td>1.189±0.056</td>
<td>0.956±0.041</td>
<td>0.499±0.023</td>
<td>0.73±0.033</td>
<td>0.974±0.035</td>
<td>1.69±0.054</td>
<td>2.99±0.13</td>
</tr>
</tbody>
</table>

The data show that increasing the thiourea concentration causes both the polarization resistance, $R_1$, and the resistance of slimes layer, $R_2$, to increase slightly. These results indicate that thiourea not only influences mass transfer across the interface of Cu/slimes, but also across the slimes layer. The values of $R_2$ and $L$ show a certain degree of disorder. This problem could be result from the fact that the pre-selected low frequency used in those tests was not low enough to complete an inductance loop measurement. Although inductance loops can be generated in a low frequency range, the low frequency ranges with respect to measuring an inductance differ from one researcher to another. In the present investigation the minimum frequency that could be reached was 0.0628 rad/sec, the inductive features in Figure 7-28 show that the inductance loops were not fully generated under this condition. When the data fitting was conducted to interpret the inductance shown in Figure 7-28, a certain degree of error could be introduced in the fitting processes.

7.4. Summary

AC impedance measurements with respect to the addition of thiourea show a significant influence on the impedance spectra. When the pure copper electrode was placed in various concentrations of thiourea under no Faradaic reaction, the resulting impedance data showed that surface coverage increased with increase in thiourea concentration. At 5 mg/L of thiourea the coverage was higher than 80%, indicating that thiourea has a natural ability to adsorb on metallic copper.
The inhibition effect of thiourea on the copper dissolution is likely achieved through changing the resistance and capacitance of the interface of Cu°/solution with respect to pure copper. The value of the electron transfer resistor (polarization resistor), $R_p$, is proportional to the thiourea concentration. The value of the Nernst diffusion layer capacitor, $C_{dl}$, decreases with increase in the thiourea concentration.

AC impedance spectra of an aged impure copper showed that thiourea changes the properties of both the interfaces of Cu°/slimes and of the slimes layer. The resistance in both the interface and the slimes layer increases with an increase in the thiourea concentration. The capacitance of both is reciprocal to the increase in thiourea concentration.

Theoretically, a current at an electrode can be defined as a measure of the charge, $q_{ch}$, transferred with respect to time, $t$, which can be expressed as the follows:

$$I = \frac{dq_{ch}}{dt} \quad (7-23)$$

The definition of the electrode capacitance without considering surface films, $C_d$, can be written as:

$$C_d = \frac{dq_{ch}}{dE} \quad (7-24)$$

where $E$ is the electrode potential.

Substituting the Eq. (7-24) to Eq.(7-23), one obtains the following equation:

$$I = C_d \frac{dE}{dt} \quad (7-25)$$

Eq. (7-25) shows that at a constant potential modulation, $dE/dt$, decreasing the capacitance will result in a decrease in the current. Since the capacitances of Cu°/slimes interface and slimes layer are all reduced by adding thiourea in the dissolution process, these indicate that thiourea hinders the dissolution rate of both pure and impure copper electrodes. This is in agreement with the results of the conventional electrochemical measurements.

The previous conventional electrochemical techniques do not show the evidence of the effect of thiourea on the formation of anode slimes. Armstrong et.al.[48] interpreted the effect of coatings on the corrosion of metal in various solutions using the following equation:
\[ C_f = \frac{\varepsilon_c \varepsilon_0 A}{I_{\text{eff}}} \]  

(7-26)

where \( C_f \) is the capacitance of diffusion layer, \( \varepsilon_c \) the dielectric constant of coatings, \( \varepsilon_0 \) the permittivity of the coatings, and \( A \) the area of an electrode surface.

The dielectric constant of copper slime layer is unknown, but it could not change in the presence of thiourea, and it can be regarded as a constant. Since the value of \( C_f \) is reciprocal to the concentration of thiourea (Table 7-7 and 7-8), the ratio of \( \frac{\varepsilon_0}{I_{\text{eff}}} \) must be decrease with increase in thiourea concentration.

In order to confirm the about conclusion, microscopic examinations were carried out. The results are shown in Figures 7-29 and 7-30.

Figure 7-29. Anodic slimes formation corresponding to impure copper dissolved in the absence of thiourea for 60 minutes. (Magnification = 16)
Figure 7-30. Anode slimes formation corresponding to the impure copper dissolved in the presence of thiourea at 10 mg/L for 60 minutes. (Magnification = 16)

Figure 7-29 shows the photograph of a stationary impure copper electrode dissolved anodically by the chronopotentiometrical control at 1910 A/m² for 60 minutes in the solution with thiourea-free. Figure 7-30 is the photograph of a stationary impure copper electrode dissolved in similar condition as the above experiment, but 10 mg/L of thiourea was added in the test electrolyte. It is like that thiourea enhances the growth of slime particles resulting in fine particles. The fine particles would increase the diffusion resistance of the slimes layer. The diffusion of copper ions could be strongly hindered by this fine particle formation. This conclusion is in agreement with the previous chronopotentiometric measurements in Chapter 5.
7.5 References


Chapter 8  Conclusions and Future Work

Conclusions

The purpose of this investigation was to study the effect of thiourea on the dissolution rate of copper electrodes in highly concentrated copper sulfate-sulfuric acid solutions. Steady state, transient state, and in-situ electrochemical techniques were chosen for simultaneous studies on the thiourea adsorption, interaction with copper ions, and mass transfer across interfaces in the vicinity of the surface of the electrodes. Data interpretation for the relative experiments leads to the following conclusions:

1. Thiourea acts as an inhibitor hindering the anodic dissolution rate of both pure copper and impure copper electrodes. The mechanism of inhibition of thiourea is likely through adsorption of thiourea on the active sites of the electrode surface.

2. Thiourea inhibition – surface coverage was directly computed by using transient state electrochemical measurements. The values of surface coverage changed from 0.65 % to 49.38 % with increase in thiourea concentration from 0.5 mg/L to 30 mg/L. These values corresponded to the polarization measurements at anodic potential of 0.34 V_SHE.

3. Most of thiourea contributed to the adsorption on the electrode surface. A small amount of thiourea interacted with cupric ion to reduce it to the cuprous form and subsequently form Cu[TU_n]^{2+}. Thiourea was also protonated to become [HTU]^+ in the acid copper sulfate.

4. Chronopotentiometry was used to study copper anode passivation. At the high current densities employed, passivation generally occurred in a relatively short time. Results showed that with the addition of thiourea, the passivation time decreased with an increase in the concentration of thiourea. The passivation time changed from 4700 seconds down to 2200 seconds with increase in the thiourea concentration from 0.5 mg/L to 30 mg/L. These values were obtained using a constant current density of 1910 A/m^2 for the dissolution of the impure copper.
5. Copper plating in the presence of thiourea was investigated using transient state electrochemical measurements. It was found out that thiourea also adsorbed on the surface of copper in the cathodic process. The surface coverage changed from 22.03 % to 84.83 % with increase in thiourea concentration from 1 mg/L to 30 mg/L. These values correspond to measurements at a cathodic potential of 0.07 V_SHE.

6. In-situ electrochemical measurements provide further information about the effect of thiourea on the anodic process. The evidence showed that adding thiourea raises the polarization resistance of the pure copper. Subsequently, the presence of thiourea causes the effective diffusion layer to increase, leading the capacitance of the diffusion layer to decrease. Both results point to the fact that thiourea adsorbs on the surface of the pure copper electrode, reducing the active area of the electrode surface. This eventually results in hindering the dissolution rate of the pure copper.

7. Characteristic changes of the impure copper electrode, aged under active dissolution and passivation conditions, can be determined using the electrochemical impedance spectroscopy (EIS). The passivated electrode showed that the polarization resistance of the Cu°/slimes interface was raised two times higher than that of the non-passivated electrode. The capacitance of slimes layer of the passivated electrode was reduced compared with the non-passivated electrode.

8. In the presence of thiourea, the EIS study showed that the capacitance of the Cu°/slimes interface of the passivated impure copper electrode was approximately two orders of magnitude smaller, than that for the non-passivated electrode. The capacitance of the slimes layer for the passivated electrode was one order magnitude smaller than that for the non-passivated electrode. The resistance of the slimes layer on the former electrode was one times higher than that for the latter.

9. The aged impure copper electrode, in the presence of a low concentration of thiourea and under active dissolution conditions, showed that the addition of thiourea decreased the capacitance of both the interface of Cu°/slimes and slimes layer, and increased the resistance of both interfaces. These results indicate that thiourea inhibition on the anodic dissolution process of impure copper not only influences the kinetic process at the interface of copper/slimes, but also changes the properties of the slimes layer. The latter phenomenon could not identified using conventional electrochemical techniques.
Future Work

1. Adsorption of thiourea on the metal surface has been reported by numerous researchers. However, there are no published data showing evidence to confirm in what kind of state thiourea adsorbs on the surface. It would be worthwhile to find suitable ways to visualize the adsorption of thiourea on the metal surface in order to identify the adsorption mechanism. Thus copper electrorefiners would benefit by being able to improve their control of the electrorefining process. An Infrared spectroscopy and Scanning Reference Electrode Technique could be used to “see” the thiourea complexes and to “map” the defects produced thiourea blocking in the surface.

2. In industrial operations, some of impurities dissolve from the impure anodes and enter the electrolyte. The behavior of thiourea on the anodic process should be investigated by introducing the common impurities in the experimental solutions. The combination measurement of potential step and rotating disk electrode would be a key tool in such an investigation.

3. Considering thiourea interacting with other species in concentrated copper sulfate-sulfuric acid solutions, it would be worthwhile to identify which species interact with thiourea under industrial copper electrorefining conditions. Since interactions would affect the consumption of thiourea.

4. The physical properties of copper anode slimes are the key to understanding copper anode passivation. In-situ electrochemical techniques, AC impedance measurements have demonstrated a powerful capability to determine these properties. The electrochemical impedance spectroscopy used in this study has a frequency limitation which hinders the present investigation. Future work could be conducted by finding a window in which the impedance spectra are generated in the low frequency range of 0.00628 rad/sec to 0.0628 rad/sec.

5. Surface examination instruments such as a transmission electron microscopy and atomic force microscopy are key tools for determining the anode slimes thickness and
pore sizes. Combining the surface examination and in-situ electrochemical measurements should provide more accurate information about the properties of anode slimes layer and mass transfer across the slimes layer.

6. Physical properties of industrial anode slimes have to be examined in order to get data on e.g. dielectric constant. With these data the AC impedance model could be modified and could be used to predict the anode slime formation and behavior in industrial operations.
Appendix I Thermodynamic Properties for Copper Sulfate-Sulfuric Acid System

Calculation of thermodynamic properties for copper and sulfur species at elevated temperatures

Since Criss and Cobble’s entropy correspondence principle is based on the careful perusal of existing high temperature entropy data, it can be used over a wide range of temperature [1]. A few researchers have obtained fairly reasonable results on Gibbs free energy, enthalpy, and entropy for aqueous species up to 150 °C [2,3,4]. This technique is applied to the calculation of the copper and sulfur species in this thesis.

An absolute entropy for an aqueous species at 25 °C can be computed by the following formula:

\[
\Delta S^{0}_{298} = \Delta S^{0} + |Z| \Delta S^{0}_{H^{+}(abs)}
\]

where \(\Delta S^{0}_{298}\) is the entropy of a species at 25 °C, \(Z\) is the valence of the species, and \(\Delta S^{0}_{H^{+}(abs)}\) is the value of modified entropy for hydrogen ion correspond to -20.92 J/mol/°C.

The Gibbs free energy of any species at elevated temperature can be expressed as:

\[
\Delta G^{0}_{T} = \Delta G^{0}_{298} + \Delta C^{0}_{p} \Theta^{T} \left( \frac{T-298}{T} \right) \Delta S^{0}_{298} (abs)/1000
\]

where \(\Delta G^{0}_{298}\) is the reaction free energy of species at 25 °C, \(\Delta C^{0}_{p} \Theta^{T}\) is a heat capacity of the species at \(T\) temperature, and \(\Theta\) is a temperature function, its values at fixed temperatures are shown in Table I-1.

### Table I-1. Values of \(\Theta\) at different temperatures

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>25</th>
<th>60</th>
<th>65</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Theta)</td>
<td>0</td>
<td>-1.97835</td>
<td>-2.57067</td>
<td>-3.23692</td>
</tr>
</tbody>
</table>

For aqueous species, the \(\Delta C^{0}_{p} \Theta^{T}\) can be represented as:
\[ \Delta C_{P}^{0} T_2^{T_2} = \frac{a_{T_2}}{\ln \left( \frac{T_2}{298} \right)} - \frac{(1 - b_{T_2})}{\ln \left( \frac{T_2}{298} \right)} \Delta S_{298}^{0} (obs) \]  

Equation (1-3) is called the Criss and Cobble Entropy Correspondence Equation, in which \( a_{T_2} \) and \( b_{T_2} \) are constants given by Criss and Cobble. The values of \( a_{T_2} \) and \( b_{T_2} \) for difference species are listed in Table I-2.

Table I-2. Values of \( a \) and \( b \) used for the Criss and Cobble Entropy Correspondence equation (data unit in cal/mol/°C).

<table>
<thead>
<tr>
<th>T K</th>
<th>simple M+</th>
<th>simple ox</th>
<th>Acid oxy M- HSO4 (-)</th>
<th>S298</th>
<th>( \Delta C_{P}^{0} T_2^{T_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( aT )</td>
<td>( bT )</td>
<td>( aT )</td>
<td>( bT )</td>
<td>( aT )</td>
</tr>
<tr>
<td>298</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>333</td>
<td>3.9</td>
<td>0.995</td>
<td>-14</td>
<td>1.217</td>
<td>-13.5</td>
</tr>
<tr>
<td>338*</td>
<td>5.102294</td>
<td>0.95041</td>
<td>-15.8306</td>
<td>1.24079</td>
<td>-15.9135</td>
</tr>
<tr>
<td>343*</td>
<td>5.771511</td>
<td>0.94151</td>
<td>-17.7174</td>
<td>1.26925</td>
<td>-17.919</td>
</tr>
</tbody>
</table>

* These values were estimated by using regression technique.

For elements and compounds, the \( \Delta C_{P}^{0} T_2^{T_2} \) can be expressed as:

\[ \Delta C_{P}^{0} T_2^{T_2} = a + bT + c'T^2 + cT^2 \]  

(1-4)

where \( a, b, c' \) and \( c \) are constants, which are listed in Table I-3.
Table I-3. Constant values input to heat capacity cal/deg/mol for elements and compounds.

<table>
<thead>
<tr>
<th>Species</th>
<th>$a$</th>
<th>$b\times10^3$</th>
<th>$c\times10^3$</th>
<th>$c\times10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>27.28</td>
<td>3.26</td>
<td>0.502</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>75.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>22.64</td>
<td>6.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>56.57</td>
<td>29.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>43.83</td>
<td>16.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>29.96</td>
<td>4.18</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>CuSO$_4$·5H$_2$O</td>
<td>61.8</td>
<td>40.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Gibbs free energy for an overall reaction at $T$ temperature can be calculated as:

$$\Delta G_T^0 = \Delta G_T^0\text{(products)} - \Delta G_T^0\text{(reactants)}$$  \hspace{1cm} (I-5)

**Example:** Calculate the following reaction free energy at $25^\circ$C.

$$\text{Cu}^{2+} + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+$$  \hspace{1cm} (I-6)

$$\Delta G_{298}^0\text{(kJ/mol)} = 65.7 - 237.178 - 134 + 0$$

$$S_{298}^0\text{(J/mol/K)} = -97.2 \quad 69.1 \quad 42.7 \quad 0$$

$$S_{298}^0\text{(abs)(J/mol/K)} = -139.04 \quad 69.1 \quad 42.7 \quad -20.92$$

According to equation (I-5), the free energy of reaction (I-6) can be evaluated:

$$\Delta G_{298}^0 = \Delta G_{298}^0\text{(CuO)} + \Delta G_{298}^0(2\text{H}^+) - \Delta G_{298}^0\text{(Cu}^{2+}) - \Delta G_{298}^0\text{(H}_2\text{O)}$$

$$= -134 + 0 - 65.7 + 237.178 = 37.478 \text{kJ/mol}$$  \hspace{1cm} (I-7)

From equation (I-1) the entropy of reaction (I-6) can be obtained:

$$\Delta S_{298}\text{(abs)} = \Delta S_{298}\text{(abs)(CuO)} + \Delta S_{298}\text{(abs)(2H}^+) - \Delta S_{298}\text{(abs)(Cu}^{2+}) - \Delta S_{298}\text{(abs)(H}_2\text{O)}$$

$$= 70.8 \text{ J/K/mol}$$  \hspace{1cm} (I-8)
The heat capacity for CuO at elevated temperature can be calculated according to equation (I-4)

$$\Delta C_{p}^0 \left[ \text{CuO} \right]_{298} = 43.83 + 16.77 \times 10^{-3} T - 5.887^2$$  \hspace{1cm} (I-9)

The heat capacity of H$_2$O does not change with temperature. Heat capacity of Cu$^{2+}$ can be estimated by using equation (I-3). The calculated values of heat capacities for the species participated in reaction (I-6) are shown as the following:

<table>
<thead>
<tr>
<th>Species</th>
<th>Cu$^{2+}$</th>
<th>H$_2$O</th>
<th>CuO$^-$</th>
<th>H$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta C_{p}^0 \left[ \text{Cu}^{2+} \right]_{298}$ (J/k/mol)</td>
<td>204.23</td>
<td>75.44</td>
<td>44.12</td>
<td>69.3</td>
</tr>
<tr>
<td>$\Delta C_{p}^0 \left[ \text{H}<em>2\text{O} \right]</em>{298}$ (J/k/mol)</td>
<td>225.14</td>
<td>75.44</td>
<td>44.36</td>
<td>100.49</td>
</tr>
<tr>
<td>$\Delta C_{p}^0 \left[ \text{CuO} \right]_{298}$ (J/k/mol)</td>
<td>230.35</td>
<td>75.44</td>
<td>44.6</td>
<td>104.68</td>
</tr>
</tbody>
</table>

Similarly, the free energy, entropy, and heat capacity at temperatures 338 and 343 K are evaluated and listed in Table I-4.

**Table I-4.** Summary of the free energy values of the species in copper-sulfur-water system at temperatures from 25-70 °C. The data unit is J/mol.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G_{298}$</th>
<th>$\Delta G_{333}$</th>
<th>$\Delta G_{338}$</th>
<th>$\Delta G_{343}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>0</td>
<td>-1206</td>
<td>-1387</td>
<td>-1569</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>65700</td>
<td>70142</td>
<td>70662</td>
<td>71190</td>
</tr>
<tr>
<td>CuO$^-$</td>
<td>-134000</td>
<td>-135575</td>
<td>-135816</td>
<td>-136059</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-148100</td>
<td>-151456</td>
<td>-151958</td>
<td>-152465</td>
</tr>
<tr>
<td>CuSO$_4$$^-$5H$_2$O$^-$</td>
<td>-1906389</td>
<td>-1857723</td>
<td>-1856736</td>
<td>-1848754</td>
</tr>
<tr>
<td>H$^+$</td>
<td>-756010</td>
<td>-758600</td>
<td>-758784</td>
<td>-758909</td>
</tr>
<tr>
<td>SO$_4$$^-$</td>
<td>-744630</td>
<td>-742598</td>
<td>-742120</td>
<td>-741581</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0</td>
<td>-3923</td>
<td>-4496</td>
<td>-5071</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0</td>
<td>539</td>
<td>575</td>
<td>599</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>-4611</td>
<td>-5282</td>
<td>-5955</td>
</tr>
<tr>
<td>H$_2$O$^-$</td>
<td>-237180</td>
<td>-239764</td>
<td>-240158</td>
<td>-240558</td>
</tr>
</tbody>
</table>
Calculation approaches to the activity of highly concentrated copper sulfate-sulfuric acid solutions

Individual ion activities in a mixed electrolyte of CuSO₄ and H₂SO₄ can be expressed as the following formulas:

\[ a_{\text{Cu}^{2+}} = \gamma_{\text{Cu}^{2+}} \cdot m_{\text{Cu}^{2+}} \]  \hspace{1cm} (I-10)

\[ a_{\text{H}^+} = \gamma_{\text{H}^+} \cdot m_{\text{H}^+} \]  \hspace{1cm} (I-11)

\[ a_{\text{SO}_4^{2-}} = \gamma_{\text{SO}_4^{2-}} \cdot m_{\text{SO}_4^{2-}} \]  \hspace{1cm} (I-12)

where \( \gamma \) is the single ion activity coefficient and \( m \) is the molal concentration.

The relationship of the activities of pure electrolytes, CuSO₄ and H₂SO₄, with the individual ion activities of Cu²⁺, H⁺, and SO₄²⁻ can be represented as:

\[ a_{\text{CuSO}_4} = (a_{\text{Cu}^{2+}})^1(a_{\text{SO}_4^{2-}})^1 = a_{\text{Cu}^{2+},\text{SO}_4^{2-}} = (m_{\text{Cu}^{2+},\text{SO}_4^{2-}} \gamma_{\text{Cu}^{2+},\text{SO}_4^{2-}})^2 \]  \hspace{1cm} (I-13)

and

\[ a_{\text{H}_2\text{SO}_4} = (a_{\text{H}^+})^2(a_{\text{SO}_4^{2-}})^1 = a_{\text{H}^+,\text{SO}_4^{2-}} = (m_{\text{H}^+,\text{SO}_4^{2-}} \gamma_{\text{H}^+,\text{SO}_4^{2-}})^3 \]  \hspace{1cm} (I-14)

where \( m_z \) is mean ionic molality, and \( \gamma_z \) is mean ionic activity coefficient.

The mean activity coefficients of CuSO₄ and H₂SO₄ are defined as:

\[ (\gamma_{\text{CuSO}_4})^2 = (\gamma_{\text{Cu}^{2+}})^1 \cdot (\gamma_{\text{SO}_4^{2-}})^1 \]  \hspace{1cm} (I-15)

\[ (\gamma_{\text{H}_2\text{SO}_4})^3 = (\gamma_{\text{H}^+})^2 \cdot (\gamma_{\text{SO}_4^{2-}})^1 \]  \hspace{1cm} (I-16)

The mean ionic molalities of CuSO₄ and H₂SO₄ can be defined as:

\[ m_{\text{CuSO}_4} = (1^1 \cdot 1^1)m_{\text{CuSO}_4} \]  \hspace{1cm} (I-17)

\[ m_{\text{H}_2\text{SO}_4} = (2^2 \cdot 1^1)m_{\text{H}_2\text{SO}_4} \]  \hspace{1cm} (I-18)

The individual ionic molality is equal to the total numbers moles of ion given by one mole of single electrolyte times the molality of the electrolyte.
\[ m_{\text{Cu}^{2+}} = (1)m_{\text{CuSO}_4} \]  
(1-19)

\[ m_{\text{H}^+} = (2)m_{\text{H}_2\text{SO}_4} \]  
(1-20)

\[ m_{\text{SO}_4^{2-}} = (1)m_{\text{H}_2\text{SO}_4} \]  
(1-21)

Since the traditional concentration scale in hydrometallurgy is expressed in terms of molarity, \( C \), mol/L, solution, which is not equal to the molality, \( m \), mol/kg, solvent. The molar concentration scale in this paper was transferred to molal scale.

The molality of a species can be computed from the density, \( d \), of solution by the relation:

\[ m_i = \frac{C_i}{d - 0.001 \sum C_j W_j} \]  
(1-22)

where \( C_j \) is the molarity of species \( j \), and \( W_j \) is the atomic weight of species \( j \). In this thesis, the density of the mixed electrolyte of \( \text{CuSO}_4 \) and \( \text{H}_2\text{SO}_4 \) was measured by using a standard picnometer.

In this present thesis, the individual ion activity coefficient was calculated based on the Bates equations [5], Gibbs-Duhem relationship, and Stokes-Robinson’s hydration theory[6]. Bates [5] developed several equations to successfully estimate the individual ion activity coefficient for the solutions of univalent chlorides and divalent chlorides.

For a divalent salt (2:1) such as \( \text{CuCl}_2 \) or \( \text{CoCl}_2 \), the Bates equations is given as:

\[ \log \gamma^+ = 2 \log \gamma^+ - \frac{h}{3} \log \alpha^+ + \log(1 + 0.18(3 - h)m) \]  
(1-23)

\[ 2 \log \gamma^- = \log \gamma^+ + \frac{h}{3} \log \alpha^+ - \log(1 + 0.18(3 - h)m) \]  
(1-24)

where \( h \) is the hydration number of a cation or electrolyte. These above equations were derived by assuming only the cation is hydrated and the anion is not. For the individual ion activity coefficient of other types of single electrolytes such as 2:2, the author, Bates, did not give any expression.

Ji[7] derived equation for the 1:2 electrolyte such as \( \text{Na}_2\text{SO}_4 \) can be written as:
\begin{align*}
2 \log \gamma_+ &= \log \gamma_\pm - \frac{4 h}{3} \log a_w - \log(1 + 0.18(3 - 2h)m) \\
\log \gamma_2- &= 2 \log \gamma_\pm + \frac{4 h}{3} \log a_w + \log(1 + 0.18(3 - 2h)m) \\
\end{align*}

and the individual ion activity coefficient 2:2 electrolytes such as CuSO₄ can be expressed as

\begin{align*}
\log \gamma_{2+} &= \log \gamma_\pm - \frac{h}{2} \log a_w \\
\log \gamma_{2-} &= \log \gamma_\pm + \frac{h}{2} \log a_w \\
\end{align*}

In practical copper electrorefining, electrolyte solutions are composed of CuSO₄ and H₂SO₄, thus the interaction of ions in the mixed electrolytes also has to be considered. Referring to Ji’s method[7] for calculating a single ion activity coefficient in aqueous solution of mixed electrolytes and acid, the sulfate ion activity coefficient can be computed by use of the following equation. Some symbols assigned as following will be used in the calculation.

\begin{align*}
m_{\text{CuSO}_4} \quad \text{molality of CuSO₄} & \quad h_{\text{CuSO}_4} \quad \text{hydration number of CuSO₄} \\
m_{\text{H₂SO}_4} \quad \text{molality of H₂SO₄} & \quad h_{\text{H₂SO}_4} \quad \text{hydration number of H₂SO₄} \\
m &= m_{\text{CuSO}_4} + m_{\text{H₂SO}_4} \\
X_{\text{CuSO}_4} &= m_{\text{CuSO}_4}/m, \quad X_{\text{H₂SO}_4} = m_{\text{H₂SO}_4}/m \\
(1-29) \\
(1-30) \\
(1-25) \\
(1-26) \\
\end{align*}

\begin{align*}
(X_{\text{CuSO}_4} + X_{\text{H₂SO}_4}) \log \gamma_{\text{SO}_4^2} &= X_{\text{CuSO}_4} \log \gamma_{\text{CuSO}_4} + X_{\text{H₂SO}_4} \log \gamma_{\text{H₂SO}_4} \\
+ \left( \frac{1}{2} h_{\text{CuSO}_4} X_{\text{CuSO}_4} + \frac{4}{3} h_{\text{H₂SO}_4} X_{\text{H₂SO}_4} \right) \log a_w \\
- X_{\text{CuSO}_4} \log[1 + 0.18(2 - h_{\text{CuSO}_4})m_{\text{CuSO}_4}] \\
- X_{\text{H₂SO}_4} \log[1 + 0.18(3 - h_{\text{H₂SO}_4})m_{\text{H₂SO}_4}] \\
+ \log \{1 + 0.18[(2 - h_{\text{CuSO}_4})m_{\text{CuSO}_4} + (3 - h_{\text{H₂SO}_4})m_{\text{H₂SO}_4}] \} \\
(1-31) \\
\end{align*}

where the $a_w$ is water activity in the mixed solutions. When the $\gamma_{\text{SO}_4^2}$ is known, the $\gamma_{\text{Cu}^2+}$ and $\gamma_{\text{H}^+}$ can be readily computed as the following:
\[
\log \gamma_{Ca^{2+}} = 2 \times \log \gamma_{CaSO_4} - \log \gamma_{SO_4} \tag{I-32}
\]

\[
\log \gamma_{H^+} = \frac{3}{2} \times \log \gamma_{H_2SO_4} - \frac{1}{2} \log \gamma_{SO_4} \tag{I-33}
\]

Meissner[8] successfully developed a technique to calculate the mean activity coefficient. In his technique he took account of the interaction between the different electrolytes, effect of temperature, and water activity variance in mixed aqueous solutions. The relationship between the mean activity coefficient and the reduced activity coefficient for one electrolyte in an aqueous solution is expressed as:

\[
\gamma_{\pm,T} = \Gamma_{ij,T} \tag{I-34}
\]

where \(\gamma_{\pm,T}\) is the mean activity coefficient and \(\Gamma_{ij,T}\) is the reduced activity coefficient for an electrolyte in the aqueous solution at \(T\) temperature. \(\Gamma_{ij,T}\) is defined as the following equation:

\[
\Gamma_{ij,T} = [1 + B_{ij,T}(1 + 0.1 I_{\text{total}})^{q_{ij,T}} - B_{ij,T}] \Gamma_T^* \tag{I-35}
\]

where \(I_{\text{total}}\) is the total ionic strength in the aqueous solution. \(q_{ij,T}\) is a number characteristic of the dissolved electrolyte at \(T\) temperature. \(B_{ij,T}\) is a function of \(q_{ij,T}\), it can be written as:

\[
B_{ij,T} = 0.75 - 0.065 q_{ij,T} \tag{I-36}
\]

\(\Gamma_T^*\) is functions of the \(I_{\text{total}}\), temperature and \(q_{ij,T}\), it can be expressed as the following:

\[
\Gamma_T^* = \exp \left(\frac{-2.303 A_T \sqrt{T}}{1 + C \sqrt{T}}\right) \tag{I-37}
\]

and \(A_T\) and \(C\) can be represented, respectively:

\[
A_T^2 = \frac{(2\pi N_0 d_1)(e^2 / DK)^3}{[1000(2.303)^2]} \tag{I-38}
\]

and

\[
C = 1 + 0.055 q_{ij,T} \exp(-0.023 I^2) \tag{I-39}
\]

\(q_{ij,T}\) is a function of temperature, at \(T\) temperature it can be estimated as:
\[ q_{ij,t} = q_{ij,25} \left\{ 1 - \frac{0.0027(t - 25)}{z_i z_j} \right\} \]  \hspace{1cm} (I-40)

For mixed aqueous solutions, Meissner\[8\] defined the value of \( q \) for one of electrolyte in the mixed electrolyte solution at 25 °C by the following equation:

\[ q_{i,2} = \Sigma_i (I_i/I_T)q_{i,2} + \Sigma_j (I_j/I_T)q_{i,j} \]  \hspace{1cm} (I-41)

The values of \( q_{Cu^{2+},SO_4^{2-}} \) and \( q_{H^+,SO_4^{2-}} \) in mixed copper sulfate and sulfuric acid solution can be obtained from the following expressions:

\[ q_{Cu^{2+},SO_4^{2-}} = \frac{I_{Cu^{2+}}}{I_{total}} q_{CuSO_4} + \frac{I_{H^+}}{I_{total}} q_{H_2SO_4} + \frac{I_{SO_4^{2-}}}{I_{total}} q_{CuSO_4} \]  \hspace{1cm} (I-42)

\[ q_{H^+,SO_4^{2-}} = \frac{I_{Cu^{2+}}}{I_{total}} q_{CuSO_4} + \frac{I_{H^+}}{I_{total}} q_{H_2SO_4} + \frac{I_{SO_4^{2-}}}{I_{total}} q_{H_2SO_4} \]  \hspace{1cm} (I-43)

The activity of water over an aqueous solution can be calculated at any temperature listing the Gibbs equation\[8\].

\[ -55.5 \log a_w^0 = \frac{2I^0}{Z_1Z_2} + 2 \int_{1}^{\Gamma^0} d\ln \Gamma^0 \]  \hspace{1cm} (I-44)

where \( a_w^0 \) is the activity of water over the aqueous solution, \( I^0 \) is the total ionic strength of the solution, \( Z_1 \) and \( Z_2 \) are the valences of species 1 and 2. \( \Gamma^0 \) is Meissner’s reduced activity coefficient. A symbol, \( \phi(I) \), is given to the integral term in above equation. The expression of \( \phi(I) \) is represented as follows:

\[ \phi(I) = \int_{0}^{I} \left\{ 0.1qBI(1 + 0.1)^{q-1} \ln[1 - B + B(1 + 0.1I)^q] - \frac{0.58807\sqrt{I}}{(1 + C\sqrt{I})^3} \right\} dI \]  \hspace{1cm} (I-45)

thus, equation (I-44) can be simplified as:
where \( \varphi(I) \) can be computed by the numerical method. Considering the mixing effect, the following equation will be used to compute the water activity in mixed electrolyte solution:

\[
(a_w)_{\text{mix}} = (a_{12w}^0)^{x_{12}} (a_{23w}^0)^{x_{23}} (a_{34w}^0)^{x_{34}} \ldots
\]  

(I-47)

**Calculation of activity in a mixed electrolyte solution**

The above mentioned approaches were applied to a hypothetical copper refining electrolyte, which is composed of 0.6 M CuSO\(_4\) and 1.8 M H\(_2\)SO\(_4\). Other aqueous ion species which may be present in the actual refining electrolyte are ignored.

For precise calculation, the values of concentration for all species in the mixed solution are converted in unit of mol/kg- H\(_2\)O. Using equation (I-22), the molar concentration of Cu\(^{2+}\), H\(^+\), and SO\(_4^{2-}\) are converted to molal concentration. The density of the solution was measured and found be 1.1912kg/l at 23 °C. Therefore,

\[
m_{\text{Cu}^{2+}} = \frac{C_{\text{Cu}^{2+}}}{1.1912 - 0.001(63.55 \times C_{\text{Cu}^{2+}} + 1 \times C_{H^{+}} + 96 \times C_{\text{SO}_{4}^{2-}})}
\]

\[
m_{\text{Cu}^{2+}} = \frac{0.6}{1.1912 - 0.001(63.55 \times 0.6 + 1 \times 3.6 + 96 \times 2.4)} = 0.653
\]  

(I-48)

\[
m_{H^{+}} = \frac{3.6}{1.1912 - 0.001(63.55 \times 0.6 + 1 \times 3.6 + 96 \times 2.4)} = 3.92
\]  

(I-49)

\[
m_{\text{SO}_{4}^{2-}} = \frac{2.4}{1.1912 - 0.001(63.55 \times 0.6 + 1 \times 3.6 + 96 \times 2.4)} = 2.611
\]  

(I-50)
The values of ionic strength, and concentration in molal and molar scales are shown in Table 1-5.

**Table 1-5.** Ionic strength, molal and molar concentration for the solution of 0.66 M CuSO$_4$ and 1.67 M H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Species</th>
<th>$C$</th>
<th>$m$</th>
<th>$I$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol/l</td>
<td>mol/kg</td>
<td>mol/l</td>
<td>mol/kg</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.6</td>
<td>0.653</td>
<td>1.2</td>
<td>1.306</td>
</tr>
<tr>
<td>H$^+$</td>
<td>3.6</td>
<td>3.92</td>
<td>1.1.8</td>
<td>1.958</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>2.4</td>
<td>2.611</td>
<td>4.8</td>
<td>5.223</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td>7.8</td>
<td>8.487</td>
</tr>
</tbody>
</table>

The parameters for Meissner’s equation of reduced activity coefficient are calculated by using equations (1-36) to (1-47), with which the mean activity coefficients of CuSO$_4$ and H$_2$SO$_4$ are determined(Table 1-6).

**Table 1-6.** Parameters for Meissner’s equation and mean activity coefficients of CuSO$_4$ and H$_2$SO$_4$ at fixed temperatures

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$q_{mix}$</th>
<th>$B_{mix}$</th>
<th>$C_{mix}$</th>
<th>$A_t$</th>
<th>$\Gamma^*_{mix}$</th>
<th>$a_{\omega_{mix}}$</th>
<th>$\gamma_{\pm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CuSO$_4$</td>
<td>H$_2$SO$_4$</td>
<td>CuSO$_4$</td>
<td>H$_2$SO$_4$</td>
<td>CuSO$_4$</td>
<td>H$_2$SO$_4$</td>
<td>CuSO$_4$</td>
</tr>
<tr>
<td>25</td>
<td>-0.1682</td>
<td>-0.6168</td>
<td>0.7609</td>
<td>0.7901</td>
<td>1</td>
<td>1</td>
<td>0.5107</td>
</tr>
<tr>
<td>60</td>
<td>-0.1643</td>
<td>-0.5877</td>
<td>0.7607</td>
<td>0.7882</td>
<td>1</td>
<td>1</td>
<td>0.5471</td>
</tr>
<tr>
<td>65</td>
<td>-0.1637</td>
<td>-0.5835</td>
<td>0.7606</td>
<td>0.7879</td>
<td>1</td>
<td>1</td>
<td>0.5534</td>
</tr>
<tr>
<td>70</td>
<td>-0.1631</td>
<td>-0.5794</td>
<td>0.7606</td>
<td>0.7877</td>
<td>1</td>
<td>1</td>
<td>0.5599</td>
</tr>
</tbody>
</table>

Employing the calculated data to equations (I-31) to (I-33), the individual activity coefficients of Cu$^{2+}$, H$^+$, and SO$_4^{2-}$ can be readily figured out. Finally, the individual activities of these ions are obtained through equations (I-10) to (I-12).
References


Appendix II. Speciation in Copper Sulfate-Sulfuric Acid System

Prior to the development of the speciation in Chapter 4, the Newton-Raphson method (also known as Newton’s method), which is probably the best known method for numerically solving systems of nonlinear equations[1,2,3], is introduced. The immense advantage of this method is that the convergence is very rapid. Unfortunately, the method is very sensitive to the choice of the initial set of values. Seed values from previous calculations are not infallible because the previous increment may have contained different precipitation conditions. Consequently, if the Newton-Raphson method is included in a larger program, the method does not always converge even when the initial estimates are near the final solution. For this reason, seed values of the calculations are based on intuition. With experience, choosing the value of exp(-0.5) as an initial guess for all variables was found to be the most reliable method. Computation time is prolonged but convergence is almost assured.

In the simple case of a system of 2 simultaneous non-linear equations of the form:

\[ f_1(x_1, x_2) = 0 \]  \hspace{1cm} (II-1)

\[ f_2(x_1, x_2) = 0 \]  \hspace{1cm} (II-2)

If \( x_1 \) and \( x_2 \) are approximate solutions to the set of equations and if \( x_1 = x_1 + \Delta x_1 \) and \( x_2 = x_2 + \Delta x_2 \) are exact solutions then;

\[ f_1(x_1 + \Delta x_1, x_2 + \Delta x_2) = 0 \]  \hspace{1cm} (II-3)

\[ f_2(x_1 + \Delta x_1, x_2 + \Delta x_2) = 0 \]  \hspace{1cm} (II-4)

Also, both \( f_1 \) and \( f_2 \) can be expanded as a Taylor’s series about \( x_1 \) and \( x_2 \). Therefore,

\[ f_1(x_1 + \Delta x_1, x_2 + \Delta x_2) = f_1(x_1, x_2) + \Delta x_1 \cdot \frac{\partial f_1(x_1, x_2)}{\partial x_1} + \Delta x_2 \cdot \frac{\partial f_1(x_1, x_2)}{\partial x_2} \]  \hspace{1cm} (II-5)

\[ f_2(x_1 + \Delta x_1, x_2 + \Delta x_2) = f_2(x_1, x_2) + \Delta x_1 \cdot \frac{\partial f_2(x_1, x_2)}{\partial x_1} + \Delta x_2 \cdot \frac{\partial f_2(x_1, x_2)}{\partial x_2} \]  \hspace{1cm} (II-6)
Thus, $\Delta x_1$ and $\Delta x_2$ must satisfy equations (II-5) and (II-6) which may be written in a matrix form as equation (II-7). The two-dimensional matrix is called the Jacobian matrix and combined with the right-hand-side vector can be solved by any matrix solver.

$$
\begin{bmatrix}
\frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} \\
\frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2}
\end{bmatrix} \begin{bmatrix}
\Delta x_1 \\
\Delta x_2
\end{bmatrix} = \begin{bmatrix}
-f_1 \\
-f_2
\end{bmatrix}
$$

The Newton-Raphson method algorithm can be described as follows:

- Assume a set of initial values for each of $x_1$ and $x_2$;
- Evaluate the augmented coefficient matrix at the points $(x_1, x_2)$;

$$
a_{ij} = \frac{\partial f_i}{\partial x_j} \quad \text{with } i = 1, 2 \text{ and } j = 1, 2
$$

and $a_{i,3} = -f_i$ with $i = 1, 2$

- iii) Use the decomposition or elimination method to solve the set of linear equations for $\Delta x_1$ and $\Delta x_2$;
- iv) Calculate $x_i = x_i + \Delta x_i$ with $i = 1, 2$;
- v) Repeat steps ii), iii) and iv) until $\max|\Delta x_i| < \varepsilon$ or $[\max|\Delta x_i|/\max|x_i|] < \varepsilon$, with $i = 1, 2$ or a fixed number of iterations.

As noted earlier, a good set of initial solution values is essential in most cases and convergence characteristics of the Newton-Raphson method can also be improved by applying under-relaxation i.e. in step iv), calculate $x_i = x_i + \alpha \cdot \Delta x_i$, $i = 1, 2$ where $\alpha$ is the under-relaxation parameter ($0 < \alpha < 1$).

**Computation of speciation for copper sulfate-sulfuric acid system**

The copper sulfate-sulfuric acid system is given as a typical example of the speciation in copper electrorefining solution. It is composed of the copper-acid species including cupric,
proton, bisulfate, sulfate ions, and ion pairs. These species are listed in Table II-1. The solution is concentrated so the activity coefficients for all species are considered.

**Table II-1 List of species involved in the copper sulfate-sulfuric acid system.**

<table>
<thead>
<tr>
<th>Copper sulfate</th>
<th>Sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$, CuSO$_4$</td>
<td>H$^+$, HS0$_4^-$, SO$_4^{2-}$</td>
</tr>
</tbody>
</table>

The system contains three mass balance for H$^+$, Cu$^{2+}$, HS0$_4^-$, SO$_4^{2-}$, and ion pair CuSO$_4$; two equilibrium constants for copper sulfate and bisulfate dissociation, respectively; two relationships for the equilibrium constant and ionic strength; and one equation for real ionic strength. For the corresponding eight parameters which are unknown, eight equations are available.

\[
2C_1 = [H^+] + [HSO_4^-] \quad \text{(II-10)}
\]

\[
C_1 + C_2 = [HSO_4^-] + [SO_4^{2-}] + [CuSO_4] \quad \text{(II-11)}
\]

\[
C_2 = [Cu^{2+}] + [CuSO_4] \quad \text{(II-12)}
\]

where $C_1$ and $C_2$ are the acid and CuSO$_4$ concentrations, respectively.

There are two equilibrium conditions

\[
Q_1 = \frac{a_{Cu^{2+}} a_{SO_4^{2-}}}{a_{CuSO_4}} = \frac{[Cu^{2+}][SO_4^{2-}]}{[CuSO_4]} \frac{\gamma_{Cu^{2+}} \gamma_{SO_4^{2-}}}{\gamma_{CuSO_4}} \quad \text{(II-13)}
\]

\[
Q_2 = \frac{a_{H^+} a_{SO_4^{2-}}}{a_{HSO_4^-}} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \frac{\gamma_{H^+} \gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}} \quad \text{(II-14)}
\]
Three equations relate to quotient constants and real ionic strength

\[
\log Q_1 = -1.993 - \frac{4.05 \sqrt{I}}{1 + 1.618 \sqrt{I}} + 0.052 I
\]  
(II-15)

\[
\log Q_2 = -2.417 + \frac{2.032 \sqrt{I}}{1 + 1.10 \sqrt{I}}
\]  
(II-16)

One equation for real ionic strength

\[
I = \frac{1}{2} \sum C_i Z_i^2 = 2[Cu^{2+}] + \frac{1}{2}[H^+] + \frac{1}{2}[HSO_4^-] + 2[SO_4^{2-}]
\]  
(II-17)

It is more convenient to use the natural logarithm because these equations can be easily represented in the Jacobian matrix.

\[
X_1 = \ln[Cu^{2+}]
\]  
(II-18)

\[
X_2 = \ln[CuSO_4]
\]  
(II-19)

\[
X_3 = \ln[H^+]
\]  
(II-20)

\[
X_4 = \ln[HSO_4^-]
\]  
(II-21)

\[
X_5 = \ln[SO_4^{2-}]
\]  
(II-22)

\[
X_6 = \ln(Q_1)
\]  
(II-23)

\[
X_7 = \ln(Q_2)
\]  
(II-24)

\[
X_8 = \ln[I]
\]  
(II-25)
Linear equations for the mass balance and equilibrium constants can be represented as:

\[
e^{x_2} + e^{x_1} = C_1 \quad \text{(II-26)}
\]

\[
e^{x_3} + e^{x_1} = C_2 \quad \text{(II-27)}
\]

\[
e^{x_1} + e^{x_1} = C_1 + C_2 \quad \text{(II-28)}
\]

\[
X_6 = \ln 0.359 + X_1 + X_5 - X_2 \quad \text{(II-29)}
\]

\[
X_7 = \ln 0.248 + X_3 + X_5 - X_4 \quad \text{(II-30)}
\]

\[
X_6 = -4.589 - \frac{9.326e^{x_2}}{1 + 1.618e^{x_2}} + 0.12e^{x_6} \quad \text{(II-31)}
\]

\[
X_7 = -5.565 + \frac{4.679e^{x_2}}{1 + 1.1e^{x_2}} \quad \text{(II-32)}
\]

\[
e^{x_6} = 2e^{x_1} + \frac{1}{2}e^{x_3} + 2e^{x_5} + \frac{1}{2}e^{x_4} \quad \text{(II-33)}
\]

Therefore, equations (II-26) to (II-33) can be rewritten in the same form as equations (II-3) and (II-4).

\[
f_1 = e^{x_1} + e^{x_2} - C_1 \quad \text{(II-34)}
\]

\[
f_2 = e^{x_3} + e^{x_1} - C_2 \quad \text{(II-35)}
\]

\[
f_3 = e^{x_1} + e^{x_1} + e^{x_3} - C_1 - C_2 \quad \text{(II-36)}
\]

\[
f_4 = X_1 + X_5 - X_2 - X_6 - 1.024 \quad \text{(II-37)}
\]

\[
f_5 = X_3 + X_5 - X_4 - X_7 - 1.396 \quad \text{(II-38)}
\]
\[ f_6 = X_6 + 4.589 + \frac{9.326e^{2X_8}}{1 + 1.618e^{2X_8}} - 0.12e^{X_8} \]  
\[ (II-39) \]

\[ f_7 = X_7 + 5.565 - \frac{4.679e^{2X_8}}{1 + 1.1e^{2X_8}} \]  
\[ (II-40) \]

\[ f_8 = 2e^{X_1} + \frac{1}{2} e^{X_2} + 2e^{X_3} + \frac{1}{2} e^{X_4} - e^{X_8} \]  
\[ (II-41) \]

The coefficients of the Jacobian matrix, the solution vector and the right-hand-side vector can be expressed as follows:

\[
\begin{bmatrix}
  e^{X_1} & e^{X_2} & 0 & 0 & 0 & 0 & 0 & 0 \\
  0 & 0 & e^{X_1} & e^{X_2} & 0 & 0 & 0 & 0 \\
  0 & e^{X_2} & 0 & e^{X_1} & e^{X_7} & 0 & 0 & 0 \\
  1 & -1 & 0 & 0 & 1 & -1 & 0 & 0 \\
  0 & 0 & 1 & -1 & 1 & 0 & -1 & 0 \\
  0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
  0 & 0 & 0 & 0 & 0 & 0 & 1 & B^* \\
  2e^{X_1} & 0 & \frac{1}{2} e^{X_2} & \frac{1}{2} e^{X_4} & 2e^{X_3} & 0 & 0 & -e^{X_8} \\
\end{bmatrix} \cdot \begin{bmatrix}
  \Delta X_1 \\
  \Delta X_2 \\
  \Delta X_3 \\
  \Delta X_4 \\
  \Delta X_5 \\
  \Delta X_6 \\
  \Delta X_7 \\
  \Delta X_8 \\
\end{bmatrix} = \begin{bmatrix}
  -f_1 \\
  -f_2 \\
  -f_3 \\
  -f_4 \\
  -f_5 \\
  -f_6 \\
  -f_7 \\
  -f_8 \\
\end{bmatrix}  
\]  
\[ (II-42) \]

Note: \( A^* = \frac{4.663e^{2X_8} + 15.089e^{X_8}}{(1 + 1.618e^{2X_8})^2} - 0.12e^{X_8} \)

\[ B^* = \frac{-2.34e^{2X_8} + 5.147e^{X_8}}{(1 + 1.1e^{2X_8})^2} \]

**Computation of speciation for copper sulfate - sulfuric acid – thiourea system**

The speciation for the copper sulfate-sulfuric acid-thiourea system when thiourea is present is slightly different from the previous case when all species are aqueous. The normal procedure is to calculate the distribution of the aqueous species shown in the above. Since the dominant species is ion pair, proton and bisulfate, the cupric ion content is much lower. As thiourea is
present in the solution, the change in the concentration of the dominant species could be ignored. Nevertheless, since the interaction products of thiourea and copper ions are mainly the subjects of investigation in Chapter 4, the species in this system are thiourea and the related interaction products. These species are listed in Table II-2.

Table II-2 List of species involved in the electrolyte containing thiourea.

<table>
<thead>
<tr>
<th>cupric ion</th>
<th>thiourea and relative interaction products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>Cu(TU)$^{2-}$, (CuTU$_2$)$^{2+}$, (CuTU$_3$)$^{2+}$, (CuTU$_4$)$^{2+}$, TU</td>
</tr>
</tbody>
</table>

There are four thermodynamic equilibria

\[
\log\left[\frac{[(CuTU)^{2+}]}{[Cu^{2+}][TU]}\right] = 0.8 \tag{II-43}
\]

\[
\log\left[\frac{[(CuTU_2)^{2+}]}{[Cu^{2+}][TU]^2}\right] = 0.9 \tag{II-44}
\]

\[
\log\left[\frac{[(CuTU_3)^{2+}]}{[Cu^{2+}][TU]^3}\right] = 1.0 \tag{II-45}
\]

\[
\log\left[\frac{[(CuTU_4)^{2+}]}{[Cu^{2+}][TU]^4}\right] = 1.1 \tag{II-46}
\]

where TU is symbol of thiourea.

There are two mass balance equations

\[
[Cu^{2+}] + [(CuTU)^{2+}] + [(CuTU_2)^{2+}] + [(CuTU_3)^{2+}] + [(CuTU_4)^{2+}] = C_{Cu^{2+}} \tag{II-47}
\]

\[
[TU] + [(CuTU)^{2+}] + [(CuTU_2)^{2+}] + [(CuTU_3)^{2+}] + [(CuTU_4)^{2+}] = C_{TU} \tag{II-48}
\]

where $C_{Cu^{2+}}$ in equation (II-47) is the concentration of cupric ion which could be obtained from the previous numerical computation with considering the dissociation of copper sulfate ion pair and bisulfate. $C_{TU}$ in equation (II-48) is thiourea concentration presented in a typical electrolyte.
solution. Equations (II-43) to (II-48) can be solved simultaneously by using previous numerical methods.

Natural logarithm is used to redefine the major species listed in Table II-2:

\[ X_1 = \ln[Cu^{2+}] \]  
\[ X_2 = \ln[CuTU]^{2+} \]  
\[ X_3 = \ln[CuTU_2]^{2+} \]  
\[ X_4 = \ln[CuTU_3]^{2+} \]  
\[ X_5 = \ln[CuTU_4]^{2+} \]  
\[ X_6 = \ln[TU] \]

Then, equations (II-43) to (II-48) can be rewritten as:

\[ X_2 - X_1 - X_6 = 1.842 \]  
\[ X_3 - X_1 - 2X_6 = 2.073 \]  
\[ X_4 - X_1 - 3X_6 = 2.303 \]  
\[ X_5 - X_1 - 4X_6 = 2.533 \]  
\[ e^{X_1} + e^{X_2} + e^{X_3} + e^{X_4} + e^{X_5} = C_{Cu^{2+}} \]  
\[ e^{X_6} + e^{X_2} + e^{X_3} + e^{X_4} + e^{X_5} = C_{TU} \]

Therefore, equations (II-55) to (II-60) can be rewritten in the same form as equations (II-3) and (II-4):

\[ f_1 = -X_2 + X_1 + X_6 + 1.842 \]  
\[ f_2 = -X_3 + X_1 + 2X_6 + 2.073 \]
\[ f_3 = -X_4 + X_1 + 3X_6 + 2.303 \]  \hspace{1cm} (II-63)

\[ f_4 = -X_5 + X_1 + 4X_6 + 2.533 \]  \hspace{1cm} (II-64)

\[ f_5 = -e^{x_1} - e^{x_2} - e^{x_3} - e^{x_4} - e^{x_5} + C_{Cu^{2+}} \]  \hspace{1cm} (II-59)

\[ f_6 = -e^{x_6} - e^{x_3} - e^{x_4} - e^{x_5} + C_{Tt^{4}} \]  \hspace{1cm} (II-60)

The coefficients of the Jacobian matrix, the solution vector and the right-hand-side vector can be expressed as follows:

\[
\begin{bmatrix}
-1 & 1 & 0 & 0 & 0 & -1 \\
-1 & 0 & 1 & 0 & 0 & -2 \\
-1 & 0 & 0 & 1 & 0 & -3 \\
-1 & 0 & 0 & 0 & 1 & -4 \\
e^{x_1} & e^{x_2} & e^{x_3} & e^{x_4} & e^{x_5} & 0 \\
0 & e^{x_2} & e^{x_3} & e^{x_4} & e^{x_5} & e^{x_6}
\end{bmatrix}
\begin{bmatrix}
\Delta X_1 \\
\Delta X_2 \\
\Delta X_3 \\
\Delta X_4 \\
\Delta X_5 \\
\Delta X_6
\end{bmatrix}
= 
\begin{bmatrix}
-f_1 \\
f_2 \\
f_3 \\
f_4 \\
f_5 \\
f_6
\end{bmatrix}
\]  \hspace{1cm} (II-61)

References


Appendix III. Standard deviations displayed in Figures in Chapter 5 and 6

Standard deviations of anodic current densities (A/cm$^2$) in Fig5-2 (p75)

<table>
<thead>
<tr>
<th>Potential (V$_{SHE}$)</th>
<th>Thiourea concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.28</td>
<td>0.010±0.001</td>
</tr>
<tr>
<td>0.32</td>
<td>0.068±0.003</td>
</tr>
<tr>
<td>0.35</td>
<td>0.156±0.009</td>
</tr>
<tr>
<td>0.40</td>
<td>0.311±0.010</td>
</tr>
<tr>
<td>0.45</td>
<td>0.443±0.013</td>
</tr>
<tr>
<td>0.50</td>
<td>0.612±0.018</td>
</tr>
<tr>
<td>0.53</td>
<td>0.622±0.020</td>
</tr>
</tbody>
</table>

Peak current density (A/cm$^2$) vs. scan rate in Fig. 5-6 (p82).

<table>
<thead>
<tr>
<th>Scan rate (mV/s)$^{1/2}$</th>
<th>Thiourea concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 mg/L</td>
</tr>
<tr>
<td>0.707</td>
<td>0.596±0.006</td>
</tr>
<tr>
<td>1.414</td>
<td>0.688±0.005</td>
</tr>
<tr>
<td>3.162</td>
<td>0.799±0.008</td>
</tr>
<tr>
<td>4.472</td>
<td>0.900±0.008</td>
</tr>
<tr>
<td>7.071</td>
<td>1.065±0.010</td>
</tr>
</tbody>
</table>

Passivation time vs. thiourea concentrations in Fig. 5-11 (p92).

<table>
<thead>
<tr>
<th>Thiourea concentration, mg/L</th>
<th>Passivation time, second</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4750±5</td>
</tr>
<tr>
<td>0.5</td>
<td>4105±5</td>
</tr>
<tr>
<td>1.0</td>
<td>3860±5</td>
</tr>
<tr>
<td>2.0</td>
<td>3716±7</td>
</tr>
<tr>
<td>3.0</td>
<td>3555±5</td>
</tr>
<tr>
<td>4.0</td>
<td>3423±5</td>
</tr>
<tr>
<td>5.0</td>
<td>3324±14</td>
</tr>
<tr>
<td>10.0</td>
<td>2772±15</td>
</tr>
<tr>
<td>20.0</td>
<td>2285±15</td>
</tr>
<tr>
<td>30.0</td>
<td>2071±20</td>
</tr>
</tbody>
</table>
Solution pH vs. time when thiourea is present in electrolytes. (Fig. 6-1, p97)

<table>
<thead>
<tr>
<th>Time min.</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>23 °C</td>
</tr>
<tr>
<td>0</td>
<td>3.301±0.004</td>
</tr>
<tr>
<td>1</td>
<td>3.278±0.001</td>
</tr>
<tr>
<td>2</td>
<td>3.229±0.002</td>
</tr>
<tr>
<td>3</td>
<td>3.204±0.001</td>
</tr>
<tr>
<td>4</td>
<td>3.180±0.001</td>
</tr>
<tr>
<td>5</td>
<td>3.165±0.001</td>
</tr>
<tr>
<td>10</td>
<td>3.063±0.002</td>
</tr>
<tr>
<td>15</td>
<td>3.006±0.001</td>
</tr>
<tr>
<td>20</td>
<td>2.934±0.001</td>
</tr>
<tr>
<td>30</td>
<td>2.869±0.001</td>
</tr>
<tr>
<td>40</td>
<td>2.812±0.001</td>
</tr>
<tr>
<td>50</td>
<td>2.811±0.001</td>
</tr>
<tr>
<td>60</td>
<td>2.810±0.001</td>
</tr>
</tbody>
</table>

Anodic current density (A/cm²) vs. time at varying concentrations of thiourea for pure copper dissolution at 0.34 V SHE. (Fig 6-3, p102)

<table>
<thead>
<tr>
<th>Time second</th>
<th>Thiourea concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 mg/L</td>
</tr>
<tr>
<td>1</td>
<td>0.161±0.0002</td>
</tr>
<tr>
<td>10</td>
<td>0.143±0.0001</td>
</tr>
<tr>
<td>150</td>
<td>0.154±0.0001</td>
</tr>
<tr>
<td>250</td>
<td>0.158±0.0001</td>
</tr>
<tr>
<td>255</td>
<td>0.125±0.0001</td>
</tr>
<tr>
<td>350</td>
<td>0.125±0.0001</td>
</tr>
<tr>
<td>400</td>
<td>0.125±0.0001</td>
</tr>
<tr>
<td>500</td>
<td>0.125±0.0001</td>
</tr>
</tbody>
</table>

Comparison of dependence of the inhibition efficiency (%) on the concentration of thiourea in the presence of low and high concentration of sulfuric acid. (Fig. 6-4, p106)

<table>
<thead>
<tr>
<th>Thiourea concentration mg/L</th>
<th>Sulfuric acid concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 g/L</td>
</tr>
<tr>
<td>4</td>
<td>35.51±0.04</td>
</tr>
<tr>
<td>10</td>
<td>52.51±0.05</td>
</tr>
<tr>
<td>20</td>
<td>60.96±0.07</td>
</tr>
<tr>
<td>30</td>
<td>65.0±0.06</td>
</tr>
</tbody>
</table>
Inhibition efficiency (%) vs. varying concentration of thiourea corresponding to the pure copper RDE at a constant FDS concentration of 10 mg/L. (Fig. 6-7, p110)

<table>
<thead>
<tr>
<th>Thiourea conc. mg/L</th>
<th>FDS conc. mg/L</th>
<th>Inhibition efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>10</td>
<td>21.1±0.03</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>32.37±0.04</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>43.22±0.04</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>49.57±0.05</td>
</tr>
</tbody>
</table>

Anodic current density (A/cm²) vs. time with respect to thiourea injection for the pure copper dissolution. (Fig. 6-8, p116)

<table>
<thead>
<tr>
<th>Time second</th>
<th>Thiourea concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.155±0.002</td>
</tr>
<tr>
<td>10</td>
<td>0.154±0.002</td>
</tr>
<tr>
<td>150</td>
<td>0.154±0.002</td>
</tr>
<tr>
<td>250</td>
<td>0.153±0.002</td>
</tr>
<tr>
<td>255</td>
<td>0.152±0.001</td>
</tr>
<tr>
<td>300</td>
<td>0.152±0.001</td>
</tr>
<tr>
<td>400</td>
<td>0.152±0.002</td>
</tr>
<tr>
<td>500</td>
<td>0.151±0.001</td>
</tr>
</tbody>
</table>

Anodic current density (A/cm²) vs. time at varying concentrations of thiourea for impure copper dissolution. (Fig. 6-9, p117)

<table>
<thead>
<tr>
<th>Time second</th>
<th>Thiourea concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.147±0.001</td>
</tr>
<tr>
<td>10</td>
<td>0.124±0.001</td>
</tr>
<tr>
<td>150</td>
<td>0.130±0.001</td>
</tr>
<tr>
<td>250</td>
<td>0.111±0.000</td>
</tr>
<tr>
<td>300</td>
<td>0.099±0.000</td>
</tr>
<tr>
<td>350</td>
<td>0.099±0.000</td>
</tr>
<tr>
<td>400</td>
<td>0.099±0.000</td>
</tr>
<tr>
<td>500</td>
<td>0.099±0.000</td>
</tr>
</tbody>
</table>
Anodic current density (A/cm^2) vs. time with respect to thiourea injection for the impure copper dissolution. (Fig. 6-10, p120)

<table>
<thead>
<tr>
<th>Time second</th>
<th>0.5 mg/L</th>
<th>1.0 mg/L</th>
<th>2.0 mg/L</th>
<th>3.0 mg/L</th>
<th>4.0 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.180±0.002</td>
<td>0.180±0.002</td>
<td>0.180±0.002</td>
<td>0.180±0.002</td>
<td>0.180±0.002</td>
</tr>
<tr>
<td>10</td>
<td>0.149±0.002</td>
<td>0.149±0.002</td>
<td>0.149±0.002</td>
<td>0.149±0.002</td>
<td>0.149±0.002</td>
</tr>
<tr>
<td>150</td>
<td>0.149±0.002</td>
<td>0.149±0.002</td>
<td>0.146±0.001</td>
<td>0.146±0.002</td>
<td>0.147±0.002</td>
</tr>
<tr>
<td>250</td>
<td>0.149±0.002</td>
<td>0.148±0.002</td>
<td>0.143±0.002</td>
<td>0.144±0.002</td>
<td>0.146±0.002</td>
</tr>
<tr>
<td>300</td>
<td>0.148±0.001</td>
<td>0.144±0.002</td>
<td>0.138±0.001</td>
<td>0.138±0.001</td>
<td>0.134±0.002</td>
</tr>
<tr>
<td>350</td>
<td>0.147±0.001</td>
<td>0.143±0.002</td>
<td>0.135±0.001</td>
<td>0.128±0.001</td>
<td>0.121±0.001</td>
</tr>
<tr>
<td>400</td>
<td>0.146±0.001</td>
<td>0.141±0.001</td>
<td>0.135±0.001</td>
<td>0.127±0.001</td>
<td>0.121±0.001</td>
</tr>
<tr>
<td>500</td>
<td>0.144±0.001</td>
<td>0.141±0.001</td>
<td>0.135±0.001</td>
<td>0.127±0.001</td>
<td>0.121±0.001</td>
</tr>
</tbody>
</table>

Cathodic current density (A/cm^2) vs. time corresponding to copper deposition by injecting thiourea at concentrations varied from 0.5 to 4 mg/L. (Fig. 6-16, p131)

<table>
<thead>
<tr>
<th>Time second</th>
<th>0.5 mg/L</th>
<th>1.0 mg/L</th>
<th>2.0 mg/L</th>
<th>3.0 mg/L</th>
<th>4.0 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.436±0.005</td>
<td>0.425±0.004</td>
<td>0.431±0.005</td>
<td>0.435±0.004</td>
<td>0.440±0.002</td>
</tr>
<tr>
<td>25</td>
<td>0.403±0.002</td>
<td>0.404±0.003</td>
<td>0.406±0.003</td>
<td>0.408±0.002</td>
<td>0.408±0.003</td>
</tr>
<tr>
<td>300</td>
<td>0.406±0.006</td>
<td>0.406±0.002</td>
<td>0.410±0.006</td>
<td>0.409±0.003</td>
<td>0.413±0.003</td>
</tr>
<tr>
<td>600</td>
<td>0.435±0.003</td>
<td>0.440±0.007</td>
<td>0.446±0.004</td>
<td>0.440±0.007</td>
<td>0.446±0.004</td>
</tr>
<tr>
<td>900</td>
<td>0.485±0.007</td>
<td>0.485±0.004</td>
<td>0.484±0.005</td>
<td>0.483±0.005</td>
<td>0.486±0.005</td>
</tr>
<tr>
<td>910</td>
<td>0.430±0.003</td>
<td>0.378±0.006</td>
<td>0.261±0.002</td>
<td>0.222±0.001</td>
<td>0.175±0.001</td>
</tr>
<tr>
<td>960</td>
<td>0.558±0.006</td>
<td>0.379±0.003</td>
<td>0.259±0.002</td>
<td>0.223±0.001</td>
<td>0.176±0.001</td>
</tr>
<tr>
<td>1100</td>
<td>0.560±0.006</td>
<td>0.383±0.003</td>
<td>0.262±0.001</td>
<td>0.226±0.001</td>
<td>0.179±0.001</td>
</tr>
</tbody>
</table>
Appendix IV. AC Impedance Measurements and Validation of Experimental Impedance Data

The Kramers-Kronig (K-K) transforms have been widely used for determining the validity of experimental impedance data. However, the application of K-K transforms has been found to fail when the experimental systems show complicated combinations of equivalent circuits.

Urquidi-Mackonald et al.[1] showed that in a simple case of impedance, which is a circuit consisting of a resistance in series with a parallel combination of a resistance and a capacitance, an inappreciable difference between the experimental data and K-K transform data was observed at low frequencies. Mansfeld et al.[2] pointed out that K-K transforms cannot be used for many of electrochemical systems, such as inhibited solutions, polymer-coated metals and anodized surface. In these cases the impedance data do not reach a DC limit in the frequency range that is experimentally accessible.

These authors suggested that the K-K transforms are a purely mathematical result and do not depend upon the existence of any physical state. The integral converge must be conducted within frequency of $\omega = 0, \omega = \infty$.

In the present investigation, some general properties of the measured impedance spectra were checked. The impedance spectrum measured immediately after the immersion of the pure copper electrode in the electrolyte should be described accurately by a single RC term in series with the electrolyte resistance. Since the depressed capacitance loop appeared, the constant phase element had to be taken into account in order to obtain a satisfactory fit. A simplified version of analysis suggested by MacDonald[3] was used. The procedure can be described briefly as follows:

- The real part of the measured impedance spectra was fitted, using the real part of the Cole-Cole equation over the measured frequency range,
- The square of distances between the measured imaginary parts and the corresponding imaginary parts of the Cole-Cole equation was calculated over the measured frequency range.
- The relative deviation of the measured imaginary part from the imaginary part corresponding to the fitted real part of the response was obtained. With these values the error of fit was calculated by using the following equation:

\[ \text{error of fit} = \sum (\text{measured imaginary part} - \text{Cole-Cole imaginary part})^2 \]
\[ r = \frac{1}{N} \sum_{i=1}^{N} \left\{ \frac{(Z'_{(\omega_i)} - Z'_{(\omega_i)c})^2 + (Z''_{(\omega_i)} - Z''_{(\omega_i)c})^2}{Z_m} \right\}^{\frac{1}{2}} \]  

(III-1)

- where \( N \) is the number of points analyzed, \( Z'_{(\omega_i)m} \) and \( Z''_{(\omega_i)m} \) are the measured real part and imaginary part of impedance, \( Z'_{(\omega_i)c} \) and \( Z''_{(\omega_i)c} \) are the calculated real part and imaginary part of impedance. \[ |Z_m| = (Z'_m Z'_m + Z''_m Z''_m)^{\frac{1}{2}} \]

- The better the equivalent circuit model the lower the error of fitting. For all experimental conditions, the error of fitting was controlled less than 5 % for the chosen model.

The equivalent circuit model, with respect to the aged impure copper experienced active dissolution, can be expressed by the following impedance equation:

\[ Z_{\text{total}} = R_1 + \frac{1}{R_2 + \frac{1}{T_1} (j\omega)^{P_1}} + \frac{1}{R_3 + \frac{1}{T_2} (j\omega)^{P_2}} + \frac{R_4 \tanh[(jT\omega)^P]}{(jT\omega)^P} \]  

(III-2)

The equivalent circuit model, corresponding to the aged impure copper experienced passivation or active dissolution in the presence of thiourea, can be described as:

\[ Z_{\text{total}} = R_1 + \frac{1}{R_2 + \frac{1}{T_1} (j\omega)^{P_1}} + \frac{1}{R_3 + \frac{1}{T_2} (j\omega)^{P_2}} + \frac{1}{R_4 + j\omega L} \]  

(III-3)

where \( T_1 \) and \( T_2 \) – frequency independent parameters corresponding to CPE\(_1\) and CPE\(_2\) respectively, \( P_1 \) and \( P_2 \) – fractional elements corresponding to CPE\(_1\) and CPE\(_2\), respectively, \( R_1 \) the solution resistance, \( R_2 \) the polarization resistance, \( R_3 \) the slime interfacial resistance, \( R_4 \) the resistance of slime.
References

