Computational Simulation of Copper (Cu) and Nickel-Copper (Ni-Cu) Alloy Electrodeposition

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Materials Science & Engineering
University of Toronto

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Abstract

A study on the electrodeposition of Cu and Ni-Cu alloys in a Hull cell was conducted using both experimental and simulation approaches. For the simulation study a commercial software package, COMSOL Multiphysics, was chosen to explore the predictive power of electrodeposition process simulation. For the relatively simple Hull cell electrodeposition configuration, the agreement between the experimental results and the simulation results were excellent. In addition to Hull cell electrodeposition, the simulation was completed for a much more challenging and industrially highly relevant inner diameter (ID) tube plating configuration without considering bubble flow inside the tube. Different parameters, for instance, tube diameter, the Ni/Cu ion ratio in the plating bath, current density, volumetric flow rate, and cathode length were analyzed regarding their sensitivities. A relative high influence was observed for certain electrodeposition parameters.
Acknowledgments

I would like to express my sincerest gratitude to my supervisor, Professor Uwe Erb, for his generous guidance, support and help throughout my graduate study process. His profound knowledge and invaluable instruction enabled me to go through my research smoothly and develop a serious working attitude which will benefit me forever. Without his precious mentorship, this thesis would not have been possible.

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Last but not least, I wish to express my acknowledgment to my family and my friends for their tremendous encouragement and support in my study.
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<th>Definition</th>
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<tbody>
<tr>
<td>BSE</td>
<td>Backscattered electron</td>
</tr>
<tr>
<td>CE</td>
<td>Current efficiency</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>HCD</td>
<td>High current density</td>
</tr>
<tr>
<td>ID</td>
<td>Inner diameter</td>
</tr>
<tr>
<td>IS</td>
<td>Ionic strength</td>
</tr>
<tr>
<td>LCD</td>
<td>Low current density</td>
</tr>
<tr>
<td>OFAT</td>
<td>One-factor-at-a-time</td>
</tr>
<tr>
<td>PCD</td>
<td>Primary current distribution</td>
</tr>
<tr>
<td>PDEs</td>
<td>Partial differential equations</td>
</tr>
<tr>
<td>RANS</td>
<td>Reynolds-averaged Navier-Stokes</td>
</tr>
<tr>
<td>RCH</td>
<td>Rotating cylinder Hull</td>
</tr>
<tr>
<td>SCD</td>
<td>Secondary current distribution</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>TCD</td>
<td>Tertiary current distribution</td>
</tr>
<tr>
<td>TDS</td>
<td>Transport of diluted species</td>
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## List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$c$</td>
<td>Concentration</td>
</tr>
<tr>
<td>$c_b$</td>
<td>Bulk concentration</td>
</tr>
<tr>
<td>$c_s$</td>
<td>Cathode surface concentration</td>
</tr>
<tr>
<td>$c_O$</td>
<td>Effective concentration of oxidation species</td>
</tr>
<tr>
<td>$c_R$</td>
<td>Effective concentration of reduction species</td>
</tr>
<tr>
<td>$C_\mu, C_{\varepsilon 1}, C_{\varepsilon 2}$</td>
<td>Constant values in $k$-$\varepsilon$ model</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$D_H$</td>
<td>Hydraulic diameter</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Pre-exponential factor of the diffusion coefficient</td>
</tr>
<tr>
<td>$E$</td>
<td>Electrode potential</td>
</tr>
<tr>
<td>$E^0$</td>
<td>Standard electrode potential at 25°C</td>
</tr>
<tr>
<td>$E_{abs}$</td>
<td>Absolute electrode potential</td>
</tr>
<tr>
<td>$E_{diff}$</td>
<td>Diffusion activation energy</td>
</tr>
<tr>
<td>$E_{eq}$</td>
<td>Equilibrium electrode potential</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>$\mathbf{F}$</td>
<td>Viscous stress tensor</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>$\Delta G^0$</td>
<td>Standard Gibbs free energy</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$I$</td>
<td>Ionic strength</td>
</tr>
<tr>
<td>$I_{tot}$</td>
<td>Total applied current</td>
</tr>
<tr>
<td>$i(x)$</td>
<td>Local current density at $x$</td>
</tr>
<tr>
<td>$i_0$</td>
<td>Exchange current density</td>
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<tr>
<td>$i_{avg}$</td>
<td>Average current density over the cathode surface</td>
</tr>
<tr>
<td>$i_l$</td>
<td>Current density in the electrolyte</td>
</tr>
<tr>
<td>$i_s$</td>
<td>Current density in the electrode</td>
</tr>
<tr>
<td>$k$</td>
<td>Pre-exponential factor</td>
</tr>
<tr>
<td></td>
<td>Turbulent kinetic energy</td>
</tr>
<tr>
<td>$K$</td>
<td>Electrode reaction rate constant</td>
</tr>
<tr>
<td>$L$</td>
<td>Length of the pipe</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons transferred during the reaction</td>
</tr>
<tr>
<td>$N$</td>
<td>Mass transport flux</td>
</tr>
<tr>
<td>$N_D$</td>
<td>Diffusion flux</td>
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<tr>
<td>$p$</td>
<td>Fluid pressure</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynold number</td>
</tr>
<tr>
<td>$s$</td>
<td>Cathode surface</td>
</tr>
</tbody>
</table>
\( T \) Absolute temperature

\( t \) Time

\( u \) Velocity of electrolyte

\( \mathbf{u} \) Liquid flow rate perpendicular to the electrode surface

\( v \) Electrode reaction rate

\( w_{\text{Ni}} \) Ni composition

\( w_{\text{Ni}'} \) Corrected Ni composition

\( W_{aT} \) Tafel Wagner number

\( x \) Normalized cathode surface coordinate

\( X \) Cathode surface distance

\( z \) Valence number

\( \alpha_a \) Anodic transfer coefficient

\( \alpha_c \) Cathodic transfer coefficient

\( \beta_{bqrs} \) Overall stability constants

\( \beta_c \) Cathodic Tafel slope

\( \delta \) Diffusion layer thickness

\( \delta_{\text{avg}} \) Average electrodeposit thickness over the cathode surface

\( \epsilon \) Characteristic length for the definition of the Wagner numbers

\( \varepsilon \) Turbulent dissipation rate
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>$\eta$</td>
<td>Overpotential</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Fluid dynamic viscosity</td>
</tr>
<tr>
<td>$\mu_T$</td>
<td>Turbulent viscosity</td>
</tr>
<tr>
<td>$\mu_m$</td>
<td>Mobility of ion</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Fluid kinetic viscosity</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Surface normal</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>Electrolyte conductivity</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>Electrode conductivity</td>
</tr>
<tr>
<td>$\sigma_K, \sigma_\varepsilon$</td>
<td>Constant values in $k-\varepsilon$ model</td>
</tr>
<tr>
<td>$\phi^l$</td>
<td>Electric potential of electrolyte</td>
</tr>
<tr>
<td>$\phi^s$</td>
<td>Electric potential of electrode</td>
</tr>
</tbody>
</table>

**Subscript**

- $aq$: Aqueous
- $b$: Bulk
- $i$: Species $i$
- $g$: Gas
- $s$: Solid
Chapter 1

Introduction

Copper (Cu) and copper alloys are widely used materials because of their excellent properties. In particular, nickel-copper (Ni-Cu) alloys, especially the commercial Monel alloy which typically contains 67% nickel and 30% copper, have been well known for a long time because of their unique properties, such as excellent corrosion resistance, high ductility, reasonable strength, and temperature tolerance [1], [2].

In order to improve the properties of certain materials, chemical or physical modifications are often required. Surface treatments are widely used to obtain better performance in terms of desired appearance, corrosion resistance, and erosion resistance. Various approaches are available as surface treatment processes, including cold spray [3], laser cladding [4], magnetron sputtering [5], plasma transferred arc deposition [6], physical vapor deposition [7] and chemical vapor deposition [8]. Compared to these approaches, electrodeposition is the most popular treatment process to produce required functional coatings with a thickness ranging from fractions of a micrometer up to some tens or even hundreds of micrometers [9]. Electrodeposition has the advantages of operating at low temperature, relatively low cost [10], [11], and simple set-up without the need for high vacuum or high temperature environments [12]. In the industrial production, the adaptability of electrodeposition is of great importance when dealing with substrates with complex geometries. Also, the electrodeposition process is very repeatable as long as the operating parameters are consistent with the technical requirements. Other benefits of electrodeposition are the easy control of the coating thickness, uniform deposit, scalability [10] and precise tailoring of the alloy composition by varying the working potential or the current density during the process [12].

Cu electrodeposition was first introduced in the early 19th century. Because of its excellent performance, electrodeposited copper has a broad range of applications such as decorative coatings, printed circuit boards, heat transfer components, and automotive parts (Figure 1-1). Ni-Cu alloy made by the electrodeposition process can obtain better properties in terms of hardness and strength because Ni in Cu provides solid solution hardening [13].
Figure 1-1. Copper coating applications in heat transfer component (left)[14] and printed circuit boards (right)[15]

1.1 Fundamentals of Electrodeposition

Electrodeposition focusses on the relationship between electricity and chemical change, or more specifically, on the conversion between electrical energy and chemical energy. A typical electrodeposition setup consists of an external electric circuit and internal electrolyte as shown in Figure 1-2. During operation, electrodes are immersed into the electrolyte with an electrical current passing through. The electrode connected to the positive terminal of the power supply is the anode, while the cathode is the electrode where the object to be plated and is connected to the negative terminal.

Figure 1-2. Schematic drawing of electrodeposition

Oxidation reaction will occur at the anode, for example, the oxidation of metal (1.1) or the oxygen evolution from water electrolysis (1.2):

\[ M_{(s)} \rightarrow M^+ + e^- \]  
\[ 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \]
At the cathode, metal ions in the electrolyte are reduced to metal (1.3) or hydrogen is generated from the reduction of protons or water (1.4):

\[ M^+ + e^- \rightarrow M_{(s)} \]  
\[ 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \]  

### 1.2 Experimental Approaches in Electrodeposition

Considering the benefits of electrodeposition as an effective surface modification technology, extensive studies have been carried out for many decades in order to develop the practical operation conditions for various deposition processes. Traditionally, there are several experimental approaches that can be applied to investigate the influence of different parameters on plating results. The conventional methodology of experimentation is the one-factor-at-a-time (OFAT) approach which evaluates the effect of a single factor or variable within each experiment by fixing the other parameters at the constant level. This classical approach can enable non-experts to carry out research without having a strong background of complex multi-factor analysis. But it is difficult with this approach to figure out the interactions among the variables and give a reasonable precision in the influence estimation of that particular variable. Because of these shortcomings, the optimization of the electrodeposition process from OFAT is impossible. Instead of OFAT, a much more scientific method regarding the optimization of multiple factors is the factorial/full factorial experimental design, which was first used in the 19th century by John Bennet Lawes and Joseph Henry Gilbert of the Rothamsted Experimental Station [16]. In a factorial design, multiple factors (two or more) with discrete levels are involved in the research and the main effect of each factor, as well as the interactions among the factors, are investigated by experiments. Different from the OFTA, all the factors in factorial design will change simultaneously in each experiment based on a carefully designed matrix. From the analysis of the results, the factorial design is capable to confirm the interactions of various factors and develop the optimal conditions in an efficient and powerful way. But considering the large number of variables or factors in the electrodeposition process such as ion concentration, current density, potential, temperature, pH, time, solution conductivity and electrolyte flow, it can be very challenging to determine an optimized process configuration by experiments alone. For example, considering a system containing 3 components with different ion concentrations, combining with all the other 7 factors, there will be at least 10
factors that need to be examined. Even if only two levels (high and low) for each factor are considered in the factorial design, there will be $2^{10}$ (or 1052) possible combinations for the experiments. Such a large amount of experiments makes this approach unfeasible in terms of time and cost. Because of the challenge by using the experimental method only, modeling and numerical simulation are becoming more attractive.

1.3 Modeling and Numerical Simulation

Modeling and numerical simulation didn’t exist until the 1940s. However, thanks to computers these fields saw a rapid development since the 1980s. Modeling is a mathematical representation of a system, which can indicate its function by equations from well-known laws of physics. With the exception of a few models, most models, due to their complexity such as multiple partial differential equations (PDEs), are very unlikely to be calculated based on analytical solutions. In this case, the numerical simulation will be unavoidable. With the innovation in digital tools especially computers, the benefits of modeling and numerical simulation are increasingly recognized. Simulation can be a much cheaper testing method compared to live experiments because no real or prototype products, measurement equipment, materials, and technicians are needed. In addition to that, more “measurements” and data are achievable simultaneously through simulation which will be either untestable or very time-consuming from experiments [17].

Specifically, the modeling and simulation method is also a cost-effective way of describing the behavior of the electrodeposition processes. Various process variables, for instance, current density, electrode potential, temperature, concentration and geometric configuration of the electrodeposition container can be included in the simulation software packages which are commercially available today. This has reshaped and expanded the application of traditional mathematical models which mostly focused on the current distribution pattern over some simplified geometries such as rotating discs or flat panels [18]. Currently, there are several commercial software packages available including Elsyca and COMSOL Multiphysics (COMSOL Ab, Stockholm, Sweden) which can be used for simulations.

However, having the advantages of numerical simulation does not necessarily mean that real experiments are no longer needed. On the contrary, the simulation will reduce the amount of experimental work but not completely replace it. In fact, many parameters required for the
simulation must be obtained through various experiments, and the adaptability of the simulation needs to be verified by different experiments as well.

1.4 Research Objective and Scope

The objective of this research is to establish electrodeposition models for Cu and Ni-Cu alloys including validation of the electrochemistry function of the software package, experimental verification of models, and prediction of electrodeposition results. The research findings are to support the design and scale-up of a very specific electrodeposition process - inner diameter (ID) tube plating. This deposition process is of particular interest to our industrial partner - Integran Technologies Inc. (Mississauga, ON, Canada) - to assess electrodeposition of Ni-Cu alloy inside a tube under different conditions, so as to provide a guideline to the application of an inner tube electrodeposition process. The effect of the various electrodeposition process variables together with electrolyte flow patterns will be studied. For this study, COMSOL Multiphysics with the Electrodeposition Module and CFD Module were selected because of COMSOL’s ability to couple the electrodeposition and flow to investigate the process of electrodeposition. The simulation of the electrodeposition process of Ni–Cu alloy has never been reported before by using similar software packages. This research is therefore novel and unique.

Initial experiments were first carried out for Cu and Ni-Cu alloy electrodeposition in the traditional Hull cell as shown in Figure 1-3 to obtain some required input parameters.

![Figure 1-3. Schematic drawing of the Hull cell](image)

The Hull cell is a trapezoidal electrodeposition container composed of two nonparallel electrodes and two insulating walls [19]. Because of the tilt of the cathode with respect to the anode, various distances between the electrodes can be achieved which will in turn result in the wide range of
current densities on the cathode surface. High current density, or HCD, is achieved at the edge nearest to the anode. On the other hand, the edge furthest to the anode will have a low current density, or LCD. The Hull cell allows the investigation of the influence of a range of current densities in a single test and is routinely used in electrodeposition experimentation [19].

The Hull cell electrodeposition process was modeled using COMSOL followed by a comparison with the experimental results in terms of coating composition, thickness, weight, current density distribution and metal ion concentration in the bath during the process of the experiments.

In addition to the Hull cell, simulation of the Ni-Cu electrodeposition process for the ID tube plating was also performed. Figure 1-4 shows a schematic drawing of the plating system. The tube wall acts as the cathode, while the anode was placed concentrically inside the tube. The electrolyte flows in the gap between the electrodes from bottom to top.

![Schematic drawing of ID tube Ni-Cu alloy plating](image)

**Figure 1-4. Schematic drawing of ID tube Ni-Cu alloy plating**

However, it is important to note that the simulation completed in this study regarding the ID plating did not consider the influence of bubble flow inside the electrolyte which is present during the industrial production. Therefore, the ID electrodeposition simulation results are only preliminary and need to be studied in further work with bubble flow involved.
Nevertheless, the results obtained from both the Hull Cell and the ID electrodeposition are expected to verify the capability of the COMSOL software package for electrodeposition simulation and develop guidelines for manufacturing industries and facilitate commercial electrodeposition of Ni-Cu alloy metal coatings.

1.5 Thesis Organization

This thesis is organized as follows. Chapter 2 will focus on the literature review to give detailed background information regarding the Cu and Ni-Cu electrodeposition in the Hull cell and modeling as well. Plating bath specifications and variables will be discussed here. For the alloy deposition, the influence of various complexing agents is provided in more depth. An introduction to the experimental configuration in terms of the specification of the Hull cell, the electrode material, power supply, along with the electrolyte used and the different agitation methods will be presented in Chapter 3 for the Cu and Ni-Cu alloy deposition, respectively. Chapter 4 presents the modeling set-up. Governing equations for electrodeposition will be introduced, as well as the flow pattern and the k-ε model used to describe turbulent flow conditions. In addition, the specific set-up in COMSOL is given regarding the geometry, diffusion layer and meshing. Then the results and discussion for Cu and Ni-Cu alloy electrodeposition will be presented for both experiments and simulation in Chapters 5. Some key features, for example, the composition, thickness, and weight of the deposits will be compared between the simulation results in the Hull cell and the experimental results. The simulation results will also be presented for the ID plating. Chapter 6 will summarize all the conclusions from the study followed by some recommendations for future work in Chapter 7.
Chapter 2

2 Theoretical Background and Literature Review

This chapter will provide the fundamental information of electrodeposition, and also review previous research regarding experimental and modeling work of Cu and Ni-Cu alloy electrodeposition processes. In addition, some results of previous applications of the COMSOL software package in electrodeposition simulation [20], [21], [22] will also be provided.

2.1 Principle of Electrodeposition

The electrodeposition process can be characterized by its thermodynamics, kinetics, and current distribution classes, which are summarized in various studies [23], [24].

2.1.1 Thermodynamics of Electrodeposition

Thermodynamics deals with the study of parameters at equilibrium conditions. Key parameters regarding the thermodynamics of electrodeposition include the electric potential, $\phi$, electrode potential, $E$, and exchange current density, $i_0$.

When an electrode is immersed into the electrolyte, because of the difference in the conductivity, the electric potential of the electrolyte and electrode at the solid-liquid interface gives the absolute electrode potential $E_{abs}$ as:

$$E_{abs} = \phi^s - \phi^l$$

(2.1)

where $\phi^s$ and $\phi^l$ are the electric potential of electrode and electrolyte, respectively.

Although $E_{abs}$ cannot be measured directly, by considering a reference electrode such as the standard hydrogen electrode (SHE), the relative electrode potential, $E$, which is the difference of the absolute value between the specific electrode and reference electrode can be used as the “real” electrode potential. Based on the electrode potential, the standard electrode potential, $E^0$, is derived as the potential of a reversible electrode at standard state with an effective ion concentration of 1M at the pressure of 1atm and the temperature of 25°C. When the equilibrium state deviates from the standard state, for the half-cell reaction of the electrode:
\[
O_x + ne \rightleftharpoons R_{ed}
\]

where \(O_x\) is the oxidation species, \(R_{ed}\) is the reduction species, \(n\) is the number of electrons transferred during the reaction, \(\bar{i}\) and \(\bar{i}\) are the reduction and oxidation current densities, respectively.

The more practical equilibrium potential, \(E_{eq}\), of a specific half-cell reaction can be calculated by equation (2.3)

\[
E_{eq} = E^o + \frac{2.3RT}{nF}\log \frac{c_O}{c_R}
\]

where:
- \(R\) is the universal gas constant, 8.314 J·mol\(^{-1}\)·K\(^{-1}\)
- \(T\) is the absolute temperature, K
- \(F\) is the Faraday constant, 96485 C·mol\(^{-1}\)
- \(c_O\) is the effective concentration of the oxidation species, mol·L\(^{-1}\), and
- \(c_R\) is the effective concentration of the reduction species, mol·L\(^{-1}\)

For the redox half-cell reaction of (2.2), the net current density of electrode, \(i\), can be expressed as:

\[
i = \bar{i} - \bar{i}
\]

At the equilibrium potential, no apparent current density can be overserved on the electrode, but that doesn’t necessarily mean the value of \(\bar{i}\) and \(\bar{i}\) are zero. The reduction current is balanced by the oxidation current. This ongoing current density in both directions is called the exchange current density, \(i_0\).

### 2.1.2 Kinetics of Electrodeposition

Thermodynamics only provides the possibility of an electrochemical reaction but without any indication of the reaction rate. Also in the practical applications, the reactions will proceed at non-equilibrium state which thermodynamics theory cannot deal with. Therefore, kinetics is adopted
to study the mechanism of electrodeposition. Typical parameters involved are overpotential, \( \eta \), and current density, \( i \).

(1) Overpotential

When current is passing through the electrodeposition circuit, electrons will move from the anode to the cathode as shown in Fig. 1-1. If the electrons are removed from the anode faster than the rate of electrochemical reaction at the anode, a depletion of electrons occurs at the anode which will change the equilibrium state of the electrode and shift the potential to a more positive value. In this state, the electrode is called “polarized”. The same occurs at the cathode, when more electrons come to the surface compared to the number of electrons that are consumed by the reaction, the buildup of electrons will also polarize the cathode with a more negative potential. The shift in the electrode potential from the equilibrium value is the overpotential which can be easily calculated by equation (2.5):

\[
\eta = E - E_{eq}
\]  

(2.5)

(2) Current density

The current density by which the reaction rate is characterized is essential for both electrolyte and electrode. Based on various mechanisms, the current density in the electrolyte, at the interface of electrolyte and electrode, and in the electrode can be presented by different equations.

- Electrolyte

In the electrolyte, the current density is proportional to the mass transport flux, \( N \), as equation (2.6):

\[
i_l = F \sum z_i N_i
\]  

(2.6)

where \( i_l \) is the current density in the electrolyte, \( A \cdot m^{-2} \), \( z_i \) is the valence of species \( i \), and \( N_i \) is the flux of species \( i \), \( mol \cdot m^{-2} \cdot s^{-1} \).

Regarding the flux, three main mechanisms, namely migration, convection and diffusion, need to be considered. The total flux can be described by the Nernst-Planck equation:
\[ N = \sum N_i = \sum (-D_i \nabla c_i + c_i \mu_{m,i} \nabla \phi_i + c_i u) \]  \hspace{1cm} (2.7)

where:

- \( D_i \) is the diffusion coefficient of species \( i \), \( \text{m}^2 \cdot \text{s}^{-1} \)
- \( c_i \) is the concentration of species \( i \), \( \text{mol} \cdot \text{m}^{-3} \)
- \( \mu_{m,i} \) is the mobility of species \( i \), \( \text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1} \)
- \( u \) is the liquid flow rate perpendicular to the electrode surface, \( \text{m} \cdot \text{s}^{-1} \)

So the current density in the electrolyte can be rewritten as:

\[ i_l = F \sum z_i N_i = -F \sum D_i z_i \nabla c_i - F \nabla \phi_i \sum z_i \mu_{m,i} c_i + Fu \sum z_i c_i \]  \hspace{1cm} (2.8)

In general, the electrolyte exhibits the electroneutrality property which means \( \sum z_i c_i = 0 \), so \( i_l \) can be calculated by (2.9):

\[ i_l = F \sum z_i N_i = -F \sum D_i z_i \nabla c_i - F \nabla \phi_i \sum z_i \mu_{m,i} c_i = -F \sum D_i z_i \nabla c_i - \sigma_i \nabla \phi_i \]  \hspace{1cm} (2.9)

where \( \sigma_i \) is the electrolyte conductivity, \( \text{S} \cdot \text{m}^{-1} \).

If the electrolyte is well agitated or continuously refreshed without experiencing any mass transport control, there is no concentration gradient in it which renders (2.10) as the expression of Ohm’s law:

\[ i_l = -\sigma_i \nabla \phi_i \]  \hspace{1cm} (2.10)

**Electrode-electrolyte Interface**

Different from the electrolyte, the current density distribution at the electrode-electrolyte interface has another mechanism. Since the current transfer is realized through the chemical reactions on the surface of the electrode, chemical kinetics is used to first describe the rate. Taking the cathode as an example, the net current density at the interface can be derived based on (2.4):

\[ i = \bar{i} - \bar{i} = nF \bar{\nu} - nF \bar{\nu} = nF \bar{\nu} c_o \exp \left( -\frac{\Delta G}{RT} \right) - nF \bar{\nu} c_o \exp \left( -\frac{\Delta G}{RT} \right) \]  \hspace{1cm} (2.11)
where:

- \( v \) is the electrode reaction rate, mol·m\(^{-2} \cdot s^{-1} \)
- \( k \) is the pre-exponential factor
- \( \Delta G \) is the Gibbs free energy, J·mol\(^{-1} \)

For the electrochemical reaction, activation energy has the following relationship with the electrode potential for reduction (2.12) and oxidation (2.13) reactions:

\[
\text{Reduction reaction: } \Delta \overline{G} = \Delta G^0 + \alpha_c FE \tag{2.12}
\]

\[
\text{Oxidation reaction: } \Delta \overline{G} = \Delta G^0 - \alpha_a FE \tag{2.13}
\]

And, \( \alpha_a + \alpha_c = n \) (2.14)

where: \( \Delta G^0 \) is the standard Gibbs free energy, \( \alpha_c \) and \( \alpha_a \) are the cathodic transfer coefficient and anodic transfer coefficient, respectively,

substituting (2.12) and (2.13) into (2.11), the net current density is changed to:

\[
i = i - \bar{i} = nF\bar{K}c_o\exp\left(-\frac{\alpha_c FE}{RT}\right) - nF\bar{K}c_R\exp\left(\frac{\alpha_a FE}{RT}\right) \tag{2.15}
\]

where \( K \) is the electrode reaction rate constant, \( K = k\exp\left(-\frac{\Delta G^0}{RT}\right) \).

At equilibrium state, for the reverse reaction of (2.2), \( i \) equals to zero, thus \( i_0 \) can be expressed as (2.16):

\[
i_0 = \bar{i}_0 = \bar{t}_0 = nF\bar{K}c_{O,b}\exp\left(-\frac{\alpha_c FE_{eq}}{RT}\right) = nF\bar{K}c_{R,b}\exp\left(\frac{\alpha_a FE_{eq}}{RT}\right) \tag{2.16}
\]

where the subscript \( b \) means bulk.

Substituting equation (2.5) and (2.16) into (2.15), the general kinetic equation (2.17) can be derived to predict the current density on the cathode at non-equilibrium state when both electron transfer and diffusion control are applied. When the mass transfer is slow compared to the reaction, the reactant concentration will show a gradient at least in the vicinity of the electrodes.
\[ i = i_0 \left[ \frac{c_{O,b}}{c_{O,b}} \exp \left( -\frac{\alpha c F \eta}{RT} \right) - \frac{c_R}{c_{R,b}} \exp \left( \frac{\alpha R F \eta}{RT} \right) \right] \]  
\text{(2.17)}

When the mass transfer condition or the diffusion influence can be neglected because of, for example, excess reactant bulk concentration, high temperature or vigorous mixing, the reaction is only controlled by electron transfer. Equation (2.17) will become the Butler-Volmer equation (2.18).

\[ i = i_0 \left[ \exp \left( -\frac{\alpha c F \eta}{RT} \right) - \exp \left( \frac{\alpha R F \eta}{RT} \right) \right] \]  
\text{(2.18)}

- **Electrode**

In general, the electrode is the metallic conductor which has very high conductivity. During electrodeposition, only electrons are transferred from or to the electrode. Current density in the electrode follows Ohm’s law which can be defined as:

\[ i_s = -\sigma_s \nabla \phi^s \]  
\text{(2.19)}

where \( \sigma_s \) is the electrode conductivity, S·m\(^{-1}\)

### 2.1.3 Current Distribution Classification

Considering different mechanisms, current distribution can be defined into 3 classes [9]: primary current distribution (PCD), secondary current distribution (SCD) and tertiary current distribution (TCD), which are summarized in Table 2-1.

Because only materials with high conductivity will be used as the electrode, current distribution inside the electrode will always follow Ohm’s law as shown in (2.19). Current distribution in the electrolyte or at the interface, however, can be characterized by different equations depending on the diffusion flux and the electrochemical reaction rate.

If the electrolyte contains excessive reactants and has excellent diffusion conditions such as vigorous mixing, the gradient in the concentration in the diffusion layer can be neglected. Therefore, the current density distribution in the electrolyte will also follow Ohm’s law, equation (2.10). Furthermore, when the electrochemical reactions at the electrode-electrolyte interface are very fast, or the influence of electrode polarization is unimportant, the electrode can be considered
as a reversible one which has the same potential value as $E_{eq}$. In this case, the current density distribution is PCD which depends on the geometry of the cell only.

If the reaction rate is not too fast to be ignored, electrode polarization or overpotential has to be considered. When the concentration effect in the diffusion layer is still negligible, the current distribution which is influenced by both effects of the electrochemical reaction and the cell geometry is called SCD.

By taking the concentration gradient within the diffusion layer into consideration, together with the effects of electrochemical reaction and geometry, TCD can be obtained.

### Table 2-1 Current Distribution Classes

<table>
<thead>
<tr>
<th>Class</th>
<th>PCD</th>
<th>SCD</th>
<th>TCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>$i_s = -\sigma_s \nabla \phi^s$</td>
<td>$i_s = -\sigma_s \nabla \phi^s$</td>
<td>$i_s = -\sigma_s \nabla \phi^s$</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>$i_l = -\sigma_l \nabla \phi^l$</td>
<td>$i_l = -\sigma_l \nabla \phi^l$</td>
<td>$i_l = -F \sum D_i z_i c_i - \sigma_l \nabla \phi^l$</td>
</tr>
<tr>
<td>Interface</td>
<td>$E = E_{eq}$</td>
<td>$i = i_0 \left[ \exp \left( -\frac{\alpha_d F \eta}{RT} \right) - \exp \left( \frac{\alpha_d F \eta}{RT} \right) \right]$</td>
<td>$i = i_0 \left[ \frac{c_o}{c_o,b} \exp \left( -\frac{\alpha_d F \eta}{RT} \right) - \frac{c_R}{c_R,b} \exp \left( \frac{\alpha_d F \eta}{RT} \right) \right]$</td>
</tr>
</tbody>
</table>

### 2.2 Copper Electrodeposition

#### 2.2.1 Bath Composition

Different types of electrodeposition baths are available for copper electrodeposition, including cyanide copper, pyrophosphate copper and acid copper [18]. Although cyanide copper solution is still used in many commercial plating processes, the relatively high toxicity problem more and more limits its application. As a consequence, the acid copper bath is becoming more attractive for copper deposition. Within the group of acidic copper solutions, sulfuric acid ($H_2SO_4$) and sulfate-based ($CuCO_4$) solution is most popular in industrial applications as well as in academic research.

Typically, the $CuSO_4/H_2SO_4$ solution process is determined by the concentration of $CuSO_4$ and $H_2SO_4$, bath conductivity, temperature and pH. Nelissen et al. [25] reported a composition of 0.3M $CuSO_4 + 1M H_2SO_4$ and operated under different current densities. A solution containing 0.56M $CuSO_4\cdot5H_2O$ and 1.4M $H_2SO_4$ was chosen by Pantleon et al. [26] to investigate the electrodeposition of Cu onto silicon wafer surfaces. In order to recover copper from acidic
solutions, Shirvanian et al. [27] prepared an electrolyte with very low CuSO$_4\cdot$5H$_2$O concentration of 0.016M and 1M H$_2$SO$_4$ at various temperatures and pH values. They found copper recovery was more efficient at low pH around 2.5 and low temperature of 20°C. Three solutions with distinct compositions were analyzed by Mattsson et al. [28] at 30°C. H$_2$SO$_4$ in the solutions was maintained as 1M, while the concentration of CuSO$_4$ varied as 1M, 0.15M and 0.022M. In order to study the copper electrowinning process, Leahy et al. [29] operated with a solution consisting of 0.8M CuSO$_4$ and 1.7M H$_2$SO$_4$ at 50°C and two current densities. Different from these studies in which the concentration of CuSO$_4$ was less than that of H$_2$SO$_4$, Chassaing et al. [30] used a bath containing 1.25 M CuSO$_4$ and only 0.5M H$_2$SO$_4$ at 26°C in order to prevent any diffusion control during copper deposition. From the above-mentioned bath formulations, it is obvious that the composition of the acidic copper plating bath is relatively flexible, and that plating at the room temperature can be used.

Furthermore, acidic solutions with a complexing agent such as citrate ion (C$_6$H$_5$O$_7^{3-}$) or chloride ion (Cl$^-$) can also be found in the literature. For example, Rode et al. [31] reported a plating bath with 0.5M CuSO$_4$ and 0.5 to 0.8M C$_6$H$_5$O$_7^{3-}$. Due to the weak acidity of C$_6$H$_5$O$_7^{3-}$, the solution pH was around 5. Sometimes a trace amount Cl$^-$ as low as 10$^{-5}$ M was added to the solution to catalyze the reduction of the copper ion (Cu$^{2+}$) [32].

2.2.2 Electrolyte Conductivity

For the electrodeposition process, the conductivity of the electrolyte is critical considering the energy consumption during the operation. Also, this parameter is required in the modeling, therefore it is important to review the literature on electrolyte conductivity.

Price et al. [33] measured the electrical conductivities of various CuSO$_4$/H$_2$SO$_4$ solutions in the application of modern electrorefining and electrowinning electrolytes. From their results, the H$_2$SO$_4$ concentration has a significant influence on the conductivity because of the presence of H$^+$ in the solution. Higher H$_2$SO$_4$ concentration in the solution will give an increase in the conductivity. A similar result was reported by Shirvanian et al. [27] when comparing the recovery efficiency of Cu at various pH values. Purcar et al. [34] reported an electrolyte consisting of CuSO$_4$ at 25°C with the conductivity of 23.2 S·m$^{-1}$ but no detailed composition was given in his study. The conductivity of the CuSO$_4$/H$_2$SO$_4$ system at different Cu ion and H$_2$SO$_4$ concentrations and temperatures, as well as more complex solutions with impurities, were investigated by Subbaiah
and Das [35]. Their work also showed a high positive correlation between the conductivity and the H$_2$SO$_4$ concentration. At the same time, an increase of Cu ion concentration (from 1.04 to 43.5 g·L$^{-1}$) was found to gradually lower the conductivity when the H$_2$SO$_4$ concentration was maintained as constant (151.3 g·L$^{-1}$). From their measurement results, this was due to the fact that the diffusion coefficient of Cu$^{2+}$, D$_{Cu}$, decreased significantly from 1.192×10$^{-9}$ to 0.856×10$^{-9}$ m$^2$·s$^{-1}$ with increasing concentration. This decrease may be caused by the interaction forces among the diffusing species, the hydration phenomena in the solution, and the increase of viscosity of the bath. The diffusion coefficient directly affected the ion mobility, which in turn affected the solution conductivity. They also studied the conductivities of complex solutions containing metallic impurities like Fe$^{2+}$, Fe$^{3+}$, Mn, Co, and Ni. An empirical equation was provided as well to calculate the conductivities considering the impurities. Table 2-2 summarized the conductivities obtained from these studies.

Table 2-2 Literature Studying of Electrical Conductivity of CuSO$_4$+H$_2$SO$_4$ Baths

<table>
<thead>
<tr>
<th>Cu$^{2+}$ concentration (g·L$^{-1}$)</th>
<th>H$_2$SO$_4$ concentration (g·L$^{-1}$)</th>
<th>Temperature (°C)</th>
<th>Conductivity (S·m$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>137</td>
<td>27</td>
<td>43.1</td>
<td>[26]</td>
</tr>
<tr>
<td>25</td>
<td>71.70</td>
<td>25</td>
<td>25.4</td>
<td>[33]</td>
</tr>
<tr>
<td>40</td>
<td>52.58</td>
<td>25</td>
<td>18.6</td>
<td>[33]</td>
</tr>
<tr>
<td>/</td>
<td>/</td>
<td>25</td>
<td>23.2</td>
<td>[34]</td>
</tr>
<tr>
<td>43.5</td>
<td>151.3</td>
<td>30</td>
<td>48.5</td>
<td>[35]</td>
</tr>
<tr>
<td>4.89</td>
<td>46.8</td>
<td>30</td>
<td>28</td>
<td>[35]</td>
</tr>
</tbody>
</table>

2.2.3 Ion Diffusivity

The diffusivity of cupric ions has an important influence on the transfer of ions from the anode to the cathode, especially at the surface of the cathode. Regarding the ion transport in the electrolyte, three types of transport will be taken into consideration: convection, migration, and diffusion. Although convection is critical for the transport in the bulk, its function within the boundary layer or Nernst diffusion layer, which is very close to the cathode surface can be neglected [36]. From kinetic studies, migration and diffusion will contribute most to the transport in the diffusion layer. The effect of migration can be derived from conductivity, while the diffusion influence requires the measurement of the diffusion coefficient.
Subbaiah et al. [35] conducted measurements of $D_{Cu}$ in CuSO$_4$+H$_2$SO$_4$ solutions by varying the concentration of Cu$^{2+}$ (1.04~43.5 g·L$^{-1}$), H$_2$SO$_4$ (46.8~450 g·L$^{-1}$) and temperature (20~60°C). An empirical equation (2.20) was developed using the experimental data:

$$D_{Cu}=10^{-5} \times (-0.57-0.00164 \text{H}_2\text{SO}_4 (\text{g} \cdot \text{L}^{-1})-0.00175 \text{Cu} (\text{g} \cdot \text{L}^{-1})+0.0607 (\text{°C})) \text{ cm}^2 \cdot \text{s}^{-1} \quad (2.20)$$

Hinatsu et al. [37] investigated $D_{Cu}$ at 25°C in 0.51M H$_2$SO$_4$ by using a wide range of CuSO$_4$ concentrations from 0.4mM to 1M. They suggested a constant $D_{Cu}$ for [CuSO$_4$] < 0.002M and an equation (2.21) to calculate $D_{Cu}$ for other CuSO$_4$ concentrations as:

$$D_{Cu}=10^{-6} \times (6.33+2.69 \log[\text{CuSO}_4]+1.62 \log^2[\text{CuSO}_4]+0.256 \log^3[\text{CuSO}_4]) \text{ cm}^2 \cdot \text{s}^{-1} \quad (2.21)$$

Quickenden and Jiang [38], [39] considered the influence of relative low Cu$^{2+}$ concentration in their work and determined the $D_{Cu}$ at 25°C. They first [38] measured $D_{Cu}$ as (7.35±0.18-(5.3±1.4) [CuSO$_4$]$^{1/2}$) × 10$^{-10}$ m$^2$·s$^{-1}$ for 0 < [CuSO$_4$] < 0.05M. In another paper [39], a value of $D_{Cu}$ as (7.80±0.25-(6.34±1.03) [Cu$^{2+}$]$^{1/2}$) × 10$^{-10}$ m$^2$·s$^{-1}$ was given for Cu$^{2+}$ concentration between 0 and 0.02M in 0.1M H$_2$SO$_4$. This paper also reviewed the values reported before by other groups.

Moats et al. [40] reported the $D_{Cu}$ values of solutions similar to electrorefining electrolytes determined through the limiting current method at a relatively high temperature of 65°C. They reported a diffusion activation energy of 19.2kJ mol$^{-1}$ which can be used in an Arrhenius type relationship. For the same electrorefining application, Leaist [41] obtained a $D_{Cu}$ value as 5.5×10$^{-10}$ m$^2$·s$^{-1}$ through a more accurate diaphragm cell method in a solution containing Na$_2$SO$_4$ and H$_2$SO$_4$ as well.

Diffusivity of CuSO$_4$ in water with a range of CuSO$_4$ concentration from 0.35 M to 1.4 M at 25°C was investigated by Emanuel and Olander [42]. The values gradually decreased from 4.95×10$^{-6}$ cm$^2$·s$^{-1}$ to 3.83×10$^{-6}$ cm$^2$·s$^{-1}$ showing that an increase in the Cu$^{2+}$ concentration will lower the diffusivity.

In this study, equation (2.20) was used to determine the copper ion diffusivity and entered into the COMSOL model. The electrolyte compositions used in this thesis were either within the range of equation (2.20) or very close to it.
2.2.4 Thermodynamics and Kinetics Parameters

The principle cathodic reaction of copper electrodeposition from acid aqueous solutions is [27]:

\[ Cu_{aq}^{2+} + 2e^- \rightarrow Cu_s \]  \hspace{1cm} (2.22)

The side reaction at the cathode is the evolution of hydrogen [27]:

\[ 2H_{aq}^+ + 2e^- \rightarrow H_2, g \]  \hspace{1cm} (2.23)

When using copper as the anode material, the main and side anodic reactions are the dissolution of copper and the evolution of oxygen [27], respectively:

Main reaction: \( Cu_s \rightarrow Cu_{aq}^{2+} + 2e^- \) \hspace{1cm} (2.24)

Side reaction: \( 2H_2O \rightarrow 4H_{aq}^+ + O_{2,g} + 4e^- \) \hspace{1cm} (2.25)

The equilibrium potential of reaction (2.22) can be calculated through (2.3) based on the operating conditions and the standard electrode potential of copper which is 0.337V (vs. SHE) [43].

The exchange current density, \( i_0 \), is another parameter to be determined through thermodynamic analysis. It has relations, from equation (2.15), with the reactant concentration and temperature. Theoretically, higher concentration and temperature will increase \( i_0 \). Since \( i_0 \) directly influences the current density with respect to equation (2.17), its value in aqueous solution has been the subject of many studies [19], [25], [27], [28], [44], [45]. Table 2-3 shows the reported values in these investigations, and the influence of temperature and concentration can be clearly seen.

**Table 2-3 Published Exchange Current Densities of CuSO₄ in Aqueous Solution**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Cu²⁺ concentration (mol L⁻¹)</th>
<th>Exchange current density (A·m⁻²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.6</td>
<td>13</td>
<td>[19]</td>
</tr>
<tr>
<td>25</td>
<td>0.3</td>
<td>25</td>
<td>[25]</td>
</tr>
<tr>
<td>35</td>
<td>0.0243</td>
<td>400</td>
<td>[27]</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>83</td>
<td>[28]</td>
</tr>
<tr>
<td>30</td>
<td>0.15</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.05</td>
<td>0.537</td>
<td>[44]</td>
</tr>
<tr>
<td>30</td>
<td>0.47</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.47</td>
<td>19.6</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.47</td>
<td>158.6</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.47</td>
<td>1268.8</td>
<td></td>
</tr>
</tbody>
</table>
Based on their experimental results, Cifuentes and Simpson [45] further provided an equation (2.26) to predict the change of the exchange current density with temperature:

$$\ln i_0 (\frac{A}{m^2}) = -\frac{20438}{T(K)} + 68.33$$  \hspace{1cm} (2.7)

The cathodic transfer coefficient $\alpha_c$ can be obtained by plotting cathodic overpotential, $\eta_c$, against the current density, $i$. Mattsson and Bockris [28] explained the method in detail in their paper and obtained an $\alpha_c$ value of 0.49 in their measurements. Similar results between 0.47 to 0.56 were also published in other studies [19], [25], [27], [30], [44], [46]. Moreover, some researchers [29], [30], [47] mentioned an increase of $\alpha_c$ or the reduction of Cu$^+$ by adding trace amount Cl$^-$ ions into the bath. But the concentration of Cl$^-$ should be carefully controlled. High Cl$^-$ concentration, such as over 0.1M, will inhibit the reduction due to lower free Cu$^{2+}$ and Cu$^+$ concentration caused by the complexation of copper species by Cl$^-$ ions.

### 2.2.5 Current Distribution in the Hull Cell

The current density plays a crucial role in the formation of structure and surface morphology of copper electrodeposits. The Hull cell can provide a broad current density range using one single test and is extensively used by many researchers [19], [21], [44], [48], [49], [50] to investigate the current density distribution over the cathode surface. In order to obtain the local current density value, both analytical and numerical solutions were given in the literature. Because of the strong nonlinear pattern in the expression, SCD and TCD results can only be obtained by numerical solutions while analytical solutions are available for PCD. Using the standard Hull cell and conformal mapping technique, West et al. [48] described a method to obtain an analytical solution of PCD for the normalized current density $\frac{i(x)}{i_{avg}}$ as (2.27):

$$\frac{i(x)}{i_{avg}} = \frac{(1-x)^{1.273}}{x^{0.359}}(0.97 + 0.763x)$$  \hspace{1cm} (2.27)

where:

- $x$ is the dimensionless distance along the cathode away from the nearest point to the anode
- $i(x)$ is the local current density at $x$, A·m$^{-2}$
- $i_{avg}$ is the average current density over the cathode surface, A·m$^{-2}$
Palli and Dey [21] compared their own and West’s analytical solutions by adopting a similar method for a modified Hull cell and found a reasonable agreement by using equation (2.28):

$$\frac{i(x)}{i_{avg}} = \frac{(1-x)^{1.3375}}{x^{0.3639}} (1.0661 + 0.5776x)$$

(2.28)

In addition, the DIN standard 50950 [51] provides an empirical solution (2.29) to calculate the local current density for the PCD class:

$$\frac{i(x)}{i_{avg}} = 2.33\log\left(\frac{1-x}{x}\right) - 0.08$$

(2.29)

for 0.059 < x < 0.814

Matlosz et al. [19] predicted the PCD and SCD numerical solutions of the traditional Hull cell from numerical algorithms and verified these by experiments. From their results, the current distribution over the surface becomes more nonuniform with increasing average current density. In contrast to the trapezoidal shape Hull cell, numerical simulations of the current distribution of a specific rotating cylinder Hull (RCH) cell (Figure 2-1) were done by Low et al. [44]. The simulated PCD can be represented by an exponential decay function.

Figure 2-1. The rotating cylinder Hull (RCH) cell, RotaHullP® used in Ref. [44]
2.2.6 Diffusion Layer Thickness

For the Cu deposition with high Cu\(^{2+}\) bulk concentration and sufficient agitation effect near the cathode surface, a concentration gradient can only be found within the diffusion layer. Because the diffusion current density is proportional to the concentration gradient when Fick’s first law of diffusion (2.30) is applied, it’s necessary to know the diffusion layer thickness for the calculation.

\[
N_D = -D \left( \frac{dc}{dx} \right) = -D \frac{c_b - c_s}{\delta}
\]  \hspace{1cm} (2.30)

where:

- \(N_D\) is the diffusion flux, mol·m\(^{-2}\)·s\(^{-1}\)
- \(c_b\) is the concentration in the bulk, mol·m\(^{-3}\)
- \(c_s\) is the concentration at the cathode surface, mol·m\(^{-3}\)
- \(\delta\) is the diffusion layer thickness, m

By using a rotating cylinder electrode, Eisenberg \textit{et al.} [52] reported thickness calculations as a function of rotation speed, rotor diameter, viscosity and diffusivity. Low \textit{et al.} [44] assumed a uniform diffusion layer thickness and provided results of a similar rotating cylinder cell with varying electrode rotation speed (132-1300 rpm). Within the speed range, the thickness varied from 20 to 100 \(\mu\)m. Nelissen \textit{et al.} [25] defined the diffusion layer as a zone where the concentration is less than 90% of the bulk value and set up different turbulent models to calculate the thickness. As a result, 10 to 30 \(\mu\)m thicknesses were found for Cu reduction under turbulent flow conditions. The value in a modified Hull cell (Figure 2-2) used for Cu deposition was set as 30 \(\mu\)m by Palli and Dey [21]. Instead of studying the diffusion layer thickness separately, recently Ibrahim and Najim [53] investigated the mass transfer coefficient, which is the ratio of diffusion coefficient to the diffusion layer thickness by using a rotating cylinder electrode as the cathode. According to their results, the value of \(\delta\) was between 17–67 \(\mu\)m at 30°C depending on the rotation rates and the copper concentration.
In this study, the diffusion layer thickness of Cu electrodeposition was set at 30μm which is in the range of all the above studies and also based on the condition that sufficient electrolyte mixing existed in the experiments.

2.3 Nickel-Copper Electrodeposition

In general, Nickel-Copper (Ni-Cu) binary alloys have been extensively studied because of their excellent corrosion resistance [54], [55], [56], [57], [58], [59], machinability, electrical conductivity and thermal properties [13]. Because copper is relatively soft, alloying with nickel is of great importance to increase the hardness [12] and the tensile strength [60] of copper. Adding copper into the nickel matrix can significantly improve the thermal stability of electrodeposited nanocrystalline nickel [61]. Considering the similar lattice parameters and the same FCC crystal structure, it is possible to obtain strain free Ni-Cu alloy films as well [62]. Ni-Cu alloys are widely used in various industrial applications, for example in the marine environment, heat exchangers and power stations [13]. Moreover, Ni-Cu alloys can be further divided into Ni-rich alloys and Cu-rich alloys based on the composition. In addition to the above properties, Ni-rich alloys can show a transition from paramagnetic to ferromagnetic behavior depending on the content of nickel [63]. Cu-rich alloys are much more suitable to be used in seawater because of their high resistance to bio-fouling [54].

Making Ni-Cu alloy by the electrodeposition process is of considerable importance as an example to demonstrate what Brenner [64] has termed “anomalous co-deposition”: it is the situation when
less noble metal (Ni) instead of the noble one (Cu) exists in significantly higher quantity in the deposit. In Ni-Cu alloy electrodeposition, this anomalous co-deposition can be explained by the influence of the metal ion concentrations in the plating bath, which is discussed in section 2.3.1. A more thorough study of the mechanism governing nickel-copper co-deposition is therefore of great importance to understand this specific anomalous electrodeposition system. The history of electrodeposition of Ni-Cu alloys can be dated back to 1912 when Bruni and Amadori first plated this material [2]. Although producing this alloy through electrodeposition attracts significant interest, the commercial application of electroplated Ni-Cu alloys is still relatively rare. Because Ni and Cu are very far apart in their standard electrode potentials (-0.25V and +0.337V, respectively), co-electrodeposition of Ni and Cu from a single solution is very challenging. Without taking special consideration, the more noble component Cu will always be deposited at first preferentially to Ni. Because of this, even maintaining the working potential at a value lower than the reduction potentials of both components, deposition of the less noble Ni is still too difficult to obtain a commercially useful alloy.

From the perspective of kinetics, the difference in the Ni and Cu reduction potentials will result in distinct overpotential values as well as reaction rates according to the equation (2.17). In order to realize the co-deposition process, either controlling the concentration or changing parameters such as the cathodic transfer coefficient $\alpha_c$ and reduction potential has to be achieved to narrow the gap in Ni and Cu reduction rate.

### 2.3.1 Influence of Ni and Cu Ion Concentrations

The concentrations of Ni and Cu ions in the solution play a critical role in the reaction rate. Decreasing the Cu ion concentration is an effective way to control its reaction rate. Yahalom and Zadok [60] and Lee et al. [65] described this in detail. When the co-deposition of two elements with distinct reduction potentials is required, a much lower concentration of the more noble metal (Cu) should be introduced together with a more concentrated solution of the other metal (Ni). Then when the cathode potential is sufficiently low to enable the reduction of both metals, Cu will quickly reach the diffusion control condition and its further deposition is inhibited, whereas the deposition of Ni will continue at a rate determined by its charge transfer property. Therefore, when the charge transfer rate becomes higher by applying higher current or lowering the potential, Ni electrodeposition is supposed to be faster proportionally. Cu deposition, however, is
disproportional because the diffusion control condition is unable to provide sufficient cupric ions to the cathode surface. Consequently, the electrodeposition rates of Ni and Cu, or the composition of the electrodeposit, can be controlled by maintaining charge transfer control for Ni and diffusion control for Cu. In Yahalom’s research [60], the content of Cu in the final electrodeposit was controlled within less than 1 wt% although Cu is the more noble metal.

The same scenario was reported in other studies as well. The sensitivity of Ni and Cu ion concentrations on the final deposit composition was described by Orinakova et al. [13]. A slight increase or decrease in the Cu ion concentration led to significant changes in the Cu content of the deposited alloy while a slight increase of Ni ions had no effect on the final composition. Eugenio et al. [47] used an electrolyte with a Ni to Cu ion molar concentration ratio ([Ni]/[Cu]) of 50 and had a Cu composition in the deposit varying between 30 at% to 40 at%, thus a significantly higher content can be found in the deposition compared to the solution. Zin et al. [66] used the same ratio of 50:1 in their work to achieve Ni contents in the alloy of up to 60%. The influence of [Ni]/[Cu] was further studied by Turonova et al. [67] by varying the ion ratio values to 17.5, 70 and 175. The Ni content can reach over 90 wt% at the highest ratio. Also, they found as long as the ratio was lower than 35, more Cu would be present in the final electrodeposit at a current density of 787.4 A·m⁻² (78.74 mA·cm⁻²). Similarly, Green et al. [68] set the [Ni]/[Cu] value of their electrolyte to 17.5 and 28, respectively, and a Ni content up to 88% was achieved at 500 A·m⁻² (50 mA·cm⁻²) for the higher ratio. Different from the aforementioned studies, much lower ratios of 4 and 9 were used by Ying [2]. Depending on the applied electrode potential, the Ni composition was varied from 5% to 28% but no Ni-rich region was obtained. In an acidic solution, Agarwal et al. [69] investigated the Ni-Cu co-deposition by using a ratio of 10 at 55°C and achieved the highest Ni composition of 77.4%. Another low ratio of 11 was adopted by Varea et al. [12] in their work to produce a smooth Cu-rich surface. From the SEM images, the decreased [Ni]/[Cu] value enabled the growth of a fairly flat deposit with up to 70 at% Cu content.

Based on the literature study, in general, relatively high [Ni]/[Cu] ratios should be considered to produce deposits with a broad range of Ni content. In this study, a ratio of 20 will be adopted in both the experiments and the simulation of the Hull cell electrodeposition.
2.3.2 Complexing Agents

In addition to changes of the concentrations of Ni and Cu ions to inhibit the rate of reduction of the more noble metal, another method to narrow the large gap in the standard reduction potentials between Ni and Cu is to add a certain complexing agent [13]. By generating a complexed substance, the reduction potential of the noble metal can be shifted to a more negative region, or the cathodic transfer coefficient is decreased to lower the activity of Cu ions. Complexants such as citric acid [1], [2], [69], [70], pyrophosphate [71] [72], ammonia [1], [73], cyanide [74], glycine [75], oxalate [76], thiosulfate [77], and tartrate for Ni-Cu-Fe alloys [78] have all been examined in past studies. The chemical formulae and structures of these complexing agents are listed in Table 2-4.

Of these agents, a plating baths containing citrate or pyrophosphate appear to be the most promising because they give good quality deposits and nickel-rich alloys with high current efficiency [68]. Specifically, the citrate bath is becoming very popular because of its intrinsic low toxicity. Furthermore, some other functions of citrate such as buffering [68], surface brightening [72] and leveling [79] further promoted its application as an agent. In practice trisodium citrate (C₆H₅Na₃O₇ or Na₃Cit) is widely used for the Ni-Cu alloy electrodeposition. For convenience, this complexing agent will also be used in the current study in both the experiments and the simulations.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Chemical Structure</th>
<th>Name</th>
<th>Chemical Formula</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate</td>
<td>C₆H₅O₇³⁻</td>
<td><img src="..." alt="Citrate Structure" /></td>
<td>Glycine</td>
<td>C₂H₅NO₂</td>
<td><img src="..." alt="Glycine Structure" /></td>
</tr>
<tr>
<td>Pyrophosphate</td>
<td>P₂O₇⁴⁻</td>
<td><img src="..." alt="Pyrophosphate Structure" /></td>
<td>Oxalate</td>
<td>C₂O₄²⁻</td>
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</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td><img src="..." alt="Ammonia Structure" /></td>
<td>Thiosulfate</td>
<td>S₂O₃²⁻</td>
<td><img src="..." alt="Thiosulfate Structure" /></td>
</tr>
<tr>
<td>Cyanide</td>
<td>CN⁻</td>
<td><img src="..." alt="Cyanide Structure" /></td>
<td>Tartrate</td>
<td>C₄H₄O₆²⁻</td>
<td><img src="..." alt="Tartrate Structure" /></td>
</tr>
</tbody>
</table>
2.3.3 Influence of pH on the Bath Stability and Alloy Deposition

Depending on the complexing agent used, the electrolyte can be acidic or basic. When using trisodium citrate as the complexing agent, the solution is supposed to be acidic with a pH value less than 6. But some studies [1], [73], [80] also investigated the results of a pH value over 9 in a bath containing trisodium citrate by adding ammonia or sodium hydroxide to the bath.

One objective to study pH effect is the need to establish the condition of a stable bath. Since it was first reported by Priscott [81], electrodeposition of Cu-Ni alloys from citrate baths has been extensively studied. In spite of its ability of high Ni content and current efficiency, a major concern of the citrate bath is its stability. Although certain citrate baths are found to be stable[1], [2], the majority precipitate after a few days of use. Green et al. [68] characterized the precipitating species from an unstable citrate bath with the concentration ratio between citrate ion and metal ions less than 1, or [Cit$^3$-]/([Ni$^{2+}$]+[Cu$^{2+}$]) < 1. Different from what had been generally assumed that the precipitate was insoluble copper citrate dehydrate complex, Cu$_2$H$_2$Cit$_2$H$_2$O, they found that the actual precipitating species was a heteronuclear copper-nickel citrate complex with a formula of Cu$_x$Ni$_{2-x}$H$_2$Cit, according to the elemental analysis. Although Cu$_2$H$_2$Cit was not the precipitate, it can still be treated as a precursor in which some of the copper ions are slowly replaced with nickel ions, leading to the eventual formation of the insoluble heteronuclear citrate complex. From the calculation of the distribution of copper citrate species as shown in Figure 2-3 as a function of pH, the experimental conditions to minimize the precursor concentration is either pH< 2 or pH> 6. Considering the very low current efficiency at pH <2, choosing a pH close to 6 is then the preferred condition. In addition, for those baths which have more Cit$^3$ than metal ions, Cu$_2$H$_2$Cit concentration can reach a significantly low value at pH around 5 [68].

By testing the stability of the solutions with various copper sulfate/citrate ratios, Chassaing et al. [82] found a ratio of no more than 1 was essential to have a stable solution. The positive correlation between pH and citrate concentration was also analyzed in their research. The influence of pH value on the ion species in the citrate bath was also investigated by the same group [31]. According to their proposed mechanism, the triply ionized citrate ion, Cit$^3$, adsorbs and blocks the electrode surface when the electrolyte has a pH less than 4. Therefore, keeping a pH value at least higher than 4 is preferred in order to facilitate the reaction on the cathode.
Figure 2-3. Distribution of copper species in a citrate bath containing 0.025 M CuSO₄, 0.70 M NiSO₄, and 0.26 M Na₃Cit at 298 K [68]

Furthermore, Rode et al. [31] carried out an extensive analysis on the complexing chemistry in copper electrodeposition from citrate bath. Their results showed that the deposition potential of Cu²⁺ is drastically shifted toward more negative potential by complex formation with citrate, and reveal that the reduction of Cu cannot be effectively inhibited until the pH is greater than 5 according to the shift. For the purpose of co-deposition of Ni and Cu where Cu deposition should be suppressed, this value can then be used as an important criterion for the preparation of a plating bath.

The effect of solution pH on Ni-Cu alloy electrodeposition results has been widely studied as well. From the common understanding, the pH values should not have a high influence on the composition of alloys if the metal ions independently exist in the solution. However, when the solution contains chelated metal ions, the pH values will play an important role in the final composition. For the acidic citrate solutions with pH 2, 4 and 6, at a relatively low current density of no more than 10 mA/cm², the Ni content drastically increased from 0.56 wt% to 37.53 wt%
with an increase in the pH from 2 to 6 [83]. More Cu deposition at low pH can be explained by the unstable complexing ions shown in Figure 2-3, at the pH lower than 4, an obvious increase in the concentration of free Cu\(^{2+}\) can be seen which will introduce more Cu in the deposit. Goranova et al. [84] contributed high Cu content at lower pH to the hydrogen evolution which improved the copper diffusion on the cathode surface. For higher pH values from 6 to 10, Sobha et al. [73] found that the copper percentage in the deposit increased from 19% to 38%, while the current efficiency was maintained at around 85%. Moreover, both Chassaing et al. [1] and Rode et al. [80] reported the catalytic effect of copper on the nickel reduction at higher pH. With the presence of Cu, the reduction potential of Ni is shifted to more positive range compared to that without Cu in the solution, which leads to the easier deposition of Ni. By using glycine as the complexing agent, Mizushima [75] performed experiments with different pH and [Cu]/[Ni] ratios. In all the experiments, the highest Ni content in the deposit was achieved at pH from 5 to 6 where the degree of Cu\(^{2+}\)-glycine complex formation reaches a maximum. But increasing the pH to 8 significantly decreased the concentration of Ni\(^{2+}\) in the solution and resulted in lower Ni content.

In the current study, the pH value of the electrolyte was selected around 5 in order to have both a stable solution and higher Ni content in the final electrodeposit.

### 2.3.4 Bath Composition

The most common ion sources used for Ni-Cu alloy deposition are nickel sulfate (NiSO\(_4\cdot6\)H\(_2\)O) and copper sulfate (CuSO\(_4\cdot5\)H\(_2\)O), together with the complexing agent trisodium citrate (C\(_6\)H\(_5\)Na\(_3\)O\(_7\)·2H\(_2\)O). It is generally accepted that the Ni concentration in the bath should be much higher than that of Cu in order to obtain the co-deposition result. But for the proportion of the complexing agent, or the ratio of [Cit] / ([Ni]+[Cu]), there is no consistent guideline in the literature. Some researchers adopt a ratio less than 1 in their works [67], [68], [70], [36], whereas the ratio over 1 can also be found in some other papers [1], [2], [31], [80]. With less citrate in the solution, in addition to the complexed species, uncomplexed metal ions exist as well. Compared to other researchers, Rode et al. [80] additionally considered the influence of the ionic strength (IS) on the bath, which was defined as

\[
I = \frac{1}{2} \sum c_iz_i^2
\]  

(2.31)

where:
$I$ is the ionic strength, mol·L$^{-1}$

$c_i$ is the molar concentration of the species $i$, mol·L$^{-1}$

$z_i$ is the charge of the species $i$

Rode et al. [80] prepared a bath with a “nominal” ionic strength of 4.4 to resemble industrial conditions.

Table 2-5 shows the main parameters of the Ni-Cu alloy plating baths studied in the literature. From the calculation results of IS, although it was not specifically stated in many studies, the values were actually around 4.4.

**Table 2-5 Characteristics of the Copper-Nickel-Citrate Plating Baths**

<table>
<thead>
<tr>
<th>[Ni] (mol/L)</th>
<th>[Cu] (mol/L)</th>
<th>[Cit] (mol/L)</th>
<th>pH</th>
<th>[Ni]/[Cu]</th>
<th>[Cit]/[Metal]</th>
<th>Nominal IS</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4-0.6</td>
<td>0.025-0.1</td>
<td>0.7</td>
<td>9.2(+NH$_3$)</td>
<td>4-25</td>
<td>&gt;1</td>
<td>&gt;4</td>
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<tr>
<td>0.181</td>
<td>0.009</td>
<td>0.255</td>
<td>5.37</td>
<td>20</td>
<td>0.135</td>
<td>2.3</td>
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</tr>
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<td>0.017</td>
<td>0.5</td>
<td>5.06</td>
<td>10</td>
<td>0.135</td>
<td>2.3</td>
<td>[2]</td>
</tr>
<tr>
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<td>0.032</td>
<td></td>
<td>4.76</td>
<td>5</td>
<td>0.135-1</td>
<td>3.42-7.16</td>
<td>[67]</td>
</tr>
<tr>
<td>0.171</td>
<td>0.019</td>
<td>0.255</td>
<td>5</td>
<td>9</td>
<td>0.135</td>
<td>2.29</td>
<td>[31]</td>
</tr>
<tr>
<td>0.7</td>
<td>0.004</td>
<td>0.1-0.7</td>
<td>4.5-4.9</td>
<td>175</td>
<td>0.135-1</td>
<td>3.42-7.16</td>
<td>[67]</td>
</tr>
<tr>
<td>0.7</td>
<td>0.025</td>
<td>0.26</td>
<td>4.12</td>
<td>28</td>
<td>~0.35</td>
<td>4.46</td>
<td>[68]</td>
</tr>
<tr>
<td>0.7</td>
<td>0.025</td>
<td>0.26</td>
<td>4.06</td>
<td>17.5</td>
<td>~0.35</td>
<td>4.46</td>
<td>[70]</td>
</tr>
<tr>
<td>0.7</td>
<td>0.025</td>
<td>0.26</td>
<td></td>
<td>56</td>
<td>~0.35</td>
<td>4.46</td>
<td>[70]</td>
</tr>
<tr>
<td>0.165</td>
<td>0.025</td>
<td>0.25</td>
<td>3-9 (+H$_2$SO$_4$ or +NaOH)</td>
<td>6.6</td>
<td>1.32</td>
<td>4.4 (+Na$_2$SO$_4$)</td>
<td>[80]</td>
</tr>
<tr>
<td>0.7</td>
<td>0.004</td>
<td>0.01</td>
<td>4.5</td>
<td>175</td>
<td>0.014-0.714</td>
<td>2.88-5.82</td>
<td>[36]</td>
</tr>
</tbody>
</table>

For the purpose of analyzing reaction mechanisms and setting up the model to represent the plating process, it is necessary to understand the species involved in the solution, possible electrochemical reactions and relevant thermodynamics and kinetics parameters. The formation of citrate complexes with nickel or copper ions can be described by the general reaction [68], [80]:

$$pcu^{2+} + qni^{2+} + rcm^{3-} + sh^+ \rightleftharpoons cu_{p}ni_{q}cm_{r}s_{h}^{(2p+2q-3r+s)+} \quad (2.32)$$
The overall stability constants, $\beta_{pqr}$ are given by

$$\beta_{pqr} = \frac{[Cu_p Ni_q Cit_r H_s]}{[Cu^{2+}]^p[Ni^{2+}]^q[Cit^{3-}]^r[H^+]^s}$$ (2.33)

where $p$, $q$, $r$, $s$ are the stoichiometric coefficients.

Based on the stability constants of various copper and nickel citrate complexes, the distribution of complexed species can be plotted with respect to the pH value. The result of copper species is presented in Figure 2-3, and Figure 2-4 shows the nickel species distribution in the same solution [68].

![Figure 2-4. Distribution of nickel species in a citrate bath containing 0.025 M CuSO$_4$, 0.70 M NiSO$_4$, and 0.26 M Na$_3$Cit at 298 K [68]](image)

It is obvious that the solution contains a large number of various complexed metal species, which makes the reactions and subsequent modeling and simulation quite challenging. In order to simplify the chemistry by considering the complexed species were CuCit$^-$ and NiCit$^-$ only, Chassaing et al. [1] and Ying et al. [2] suggested to use excess citrate while Podlaha et al. [36]
maintained the solution pH of approximately 4.5. In the current study, the bath is made based on excess citrate and an ionic strength of 4.4. So only the CuCit⁻ and NiCit⁻ are taken into account in the following electrochemical reduction analysis and computational simulation.

2.3.5 Influence of Current Density

Co-deposition of Ni and Cu is designed in a way that Cu will experience mass transfer control while Ni reduction will be mainly controlled by the charge transfer process. It is then obvious that changing current density is an effective way to adjust the composition of the deposit. Increasing the current density resulted in more negative cathode potential which is a benefit for the reduction under charge transfer control condition. From the appearance of the deposit, it is very easy to find that at lower current density the deposit is copper-coloured and is bright, uniform, smooth, and metallic. At higher current density, it is greyish indicating the presence of more Ni [13].

An extensive investigation was performed by Stout et al. [74] regarding the electrodeposition of copper-nickel alloys. In their studies, a series of current densities of 5-60 mA·cm⁻² was employed. An analysis of the results indicated that the deposition of Cu was favored at low current densities. Almost no Ni was obtained in the deposit at the lowest current density even when the Ni concentration was 4 times higher than that of Cu in the electrolyte. In contrast, a significant increase can be found in the Ni concentration from 12.9% to 77.4% when increasing the current density from 50 mA·cm⁻² to 250 mA·cm⁻² by using an electrolyte with a [Ni]/[Cu] of 10 [69]. At pH of 9 and relative lower current densities from 2.5 to 20 mA·cm⁻², Sobha et al. [73] reported that the high copper contents in Ni-Cu alloy deposits were obtained at current densities less than 7.5 mA·cm⁻². However, the effect of current density on metal content was far less pronounced when the current density was between 7.5 to 20 mA·cm⁻². This indicates that the reduction of more noble metal (Cu) was preferred at lower current densities. In addition to the composition, current density also has some effects on the grain size and morphology of the electrodeposit [84]. The crystallite size decreases with increasing current density. At the same time, an increase in the roughness and dendritic growth were observed at higher current density.

2.3.6 Thermodynamics and Kinetics

Thermodynamic and kinetic analysis are closely related to the electrochemical reactions on the electrode surface, specifically, the reduction on the cathode surface. For the co-deposition of Ni
and Cu in the citrate bath, multiple reactions are assumed to occur including at least the reduction of Ni and Cu, and perhaps the evolution of hydrogen and oxygen as well [85].

Before discussing the alloy deposition, it is of interest to look briefly at the single metal deposition. Cu deposition was discussed previously in section 2.1, while single Ni deposition without complexing agent has also been extensively investigated [13], [86], [87], [88], [89] because of its wide application as decorative and magnetic materials. It is generally accepted in these papers that the reduction of Ni within un-buffered electrolytes can be separated into several steps [13], [86]:

\[
Ni^{2+} + H_2O \rightleftharpoons Ni(OH)^+ + H^+ \tag{2.34}
\]

\[
Ni(OH)^+ + e^- \rightleftharpoons Ni(OH)_{ads} \text{ (slow)} \tag{2.35}
\]

\[
Ni(OH)_{ads} + Ni^{2+} + 2e^- \rightleftharpoons Ni + Ni(OH)_{ads} \tag{2.36}
\]

\[
Ni(OH)_{ads} + e^- \rightleftharpoons Ni + OH^- \tag{2.37}
\]

In reaction (2.34), an intermediate species, \(Ni(OH)^+\), is generated through a homogeneous chemical reaction. A slow electron transfer (2.35) takes place at the same time to produce an adsorbed product \(Ni(OH)_{ads}\) on the cathode surface, which participates in the following two parallel fast electrochemical reactions (2.36) and (2.37) leading to the formation of metallic nickel.

Widayatno [90] studied the kinetic parameters of Ni reduction including the exchange current density and charge transfer coefficient by using both analytical and graphical methods. The Bulter-Volmer equations (2.18) with first-order species dependencies was applied to set up the model. From the analytical results, the exchange current density and cathodic charge transfer coefficient were \(1.6 \times 10^{-4} \text{ mA}\cdot\text{m}^{-2}\) and 0.39, respectively.

Some studies were done on the investigation of the thermodynamics and kinetics of the co-electrodeposition of Ni and Cu in citrate baths. The polarization technique is mostly used for the study of the Ni-Cu electrodeposition mechanism [2], [80], [36]. In addition, Chassaing et al. [1] also employed electrochemical impedance techniques to investigate the reaction path. All studies revealed mass transport control in the diffusion layer for the reduction of Cu with a low concentration in the bath.
Chassaing *et al.* [1] investigated a complexing citrate-ammonia solution with a pH value of 9.2. With the presence of NiSO₄, the Cu deposition is inhibited. The partial Ni reduction curve, however, shows the catalyzing effect of Cu²⁺ because of a larger slope. Using the impedance spectra, a two-step discharge of complexed Cu species has been confirmed with a much lower rate constant for the first step which generated the intermediate CuCit²⁻ on the electrode surface. The reduction of Ni can be treated as the reaction of Ni²⁺ only without considering the Cit³⁻ in their experiment. Impedance spectra also showed a two-step discharge of Ni²⁺ involving an intermediate adsorbate, Ni⁺ₐds, generated from the first step. Following this observation, Chassaing *et al.* [1] proposed a reaction model for the parallel discharge of CuCit⁻ and Ni²⁺ containing 7 reactions. For the reduction of Ni in the alloy, they specifically used the concept of catalytic active sites which were nucleated from the Ni⁺ₐds and continuously renewed during the electrodeposition from the association of one Ni and several Cu ions.

A similar bath was used by Ying *et al.* [2] [85] which had a higher citrate concentration and a pH around 5. In order to understand the fundamental mechanism of the co-deposition process, a wide range of potentials were applied in their research. From the polarization results, five electrochemical reactions were found to occur during the electrodeposition including the reduction of hydrogen ion from the dissociation of hydrogenated citrate ions, and the reduction of dissolved oxygen, Cu ion, Ni ion and water when gradually increasing the negative potentials. But a comparison of the current density of Cu deposition with the combined current densities of hydrogen evolution from citrate dissociation and oxygen reduction revealed more than one order of magnitude difference. Thus, only the reduction of Cu ions, Ni ions, and water were considered in their model. Furthermore, the bulk concentrations of 16 species including not only the metal ion species but also H₃Cit, H₂Cit⁻, HCit²⁻, Cit³⁻, HSO₄⁻, SO₄²⁻, H⁺ and OH⁻ were calculated through the equilibrium constant, material conservation and electroneutrality condition. Different from some other studies which considered a series of metal ions or complexed metal species in the solution, only 4 complexed and 2 single metal species were included in the calculation. For the experimental condition used, the complexed Ni and Cu species that existed in the solution were determined as CuCit⁻ and NiCit⁻, respectively, which had concentrations more than 8 to 10 orders of magnitude greater than other possible complexed or single metal ions. Consequently, the following reactions were proposed to occur at the electrode surface:

\[ \text{CuCit}^- + 2e^- \rightarrow \text{Cu} + \text{Cit}^{3-} \]  (2.38)
\[ NiCit^- + 2e^- \rightarrow Ni + Cit^3^- \quad (2.39) \]

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2.40) \]

In terms of the kinetics, the Bulter-Volmer equations (2.18) with first-order species dependencies is used to explain the mechanism. For the Cu reduction reaction (2.38), since it can occur independently, the thermodynamic and kinetic parameters, such as the diffusion coefficient, transfer coefficient, exchange current density, and equilibrium potential, can be determined accurately. For the Ni reduction (2.39) and hydrogen evolution (2.40), the determination of these parameters is difficult given the fact that multiple reactions are occurring. Thus, they are inferred from the model-experimental fit of the cathodic polarization curve. The verification of the model indicates the validity and predictability of these parameters, specifically, in the co-deposition region with lower Cu concentration in the bath. Table 2-6 summarizes the data reported by Ying et al. [85] except for the exchange current density of the reaction (2.40), for which the value of 0.07 mA·cm\(^{-2}\) from Ref. [36] was adopted to get best fitting result.

Table 2-6 Mass Transport and Kinetic Parameters for Ni-Cu Co-electrodeposition

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Exchange Current Density (i_0) (mA·cm(^{-2}))</th>
<th>Cathodic Transfer Coefficient (\alpha_c)</th>
<th>Equilibrium Potential (E_{eq}) vs SHE (V)</th>
<th>Diffusion Coefficient (D) (m(^2)·s(^{-1}))</th>
<th>Bulk Concentration (c_b) (mol·L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.38)</td>
<td>2.6</td>
<td>0.084</td>
<td>0.161</td>
<td>2.1×10(^{-10})</td>
<td>0.019</td>
</tr>
<tr>
<td>(2.39)</td>
<td>0.1</td>
<td>0.45</td>
<td>-0.427</td>
<td>2.5×10(^{-12})</td>
<td>0.171</td>
</tr>
<tr>
<td>(2.40)</td>
<td>0.07</td>
<td>0.25</td>
<td>-0.584</td>
<td>5.5×10(^{-9})</td>
<td>8.71×10(^{-6})</td>
</tr>
</tbody>
</table>

These parameters are critical for the purpose of modeling and simulation and were used for the subsequent analysis in this study.

Podlaha et al. [36] modeled the co-deposition in a citrate bath with higher total metal ion concentration. Because of the excess of metal ions, both complexed and uncomplexed metal ions are available in the bath. The model focuses on the species in the diffusion layer and includes the mass transfer and interfacial kinetics. In the diffusion layer which is very close to the electrode surface, forced convection plays a small role and is negligible. Moreover, the ion migration effect is considered small when sufficient ions other than the deposited ones exist in the electrolyte. As a consequence, only the diffusion flux is considered within the boundary layer. The kinetics is described by Bulter-Volmer equation as well. Same as the study of Ying et al. [2] [85], the
complexed metal ions are NiCit\(^-\) and CuCit\(^-\) with the initial pH of 4.5. In addition to the reactions (2.38) ~ (2.40), the deposition of uncomplexed species and hydrogen evolution are also taken into account. The transport properties, for example the diffusion coefficient, of the complexed species are measured or estimated. The thermodynamic and kinetic parameters are adapted from Ying et al. [85] or fitted from experimental data.

Rode et al. [80] determined the species that existed in the bath with pH varying from 3 to 9 according to the formation constant and proposed a simple model to represent the parallel reactions which occur on the cathode surface. The partial-current electrodeposition kinetics of nickel-copper co-deposition was selected to compare with the results of single-metal deposition of nickel and copper alone. Partial-current polarization behavior for nickel in the co-deposition condition showed a significant catalytic effect by the presence of Cu on the reduction of Ni by shifting the reduction potential to more positive values. For pH values between 5 and 7, they used the direct discharge of NiCit\(^-\) pseudo-species to resemble the deposition of all the active species of Ni, consisting not only the free Ni\(^{2+}\) ion but also all complexed species. The concentration of these pseudo-species were equaled to the total bulk concentration of Ni. They finally described the kinetics of Ni reduction by using a simple Tafel activation and first-order species dependencies.

The steady-state partial-current polarization result for Cu in co-deposition, however, was found to be identical to that observed for single-metal deposition. In their another paper [31] studying the deposition of Cu in citrate solution, the polarization results revealed three possible reduction species, which were the Cu\(^{2+}\) (pH < 2), pseudo-species CuCit\(^-\) and binuclear species at high pH [91], Cu\(_2\)Cit\(_2\)H\(_2\)\(^4+\) or CuNiCit\(_2\)H\(_2\)\(^4-\). The kinetic mechanism of all these three reduction reactions was also defined by the Tafel equation and first-order species dependencies. Similar to the case of Ni, the concentration of the pseudo-species CuCit\(^-\) was controlled by the Cu content in the bath. For a bath containing excess citrate and a pH value of 5, the contributions of free Cu\(^{2+}\) ion and Cu\(_2\)Cit\(_2\)H\(_2\)\(^4+\) or Cu\(_{Ni}\)Cit\(_2\)H\(_2\)\(^4-\) were negligible.

### 2.4 Mathematical Modeling

The large number of electrochemical and operational parameters, such as temperature, agitation, pH, concentration, and conductivity, involved in the electrodeposition process make the prediction of the results extremely difficult. As mentioned before, even for the single Cu reduction in the Hull cell, analytical or numerical calculation is only available for the primary current distribution
pattern, which is rarely found in practice. Alloy deposition is more challenging considering the complexing agents, buffer capacity and the interactive effects within various elements. The increasing capabilities of computers has recently enabled it to carry out the simulation of rather complex electrochemical processes. Although not all parameters can be considered in the simulation, computer-aided modeling and simulation are extremely useful to at least qualitatively predict the relationships among various parameters.

2.4.1 Electrodeposition

In the absence of mass-transfer limitation or concentration gradients, only charge transport with normal ohmic resistivity is applied for the electrolyte according to equation (2.10). So the current density can be solved by the distribution of the potential inside the electrolyte [19], [21], [44], [92], [93]. By using Laplace’s equation, the potential distribution is calculated from:

\[ \nabla^2 \phi = 0 \quad (2.41) \]

Along the cathode surface, the current density thus can be described by the equations shown in Table 2-1 for the PCD and SCD. Boundary conditions given by Palli and Dey [21] along the cathode and the insulating walls are, respectively:

\[ \int (\xi \cdot i) ds = i_{avg} \quad (2.42) \]

\[ \frac{\partial \phi}{\partial \xi} = 0 \quad (2.43) \]

where \( \xi \) is the surface normal, \( s \) is the surface of the cathode.

When the mass-transfer influence is considered in the model, then the basic principles of both concentration gradient and interfacial kinetics are applied in the mathematical model of electrodeposition to evaluate the surface concentration of metal ions [86], [85], [94] and current density at the interface [20]. Laitinen et al. [20] and Ying et al. [85] used the Nernst-Planck equation (2.25) to describe the mass balance equation for each involved species \( i \):

\[ \frac{\partial c_i}{\partial t} = -\nabla \cdot N_i \quad (2.44) \]

where:

- \( c_i \) is the concentration of species \( i \) in the diffusion layer, \text{mol} \cdot \text{L}^{-1}
\( t \) is the time, s

\( N_i \) is the mass flux of species \( i \) calculated from Nernst-Planck equation (2.7), mol\cdot m^2\cdot s^{-1}

Both the mass transport flux and the electrochemical reaction have to be in balance at the interface [94], thus the flux of each species \( i \) equals the amount of the species consumed by the electrode reactions at the interface:

\[
N_i = \frac{i_i}{z_i F}
\]  

(2.45)

Combining with the expression of \( i \) in equation (2.17) at the interface, Hessami and Tobias [86], Ying et al. [85], and Brunner et al. [94] set up their models with the boundary conditions of overpotential \( \eta \) (1.9) and

\[
c_i = c_b \text{ at the diffusion layer and bulk boundary} \quad (2.46)
\]

### 2.5 Previous Applications of COMSOL Multiphysics Software in Electrodeposition

COMSOL Multiphysics, a finite element based software package, with its Electrodeposition Module is receiving more and more attention in the electrodeposition computational simulation field. As a cross-platform analysis, solver and multiphysics simulation software, its capability of coupling different physics is critical for this study since not only electrodeposition but also flow effects will be considered.

Laitien et al. [20] introduced a novel 3D electroplating tank layout for the electrodeposition of trivalent chromium and studied its feasibility by a 3D simulation model in COMSOL. The process of setting up the 3D configuration showed the ability of COMSOL in terms of its component building aspect. In addition to the electrodeposition, their model also coupled fluid flow by taking a recirculation flow into account and applying periodic boundary conditions at the inlet and outlet. The simulation result proved that the operation principle of the tank was feasible and fairly uniform coating thicknesses were obtained. Certain deviations in the thickness of the coating between the measured and simulated value were attributed to the unclear bath chemistry and process parameters.
The simulation of a modified Hull cell for the electrodeposition of copper was reported by Palli and Dey [21]. Regarding the current distribution, the simulated PCD result was found in good agreement with the analytical and numerical results using mathematical models. Moreover, COMSOL enabled the numerical analysis of the other two current distributions, SCD and TCD, as well. A significant difference can be found when considering the influence of electrode reaction kinetic and concentration gradient in the simulation. Under their experimental conditions, secondary or tertiary distribution results from the simulation were shown to be more accurate in predicting the actual plating situation.

Lima et al. [22] studied the tertiary Nernst-Planck interface in the Hull cell for copper electrodeposition by using COMSOL. Except for the traditional Hull cell structure, a modified cylinder shape “Hull cell” which represents a standard geometry in production was analyzed in both 2D and 3D. Based on the simulation results, improved design with respect to the cylinder shape cell was achieved. The current density decreased with the increase of the distance between cathode and anode. Their work provided a good foundation for the development of subsequent physical models.

In addition, component building feature of COMSOL enables the setup of 1D, 2D or the much more complicated 3D geometries in the model.
Chapter 3

3 Experimental Setup

Two series of experiments were completed in this study. Cu deposition in a standard and well-accepted Hull cell was first studied with various plating times and agitation conditions. Current density distribution, deposit thickness, and weight were investigated for further analysis. Following the single metal deposition, Ni-Cu alloy co-deposition was carried out also in the Hull cell. In addition to analyzing the thickness and weight, composition measurements were also a critical part of the analysis of alloy electrodeposition results. All the experiments in this study were performed galvanostatically using a DC power supplied by a Dynatronix 999-1086-01 Pulse Power Supply. The experimental setup of this part of the study is shown in Figure 3-1 for Cu single metal and Ni-Cu alloy electrodeposition, respectively.

Figure 3-1. Experimental setup of Cu electrodeposition (left) and Ni-Cu electrodeposition (right) in a Hull cell

3.1 The Hull Cell

For both series of experiments, a standard 267 ml Hull cell (Kocour Company, Chicago, IL, USA) was used with dimensions shown in Figure 3-2. All the cathodes were commercially available brass test plates with a size of 100 mm by 75 mm supplied with a thin protection polymer film attached on the working surface. When the solution level in the cell was 45 mm high, it equaled to a total volume of approximately 250 ml in the cell. The anode was either a piece of corrugated
copper or a piece of flat nickel with the dimension of 61 mm by 64 mm. Both the cathode and anode materials were provided by Integran Technologies Inc. (Mississauga, ON, Canada).

![Figure 3-2. The 267 ml Hull cell with dimensions in mm](image)

3.2 Electrolyte

The solution for the Cu electrodeposition mainly contained copper sulfate (CuSO$_4$·5H$_2$O) and sulfuric acid (H$_2$SO$_4$) with a trace amount of hydrochloric acid (HCl). From the literature review, trace amount Cl$^-$ in the bath would catalyze the reduction of copper ion (Cu$^{2+}$) [32]. Also, the composition of the bath for Cu electrodeposition can vary significantly from study to study. In the current investigation, the concentration of each component was chosen according to the industrial process used by Integran Technologies Inc. as follows:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration $\text{g}\cdot\text{L}^{-1}$</th>
<th>Concentration $\text{mol}\cdot\text{L}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$·5H$_2$O</td>
<td>190</td>
<td>0.76</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>70</td>
<td>0.72</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>25 (ppm)</td>
<td>$1.4\times10^{-3}$</td>
</tr>
</tbody>
</table>

Agitation in the bath, especially at the surface of the cathode, is needed for the Cu deposition to avoid the mass transport control conditions. A portable air pump was used to purge air into the solution from a sparger placed at the bottom right in front of the cathode to generate a continuous
bubble agitation effect. Figure 3-3 shows the sparger and the bubble agitation effect. All the experiments for Cu deposit were carried out at room temperature.

![Image showing sparger](image)

**Figure 3-3. Air sparger agitation for Cu electrodeposition in a Hull cell**

For the co-deposition of Ni-Cu alloy, the solution used in the experiments consisted of nickel sulfate (NiSO₄·6H₂O), copper sulfate (CuSO₄·5H₂O), and trisodium citrate (Na₃Cit·2H₂O). A small amount of sulphuric acid (H₂SO₄) was also used to adjust the pH to 5. According to the literature review, co-deposition of Ni and Cu requires a significant excess concentration of Ni. The [Ni]/[Cu] ion concentration ratio was chosen as 20 in this study and a Cu ion concentration of 0.0175 mol·L⁻¹ was used to represent the Integran industrial process. In addition, 0.5 mol·L⁻¹ Na₃Cit was added to obtain an overall ionic strength of 4.4 in order to simulate the real production conditions. Thus, the final composition of Ni-Cu alloy plating bath was:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration g·L⁻¹</th>
<th>Concentration mol·L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄·6H₂O</td>
<td>92</td>
<td>0.35</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>1.12</td>
<td>0.0175</td>
</tr>
<tr>
<td>Na₃Cit·2H₂O</td>
<td>147</td>
<td>0.5</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>3.43×10⁻³</td>
<td>3.5×10⁻⁵</td>
</tr>
</tbody>
</table>

Table 3-2. Ni-Cu Alloy Co-deposition Bath Composition

Better mixing in the bath was also required for the Ni-Cu alloy electrodeposition so that the Ni reduction is not affected by mass transport control. Different from that of Cu deposition, agitation for the alloy deposition was realized by a reciprocating agitator which was placed in front of the cathode as shown in Figure 3-4 (a) and moved back and forth continuously during the experiment. Alloy deposition was performed at a temperature of about 60°C to represent the real production conditions.
process. Heating of the electrolyte was done by a heater installed at the bottom and a temperature controller which were shown in Figure 3-4 (b).

Figure 3-4. Agitation (left) and heating (right) for Ni-Cu alloy co-electrodeposition

3.3 Experimental Procedure

Prior to deposition, the protection polymer film was peeled off and the cathode was weighed. After that, 3M (TC158) tape was applied to mask the entire back side and the top 30 mm of the working surface of the cathode, leaving a 100 mm by 45 mm exposed working area in the solution. The cathode plate was then degreased with an alkaline solution provided by Integran Technologies Inc. (Mississauga, ON, Canada) and activated by immersing in an aqueous 10% sulphuric acid solution for 15 seconds. The same sulphuric acid solution was also applied for the activation of the copper or nickel anodes for 10 minutes in order to remove any oxides and possible contamination on the surface. Cu samples were plated at a constant current of 2A for various times and agitation conditions, while Ni-Cu alloy deposition used different total currents. The experimental conditions for each experiment are summarized in Table 3-3.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Cu Electrodeposition</th>
<th>Ni-Cu Alloy Electrodeposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (mins)</td>
<td>Current (A)</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 3-3. Experimental Conditions for Cu and Ni-Cu Electrodeposition
Following the electrodeposition run, each sample was taken out of solution and rinsed with distilled water. Subsequent to cleaning, the tape was removed, and the sample was rerinsed and dried using compressed air prior to the weight measurement. Finally, the sample (Figure 3-5a) was cut at about 25 mm from the bottom to produce one 5 mm by 100 mm strip (Figure 3-5b). To allow for metallographic examination mounting, the strip was further cut into equal 5 pieces with dimensions of 5 mm by 20 mm each (Figure 3-5c). All cutting procedures were done using a Struers Minitom diamond blade with adequate coolant.

![Figure 3-5. Schematic drawing of sample preparation for analysis](image)

The sections of each sample were then mounted in epoxy resin with the cross-section of deposit exposed at the surface (Figure 3-6).

![Figure 3-6. Cu deposit sample mounted in nickel epoxy puck (left) and Ni-Cu alloy deposit sample mounted in epoxy puck (right)](image)

Buehler EpoxiCure 2 resin and supplementary hardener were used to mount the sample at room temperature. For the Cu electrodeposits, Buehler conductive nickel filler powder was also added into the epoxy to enhance the electrical conductivity of the samples. Each sample was numbered carefully for further analysis. The mounted samples were ground with different grit size SiC papers.
(320, 400, 800, 1500, 2500) followed by a polishing procedure which was carried out on the 8” Buehler Microcloth polishing pad using 3μm and 1μm diamond particles. The samples were sonicated in ethanol for 10 minutes to remove any residual grease or particles from the surface. After the thickness and composition measurements, one from each of Cu and Ni-Cu samples were selected to conduct vibratory polishing on a 12” Buehler Microcloth and Buehler Vibromet at 20% intensity and ion milling (Hitachi IM4000 Plus using Ar ions at the acceleration voltage of 4kV for 0.5-1 minutes) for the purpose of grain size analysis in the scanning electron microscope (SEM).

For the sample of experiment 3 of Cu deposition and experiment 2 of Ni-Cu alloy deposition, another one 5 mm by 100 mm strip was cut to produce the sections following the same procedure as above. After cleaning the surface, these pieces were used to observe the surface morphology.

3.4 Material Characterization Techniques

For the purpose of this study, several material characterization techniques were employed to analyze the thickness, composition, and surface morphology of the plated materials of interest.

3.4.1 Scanning Electron Microscopy

Two kinds of scanning electron microscopes (SEMs) were used for this project: Hitachi SU3500 for surface morphology and Hitachi SU5000 for deposit thickness and grain size analysis on the cross-sections of the samples. Surface morphology characterization was carried out by using the second electron (SE) detector with a working voltage of 10 kV for both Cu and Ni-Cu deposit samples. Characterizing the cross-sections of the samples required a higher voltage between 15-20 kV. In order to have a better contrast between the substrate and the electrodeposit, the backscattered electron (BSE) signal was analyzed, especially for the Cu deposit.

3.4.2 Energy Dispersive X-Ray Spectroscopy

Energy Dispersive X-Ray Spectroscopy (EDS) (Bruker, XFlash 6|60) in combination with the Hitachi SU5000 was used to obtain the composition of Ni-Cu alloy samples as well as their thickness. Since the thicknesses of the alloy deposits were relatively low, element mapping from the EDS could give more accurate thickness measurement by showing distinct color contrast between the deposit and the substrate.
Chapter 4

4 Modeling Setup

This chapter focuses on the simulation modeling setup in the COMSOL Multiphysics software package. Starting with pure Cu deposition, modeling results were compared with the experimental results and generally good agreement was found. For the alloy electrodeposition, the simulation was first set up and then modified according to the experimental results. Then the result predicted by the model under new conditions was verified by comparing with the corresponding experimental results. In addition to the Hull cell deposition, the simulation was also done for the ID tube Ni-Cu alloy deposit which was described in 1.4 without considering the flow of bubbles in the electrolyte.

2D models were chosen for the simulation of both Hull cell and ID tube plating processes (Appendix C). Considering the strong agitation effect in the Hull cell, it is reasonable to assume that the electrolyte properties are the same at different heights in the cell. Therefore, the 2D cross-section plane parallel to the bottom was used in the simulation. Regarding the ID tube plating, various factors including concentric anode placement, incompressible fluid, and turbulence flow allowed the axial cross-section of the electrolyte to be the representative plane for the simulation.

4.1 Simulation Parameters

In this study, all major parameters involved in the electrodeposition process such as electrolyte conductivity, concentration, exchange current density, equilibrium potential, diffusion coefficient, and transfer coefficient can be defined as the input parameters in COMSOL. The parameters derived from the literature review will be applied first and fitted later by comparing with the experimental results.

For the pure copper deposition in the acid solution, the model should take into account two ionic species: Cu$^{2+}$ and H$^+$. On the other hand, for the Ni-Cu alloy electrodeposition, at least three ionic species, NiCit$^-$, CuCit$^-$, and OH$^-$, must be included in the model [85]. The relevant parameters should be defined prior to the calculation. Some of these parameters, for example, geometry, temperature, ion concentrations, current (or current density), conductivity of the bath and flow rate were known from the preset or measured values. Other parameters, especially the electrochemical
parameters, such as equilibrium potential, transfer coefficient, diffusion coefficient, and exchange current density were selected based on the literature review specified in Chapter 2. However, since the experimental temperature in most of the studies in literature was room temperature which is much lower than the temperature of about 60°C used in this study for the Ni-Cu alloy deposition, some parameters such as diffusion coefficient and exchange current density needed to be corrected accordingly. Calculation of the corrections is shown in Appendix A.

4.1.1 Diffusion Layer Thickness of Ni-Cu Alloy Electrodeposition

For the case of Ni-Cu alloy deposition in the Hull cell, very limited information could be found in the literature regarding the diffusion layer thickness. For the configuration used in this study, the cathode surface can be approximated as a flat electrode with laminar flow. Levich [95] first introduced an equation (4.1), which was also adopted by Tobias et al. [96] and Di [97] in their works, to calculate the diffusion layer thickness under such conditions:

\[
\delta_i = 3 \left( \frac{D_i}{\nu} \right)^{\frac{1}{3}} \left( \frac{\nu X}{u} \right)^{\frac{1}{2}}
\]  

(4.1)

Where:

- \( \delta \) is the diffusion layer thickness, m
- \( D_i \) is the diffusion coefficient of species \( i \), m²·s⁻¹
- \( \nu \) is the kinetic viscosity of the liquid, mol·m²·s⁻¹
- \( X \) is the coordinate along the plate counting from the edge, m
- \( u \) is the velocity of the electrolyte, m s⁻¹

The initial input values of the average \( \delta \) of NiCit⁻ and CuCit⁻ ions using the Hull cell were calculated in Appendix B based on (4.1). It should be noted that at the two ends of the cathode where the agitation plate could not reach, \( \delta \) was higher and the value was eventually obtained through the model fitting.

The alloy electrodeposition inside the tube, however, is a new application and no information regarding the diffusion layer thickness is available. Based on the Reynolds number (Re) in Appendix B, the flow pattern at the simulation condition is turbulent flow which means a uniform thickness can be assumed for both NiCit- and CuCit- ions. In the simulation, a range of thickness from 30 to 90 \( \mu \)m is investigated to compare the simulation results at different \( \delta \) values.
The main parameters applied in the simulation are provided in Table 4-1 for the Hull cell simulation and Table 4-2 for the ID tube plating simulation.

### Table 4-1. Main Parameters Applied in the Hull Cell Simulation

<table>
<thead>
<tr>
<th>Name</th>
<th>Unit</th>
<th>Cu</th>
<th>Ni-Cu</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma )</td>
<td>[S/m]</td>
<td>21</td>
<td>9.6</td>
<td>Electrolyte conductivity</td>
</tr>
<tr>
<td>( I )</td>
<td>[A]</td>
<td>2</td>
<td>1, 2</td>
<td>Applied total current</td>
</tr>
<tr>
<td>( \delta_{\text{Cu}} )</td>
<td>[m]</td>
<td>( 3 \times 10^{-5} )</td>
<td>-</td>
<td>Diffusion layer thickness of Cu(^{2+}) at 25°C</td>
</tr>
<tr>
<td>( \delta_{\text{Ni}} )</td>
<td>[m]</td>
<td>-</td>
<td>( 2.1 \times 10^{-5} )</td>
<td>Average diffusion layer thickness of NiCit(^{-}) at 60°C</td>
</tr>
<tr>
<td>( \delta_{\text{Cu}} )</td>
<td>[m]</td>
<td>-</td>
<td>( 9.3 \times 10^{-5} )</td>
<td>Average diffusion layer thickness of CuCit(^{-}) at 60°C</td>
</tr>
<tr>
<td>( \rho_{\text{Ni}} )</td>
<td>[kg/m(^3)]</td>
<td>-</td>
<td>8908</td>
<td>Density, nickel</td>
</tr>
<tr>
<td>( \rho_{\text{Cu}} )</td>
<td>[kg/m(^3)]</td>
<td>8960</td>
<td>8960</td>
<td>Density, copper</td>
</tr>
<tr>
<td>( M_{\text{Ni}} )</td>
<td>[g/mole]</td>
<td>-</td>
<td>58.69</td>
<td>Molar mass, nickel</td>
</tr>
<tr>
<td>( M_{\text{Cu}} )</td>
<td>[g/mole]</td>
<td>63.55</td>
<td>63.55</td>
<td>Molar mass, copper</td>
</tr>
<tr>
<td>( i_{0\text{Cu}} )</td>
<td>[A/m(^2)]</td>
<td>13</td>
<td>-</td>
<td>Exchange current density, Cu(^{2+}) reaction</td>
</tr>
<tr>
<td>( i_{0\text{Ni}} )</td>
<td>[A/m(^2)]</td>
<td>-</td>
<td>14</td>
<td>Exchange current density, NiCit(^{-}) reaction</td>
</tr>
<tr>
<td>( i_{0\text{CuCit}} )</td>
<td>[A/m(^2)]</td>
<td>-</td>
<td>280</td>
<td>Exchange current density, CuCit(^{-}) reduction</td>
</tr>
<tr>
<td>( i_{0\text{OH}} )</td>
<td>[A/m(^2)]</td>
<td>-</td>
<td>1.2</td>
<td>Exchange current density, H(_2)O reduction</td>
</tr>
<tr>
<td>( c_{0\text{Cu}} )</td>
<td>[mol/l]</td>
<td>0.76</td>
<td>-</td>
<td>Initial concentration, Cu(^{2+}) ion</td>
</tr>
<tr>
<td>( c_{0\text{Ni}} )</td>
<td>[mol/l]</td>
<td>-</td>
<td>0.35</td>
<td>Initial concentration, NiCit(^{-}) ion</td>
</tr>
<tr>
<td>( c_{0\text{CuCit}} )</td>
<td>[mol/l]</td>
<td>-</td>
<td>0.0175</td>
<td>Initial concentration, CuCit(^{-}) ion</td>
</tr>
<tr>
<td>( c_{0\text{OH}} )</td>
<td>[mol/l]</td>
<td>-</td>
<td>( 3.16 \times 10^{-10} )</td>
<td>Initial concentration, OH(^{-}) ion</td>
</tr>
<tr>
<td>( D_{\text{Cu}} )</td>
<td>[m(^2)/s]</td>
<td>( 7.4 \times 10^{-10} )</td>
<td>-</td>
<td>Diffusivity, Cu(^{2+})</td>
</tr>
<tr>
<td>( D_{\text{Ni}} )</td>
<td>[m(^2)/s]</td>
<td>-</td>
<td>( 3.45 \times 10^{-11} )</td>
<td>Diffusivity at 60°C, NiCit</td>
</tr>
<tr>
<td>( D_{\text{CuCit}} )</td>
<td>[m(^2)/s]</td>
<td>-</td>
<td>( 2.9 \times 10^{-9} )</td>
<td>Diffusivity at 60°C, CuCit(^{-})</td>
</tr>
<tr>
<td>( D_{\text{OH}} )</td>
<td>[m(^2)/s]</td>
<td>-</td>
<td>( 5.5 \times 10^{-9} )</td>
<td>Diffusivity, OH</td>
</tr>
<tr>
<td>( E_{\text{eq}} )</td>
<td>[V]</td>
<td>0.333</td>
<td>-</td>
<td>Equilibrium potential, Cu(^{2+})/Cu reduction vs SHE</td>
</tr>
<tr>
<td>( E_{\text{eq}} )</td>
<td>[V]</td>
<td>-</td>
<td>-0.427</td>
<td>Equilibrium potential, NiCit(^{-})/Ni reduction vs SHE</td>
</tr>
<tr>
<td>( E_{\text{eq}} )</td>
<td>[V]</td>
<td>-</td>
<td>0.161</td>
<td>Equilibrium potential, CuCit(^{-})/Cu reduction vs SHE</td>
</tr>
<tr>
<td>( E_{\text{eq}} )</td>
<td>[V]</td>
<td>-</td>
<td>-0.566</td>
<td>Equilibrium potential, H(_2)O/H(_2) reduction vs SHE</td>
</tr>
<tr>
<td>( \alpha_{\text{a}} )</td>
<td>Cu</td>
<td>1.5</td>
<td>-</td>
<td>Anodic transfer coefficient, Cu(^{2+})/Cu</td>
</tr>
<tr>
<td>( \alpha_{\text{c}} )</td>
<td>Cu</td>
<td>0.5</td>
<td>-</td>
<td>Cathodic transfer coefficient, Cu(^{2+})/Cu</td>
</tr>
<tr>
<td>( \alpha_{\text{a}} )</td>
<td>NiCit</td>
<td>-</td>
<td>1.55</td>
<td>Anodic transfer coefficient, NiCit(^{-})/Ni</td>
</tr>
<tr>
<td>( \alpha_{\text{c}} )</td>
<td>NiCit</td>
<td>-</td>
<td>0.45</td>
<td>Cathodic transfer coefficient, NiCit(^{-})/Ni</td>
</tr>
<tr>
<td>( \alpha_{\text{a}} )</td>
<td>CuCit</td>
<td>-</td>
<td>1.916</td>
<td>Anodic transfer coefficient, CuCit(^{-})/Cu</td>
</tr>
<tr>
<td>( \alpha_{\text{c}} )</td>
<td>CuCit</td>
<td>-</td>
<td>0.084</td>
<td>Cathodic transfer coefficient, CuCit(^{-})/Cu</td>
</tr>
<tr>
<td>( \alpha_{\text{a}} )</td>
<td>OH(^{-})</td>
<td>-</td>
<td>1.75</td>
<td>Anodic transfer coefficient, H(_2)O/H(_2)</td>
</tr>
<tr>
<td>( \alpha_{\text{c}} )</td>
<td>OH(^{-})</td>
<td>-</td>
<td>0.25</td>
<td>Cathodic transfer coefficient, H(_2)O/H(_2)</td>
</tr>
</tbody>
</table>
Table 4-2. Main Parameters Applied in the ID Tube Plating Simulation

<table>
<thead>
<tr>
<th>Name</th>
<th>Unit</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma )</td>
<td>[S/m]</td>
<td>16</td>
<td>Electrolyte conductivity</td>
</tr>
<tr>
<td>( T )</td>
<td>[K]</td>
<td>343.15*, 333.15, 323.15</td>
<td>Electrolyte temperature</td>
</tr>
<tr>
<td>( i )</td>
<td>[A/m²]</td>
<td>100, 300, 500*, 700, 900</td>
<td>Applied current density</td>
</tr>
<tr>
<td>( ID_c )</td>
<td>[m]</td>
<td>9.525×10⁻³* 1.27×10⁻² 2.54×10⁻²</td>
<td>Inner diameter of the cathode</td>
</tr>
<tr>
<td>( OD_a )</td>
<td>[m]</td>
<td>3.175×10⁻³</td>
<td>Outer diameter of the anode</td>
</tr>
<tr>
<td>( L )</td>
<td>[m]</td>
<td>0.3</td>
<td>Length of the pipe</td>
</tr>
<tr>
<td>( u )</td>
<td>[m/s]</td>
<td>0.39</td>
<td>Annular flow velocity</td>
</tr>
<tr>
<td>( \delta )</td>
<td>[µm]</td>
<td>30,50*,70,90</td>
<td>Diffusion layer thickness at cathode surface</td>
</tr>
<tr>
<td>( \rho_{Ni} )</td>
<td>[kg/m³]</td>
<td>8908</td>
<td>Density, nickel</td>
</tr>
<tr>
<td>( \rho_{Cu} )</td>
<td>[kg/m³]</td>
<td>8960</td>
<td>Density, copper</td>
</tr>
<tr>
<td>( M_{Ni} )</td>
<td>[g/mole]</td>
<td>58.69</td>
<td>Molar mass, nickel</td>
</tr>
<tr>
<td>( M_{Cu} )</td>
<td>[g/mole]</td>
<td>63.55</td>
<td>Molar mass, copper</td>
</tr>
<tr>
<td>( i_{0_{NiCt}} )</td>
<td>[A/m²]</td>
<td>14*, 7.3</td>
<td>Exchange current density, NiCt reaction</td>
</tr>
<tr>
<td>( i_{0_{CuCt}} )</td>
<td>[A/m²]</td>
<td>280*, 160</td>
<td>Exchange current density, CuCt reduction</td>
</tr>
<tr>
<td>( i_{0_{OH}} )</td>
<td>[A/m²]</td>
<td>1.2*, 1</td>
<td>Exchange current density, H₂O reduction</td>
</tr>
<tr>
<td>( c_{0_{NiCt}} )</td>
<td>[mol/l]</td>
<td>0.312, 0.511*, 0.624, 0.78</td>
<td>Initial concentration, NiCt ion</td>
</tr>
<tr>
<td>( c_{0_{CuCt}} )</td>
<td>[mol/l]</td>
<td>0.0156</td>
<td>Initial concentration, CuCt ion</td>
</tr>
<tr>
<td>( c_{0_{OH}} )</td>
<td>[mol/l]</td>
<td>3.16×10⁻¹⁰</td>
<td>Initial concentration, OH ion</td>
</tr>
<tr>
<td>( D_{NiCt} )</td>
<td>[m²/s]</td>
<td>6.25*, 3.45, 1.84×10⁻¹¹</td>
<td>Diffusivity at 70°C, 60°C, and 50°C, NiCt⁻</td>
</tr>
<tr>
<td>( D_{CuCt} )</td>
<td>[m²/s]</td>
<td>5.25*, 2.9, 1.54×10⁻⁹</td>
<td>Diffusivity at 70°C, 60°C, and 50°C, CuCt⁻</td>
</tr>
<tr>
<td>( D_{OH} )</td>
<td>[m²/s]</td>
<td>5.5×10⁻⁹</td>
<td>Diffusivity, OH⁻</td>
</tr>
<tr>
<td>( \tilde{E}<em>{eq</em>{NiCt}} )</td>
<td>[V]</td>
<td>-0.427</td>
<td>Equilibrium potential, NiCt⁻ reduction vs SHE</td>
</tr>
<tr>
<td>( \tilde{E}<em>{eq</em>{CuCt}} )</td>
<td>[V]</td>
<td>0.161</td>
<td>Equilibrium potential, CuCt⁻ reduction vs SHE</td>
</tr>
<tr>
<td>( \tilde{E}<em>{eq</em>{OH}} )</td>
<td>[V]</td>
<td>-0.566</td>
<td>Equilibrium potential, H₂O reduction vs SHE</td>
</tr>
<tr>
<td>( \alpha_a_{NiCu} )</td>
<td></td>
<td>1.55</td>
<td>Anodic transfer coefficient, NiCt/Ni</td>
</tr>
<tr>
<td>( \alpha_c_{NiCu} )</td>
<td></td>
<td>0.45</td>
<td>Cathodic transfer coefficient, NiCt/Ni</td>
</tr>
<tr>
<td>( \alpha_a_{CuCu} )</td>
<td></td>
<td>1.916</td>
<td>Anodic transfer coefficient, CuCt/Cu</td>
</tr>
<tr>
<td>( \alpha_c_{CuCu} )</td>
<td></td>
<td>0.084</td>
<td>Cathodic transfer coefficient, CuCt/Cu</td>
</tr>
<tr>
<td>( \alpha_a_{OH} )</td>
<td></td>
<td>1.75</td>
<td>Anodic transfer coefficient, H₂O/H₂</td>
</tr>
<tr>
<td>( \alpha_c_{OH} )</td>
<td></td>
<td>0.25</td>
<td>Cathodic transfer coefficient, H₂O/H₂</td>
</tr>
</tbody>
</table>

* Indicates the default condition for the simulation

4.2 Hull Cell Modeling

The 2D modeling setup of the Hull cell started with the definition of the calculation domain with the same geometry as the one used in the experiments shown in Figure 4-1. A certain thickness of the diffusion layer was considered for both Cu and Ni-Cu co-deposition simulations as specified in section 4.1. For the Hull cell modeling, only the electrodeposition physics was implemented in
the simulation. The fluid flow caused either by the natural convection due to density differences or the forced convection because of agitation were not taken into account.

The calculation domain was then meshed into subdomains of the free electrolyte region and the diffusion layer region by different methods in COMSOL: “free triangle” for the free electrolyte region and “quad” for the diffusion layer region. Because of the different diffusion layer thicknesses of NiCit and CuCit ions, two layers have to be considered with respect to the alloy model meshing. Figure 4-2 shows the meshing results of the pure Cu metal and Ni-Cu alloy electrodeposition models with the meshing in the diffusion layer shown in the inset figures. It is obvious that the relatively thin diffusion layer requires much finer meshing compared to the free electrolyte region. In order to increase the calculation accuracy, quads type mesh was applied for the diffusion layer considering its regular parallelogram geometry. The final Cu deposition model had 6318 total meshing elements including 4818 triangles and 1500 quads, and the model for Ni-Cu alloy deposition had 11374 total meshing elements with 6374 triangles and 5000 quads.

![Figure 4-1. Hull cell geometry and boundary set up in COMSOL](image-url)
Figure 4-2. Meshing results of the Cu (left) and the Ni-Cu (right) electrodeposition models

Simulation of all three current distribution classes, PCD, SCD, and TCD, were carried out first for the Cu deposition in the Hull cell. The validity of the software in terms of the physics, accuracy, and electrochemistry was assessed by comparing the simulation results with the results reported in the literature or obtained from the experiments. No change in the Cu ion concentration was considered in PCD and SCD simulation. TCD, however, was allowed to include a gradient of the concentration. Considering the agitation effect in the bath and the Cu anode dissolution to replenish the consumed Cu ions, the Cu concentration can be treated as constant in the bulk while the gradient will only exist in the diffusion layer. Then the TCD simulation can be realized in COMSOL by combining SCD with the “transport of diluted species” (TDS) to simplify the calculation.

Mathematical simulation of Ni-Cu co-deposition has to include the mass transport influence or the TCD class because, depending on the operating conditions, the cathode surface concentration of the reactants always differ from their bulk concentration. Therefore alloy simulation is performed with TCD by the combination of SCD and TDS as well. Constant NiCit˚ ion concentration is used in the bulk when applying pure Ni as the anode material. Whereas, the bulk CuCit˚ concentration is decreasing during the electrodeposition which is reflected in the simulation by defining the concentration as a function of time.
4.3 ID Tube Plating

Similar to the Hull cell case, ID tube plating modeling was built by using the 2D “rotation” model with identical geometry as what used by Integran Technologies Inc. in the production process. In addition to the electrodeposition, the flow model is also coupled to simulate the moving condition inside the electrolyte. Figure 4-3 presents both model configuration with the outline and boundary definition.

![Diagram](image)

**Figure 4-3. ID tube plating model of electrodeposition (left) and flow (right)**

For meshing, the electrolyte domain is again divided into the free electrolyte region and the diffusion layer region. Since both regions are relatively small with a regular rectangular shape, only the “quad” tool in COMSOL was used to mesh these two regions as shown in Figure 4-4 (only the bottom part is presented in order to clearly indicate the meshing result). Much finer meshing was required in the diffusion layer region to calculate the flow condition and deposition process more precisely. Due to the regular rectangular geometry, quads type mesh was chosen for both the bulk and diffusion layer. Finally, the model had 748 elements consisting of 600 quads, 140 edge and 8 vertex elements.

The electrodeposition simulation of the ID tube plating was completed with TCD method in COMSOL. The moving electrolyte inside the tube enables the continuous replenishment of NiCit
and CuCit, which have a constant concentration in the bulk up to the boundary of the diffusion layer.

\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[ -p \mathbf{I} + \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \right] + \mathbf{F} \quad (4.2)
\]

and

\[
\rho \nabla \cdot \mathbf{u} = 0 \quad (4.3)
\]

Where:
- \( \rho \) is the fluid density, kg·m\(^{-3}\)
- \( \mathbf{u} \) is the fluid velocity vector, m·s\(^{-1}\)
- \( p \) is the fluid pressure, Pa
- \( \mu \) is the fluid dynamic viscosity, Pa·s
- \( \mathbf{F} \) is the viscous stress tensor, Pa

One of the most used turbulence models for industrial applications is the \( k-\varepsilon \) turbulence model to solve RANS equations. COMSOL provides the standard \( k-\varepsilon \) model [98], which introduces two additional transport equations and two dependent variables: the turbulent kinetic energy, \( k \), and the turbulent dissipation rate, \( \varepsilon \).

The transport equation of \( k \) is:
\[
\rho \frac{\partial k}{\partial t} + \rho \mathbf{u} \cdot \nabla k = \nabla \cdot \left[ \left( \mu + \frac{\mu_T}{\sigma_k} \right) \nabla k \right] + P_k - \rho \epsilon
\] (4.4)

Where the turbulent viscosity \( \mu_T \) is modeled as:

\[
\mu_T = \rho C_{\mu} \frac{k^2}{\epsilon}
\] (4.5)

and the production term \( P_k \) is:

\[
P_k = \mu_T \left[ \nabla \mathbf{u} : (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} (\nabla \cdot \mathbf{u})^2 \right] - \frac{2}{3} \rho k \nabla \cdot \mathbf{u}
\] (4.6)

The transport equation for \( \epsilon \) is

\[
\rho \frac{\partial \epsilon}{\partial t} + \rho \mathbf{u} \cdot \nabla \epsilon = \nabla \cdot \left[ \left( \mu + \frac{\mu_T}{\sigma_\epsilon} \right) \nabla \epsilon \right] + C_{\epsilon_1} \frac{\epsilon}{k} P_k - C_{\epsilon_2} \rho \frac{\epsilon^2}{k}
\] (4.7)

\( C_{\mu}, C_{\epsilon_1}, C_{\epsilon_2}, \sigma_k, \) and \( \sigma_\epsilon \) are the constant with values selected in the model as in Table 4-3:

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{\mu} )</td>
<td>0.09</td>
</tr>
<tr>
<td>( C_{\epsilon_1} )</td>
<td>1.44</td>
</tr>
<tr>
<td>( C_{\epsilon_2} )</td>
<td>1.92</td>
</tr>
<tr>
<td>( \sigma_k )</td>
<td>1.0</td>
</tr>
<tr>
<td>( \sigma_\epsilon )</td>
<td>1.3</td>
</tr>
</tbody>
</table>

4.4 Convergence of Simulation

Considering the strong nonlinear characteristics of the equations involved in the electrodeposition process, model convergence is a critical factor affecting the simulation process. In order to minimize the non-convergent issue, special measures such as the dimension of the calculated domain, the meshing method, the interface boundary condition and the turbulent flow model are taken into consideration in this study. By carefully selecting and integrating these measures, the convergence of simulation is eventually guaranteed. Detailed discussion on the convergence of the simulation is provided in Appendix C.
Chapter 5

5 Results and Discussion

This chapter presents the characterization results, including weight, thickness, composition, grain size and surface morphology, of the experiments for both Cu and Ni-Cu alloy electrodeposition in the Hull cell. A comparison of the simulation results with the experimental results will be also provided with analysis and discussion. The thickness and composition distribution will be plotted based on the SEM and EDS characterization data of all the samples at different positions on the cross-section surface. The complete datasheets of the measurement are presented in Appendix D.

For the ID tube Ni-Cu alloy plating, the simulation results are presented in terms of the distribution of composition, concentration and thickness along the pipe. Moreover, the influence of cathode diameter, flow rate, Ni/Cu ratio, and cathode length on the final deposit results are predicted by the simulation for ID tube plating.

5.1 Cu Deposition in the Hull Cell

5.1.1 Experimental Results

As specified in Table 3-3, a total of 5 experiments were carried out for Cu deposition in the Hull cell. The surface images of the entire plates in Figure 5-1 show the significant influence of agitation inside the bath. Current density increases from the right to the left on the surface according to section 1.4. The coordination system used in the study is shown in Figure 5-1 (a) as well.

![Figure 5-1](image)

Figure 5-1. The surface appearance of Cu electrodeposits in the Hull cell at (a) 15mins with agitation, (b) 30mins with agitation, (c) 45mins with agitation, (d) 5mins without agitation, (e) 30mins without agitation
For the 3 experiments with agitation, the surfaces are smooth and almost identical to each other with reddish brown color no matter how long the plating time was. However, a black or “burned deposit” area can be found in the HCD region for the last two experiments without agitation. Furthermore, the burned region is larger at the top which can be attributed to the edge effect due to the taping of the brass substrate plates. Since the reduction of Cu is very fast at the HCD edge, the depleted Cu ions cannot be replenished without sufficient agitation, which will change the electrochemical reaction to the water reduction to produce hydrogen and hydroxide ions. The plated material at the burned area is porous and easily peels off. Since burned deposits should be avoided in a real production process, its characterization and simulation will not be included in this study.

5.1.1.1 Surface Morphology

Although the electrodeposition results show a relatively smooth surface in terms of its appearance at low magnification, the surface morphology of experiment 3 characterized by SEM clearly shows roughness on the micro-scale and a significant influence of current density at various positions as shown in Figure 5-2 a - e.

Figure 5-2. Surface morphology of experiment 3 at selected locations

From the commonly-used scale (see Appendix E) which is designed specifically for Hull cell testing, the approximate local current densities at positions from (a) to (e) are 90, 50, 27, 13 and 2
mA·cm$^{-2}$, respectively. The image obtained at a lower current density or lower overpotential, Fig 5-2 e, shows many small grains with some larger (10-20 μm) grains randomly distributed in the small-grain matrix. When the current density is increased to (d), the surface shows predominantly of 20 μm more faceted crystals. It is interesting to note that the grains in Fig 5-2 d have a preferential octahedral shape which was earlier reported by Mercado et al. [99] as well. A detailed mechanism of the formation of this prism structure was given by Banthia et al. [100]. When the current density is further increased (Fig 5-2 c, b, a), the rapid deposit growth rate makes the small grains unresolvable. The deposits then show the typical cauliflower structure.

5.1.1.2 Grain Size and Structure

Figure 5-3 and Figure 5-4 show the cross section grain structure of experiment 3 at X=80mm and X=10mm, respectively, which reflect the influence of different current density on the grain morphology in the deposit. Theses samples were prepared by vibratory polishing and ion milling which is described in section 3.3.

It can be seen from the figures that the boundary between the deposit and the substrate can be clearly distinguished at both current densities. Initially reduced metal atoms arrive in random positions on the cathode surface without necessarily minimizing the energy [101] giving the growth of extremely fine grains at the substrate surface shown in Figure 5-3 (a)(b) and Figure 5-4 (a)(b). With increasing deposit thickness, however, crystals having a specific plane and surface energy will preferentially grow in order to minimize the total surface energy and form larger crystals. But the final crystal structures at various current densities are dramatically different from each other. At X=80mm where the current density is low, grains appear to have equiaxed shape with a small aspect ratio and a size from 1μm to 5 μm. On the other hand, at high current density shown in Figure 5-4 (a) where X=10mm, the crystals have an obvious columnar shape with an aspect ratio of 100 or more, indicating specific crystal directions have a significant growth advantage over other directions. Further analysis of Figure 5-4(b) shows that in the region less than 10 μm from the substrate, although columnar crystals have been generated, there are still a large number of non-columnar grains, which are no longer present at the top region shown in Figure 5-4(c), where only columnar crystals can be found. The width of the columnar crystal can be determined from Figure 5-4(d) and is generally no more than 1 μm.
Figure 5-3. Crystal size and structure of experiment 3 at (a) X= 80mm. In (b), the corresponding magnified image of (a) is shown.

Figure 5-4. Crystal size and structure of experiment 3 at (a) X= 10 mm. In (b), (c), and (d), the corresponding magnified images of (a) are shown.
5.1.1.3 Electrodeposition Mass

A high precision scale was used to measure the weight of the cathode before and after electrodeposition to calculate the weight of the electrodeposits. These values are then compared with the theoretical weights calculated from Faraday’s Law (5.1) in Table 5-1.

\[ m = \frac{I_{tot} \cdot M}{nF} \]  

(5.1)

where:

- \( m \) is the theoretical deposit mass, g
- \( I_{tot} \) is the total applied current, 2 A
- \( t \) is the plating time, s
- \( M \) is the molar mass of copper, 63.55 g·mol\(^{-1}\)
- \( n \) is the number of electrons, 2 for the case of Cu
- \( F \) is Faraday constant, 96485 C·mol\(^{-1}\)

Table 5-1. Comparison of Experimental and Theoretical Electrodeposition Mass

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Experimental Mass (g)</th>
<th>Theoretical Mass (g)</th>
<th>Deviation (%)</th>
<th>Agitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.59</td>
<td>0.593</td>
<td>0.51</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>1.18</td>
<td>1.186</td>
<td>0.51</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>1.77</td>
<td>1.778</td>
<td>0.45</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>0.196</td>
<td>0.198</td>
<td>1.01</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>1.14</td>
<td>1.186</td>
<td>3.88</td>
<td>No</td>
</tr>
</tbody>
</table>

Low deviation values of the plating results with agitation means almost all the current applied into the system is used to reduce copper ions into copper metal. The relative lower efficiency for the experiments without agitation can be attributed to the generation of hydrogen.

5.1.1.4 Electrodeposition Thickness

For the five 5mm × 20mm pieces made from each experimental deposit sample, four positions are selected for each piece to measure the thickness, therefore, a total of twenty measurement results are available for each sample to compare with the simulation results. Appendix D provides the complete thickness measurement results of Cu electrodeposition experiment 1, 2 and 3 (Table 3-3). Figure 5-5 illustrates the thickness value measurement of experiment 3 by using SEM images at randomly selected locations on the sample as an example.
5.1.2 Simulation Results

5.1.2.1 Current Density Distribution

All three current distribution classes are simulated and compared as shown in Figure 5-6, where current density, $i$, is plotted against the normalized cathode surface coordinate, $x$, which equals to the X value (mm) divided by the entire length of the cathode (100 mm). $x = 0$ is the closest end (HCD) of the cathode from the anode, and $x = 1$ corresponds to the furthest end (LCD) of the cathode from the anode. The normalized surface coordinate is used in order to compare with the results reported in the literature which had various cathode width. All three curves are not uniform and decrease rapidly from over 200 mA·cm$^{-2}$ to near 0 along $x$. It is obvious that the curves of SCD and TCD are almost identical to each other, and the curve of PCD is also quite similar with only a slightly higher slope when $x$ approaches 0 and 1. The uneven distribution of all the three results is quite different from what was reported by Palli et al. [21] and Low et al. [44] at lower current.
density. In their studies, they found for PCD to TCD, the current distribution curves would become much more uniform and eventually approach the average current density. This discrepancy can be explained by using the Tafel Wagner number, $W_{aT}$, defined as:

$$W_{aT} = \frac{\beta_c \sigma}{i_{avg} \epsilon}$$  \hspace{1cm} (5.2)

Where:

- $\beta_c$ is the cathodic Tafel slope, 118 mV
- $\epsilon$ is the characteristic length of the system, 10 cm (cathode length for this case)

$W_{aT}$ is a measure of the uniformity of the current distribution: the higher of $W_{aT}$, the more uniform of the current distribution [19]. At low $W_{aT}$, the distribution of SCD or TCD becomes very nonuniform and approaches the PCD class.

![Graph showing current distribution classes](image)

**Figure 5-6. Simulation results of various current distribution classes**

$W_{aT}$ values reported in the literature and for this study are given in Table 5-2. The high current density chosen in this study leads to the much lower $W_{aT}$ value and thus a non-uniform current distribution regardless of the category.

<table>
<thead>
<tr>
<th>$i$, mA·cm$^2$</th>
<th>Palli et al. [21]</th>
<th>Low et al. [44]</th>
<th>Matlosz et al. [19]</th>
<th>This Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-8.2</td>
<td>0.01-20</td>
<td>0.94-23.6</td>
<td>44.4</td>
<td></td>
</tr>
<tr>
<td>1.1-4.6</td>
<td>0.11-229.7</td>
<td>0.063-1.6</td>
<td>0.053</td>
<td></td>
</tr>
</tbody>
</table>

**Table 5-2. $W_{aT}$ Values Reported in the Literature and for This Study**
TCD simulation results are then compared with the reported analytical and empirical solutions in Figure 5-7 in terms of normalized current density, which is the ratio of local current density, $i$, to the average current density, $i_{avg}$. Because all the solutions in the literature were achieved by assuming a primary current distribution, they have a larger slope compared to the current TCD simulation results. However, because of the lower $W_{at}$ used in this study, the difference among the curves is relatively small.

![Graph](image)

**Figure 5-7. Normalized current density reported in literature and from this study**

According to Faraday’s Law, the local and average current densities can be calculated as:

$$i = \frac{\delta \rho n F}{t M} \quad \text{and} \quad i_{avg} = \frac{\delta_{avg} \rho n F}{t M}$$  \hspace{1cm} (5.3)

Therefore, the experimental normalized current density, $\frac{i}{i_{avg}}$, can be obtained from the normalized thickness, $\frac{\delta}{\delta_{avg}}$, by measuring the thickness at different locations. Figure 5-8 presents a comparison of the normalized current density between the simulation and the experiments. The results are in excellent agreement which confirms that the simulation is a good representation of the current distribution characteristics on the cathode in the Hull cell. As a consequence, the electrochemical simulation results of COMSOL can be considered reliable and be used in other research aspects.
5.1.2.2 Electrodeposition Thickness

The experimental results of the thickness are compared with the simulated ones in Figure 5-9. It is clearly seen that the thickness measured under all experimental conditions matches the corresponding simulation results very well with negligible deviation.

5.1.2.3 Electrodeposit Mass

The simulated mass is calculated based on the integration of the current density on the cathode surface and Faraday’s Law. The comparison between the experiments and the simulation as shown in Table 5-3 indicates the excellent consistency among the results.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Experimental Mass (g)</th>
<th>Simulation Mass (g)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.59</td>
<td>0.593</td>
<td>0.51</td>
</tr>
<tr>
<td>2</td>
<td>1.18</td>
<td>1.186</td>
<td>0.51</td>
</tr>
<tr>
<td>3</td>
<td>1.77</td>
<td>1.778</td>
<td>0.45</td>
</tr>
</tbody>
</table>

5.1.2.4 Cathode Overpotential and Surface Concentration

In addition to providing some results to compare with the experimental results, simulation can also provide results which are hardly measured in the experiment. Figure 5-10 shows the distribution of overpotential, $\eta$, and Cu$^{2+}$ concentration on the surface of the cathode at the end of experiment 3. It is known that the overpotential will directly influence the reaction rate, and then change the cathode surface Cu$^{2+}$ concentration. From Fig 5-10, it is evident that at $x=0$ where the highest overpotential is obtained, the corresponding Cu$^{2+}$ concentration reaches its lowest value because of the very fast reaction. However, a highest concentration of 0.76mol·L$^{-1}$ is obtained at the furthest end of the cathode where $\eta$ is very low. It can also be seen in Fig 5-10 that the concentration drops rapidly at the high overpotential region which can be explained by the exponential relation between the reaction rate, $i$, and $\eta$ according to equation (2.17).

![Figure 5-10. Cathode overpotential and surface Cu$^{2+}$ concentration of experiment 3](image-url)
5.2 Ni-Cu Co-deposition in the Hull cell

Three experiments were carried out for Ni-Cu co-deposition using various parameters in terms of temperature, time and current as specified in table 3-3. Out of these experiments, experiment 2 was selected to use as the input information for the fitting of the model to obtain some necessary parameters, such as diffusion coefficient and bath conductivity. The fitted parameters are then used to predict the result of experiment 1 in terms of composition, thickness, and mass. Finally the validity of the model is determined by comparison with the measured results of experiment 1.

Moreover, since the accuracy of the experimental process has an important impact on the model fitting and verification, experiment 3 which has very similar conditions as experiment 2 is used to investigate the repeatability of the experiments by comparison with experiment 2.

5.2.1 Experimental Results

The surface appearance of all the samples is presented in Figure 5-11 a-c corresponding to experiments 1 to 3 in the alloy electrodeposition. In contrast to single Cu deposit (Fig 5.1 a-c), the results of Ni-Cu alloy deposit in the Hull cell show distinct changes in the surface appearance along the X-axis. For the low current case of experiment 1, the surface can be roughly divided into 6 regions from I to VI in Figure 5-11(a) according to the appearance, while for the higher current case of experiment 2 and 3, one additional burned area VII exists at the HCD end as shown in Figure 5-11(b) and (c). By using the 267 ml Hull cell scale (see Appendix E), a similar local current density is obtained for the same region regardless of the total applied current. Table 5-4 summarizes the appearance and corresponding current density at each region.

![Figure 5-11. The surface appearance of Ni-Cu alloy deposit in the Hull cell](image)
The low current density preferentially deposits copper, as can be seen from the much larger reddish color region I in experiment 1. Increasing the current density will result in more Ni reduction in the deposit as the color changes to grey or even darker. Region III which shows a mirror-like surface finish is likely more attractive for industrial application. It should be noted that the boundary lines between the respective regions are not perpendicular to the X-axis, indicating that the alloy composition is different along the Y direction at the same X position, which can be attributed to the non-uniform stirring in the bath.

Table 5-4. Appearance and Local Current Density of Ni-Cu Alloy Deposition

<table>
<thead>
<tr>
<th>Region</th>
<th>Appearance</th>
<th>Local Current Density (mA·cm⁻²)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Reddish</td>
<td>0-3 0-1</td>
</tr>
<tr>
<td>II</td>
<td>Grey</td>
<td>3-9 1-8.5</td>
</tr>
<tr>
<td>III</td>
<td>Mirror</td>
<td>9-12 8.5-13</td>
</tr>
<tr>
<td>IV</td>
<td>Bright</td>
<td>12-20 13-20</td>
</tr>
<tr>
<td>V</td>
<td>Grey</td>
<td>20-45 20-45</td>
</tr>
<tr>
<td>VI</td>
<td>Black &amp; Grey</td>
<td>&gt;45 &gt;45</td>
</tr>
<tr>
<td>VII</td>
<td>Burned</td>
<td>&gt;45 1-110</td>
</tr>
</tbody>
</table>

*: Values are read from the Hull cell scale (Fig 11-1)

5.2.1.1 Surface Morphology

The surface morphologies at several of locations (a-l) of sample 2 are shown in Figure 5-12 a to l, which clearly indicate the development of surface roughness and its relation with the appearance of the deposit.

Small nodules with a size of no more than 1 µm can be found in the low current density regions from (a) to (c). It is obvious that the density of the nodules decreases with increasing current density. The entire surface is covered with the nodules in (a) while about half the surface is smooth in (c) and most nodules are very small. The disappearance of nodules eventually gives rise of the mirror-like surface in (d) to (e) where a featureless smooth surface is produced. Position (f), which is at the boundary between the mirror and grey color region, still maintains a relatively smooth surface but a lightly cracked coating begins to develop as shown in the image. The cracking and large nodule formation is becoming more significant from (g) to (i) when the current density is further increased. At even higher current density, the cauliflower-like structure can be formed on the surface as presented in (j) and (k). At the highest current density position (l), a dendrite
structure is generated. Overall, the change in growth morphology with increasing current density/overpotential is very similar to what was earlier described in literature [100].

Figure 5-12. Surface morphologies of experiment 2 at selected locations
5.2.1.2 Grain Size and Structure

Cross-sectional grain structure images at two representative positions on the deposit from experiment 1 are shown in Figure 5-13 and Figure 5-14. At X=95mm where the current density is very low, the image represents the Cu-rich region (Fig 5-13). The image for X=60mm (Fig 5-14), however, is in the Ni-rich region. Significant difference in terms of the grain size and shape can be found between these two regions: the Cu-rich region has a relatively large grain size of around 100-200nm with a distinct equiaxed crystal shape. For the Ni-rich region, the overall grain size is decreased significantly. Similar to the pure Cu electrodeposition, the smallest grains are formed at the interface between the substrate and deposit. But the upper part in the deposit does not show the obvious increase in the size of the grains. Although some grains have a columnar shape, a large number of fine equiaxed crystals having a size of 20-50 nm are also present as shown in Figure 5-14 d. Nady and Negem [57] observed similar results in their research that the Cu-rich region in Ni-Cu alloy electrodeposition had grain sizes ranging from 62 to 120 nm, and the grain size of the Ni-rich region was between 13 to 47 nm. Comparison with the Cu electrodeposition result demonstrates there are much smaller nano-size grains in Ni-Cu alloy electrodeposits which was also reported by some other studies [66], [69], and [83].

![Figure 5-13. Crystal size and structure of electrodeposits from experiment 1 at (a) X= 95 mm. In (b), the corresponding larger magnification image of (a) is shown](image-url)
Figure 5-14. Crystal size and structure of electrodeposit from experiment 1 at (a) X = 60 mm. In (b), (c), and (d), the corresponding higher magnification images of (a) are shown.

5.2.1.3 Electrodeposit Mass

The same scale used for Cu electrodeposit was chosen for measuring the weight of the cathodes before and after electrodeposition to calculate the weight of Ni-Cu alloy. However, it is difficult to obtain the theoretical weight from Faraday’s Law because the respective current densities for the Ni and Cu reduction and hydrogen evolution cannot be separated from the total current. The measurement results for all the experiments are presented in Table 5-5 together with the weight when assuming only Ni or Cu is reduced. It is obvious that the deposit mass is much lower than the results of the reduction of either pure Ni or Cu, meaning a significant amount of hydrogen is produced during the electrodeposition process.
Table 5-5. Measured and Assumed Mass of Ni-Cu Electrodeposition

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Measured Mass (mg)</th>
<th>Assumed Mass of Pure Ni Reduction (mg)</th>
<th>Assumed Mass of Pure Cu Reduction (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>259.6</td>
<td>383</td>
<td>414</td>
</tr>
<tr>
<td>2</td>
<td>270.8</td>
<td>547</td>
<td>593</td>
</tr>
<tr>
<td>3</td>
<td>285.8</td>
<td>547</td>
<td>593</td>
</tr>
</tbody>
</table>

5.2.1.4 Alloy Composition and Thickness

Cross-sectional EDS mapping results regarding the composition of Ni-Cu electrodeposit with the corresponding line scan results at some selected positions of experiment 3 are shown in Figure 5-15 (a) (c) (e) (g) and (b) (d) (f) (h), respectively. Not only can the composition data be obtained from the EDS analysis, but the thickness of the deposit is also calculated by taking the average value of at least three measurements at each position, for example, as indicated by the black arrows in Figure 5-15 (c).
Figure 5-15. EDS mapping results at selected positions of experiment 3. In (b), (d), (f), and (h), the corresponding line scan images are shown. (red: Ni, green: Cu, purple: Zn, yellow: C, I: substrate, II: transition region, III: deposit, IV: transition region, V: epoxy)

The composition and thickness measurement methods illustrated above are applied for the measurement of samples from experiment 1 and 2 as well. For each deposit sample, in total 25 locations were selected to perform EDS mapping analysis. The local composition of the bulk alloy is analyzed and recorded to plot the distribution of composition over the cathode surface. Figure 5-16 provides the measurement results of experiment 2 as an example. The complete measurement results of the composition of experiments 1, 2 and 3 are provided in Appendix F. Under the operating conditions of this study, experiment 2 shows a distribution of 26% to 72% regarding the Ni content along the cathode surface, indicating a strong influence of current density on the Ni-Cu co-electrodeposition. At the lower current density region, the electrode potential is low as well which is beneficial for the reduction of Cu, so a Cu-rich region existed between X= 80 to 100 mm. When the current density increases, Ni reduction becomes easier because of the more negative electrode potential, leading to much higher Ni content in the deposit until reaching the highest value at X=40 mm. Further increases in the current density after this point will significantly
promote the hydrogen evolution, which in turn inhibits the total metal reduction reactions and reduces its partial current density. This is similar to the case at low current densities where the Cu reduction is more preferential and the Ni content tends to decrease. More Cu reduction can also be attributed to that the diffusion controlled Cu reduction process is improved by the more vigorous agitation effect because of the hydrogen evolution. The average Ni composition over the entire surface is also evaluated, for instance, for experiment 2 as shown Figure 5-16 (right) by integrating the measured value against the X-axis. The data of 58.1% was obtained for experiment 2, which will be compared with the simulated value later.

Figure 5-16. Local (left) and average (right) Ni composition of Ni-Cu alloy electrodeposits

Figure 5-17 shows the thickness distributions of experiment 2 on the cathode from the EDS mapping analysis. Appendix D provides the complete thickness measurement results of alloy experiment 1, 2 and 3. The majority of the thickness values are between 6 to 10 μm except for the lower current density region and it is relatively scattered in the measurement results. Although these results are compared with simulated values later in the text, it should be noted that thickness measurement values may only be used as a reference due to possible errors from the EDS technique.

(1) Interaction volume at an accelerating voltage of 20kV. Because the three elements (Ni, Cu and Zn) involved in this study have very high Kα values (7.480keV, 8.046keV, and 8.637keV, respectively), a high acceleration voltage of 20 kV was required. This will introduce an interaction volume of approximately 2 μm with the associated uncertainty at
the substrate-deposit interface (Figure 5-18). Because the brass substrate plate contains copper, the interaction volume will affect the copper concentration measurement in regions close to the substrate-deposition interface;

(2) **Uneven free surface.** For example, in Figure 5-15 (c), the uneven surface could result in a difference of 2μm in the thickness;

(3) **Transition regions.** Figure 5-15(h) shows the position of the transition regions II and IV. The two interfaces within these regions are difficult to be defined precisely which also give a total uncertainty of about 3μm.

![Graph](image)

**Figure 5-17. Alloy thickness measurements for experiment 2**

![Diagram](image)

**Figure 5-18. Schematic drawing of the interaction volume**
The composition and thickness of experiment 1 will be presented in section 5.2.3 together with the model verification. The comparison between experiment 2 and 3 in terms of the composition and thickness will be conducted in section 5.2.4 to show the reproducibility of the experiments.

5.2.2 Simulation Results of Experiment 2

Simulation is carried out at first to fit the experimental results of experiment 2 regarding the composition, thickness, and mass in order to verify or obtain some critical parameters, such as the diffusion coefficient, reduction potential, and transfer coefficient.

5.2.2.1 Ni Composition

Figure 5-19 shows the simulation results for the Ni composition along the cathode surface of experiment 2. The experimental data (from Fig. 5-16) is also included for comparison purpose. In general good agreement is found between the simulated and the experimental results for both experiments with the exception of the high Ni content region, where the simulation results are slightly lower than the experimental ones with a deviation about 3%. This small deviation may be due to the not fully representative initial parameters, for example, the diffusion coefficient of CuCit. Given the complex case of alloy deposition simulation, a deviation of 3% can be acceptable.

![Figure 5-19. Comparison of the simulated and the measured Ni composition of experiment 2](image-url)
As shown in Figure 5-16, in addition to the local composition, the average composition is another way to verify the accuracy of the simulation. The calculation of the Ni average composition results in 58.6% and 59.1% for the simulation and the measurement of experiment 2, respectively. The agreement is within 1%.

5.2.2.2 Electrodeposit Thickness

Simulation result of the electrodeposit thickness of experiment 2 is shown in Figure 5-20 in comparison of experimental data (from Fig. 5-17). It’s obvious that the simulation can in general follow the trend in the distribution of thickness on the cathode surface. The increasing thickness from $X = 100$ mm to $X = 40$ mm in simulation presents more electrodeposited metal due to the increase in the current density. However, beyond this point as depicted for the range between $X = 0$ to $X = 40$ mm, further increase in the current density will lower the thickness of the deposit due to the more severe evolution of hydrogen which consumes more and more of the applied current, thereby reducing the metal reduction and the deposit thickness.

While the general trends for deposit thickness are similar for the simulation and the experiment, comparison of individual points indicates a relatively high difference of around 2 $\mu$m at some positions, for example, the low current density region. Furthermore, in areas with thicker simulation results, the measurement results also have a certain deviation. The reasons could be the possible errors during the thickness measurements, which were discussed in section 5.2.1.4: interaction volume, uneven free surface, and transition regions at the interface.

Different from the local thickness results, a comparison of the average values between the simulation and the measurement has a much smaller deviation of 1.8% for experiment 2. The average thickness of the simulation is 6.89 $\mu$m, and the measurement has a result of 6.77 $\mu$m. This good agreement is due to the fact that both positive and negative thickness deviations existed in the local measurements which cancel each other out when taking the average from the experimental results. Thus the average experimental thickness is much closer to the average simulated thickness.
5.2.2.3 Electrodeposit Mass

Not only is the total mass of the electrodeposit of importance, the respective mass of Ni and Cu in the deposit of experiment 2 can also be obtained in the simulation as shown in Table 5-6. This table presents the experimental results of the total, Ni, and Cu mass, which are calculated from the average composition value, in comparison with the corresponding simulation results. As seen from the table, the small deviations between the simulation and experiment reveal an excellent agreement and further proves the reliability of the model.

Table 5-6. Electrodeposition Mass of Simulation and Measurement of Experiment 2

<table>
<thead>
<tr>
<th>Item</th>
<th>Simulation (mg)</th>
<th>Experiment (mg)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>268.9</td>
<td>270.8</td>
<td>-0.7</td>
</tr>
<tr>
<td>Cu</td>
<td>111.4</td>
<td>110.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Ni</td>
<td>157.5</td>
<td>160</td>
<td>-1.6</td>
</tr>
</tbody>
</table>

5.2.2.4 Current Density Distribution

Fitting the aforementioned experimental results allowed to determine the critical parameters to generate the current density distribution as shown in Figure 5-21 for experiment 2. The almost constant partial current density for the Cu reduction indicates a mass-transfer control mechanism for this reaction, where the current density or overpotential distribution on the cathode surface has
negligible influence on its reaction rate. It is obvious in Figure 5-22 that the concentration of CuCit’ is close to 0 over the entire cathode surface.

Figure 5-21. Current density distribution of experiment 2

In contrast, the hydrogen (H₂) evolution partial current density shows a very strong relationship with the X position, or the overpotential on the cathode. Almost no H₂ is found when X > 40mm where the overpotential is low. As X approaches 0 where the highest overpotential is expected, the reaction rate of H₂ evolution increases exponentially as seen in Figure 5-21, indicating the charge transfer control mechanism of the H₂ evolution reaction which is very sensitive to the overpotential.

The partial current density of the Ni reduction, however, shows a small peak at X around 40 mm, where the surface concentration of NiCit’ approaches 0 according to Figure 5-22. Therefore in the range of X = 40 to 100 mm where the surface concentration of NiCit’ is high enough, the reaction is under charge transfer control. Beyond that point in the interval of X =0 to 40 mm, the much lower NiCit’ concentration changes the reaction mechanism to mass transfer control with a gradually decreasing partial current density for Ni reduction. In summary, the simulation result reveals a combined control mechanism for the Ni reduction in Ni-Cu alloy electrodeposition.
5.2.3 Verification and Prediction of the Simulation

The purpose of modeling is not just to fit the existing experiments. More important is to predict the plating behavior at different operating conditions. Also, it is expected to use the modeling result as a guideline to determine the operating conditions necessary to achieve the required deposit composition.

In the following, a validity test of the alloy model is performed by predicting the results of experiment 1 with the same thermodynamic and kinetic parameters obtained from experiment 2 fitting process. This study will concentrate on predicting and then verifying the composition, thickness and mass of experiment 1 which is electrodeposited at a different time, temperature, and current compared to experiment 2 (Table 5-7).

Table 5-7. Main Operating Parameters of Experiment 1 and Experiment 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plating Time, t</td>
<td>min</td>
<td>21</td>
<td>15</td>
</tr>
<tr>
<td>Total Current, I</td>
<td>A</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Temperature, T</td>
<td>°C</td>
<td>57</td>
<td>61</td>
</tr>
</tbody>
</table>

After the verification, a brief demonstration on choosing the optimum bath composition and applied current density by using the modeling result will be presented.
5.2.3.1 Verification of the Simulation

5.2.3.1.1 Ni Composition

The theoretical alloy composition predicted by modeling for experiment 1 as a function of cathode surface position is indicated in Figure 5-23 by the solid line. Compared to the results of experiment 2 which is operated at a higher current, a significant larger Cu-rich region can be found in the simulation result of experiment 1 from $X = 60$ to 100 mm. This is consistent with the large reddish sample area of experiment 1, as seen in Fig. 5-11. Furthermore, the highest Cu content of over 95% in the alloy is found at the LCD, which is much higher than that found in experiment 2. This indicates more favorable reduction of Cu at low applied current. Regarding the Ni content, it is obvious that the peak Ni composition from the simulation is quite similar to the result of experiment 2 (Fig. 5-19), but with the peak position shifted to the left.

![Graph showing Ni composition vs. cathode surface distance](attachment:graph.png)

**Figure 5-23. Comparison of the simulated and the measured Ni composition of experiment1**

The simulation is then verified by comparing with the experimental results which are superimposed in the figure as red squares. They correspond to each other especially well at the high current density region. This region is also the Ni-rich region, or when the cathode surface distance is less than 60 mm. The highest Ni content in measurement and simulation are 71.6% and 68.1%, respectively. In the Cu-rich region, however, a relatively large difference in the Ni composition value of up to 11% can be found. This deviation may be due to the calculated diffusion
layer thickness of NiCit (Appendix B 9.2) within this region not perfectly matching the real experimental thickness which is difficult to measure in practice. This will cause a certain deviation in the calculation of Ni content for the simulation. However, the more likely cause is the influence of substrate material (brass or Cu-Zn alloy) on the measurement of Cu during EDS analysis. The high accelerating voltage used in EDS analysis results in a larger interaction volume of about 2 μm. For the region where the deposit is thin, the analysis results may be affected by the substrate because part of the X-ray signal from the substrate could also be included in the measurement. Therefore, the measured Cu content in the thin deposit may be higher than its actual value since the substrate material also contains copper. This can also result in the measured Ni content being lower than the actual result. In order to obtain more accurate composition data at the thin deposit region, the substrate influence should be removed from the deposit measurement. The substrate used in this experiment has a composition of 67 wt% Cu and 33 wt% Zn, and there is no Zn formed in the deposit. Therefore the amount of Cu originated from the substrate in the EDS analysis can be indirectly obtained by using the measured amount of Zn.

Table 5-8 shows the EDS mapping results of Ni, Cu and Zn content at positions of 3 μm or less in thickness. These positions are more likely to be affected by the interaction volume effect. The significant amounts of Zn in all results indicates a strong influence from the substrate.

The local Ni composition, w_Ni, in Figure 5-23 is automatically calculated in the EDS analysis by considering Ni and Cu content as:

\[
    w_{Ni} = \frac{Ni(\text{wt} \%)_{\text{Ni}}}{{Ni(\text{wt} \%)_{\text{Ni}} + Cu(\text{wt} \%)_{\text{Cu}}}} \times 100\%
\]

(5.3)

Obviously, this calculation is more reliable when the influence of the substrate is negligible. But in this case, it should be corrected since the contribution of the substrate cannot be ignored. Based on the composition of the substrate, the amount of Cu from the substrate will be 2 times of the Zn amount, so the corrected Ni composition, w_Ni’, is obtained by,

\[
    w_{Ni}' = \frac{Ni(\text{wt} \%)_{\text{Ni}}}{Ni(\text{wt} \%)_{\text{Ni}} + Cu(\text{wt} \%)_{\text{Cu}} - 2 \times Zn(\text{wt} \%)} \times 100\%
\]

(5.4)

The difference between w_Ni and w_Ni’ can be clearly seen in Table 5-8. As mentioned earlier, the local Ni composition will be lowered because of the excess Cu introduced from the substrate.
at the thin deposit region. As the thickness of the deposit increases, this effect will be significantly reduced. This may explain the reason why the modeling results are poor in the copper-rich region where the thickness is low, while it is in good agreement with the measured results at the nickel-rich region which has a much thicker deposit.

Table 5-8. Characterization of Ni Content at Selected Positions

<table>
<thead>
<tr>
<th>Analysis</th>
<th>X=98mm</th>
<th>X=94mm</th>
<th>X=90mm</th>
<th>X=86mm</th>
<th>X=82mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (μm)</td>
<td>1.68</td>
<td>2.29</td>
<td>2.08</td>
<td>1.88</td>
<td>2.79</td>
</tr>
<tr>
<td>Ni (wt%)</td>
<td>2.40</td>
<td>2.44</td>
<td>4.17</td>
<td>13.11</td>
<td>12.79</td>
</tr>
<tr>
<td>Cu (wt%)</td>
<td>80.79</td>
<td>83.8</td>
<td>86.77</td>
<td>78.1</td>
<td>79.52</td>
</tr>
<tr>
<td>Zn (wt%)</td>
<td>16.81</td>
<td>13.74</td>
<td>8.79</td>
<td>8.79</td>
<td>7.69</td>
</tr>
<tr>
<td>w_Ni (%)</td>
<td>2.88</td>
<td>2.83</td>
<td>4.59</td>
<td>14.4</td>
<td>13.9</td>
</tr>
<tr>
<td>w_Ni* (%)</td>
<td>4.76</td>
<td>4.15</td>
<td>5.92</td>
<td>18.5</td>
<td>17.2</td>
</tr>
</tbody>
</table>

In terms of the average Ni composition, a good fit between the simulation and experiment can be obtained with the corresponding values of 48.1% and 46.6%, respectively, even without considering the correction of w_Ni. In particular, if the data of the area with a thickness less than 3μm is not considered, almost identical average values of 56.5% and 56.8% are obtained, indicating an excellent match between the simulation and experiment when the deposit is thick enough to minimize the influence of interaction volume.

5.2.3.1.2 Electrodeposit Thickness

The solid line in Figure 5-24 indicates the predicted thickness distribution over the cathode surface of experiment 1 from the simulation. Like the previous results of experiment 2 (Fig. 5-20), the thickness gradually increases from the LCD edge to its highest value of about 10 μm at the highest Ni content position and then drops to about 6.5 μm at the HCD end. This trend can be explained by the increasing electrodeposited metal with the increasing current density prior to the highest point and then the inhibited metal reduction process because of the hydrogen evolution after that point. When the prediction is compared with the measurement result of experiment 1, a reasonable match is found in the middle region of X from 25 mm to 80 mm which is the area with the minimum measurement deviation. When X is larger than 80 mm, this corresponds to a deposit thickness of less than 3μm. Here, the measurement results are not quite reliable because of the interaction volume effects which causes the substrate to influence the EDS results. For the measurements at positions from 0 to 25 mm, the deviation from the uneven free surface is the main cause. In addition to this, in the X range of 0 to 10 mm, the less dense structure of the deposit due to the severe
hydrogen evolution would make the measured thickness higher than its theoretical value. In general, the good agreement of the middle part illustrates the reliability of the model. Moreover, the average thickness from the prediction, 6.74µm, is fairly consistent with that of the experimental value, 6.46µm, having a deviation of only 4.3%.

![Graph showing comparison between simulated and measured thickness](image)

**Figure 5-24. Comparison of the simulated and the measured thickness of experiment 1**

### 5.2.3.1.3 Electrodeposit Mass

As can be seen from Table 5-9, the agreement between the predicted and the measured electrodeposit mass is very good. The slightly higher deviation in Ni content can be contributed to the possible measurement error in the Cu-rich region discussed above.

<table>
<thead>
<tr>
<th>Item</th>
<th>Simulation (mg)</th>
<th>Experiment (mg)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>273</td>
<td>260</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>142</td>
<td>139</td>
<td>2.2</td>
</tr>
<tr>
<td>Ni</td>
<td>131</td>
<td>121</td>
<td>8.3</td>
</tr>
</tbody>
</table>

### 5.2.3.1.4 Current Density Distribution

For experiment 1, the predicted current density distribution can be plotted against the position on the cathode as shown in Figure 5-25 (left). The prediction of current density is overall consistent
with the distribution pattern of the deposit Ni composition and thickness. From the partial current density distribution, the kinetic mechanism for all three reactions is the same as for experiment 2. CuCit\(^-\) reduction is under the mass-transfer control which is also clear from its cathode surface concentration curve in Figure 5-25 (right). The hydrogen evolution curve depicts the typical charge transfer control process. It is worth noting that the partial current densities of hydrogen evolution over the cathode are considerably lower than the corresponding values in experiment 2 (Fig. 5-21), indicating this side reaction is inhibited at lower applied current and a higher current efficiency is hence expected. The gradually increasing partial current density of NiCit\(^-\) reduction from X=100 mm to X=25 mm along with the increase in overpotential shows the charge transfer control mechanism. However, when X is less than 25 mm, the low cathode surface concentration of NiCl\(^-\) shown in Figure 5-25 (right) will change the mechanism to the mass transfer control process, and the Ni reduction partial current decreases with the further decrease in the concentration.

**Figure 5-25. Simulation of the current density distribution (left) and the cathode surface concentration (right) of experiment 1**

In summary, the simulation and experimental results match fairly well, indicating the validity of the model.

### 5.2.3.2 Determination of the Optimum Conditions by Modeling

One of the objectives of this study was to reasonably model the Ni-Cu alloy deposition process in order to determine the optimum operating conditions to plate Monel alloy which contains about 67% nickel. From the literature study, the Ni/Cu ions ratio in the bath and the current density are
the most sensitive variables influencing the final electrodeposited alloy composition. Although only one bath composition was used in the study (Table 3-1), the results of other compositions as well as the optimum current density can also be predicted by using the model.

Figure 5-26 illustrates the effect of bath composition on the deposit composition by using the model setup of experiment 2 with the same initial [CuCit\(^-\)] of 0.0175 mol·L\(^{-1}\). A wide range current densities from 0 to 150 mA·cm\(^{-2}\) were investigated to mimic typical industrial processes. It is evident that the current density has a significant influence on the final Ni content. The influence of the [NiCit\(^-\)]/[CuCit\(^-\)] ratio, however, depends on the control mechanism of NiCit\(^-\) reduction. In the lower current density region where the reduction of NiCit\(^-\) is controlled by the electron transfer step, the almost overlapping curves among various [NiCit\(^-\)]/[CuCit\(^-\)] ratios in Figure 5-26 (left) indicate a very small influence of concentration. The concentration does not play a critical role in the deposit composition until the reaction becomes mix-controlled by the electron transfer and mass transfer processes: the higher [NiCit\(^-\)]/[CuCit\(^-\)] ratio, the higher the Ni content in the deposit.

**Figure 5-26. Modeling prediction of Ni composition (left) and current efficiency (right) as a function of current density at various bath compositions**

Under the simulation condition, an initial ratio of 10:1 cannot give the Monel alloy composition for any current density, while for the other three ratios, two possible current densities for each are available as labeled “a” to “f” to produce the Monel alloy containing 67% Ni. It should also be noted that the ratios indicated here are based on the initial bath composition. In order to mimic the configuration of experiment 2 where the anode is nickel, the bulk concentration of NiCit\(^-\) is
maintained as constant during the simulation, but a gradual decrease in the bulk concentration of 
CuCit must be considered because of the consumption of CuCit ions. This depletion is calculated
to reach about 45% of total initial CuCit ion, which means that the real ratio at the end of
deposition should be roughly doubled. Although six possible conditions are given in Fig. 5-26
(left), it does not mean that all these conditions are acceptable in the industrial production. The
choice has to be done together with the current efficiency (CE), which is the proportion of the total
applied current density used for the metal reduction, predicted by the model as shown in Figure
5-26 (right). Based on the prediction, for all the Monel plating conditions, the corresponding bath
composition, current density, and current efficiency are indicated in Table 5-10.

From Table 5-10, the significantly high current efficiencies of conditions a, b, and c make them be
the possible candidates for further investigation.

<table>
<thead>
<tr>
<th>Item</th>
<th>Operating Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>[CuCit\textsuperscript-], mol\cdot L\textsuperscript{-1}</td>
<td>0.0175</td>
</tr>
<tr>
<td>[NiCit\textsuperscript-]/[CuCit\textsuperscript-]</td>
<td>40:1</td>
</tr>
<tr>
<td>i, mA\cdot cm\textsuperscript{-2}</td>
<td>27</td>
</tr>
<tr>
<td>CE, %</td>
<td>98.7</td>
</tr>
</tbody>
</table>

The above considerations just give a simple example of determining the operating conditions for
a very specific Ni composition by simulation. In reality any Monel type deposit with the Ni
composition between 63% and 67% is not expected to show major differences in properties [102].
For this reason, the target composition of 67% can be relaxed to 63% as shown in Figure 5-28.
The possible current densities at each [NiCit\textsuperscript-]/[CuCit\textsuperscript-] ratio to produce the Monel alloy will be a
range instead of the fixed value in Table 5-10. For example, the current density range for the ratio
of 20 is between 24 and 29 mA\cdot cm\textsuperscript{-2} which can be seen in Fig. 5-27.
5.2.4 Experimental Repeatability

As can be seen from the previous discussion, the accuracy of the experimental process has an important impact on the fitting and verification of model. Therefore, in addition to experiment 2, another experiment (experiment 3) which has very similar electrodeposition conditions (Table 3-3) was conducted and compared with experiment 2 in terms of mass, composition, and thickness to investigate the repeatability of the experimental process.

5.2.4.1 Electrodeposit Mass

As can be seen from the Table 5-5, the deposit mass of experiment 2 and 3 are 270.8g and 285.8g, respectively. The deviation of about 5.5% in the results shows the similarity and the repeatability of the two experiments with respect to the mass. In particular, considering that the slightly higher temperature in experiment 3 should result in more deposit, then the mass deviation would be even smaller if the experimental conditions are completely consistent.
5.2.4.2 Ni Composition

![Graph showing Ni composition over cathode surface distance]

**Figure 5-28. Local Ni composition of Ni-Cu alloy electrodeposition in experiments 2 and 3**

The EDS analysis results of local Ni composition of experiments 2 and 3 are shown in Figure 5-289. It is obvious that the composition distribution over the cathode surface of the two experiments are almost identical to each other, especially in the X range of 0 to 70 mm. Both experiments show a similar distribution regarding the Ni content with the highest value of 72.8% and 72.1% for experiments 2 and 3, respectively. The values of the average Ni composition of the two experiments, 59.1% and 56.6%, also indicate a reasonable match.
5.2.4.3 Deposit Thickness

![Deposit Thickness Graph](image)

**Figure 5-29. Deposit thickness of Ni-Cu alloy electrodeposition in experiments 2 and 3**

Figure 5-29 shows the deposit thickness distribution of experiments 2 and 3. As for experiment 2, relatively scattered results can be found for experiment 3. Most of the measured values are very close even overlapping, indicating the good agreement and repeatability between the experiments. The consistency of the two experiments can also be seen from the average thickness value. Experiment 2 has an average thickness of 6.77 μm, while the value of experiment 3 is 6.97 μm with the deviation of 3% only.

From the above comparison and discussion in terms of the mass, composition and thickness, the repeatability of the alloy electrodeposition experiments can be clearly identified.
5.3 Inner Diameter Tube Plating

Simulation of the inner diameter (ID) tube plating (Figure 4-3) was done by using the thermodynamics and kinetic parameters established in section 5.2. The plating results at the default conditions (Table 5-11) along the tube was first studied in section 5.3.1. Then the influence of variables such as current density, diameter, flow rate, and the diffusion layer thickness was evaluated in section 5.3.2. Three reactions described by (2.38), (2.39), and (2.40) on the cathode are considered during the simulation in order to reproduce the industrial process.

Table 5-11. Default Conditions for ID Tube Plating Simulation

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>pH</th>
<th>Cathode Inner Diameter (mm)</th>
<th>Anode Outer Diameter (mm)</th>
<th>NiCit(^{-}) bulk concentration (mol(\cdot)L(^{-}))</th>
<th>CuCit(^{-}) bulk concentration (mol(\cdot)L(^{-}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>3.5</td>
<td>9.525</td>
<td>3.175</td>
<td>0.511</td>
<td>0.0156</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrolyte Density (kg(\cdot)m(^{-}))</th>
<th>Applied Current Density (mA(\cdot)cm(^{-}))</th>
<th>Electrolyte Linear Velocity (m(\cdot)s(^{-}))</th>
<th>Electrolyte Volume Flowrate (L(\cdot)min(^{-}))</th>
<th>Tube Length (mm)</th>
<th>Diffusion Layer Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1090</td>
<td>50</td>
<td>0.39</td>
<td>1.5</td>
<td>300</td>
<td>50</td>
</tr>
</tbody>
</table>

5.3.1 Simulation Results at Default Condition

5.3.1.1 Cathode Surface Concentration Distribution

Different initial concentrations of NiCit\(^{-}\) and CuCit\(^{-}\) lead to the various reaction mechanisms according to the concentration distribution on the cathode surface shown in Figure 5-30. Along the height of the tube, [NiCit\(^{-}\)] gradually decreases from 0.511 mol\(\cdot\)L\(^{-}\) to 0.36 mol\(\cdot\)L\(^{-}\) (Fig. 5-29 left) and its reduction is mainly controlled by the electron transfer process. In contrast, a much faster reaction rate in the reduction of CuCit\(^{-}\) gives a sharp decrease in the concentration of CuCit\(^{-}\) to almost 0 mol\(\cdot\)L\(^{-}\) within the first 75 mm (Fig. 5-29 right), indicating a mass transfer control process.
Figure 5-30. Cathode surface concentration distribution of NiCit\(^-\) (left) and CuCit\(^-\) (right) in ID plating simulation

5.3.1.2 Ni Composition and Current Density Distribution

According to the simulation result as shown in Figure 5-31 (left), the Ni content increases significantly from 0 to 42% along the tube within about 75mm, which fits well the trend of concentration change of CuCit\(^-\). After that, since the mechanism of these two reduction reactions do not change during the plating process under the default conditions, the Ni content remains basically constant up to the tube outlet (Y=300mm).

The composition distribution is related to the corresponding reaction rate or the partial current density distribution along the cathode. Figure 5-31 (right) provides the partial current density distribution of the three reactions as well as the total current density. It is evident that near the inlet region (Y=0 mm), determined by its inherent thermodynamics and kinetic parameters, most of the current density comes from the CuCit\(^-\) reduction. But decreasing concentration rapidly lowers the CuCit\(^-\) reduction current density to a constant value about 28mA·cm\(^{-2}\). At the same time, the partial current density of NiCit\(^-\) reduction steadily increases to a constant value of about 20 mA·cm\(^{-2}\). Therefore, the composition remains almost unchanged after certain height. The hydrogen evolution is suppressed on the entire surface according to its extremely low current density. The current efficiency of the plating process is thus very high.
5.3.1.3 Thickness Distribution

The thickness of the deposit is proportional to the current density of metal reduction based on Faraday’s law (Equation 5.3) which is evident in Figure 5-32 when compared with the total current density curve in Figure 5-31.

Although the thickness distribution is uniform on most parts of the cathode surface, a significant higher value is found at the inlet region (Y=0mm). This is due to the very fast reduction of Cu at the inlet region according to its partial current density which can be found in Figure 5-31 (right).
Moreover, according to the simulation result, the non-uniform thickness length increases with longer plating time. In order to lower the inlet thickness and prevent the growth of the non-uniform length, insulating a certain length of the anode at the inlet part may be a choice. The Cu reduction at the inlet will be inhibited greatly because of the lower local current density, and a more uniform thickness distribution is hence expected.

5.3.1.4 Flow Velocity Distribution

The flow profile of the electrolyte in the ID plating at the default condition can be characterized by using the Reynolds number (Re) in Equation 5.4. Since Re > 2300, the flow profile is turbulent flow under the experimental condition.

\[
\text{Re} = \frac{\rho UD_H}{\mu} = \frac{1090 \times 0.39 \times 0.00635}{0.4 \times 10^{-3}} = 6748
\]  

(5.4)

where:

- \( \rho \) is the electrolyte density, 1090 kg·m\(^{-3}\)
- \( U \) is the velocity of electrolyte, 0.39 m·s\(^{-1}\)
- \( D_H \) is the hydraulic diameter, 0.00635 m
- \( \mu \) is the dynamic viscosity at 70°C, 0.4×10\(^{-3}\) Pa·s

Figure 5-33 (left) clearly shows the variation of velocity over the cathode surface along the flow path. The highest velocity only exists at the inlet followed by a significant drop due to the friction effect of the wall. But different from the laminar flow which will reach 0 at the pipe wall, there is still a certain velocity of 0.31 m/s at the wall under turbulent flow conditions. Figure 5-33 (right) indicates the velocity distribution in radical direction by investigating the cross-section at various heights near the inlet. An opposite development trend in the bulk and at the electrode surfaces can be found. According to the simulation, two transit regions with lower velocity than the initial velocity can be seen at anode and cathode surfaces right after the inlet, accompanied by an increasing velocity in the bulk. The thickness of these two regions gradually increases until \( Y = 50 \) mm where the flow is fully developed (Fig. 5-32 left). Beyond that position, the thickness of these regions will remain as constant up to the tube outlet.
5.3.2 Sensitivity Analysis

The cathode diameter, NiCit/CuCit$^-$ ion ratio together with two current densities of 50 mA·cm$^{-2}$ and 90 mA·cm$^{-2}$, electrolyte flow rate, and cathode length were chosen in this study for the sensitivity analysis. For all analyses, the sensitivity of these factors was investigated by the simulated Ni composition in the deposits, which is also one of the most important issues in the real production process. Moreover, the concentration distribution over the cathode surface was used to explain the possible reaction mechanism. To simplify the analysis, all the inlet CuCit$^-$ ion concentrations discussed below were maintained at their default value of 0.0156 mol·L$^{-1}$. According to section 5.3.1.1 and 5.3.1.2, the reduction of CuCit$^-$ will be controlled by the mass transfer process in all the following analyses. Therefore, only the NiCit$^-$ concentration simulation results were provided and analyzed below.

5.3.2.1 Cathode Diameter

Three cathodes with various inner diameters, $\frac{3}{8}$", $\frac{1}{2}$", and 1" (9.525mm, 12.7mm, and 25.4mm, respectively) were applied for the analysis. Changing the diameter will vary either the linear velocity or the volume flowrate from the default conditions (Table 5-11). To address this issue, the analysis was done by using either the default linear velocity (0.39 m/s) or the default volumetric flow rate (1.5 L/min). All the other parameters were remained the same as the default values.
5.3.2.1.1 Default Linear Velocity

Under the condition of default inlet linear velocity of 0.39 m/s, all three diameters still result in the turbulent flow profile to which the model can be applied. The diffusion layer thickness will be the same as well. As indicated in Figure 5-34 (left), the simulated results of Ni content distribution along the cathode does not show a significant difference among these tubes. Prior to the fully developed flow, the larger cathode diameter initially has a slightly lower Ni content, but a slightly higher value when Y is beyond 50 mm. These almost identical distribution curves indicate a similar reduction mechanism of NiCit\(^{-}\) among various cathodes. From Figure 5-34 (right), the surface concentrations of NiCit\(^{-}\) in all three cases are almost identical and high enough to keep the reaction mechanism in the electron transfer control region.

According to the simulation results, the linear velocity should be maintained the same when varying the size of the cathode in the industrial process to obtain deposits with similar composition.

![Figure 5-34. Distribution of Ni composition (left) and surface concentration of NiCit\(^{-}\) (right) at constant linear velocity (0.39m-s\(^{-1}\)) with different cathode diameters](image)

5.3.2.1.2 Default Volumetric Flow Rate

Keeping the same volumetric flow rate for different cathodes results in various linear velocities and, in turn, different diffusion layer thicknesses, which will affect the Ni composition results significantly as shown in Figure 5-35 (left).
According to the simulation result, a higher Ni composition can be obtained for the larger cathode when Y is less than 175 mm. This can be explained by the difference in the diffusion layer thickness caused by the various linear velocities. According to Levich [95] and other studies [19] [92], the diffusion layer thickness is inversely proportional to the square root of the linear velocity $u (u^{-0.5})$. The default thickness for 3/8” cathode was chosen as 50 µm according to Appendix B. The corresponding diffusion layer thicknesses for all the cathode diameters are shown in Table 5-12 by using the default volumetric flow rate of 1.5 L·min⁻¹. It’s obvious that the thickness will increase along with the larger cathode diameter. The reduction of CuCit⁻, which is controlled by the mass transfer process, is much more sensitive to the diffusion effect compared to the reduction of NiCit⁻. The negative effect of increasing in the diffusion layer thickness on the reaction rate of CuCit⁻ reduction is higher than that of NiCit⁻ reduction. Therefore, the Ni composition increases with increasing cathode diameter as shown in Fig. 5-34 (left).

**Table 5-12. Diffusion Layer Thickness for Various Cathode Diameters**

<table>
<thead>
<tr>
<th>Volume Flow, V (L·min⁻¹)</th>
<th>Cathode Inner Diameter, IDc (inch)</th>
<th>Linear Velocity, $u$ (m·s⁻¹)</th>
<th>$u^{-0.5}$</th>
<th>Diffusion Layer Thickness, $\delta$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>3/8</td>
<td>0.39</td>
<td>1.6</td>
<td>50</td>
</tr>
<tr>
<td>1.5</td>
<td>1/2</td>
<td>0.21</td>
<td>2.2</td>
<td>69</td>
</tr>
<tr>
<td>1.5</td>
<td>1</td>
<td>0.05</td>
<td>4.47</td>
<td>100*</td>
</tr>
</tbody>
</table>

*: Determined from the simulation
However, the increase in the diffusion layer thickness also hinders the transport of NiCit\(^-\) to the cathode surface. When the thickness is too large that the consumed NiCit\(^-\) on the cathode surface cannot be replenished because of the poor diffusion effect, the reduction of NiCit\(^-\) may be convert to mass transfer control. Under this condition, the reduction of CuCit\(^-\) will be the prominent one again, resulting in a decrease in the Ni composition as is the case of the 1” diameter cathode.

The above assumed mechanism can be verified by the simulated NiCit\(^-\) concentration results shown in Figure 5-35 (right). First, the increase in the diffusion layer thickness inhibits the diffusion effect of NiCit\(^-\). In general, the larger the cathode diameter, the faster the surface concentration drops along the flow direction. Second, the 1/2” diameter cathode can still maintain relatively high concentration over the entire surface regardless the change in the diffusion layer thickness. Therefore, a constant Ni composition can be obtained after a certain distance according to sections 5.3.1.1 and 5.3.1.2. Finally, the 1” diameter cathode experiences a fast decline in the NiCit\(^-\) concentration to almost 0 at Y = 125 mm, which changes the reduction mechanism of NiCit\(^-\) to the mass transfer control and corresponds to the change in the Ni composition distribution.

5.3.2.2 NiCit\(^-\)/CuCit\(^-\) Ratio and Current Density

According to the literature review in section 2.3.1, the Ni/Cu ion ratio in the bath together with the applied current density are expected to play a critical role in determining the final deposit composition. This influence was studied by comparing the deposit composition results of four different NiCit\(^-\)/CuCit\(^-\) ion ratios (20, 33, 40, and 50) at two current densities (50 mA·cm\(^{-2}\) and 90 mA·cm\(^{-2}\)).

Figure 5-36 (left) shows the Ni composition distribution of the four ratios at the current density of 50 mA·cm\(^{-2}\). It is obvious that the compositions of the deposits are almost identical for all the ratios. Therefore, it is reasonable to assume that the other three ratios will follow the same reduction mechanism as the default ratio of 33 (0.511/0.0156, see Table 5-11). According to section 5.3.1, the reduction of NiCit\(^-\) and CuCit\(^-\) under default condition should be controlled by charge transfer and mass transfer, respectively. In order to verify the assumption, the NiCit\(^-\) concentration over the cathode surface of the four ratios was simulated as shown in Figure 5-36 (right). It can be seen that although all the NiCit\(^-\) concentrations will decrease along the cathode, they are still high enough to prevent the occurrence of mass transfer control.
Figure 5-36. Distribution of the Ni composition in the deposit (left) and the NiCit⁻ ion concentration (right) at various NiCit⁻/CuCit⁻ ratios and 50 mA·cm⁻²

As a comparison, the influence of higher current density of 90 mA·cm⁻² was studied as well in terms of the Ni composition and NiCit⁻ concentration. The results are shown in Figure 5-37. Not surprisingly, increasing the current density is more beneficial to the reduction of NiCit⁻, leading to a much higher Ni composition in the deposits as indicated in Figure 5-37 (left). But different from the other ratios, there is a peak value of 73% for the ratio of 20, followed by a significant decline to 45% at the end of the cathode (Y=300mm). Based on the discussion in section 5.3.2.1.2, it is reasonable to assume that the reduction of NiCit⁻ for the ratio of 20 has become mass transport control after a certain distance on the cathode. But different from the influence of the diffusion layer thickness in that section, in this case, it can be attributed to the combined effect of the higher current density and lower surface NiCit⁻ concentration: the fast NiCit⁻ consumption on the cathode caused by the high current density may not replenish Ni²⁺ in time from the bath, resulting in extremely low NiCit⁻ concentration on the cathode surface.

The NiCit⁻ concentration was then simulated as shown in Figure 5-37 (right). It is evident that only the ratio of 20 has a rapid drop in the NiCit⁻ concentration to near 0, which matches the change in the composition very well.
Figure 5-37. Distribution of the Ni composition in deposit (left) and the NiCit⁻ ion concentration (right) at various NiCit⁻/CuCit⁻ ratios and 90 mA·cm⁻²

In fact, not only is there a significant fluctuation in the Ni content at the lowest ratio, but even at the default ratio of 33, the content will also decrease to some extent at the end of the cathode as shown in Figure 5-37 (left), indicating that in the production process, the NiCit⁻/CuCit⁻ ratio should be considered in parallel with the current density in order to obtain a constant composition over the entire cathode length.

5.3.2.3 Electrolyte Volumetric Flow Rate

In the actual production process, the volumetric flow rate of the electrolyte, V, can be adjusted within certain limits as required. It is therefore of interest to investigate the possible influence of the flow rate on the final deposit composition. Changing the flow certainly varies the linear velocity, u, inside the tube and affects the composition via the different diffusion layer thicknesses, δ. Table 5-13 gives the volume flow investigated in the simulation together with the corresponding δ.

<table>
<thead>
<tr>
<th>V (L·min⁻¹)</th>
<th>u (m·s⁻¹)</th>
<th>δ (μm)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>0.12</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.2</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.39</td>
<td>50</td>
<td>Default condition</td>
</tr>
<tr>
<td>4</td>
<td>1.09</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>
The difference in the Ni composition is obvious in Figure 5-38 (left) with respect to the various flow rates. It is reasonable that the thinner the diffusion layer, the more likely it is that the reduction of the mass-transfer controlled CuCit\(^-\) will preferly occur, leading to a lower Ni content. The concentration distribution of CuCit\(^-\) in Figure 5-38 (right) also reveals a much higher value over almost the entire cathode surface at \(\delta=30\mu m\) thickness. The main controlling factor, however, for the NiCit\(^-\) reduction is still the electron transfer based on its relatively higher concentration.

**Figure 5-38. Distribution of the Ni composition (left) and the CuCit\(^-\) concentration (right) at various volumetric flow rates (inset: NiCit\(^-\) concentration distribution)**

But it should be noted that the above analysis with almost constant Ni composition on most of the cathode surface is valid only when the reduction of NiCit\(^-\) is mostly controlled by the charge transfer step. Any factor which may change the mechanism to mass transfer control, for example, low velocity, high current density or low initial concentration, will dramatically influence the composition distribution profile as shown in Figure 5-35 (left) and Figure 5-37 (left).

### 5.3.2.4 Cathode Length and Current Density

The total cathode length is another concern in the ID plating process in terms of the possible change in the composition. It can be seen from the previous simulation results that the NiCit\(^-\) concentration on the cathode surface will gradually decrease along the flow direction in all cases. Although in most cases the Ni composition can be treated as constant after a certain distance \(Y\) on the cathode, the effect of decreasing concentration on the composition cannot be neglected when the tube is becoming longer. It is for this reason that the sensitivity with respect to cathode length \(Y\) was
investigated. In addition to the length, current density is often varied as well in the production process of ID plating, which also has a significant influence on the composition. Therefore, the influence of cathode length on the composition is evaluated here by using various lengths and different applied current densities.

Figure 5-39 shows the simulated results of Ni composition against different lengths and current densities. For all the applied current densities, a maximum Ni content, $w_{max}$, the value of which depends on the cathode length can be found at about $Y = 50$ mm, which then was followed by a gradual decline to the composition, $w_{end}$, at the end of the cathode, which needs to be addressed in the simulation. In order to compare the degree of decline, a specific value, $\frac{w_{max}}{w_{end}}$, is used to illustrate the non-uniformity of the composition along the tube wall. According to the industrial practice at Integran Technologies Inc. (Mississauga, ON, Canada), a ratio of 1.15 is regarded as the criteria of the maximum acceptable deviation. Table 5-14 shows the calculation results of $\frac{w_{max}}{w_{end}}$ as a function of current density and cathode length.

By using the ratio, the maximum lengths significantly differs from each other depending on the applied current density. For example, a total length of 2m can be applied for the current density of 30 mA·cm$^{-2}$. When the current density reaches 90 mA·cm$^{-2}$, however, the available length is only 0.4m.
Figure 5-39. Influence of cathode length on the deposit composition at current densities of
(a) 30, (b) 50, (c) 70, (d) 90 mA·cm$^{-2}$

As can be seen from the above, although the experimental verification is not carried out for the ID
plating, the simulation can still give the reasonable qualitative analysis results. Through the
simulation results of the Ni composition and the ion concentration on the cathode surface, the
sensitivity analysis of the different factors can also be initially obtained.
Table 5-14. $w_{\text{max}}/w_{\text{end}}$ Value at Different Cathode Length and Applied Current Densities

<table>
<thead>
<tr>
<th>Length (m)</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni content</td>
<td>$w_{\text{max}}$ (%)</td>
<td>$w_{\text{end}}$ (%)</td>
<td>$w_{\text{max}}/w_{\text{end}}$</td>
<td>$w_{\text{max}}$ (%)</td>
<td>$w_{\text{end}}$ (%)</td>
<td>$w_{\text{max}}/w_{\text{end}}$</td>
</tr>
<tr>
<td>$i=30$ (mA/cm$^2$)</td>
<td>12.8</td>
<td>12.6</td>
<td>1.02</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$i=50$ (mA/cm$^2$)</td>
<td>42.5</td>
<td>41.1</td>
<td>1.03</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$i=70$ (mA/cm$^2$)</td>
<td>59.6</td>
<td>56.7</td>
<td>1.05</td>
<td>60.6</td>
<td>56</td>
<td>1.08</td>
</tr>
<tr>
<td>$i=90$ (mA/cm$^2$)</td>
<td>69.3</td>
<td>63.8</td>
<td>1.09</td>
<td>70.8</td>
<td>60.8</td>
<td>1.16</td>
</tr>
</tbody>
</table>

$\rightarrow$: Simulation is not performed at this length

$/\$: Simulation is not performed at this length because the maximum deviation has been met before
6 Conclusions

In the first part of this study, Cu and Ni-Cu alloy electrodeposition experiments in a Hull cell were conducted at various working conditions followed by a simulation using COMSOL to investigate the possibility of using modeling to fit and predict the result of electrodeposition. For the second part of this thesis, the parameters obtained from the Hull cell simulation were then used in COMSOL to study the inner diameter tube plating under default conditions and the influence of different parameters on the electrodeposition results.

6.1 Cu Electrodeposition in the Hull cell

(1) In general, agitation had a significant influence on the final appearance of all studied electrodeposited Cu samples. A reddish and smooth surface was obtained with agitation while a burned deposit was observed without agitation. The electrodeposited mass matched the theoretical results well, indicating a high current efficiency during electrodeposition.

(2) Surface morphology, grain size, and deposit thickness analyses showed that the current density was a decisive factor in determining the shape of the grains on the surface, the cross-sectional structure of the grains, and the thickness distribution over the cathode surface. Equiaxed and columnar grain structures were observed at low and high current densities, respectively.

(3) Almost identical current density distribution profiles were found in the simulation for primary current distribution, secondary current distribution and tertiary current distribution, which was attributed to the much lower Tafel Wagner number ($W_{aT}$) used in this study that resulted in these highly non-uniform features.

(4) All the simulation results in terms of the normalized current density, thickness, and mass were in excellent agreement with both previous literature results and the experimental results, showing that the modeling method for Cu electrodeposition yielded reliable results.

6.2 Ni-Cu Alloy Electrodeposition in the Hull Cell

(1) Different regions on the surface were found in the electrodeposited samples. Lower current density gave rise to high Cu content in the deposits, and as the current density increases,
the appearance became gray because of the higher Ni content. The current efficiencies in these experiments were lower.

(2) The surface morphology varied from the growth process of grains to a featureless smooth surface with mirror finish depending on current density. Nano-size equiaxed crystal structure was obtained in the high Cu content region, while the Ni-rich region had an even smaller grain size of 20-50 nm.

(3) Fitting results showed a reasonable agreement between the simulation and the experiment regarding the local and average composition as well as the deposit weight. The relatively higher differences in the thickness at some cathode locations were attributed to uncertainties in the experimental analysis due to the interaction volume, uneven free surface, and the transition regions. The high H\textsubscript{2} evolution partial current density in the simulation at the nearest end of the Hull cell explained the reason for the low current efficiency. Moreover, modeling result of the ion concentration on the cathode surface indicated a mass-transfer control mechanism of Cu reduction and a mixed control mechanism for the Ni reduction depending on the current density.

(4) It was observed that the predicted composition, thickness, and electrodeposited mass are fairly consistent with the experimental results which further proved the reliability of the modeling approach. The deviation in the composition at the Cu-rich region was mainly attributed to the influence of the substrate on the EDS analysis. Thickness deviations were mainly due to the uneven coating surface from the hydrogen evolution.

(5) Optimum conditions for plating Monel alloy were investigated by modeling, according to which the Ni/Cu ion ratio and current density had interacting effects on the composition. The Ni/Cu ion ratio in the plating bath does not affect the composition until the current density is sufficiently high to trigger mixed control in the Ni reduction mechanism and result in a positive correlation between composition and concentration. The optimum operating conditions also considered the current efficiency.
6.3 Inner Diameter Tube Plating Simulation

(1) Simulation results at the default conditions revealed the electron-transfer control and mass-transfer control mechanisms for the Ni and Cu reduction, respectively. An almost constant composition can be expected on the cathode except for a certain distance from the inlet of the tube. A uniform increase in the thickness was obtained due to the continuously replenished bath. In terms of flow, a fully developed profile was formed after 50 mm.

(2) Changing the diameter of the tube when keeping volume flow constant, or varying the volume flow for the fixed tube changes the linear velocity of the electrolyte in the tube. This greatly affects the composition of the deposit because of the change in the diffusion layer thickness. However, if the linear velocity is maintained constant, changing the diameter of the tube only had a small influence on the composition.

(3) The Ni/Cu ion ratio and current density showed combined effects on the deposit composition. A lower ion ratio presented an obvious decline in the Ni composition at high current density.

(4) The influence of the tube cathode length on the composition was addressed at various lengths and current densities. In order to obtain a uniformly distributed composition, the length has to be chosen based on the applied current densities.

(5) This study can be used as a guideline for the industrial process to predict electrodeposition results and optimize operating conditions such as ion ratios, current density, and volumetric flow rate.
7 Recommendations for Future Work

The following areas should be considered as future work:

(1) Critical thermodynamics and kinetics parameters of Ni-Cu alloy electrodeposition should be further studied. The parameters such as diffusion coefficient, exchange current density, and transfer coefficient of the NiCit- and CuCit- reduction reactions were determined in the simulation to have a significant influence on the results. These values, however, are either rarely mentioned in the literature or vary greatly from study to study. A systematic measurement of these parameters through carefully designed experiments will greatly improve the adaptability and reliability of the simulation.

(2) Simulation of eccentrically arranged ID tube plating should be performed. The modeling completed in this study for the ID plating was set up in the way that the anode and the cathode are concentrically placed, which is difficult to be maintained in the actual production process. Because of the narrow gap between the anode and the cathode, small deviations may have a significant effect on the results. Therefore, the simulation of an eccentric arrangement may have more practical significance.

(3) Bubble flow during ID tube plating simulation should be considered. In this study, the simulation results for ID plating were not verified by experiments because bubble flow occurring in the actual electrodeposition process was not included in the simulation. Bubble flow is believed to increase the mixing effect of the bath, which in turn may affect the plating results. Introducing bubble flow into the simulation will make the results more representative of the actual industrial process.

(4) Experiments of ID tube plating similar to the simulation configuration should be carried out. Such experiments are not only required to verify the simulation, but also helpful to determine the input parameters of simulation through fitting the experimental results.
References


Schichtdicke,” TAB 175, Beuth Verlag GmbH, Berlin, Germany, 1983.


[90] T. Widayatno, “Kinetics of Nickel Electrodeposition from Low Electrolyte Concentration and at A Narrow Interelectrode Gap,” in International Conference of Chemical and


Appendices

8 Appendix A – Temperature Correction of Parameters

This appendix provides the calculation process for the temperature correction of some electrochemical parameters in the simulation of Ni-Cu alloy co-electrodeposition.

8.1 Diffusion Coefficient

From the literature [85], the diffusion coefficients, \( D \), of CuCit' and NiCit' ions at 22°C (295.15 K) are \( 2.1 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1} \) and \( 2.5 \times 10^{-12} \text{ m}^2\cdot\text{s}^{-1} \), respectively. The simulation was done first for experiment 2 of Ni-Cu alloy electrodeposition (Table 3-3). From the fitting results, the \( D \) values at the experimental temperature of 61°C (334.15 K) were \( 3.08 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1} \) and \( 3.67 \times 10^{-11} \text{ m}^2\cdot\text{s}^{-1} \), respectively. Temperature influence on the diffusion coefficient can be expressed by the Arrhenius-type equation 8.1 as:

\[
D = D_0 \cdot \exp\left(-\frac{E_{\text{diff}}}{RT}\right)
\]  

(8.1)

where:
- \( D_0 \) is the pre-exponential factor, \( \text{m}^2\cdot\text{s}^{-1} \)
- \( E_{\text{diff}} \) is the diffusion activation energy, \( \text{kJ}\cdot\text{mol}^{-1} \)
- \( R \) is the universal gas constant, \( 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \)
- \( T \) is the absolute temperature, \( \text{K} \)

Based on the \( D \) value of CuCit' at \( T_1=295.15 \text{ K} \) and \( T_2=334.15 \text{ K} \), the diffusion activation energy \( E_{\text{diff}} \) of CuCit' ions can be calculated from equation 8.2.

\[
E_{\text{diff}} = \frac{R \cdot \ln\left(\frac{D_1}{D_2}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \frac{8.314 \times \ln\left(\frac{2.1 \times 10^{-10}}{3.08 \times 10^{-9}}\right)}{\left(\frac{1}{334.15} - \frac{1}{295.15}\right)} = 56.5 \text{kJ} \cdot \text{mol}^{-1}
\]

(8.2)

In order to simplify the simulation, it’s assumed that NiCit' ions have the same \( E_{\text{diff}} \) value as that of CuCit'. The diffusion coefficient at other experimental temperatures can be obtained by substituting \( E_{\text{diff}} \) into (8.1). Table 8-1 shows the corresponding \( D \) values of the various experiments.
Table 8-1. Diffusion Coefficients of NiCit⁻ and CuCit⁻ Ions at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$D_{\text{NiCit}^-} \times 10^{11}$ (m²·s⁻¹)</th>
<th>$D_{\text{CuCit}^-} \times 10^9$ (m²·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>2.87</td>
<td>2.41</td>
</tr>
<tr>
<td>60</td>
<td>3.45</td>
<td>2.90</td>
</tr>
<tr>
<td>61</td>
<td>3.67</td>
<td>3.08</td>
</tr>
<tr>
<td>62</td>
<td>3.9</td>
<td>3.28</td>
</tr>
</tbody>
</table>

8.2 Exchange Current Density

Because of its sensitivity to the temperature, the exchange current density, $i_0$, is required to be modified for the Ni-Cu alloy electrodeposition as well. According to equation (2.16), $i_0$ has a proportional relation as follows:

$$i_0 \propto \exp \left( -\frac{\Delta G}{RT} \right) \cdot \exp \left( -\frac{\alpha_c F E_{eq}}{RT} \right)$$  \hspace{0.5cm} (8.3)

So the $i_0$ values at two different temperatures can be expressed as:

$$\frac{i_{01}}{i_{02}} = \frac{\exp \left( -\frac{\Delta G}{RT_1} \right) \exp \left( -\frac{\alpha_c F E_{eq}}{RT_1} \right)}{\exp \left( -\frac{\Delta G}{RT_2} \right) \exp \left( -\frac{\alpha_c F E_{eq}}{RT_2} \right)} = \exp \left[ \frac{\Delta G + \alpha_c F E_{eq}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$  \hspace{0.5cm} (8.4)

Table 2-6 provides the values of $i_0$, $\alpha_c$, and $E_{eq}$ for the three reactions (2.38) (2.39) (2.40) in the co-deposition of Ni and Cu at 22°C (295.15 K). The corresponded $i_0$ values at 60°C (333.15 K) are calculated according to (8.4) as 280, 14, and 1.2 A·m⁻², respectively, for the involved three electrochemical reactions. The activation energy used in the calculation for the reduction of Cu, Ni and water were chosen from the literatures [103], [104], and [105].
Appendix B – Diffusion Layer Thickness in Alloy Electrodeposition Simulation Using the Hull Cell

The flow pattern over the surface of the cathode in the Hull cell and the tube is first determined in this appendix. The diffusion layer thickness in the Ni-Cu alloy co-deposition in the Hull cell and inside the tube is then calculated based on the flow pattern results, respectively.

9.1 Flow Pattern Determination

9.1.1 Hull Cell Simulation

Equation (4.1) is effective only for laminar flow over a flat cathode surface. The flow pattern of the electrolyte in the Hull cell at the surface can be determined by using the Reynolds number (Re):

\[
Re = \frac{\rho u D_H}{\mu} = \frac{1090 \times 0.56 \times 0.001}{0.466 \times 10^{-3}} = 1311
\]

(9.1)

where:

- \( \rho \) is the electrolyte density, 1090 kg·m\(^{-3}\)
- \( u \) is the velocity of electrolyte, 0.56 m·s\(^{-1}\)
- \( D_H \) is the hydraulic diameter (distance between agitation plate and cathode), 0.001 m
- \( \mu \) is the dynamic viscosity at 60°C, 0.466×10\(^{-3}\) Pa·s

Since Re<2300, the flow pattern is laminar flow under the experimental conditions.

9.1.2 Inner Diameter Tube Plating Simulation

Flow in the tube is the annular type with a flow rate of 0.39 m·s\(^{-1}\) and hydraulic diameter of 6.35×10\(^{-3}\) m according to Integran Technologies Inc.’s production process. At 70°C, the Reynolds number (Re) inside the tube is:

\[
Re = \frac{\rho u D_H}{\mu} = \frac{1090 \times 0.39 \times 6.35 \times 10^{-3}}{0.4 \times 10^{-3}} = 6748
\]

(9.2)

From the Re number, the flow pattern of the inner diameter tube plating will be the turbulent flow.
9.2 Diffusion Layer Thickness

9.2.1 Hull Cell Simulation

From equation (4.1), the diffusion layer thickness, $\delta$, increases along the cathode surface for single-direction flow. The reciprocating bar in this study, however, is moving back and forth in front of the surface. Therefore, $\delta$ at the midpoint of the moving distance is the more representative average value of the actual situation. In the experiments, there is a “dead zone” located at each end to which the agitation plate can not move. Each time the actual moving distance of the plate is around 7 cm, giving 3.5 cm at the midpoint. So the average $\delta$ at 60°C of NiCit$^-$ ions, for example, is:

$$\delta_{\text{NiCit}^-} = 3 \left( \frac{D_{\text{NiCit}^-}}{\nu} \right)^{\frac{1}{3}} \left( \frac{\nu X}{u} \right)^{\frac{1}{2}} = 3 \times \left( \frac{3.45 \times 10^{-11}}{4.27 \times 10^{-7}} \right)^{\frac{1}{3}} \left( \frac{4.27 \times 10^{-7} \times 0.035}{0.56} \right)^{\frac{1}{2}} = 2.1 \times 10^{-5} \text{ m} = 21 \mu\text{m} \ (9.3)$$

Similarly, the values at other temperatures as well as that of CuCit$^-$ ions can also be calculated based on the diffusion coefficient values. Table 9-1 presents the average $\delta$ values of NiCit$^-$ and CuCit$^-$ ions at various temperatures.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$\delta_{\text{NiCit}^-}$ (µm)</th>
<th>$\delta_{\text{CuCit}^-}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>20</td>
<td>87</td>
</tr>
<tr>
<td>60</td>
<td>21</td>
<td>93</td>
</tr>
<tr>
<td>61</td>
<td>22</td>
<td>95</td>
</tr>
<tr>
<td>62</td>
<td>22</td>
<td>97</td>
</tr>
</tbody>
</table>

9.2.2 Inner Diameter Tube Plating Simulation

The diffusion layer thickness can be assumed as constant inside the tube because of the thorough mixing effect generated by the turbulent flow. It is reasonable to assume a uniform thickness between 30 to 100 µm according to references [21], [20], [36], and [46]. As for the default condition, a thickness of 50 µm was adopted.
10 Appendix C – Convergence of Simulation

Various measures that were taken in this study to improve the quality of models for better convergence are introduced in this appendix. Severe non-linear relationships among parameters in electrodeposition simulation sometimes makes the calculation process very challenging in terms of its convergence. For the ID tube plating, flow physics coupled in the calculation further increases the difficulty to achieve a convergent result. Therefore, it is necessary to optimize the model or carefully select the boundary conditions for calculation purposes.

10.1 2D Configuration Domain

It is generally accepted that the higher the dimension in model, the harder the calculation. In order to simplify the calculation, 2D instead of 3D domains are used for both Hull cell and ID tube plating. Considering the structural characteristics of the two cells, a representative plane can be chosen to serve as the calculation domain. Figure 10-1 shows the selection of 2D representative plane for the Hull cell. The highlighted trapezoidal 2D planar area is the computational domain for the numerical simulation.

![Figure 10-1. 2D computational domain of Hull cell simulation](image)

For the ID tube plating, the computational domain can be further simplified to a 2D axisymmetric structure as indicated in the highlighted area of Figure 10-2. By rotating the domain around the centre line, the simulation results for the tube plating can be achieved.
10.2 Meshing Method

In the process of meshing, special considerations are given to the region which experiences rapid change in some parameters to improve the accuracy and convergence.

1. **Much smaller size mesh in the diffusion layer.** Based on the reduction mechanism, the diffusion layer will have a significant concentration gradient compared to the bulk area. Therefore, much finer mesh is applied in this region as shown in Figure 4-2 and Figure 4-4 to ensure the calculation quality.

2. **Higher density mesh in the more sensitive regions.** Areas such as the HCD edge of the Hull cell or the inlet of ID tube plating are the more sensitive ones. Significant faster growth of the electrodeposit, severe hydrogen evolution or change in the fluid linear velocity occur at these positions. In this study, the “distribution” feature of COMSOL is applied to increase the density of the mesh in these areas as seen in Figure 10-3.
10.3 Interface Boundary Conditions

The interface boundary conditions between electrode and electrolyte applied in COMSOL can be defined by average current density, total current, electric potential, or electrode potential. Although the average current density or total current is usually fixed in the production process, it is quite challenging by using current / current density as the boundary condition at the beginning of the simulation. As found in Figure 10-4 (left), this condition requires both current/current density and its corresponding initial boundary potential as input parameters. When they do not match each other reasonably well, the calculation cannot proceed successfully.

Instead of using current/current density, the electric potential is applied first as the boundary condition in this study. From Figure 10-4 (right), only the potential value is required for this case, which significantly improves the non-convergence problem. For each potential, the corresponding current/current density can then be obtained from simulation. A relationship between...
current/current density and potential is then established which can be used to define the input values for the current/current density boundary conditions.

10.4 Turbulent Flow Model

According to Appendix B, the flow condition for the ID tube plating is turbulent flow. Various models are capable to describe the turbulent process, among which the Reynolds-averaged Navier-Stokes (RANS) models are the most popular ones. In particular, standard $k$-$\varepsilon$ and $k$-$\omega$ models in RANS are both widely used. Table 10-1 shows a comparison between these two models. It is obvious that for the ID tube plating which does not contain strong swirling flow condition, the standard $k$-$\varepsilon$ model is a better choice because of its good convergence property.

<table>
<thead>
<tr>
<th>Model</th>
<th>Standard $k$-$\varepsilon$ Model</th>
<th>Standard $k$-$\omega$ Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength</td>
<td>• Good convergence</td>
<td>• Near-wall interaction</td>
</tr>
<tr>
<td></td>
<td>• Not memory-intensive</td>
<td>• Turbomachinery</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Strong vortices swirling flows</td>
</tr>
<tr>
<td>Limitation</td>
<td>• No-slip walls</td>
<td>• Difficulty of convergence compared to $k$-$\varepsilon$</td>
</tr>
<tr>
<td></td>
<td>• Adverse pressure gradients</td>
<td>• Sensitivity to initial conditions</td>
</tr>
<tr>
<td></td>
<td>• Strong curvatures</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Jet flows</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Difficulty solving for $\varepsilon$</td>
<td></td>
</tr>
</tbody>
</table>
11 Appendix D – Thickness Measurement Results

Thickness measurement results, \( \delta \), for all the samples of both Cu and Ni-Cu electrodeposition are presented in this appendix. In order to compare with the results reported in the literature which had various cathode width, the normalized cathode surface coordinate, \( x \), which equals to the X value (cm) of each position divided by the entire length of the cathode (10 cm) is introduced in the results. For the Cu electrodeposition, the theoretical average thickness, \( \delta_{avg} \), and the normalized thickness value, \( \frac{\delta}{\delta_{avg}} \) are calculated as well in order to obtain the normalized current density value, \( \frac{i}{i_{avg}} \), as explained in section 5.1.2.1.

11.1 Cu Electrodeposition

Three sets of thickness data are collected for experiments 1 to 3 by using SEM. For single metal deposition, the theoretical average thickness can be calculated by rewriting Faraday’s Law as:

\[
\delta_{avg} = \frac{ItM_{Cu}}{nF\rho_{Cu}A} \times 10^6
\]

where:

- \( \delta_{avg} \) is the theoretical average thickness, \( \mu m \)
- \( \rho \) is the density of copper, 8960 kg·m\(^{-3} \)
- \( A \) is the cathode area, 0.0045 m\(^2 \)

It is calculated that the average thickness for experiments 1 to 3 are 14.81\( \mu \)m, 29.61\( \mu \)m, and 44.42\( \mu \)m, respectively. Then the normalized thickness can be obtained from \( \frac{\delta}{\delta_{avg}} \). All the measurement results of Cu electrodeposition thickness are shown in Table 11-1 to Table 11-3.

11.2 Ni-Cu Alloy Electrodeposition

The thickness of alloy electrodeposition is calculated based on the average value at each position according to section 5.2.1.4. Results of alloy electrodeposition experiment 1, 2, and 3 are shown in Table 11-4 to Table 11-6.
### Table 11-1. Thickness Measurement Results of Cu Electrodeposition Experiment 1

| No. | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | 14  | 15  | 16  | 17  | 18  | 19  | 20  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| X  | 4   | 8   | 12  | 16  | 23  | 27  | 31  | 35  | 43  | 47  | 51  | 55  | 64  | 68  | 72  | 76  | 84  | 88  | 92  | 96  |
| x  | 0.04| 0.08| 0.12| 0.16| 0.23| 0.27| 0.31| 0.35| 0.43| 0.47| 0.51| 0.55| 0.64| 0.68| 0.72| 0.76| 0.84| 0.88| 0.92| 0.96|
| δ  | 38  | 29  | 25  | 22  | 19.47| 18.4| 15.7| 14  | 13.1| 11.6| 10.8| 8.13| 7.6 | 9.7 | 6   | 5   | 4   | 0   | 0   |     |
| δ/δavg | 2.57| 1.96| 1.69| 1.49| 1.31| 1.24| 1.06| 0.95| 0.88| 0.78| 0.74| 0.73| 0.55| 0.51| 0.66| 0.41| 0.34| 0.27| 0   | 0   |

### Table 11-2. Thickness Measurement Results of Cu Electrodeposition Experiment 2

<table>
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<th>17</th>
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<td>92</td>
<td>96</td>
</tr>
<tr>
<td>x</td>
<td>0.04</td>
<td>0.08</td>
<td>0.12</td>
<td>0.16</td>
<td>0.24</td>
<td>0.28</td>
<td>0.32</td>
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<td>0.44</td>
<td>0.48</td>
<td>0.52</td>
<td>0.56</td>
<td>0.64</td>
<td>0.68</td>
<td>0.72</td>
<td>0.76</td>
<td>0.84</td>
<td>0.88</td>
<td>0.92</td>
<td>0.96</td>
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<tr>
<td>δ</td>
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<td>51.6</td>
<td>43.8</td>
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<td>23.5</td>
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<td>22</td>
<td>18</td>
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<td>11</td>
<td>9.9</td>
<td>7.5</td>
<td>6</td>
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<td>4.2</td>
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<td>δ/δavg</td>
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<td>1.48</td>
<td>1.27</td>
<td>1.07</td>
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<td>0.69</td>
<td>0.74</td>
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<td>0.51</td>
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### Table 11-3. Thickness Measurement Results of Cu Electrodeposition Experiment 3

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<th>17</th>
<th>18</th>
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<tr>
<td>X</td>
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<td>12</td>
<td>16</td>
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<td>x</td>
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<td>0.08</td>
<td>0.12</td>
<td>0.16</td>
<td>0.24</td>
<td>0.28</td>
<td>0.32</td>
<td>0.36</td>
<td>0.44</td>
<td>0.48</td>
<td>0.52</td>
<td>0.56</td>
<td>0.64</td>
<td>0.68</td>
<td>0.72</td>
<td>0.76</td>
<td>0.84</td>
<td>0.88</td>
<td>0.92</td>
<td>0.96</td>
</tr>
<tr>
<td>δ</td>
<td>108</td>
<td>87</td>
<td>75</td>
<td>63.5</td>
<td>54.5</td>
<td>49.5</td>
<td>43.4</td>
<td>40</td>
<td>37</td>
<td>45</td>
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<td>28.9</td>
<td>24</td>
<td>22</td>
<td>20.5</td>
<td>16</td>
<td>10.2</td>
<td>8.9</td>
<td>7.2</td>
<td>7</td>
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<tr>
<td>δ/δavg</td>
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<td>1.96</td>
<td>1.69</td>
<td>1.43</td>
<td>1.23</td>
<td>1.11</td>
<td>0.98</td>
<td>0.90</td>
<td>0.83</td>
<td>1.01</td>
<td>0.71</td>
<td>0.65</td>
<td>0.54</td>
<td>0.50</td>
<td>0.46</td>
<td>0.36</td>
<td>0.23</td>
<td>0.20</td>
<td>0.16</td>
<td>0.16</td>
</tr>
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</table>
Table 11-4. Thickness Measurement Results of Ni-Cu Electrodeposition Experiment 1

| No. | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | 14  | 15  | 16  | 17  | 18  | 19  | 20  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| X (mm) | 4.5 | 8.5 | 12.5| 16.5| 20  | 24  | 28  | 32  | 36  | 40  | 43  | 47  | 51  | 55  | 59  | 62  | 66  | 70  | 74  | 78  |
| x    | 0.045 | 0.085 | 0.125 | 0.165 | 0.2 | 0.24 | 0.28 | 0.32 | 0.36 | 0.4 | 0.43 | 0.47 | 0.51 | 0.55 | 0.59 | 0.62 | 0.66 | 0.7 | 0.74 | 0.78 |

<table>
<thead>
<tr>
<th>No.</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>24</th>
<th>25</th>
</tr>
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<tbody>
<tr>
<td>X (mm)</td>
<td>82</td>
<td>86</td>
<td>90</td>
<td>94</td>
<td>98</td>
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<tr>
<td>x</td>
<td>0.82</td>
<td>0.86</td>
<td>0.9</td>
<td>0.94</td>
<td>0.98</td>
</tr>
<tr>
<td>δ (µm)</td>
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<td>1.88</td>
<td>2.08</td>
<td>2.29</td>
<td>1.68</td>
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</tbody>
</table>

Table 11-5. Thickness Measurement Results of Ni-Cu Electrodeposition Experiment 2

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<th>1</th>
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<tr>
<td>X (mm)</td>
<td>2.5</td>
<td>6.5</td>
<td>10</td>
<td>14.5</td>
<td>18.5</td>
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<td>54</td>
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<td>61</td>
<td>65</td>
<td>69</td>
<td>73</td>
<td>77</td>
</tr>
<tr>
<td>x</td>
<td>0.02</td>
<td>0.06</td>
<td>0.1</td>
<td>0.14</td>
<td>0.18</td>
<td>0.22</td>
<td>0.26</td>
<td>0.3</td>
<td>0.34</td>
<td>0.38</td>
<td>0.42</td>
<td>0.46</td>
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<td>0.61</td>
<td>0.65</td>
<td>0.69</td>
<td>0.73</td>
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<td>δ (µm)</td>
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<td>8.55</td>
<td>6.75</td>
<td>8.47</td>
<td>8.22</td>
<td>8.16</td>
<td>8.49</td>
<td>7.90</td>
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<td>7.74</td>
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<td>6.14</td>
<td>5.62</td>
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<table>
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<tbody>
<tr>
<td>X (mm)</td>
<td>82</td>
<td>86</td>
<td>90</td>
<td>94</td>
<td>98</td>
</tr>
<tr>
<td>x</td>
<td>0.82</td>
<td>0.86</td>
<td>0.9</td>
<td>0.94</td>
<td>0.98</td>
</tr>
<tr>
<td>δ (µm)</td>
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<td>3.65</td>
<td>2.94</td>
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<tr>
<td>$x$</td>
<td>0.03</td>
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<td>0.11</td>
<td>0.15</td>
<td>0.19</td>
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<tr>
<td>$\delta$ (µm)</td>
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<td>7.06</td>
<td>8.71</td>
<td>8.63</td>
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<td>21</td>
<td>22</td>
<td>23</td>
<td>24</td>
<td>25</td>
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<tr>
<td>$X$ (mm)</td>
<td>83</td>
<td>87</td>
<td>91</td>
<td>95</td>
<td>99</td>
</tr>
<tr>
<td>$x$</td>
<td>0.83</td>
<td>0.87</td>
<td>0.91</td>
<td>0.95</td>
<td>0.99</td>
</tr>
<tr>
<td>$\delta$ (µm)</td>
<td>2.77</td>
<td>3.92</td>
<td>4.62</td>
<td>1.57</td>
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</table>

Table 11-6. Thickness Measurement Results of Ni-Cu Electrodeposition Experiment 3
12 Appendix E – Hull Cell Scale

The trapezoidal shape of the Hull cell allows the distribution of various current densities on the cathode. In order to measure the local current density, a specific Hull cell ruler or Hull cell scale can be used as shown in the Fig 11-1. Hull cell scale is a calibrated ruler for the interpretation of the local current densities at an applied total current of 1, 2, 3, and 5 amps, respectively.

Figure 12-1. The Hull cell scale used in this study
Appendix F – Composition Measurement Results

The composition measurement results (expressed as Ni%) at selected X positions for experiment 1, 2, and 3 of Ni-Cu electrodeposition are presented in this appendix.

Table 13-1. Composition Measurement Results of Ni-Cu Electrodeposition Experiment 1

<table>
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<td>40</td>
<td>43</td>
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<tr>
<td>x</td>
<td>0.045</td>
<td>0.085</td>
<td>0.125</td>
<td>0.165</td>
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<td>0.24</td>
<td>0.28</td>
<td>0.32</td>
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<td>0.4</td>
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<td>Ni (%)</td>
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Table 13-2. Composition Measurement Results of Ni-Cu Electrodeposition Experiment 2

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<td>0.1</td>
<td>0.14</td>
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<td>0.22</td>
<td>0.26</td>
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<td>0.38</td>
<td>0.42</td>
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<td>0.5</td>
</tr>
<tr>
<td>Ni (%)</td>
<td>45.8</td>
<td>47.7</td>
<td>51.7</td>
<td>59.7</td>
<td>62.5</td>
<td>63.9</td>
<td>66.7</td>
<td>69.2</td>
<td>70.5</td>
<td>72.4</td>
<td>71.6</td>
<td>72.8</td>
<td>71.7</td>
</tr>
</tbody>
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Table 13-3. Composition Measurement Results of Ni-Cu Electrodeposition Experiment 3

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<th>No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>X (mm)</td>
<td>3</td>
<td>7</td>
<td>11</td>
<td>15</td>
<td>19</td>
<td>24</td>
<td>28</td>
<td>32</td>
<td>36</td>
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<td>52</td>
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<tr>
<td>x</td>
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<td>0.07</td>
<td>0.11</td>
<td>0.15</td>
<td>0.19</td>
<td>0.24</td>
<td>0.28</td>
<td>0.32</td>
<td>0.36</td>
<td>0.4</td>
<td>0.44</td>
<td>0.48</td>
<td>0.52</td>
</tr>
<tr>
<td>Ni (%)</td>
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<td>47.8</td>
<td>54.4</td>
<td>61.8</td>
<td>63.2</td>
<td>64.9</td>
<td>66.8</td>
<td>69.3</td>
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<td>72.8</td>
<td>72.5</td>
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<td>69.8</td>
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</tbody>
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