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Effect and interactions of commercial additives and chloride ion in copper electrowinning

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EFFECT AND INTERACTIONS OF COMMERICIAL ADDITIVES AND CHLORIDE ION IN COPPER ELECTROWINNING

by

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A THESIS

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ABSTRACT

This thesis is to understand and compare the effects and interactions of modified polysaccharide (HydroStar), polyacrylamide (Cyquest N-900) and chloride ion on copper electrowinning. A study of the nucleation and growth was conducted in a synthetic electrolyte (40 g/L Cu, 160 g/L H_2SO_4, 20 mg/L Cl^-) with the addition of HydroStar or Cyquest N-900 using potential step measurements. The current responses generated were compared to theoretical models of nucleation and growth mechanisms. The nucleation and growth mechanism changed as function of potential and the presence of organic additives. The nucleation and growth mechanisms were confirmed using scanning electron microscopy (SEM). At low overpotentials, electrodeposition from the electrolyte without additives proceeded by progressive nucleation with three-dimensional (3-D) growth. The addition of HydroStar produced smaller nuclei and changed the mechanism to progressive nucleation and 2-D growth. Cyquest N-900 used there appeared to be progressive nucleation with 2-D growth and polarize the cathodes. In addition, instantaneous nucleation under diffusion control occurred at high overpotentials.

Chloride ion and its interaction with HydroStar and Cyquest N-900 were further characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The trends observed from Nyquist plots and equivalent circuit models were consistent with the CV results. Chloride, on its own, depolarized copper electrodeposition, while chloride ion associated with Cyquest N-900 inhibited the reaction. It is proposed that Cl^- acted as a bridging ligand between copper and Cyquest N-900. The addition of HydroStar depolarized copper deposition, but it did not interact with chloride.

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This thesis is dedicated to my dearest parents, Guanbo Cui and Xiuyue Bo.

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SECTION

1. INTRODUCTION

This section describes the background to the project in this thesis. Electrometallurgy is the last process for the recovery and therefore produces copper from the mining industry. Copper electrometallurgy contains electrorefining and electrowinning depending on whether the copper mineral is processed by pyrometallurgy or hydrometallurgy. A 2013 survey indicated that over 4.5 million tonnes of copper were processed per year from electrowinning operations [1].

In copper electrowinning, copper is usually electrodeposited on 316L stainless steel cathodes for six to seven days. Then copper is harvested, washed and sold to market. As such, the control of copper quality during electrodepostion is of great significance. Numerous parameters influence the copper electrowinning process, with the most significant being electrode placement, electrode vertically, temperature, current density, electrolyte concentration and additives [1-48].

Additives, such as organic smoothing agents, control the nucleation and growth of copper during the deposition process. The additives allow the production of smooth copper deposits free of voids and porosity. Without the uses of additives, copper deposits have a tendency to develop into column crystals and eventually lead to dendrite growth with voids between the crystals. Guar has traditionally been the preferred a smoothing agent in copper electrowinning for about forty years. However, there has been a trend to replace guar with lower-cost smoothing additives in the copper electrowinning industry [1-2, 18-24]. Chloride ions are naturally present with 20-30 mg/L in the electrolyte.

New products like modified polysaccharides (HydroStar ®) and polyacrylamide (Cyqueset N-900) have been developed and are new used as replacements for guar in commercial tankhouses [45]. The use of modified polysaccharide (HydroStar) was first reported by Sandoval et al [32]. After several tests, HydroStar exhibited improved cathode quality and lower cost than guar products, which made it as an attractive cathode smoothing candidate. Polyacrylamide has also been reported to produce smoother, brighter and more compact copper electrodeposits than guar [24-26].

Based on these achievements, a limited amount of work has been conducted to examine and characterize the electrochemical properties of these two organic additives. It is known to us that Cyquest N-900 could polarize and HydroStar neither depolarize nor polarize the copper deposition process under certain conditions [19-20]. However, the initial nucleation and growth of copper on stainless steel cathodes in the presence of either of these two additives has not been reported. In addition, chloride ion and its interaction with these two additives need to be investigated since chloride is present in electrowinning electrolytes and is known to interact with other organic smoothing agents [27, 36-38, 53-54].

1.1. THESIS OBJECTIVES

The objective of this thesis is to understand and compare the effects and interactions of modified polysaccharide (HydroStar), polyacrylamide (Cyquest N-900) and chloride ion in copper electrowinning. A literature review is presented on copper electrowinning and nucleation and growth mechanisms fundamentals and some parameters influencing electrowinning in Section 2. In paper I, potential step measurements were employed in a synthetic electrolyte (40 g/L Cu, 160 g/L H_2SO_4, 20 mg/L Cl^-) with and without the addition of HydroStar or Cyquest N-900 to study the initial nucleation and growth of copper. The current responses generated were compared to theoretical models of nucleation and growth mechanisms. The nucleation and growth mechanism changed as a function of potential and the presence of additives. The nucleation and growth mechanisms were confirmed using scanning electron microscopy (SEM) results. In paper II, an electrochemical study was performed on chloride ion and its interaction with HydroStar and Cyquest N-900. Cyclic voltammetry was employed to determine depolarization/polarization effects. Electrochemical impedance spectroscopy (EIS) was conducted to gain insight into the kinetics of the electrochemical system

2. LITERATURE REVIEW

2.1. BACKGROUND

The production of copper by conventional methods is shown in Figure 2.1 [1].

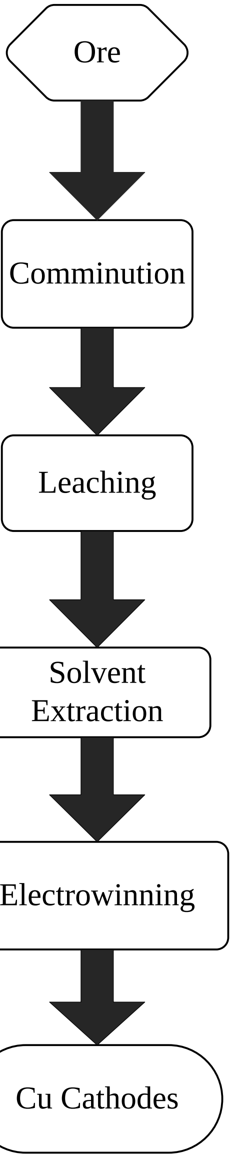

Figure 2.1. Schematic Diagram of Conventional Copper Processing Adapted from [1]

Primary copper production starts from the extraction of copper-bearing ores. There are three methods of copper mining: underground, open pit and solution mining. Open-pit mining is the predominant way used to extract large, low grade deposits all over the world. The type of ore extracted determines the process that will be applied for copper production. Sulfide ores are traditionally processed by flotation, smelting and electrolytic refining. Oxide ores are treated using leaching, solvent extraction and electrowinning. Some sulfide ores are using bio-leaching methods [1-5].

In the hydrometallurgy process, the pretreated oxide ore is acid leached in tanks or hill size heaps in order to produce a copper sulfate solution. The leach solution is collected and sent to the solvent extraction process where copper is selectively extracted into an organic phase containing a mixture of hydroxyoximes. The copper bearing organic phase is then cycled to the stripping stage where the copper is released into a solution of a high acidity. Finally, the copper rich solution obtained is used as electrolyte in electrowinning where copper metal cathodes of 99.99% purity are produced [1-5].

2.2. COPPER ELECTROWINNING DESCRIPTION

Hydrometallurgical extraction of copper produces 20-25% of the world's refined copper. Therefore, recovering high-purity copper by electrowinning on a large scale at reasonable costs is of great importance. The electrowinning process involves the input of electrical energy to reverse the process of metal dissolution, which essentially is the same as the recharging of a battery [2]. A schematic view of a copper electrowinning cell is shown in Figure 2.2 [1].

Water is decomposed at the anode which releases oxygen.

$$H_2O \rightarrow H^+ + OH^- \rightarrow 0.5O_2 + 2H^+ + 2e^- \qquad E°=1.23V \qquad (1)$$

The cathode reaction is the deposition of copper metal:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E°=0.34V \qquad (2)$$

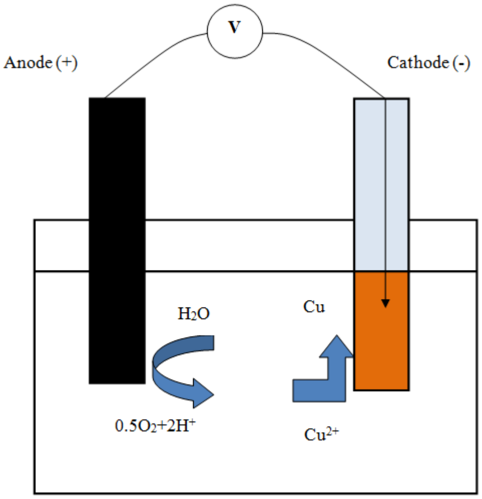

Figure 2.2. Schematic View of a Copper Electrowinning Cell Adapted from [1]

Therefore, the net electrowinning reaction including sulfate ions is:

$$Cu^{2+} + SO_4^{2-} + H_2O \rightarrow Cu^0 + 0.5O_2 + 2H^+ + SO_4^{2-} \qquad (3)$$

The oxygen enters the atmosphere. The copper is sent to melting and fabrication.

Since the 1980's, the use of stainless-steel cathodes as the substrate for copper deposition and the automation of stripping has increased significantly. Additionally, to reduce the environmental concerns and energy consumption, alternative anodes are being developed and employed. The promising anodes are titanium anodes with a precious metal oxide coating based on RuO_2 or IrO_2. These anodes will consume less energy and eliminate lead sludge and lead contamination on the products [3-8].

The electrolyte from copper electrowinning typically contains 40-45 g/L Cu^{2+} and 160-180 g/L H_2SO_4, 1-3g/L Fe and 100-200 mg/L cobalt. The presence of cobalt is to prevent the lead anode corrosion. The presence of iron is from solvent extraction process. Metal cathodes and anodes are immersed into this $CuSO_4$ and H_2SO_4 electrolyte.

Modern electrolytic cells are usually made of polymer concretes or with chemical resistant lining, such as welded or spray-coated polyvinyl chloride (PVC). The spacing between the anodes and cathodes are designed to be 50 mm in order to accommodate more plating capacity. The number of cathodes is usually 60-84 per electrolytic cell. The electrodes are connected in parallel but the cells in a tankhouse are connected in series.

2.3. ELECTROCHEMICAL NUCLEATION AND GROWTH FUNDAMENTALS

The quality of the electrowon copper is determined by many factors. The first stage of the nucleation and growth on the substrate surface is, in fact, a very important aspect for electrowon copper. The mechanism of copper nucleation and growth has been studied in two aspects of electrochemical and structural. The mechanistic aspects of lattice formation process have been examined by scanning (SEM) and transmission microscopy (TEM). Some electrochemical techniques were followed by morphological studies by atomic force microscopy (AFM).

Several methods have been published to determine nucleation and growth mechanism. Among them, current-time relationships have been established and documented by Fleischmann and Thirsk and Harrison [10-12]. They described the early stages of metal deposition for specific types of nucleation and crystal growth under kinetic control. Nuclei prefer to form at energetically favorable sites. Whether a particular site is favorable or not depends on its surface energy and the magnitude of the applied cathodic potentials. Two types of nucleation may occur: progressive or instantaneous. Progressive nucleation is the formation of new nuclei in an area close to previously formed nuclei at a later time. Instantaneous nucleation occurs when a number of equal sized nuclei form on the substrate at one time. Three different morphologies (one-dimensional (1-D) or two-dimensional (2-D) or three-dimensional (3-D)) can be observed after nucleation occurs. Growth is also controlled by kinetic or diffusion. For kinetic control, the rate-determining step is represented by the incorporation of the metal into the growth. For diffusion control, the rate-determining step is the mass transfer of the metal deposited to the surface of the growing nucleus.

These various nucleation and growth mechanisms were modeled for constant potential conditions [10]. Those models show the relationship between current density and time. Current density is related to different power of time ranging from 0.5-3.For kinetic control, the following expressions were developed.

For 2-D growth after instantaneous nucleation,

$$i= (2zF\pi MhN_0k^2/\rho)\ t \quad (4)$$

For 2-D growth after progressive nucleation,

$$i= (zF\pi MhAk^2/\rho)\ t^2 \quad (5)$$

For 3-D growth after instantaneous nucleation,

$$i= (2zF\pi M^2N_0k^3/\rho^2)\ t^2 \quad (6)$$

For 3-D growth after progressive nucleation,

$$i= (2zF\pi M^2Ak^3/3\rho^2)\ t^3 \quad (7)$$

When growth is of diffusion controlled, the expressions are:
For 3-D growth after instantaneous nucleation,

$$i= (8\pi zFN_0M^2C^3D^{3/2}/\rho^2)\ t^{1/2} \quad (8)$$

For 3-D growth after progressive nucleation,

$$i= (16\pi zFAM^2C^3D^{3/2}/3\rho^2)\ t^{3/2} \quad (9)$$

For Equations (4)-(9), i is the current density (A/m^2), M is molecular weight, ρ is density, C is copper ion concentration (mol/cm^3) , D is the diffusion coefficient, t is time, k is the reaction rate constant, h is the nuclei height, L^2 the cross section and θ the coverage. A is defined as the adjusted nucleation rate constant and N_0 the total number of sites available for nucleation. F is Faraday constant and z is the number of electrons transferred.

Research has been conducted to gain the fundamental information on the initial nucleation and growth based on the models above. The current-time data generated from potentiostatic step experiments can be fit into the various models and the nucleation and growth mechanism determined. For example, Beshore et al. [13] investigated the zinc instantaneous nucleation mechanism in the absence and presence of antimony and glue by this method.

Potential step measurement has been used to study the nucleation and growth in copper electrodeposition. The current transients for additive-free electrolyte and in the presence of chloride, glue and/or thiourea were examined and confirmed by SEM micrographs [9]. The data provided by the nucleation studies helped to establish a more quantitative measure of the effect of various additives found in copper electrorefining on copper electrodeposition on stainless steel cathodes. This preliminary investigation led to more studies on the nucleation and growth of various additives on different substrates for copper deposits.

Potentiostatic pulses and SEM examination were performed to characterize the mechanism of nucleation and growth of copper on titanium substrates [14]. The results showed that most of the copper nucleation occurred in the first milliseconds. The nucleation and growth of copper was strongly dependent on the potentials and electrolyte temperature.

Current and potential step experiments were also conducted to evaluate the initial stage of copper nucleation and growth on thermally oxidized 316 L stainless steel substrates. Zhou and O’Keefe [18] showed that the copper electrocrystallization process was influenced by the temperature employed in oxidizing the stainless steel.

The influence of nucleation potential, nucleation time and growth potential on the surface roughness of copper foil deposits on titanium substrates were examined by Getrouw and Dutra [48]. Based on the Thirsk [12] model for different experimental conditions, mechanisms for copper nucleation were determined with the aid of potentiostatic current transients. It showed that the surface roughness of copper foil deposits was a function of not only the nucleation process, but also the growth process and the lowest roughness was related to a pre-potential step at -0.59 V for 10 ms on a titanium substrate.

The surface properties of stainless steel substrates can affect copper nucleation [16]. The surface of the stainless steel blanks were characterized with electrochemical and mechanical methods. It indicated that increasing surface roughness of the substrates correlated with lower copper growth.

Nucleation and growth of copper electrodeposits on chromium plated electrodes were reported under potentiostatic conditions [49]. Copper initially nucleated and grew according to 3-D diffusion controlled progressive nucleation process, and later according to an instantaneous nucleation process. These appeared to be associated with the IR drop across the Cr layer reducing the driving force for the electrodeposition for copper under potentiostatic plating conditions.

2.4.EFFECT OF DIFFERENT PARAMETERS IN COPPER ELECTROWINNING

During the copper electrodeposition process, there are several parameters that affect the final copper quality. These include temperature, current density, and additives (organic and chloride)

2.4.1. Temperature. According to Robinson et al. [45], copper electrowinning plants usually operated within a temperature range of 35 to 55 °C. Tankhouses associated with solvent extraction plants use temperature ≤ 40°C. Hence, there is not a universal optimum operation temperature. The best temperature of each plant needs to be determined by its operating conditions. This significant parameter influences the electrowinning process in different ways.

It has been recorded that the change of electrolyte temperature affects the cathode deposit and its structure. According to Pradhan et al., increasing temperature from 30-60 °C leads to rougher cathode deposits [50]. Experiments were conducted by O’Keefe and Hurst, the results showed that the lacy copper could be obtained at the over 40 °C [35].

The initial stage of copper nucleation and growth on titanium is dependent on the electrolyte temperature reported by Dutra et al [14]. Two sets of experiments were done at 45 °C and 65 °C. It reported that a higher temperature promoted copper nucleation and growth.

Therefore, a vigorous control of temperature, depending on other parameters such as current density and additive concentrations is required in order to produce high quality of copper cathodes.

2.4.2. Current Density. Operating plants use a range of current densities of 200-450 A/m2 [45]. If the current density goes beyond the limit point, the deposit will become powdery and hydrogen gas will evolve According to Winand [55], it should be possible to produce acceptable deposits at up to 80-90% of the value of the limiting current density. However, in practice the applied current density is usually less than 50% of the estimated limiting current density. This limit is set due to an uneven current distribution in the tank house and to the tendency of deposit morphology toward nodulation and dendrite formation.

2.4.3. Organic Additives. It is common practice to use the additives to obtain smooth and dense cathodes in copper electrowinning tankhouses. The addition of even small amounts of certain substances in the deposition baths will cause significant changes in the properties of the copper products. Organic additives significantly influence the current-potential relationship because of their competition for surface coverage with the components in the electrolyte. Recent reviews have tried to summarize their different effects in copper electrowinning.

Additives usually are classified as brighteners, levelers, depolarizers or grain refiners [21-28]. Levelers or smoothing additives generally lead to a geometric change on the deposit surface which tends to redistribute the growth rates. These kinds of additives have the ability to deposit thicker in small recesses. Brightening additives act as orienting grain structure and modify the nucleation process. A grain refiner may predominantly control of nucleation of new crystallites. Depolarizers enhance the formation of dendrites rather than new nuclei. The synergistic process between levelers and grain refiners are aimed at improving the copper deposit quality and a reduction of short-circuits caused by dendrites.

Thiourea is used as a grain refiner during copper electrowinning and electrodeposition. Kang and Kim [51] confirmed the effect of thiourea on the copper electrochemical nucleation. The results show that thiourea was found to react with copper leading to the generation of CuS. The CuS adsorption seems to inhibit the initial nucleation of copper resulting in the formation of smaller copper grains compared to those forming in the absence of thiourea. However, it has been established that thiourea decompose leading to contamination of the cathodic deposit with sulfur.

Guar has traditionally been used additive in copper electrowinning if the electrolyte is produced from solvent extraction. It is a naturally occurring galacto-mannan polymer, a polysaccharide, used as flocculant and coagulant with typical molecular weights ranging from 200,000 to 500,000 Da [25]. It has been used as a leveling agent for more than forty years to produce bright and dense copper deposit. Vereecken and Winand studied the effect of guar on the quality of copper deposits in the industrial copper sulfate solution at 200A/m^2 and 50 °C. They showed that the surface quality of copper obtained with guar was better than that with certain polyacrylamides.

However, there has been a trend to replace guar with lower-cost smoothing agents in copper electrowinning. Pye and Schurz [47] proposed the use of polyacrylamide (as shown in Figure 2.3) in copper electrowinning as early as 1957. They claimed that polyacrylamide could be dissolved into the water or electrolyte. The use of polyacrylamide as an inhibitor was done by Vereecken and Winand [43]. They compared the results in the aspects of deposit quality, the structure, the galvanic potential with commonly used guar. Addition of polyacrylamide to acid copper sulfate did not produce deposits as smooth as those with guar.

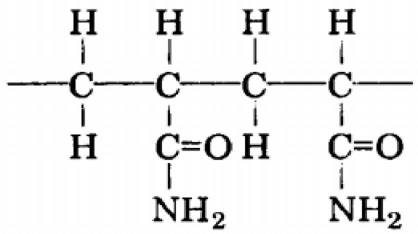

Figure 2.3. General Formula of Polyacrylamide

In recent years, Fabian reported that an activated polyacrylamide (APAM) could be used as a leveling and brightening agent. In Fabian’s work [25-26], bench scale continuous electrowinning tests were carried out to assess APAM and guar in copper electrodeposition at 50 °C. These tests indicated that the deposits with APAM were brighter and produced smaller crystallite sizes than those obtained with guar. The cross section results showed that APAM produced a tight columnar copper deposit and guar produced a porous copper deposit. Therefore, they inferred that APAM favored a higher nucleation rate and greater three dimension crystallite growth than guar.

Modified polysaccified have also been commercialized by Freeport-McMoRan Technology Center [32] in recent years. Based on a series of bench scale electrowinning cell tests, EPC-4201 (under the trade name of HydroStar ®) exhibited a low sulfur content and higher cathode density than guar. It showed that HydroStar had no affect on the electrowinning cell voltage, current efficiency, cathode lead content and solvent extraction phase separation time. Therefore, the low cost combined with cathode quality improvements has made HydroStar an attractive candidate additive in copper electrowinning.

While modified polysaccharide (HydroStar) and polyacrylamide (Cyquest N-900) are new developed products and are being used commercially, only a few electrochemical studies have been reported. Moats and Derrick [20] used a galvanodynamic method to examine numerous organic additives including HydroStar and a polyacrylamide in room temperature synthetic electrolyte. According to their conclusions, HydroStar had no measurable polarization effect or plating potentials. However, the polyacrylamide polarized the plating potential but not on the potential of nucleation on a stainless steel cathode.

Helsten and Moats [19] investigated three organic additive systems (HydroStar, a polyacrylamide N-100 and a 50/50 ration of guar and HydroStar). One hour deposition and galvanodynamic tests were performed to evaluate the additive effect. Even though smoother deposits were produced with increasing concentrations of additives, no correlation was found between polarization and surface roughness.

Since previous investigation employed a non-traditional electrochemical method to evaluate these two additives, Moats et al. [44] used traditional methods like cyclic voltammetey (CV) and electrochemical impedance spectroscopy (EIS) to further illustrate Cyquest N-900 has a polarization effect while HydroStar has minimal effect on electrochemical response.

Other additives such as gelatin, animal glue and various mixtures of additives are commonly used as levelling and brightening agents in copper electrodeposition and electrorefining. As these are not commonly used in solvent extraction-electrowinning tankhouses, they were not reviewed for this thesis.

2.4.4. Chloride Ions. The presence of chloride ions in electrowinning electrolyte is the result of the transfer of chloride through solvent extraction. Chloride ion is commonly presented in copper electrowinning usually in the range of 20 to 30 mg/L in commercial tankhouse [45]. Therefore, understanding the effect of chloride ion on deposition process is of central importance for understanding the combined effect of all the other additives.

The effect of chloride has been the subject of considerable research. From an electrochemical perspective, chloride ions depolarize the copper reduction process at low concentration (few mM) [33-37]. Ilgar reported that the addition of 20 mg/L chloride slightly depolarizes the electrode reaction at higher overpotentials [52]. Sun and O’Keeefe [9] claimed that 40 mg/L chloride ions increased the rate of reaction possibly due to the formation of copper-chloride complexes. At the same time, their results confirmed that the early stage of copper nucleation mechanism was not affected by the presence of chloride ions.

Recently, electrochemical techniques like cyclic voltammetry and electrochemical impedance spectroscopy (EIS) studies have revealed that chloride has a catalytic action on copper electrodeposition [36]. These studies concluded that the presence of chloride ion, at potentials used during electroplating, accelerates the reduction of copper through the formation of CuCl at the electrode surface:

$$\mathrm{Cu^{2+} + Cl^{-}_{ads} + e = CuCl_{ads}} \qquad E° = 0.582\,V_{SHE} \qquad (10)$$

$$\mathrm{CuCl_{ads} + e = Cu + Cl^{-}} \qquad E° = 0.181\,V_{SHE} \qquad (11)$$

This chloride-mediated mechanism proceeds in parallel with the copper reduction reactions, which leads to an acceleration of the overall reduction kinetics. Therefore, the formation of CuCl has an effect on the deposition of copper [36-42].

In the viewpoint of crystallographic, chloride ions are able to change the crystallographic orientation of cathode deposits [34-35]. Cathodic copper deposits has the (111) orientation in the absence of chloride ions and the order of preference for different planes is (111)> (200)> (220)> (311)> (222). With the addition of 5 mg/L of chloride, the order of preference has changed to the planes of (220) > (111) > (311) > (200) > (222). Increasing the chloride concentrations to 10 mg/L, all of the XRD peaks will not change the preferred orientation and this indicates a more random crystallographic structure [33-35, 50].

In commercial tankhous, chloride concentration must be kept below 30 mg/L when plating on the stainless steel cathodes to prevent the formation of Cl_2 gas [1, 45] according to Equation (12):

$$2Cl^- + \frac{1}{2}O_2 + H_2O \rightarrow Cl_2 + 2OH^- \tag{12}$$

This leads to pitting corrosion on the stainless steel, which makes the copper deposition difficult to detach.

Since chloride ions and organic additives are used together in commercial tankhouses, it is necessary to examine the interaction of chloride and additives in electrowinning process. Ativated polyacrylamide (APAM) and chloride ions acted as a suppressor/ inhibitor for copper electrodeposition [24-25]. A possible explanation might be the bonding of APAM with cuprous ions and chloride ions (APAM-Cu^+-Cl^-), which made activated polyacrylamide appear to be more specifically adsorbed at the electrode. In addition, a mathematical model in Figure 2.4 was proposed to describe the role of chloride ion and polyethylene glycol (PEG) in copper electrodeposition based on Raman spectroscopy (SERS) [53-54]. This model assumes adsorbed Cl^- was involved in binding of PEG to copper surface. It identified a critical Cl^- fractional coverage (θ^*) at which PEG completely covered the copper surface. This model was further confirmed in Chen's

[46] work using electrochemical techniques like electrochemical impedance spectroscopy and linear sweep voltammetry. It indicated that adsorption of PEG on the copper surface required the presence of chloride ions to act as a bridge between PEG and the electrode surface.

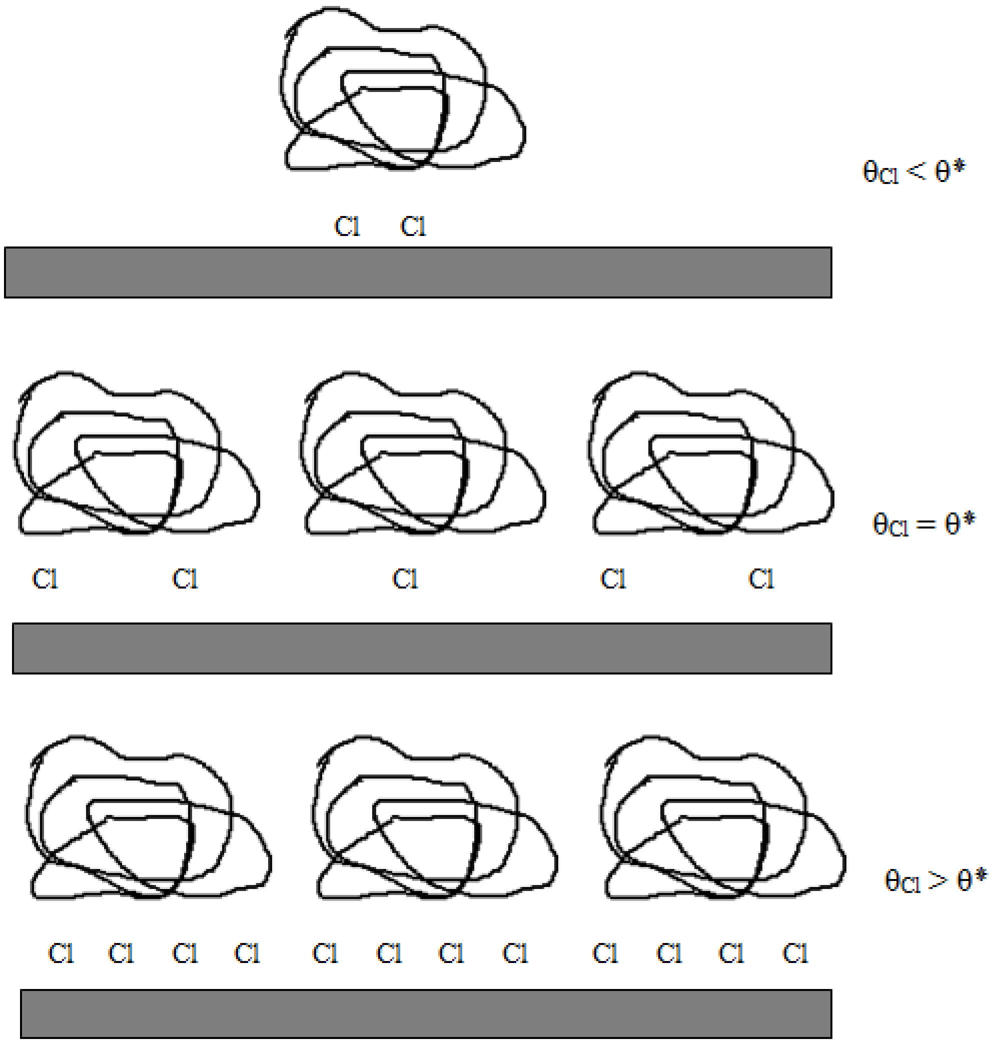

Figure 2.4. Schematic View of a Cross Section Illustrating the Cl^- and PEG Adsorbed Layers at Three Chloride Coverage Adapted From [46]. θ*is the Cl^- Critical Coverage Relative to Full Coverage. Cu^+ Believed to Link PEG and Cl^- is Not Shown

2.5. ELECTROCHEMICAL TECHNIQUES

The interaction between the chloride ions and organic additives during the copper electrowinning can be investigated using electrochemical techniques. Therefore, several electrochemical techniques were employed in this study and are described in the following sections.

2.5.1. Voltammetry. In a voltammetry, a potential scan to observe changes in current as a function of voltage. Two common methods are linear sweep and cyclic voltammetry. In linear sweep voltammetry (LSV), the potential of the working electrode versus a reference electrode is varied continuously with time while the current is measured as a function of potential. Cyclic voltammetry (CV) is like LSV in the use of a constant scan rate; however, the potential is cycled between two values. The cycling process can be repeated several times to determine how the reaction is affected. The measured current is generated as a function of the potential versus the reversible potential of the reaction in question, the sweep rate, the surface area et al.

2.5.2. Chronopotentiometry. This is an electrochemical technique in which a constant current is applied between the electrodes for a period of time. During this period of time, the potential of one electrode is monitored as a function of time with respect to a reference electrode.

2.5.3. Potential Step Measurements. A cathodic potential versus a reference potential is applied using a step function for the potential step experiments. The resulting current is measured as a function of time and stored for further analysis of nucleation mechanism.

2.5.4. Electrochemical Impedance Spectroscopy (EIS). In an EIS experiment, the response analysis to a periodic small amplitude AC signal applied to a target system provides electrochemical information about the system structure, electrode interface and relevant reactions. Based on this information, an equivalent circuit can be constructed to model the system. Dissolution and deposition of metals near the reversible potential can typically be modeled using a simple resistance-capacitor (RC) circuit as shown in Figure 2.5. The modeling of EIS data has to be performed carefully and in conjunction with other electrochemical techniques.

2.6. SUMMARY

The aim of this chapter is to primarily provide background information about the presence of organic additives and chloride in copper electrowinning process. The nucleation and growth of copper electrodeposits needs to be controlled by carefully selected concentrated organic additives and chloride to eliminate the formation of dendrites. The nucleation and growth mechanism and electrochemical behavior of modified polysaccharide (HydroStar) and polyacrylamide (Cyquest N-900) in copper electrowinning have not been extensively documented in open literature compared with glue, thiourea in electrorefining process. Study of chloride and its interaction with these two organic additives is lacking. Therefore, a better understanding of the influence of HydroStar, Cyquest N-900 and chloride ion during copper electrowinning process is presented.

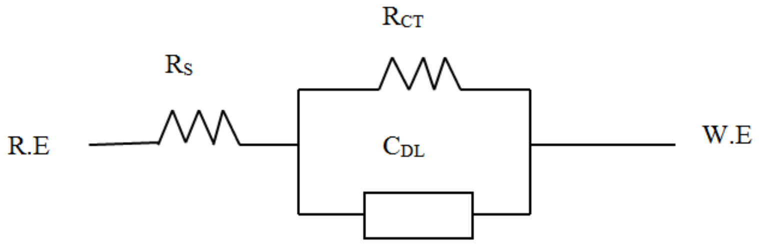

Figure 2.5. EIS Equivalent Circuit Modeling with Reference Electrode (R.E), Solution Resistance (R_S), Charge Transfer Resistance (R_{CT}), Double Layer Capacitance (C_{DL}), Working Electrode (W.E).

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PAPER

I. Effect of commercial electrowinning additives on the nucleation and growth of copper on stainless steel

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Abstract

A study of the nucleation and growth of copper deposited on 316 L stainless steel was conducted in the presence of modified polysaccharide (HydroStar ®) and polyacrylamide (Cyquest N-900) in a synthetic electrowinning electrolyte (40 g/L Cu, 160 g/L H_2SO_4, 20 mg/L Cl^-, 40°C) without external agitation using a potentiostatic technique. At low overpotentials, electrodeposition from the electrolyte without additives proceeds by progressive nucleation with three-dimensional (2-D) growth. Due to discontinuous deposits, it causes the roughest surface after two hours of electrodeposition. Using Cyquest N-900 used does not change the mechanism but polarizes the cathode reaction and produces smaller nuclei. However, the addition of HydroStar changed the mechanism to progressive nucleation and 2-D growth. HydroStar also creates finer structures and contributed to a smoother surface. At high overpotentials, instantaneous nucleation under diffusion control occurred. Therefore, copper nucleation and growth mechanism changes with potentials and presence of organic additives.

Key words: Copper, Electrowinning, Organic additives, Modified polysaccharide, Polyacrylamide, Nucleation and growth

Introduction

Approximately twenty percent of the world’s refined copper is produced from acidified sulfate solution by electrowinning. In electrowinning, copper is electrodeposited mostly on AISI 316L stainless steel cathodes for 6-7 days, after which the copper is stripped from the substrate (Schlesinger, Sole, Davenport, 2011). Electrodeposition consists of a series of processes from bulk diffusion, charge transfer, surface diffusion, nucleation and crystallization. However, the initial stages of nucleation and growth are important as they will likely control the resulting structure of the deposit.

The nucleation and growth of an electrodeposited phase is a complicated process. Harrison and Thirsk (1972) proposed several nucleation and growth mechanisms which could be determined using a potential-step technique. A first order nucleation law is assumed during the potentiostatic pulse measurement. The total number of nuclei, N, versus time adheres to a relationship such as:

$$\mathrm{N} = \mathrm{N}_0[1 - \exp(-A't)] \tag{1}$$

where nucleation time is t, A' is the nucleation rate constant and N_0 the total number of available sites for nucleation. Two types of nucleation may occur: progressive and instantaneous. Progressive is the formation of new nuclei in an area close to previously formed nuclei at a later time. Instantaneous nucleation occurs when a number of equal sized nuclei form on the substrate at one time. Growth of electrodeposition can occur in one, two or three dimensions (Thirsk and Harrison, 1972).

The control of nucleation and growth is affected by several parameters: current density, temperature, electrolyte concentration and organic smoothing additives. Extensive work has been carried out on the nucleation and growth of copper in the micro-electronics industry (Grujicic and Batric, 2002). For copper electrodeposition on stainless steel, the studies have been more limited. Surface properties of stainless steel can affect on the copper nucleation (Aromaa, Stefanova, Forsén, 2012). Increasing surface roughness is associated with lower copper growth. Urda-Kiel (1999) also concluded that thicker oxide layers on AISI 304 stainless steel led to lower nucleation. The copper electrocrystallization process was influenced by surface pretreatment on 316 L stainless steel. Dense, uniform and fine copper nuclei were obtained on stainless steel substrate oxidized in air at 200-300 °C (Zhou and O'Keefe, 1998). Bonou (1994) reported that the first stage was the formation of copper crystallites by a 3-D nucleation process on the air formed oxide layer. As the kinetics was mass transfer controlled, part of the applied current was to reduce this oxide layer, with formation of new sites for the copper deposition.

In order to achieve required product quality, small amounts of organic additives are added to influence the deposits brightness and surface roughness. Sun and O'Keefe (1992) reported the nucleation and growth mechanism in 40g/L Cu, 180g/L H_2SO_4 in the presence of thiourea or glue on a stainless steel cathode. The experiments showed copper formed by progressive nucleation and three-dimensional (3-D) growth under diffusion control in additive-free electrolyte. Addition of glue did not change the mechanism but increased the number of nuclei formed on the surface. The addition of thiourea changed the mechanism to instantaneous nucleation with 3-D growth under kinetic control.

The use of modified polysaccharide products (DXG-7 and HydroStar®) and a polyacrylamide (Cyquest® N-900) have been recently reported in commercial copper electrowinning tankhouses (Robinson et al. 2013) but very few electrochemical studies have been published. Fabian et al. (2007) claimed that the addition of activated polyacrymides in the electrolyte could lead to smoother deposits than guar. Moats and Derrick (2012) explored the nucleation and plating overpotentials using a galvano-dynamic method in the presence of various organic additives. The plating potentials revealed that HydroStar did not polarize the copper electrodeposition potential while a polyacrylamide had a polarizing effect on plating, but not on nucleation. Helsten and Moats (2013) investigated the nucleation and plating potential using the same technique for HydroStar and Cyquest N-900. They concluded that varying chloride or HydroStar concentrations appeared to have little effect on the nucleation and plating potentials but smoothed the deposit surface. Increasing concentrations of N-900 decreased the plating potentials and surface roughness but did not influence the nucleation potential.

Moats, Luyima and Oliveria (2014) continued the examination HydroStar and Cyquest N-900 on copper electrodeposition by using traditional methods of cyclic voltammetry and electrochemical impedance spectroscopy. Even though the two additives showed no apparent difference on the nucleation overpotential, Cyquest N-900 polarized the copper deposition reaction upon the return sweep. It also indicated that Cyquest N-900 increased the reaction’s charge transfer resistance and created a second low frequency loop.

The main purpose of this work is to examine the nucleation and growth mechanism in the presence of HydroStar and Cyquest N-900 at low and high plating potentials. In addition, scanning electron microscope (SEM) micrographs at 10 and 30 seconds deposition are examined to verify the proposed mechanism. Finally, surface roughness of two hour electrodepositions were examined to determine if an interaction between current density and additive concentration was observed.

Materials and methods

Electrolyte

A synthetic electrolyte was prepared from Fisher certified grade cupric sulfate pentahydrate, sodium chloride and reagent grade sulfuric acid to produce a base electrolyte with a room temperature composition of 40 g/L copper, 20 mg/L chloride and 160 g/L sulfuric acid. All experiments were conducted at 40 °C ±1°C without external agitation.

The organic additives were commercial products, HyrdroStar® and Cyquest N-900. They were provided by an industrial partner. HydroStar® is a modified polysaccharide produced by ChemStar. Cyquest N-900 is a polyacrylamide produced by Cytec Industries. The additives were predissolved in water at a concentration of 3.5 g/L. Required amount of the additive was added into the electrolyte 30 minutes before each experiment.

Apparatus

A three electrode cell was employed for all electrochemical measurements. The electrowinning cell was a 300 mL glass vessel with a plastic cover. The working electrode was a 316L stainless steel plate. Prior to each experiment, the stainless steel plate was prepared by successful polishing using 180, 400 and 600 grit silicon carbide sandpaper in order to obtain a smooth, even surface for copper electrodeposition. After polishing, each stainless steel was washed by de-ionized water (DI) in an ultrasonic cleaner. Then the stainless steel plate was masked with chemical resistant non-conductive tape, leaving the top centimeter untaped for electrical connection. A deposition area of 2.25 cm^2 was carefully cut-out by a template. Additional tape was applied to ensure the electrolyte only contacted the deposition area. The counter electrode was IrO_2-Ta_2O_5 coated titanium mesh which was washed with DI water and acetone between experiments. The distance between the working electrode and counter electrode was kept at ~3 cm for all experiments. The reference electrode used was a double junction mercury sulfate electrode (Fisher Scientific model number 5771425003B). All potentials were converted to standard hydrogen electrode potential (SHE) and reported as such. The electrodes were put into the electrolyte 20 minutes prior to the experiment to reach the target temperature of 40°C.

For electrochemical testing, a Gamry Reference 3000 Potentiostat/ Galvanostat connected to a computer and controlled by Gamry software was used. Three different electrochemical experiments were conducted: (1) linear sweep voltammetry, (2) potentiostatic, (3) chronopotentiometry. Linear sweep voltammetry (LSV) was employed by sweeping the potential from 0.28V to 0.05V vs. SHE at a scan rate of 1mV/s. During the potentiostatic measurements, the potential was stepped to a specific value and held for five seconds while current was measured versus time at a sample frequency rate of 1000 Hz. Chronopotentiometey was also conducted with constant current control to produce two hour copper electrodeposits at current densities from 30 mA/cm^2 to 70 mA/cm^2 in the presence of various concentrations of organic additives.

Surface roughness measurements were performed using a HiRox KH-8700 digital microscope on the copper deposits without removal from the stainless steel cathodes. The roughness was measured using a 3-D profile image with 0.05μm/pulse precision and 30 mm of automated travel distance. The measurement process was repeated eight times on the copper deposits on distributed lines away from the edges of the deposit.

Results and discussion

Linear sweep voltammetry

Before discussing the effect of organic additives on the nucleation and growth of copper, linear sweep voltammetry was conducted to determine their effects on Cu^{2+} reduction. Experiments in this study were performed in the base electrolyte with or without the addition of 2.5 mg/L HydroStar or Cyquest N-900. All solutions tested in this study contain 20 mg/L Cl^-. This was chosen to reflect the conditions most common in commercial copper electrowinning tankhouses (Robinson, 2013). Others have reported that Cl^- addition to acidified copper sulfate depolarizes copper deposition (Lakshmanman, Mackinnon, Brannen, 1977, Shao, Pattanaik, Zangari, 2007).

The LSV results are shown in Fig. 1. The addition of Cyquest N-900 to the electrolyte caused the current density to decrease compared to the base electrolyte. This indicates the polarizing or inhibition effect of Cyquest N-900. The addition of HydroStar produces a curve almost identical to that of the base solution. HydroStar does not appear to polarize the reaction. These results confirm previous findings measured by other electrochemical methods (Moats, 2012, 2013, 2014).

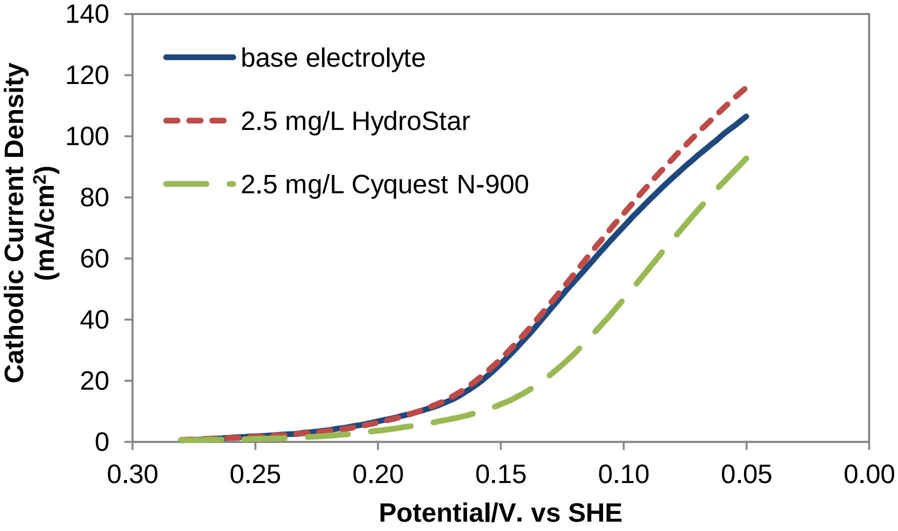

Figure 1 – Linear sweep voltammogram for copper electrodeposition from 0.28 V to 0.05 V vs.SHE, scan rate 1 mV/s. Base electrolyte: 40 g/L Cu^{2+}, 160 g/L H_2SO_4, 20 mg/L Cl^-, 40°C.

Nucleation and growth mechanism

In order to understand the effect of additives on copper nucleation and growth, potentiostatic experiments were conducted. A typical current-time behavior in the base electrolyte is shown in Fig. 2. A potential of 0.14V vs. SHE was applied for five seconds. According to Sun and O’Keefe (1992), three characteristic regions are typically presented in potentisostatic responses of copper electrodeposition. In the first milli-seconds, there is an initial pulse due to the charging of the double layer. This pulse was not revealed in our experiments. A similar response was also observed by other researchers (Zhou and

O'Keefe, 1998).The second region is induction. During the induction of copper nuclei, the current remains low. The induction period in these experiments appears to be around 0.2 seconds. As the copper nucleates and grows, the current density increases with time into the third region, where nuclei form and grow.

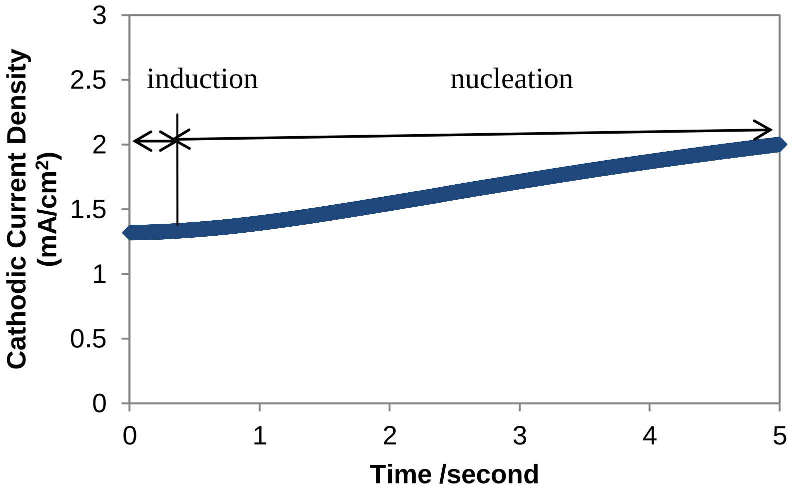

Figure 2 – Current-time relationship for the nucleation and initial growth of copper on 316 L stainless steel in 40 g/L Cu, 160 g/L H_2SO_4, 20 mg/L Cl^- at the applied potential of 0.14 V vs. SHE, no external agitation, 40°C.

The current-time data obtained in each solution and applied potential was examined to determine nucleation and growth behavior of the electrodeposited phase. A summary of the various nucleation and growth models and their resulting relationships between current density and time are presented in Table 1 (Thirsk and Harrison, 1972). At constant potential, the current density (i) is proportional to t^n (n=0.5, 1, 1.5, 2, 2.5, 3).To determine the nucleation mechanism, the induction time t_0 is excluded from time, t. The induction time t_0 did not vary significantly in our experiments.

For Equations 2-9, i is the current density (A/m^2), M is molecular weight, ρ is density, C is copper ion concentration (mol/cm^3) , D is the diffusion coefficient, t is time, k is the reaction rate constant, h is the nuclei height, L^2 the cross section and θ the coverage. A is defined as the adjusted nucleation rate constant and N_0 the total number of sites available for nucleation. F is Faraday constant and z is the number of electrons transferred (Thirsk and Harrison, 1972).

Table 1 – Current density-time relationship for potentiostatic nucleation and growth (Thirsk and Harrison, 1972)

Expression	Nucleation Type	Growth Type	Control Regime	Equation
$\mathrm{i} = 8\mathrm{zF}\pi \mathrm{N}_0 M^2 \mathrm{C}^3 \mathrm{D}^{3/2} \mathrm{t}^{1/2} / \rho^2$	instantaneous	3D	diffusion	2
$\mathrm{i} = 2\mathrm{zFAL}^2\mathrm{kt}$	progressive	1D	kinetic	3
$\mathrm{i} = \mathrm{zFh}\rho\pi\theta^2\mathrm{DAt/M}$	progressive	2D	diffusion	4
$\mathrm{i} = 2\mathrm{zF}\pi\mathrm{MhN}_0 k^2 \mathrm{t}/\rho$	instantaneous	2D	kinetic	5
$\mathrm{i} = 16\mathrm{zF}\pi\mathrm{AM}^2\mathrm{C}^3\mathrm{D}^{3/2}\mathrm{t}^{3/2} / 3\rho^2$	progressive	3D	diffusion	6
$\mathrm{i} = \mathrm{zF}\pi\mathrm{MhAk}^2 t^2 / \rho$	progressive	2D	kinetic	7
$\mathrm{i} = 2\mathrm{zF}\pi\mathrm{M}^2 N_0 \mathrm{k}^3 \mathrm{t}^2 \rho^2$	instantaneous	3D	kinetic	8
$\mathrm{i} = 2\mathrm{zF}\pi\mathrm{AM}^2 h\mathrm{Ak}^3 t^3 / 3\rho^2$	progressive	3D	kinetic	9

Using the linear sweep voltammetry results, three potentials were selected to provide a range of current densities. Nucleation was examined at 0.05V, 0.12V and 0.14V vs. SHE. Electrolytes with and without the addition of 2.5 mg/L HydroStar or Cyquest N-900 were evaluated at each potential.

Current density vs. time plot for the three electrolytes when the cathode was held at 0.14V vs. SHE are shown in Figure 3. The curves for the base electrolyte and HydroStar are similar in current density to each other. The current density of Cyquest N-900 is less than the other two as expected from the LSV results.

Each data set was examined using each of the models shown in Table 1. The model that produced the highest correlation coefficient, R^2 ,was chosen as the mechanism model. A summary of the n values and nucleation and growth mechanism for copper deposition at 0.14 V in each electrolyte is presented in Fig.3 and Table 2. The linear regression analysis indicates strong correlation with the models. The initial nucleation and growth of copper in the electrolyte without organic additives appears to be progressive nucleation with 3-D growth under diffusion control, which confirms the findings of Sun and O'Keefe (1992). Even though Cyquest N-900 has a polarizing effect at this concentration, the nucleation and growth was also progressive nucleation with 3-D growth under diffusion control similar to the base electrolyte. The addition of HydroStar to the electrolyte appears to change the nucleation and growth mechanism to progressive nucleation with 2-D growth under diffusion control based on SEM micrograph observations.

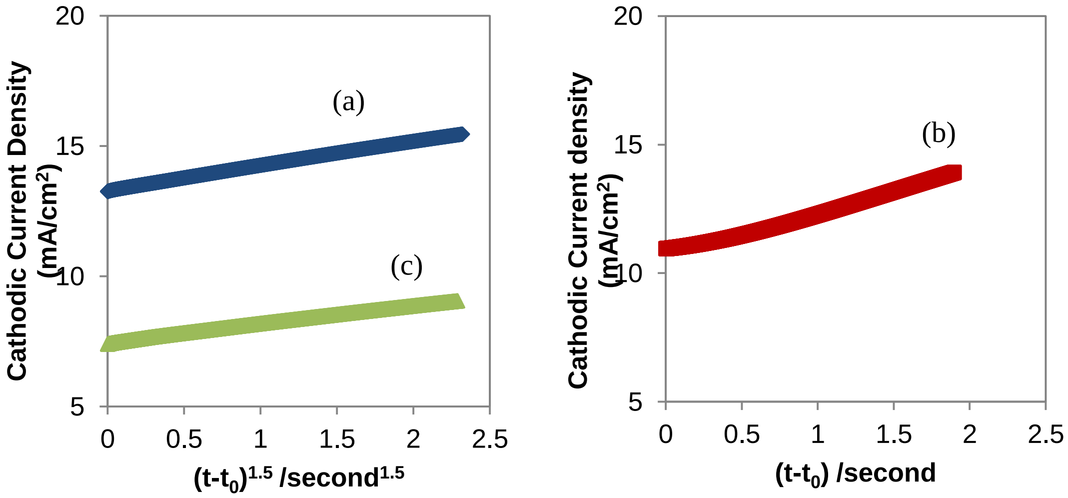

Figure 3 – Current density-time relationship at applied potential of 0.14 V vs. SHE. (a) base electrolyte (b) base electrolyte+2.5 mg/L HydroStar (c) base electrolyte+2.5 mg/L Cyquest N-900.

As the current densities generated at 0.14 V were below those typically employed in commercial operations, a constant potential of 0.12 V vs. SHE was evaluated to generate slightly higher current densities. The current density-time curves and summary of nucleation models at 0.12 V vs. SHE are presented in Fig. 4 and Table 3, respectively. The data and analyses indicate that copper nucleation and growth in the base electrolyte and HydroStar did not change as potentials decreased from 0.14V to 0.12V vs. SHE. However, the mechanism in the presence of Cyquest N-900 changed to progressive nucleation, 2-D growth with diffusion control concluded from our SEM analysis.

Table 2 – Current density-time relationship for the nucleation of copper at 0.14 V vs. SHE

Additive (mg/L)	Equations	n values	Nucleation Mechanism
0	$i = 9.47(t-t_0)^n + 132.96$ $R^2 = 0.999$	1.5	3D,progressive, diffusion
2.5 HydroStar	$i = 16.31(t-t_0)^n + 107.15$ $R^2 = 0.993$	1	2D,progressive, diffusion
2.5 Cyquest N-900	$y = 7.17(t-t_0)^n + 74.52$ $R^2 = 0.998$	1.5	3D,progressive, diffusion

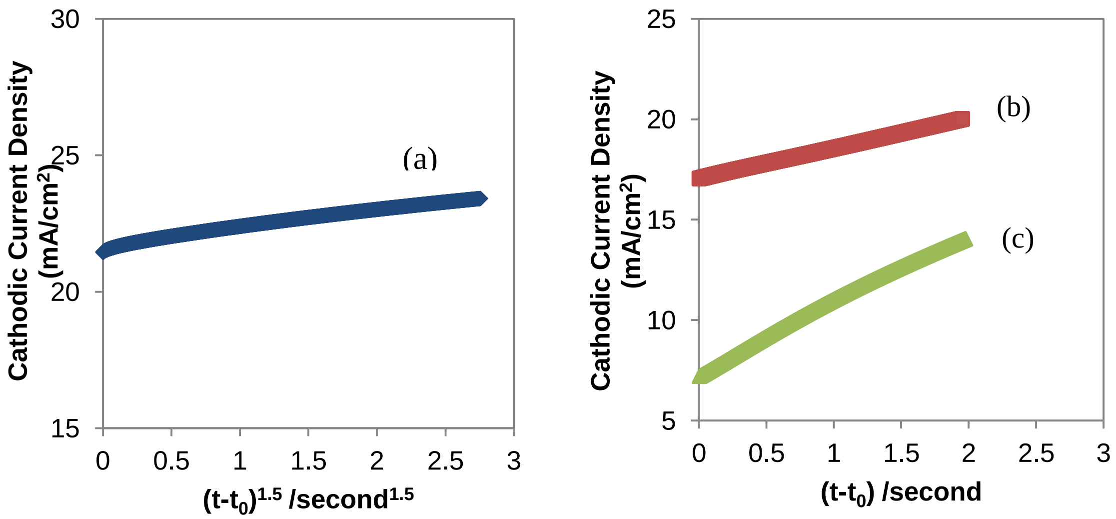

Figure 4 – Current density-time relationship at applied potential of 0.12 V vs. SHE. (a) base electrolyte (b) base electrolyte+2.5 mg/L HydroStar (c) base electrolyte+2.5 mg/L Cyquest N-900.

Table 3 – Current density-time relationship for the nucleation of copper at 0.12 V vs. SHE.

Additives (mg/L)	Equations	N values	Nucleation mechanism
0	$i = 6.85(t-t_0)^n + 216.50$ $R^2 = 0.987$	1.5	3D,progressive, diffusion
2.5 Hydrostar	$i = 35.22(t-t_0)^n + 73.92$ $R^2 = 0.997$	1	2D,progressive, diffusion
2.5 Cyquest N-900	$i = 15.06(t-t_0)^n + 170.63$ $R^2 = 0.999$	1	2D,progressive, diffusion

During harvesting, significantly higher current densities can be observed in commercial electrowinning. To evaluate this situation, the cathodic potential was set to 0.05 V vs. SHE and current density was measured versus time. The resulting plots are shown in Fig. 5. As expected, the current densities observed are much higher. Analysis of the data indicates the nucleation and growth mechanism for each electrolyte was instantaneous nucleation and three- dimensional growth with diffusion control as shown in Table 4.

SEM analysis

While the nucleation and growth study was conducted at constant potentials, industrially constant current conditions are employed. Figure 6 presents the potential during the 30 seconds deposition in these electrolytes. Nucleation occurs during the initial several seconds. A series of SEM micrographs of copper deposits at 30 mA/cm^2 on stainless steel (10 seconds and 30 seconds) were taken and are shown in Figs. 7-9.

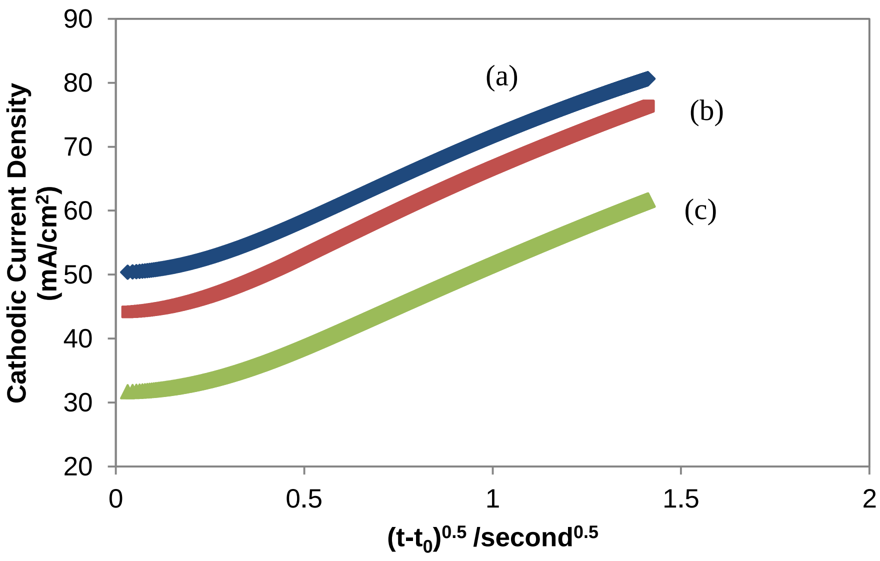

Figure 5 – Current density-time relationship at applied potential of 0.05 V vs. SHE. (a) base electrolyte (b) base electrolyte+2.5 mg/L HydroStar (c) base electrolyte+2.5 mg/L Cyquest N-900.

Table 4 – Current density-time relationship for the nucleation of copper at 0.05 V vs. SHE.

Additive (mg/L)	Equations	n values	Nucleation Mechanism
0	$i = 246.71(t-t_0)^n + 269.52$ $R^2 = 0.998$	0.5	3D, instantaneous, diffusion
2.5 HydroStar	$i = 257.97(t-t_0)^n + 405.12$ $R^2 = 0.998$	0.5	3D, instantaneous, diffusion
2.5 Cyquest N-900	$i = 245.07(t-t_0)^n + 467.28$ $R^2 = 0.998$	0.5	3D, instantaneous, diffusion

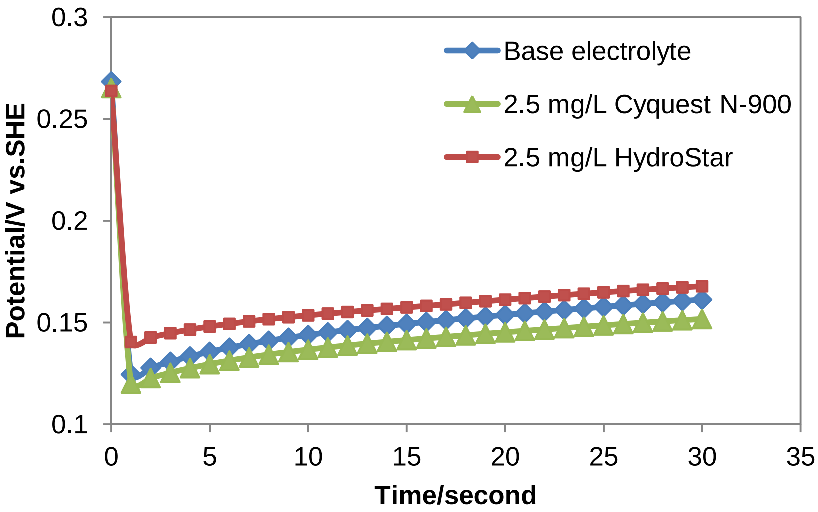

Figure 6 – Potential versus time for 30 seconds deposition in base electrolyte, 2.5 mg/L HydroStar and Cyquest N-900. 40 g/L Cu, 160 g/L H_2SO_4, 20 mg/L Cl^-, 40 °C, no external agitation, 316 L stainless steel substrate.

The deposits from the base electrolyte (Fig. 7) show that nuclei are growing in a hemi-spherical shape (three-dimensions), and the distribution of size indicates varying ages of nuclei. The increase number of nuclei with time increasing from 10 seconds to 30 seconds suggests that nuclei are continuing to form over time. These observations are in agreement with the mechanism of progressive nucleation and 3-D growth at 0.14 V vs. SHE in base electrolyte. This phenomenon is similar to previous observations (O'Keefe, 1992, 1998).

The SEM micrographs in Fig. 8 presents the copper nuclei and growth exhibited in the presence of HydroStar. The crystal size is smaller with HydroStar containing electrolytes than that from base electrolytes. Some size variations indicate the nuclei form progressively. Due to the nucleation potential approximately 0.14 V vs. SHE, the mechanism is to be progressive nucleation and 2-D growth under diffusion control. It is also noted that the copper nucleate along the direction of polishing stainless steel, which indicates the polishing direction might be the favorable growth site as indicated by others (Aromaa, 2012).

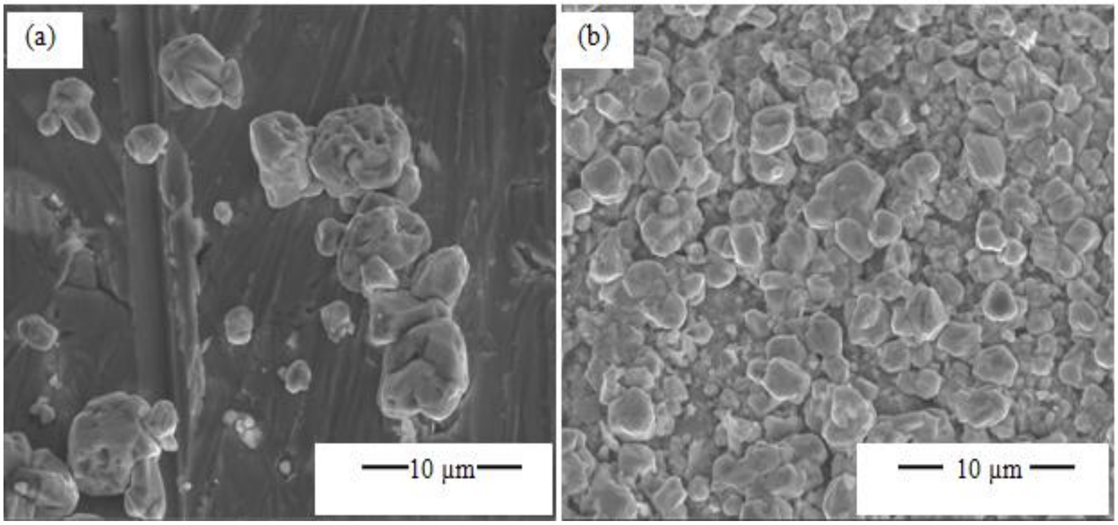

Figure 7 – SEM micrographs of copper crystals on 316 L stainless steel in base electrolyte at 30 mA/cm^2. (a) 10 seconds and (b) 30 seconds deposition.

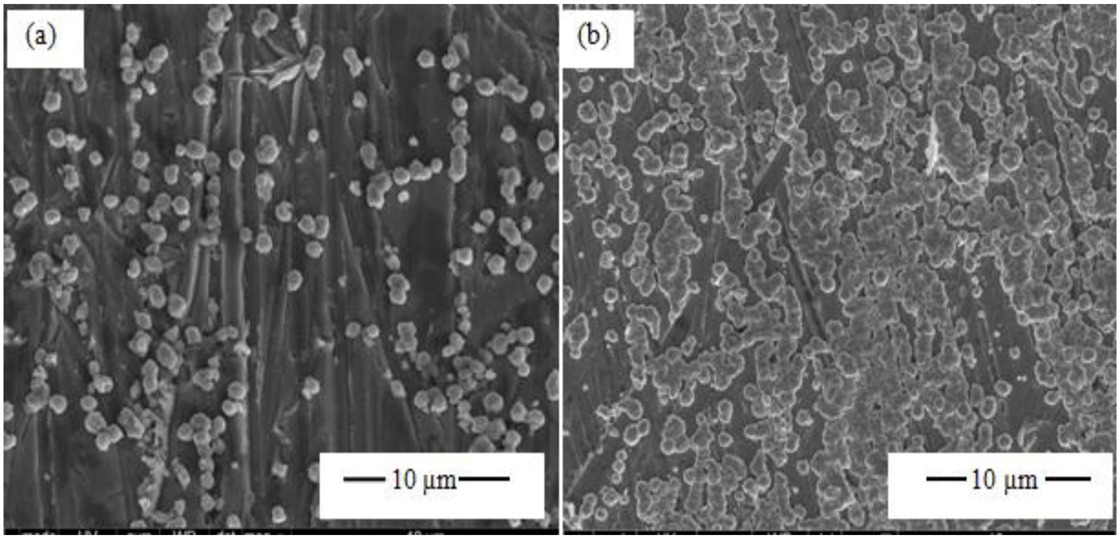

Figure 8 – SEM micrographs of copper crystals on 316 L stainless steel in base electrolyte with addition of 2.5 mg/L HydroStar at 30 mA/cm^2. (a) 10 seconds and (b) 30 seconds deposition.

It is shown in Fig. 9 (a) that the nuclei sizes formed in the presence of Cyquest N-900 are smaller than those from the base electrolyte. The number of nuclei is less than in the presence of HydroStar. The evolution of copper nuclei with time is presented in Fig. 9

(b). The relative uniform coverage and refinement of grains relative to the base electrolyte is attributed to the addition of Cyquest N-900. The nuclei size variation indicates progressive nucleation and 2-D growth.

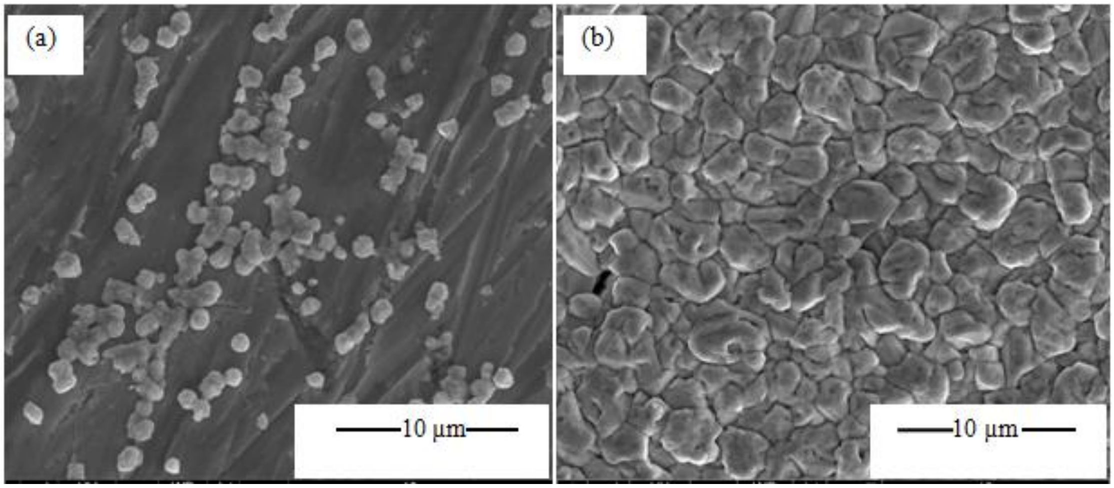

Figure 9 – SEM micrographs of copper crystals on 316 L stainless steel in base electrolyte with addition of 2.5 mg/L Cyquest N-900 at 30 mA/cm^2. (a)10 seconds and (b) 30 seconds deposition.

Surface roughness

The initial steps of copper nucleation and growth are particularly important for the quality of copper products, because a homogeneous covering of the entire surface of the electrode are critical to obtain copper deposits with low surface roughness. Therefore, two hours copper electrodeposition experiments were conducted in electrolytes with and without HydroStar or Cyquest-900 at 30, 40 and 70 mA/cm^2 to examine if surface roughness changes as a function of current density or nucleation and growth mechanism. The substrate is 316L stainless steel. Table 5 shows the average cathodic potentials at the current densities utilized above.

Table 5 – Current densities versus cathodic potential (V vs. SHE) in base electrolyte and in the presence of HydroStar or Cyquest N-900

Current Density (mA/cm^2)	Base electrolyte (V vs. SHE)	2.5 mg/L HydroStar (V vs. SHE)	2.5 mg/L Cyquest N-900 (V vs. SHE)
30	0.144	0.146	0.128
40	0.122	0.124	0.106
70	0.076	0.078	0.064

The expression of R_Z is shown as below.

$$R_Z=Y_P+Y_V \tag{10}$$

This value is obtained by removing the standard length from the roughness curve in the direction of the mean line. Then add the height Y_P to the highest point and the depth from the removed mean line to the lowest point Y_V. R_Z indicates the roughness as a function of the highest peak, which in practice would most likely to lead a short circuit.

Average surface roughness R_Z values are plotted versus current densities in Fig. 10. It can be observed that the R_Z values increase significantly in base electrolytes and HydroStar-containing electrolytes. Conversely, when the current density was 70 mA/cm^2, surface roughness in the presence of Cyquest N-900 remained almost the same. The results indicated that Cyquest N-900 is likely a better smoothing agent than HydroStar.

Since surface roughness is related to adsorption, the overall results suggest that Cyquest N-900 is more specifically adsorbed than HydroStar at the electrode interface. This adsorption associated with polarization behaviors thus inhibit the formation of dendrites, which contributes to the smoother surface in Cyquest N-900 containing solution. As a progressive nucleation mechanism is indicated versus the base electrolyte at 30 and 40 mA/cm^2, new copper nuclei grow on the previously deposited copper. After two hours, copper deposition is discontinuous and incomplete on stainless steel substrate. This leads to a higher surface roughness. Instantaneous nucleation is indicated in HydroStar-containing solutions at 30 and 40 mA/cm^2, therefore smaller crystal sizes are exhibited on the substrate. Due to a limit current density of 70 mA/cm^2, the nucleation and growth mechanism might be controlled by mass transfer and therefore thicker and rougher deposits are produced. However, the surface roughness of Cyquest N-900 at the limit current density seems to be unexpected and needs to be inverstigated.

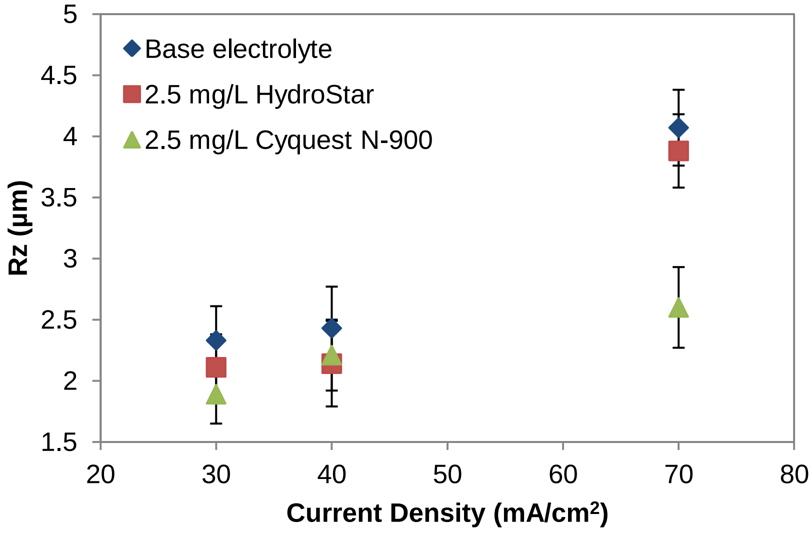

Figure 10 – Surface Roughness of two hours deposits versus current densities, 2.5 mg/L HydroStar and Cyquest N-900. 40 g/L Cu, 160 g/L H_2SO_4, 20 mg/L Cl^-, 40 °C, no external agitation, 316 L stainless steel substrate.

Conclusions

A traditional three electrode cell was employed to conduct linear sweep voltammetry and potentiostatic measurements to characterize the effect of HydroStar and Cyquest N-900 on copper electrowinning.

Based on the nucleation and growth theory developed by Thirsk and Harrison, good agreement was achieved between the theory and SEM micrographs and surface roughness results. The mechanism for copper deposited on 316 L stainless steel in 40 g/L Cu, 160 g/L H_2SO_4, 20 mg/L Cl^-, 40°C electrolyte appears to be progressive nucleation and 3-D growth under diffusion control. Due to discontinuous deposition on a stainless steel blank, it produces the roughest surface after two hours electrodeposition.

Small addition (2.5 mg/L) of polyacrylamide (Cyquest N-900) polarizes the cathodic reaction. At a current density commonly used in tankhouses, the nucleation and growth mechanism appears to also be progressive nucleation and 2-D growth in the solutions containing Cyquest N-900. The polarization appears to create smaller nuclei which lead to a finer grain structure. The polymer also appears to provide leveling of the longer term deposit.

Modified polysaccharide (HydroStar) is neither a depolarizer nor polarizer on the electrode surface, however produces smaller nuclei than the base electrolyte and changes growth from 3-D to 2-D while the nucleation is still progressive. The finer structure and 2-D growth appears to be the source of the smoothing agent of HydroStar.

This work shows that potentiostatic measurement associated with SEM micrographs and surface roughness are effective to analyze the copper deposition process and surface quality. Future work will be focused on the effect of organic additives and their interactions with chloride ions on copper electrodeposition.

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II. Chloride ion and its interaction with commercial additives in copper electrowinning

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Abstract

Chloride ion and its interaction with Cyquest N-900 (a polyacrylamide) and HydroStar® (a modified polysaccharide) during copper electrodeposition is explored using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrochemical results revealed that chloride ion (up to 40 mg/L) on its own depolarized the copper deposition reaction, while chloride plus Cyquest N-900 inhibited depolarization. It is proposed that chloride ion acted as a bridging ligand between copper and Cyquest N-900. Addition of 2.5 mg/L HydroStar depolarized copper deposition reaction, but this behavior did not change at the chloride concentrations tested.

Key words: Copper electrowinning, Chloride, HydroStar, Cyquest N-900, Cyclic voltammetry, Electrochemical impedance spectroscopy

Introduction

Electrowinning is a major production method to obtain high purity copper in modern tankhouses. Copper is electrodeposited on stainless steels; and then stripped, washed and sold. Significant improvements in the quality of copper electrodeposits have been made over the last few decades. Temperature, additives, current density, electrolyte concentrations and agitation are now known to influence the quality of copper electrodeposits (Moats and Derrick, 2012).

Among those factors, the addition of small quantities of organic additives has been recognized to significantly improve the properties of copper deposits. These additives are critical in the prevention of dendrite growth and production of smooth, dense cathode deposits. Chloride ion and organics are known to affect the nucleation and growth process of copper electrodeposition (Lakshmanan, 1977, O'Keefe, 1978, Ilgar, 1997, Hebert et, 2005). Therefore, understanding the chloride ions effect and its interaction with recently implemented organic additives are of importance to copper electrowinning or electrodeposition.

The influence of chloride on copper deposit ion has been the subject of considerable research. It is generally agreed that chloride ions depolarize the copper deposition process at low chloride concentrations (few mM), because chloride catalyzes the $Cu^{2+} \rightarrow Cu^{+} + e^{-}$ rate-limiting step of this process (O'Keefe, 1978, Ilgar, 1997, Hebert, 2005, Shao, 2007). Guar has been industry-standard organic additive for copper electrowinning. The interaction between chloride ions and guar has been reported using a rotating cylinder electrode experimental arragement. Results showed that guar and Cl^{-} did not inhibit for copper electrodeposition (Fabian, 2007, 2009).

Guar, however, is relatively expensive. Recently, the use of modified polysaccharide (HydroStar®) and polyacrymide products (Cyquest N-900) have attracted the attention in copper electrowinning plants as a cheaper replacement for guar products (Robinson, 2013).

Since the use of modified polysaccharide and polyacrylamide is still developing, a limited amount of electrochemical studies have been published and some mechanisms still remain unclear. Winand et al. (1976) compared the copper quality obtained with polyacrylamide against guar in electrowinning. The conclusion was guar produced better quality with polyacrylamide . However, there are many different types of polyarylamides. Fabian et al. (2007) compared the effects of an activated polyacrylamide (APAM) to guar on deposited copper. The later study indicated that activated polyacrylamide produced smoother and brighter deposits than guar. In addition, the activated polyacrylamide and chloride ion acted as a suppressor to copper deposition, which the authors indicated by have been due to an APAM-CuCl complex.

Nucleation and plating potentials were measured and compared in the presence of either chloride, HydroStar (a modified polysaccharide) or N-100 (Cytec polyacrylamide product) by Helsten and Moats (2013). It was found that varying concentration of chloride or HydroStar had little influence on the nucleating and plating potentials. However, N-100 in the presence of chloride appeared to polarize copper deposition. Moats and Derrick (2012) also investigated HydroStar and a different polyacrylamide by a galvanodynamic method and illustrated that this polyacrylamide had a polarizing effect while HydroStar had a leveling effect with an unclear mechanism. These phenomena were further illustrated by means of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) (Moats, Luyima, Oliveira, 2014).

The past research revealed the effect of various concentrations of modified polysaccrides and polyacrylamide on copper electrodeposition. However, the interaction between the chloride and these organic additives still remains unknown. Thus, the interaction of chloride ion, a modified polysaccharides (HydroStar®) and polyacrylamide (Cyquest N-900) during copper electrodeposition was examined in a synthetic electrowinning electrolyte. Electrochemical tests like cyclic voltammetry and electrochemical impedance spectroscopy were employed to investigate electrochemical fundamentals.

Material and methods

Electrolyte preparation

The synthetic electrolyte was prepared from Fisher grade reagents: copper sulfate pentahydrate, sulfuric acid and sodium chloride. De-ionized water was used in all electrolyte preparation. Organic additives, HydroStar® and Cyquest N-900, are commercial products and were provided by a copper mining company. HydroStar® is a modified polysaccharide product produced by ChemStar. Cyquest N-900 is a polyacrylamide product produced by Cytec Industries.

For all the experiments, the starting concentrations of copper and sulfuric acid were 40 g/L and 160 g/L, respectively. Chloride concentration was examined at various concentrations. The organic additives were pre-dissolved into the de-ionized water to produce stock solutions. The desired concentration of additive was added to the electrolyte 30 minutes before the experiments.

Electrowinning cell

A conventional three electrode cell system was used for all the experiments. The temperature was controlled at 40±1 °C in an Isotemp 128 water bath (Fisher Scientific). No external agitation was provided to the electrolyte within the cell.

The working electrode was a 316L stainless steel plate. The stainless steel cathode was polished using 120, 400, 600 grit silicon carbide papers to obtain a uniform surface prior to each experiment. After polishing, the cathodes were washed with de-ionized water and then acetone followed by drying with compressed air. Chemical resistant non-conductive tape was used to leave an area of 2.25 cm^2 on the surface. Additional tape was applied to make sure that the electrolyte only contacted the exposed surface area. The counter electrode was a mixed metal oxide coated titanium mesh which washed with de-ionized water and acetone before each experiment. The distance between the working electrode and counter electrode was about 3 cm for all experiments. The reference electrode used was double junction mercury sulfate electrode (MSE) from Fisher Scientific. All the potentials in this work are reported relative to standard hydrogen electrode potential (SHE).

Electrochemical methods

The electrochemical experiments were measured using a Gamry Instruments Reference 3000 Potentiostat/Galvanostat/ZRA. The data was collected using Gamry software pre-installed on a personal computer. For cyclic voltammetry, the cathodic potential was cycled between 0.28 and 0.05 V vs. SHE with a scan rate of 1 mV/s. The current data was converted to current density after dividing by the known surface area.

Electrochemical impedance spectroscopy (EIS) was conducted after copper deposition for 15 minutes at a fixed potential of 0.12 V vs. SHE in a potentiostatic mode. The EIS tests used a DC potential of 0.12 V vs SHE with a 5 mV AC perturbation over the frequency range of 100 KHz to 0.1 Hz. Gamry Echem Analyst Software 6.04 was employed to perform the circuit design, data process and impedance parameter estimation.

Results and discussion

Cyclic voltammetry (CV)

A typical cyclic volatammogram of copper electrodeposition on a stainless steel cathode is presented in Fig. 1.

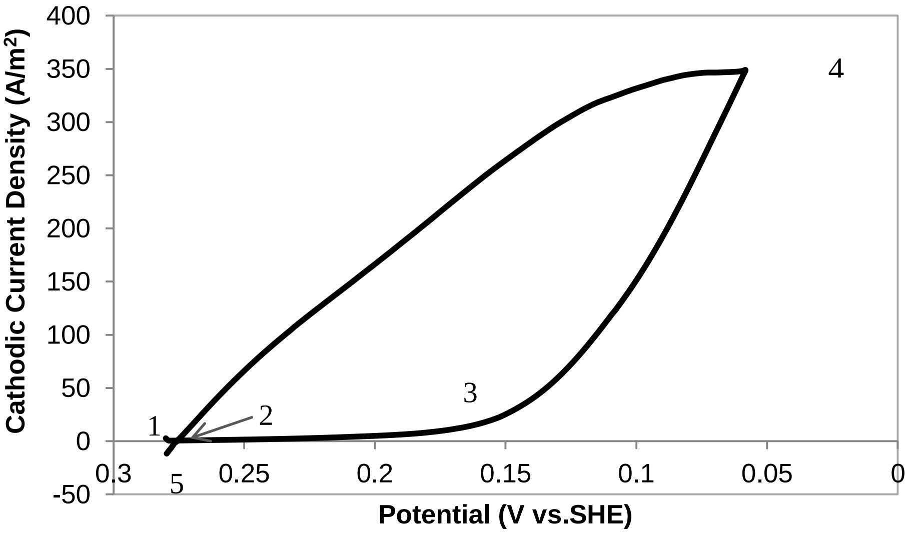

Figure 1 – Typical cyclic voltammogram of copper electrodeposition on 316 L stainless steel blank, 40 g/L Cu^{2+}, 160 g/L H_2SO_4, 40 °C, no external agitation. Scan from 0.28 V to 0.05 V vs. SHE, scan rate 1 mV/s.

The voltage sweep started from point 1 at 0.28 V vs. SHE. Point 2 is the equilibrium point. It is the potential at which the curve 4-5 crosses the zero current line. The increase of current density to point 3 indicates charging of the electrode double layer and point 3 is the approximate potential at which copper nucleates on the stainless steel cathode. The curve 3-4 represents the polarization overpotential as copper grows on the stainless steel substrate. The curve from 4-5 occurs as the potential was reversed and causes copper deposition to occur on freshly deposited copper. This leads to a higher current density than measured from 3-4. The process 3-4-5 is a non-steady state condition during which the stainless steel blank was increasingly covered by copper. Curve 2-5 represents the dissolution of the formally deposited copper. Therefore, the shape of the curve is dependent on the voltage limits.

Electrochemical or physical parameters in the system determine the polarization or depolarization behaviors. Assuming the electrochemical parameters (e.g., same applied potential) and physical set up (e.g.,same cathode surface polishing) are constant for all experiments, the addition of chloride ions or two organic additives may lead to a depolarization or polarization effect. Figure 2 shows an example of cyclic voltammograms in chloride-containing electrolytes with and without the addition of 2.5 mg/L HydroStar or Cyquest N-900. It can be observed that no chloride exhibits the lowest current density in Fig. 2-(a). Increasing the chloride concentrations to 10 mg/L increased the overall current densities. The addition of more Cl^- had little effect. This indicates that the presence of chloride depolarizes the deposition reaction. This confirms previous reports [Gabrilli, 2006, Shao 2007, Fabian 2007, 2009, Pasquale, 2008]. In the presence of HydroStar, the addition of chloride had no effect in Fig. 2-(b). It appears HydroStar alone accelerate the rate of copper deposition and chloride does not affect the reaction further. However, in the presence of Cyquest N-900 as in Fig. 2-(c), the addition of chloride assists polarizing in the deposition process. Increasing the chloride concentration leads to further inhibition of copper deposition.

To further illustrate the interactions between chloride and the organics, current densities at 0.12 V vs. SHE from the returning sweep are illustrated in Fig. 3. During the growth of copper deposits, the presence and concentration of chloride has a significant effect. This has been attributed to the formation of a CuCl complex which accelerates the copper reduction reaction rate at a fixed potential (Shao, 2007). Conversely, the current density during the copper plating process in the presence of chloride and Cyquest N-900 decreases up to 40 mg/L chloride concentration. The interaction of Cyquest N-900 with Cl^- appears similar to previous research with polyenthylene glycol and Cl^- (Hebert, 2005, Chen, 2008).The results from HydroStar-containing solutions fluctuate very little compared to chloride and Cyquest N-900 series, but indicate a depolarizing effect if no Cl^- is present.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is an effective tool to characterize electrode processes and gain insight into the kinetics of the electrochemical system. EIS is able to determine solution resistance (R_S), rate of charge-transfer resistance (R_{CT}), double layer capacitance (C_{DL}) and their phenomena (Fabian, 2009). EIS results obtained at a fixed potential with a frequency scan are shown in a Nyquist plot (Fig. 4) in which the negative imaginary impedance is plotted versus real impedance. The EIS data can also be analyzed using an equivalent circuit model and the parameters like R_S, R_{CT} and C_{DL} estimated. EIS combined with equivalent circuit models assist in directly quantifying the electrochemical reactions rate compared to chronopotentiometry or cyclic voltammetry measurements. Therefore, this technique has been widely used in evaluation copper electrodeposition in the presence of some additives like guar, activated polyacrylamide or polyethylene glycol (PEG) (Hebert, 2005, Chen, 2008).

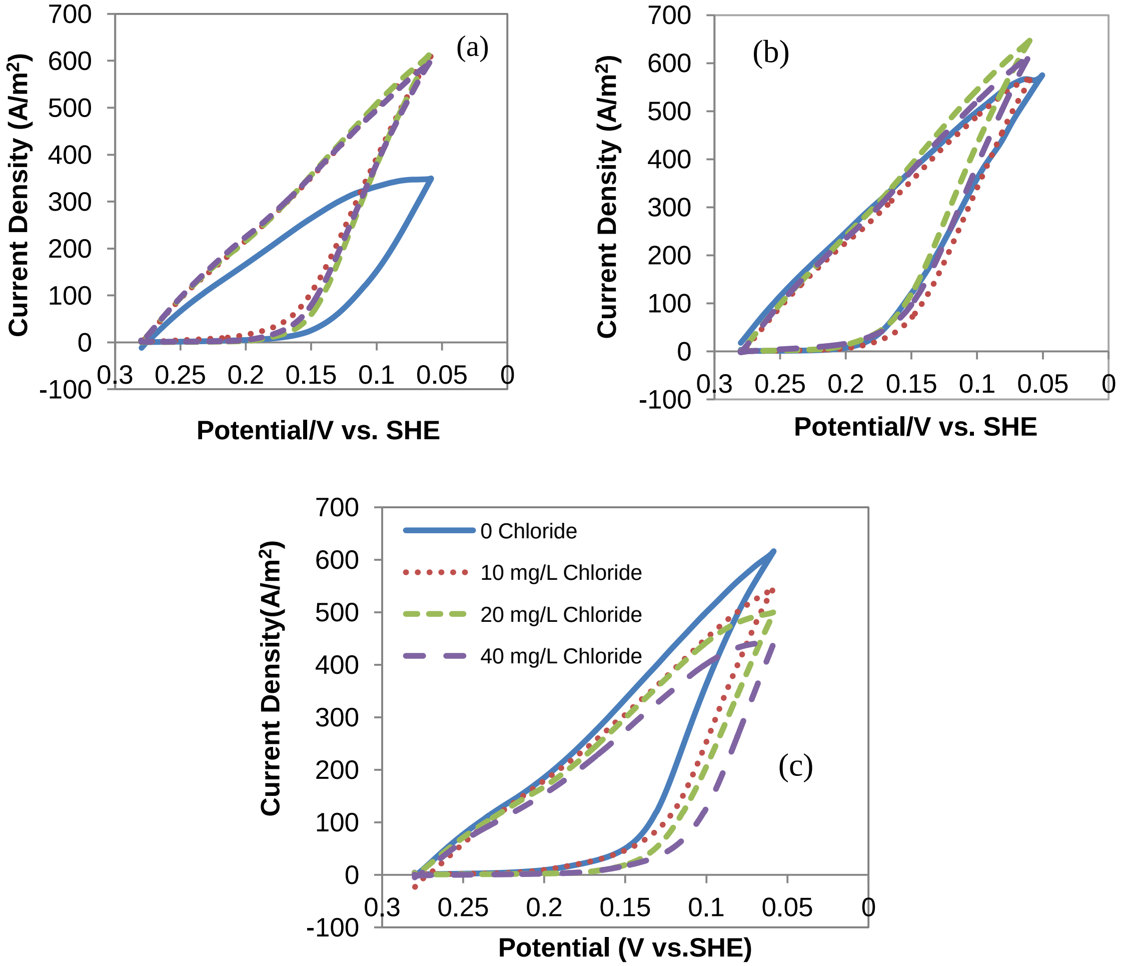

Figure 2 – Cyclic voltammogram. (a) 0-40 mg/L chloride-containing electrolytes, (b) 0-40 mg/L chloride +2.5 mg/L HydroStar, (c) 0-40 mg/L chloride+2.5 mg/L Cyquest N-900. Base conditions: 40 g/L Cu, 160 g/L H_2SO_4, 40 °C, no external agitation,316 L stainless steel blank, 1mV/s sweep rate.

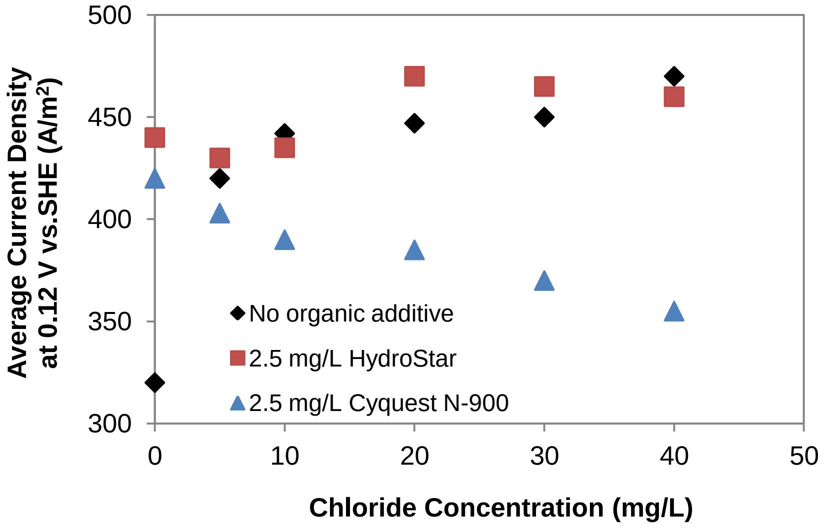

Figure 3 – Effect of chloride ions and organic additives on average potential at 300 A/m^2 on returning sweep. Base electrolyte: 40 g/L Cu, 160 g/L H_2SO_4, 40 °C, no external agitation,316 L stainless steel blank, 1mV/s sweep rate.

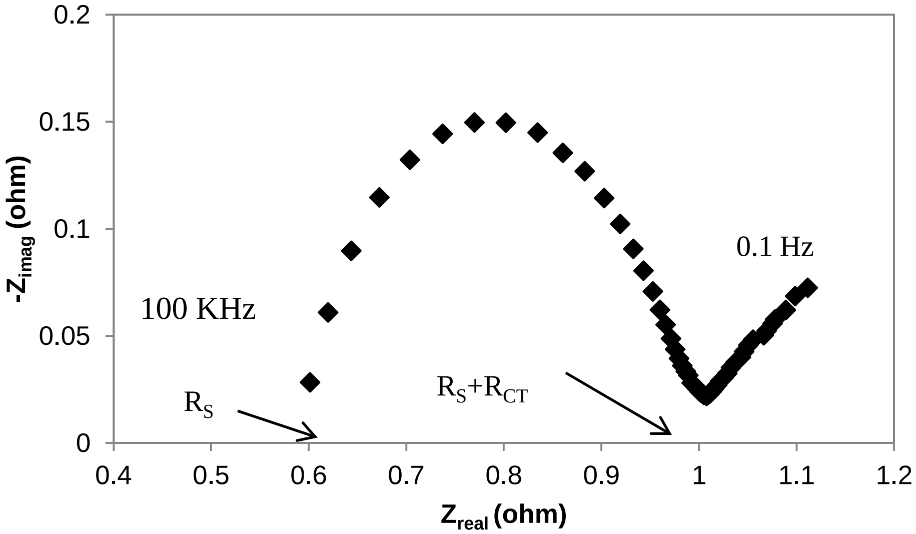

Figure 4 – A Nyquist plot of EIS data for copper electrodeposition in 40 g/L Cu, 160 g/L H_2SO_4, 40°C, no external agitation. 15 minutes copper deposition at 0.12 V vs. SHE prior to EIS, DC potential 0.12 V vs. SHE with AC potential of 5 mV.

EIS measurements and equivalent circuit modeling have been performed to understand the charge transfer resistance and double layer capacitance in the presence of chloride ions with or without HydroStar or Cyquest N-900. A Nyquist plot is shown in Fig. 4 for copper elelctrodeposition in an additive free electrolyte (40 g/L Cu, 160 g/L H_2SO_4, 40 °C, no external agitation). It depicts the real impedance versus the negative of the imaginary impedance which characterizes the capacitance or impedance of the system. Impedance semicircle/arcs are shown on the plot and the shapes or diameters of the curves indicate governing mechanism. The intercept at the highest frequencies of the loop with the real axis indicates the solution resistance (R_S). Also, the real axis on the other side intercept is the sum of solution resistance and charge transfer resistance or polarization resistance (R_S+R_{CT}). Therefore, the diameter of the semicircle at high frequency is related to the resistance of charge transfer (R_{CT}). The height of the loop is related to the double layer capacitance.

EIS is also performed at low frequency (0.1 Hz) where further observations can be made. It can be seen from Fig. 4 that there is an arc with a slope of about 45° to the real axis. This shape indicates Warburg impedance, which is caused by the diffusion of copper ions across the boundary layer at low frequency in the non-agitated solution used in these experiments.

Figure 5 shows the Nyquist plots determined from EIS experiments conducted in electrolytes containing various concentrations of chloride (0-40 mg/L) with no organic additives at a potential 0.12 V vs. SHE. One semicircle is observed at high frequency and a ~45° straight line is observed at low frequency. A dominant capacitive loop corresponding to the charge transfer resistance and double layer capacitance is present at high frequency. This loop is well defined in each electrolyte and comes from the charge transfer from Cu^{2+} to Cu^{+}. The diameter of this semicircle is the value of charge transfer resistance (R_{CT}) and generally decreases with the increasing concentration of chloride ions. The same results were also reported by Shao and Zangari (2007). The lower frequency loop represents the Cu^{2+} diffusion to Cu in deposition process.

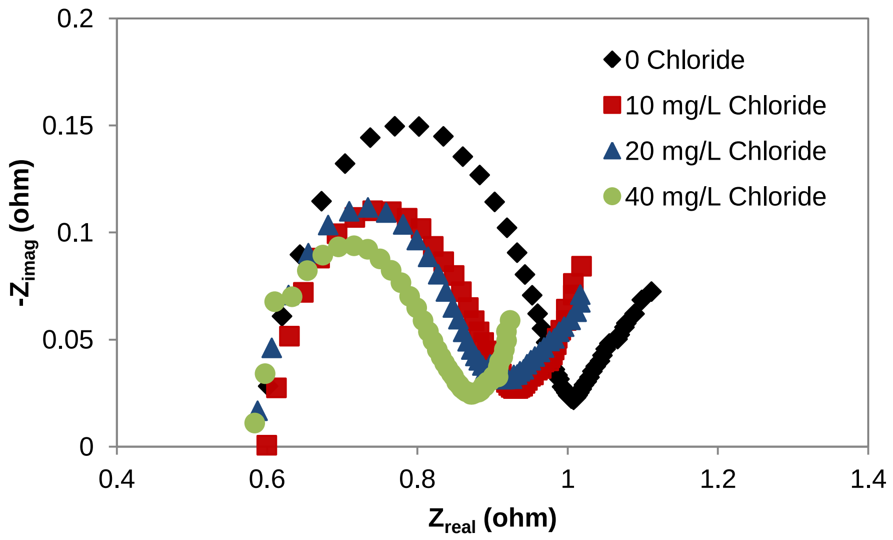

Figure 5 – A Nyquist plot of EIS data for copper electrodeposition with 0-40 mg/L chloride in 40 g/L Cu, 160 g/L H_2SO_4, 40°C, no external agitation. 15 minutes copper deposition at 0.12 V vs. SHE prior to EIS, DC potential 0.12 V vs. SHE with AC potential of 5 mV.

Profound changes are observed in the EIS measurements (Fig. 6) in Cyquest N-900 containing electrolytes for various chloride concentrations. The high frequency capacitive loop is related to charge transfer reaction. Conversely, the shapes of the semicircle at higher frequency with the addition of Cyquest N-900 are increasing up to 40 mg/L chloride concentration. It indicates that the corresponding charge transfer resistance increases with increasing Cl^- in the presence of Cyquest N-900, coinciding with a reduction of deposition current density observed in the CV plot. A possible explanation is that the complex bonding among Cyquest N-900 and cupric ions and chloride ions form on the electrode surface. This reaction product is similar to PEG-CuCl (Chen, 2008) and APAM-CuCl (Fabian, 2009) complex produced by others. The low frequency loop is attributed to the addition of Cyquest N-900 and causes another boundary layer. Adsorption of Cyquest N-900 appears to form of inductive loop at low frequency in the presence of increasing chloride concentration. The root cause of this inductive loop was not evaluated in this study.

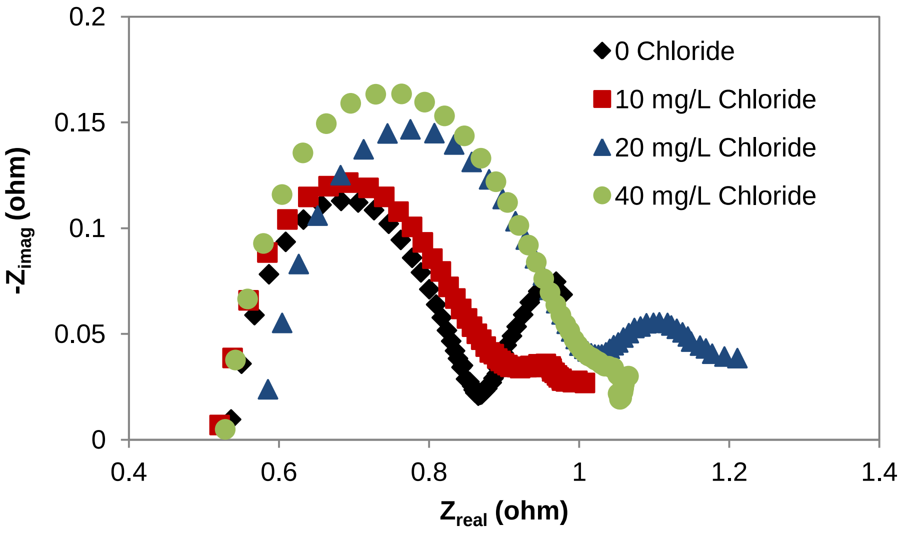

Figure 6 – A Nyquist plot of EIS data for copper electrodeposition with 0-40 mg/L chloride+2.5 mg/L Cyquest N-900 in 40 g/L Cu, 160 g/L H_2SO_4, 40°C, no external agitation. 15 minutes copper deposition at 0.12 V vs. SHE prior to EIS, DC potential 0.12 V vs. SHE with AC potential of 5 mV.

Nyquist plots obtained in the solutions of chloride and 2.5 mg/L HydroStar are provided in Fig.7. The shapes of the impedance spectra were not to be affected significantly by chloride addition in the presence of HydroStar. The diameters of the high frequency loop exhibit some variation, but it appears HydroStar disrupts the depolarization mechanism seen earlier in the chloride-only EIS data.

To further understand the EIS data, an equivalent circuit model was employed. The equivalent circuit describes the Faradic electrode process and consists of resistors and capacitance as depicted in Fig. 8. To model this electrochemical system between the working electrode and the reference electrode, the solution resistance (R_S) is placed in series with a constant phase element which models the double layer capacitance (C_{DL}). As the components of Faradic impedance are non-ideal, the double layer capacitance is placed in parallel with charger transfer or polarization resistance. Low frequency data is often modeled with a third resistor (R_3) and a parallel CPE capacitance (C_3).

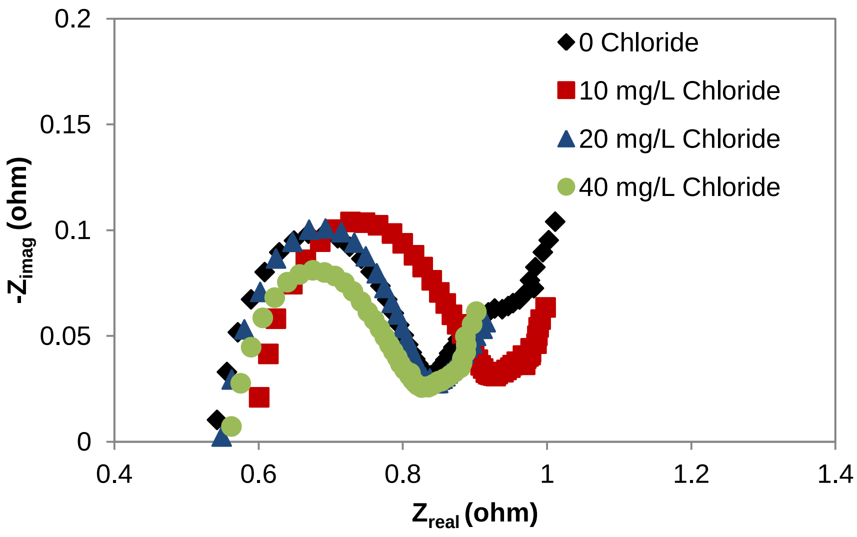

Figure 7 – A Nyquist plot of EIS data for copper electrodeposition with 0-40 mg/L chloride+2.5 mg/L HydroStar in 40 g/L Cu, 160 g/L H_2SO_4, 40°C, no external agitation. 15 minutes copper deposition at 0.12 V vs. SHE prior to EIS, DC potential 0.12 V vs. SHE with AC potential of 5 mV.

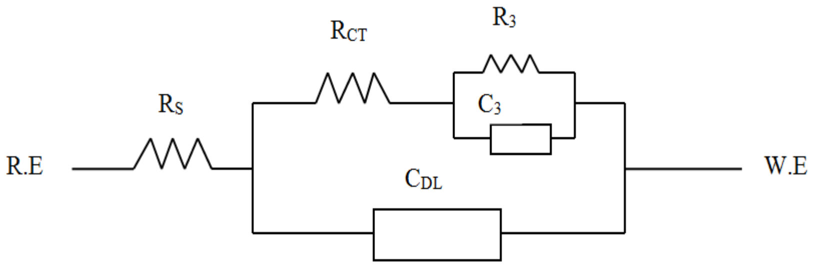

Figure 8 – EIS equivalent circuit with reference electrode (R.E), solution resistance (R_S), charge transfer resistance (R_{CT}), double layer capacitance (C_{DL}), capacitance (C_3) and resistance (R_3), working electrode (W.E).

The calculated charge transfer resistances from the equivalent circuit modeling are shown in Fig. 9. When no organic additive was present, charge transfer resistance decreased significantly when chloride was added at 5 mg/L, confirming again that chloride depolarizes the copper reduction process. The R_{CT} values continue to decrease slightly up to 40 mg/L chloride concentration. The phenomenon is consistent with the CV data in Fig. 3.

In the Cyquest N-900 containing solution, N-900 does not depolarize the reaction without chloride present. However, addition of chloride increases the charge transfer resistance. It is believed that the chloride ions play the role of bridging ligand and thus promote Cyquest N-900 adsorption similar to reports on the interaction of PEG and Cl^- (Chen, 2008). The presence of Cyquest N-900 and chloride polarizes the $Cu^{2+} \rightarrow Cu^{+} + e^-$ reduction. Only chloride ions form a thin layer on the electrode surface, the addition of extra chloride does not further Cyquest N-900 adsorption. This is supported by the plateau R_{CT} values at higher concentrations.

The addition of HydroStar appears to depolarize copper electrodeposition by lowering R_{CT}. It appears that chloride does not interact with HydroStar as adding chloride concentration up to 40 mg/L does not change this behavior substantially. From this point of view, the mechanism of HydroStar in copper electrodeposition process is still not clear.

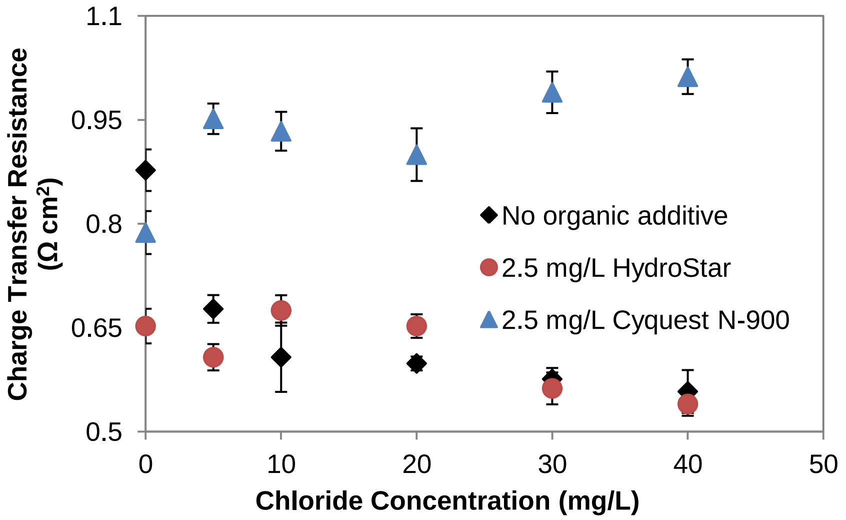

Figure 9 – Charge transfer resistance data of EIS modeling with addition of HydroStar or Cyquest N-900 in the electrolytes containing 0-40 mg/L chloride.

Double layer capacitance data obtained from EIS modeling are plotted in Fig. 10. These values exhibit similar trend as charge transfer resistance data. C_{DL} data decreases with the addition of chloride concentrations as previously reported (Chen, 2008). The physical meaning of C_{DL} values are difficult to interpret with the presence of two organic additives. More work needs to be done to confirm this observation and determines the meaning.

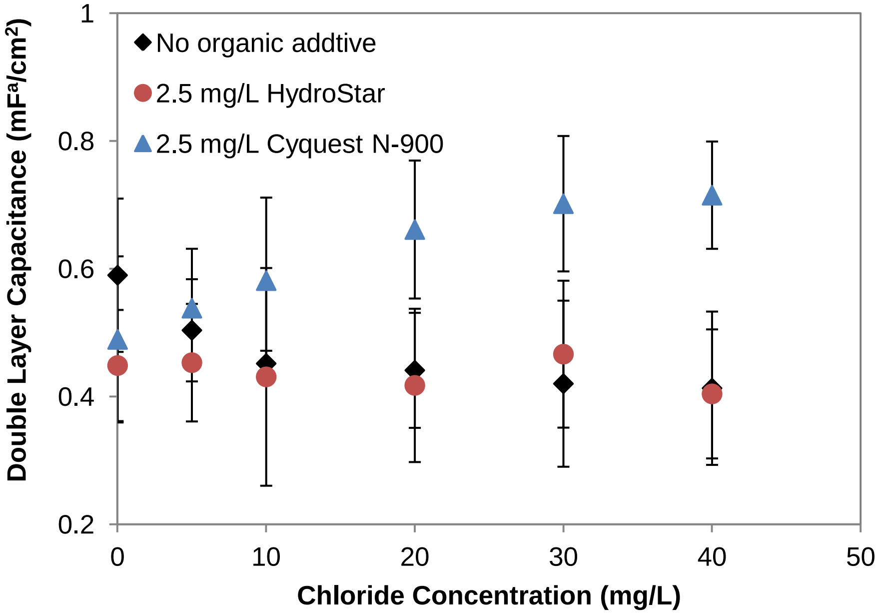

Figure 10 – Double layer capacitance data of EIS Modeling with addition of HydroStar or Cyquest N-900 in the electrolytes containing 0-40 mg/L chloride, a is CPE exponent and has a value ~0.7-0.8

Conclusions

Cyclic voltammetry and electrochemical impedance spectroscopy were employed to characterize the individual roles and interactions of chloride, Cyquest N-900 and HydroStar in a synthetic copper electrowinning electrolyte (40 g/L Cu, 160 g/L H_2SO_4, 40 °C) without external agitation.

The chloride ion on its own depolarizes copper electrodeposition, while chloride ion associated with Cyquest N-900 inhibits the reaction. The former is believed to be caused by CuCl complex forming, and the latter might be due to the adsorption of a

Cyqueset N-900 upon the complex with Cu^{2+} and Cl^- .The addition of HydroStar depolarized copper deposition and appears not to interact with chloride.

This is further illustrated in EIS and equivalent circuit modeling data. The Nyquist plots for organic additive-free electrolytes are observed a high-frequency capacitive loop with a reduction of charge transfer resistance with increasing chloride. In the presence of Cyquest N-900, the R_{CT} values increase with the addition of chloride ions but plateau with increasing Cl^- content. This seems to indicate Cl^- is acting as a bridging ligand between copper and Cyquest N-900. Addition of HydroStar to the electrolyte seems to depolarize the deposition reaction but it does not alert its behavior at the chloride concentrations tested. The trends observed from Nyquist plots and equivalent circuit models are consistent with the CV results.

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SECTION

3. CONCLUSIONS

The results of this work highlight the influence and interactions of modified polysaccharide (HydroStar), polyacrylamide (Cyquest N-900) and chloride ion during the copper electrowinning process. The most important conclusions are:

Copper nucleation and growth mechanisms changed with potential and the presence of organic additives. At lower overpotentials, the deposition mechanism appears to be progressive nucleation and 3-D growth with diffusion control in a synthetic electrolyte (40 g/L Cu, 160 g/L H_2SO_4, 20 mg/L Cl^-). Because of discontinuous deposits, it leads to the roughest surface after two hours electrodeposition. The introduction of Cyquest N-900 does not change the mechanism but polarize the cathode reaction, which appears to produce smaller nuclei. However, small addition of HydroStar changes the mechanism to progress nucleation and 2-D growth with diffusion control. It also produced finer structure and contributes to smoothing agent.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were employed to further examine the chloride ion and its interaction with HydroStar and Cyquest N-900. CV results indicated that chloride ion depolarizes copper electrodeposition. However, chloride ion associated with Cyquest N-900 inhibits the reaction, which might be due to the adsorption of a Cyquest N-900 upon the complex with Cu^{2+} and Cl^-. On the other hand, the addition of HydroStar depolarizes copper deposition and does not appear to interact with chloride.

The phenomena were investigated further by EIS and equivalent circuit modeling. The Nyquist plots for organic additive-free electrolytes are characterized by a high-frequency capacitive loop with a reduction of the charge transfer resistance with increasing chloride concentration. In the presence of Cyquest N-900, the R_{CT} values increased with the addition of chloride ions but plateaued with increasing Cl^- content. This indicates Cl^- is playing a role as a bridging ligand between copper and Cyquest N-900. The addition of HydroStar to the electrolyte appears to depolarize the deposition reaction but it does not alert its behavior at the chloride concentrations investigated.

VITA

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