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EVALUATION OF ELECTROCHEMICAL TECHNIQUES FOR THE QUANTIFICATION OF GLUE IN COPPER ELECTROWINNING ELECTROLYTES

Bachelor Thesis

by

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1 Introduction

Copper electrorefining is the purification process where anode slabs with around 98% copper content are introduced and dissolved in electrolyte solution to produce cathodes that contains 99.99% pure copper through re-deposition. Major amount of copper is produced through this process. In 2015, total 23 million tons of copper have been refined, in which 18.9 million tons of copper was produced by electrorefining process, and the amount of electrowon copper was 4 million tons [1].

For the production process, it is very efficient and less energy intensive when the current density is high. However, when the current density is high, electrodeposition of copper generates cathode copper with lot of irregularities, such as needles and nodules.

Uneven and irregular surfaces of copper can be avoided with presence of additives in the electrolyte solution. Glue is a leveling agent used for electrorefining process, and it is considered the most effective and strongest additive of all. Glue acts as a resistance barrier on the cathode surface and it greatly influence electrodeposition. Long chain of protein molecules of glue are attracted to the negatively charged cathode. Since glue molecules are positively charged in solution, they are selectively adsorbed on the areas where the field strength is high. Such locations are edges, nodules and needles on the cathode surface. The adsorption of glue takes place at these areas by minimizing needles, edges and dendrites, therefore, purer cathode copper with smoother and denser surface can be obtained.

Both low dosage and over dosage of glue result insufficient quality of electrodeposition. As a common experience, glue is mostly added excessively than deficiently dosing. A big drawback of over dosing is that glue increases the polarization resulting high voltage of a cell. When the quantification of glue is accurately measured and maintained, energy consumption can be diminished significantly.

Glue consists of a mixture of various protein molecules, so that the chemistry of glue is complex. This feature of the glue makes the chemical analysis very complicated. A conventional chemical analysis can take about 48 hours. Unfortunately, electrorefining is continuous process, the glue concentration must be monitored and controlled in simultaneously.

Based on glue impact on polarization of cathode, electrochemical methods of measuring glue concentration in electrolyte has been actively researched and developed in past. Modern electrorefining plants mainly use galvanostatic method for measurement, in which potential time response is measured as the current is constant. Although this method was formerly known as reliable and less costly, the preparation of the work, the calibration, and calculation processes are very time consuming and repeated many times.

Therefore, simple and accurate measuring methods must be investigated and studied for electrorefining plants in the future for a better performance. This thesis mainly focused on electrochemical techniques that used to study glue behaviour in electrolyte.

Furthermore, glue changes the electrodeposition of cathode by changing their morphological behavior and kinetics of the crystal growth. To determine glue effects on electrodeposition, instantaneous nucleation and progressive nucleation mechanisms of copper have been studied in this work.

Synthetic electrolyte solutions have been prepared, and cyclic voltammetry, chronoamperometry, differential pulsed voltammetry techniques have been performed to investigate how glue affects the electrodeposition in electrolyte solution. The main characteristic of these methods is that potentiostatic approach gives a distinctive opportunity to measure the change of current density while the potential between a working and reference electrode is kept constant. As a result, this method enables us to study cathodic behavior of a cell.

2 Literature review

2.1 *The characteristics of copper*

Copper is one of the most used metals in industry. It is a red orange ductile, malleable and corrosion resistant metal that has a bright metallic luster. Brass and bronze are one of the widely used copper alloys. The concentration of copper in the earth crust exceeds 50 ppm which makes copper 26th abundant element on the earth [2].

Atomic number of copper is 29, and it has two natural isotopes, ^{63}Cu (68.94%) and ^{65}Cu (31.06%). Besides, other nine synthetic artificial isotopes are currently known [3].

In ambient condition, copper has cubic closest-packed (CCP) lattice structure and a density of 8.93g/cm^3. Thermal conductivity of copper is the second highest of all metals, therefore this makes copper a suitable material for a high quality piping of heat exchangers and heat sinks [4]. Due to its highly electrical conductive behavior, it is mainly used as wiring and engine metal for electrical equipment. Other application areas include architecture, automotive, telecommunications, construction, marine and energy. Approximately 830 million tons of copper reserves has been estimated in 2019 [5].

2.2 Copper processing

The processing of copper depends on the mineralogy of ores. It determines how the metal will be extracted economically from ores. Only 20 out of 200 copper bearing minerals are the principal for copper extraction. Copper minerals naturally occur in two different groups according to their chemical constituents which includes sulfidic minerals and oxidized minerals (carbonates, oxides, sulfates and hydro-silicate minerals) [6]. The deposition is another criteria for mineral grouping, which is responsible for different processing stages.

In mineral processing, the main two processes are used to convert the copper ore into pure copper cathode with purity of 99.99%. The choice of process related to the type of ore. Copper sulfide type of ore, such as chalcopyrite and chalcocite, undergo hydrometallurgical process due to its relatively richer content of copper, whereas oxidized ores that are closer to the surface of the ground goes through hydrometallurgical process [2].

Both of the processing routines require the mining, transportation and ore preparation must be carried out for better handling of the bulk solids. The ores near the surface are extracted by open pit mining by digging deeper into the earth by time. As for the ores which formed deep in the earth crust, underground mining is used. Those ores placed deep down in the earth tend to have high grade and less oxidized copper. It makes the enrichment process easier.

Once the ore is mined, it is transported and delivered to primary crusher for a size reduction. For further steps, secondary and sometimes tertiary crushers prepare the ore to the grinding and milling processes to liberate copper minerals from the gangue minerals in pyrometallurgical processing. Mostly the product of the crushers is directed to hydrometallurgical process by leaching the piled heap of ore [4].

Pyrometallurgical processing

The name of this process is derived due the application of heat that is used to extract and purify metal. As shown in Figure 1, sulfide ore must undergo a series of physical treatment processes, so that the content of copper increases as the ore goes through the steps.

The grinding and milling of copper continues until it reaches close to the liberation size of copper which has been found 125 µm [7]. Once the copper minerals reach the certain degree of liberation, the ore is mixed with liquid to form slurry for preparation of the first step of the pyrometallurgical process called the froth flotation. The basic principle of this step is that valuable minerals in the ground ore slurry are separated from the gangue by means of flotation. The flotation process consists of mixing the ore slurry from the grinding process in an agitated cell in which air and reagents are introduced. The combination of the agitation, air, and chemicals creates bubbles where the mineral particles are attached. The bubbles rise through the agitated slurry to form a froth layer on top of the cells. The froth layer, containing a significant amount of the valuable minerals, is continuously removed from the cell. After further treatment in various other sections of the flotation circuit, this froth becomes the final concentrate, which contains the vast majority of the copper minerals [8].

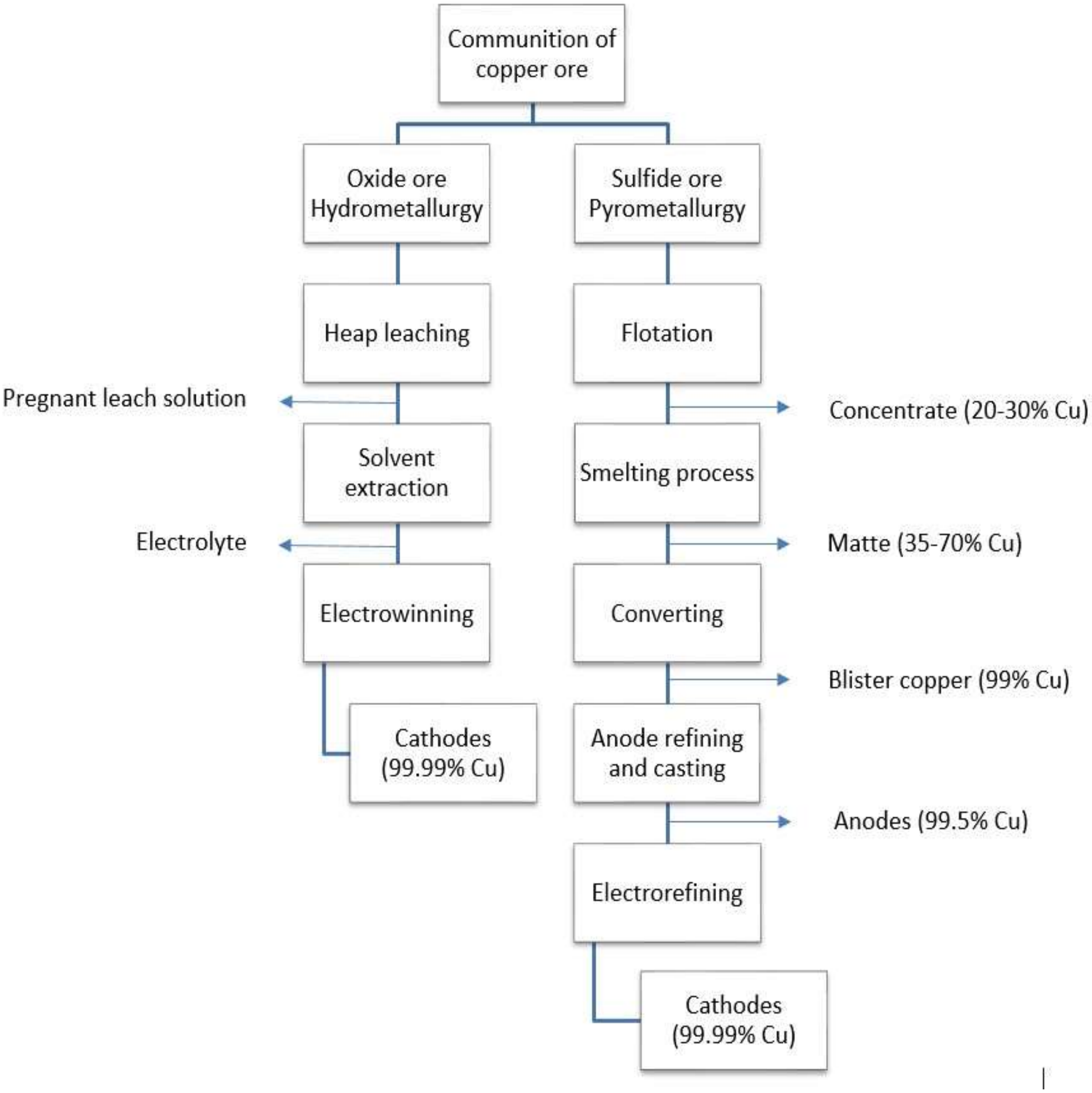

Figure 1 Copper processing flowsheet

Secondly, the concentrate which contains 20-30% copper is subjected to the smelting furnace to reach 1500°C [9]. The furnace produces a molten liquid of the concentrate which is later sent to slag-settling furnace. Matte is created from this process contains 35-70% copper, iron, sulfur, silica and other element.

To more pure product, impurity elements must be eliminated from the matte such as iron, sulfur and silica. Third step called converting helps the matte to get rid of impurities and it delivers very pure copper with content about 98%. Such blister copper hold certain amount of oxygen inside.

The color changing of the blister copper occurs as oxygen in the copper escapes and it turns yellow to blue-green due to loss of oxygen in anode smelter. After this stage, the resulting poured and molten copper cools down and forms anode which contains 99% copper and 1% impurities.

The last process of pyrometallurgical copper processing is called electrorefining. This is normal electrolysis process to produce cathode copper where the anode copper is dipped in the mixture of copper sulfate, sulfuric acid and additives. When electric power is applied, the current goes through and positive copper ions move from anode to cathode where copper deposits and other impurities sink down to the bottom of electrolysis tank. Such impurities often contain precious metals - gold and silver. The process takes about 14 days until anode copper fully dissolves and form cathodes with 99.99% copper content. Final product can be used for different applications such as wiring and plating [2].

Hydrometallurgical processing

This process involves aqueous solutions to produce copper from oxide ores. The advantage of the process is the possibility of extraction of copper at ambient temperature without a very high energy demand. Total three steps, are required for a conversion of oxide ores to pure copper plates, include heap leaching, solvent extraction and electrowinning.

The process starts with leaching the ore with aqueous solutions to dissolve metal into the solution. Mostly, the ores with low grade, which cannot be extracted by pyrometallurgical process with profit, goes through this process. Additionally, oxidized minerals do not respond to conventional flotation technique due to its physicochemical characteristic. On the top of impenetrable layer, crushed ore is placed forming heap with a small slope. When leaching reagent such as sulfuric acid, is sprinkled from the top, the copper dissolves in the solution, penetrate through the pile and collected in the pool. Copper solution collected is called pregnant leach solution, and it contains roughly 60-70% copper.

The solvent extraction is the method to separate pure copper solution from impure pregnant leach solution. To do so, the leach solution is mixed with an extractant which is mostly selective organic liquid and copper migrates to organic liquid leaving impurities in pregnant solution. Next stripping process involves a different aqueous solution (mostly sulfuric acid) to strip copper from organic phase. Solvent extraction can have one to several stages to fully separate copper from the solution.

Electrowinning, the last step of hydrometallurgical extraction of copper, is electrolysis process. Unlike electrorefining, electrowinning employs inert electrode which is commonly made out of lead, in copper electrolyte solution from solvent extraction step. The applied electrical current goes through anode electrode, and carried positive copper ions migrate from the solution, then positive ions electrodeposits on cathode plate forming very pure cathode copper. Impurities such as gold and silver deposited on the bottom of the electrowinning tank [10].

2.3 Copper electrolytic processes

During copper production from the ore, nearly all copper is treated by an electrolytic process. Based on their origin, copper is produced from either electrorefining anodes or electrowon from copper electrolyte solution.

Electrorefining

Electrorefining is limited by a) copper recovery from impure anode into copper sulfate and sulfuric acid electrolyte by electrochemical dissolving and b) electro plating of copper without anode impurities. The produced copper is free of impurities, and gold and silver can be recovered as byproducts. The copper content is enhanced up to 99.99% from 98.5%.

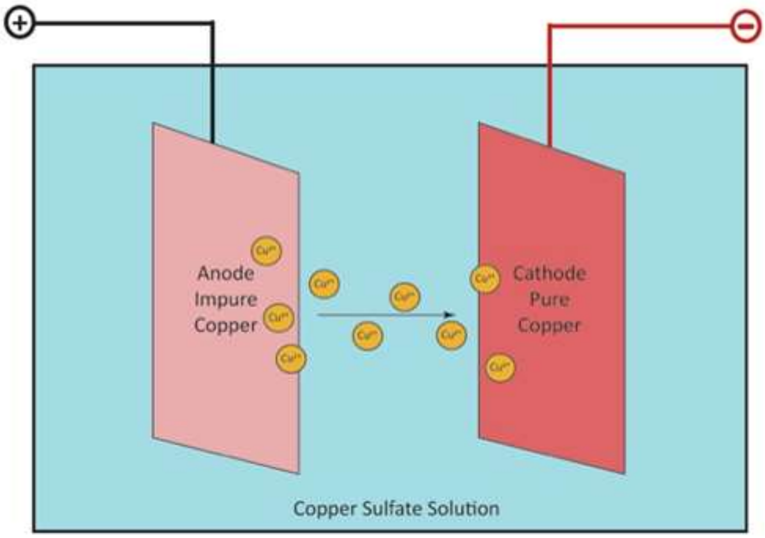

Figure 2 Copper electrorefining [11]

As illustrated on Figure 2, the applied current goes between anode slabs and cathode in electrolyte solution carrying copper ions. Deposition process can be divided into 3 subprocesses.

1) When the anode copper is dissolved in the electrolyte solution, it produces copper cations and electrons.

Equation 1

$$Cu_{anode}^{0} \rightarrow Cu^{2+} + 2e^{-} \qquad E^{0} = -0.34\,V$$

2) Due to convection and diffusion, positively charged Cu^{2+} ions in electrolyte are attracted and travel to negatively charged cathode as electrons produced from Equation 1 move through cathode and power supply

3) Copper metal is formed and electrodeposited on surface of cathode by recombining copper cations and electrons

Equation 2

$$Cu^{2+} + 2e^{-} \rightarrow Cu_{cathode}^{0} \qquad E^{0} = +0.34\,V$$

Overall reaction of electrorefining is expressed in Equation 3.

Equation 3

$$Cu_{impure}^{0} \rightarrow Cu_{pure}^{0} \qquad E^{0} = 0.00\,V$$

Anode impurities are left in the electrolytic solution, so that the resulting cathode has higher purity than starting anode slabs. The main impurity materials are Ag, As, Au, Bi, Co, Fe, Ni, O, Pb, S, Sb, Se and Te [12]. If the impurity has more negative reduction potential than copper, such as As, Bi, Co, Fe, and Ni, it dissolves into the solution under the applied potential. Because lower potential of copper is applied to the cell, the dissolved impurities cannot deposit on the cathode. To inhibit an accumulation of these impurities in the electrolyte solution, constant purification must takes place from the recycled bleed stream [13].

On the other way, the elements with more positive reduction potential stay in solid anode, including Ag, Au and Pt. As copper ions enters to the solution from anode, these impure elements sink down to the bottom of the tank and form anode slime. Anode slimes are continuously removed and recovered from the cell [14].

Depending on the source of anode copper, the concentration of each elements in electrolytic solution can vary. As shown in Table 1, the most typical copper electrolyte contain 40-50 g/L Cu, 170-200 g/L H_2SO_4, 10-20 g/L Ni, less than 20 g/L As and other impurities [15].

Table 1 Compositions of Copper Refining Electrolytes Table [15]

Component	Concentrations
Cu	35-60 (typical 45-50) g/L
H_2SO_4	120-210 (typical 150-200) g/L
Cl	0.01-0.06 g/L
As	2-30 g/L
Bi	0.01-0.7 g/L
Fe	0.1-3 g/L
Ni	0.3-25 g/L
Sb	0.002-3 g/L
Glue (protein colloids)	35-350 g/t Cu cathode
Thiourea	30-140 g/t Cu cathode
Avitone	0-60 g/t Cu cathode

Concentration of each element can influence directly to the refining process. Higher electrical conductivity and energy efficiency can be reached by increasing the concentration of H_2SO_4 in solution, although concentrations of Cu and Ni decreases the conductivity. Passivation of anode and very viscous electrolyte may occur due to exceeding amount of copper in solution [16]. As well as purity of cathode is influenced by Cu concentration because of increased solids in suspension. Organic agents and chloride are added to improve purity of cathode deposit [17].

Operating conditions of electrorefining

Industrial electrorefining cells requires direct current power supply. Theoretical potential must apply to the cell is 0.00 V according to Equation 3. However, overvoltage on the cathode and overvoltage for dissolving copper from anode, ohmic drops for electrolyte and hardware must be included for the applying potential between anode and cathode [18]. 3-6 m long cells with stainless steel blanks as the starting cathode are commonly operated in industry for electrorefining. Anode is 4-5 cm thick impure copper with a mass of 300-400 kg. Typically between 20 and 40 cells are connected in series. Current density of 400 A/m^2 is optimally used in industrial operation [2]. Although rapid copper plating can be reached by increasing current density, too high current density causes passivation of anode by converting anode Cu into Cu^{2+}

ions on the anode faster than the ions can travel to the cathode. Consequently, excess Cu^{+2} forms $CuSO_4 \cdot 5H_2O$ precipitation layer on anode that the precipitation insulates the anode from the electrolytic solution causing obstruction of the further oxidation process [16]. Anode passivation can be inhibited by adjusting current density below 300 A/m^2 in operation. Otherwise, increasing temperature by dissolving formed precipitation or adding more chloride in electrolyte can help to avoid passivation [19].

The operation temperature of electrolytic solution is approximately 65°C. Regardless the cost and energy intensive process of heating the electrolytic cell, the advantages of higher temperature are beneficial for deposition of copper. As the temperature increases, the solubility of $CuSO_4$*$5H_20$ increases, so that the hydrate doesn't crystallize on the anode slab. Moreover, electrolyte density and viscosity decreases as the temperature raises. Heating also helps the electrochemical reaction to occur quickly. On the other hand, too high temperature destroy the structure of organic additives and it results evaporation of the solution [20].

Solid particles in electrolyte originates from the anodes' breakdown, slimes and mold coating from casting of the anodes. Such insoluble particles creates highly viscous electrolyte and they start grow on cathode. As a result, rough grains and dendrites get built, so that the filtration of electrolyte is crucial.

Electrowinning

Electrowinning differs from electrorefining by its inert anode electrode mostly made out of lead alloy sheets or sometimes made out of indium oxide-coated titanium. The process involves the submerging of metal cathodes and inert anodes into a pure copper electrolyte containing $CuSO_4$ and H_2SO_4, applying a direct current to electrode and electroplating of metallic copper from the electrolyte. Typical cathodes are made out of stainless steel. After 6 to 7 days, the plated copper is taken out and stripped by a machine [2]. The main principle behind electrowinning can be expressed as following steps.

The cathode reaction of electrowinning is identical to the electrorefining reduction [2].

$$Cu^{2+} + 2e^- \rightarrow Cu^0_{cathode} \qquad E^0 = +0.34\,V$$

Equation 2a

However, the anode reaction is dissimilar, in which oxygen gas and protons are obtained from the decomposition reaction of water [2].

Equation 4

$$H_2O \rightarrow H^+ + OH^- \rightarrow 0.5\,O_2 + 2\,H^+ + 2e^- \qquad E^0 = -1.23\,V$$

With the presence of the sulfate ions, the total electrowinning reaction [2]:

Equation 5

$$Cu^{2+} + SO_4^{2-} + H_2O \rightarrow Cu^0 + 0.5O_2 + 2H^+ + SO_4^{2-} \qquad E^0 = -0.89\,V$$

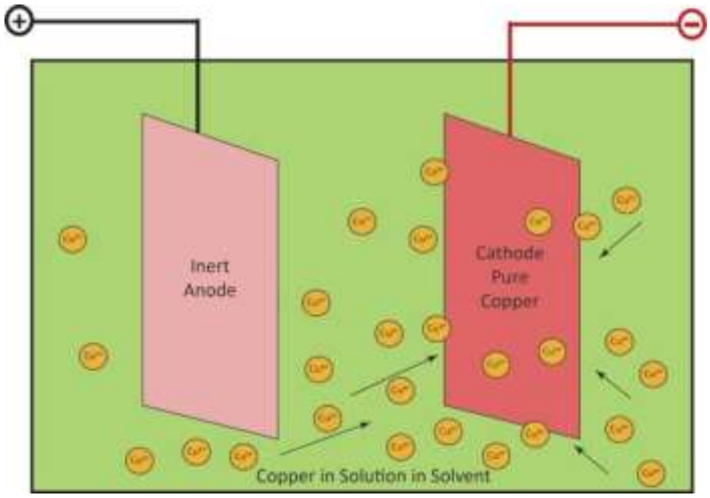

Figure 3 Copper electrowinning process [11]

Modern anodes of electrowinning is made out of the alloy of Pb with Sn and Ca. As time passes, anodes form PbO_2 layer resulting the corrosion in acidic electrolyte. Components of the anode can dissolve in the electrolyte solution or go down to the bottom of the cell forming solid anode sludge. Solid sludge is often sent for recovery of lead [21].

The extracted copper solution from solvent extraction normally contains 45 g/L Cu^{2+} and 170 g/L H_2SO_4. The concentration of sulfuric acid is strictly defined due to its highly corrosive nature. From the electrowinning, sulfuric acid is regenerated, and it is sent back to solvent extraction (SX) step to strip the Cu^{2+} from the loaded organic phase. New solution from SX is then mixed with a bleed of spent electrolyte (with concentration of 5 g/L Cu^{2+}) for recirculation [22].

Operating conditions of electrowinning

Electrical potential needed for electrorefining is 0.34 V, but electrowinning process must meet the potential requirement of 2.0 V. Although the theoretical potential needed for the reaction is 0.89 V according to Equation 4, overvoltage for copper electrodeposition at cathode, overvoltage for formation of oxygen at anode, ohmic potential drops in electrolyte and for hardware (rectifier) must be added to calculate potential needed to apply between anode and cathode. Current densities of modern plants are within the range of 200 and 450 A/m^2 [18]. Although the copper plating is faster at high current density, an impractical current density can result nodular, less pure, and nodular cathode.

Conductivity of the electrolyte influences greatly to the power consumption. 45 – 55 °C is optimum for conductivity. Although acidity enhances the electrical conductivity, it immensely degrades organic phase in SX [2].

2.4 Additives used in electrorefining and electrowinning electrolytes

Electrorefining grain refining agents

Thiourea is the principal grain refining agent that is added in electrolyte. A grain refiner thiourea $(NH_2)_2CS$ prevents the further growth of existing crystals and it helps newly growing copper nuclei to form. Thiourea firstly reduce Cu^{2+} to Cu^{+} and produces cationic complex with Cu^{+} on the surface of cathode, and inhibit the growth of crystals. An excess amount of thiourea leads to high adsorption on the copper surface, then sulfur impurities on the cathode will increase.

Avitone is a patented sodium sulfonated liquid. When it is used with glue with proper amount, it makes the cathode deposit smooth and dense. If insufficient amount of Avitone in electrolyte is added, the cathode tends to trap slimes that stays as a contaminant [23].

When chloride co-adsorb with thiourea, it enhances and brighten the cathode copper. It is one of the grain refining agent. HCl and NaCl is widely used to produce Cl^- ions as it disassociates. However higher amount of Cl^- concentration accelerates the corrosion of steel cathode blanks [2]. The Reatrol system is broadly used for thiourea control [24].

Electrorefining leveling agents

Protein colloid bone glues are used as leveling agents with varying concentrations of 50-120 gr/t copper in all copper refineries. The glue molecules have a relatively high molecular weight of 10 000 – 30 000 gr/mol due to its long and polymeric protein molecules [15]. It generates large cations in the copper electrolyte.

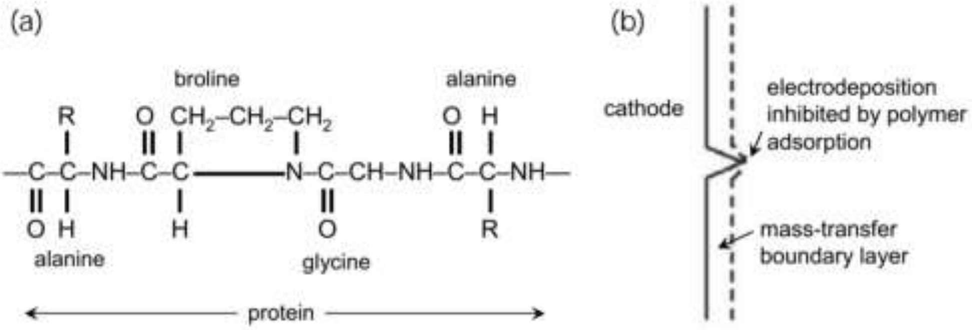

Figure 4 a) Structure of glue molecules consists of series of amino acids linked together as forming large protein chain, and b) the leveling mechanism of the glue [25]

The glue helps the growth of the smooth cathode layer as it deposits on negatively charged uneven surface of copper grains. When the copper grains start electrodepositing in unusual way by forming spike shapes, the electric field of this area increases [25]. At this area, glue creates electrically resistant barrier at the unusual growing grains and block the further formation of such tips of the protruding crystals. As a result, the dense and level growth of crystals are formed on the surface of cathode. If the glue concentration is higher than normal amount, rough and brittle deposit is obtained. Contrarily, too low concentration leads to nodulation.

Decomposition of glue in the copper electrolyte occurs after 1.5 to 2 hours at elevated temperatures and low pH value. Sulfuric acid catalyzes the degradation of the glue molecules. For that reason, it is essential to ensure constant monitoring and maintenance. Predominantly The CollaMat system is used for quantifying concentration of glue [2].

Electrowinning additives

Most widely used additive of electrowinning is Guar gum (150 – 400 g/t of cathode) which acts as a smoothing agents as similar as the glue in electrorefining process, but it is more adapted to the SX organics. Starched such as polysaccharides and polyacrylamides are also in extensive use. More than 300 A/m^2 current density causes harm to the smoothing agents by breaking them down [23].

In some electrowinning processes, chloride ions are present in SX solution, or hydrochloric acid is added into the electrolyte, because it improves the quality of copper deposit by forming dense and fine grains. The concentration remains under 30 mg/L to prevent the corrosion of equipment [2].

Co^{2+} ions in the electrolyte assists oxygen gas formation on the anode instead of Pb oxidation. It preserves the PbO_2 on the surface of anode and prevents Pb to contaminate the cathode copper, so that promotes the anode life [26].

2.5 Glue behavior in the electrolyte

Nowadays electrorefining processes are operating at higher current densities than they were ever been before. Although, no significant invention has been developed in last 100 years, the efficiency was improved greatly by applying higher current density and increasing the space time yield. Raising the current density is considered very efficient for energy usage resulting the reduced plant size and higher production rate. Nevertheless, a greater current density leads to uneven and rougher cathode surfaces. As copper deposits unevenly, impurities are included on the surface of cathode proceeding a poor quality of cathode and it reduces current efficiency by causing short circuits in the system. To suppress that effect, grain refining and leveling agents are added into the electrolytic solution by obtaining smooth, dense and pure copper [27].

The common additives used in electrorefining process are glue, thiourea, Avitone and chloride ion. The purpose of such additives in copper electrorefining is to produce high quality cathodic copper [14]. Glue is protein colloid. Thiourea and glue are common organic additives used for producing smooth, thick, coherent deposits in modern tank houses. Furthermore, the chloride ion is an essential part of the standard suite of adding agents. Such additives affect the electrocrystallization of copper in various ways: glue (protein colloid) acts as a leveling agent, and thiourea and chloride ions act as grain refiners [14].

In refinery electrolyte, addition organic compounds are carefully added to control possible damaging effects, and amount of the glue must kept stable. The compounds has great impact on the deposition on the cathode by changing their morphological behavior and kinetics of the crystal growth. Glue is produced naturally and it consists of many different polypeptides. Unlike thiourea and chloride, glue has no defined chemical structure, so that measuring the amount of glue in the electrolyte is complicated. However, it is difficult to maintain the same condition all the time, as the glue becomes ineffective due to loss in the tankhouse [28]. The glue loss occurs when it is adsorbed onto slime as well as the hydrolysis of glue with help of sulfuric acid as a catalyst.

When the cathode surface has edges, needles and nodules, a field strength rises dramatically. Glue is adsorbed on such areas with high field strength and the isolation layer of glue is formed to decrease a polarization as the layer stops the growth of needles and uneven surface. The glue is desorbed after the cathode copper surface has become even and the field strength has decreased. It is predicted that negatively charged cathode attracts positive and protonated protein molecules. The diffusion layer of cathode is influenced by glue molecules, and protein molecules changes zeta potentials. Electro-adsorption and desorption of the glue can take place over and over again based on a field strength of the cathode surface [29].

Since glue changes the polarization of the surface and it was unknown what type and size of glue molecules adsorbs on the copper surface, conventional chemical analysis is not suitable for measuring the amount of glue.

Both low dosage and over dosage of glue result insufficient quality of electrodeposition. As a common experience, glue is mostly added excessively than deficiently dosing. A big drawback of over dosing is that glue increases the polarization resulting high voltage of a cell. When the quantification of glue is accurately measured, energy consumption can be diminished significantly [30].

2.6 Methods for quantifying glue

To measure concentrations of the glue and other organic substances in the electrolyte, 30 years ago the operators has been relying on their experience gained empirically. But nowadays, there are several methods that are readily available [30].

The quantification of glue concentration in electrorefining tank is complicated and time consuming. Chemical analysis involves the precipitation of glue from the electrolyte solution at the isoelectric point and column chromatography with an ion-exchange resin. The analysis normally takes up to 48 hours. Conventionally, hydrolyzed amino acid compounds of the glue are determined by chemical analysis after boiling it under acidic condition for 24 hours [31].

To overcome this long chemical procedure, the electrochemical methods for the glue measurement has been established based on a change of polarization of the cathode that is caused by the glue molecules. In 1976, the first accurate method of glue measurement that has based on the polarization has been developed by Anderson, Budd and Strachan. The main principle behind this method was the fact that polarization is affected when the glue is added in the system. To measure amount of glue, the polarization curve was being used. Two curves are plotted to compare before and after the hydrolysis of glue has taken place when heat is applied. The first scan curve represents the sample of fresh electrolyte, while another curve is plotted after destroying the glue molecules at a high temperature [32]. This method promotes a great advantage to determine amount of glue in the multicomponent electrolyte by simply comparing the curve [30]. Despite the possibility of quantification, main drawback of the method was a complex calibration of each curves with different concentration of adjacent ions such as Cu^{2+} and Ni^{2+}. Also, other leveling and refining addition agents the changes the polarization curve when the glue is completely destroyed by heat. Therefore, accuracy of the method was slightly unreliable.

Adopting Anderson *et al* rapid electrochemical method, another measurement technique has been evolved. It gave refineries an opportunity to easily interpolate the glue concentration from a calibration curve that has been plotted by measuring cathodic overpotential. In addition to the previous method, they added a separation process of glue by filtering ultrafine molecules of organic compounds in the electrolyte [31]. Although, this technique has not been dedicated for continuous operation of electrorefining processes in industry.

Fabricius and Sundholm [33] studied the effect of glue using impedance technique. As glue is adsorbed on the cathode surface, impedance diagrams has been plotted. As a result, higher overpotential correlated to the lower frequencies as the diagram. Moreover, impedance reduces as the amount of glue decreases resulting the hydrolysis of glue.

Nowadays, most of the refineries use CollaMat system that has been developed by former Norddeutsche Affinerie (now Aurubis AG). CollaMat system gives an advantage to effectively control glue concentration correlated to acid concentration and temperature. The process has been proven experimentally and practically by using it on-line processes. The system uses special cells, which are operated continuously with pre-defined conditions while the measurement is performed. Glue concentration is determined using the kinetic data, including degradation rates depending on temperature and concentration of acid, from measurements of the cells. By continuously monitoring by CollaMat system, overdosing can be avoided. Measuring the change of polarization is more reliable than other methods, since it has already taken a degradation of glue and glue activity into account. To make the system more reliable and less costly, the system works without reference electrode which has been used conventionally. Every new measurement consists of 10 min of measuring phase and 2 min of regeneration phase [30]. A concentration of 0.1 mg/L of active glue is required for the electrolyte solution of CollaMat system. The measurements of glue is made for both discharged and inflowing electrolyte. The system uses galvanostatic measurements where the potential time response is recorded as the current is kept constant. Once the potential time curve is plotted from the measurement, the glue content can be determined by using the maximum increase of the curve [30].

According to Blechta *et al*. described the galvanostatic technique, where the potential between a reference electrode and cathode in the electrolyte is measured at constant current [34]. Potential time curves, as shown in Figure 5a, are plotted with respect to various glue concentrations. From the curve, so called potential shift (PS) curve which correlates to the glue content has to be calibrated as represented in Figure 5b. Operating condition for this technique is acquired at 65 °C when the current density is 300 A/m^2. Calibration curve then be used to calculate third-order polynomial best fit equation for glue analysis [34]. The location of calibration curve is greatly affected by copper concentration, and slightly dependent on acid content, hydrolysis of compounds and organic additives due to their ability to cause changes on cathode potential. To prevent obtaining misleading information from calibration curve, electrolytes with different copper concentrations are used for generating a certain number of calibration curves. Content of nickel and sulfuric acid on calibration curve is inconsiderably small, but Termind (additive made of lignin sulfonate) changes the polarization and decreases effect of glue in electrolyte [34].

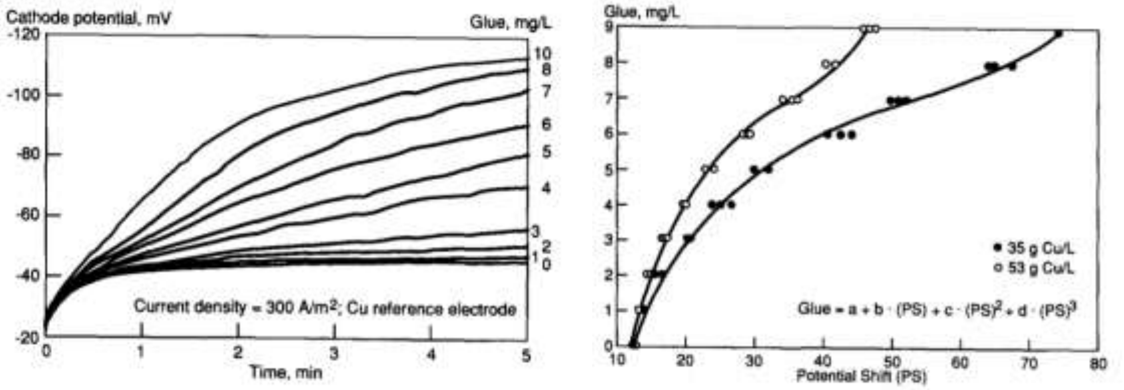

Figure 5 a) Potential time curve at different glue concentrations b) calibration curve of glue as a function of potential shift [34]

The calculation of glue is time consuming and complicated process. It takes long time to prepare for the measurement, and the number of repeated measurements is large. The simpler and easier method to measure glue must be developed.

2.7 Glue degradation

Only glue molecules with a certain molar mass has effects on electrodeposition of copper. Molar masses of more than 10 000 units are considered as active glue which positively influence electrorefining process [31]. Glue activity is defined as the ability to form resistance barrier on cathode surface. Activity is measured by overpotential. The activity of a glue differs in dissimilar electrolytes with same amount, therefore, the amount of glue in different electrolytes must be altered for the optimal deposition of copper. Glue activity curve is plotted after the fresh glue is introduced into copper electrolyte which contains no active glue. The main reason behind the increment of curve is the breaking off long and inactive glue molecules into new active molecules, in which the number of newly created glue molecules exceeds the amount of degraded molecules [34]. Accordingly, the activity of glue increases. Glue activity decreases as a result of hydrolysis of glue molecules where the size of molecules become smaller than optimal size and it is no longer able to form a resistance barrier on the copper surface. Degradation products, such as glycine, has no effect on cathode potential current density [35].

Length and size of molecules in glue are not always consistent. There are long, medium and small molecules co-exists. Medium sized glue molecules are 10 to 20 times more active than 10 to 20 time longer molecules. The increase of activity is due to creation of optimal medium-sized molecules which are the most active molecules for electrodeposition process [34].

The degradation rate is not dependent on initial concentration of glue but acid concentration, since the reaction of glue degradation is “pseudo first order”. The rate is zero order regarding to initial concentration of the polypeptides and first order in respect of acid concentration. For the glue molecules with molar mass less than 10 000 units, the hydrolysis process is rapid and occurs in 40 to 80 min in electrolyte solution. The degradation rate can be expressed as shown on Equation 6 [35].

Equation 6 Glue degradation rate [35]

$$\frac{1}{(M_n)_t} = \frac{1}{(M_n)_0} + k't$$

where $(M_n)_t$ is number average molar mass at time t, and $(M_n)_0$ is number average molar mass at time zero. Degradation rate constant has been found as shown Equation 7 where $[A]$ is sulfuric acid concentration and k is intrinsic rate constant of glue in min^{-1}.

Equation 7 [35]

$$k' = \frac{k[A]}{(M_n)_0}$$

In electrolyte, sulfuric acid acts as catalyst to hydrolyze glue molecule, so that excess amount of acid must be avoided. Glue activity rises up to a certain point and it decreases back remarkably in only 10 to 50 min. Glue is consumed by inclusion of cathode, slime adsorption hydrolysis of glue due to temperature and acid content [30].

Animal glue is a product of hydrolyzing animal tissue collagen [36]. Chemistry of aqueous collagen protein molecules are complicated and it is not enough studied. The critical average molar mass, is where the most of glue molecules lose their activity, has been defined as 3700 [35].

Hydrolysis of glue with respect to temperature follows Arrhenius equation where rate constant has linear relationship with temperature. Glue degradation process is statistical, therefore hydrolysis occurs 10 to 20 times faster than medium sized ones as the glue size diminishes about 10 to 20 times [34].

Table 2 Protein Standards [35]

Name	Approximate molar mass (u)
Blue dextrane	2 000 000
Thyroglobulin	669 000
Apoferritin	443 000
B-amylase	200 000
Alcohol dehydrogenase	150 000
Albumine, bovine serum	66 000
Carbonic anhydrase	29 000
Cytochrome C	12 400
Gly-gly-gly-gly-gly-gly	360
Gly-gly-gly-gly-gly	303
Gly-gly-gly-gly	246

Chemical and physical properties of glue has been studied on CRODA glue, TAKASHIMA glue ad NITTA glue by Saban eds. [35].

Viscosity of one of glue samples was 80 mps at 12.5 pct when temperature was 60 °C. At 60 °C, Bloom grams was 250 which correlates to high Bloom value, and average molecular mass of 50 000 to 100 000 units. Higher Bloom gram correlates to longer the chain of glue. Isoelectric point varied between pH 5.10 and 5.50 at 40 °C. Moisture of 10.85 – 13.20 pct, ash mass of 1.8 - 2.47 pct, and grease mass of 0.25 – 1.14 pct has been obtained [35].

Table 3 Elemental analysis results of three different glue products [35]

Elemental analysis	Mass (pct)
C	45.60 to 48.77
H	6.48 to 6.58
N	16.61 to 17.25
S	0.07 to 0.25
O	27.33 to 30.95

3 Materials and Methods

In this work, cyclic voltammetry, differential pulsed voltammetry and chronoamperometry techniques were used to determine kinetics of deposition and morphological change of the copper on cathode.

3.1 Electrochemical techniques

In electrochemical methods, the interrelation of electrical and chemical processes can be described by interface between electrode and electrolyte in electrochemical cell. By definition, electrode is an electronic conductor which carries the charge by the movement of electrons, while electrolyte is an ionic conductor which transports the charge by movement of ions [37].

Galvanostatic and potentiostatic electrochemical modes can be distinguished by how the measurement is performed between electrodes in a cell. Galvanostatic mode records the potential time as the current is kept constant or stepped, whilst potentiostatic method records current flow as the potential between electrodes remains unchanged [38].

Experimental setup for electrochemical cell includes 3 electrodes, which are counter electrode, reference electrode and working electrode. Working electrode is the principal electrode where the chemical reaction takes place, whilst main function of reference electrode is to provide stable electrode potential so that accurate potential between these 2 electrodes can be adjusted. Thirdly, the counter electrode is an inert electrode that is intended to close the current circuit. As mentioned before, potentiostatic measures current flow between working and counter electrodes when the potential between working and reference electrodes is kept constant. Current can be measured as a function of potential or time or charge passed through the systems [37]. Based on the different methods of measurement, potentiostatic techniques have been derived, such as voltammetry, polagraphy, chronoamperometry and coulometry.

For voltammetry technique, the current is measured as a function of potential resulting a voltammograms (current-potential plot). This technique is commonly used in chemical analysis, because voltammograms indicate the electron transfer between the surface of electrode and the species in electrolyte solution. Voltammetry can be divided into different types based on the potential control mode, including linear sweep voltammetry, cyclic voltammetry, pulsed voltammetry, square wave voltammetry, alternating current voltammetry and stripping voltammetry [39].

Cyclic voltammetry

Cyclic voltammetry is most commonly used technique, because it provides various information about reduction and oxidation potentials, oxidation states, chemical processes due to electron transfer, electron transfer rate and adsorption effect [40]. It measures the current response of the electrode to a linearly altering potential. As shown in Figure 6, the measurement commences from the potential where no electrode process takes place. Due to electrochemical active species in the electrolyte solution, anodic current peak $E_{p,a}$ is observed at the peak current $I_{p,a}$. Once anodic current peak decreases, it reaches Eswitch where the potential starts sweeping back to the cathodic peak current $E_{p,c}$ at the peak current $I_{p,c}$. Peak current magnitude can be calculated using Randles-Sevcik equation, where I_p stands for the peak current, n is number of electron transferred, *F* for Faraday constant, *A* for the electrode area, *c* for the concentration of species in electrolyte, *R* for gas constant, *T* is absolute temperature, *D* for diffusion coefficient, and v is scan rate [41].

Equation 8 Randles Sevcik equation of peak current

$$I_p = 0.446nFAc\sqrt{\frac{nFvD}{RT}}$$

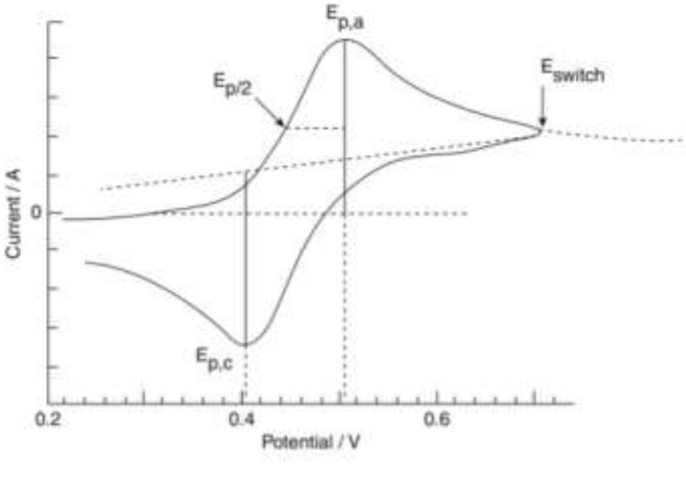

Figure 6 Cyclic voltammetry

Alternatively, bell-shaped symmetric oxidation and reduction peak can occur when the reaction is electrochemically reversible. In that case, peak current is expressed as Equation 7 where *Γ* is surface concentration, and therefore the scan rate is linerly proportional to the peak current [38].

Equation 9 Peak current for reversible reactions

$$I_p = \frac{n^2F^2}{4RT}vA\Gamma$$

Between *E₀* and *Eₚ*, Buttler-Volmer equation is used in Equation 8. The equation involves kinetics of the electrode, where *α* as a transfer coefficient, and k_0 for rate constant of the deposition [42].

Equation 10 Buttler-Volmer eqution

$$lnI_p = \ln(0.227nFck^0) + \frac{\alpha nF}{RT}(E_p - E_0)$$

Copper reduction reaction is not affected by pH of the solution. According to Uchikoshi and Kekesi [43], equilibrium constants (K_1, K_2, K_3) have been found as shown for copper reduction reactions.

$Cu^{+1} + e^- \rightarrow Cu^0, \qquad logK_1 = 8.80$

$Cu^{+2} + 2e^- \rightarrow Cu^0, \qquad logK_2 = 11.38$

$Cu^{+2} + e^- \rightarrow Cu^{+1}, \qquad logK_3 = 2.68$

Equilibrium potentials E_1, E_2 and E_3 can be calculated by substituting Nernst equations as described on Equation 2 and 3,

Equation 11 Nernst equation for copper (I) reduction

$$E_1 = E_1^0 + \frac{RT}{F}\ln\left(\frac{a_{Cu^+}}{a_{Cu^0}}\right)$$

Equation 12 Nernst equation for copper (II) reduction to metal copper

$$E_2 = E_2^0 + \frac{RT}{2F}\ln\left(\frac{a_{Cu^{+2}}}{a_{Cu^0}}\right)$$

Equation 13 Nernst equation for copper (II) to copper (I)

$$E_3 = E_3^0 + \frac{RT}{F}\ln\left(\frac{a_{Cu^{+2}}}{a_{Cu^+}}\right)$$

where E^0_1, E^0_2 and E^0_3 are the standard reduction potentials, *T* is the absolute temperature, *R* is the molar gas constant, *F* for Faraday constant and a for activity of subscripted electro active species. Theoretical standard reduction potentials are $E^0_1 = 0.52$ *V*, $E^0_2 = 0.34$ *V* and $E^0_3 = 0.16$ *V.*

Differential pulse voltammetry

This is one of the voltametric techniques where superimposition of potential pulses takes place to a linear varying potential or to a staircase ramp potential. This technique measures current right before applying each pulse and right before end of each pulse, then resulting difference is amplified. In Figure 6, the currents being measured are specified as a dot. And the difference ΔE_p is the output and pulse time t_p is measured [44].

The technique is widely used for investigation of chemical reactions, kinetics and mechanisms. The main advantage of this method is the higher sensitivity. Some cases, it can allow the user to measure in ppb (parts per billion) level [39]. Therefore, it can give us more precise information about reduction process of copper deposition than cyclic voltammetry.

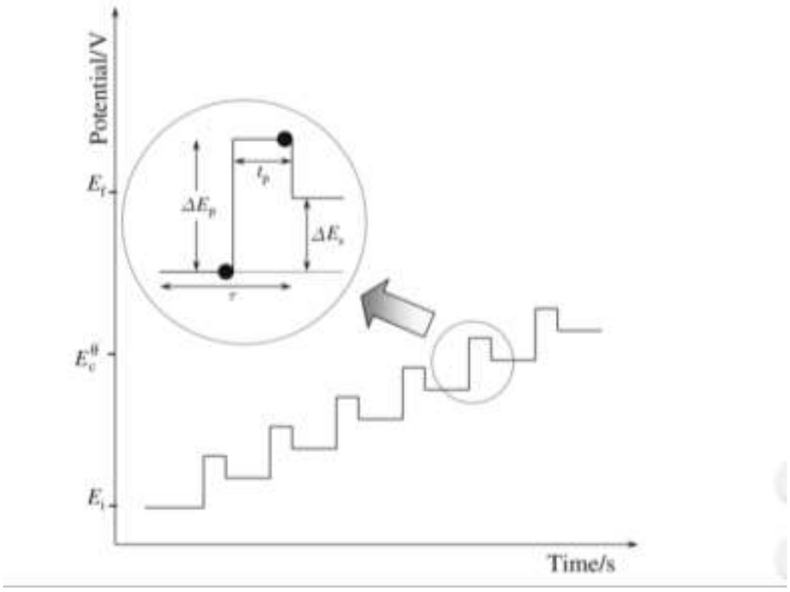

Figure 7 Differential pulse voltammetry potential waveform [39]

The shape of differential pulse voltammogram is peak shaped. Therefore, peak height of ΔI_p can be calculated using Equation 14 for the reversible system, where A is electrode area, n is the number of electron transferred, D for diffusion coefficien, c_{ox} os the substrate concentration, t_p is pulse time, and σ is expressed as follows, $\sigma = \exp(nF\Delta E_p/2RT)$ [39].

Equation 14

$$\Delta I_p = \frac{nFAD^{\frac{1}{2}}c_{ox}}{\pi^{\frac{1}{2}}t_p^{\frac{1}{2}}}\left(\frac{1-\sigma}{1+\sigma}\right)$$

It can bee seen that the peak potential ΔE_p reduces as the ratio $(1+\sigma)/(1+\sigma)$ decreases until the value goes to zero. Furthermore, peak potential formula is shown in Equation 15, where $E^{o'}_c$ is formal potential [37].

Equation 15

$$E_p = E^{o'}{}_c + \frac{RT}{nF}\ln\left(\frac{D_{Red}}{D_{ox}}\right)^{1/2} - \frac{\Delta E_p}{2}$$

The peak width at half height, $w_{1/2}$ can be found as shown in Equation 16 when the ΔE_p is considerably small at 25 °C. For copper reduction, this value is 45.2 mV.

Equation 16

$$w_{1/2} = 3.52\ RT/nF$$

Chronoamperometry

Features of macroscopic deposit of copper, such as smoothness and brightness, are defined by early stage of the electrocrystallization. These are strongly related to the nucleation process.

As the glue molecules changes polarization of cathode, overpotential generally determines the nucleation mechanism. Chronoamperometry is a classical electrochemical technique, in which the current transient measurement is made while the potential of working electrode is stepped [42]. The method is dedicated to study diffusion controlled electrochemical reactions and other complicated electrochemical mechanisms. The chronoamperometry measurements are performed by first applying a certain potential value where no faradaic reaction takes place, then stepping the potential to the value at which the electrochemical reaction of interest occur. The measurement results gives a big data file which has been measured rapidly [45].

Cyclic voltammetry exhibits qualitatively that the nucleation is present, whereas chronoamperometry technique is commonly used to investigate nucleation and growth of crystals on the electrode. During the chronoamperometry measurement, the rate of mass transfer of copper ions to the electrode surface controls the system transition from no reaction to the steady state reaction. Until the steady-state is achieved, a current transient occurs. This transition can be expressed by the Cottrell equation Equation 17.

Equation 17

$$j = \frac{nFD^{\frac{1}{2}}c_0}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}}$$

In the equation, current density is denoted as *j*, *n* for number of electrons involved; *F*, Faraday constant; *D* stands for diffusion coefficient; $c_{0,}$ concentration of the species and *t*, time.

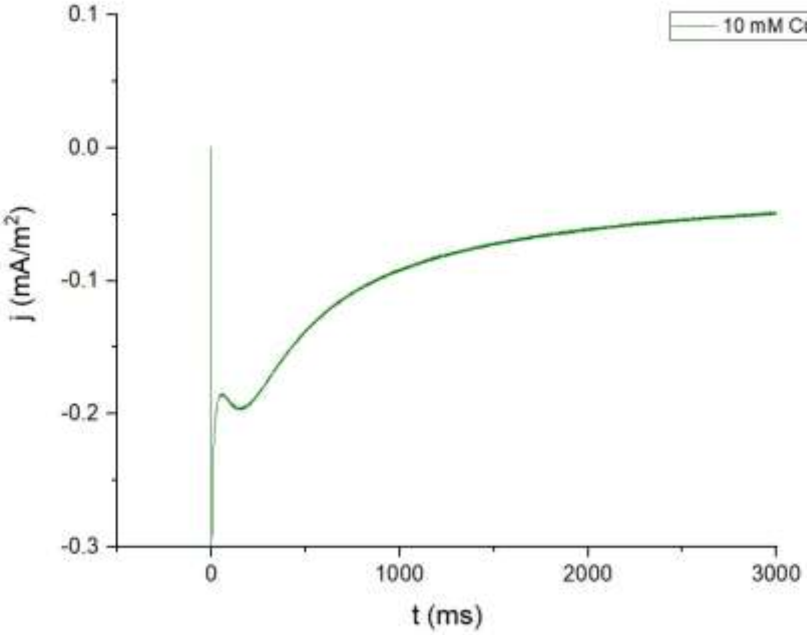

Figure 8 Chronoamperometry measurement of $CuSO_4$ solution on Cu working electrode

Copper reduction Cu^{2+} to Cu^0 is diffusion controlled [46]. In that case, nuclei grows on the available area of the surface for the reaction. Growth of the nuclei in this case is 3D, in which growth rate of nuclei with respect to electrode surface directions is identical or comparable parallel and perpendicular [47]. Typical chronoamperometry measurement is shown in Figure 8. The main mechanism of the technique can be explained as follow. In the beginning, the current increases as the new surface area starts to develop when the nucleation is involved. The more nucleation takes place, nuclei the overlapping is initiated. Every copper nucleus has its own diffusion zone that has been defined, showing the mass supplying mechanism for continuous growth. Because the diffusion zones are broader than the underlying nuclei, eventually the overlapping zones would contain the entire electrode area. Further reaction strictly follows the rate of the mass transfer through the control area of the diffusion zone. Growth of already created copper nuclei can proceed, or more nucleation can begin on different sites within the diffusion zone. Both of the mentioned path is controlled by the steady state conditions, as represented by the Cottrell equation.

Current transient, is provided by chronoamperometry technique, were used by Scharifker and Hills [48, 49]. According to them, the nucleation mechanism can be described by a mathematical models. The main two limiting nucleation mechanisms are the instantaneous nucleation and the progressive nucleation. Progressive nucleation represents the fast growing nuclei on various active sites that were activated during the electroreduction process. As for instantaneous mechanism is described as a slow growth of nuclei on the few active sites that were activated at the same time [49].

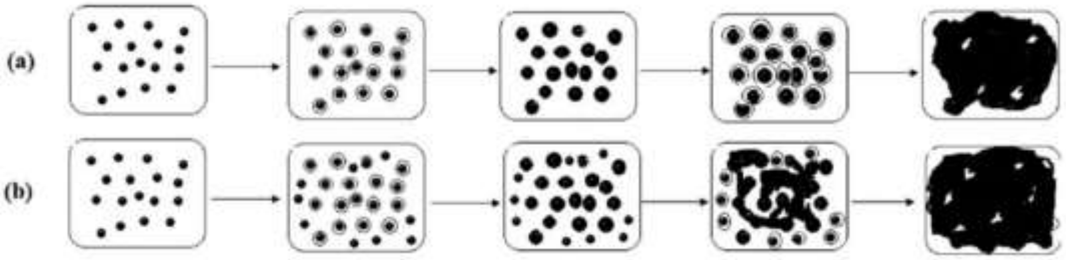

Figure 9 a) Instantaneous nucleation and b) progressive nucleation illustration [47]

As illustrated on Figure 9, instantaneous nucleation only occur when the nuclei growth takes place on only their previously defined positions on the substrate surface without formation of new nuclei. Therefore, nuclei size is large and it results rough surface of the deposition. This nucleation mechanism must be avoided during electrorefining. Contrarily, progressive nucleation creates flatter and denser surface due to the small particle size on the surface. Progressive nucleation mechanism is more favorable for electrodeposition of the copper. In progressive nucleation, nuclei growth occur not only on the already existing positions, as well as other new nuclei [47].

Equation 18 Mathematical model of instantaneous nucleation

$$\frac{j^2}{j_{max}^2} = 1.9542\left(\frac{t}{t_{max}}\right)^{-1}\left\{1 - \exp\left[-1.2564\left(\frac{t}{t_{max}}\right)\right]\right\}^2$$

Equation 19 Mathematical model of progressive nucleation

$$\frac{j^2}{j_{max}^2} = 1.2254\left(\frac{t}{t_{max}}\right)^{-1}\left\{1 - \exp\left[-2.3367\left(\frac{t}{t_{max}}\right)^2\right]\right\}^2$$

According to Equation 18 and Equation 19, j_{max} (A/cm^2) and t_{max} (s) are the current and time at the peak of increasing and decreasing portion of the current transient. Using current maximum, kinetic parameters can be found, including nuclear number density, nuclear rate constant and diffusion coefficient. Applying acquired data of chronoamperometry measurements, j_{max} and t_{max} can be predicted using the model [48]. On Equation 20, N_0 stands for nuclei population density (cm^{-2}), F for Faraday's constant, c for concentration of species in the bulk, V_m for molar volume.

Equation 20 Nuclei population

$$N_0 = 0.065\left(\frac{1}{8\pi c V_m}\right)^{\frac{1}{2}}\left(\frac{nFc}{i_{max}t_{max}}\right)^{2}$$

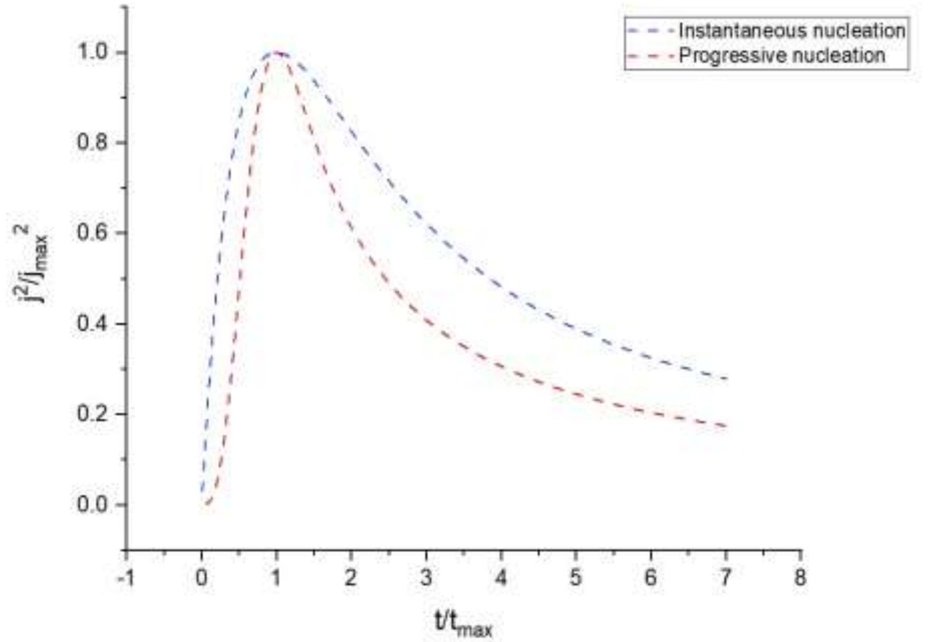

Figure 10 Graphical illustration of Instantaneous and Progressive nucleation

Mathematical models of progressive and instantaneous nucleation mechanisms can be graphically illustrated as shown in Figure 10. Both of the curve increases in steeply until it reaches the maximum which occurs about the time ratio equals 1. After the maximum value, progressive nucleation's curve decreases with sharp slope due to newly forming nuclei on the various active sites, whilst instantaneous nucleation's curve declines slowly.

Since copper deposition is 3D multiple nucleation, acquired data has been analyzed using theoretical models of Scharifker and Hills [48]. The models proposed that there are 3 stages of electrodeposition, stage 1, stage 2 and stage 3. At the first stage, the nuclei starts to grow on substrate nuclei where $\frac{t}{t_{max}} < 1$. The ratio of time and time required to reach current peak is approximately 1, newly grown nuclei forms accumulation (coalescence) or overlap of diffusion zones around them. Further growth of copper layer will occur at the last stage where the ratio equals more than 1.

3.2 Sample preparation

In this work, two different synthetic electrolyte solutions were prepared for the electrochemical measurement to investigate the effect of glue. The solutions differ from each other with the presence of glue.

1. *10 mM copper sulfate ($CuSO_4$), 100 mM sodium sulfate (Na_2SO_4) and 10 mM sulfuric acid (H_2SO_4) solution*

   The electrolyte solutions were prepared using the following commercially available reagents.

Table 4 Reagents used for preparation of the electrolyte solutions

Reagent name	Chemical formula	Molar mass (g/mol)
Copper sulfate pentahydrate	$CuSO_4 \cdot 5H_20$	249.69
Sodium sulfate	Na_2SO_4	142.20
Sulfuric acid 98%	H_2SO_4	98.08

2. *10 mM copper sulfate ($CuSO_4$), 100 mM sodium sulfate (Na2SO4), 10 mM sulfuric acid (H_2SO_4) and 50 mg/l glue solution*

   Unlike the first electrolyte solution, glue has been added into the electrolyte. Due to lower solubility of glue in aqueous solution at low temperature, the solution was heated for 15 min up to 62°*C.*

10 mM Na2SO4 has been used as background electrolyte to improve the conductivity of a solution.

3.3 Electrochemical measurements and equipment

Location and duration

All measurements have been made at Faculty 2 Chemistry laboratory of TU Bergakademie Freiberg. The experimental part was conducted from 10th January to 26th February, 2020.

Equipment

Gamry Galvanostat/Potentiostat instrumentation has been used for electrochemical measurements of sample electrolytes. A three electrode system was used as shown in Figure 11.

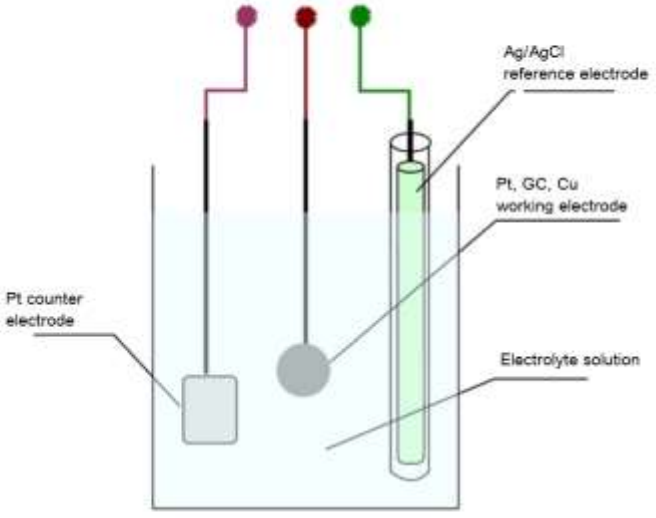

Figure 11 Systematic representation of three electrode system [50]

1. Reference electrode was chosen as silver/silver chloride (Ag/AgCl) electrode in a potassium chloride KCl solution.
2. Counter electrode was made of platinum (Pt) sheet.
3. Working electrodes has been chosen differently based on their voltagrams, potential window and absorptivity. Platinum (Pt), Copper (Cu) and Glassy carbon (GC) electrodes were used for electrochemical measurements. Cu electrode is more preferable in the experimental part since industrial cathode are made of copper. Deposition potential of copper tends to be high on foreign substrate, such as Pt and GC electrodes, to compare with the electrode that made out of copper due to crystallographic substrate-metal misfit.

Three different electrochemical techniques have been used to investigate influence of glue in synthetic electrolyte solutions.

1. Cyclic voltammetry was used to study reduction potential of copper and their changes after adding glue in copper electrolyte.
2. Chronoamperometry technique determines the nucleation mechanism of the copper on a working electrolyte.
3. Differential pulsed techniques measurements are demonstrated in this work.

Polishing, rinsing and drying of working electrode were performed using 0.3 µm alumina paste before every measurement. All measurements have been done at ambient temperate (23 ± 2 °C).

Measurement parameters

Table 5 Experimental parameters

Electrochemical technique	Parameters
Cyclic voltammetry	Pt electrode Potential high limit: 0.7 V, Potential low limit: -0.5 V GC electrode Potential high limit: 0.8 V, Potential low limit: -0.5 V Cu electrode Potential high limit: 0.15 V, Potential low limit: -0.5 V Current maximum: 1 mA, Final potential: 1 V Electrode area: 0.00785 cm^2 Scan rate: 50 mV/s, Step size: 1 mV, Cycles 3
Chronoamperometry	Step voltage 1: -0.4, -0.3, -0.2, -0.1, 0, +0.1, +0.2 V Step voltage 2: +0.4 V (Potential was stepped from step voltage 1 to step voltage 2. Various step voltages 1 were chosen.) Pre-step delay time: 5 s, Step 1 time: 15 s, Step 2 time: 15 s Sample period: 0.0001 s Max current: 1mA, Current density limit: 150 mA/cm^2 PF Corr. : 50 Ω Equilibrium time: 0 s Electrode area: 0.00785 cm^2
Differential pulsed voltammetry	Initial potential: -0.4 V, Final potential: +0.6 V Step size: 2 mV Pulse size: 25 mV, Electrode area: 0.00785 cm^2 Equilibrium time: 15 s, PF Corr : 50 Ω

3.4 Software for data acquisition and analysis

Gamry Potentiostat uses *Gamry Framework™* program. Structure of the electrode interface and the mechanisms if the electrochemical reactions are studied using the software.

The software provides user main three opportunity that includes running experiments, editing scripts of the experiments, and starting up *Gamry Echem Analyst™. Framework™* is data acquisition program which provides useful electrochemical research techniques, such as cyclic voltammetry, liner sweep voltammetry, chronoamperometry, chronopotentiometry etc. In this work, only experiments were performed using physical electrochemistry category of Framework.

Echem Analyst™ software is used together with Framework for data analysis. Once the data is generated by Framework, Echem Analyst can be used for analysis. It can run all types of data that came from different experiments. Alternatively, it is used to extract the data from the Framework in different file types [51].

Additionally, most of the data analysis has been made on Excel® software of Microsoft and OriginLab 2020.

4 Results and Discussion

4.1 Studying effect of glue in copper solution using cyclic voltametric technique

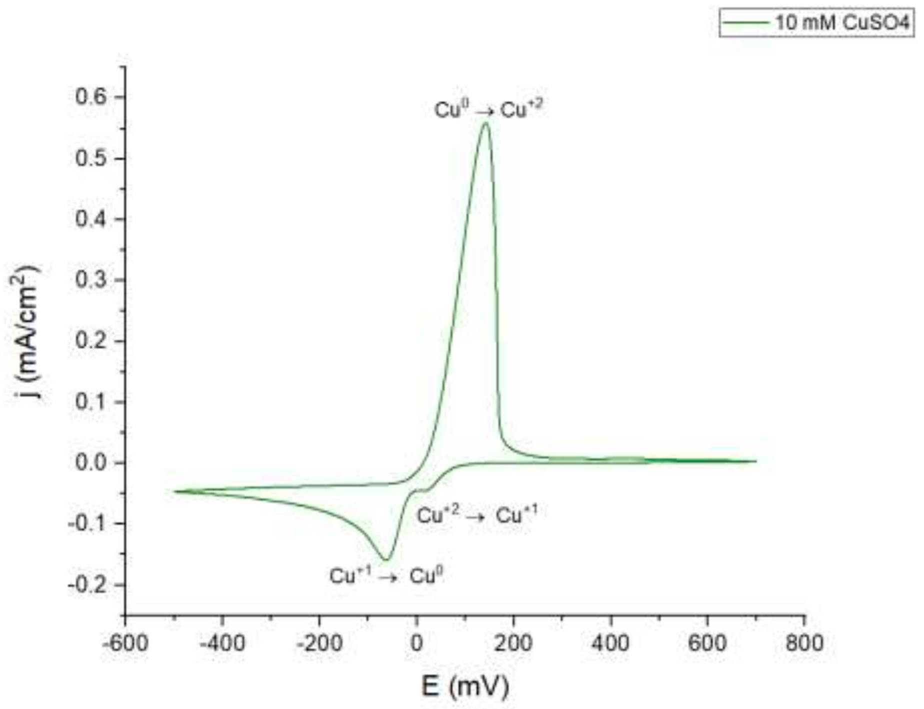

Figure 12 Cyclic voltammograms of $CuSO_4$ solution measured on GC working electrode

Cyclic voltammetry of copper sulfate solution has been studied. In Figure 12, the cycle commenced at +700 mV and reversed at -500 mV when the working electrode was chosen as glassy carbon electrode. Firstly, no current was produced until potential of -70 mV was reached. From this point, cathodic current started increasing and formed a peak at -20 mV which corresponds to following reaction of copper reduction $Cu^{2+} + e^- \rightarrow Cu^+$. After the peak, cathodic current kept increasing and formed a larger peak at -70 mV in which the reaction responsible for the peak is $Cu^{+} + e^{-} \rightarrow Cu^{0}$. According to Uchikoshi and Kekesi, Cu^{2+} species in sulfuric acid does not form cuprous ion in the solution, but cuprous ion forms when the Cl^{-} ion is in present in the electrolyte [43].

When it swept reversely, current density crossed zero and turned into anodic current. Sweeping in positive direction resulted anodic peak at +170 mV, which correlates with the oxidation reaction of $Cu^{0} \rightarrow Cu^{2+}$. At current density of 0, oxidation reaction was completed.

By reason of crystallographic substrate-metal misfit, deposition potential of copper tends to be high on foreign substrate to compare with the electrode that made out of copper [46]. Ag/AgCl standard electrode potential against SHE is 0.23 V. Although it is hard to determine redox potential due to double peak cathodic currents, it is estimated around 0.355 V, so that reduction potential of copper is slightly higher than redox potential of 0.34 V after taking Ag/AgCl standard potential into account.

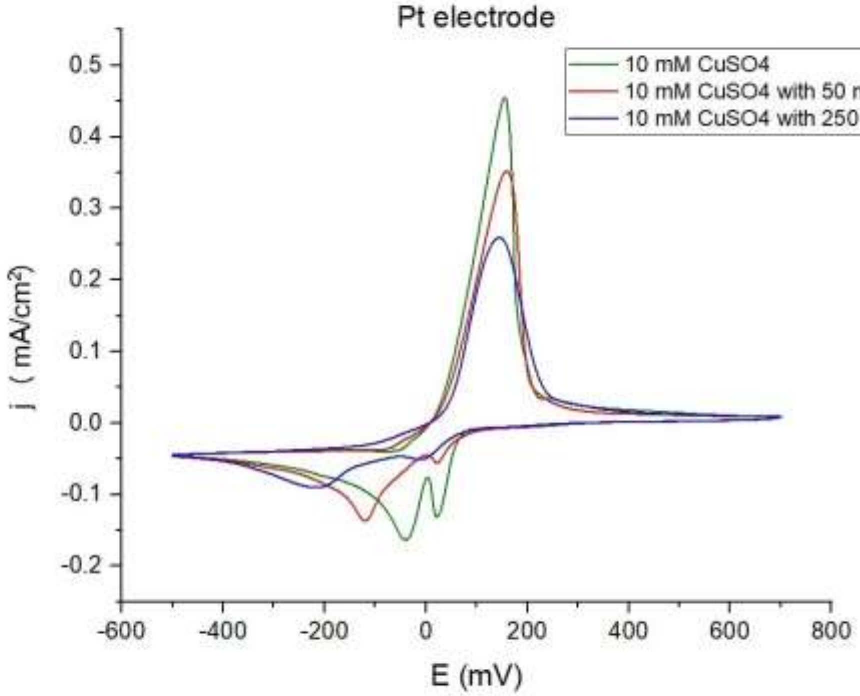

Figure 13 Cyclic voltammetry results of the copper electrolytes using Pt as a working electrode

As explained on Figure 13, each cycle was swept from initial potential to the final potential on Figure 12. When the Pt was chosen as a working electrode, initial potential and final potentials has been chosen +0.7 V and -0.5 V respectively. Since glue influences only the electrodeposition of the copper on the cathode surface, reduction reaction was only in the interest of this study. After starting the measurement, current density drop initiated at +0.1 V for the electrolytes with different concentrations. All of the voltammograms shows two peaks each, representing reduction of copper (II) to copper (I) and copper (I) to copper (II) as expressed in Figure 5. For the copper solution with 10 mM concentration, 2 peaks have been occurred at +0.02 V and -0.04 V respectively. When the 50 mg/L glue was added into the solution, first peak current density of copper (II) reduction was diminished as comparison to copper electrolyte without glue content. 2 reduction reactions occur at +0.015 V and -0.12 V each. Third electrolyte solution with 250 mg/L glue has been measured, and it results the more reduced peak current density. Reduction potentials have been observed at 0 V and -0.21 V.

It was observed that the peak current density and the area in the negative region decrease as the content of glue increases. Moreover, a significant shifting of reduction potential of copper (I) to elemental copper has been obtained when the glue is added. From the results, it is proposed that glue destabilizes Cu^{+} species and stabilizes Cu^{2+}, and more glue content can possibly eliminate one step and directly convert Cu^{2+} to Cu^{0}.

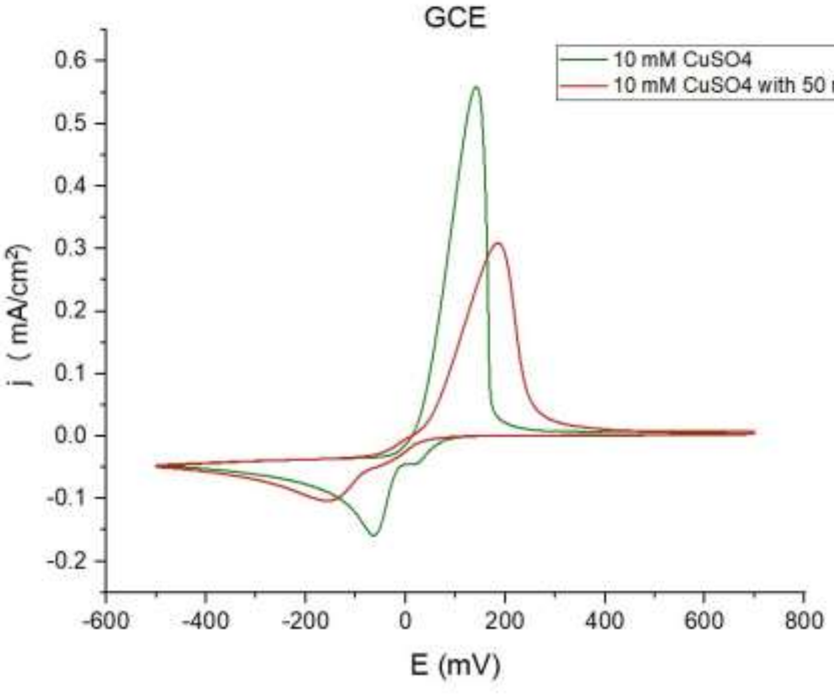

Figure 14 Cyclic voltammetry results of the copper electrolytes using Glassy Carbon as a working electrode

During the cyclic voltametric measurement on GCE as a working electrode, initial potential and final potentials has been chosen +0.8 V and -0.5 V respectively in Figure 14. Once the measurement has commenced, current density was constant until it reaches +0.1 V where the peak current density started to form. All of the voltammograms shows two peaks each, representing reduction of copper (II) to copper (I) and copper (I) to copper (II) as expressed in Figure 5. Copper solution containing 10 mM $CuSO_4$, 2 peaks have been occurred at +0.02 V and -0.05 V respectively. When the electrolyte with 50 mg/L glue was measured, same trend has been observed, as first peak current density of copper (II) reduction was diminished as comparison to copper electrolyte without glue content. In that case, reduction peaks took place at 0 V and -0.1 V each.

Identically, the peak current density and the area of negative region decrease as the content of glue increases as represented on Pt electrode. More cathodic shifting of potential for copper (I) to elemental copper has been observed when the glue is added. Unlike Pt electrode measurement, initial peak current density of copper (II) to copper (I) was smaller, and nearly flat peak has been measured. This can be interpreted that glue stabilizes copper ions due to more negative potential needed to reduce. The results indicate that the electrodeposition process is limited by charge transfer rate. Charge transfer and mass transport of electroactive species occur at the same time.

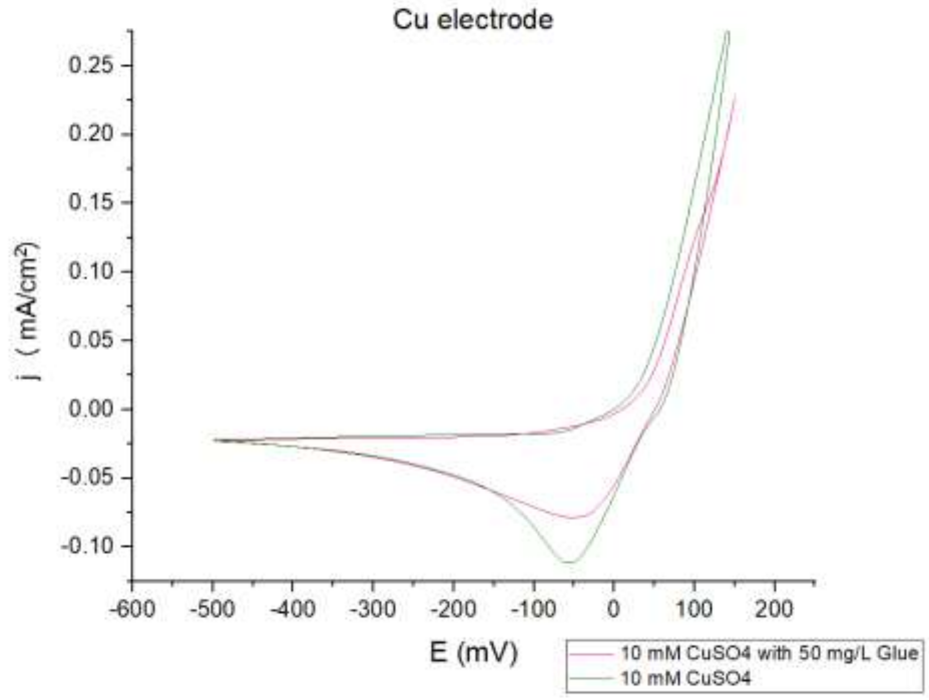

Figure 15 Cyclic voltammetry results of the copper electrolytes using Cu as a working electrode

Cyclic voltametric measurement on Cu working electrode is slightly different than other measurements that have been made on different electrodes. Initial potential and final potentials has been chosen +0.15 V and -0.5 V respectively due to dissimilar potential window of the electrode. Peaks of current density formed at -0.05 V for both cases. As copper solution containing 10 mM $CuSO_4$ showed peak current density at -0.13 mA/cm^2. For the electrolyte with 50 mg/L glue, a peak at -0.09 mA/cm^2 has been observed.

Similar to the other electrodes, the peak current density decreases as the content of glue increases for Cu electrode. No cathodic shifting of potential for copper (II) to elemental copper has been observed when the glue is added. Furthermore, no copper (II) to copper (I) reduction peak has been obtained, but only one peak for the reduction occurred. It is predicted that the reduction has not been appeared on the voltammograms due to small potential window of the Cu electrode.

Cyclic voltammetry results show us that the cathodic shift of the peak current potential occurs for the higher concentration of the glue. Also, the area in the negative region gets smaller with increasing amount of glue in the electrolyte. It clearly shows that glue decreases the polarization of the surface. Magnitude of peak currents is reduced as glue is added. The results suggest that glue destabilizes Cu^+ species and stabilizes Cu^{2+}, and higher concentration of glue can potentially convert Cu^{2+} to Cu^0. With help of further data acquisition, the quantification of the glue can be done using cyclic voltammetry based on the difference of reduction potential as glue influences it. Although, old literatures suggest that cyclic voltammetry cannot provide accurate concentration of the glue [31].

4.2 *Studying the effect of glue in copper electrolyte solution using differential pulse voltametric measurements*

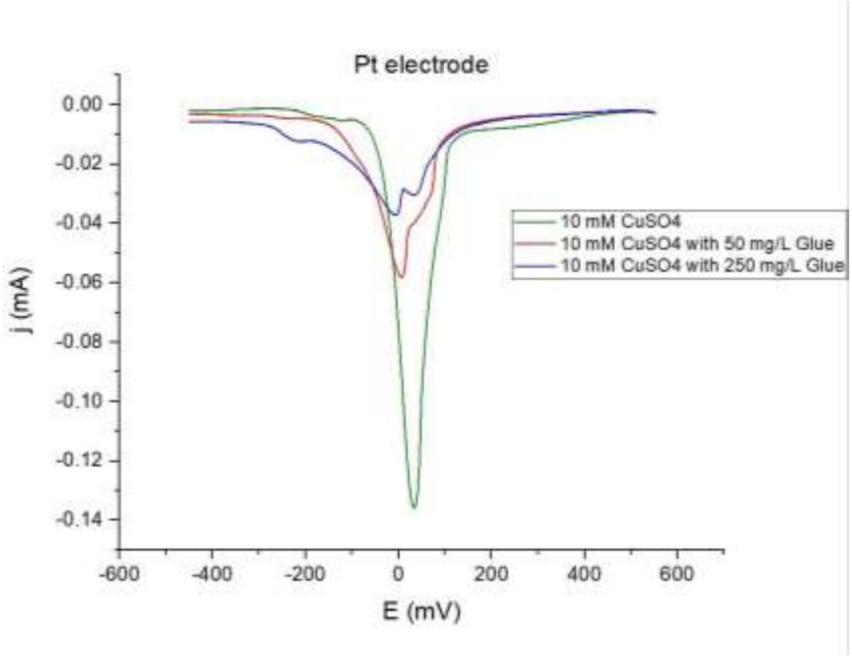

Figure 16 Differential pulsed voltammetry results of copper electrolytes using Pt as a working electrode

In this experiment, initial potential has been set -0.4 V, and final potential has been adjusted +0.6 V

From the differential pulse voltammograms, it can be seen that 2 step reduction process occurs when the amount of glue is higher. When there is no glue in the solution peak current potential has been found at +0.04 V. Addition of 50 mg/L glue results the peak potentials at +0.01 V and +0.08 V respectively. 250 mg/L inclusion in the electrolyte changed the peak potentials slightly to the cathodic side at 0.0 V and +0.03 V each.

Although the differential pulsed voltammograms did not agree with cyclic voltammograms, it is predicted that DPV measurement is insensitive to electrochemical irreversible processes creating high current peak, and it makes the voltammograms hard to distinguish.

4.3 Studying the effect of glue in copper electrolyte solution using chronoamperometry technique

. The data from the chronoamperometry measurements were obtained when the potential was stepped to various potentials between +0.4 and -0.4 V. In this range, the copper deposition has been observed by cyclic voltammetry.

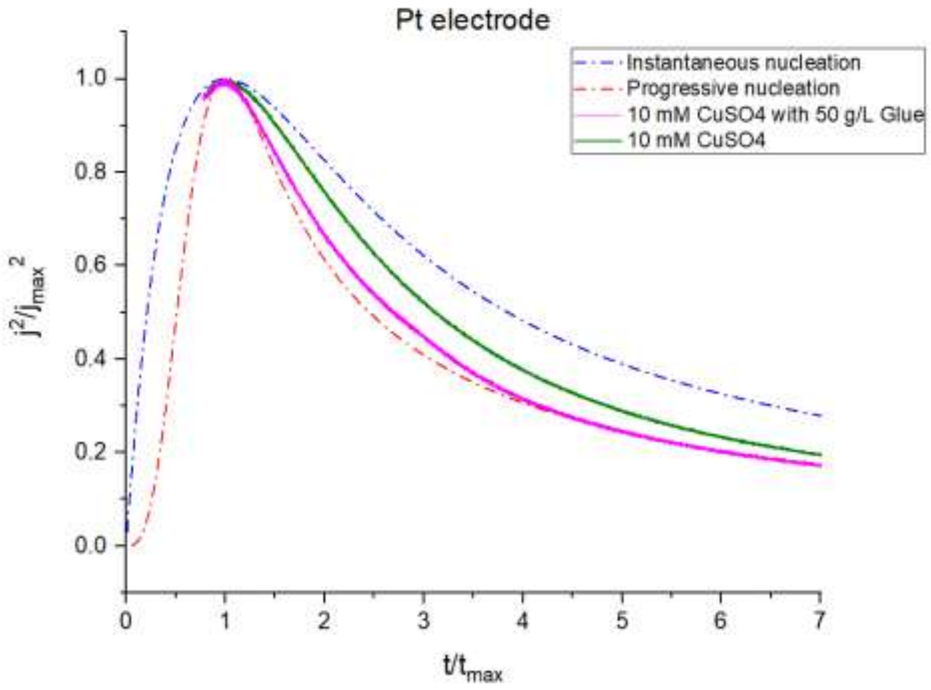

Figure 17 Chronoamperometry results of the copper electrolytes, Pt as a working electrode

As shown in the Figure 18, stage 1 occurs during the increase of the curve to the maximum point of current. Figure 16 only represents the two curves where the potential is stepped between -0.2 and +0.4 V, because the more clearer and defined peaks were observed in this step. New nuclei begin forming in stage 1. At stage 2, copper nuclei accumulate on the surface as it is expressed as maxima of the curve. Final stage 3, further growth on the layer of copper takes place. According to the result, curve for copper solution with glue fits well to theoretical model for progressive nucleation at every stage, whilst copper solution curve occurs between progressive and instantaneous at stage 3 only. This deviation occurs to instantaneous nucleation whose growth is both diffusion controlled and kinetics controlled [52].

On the glassy carbon and copper electrodes, electrochemical measurement results follow mathematical models. Almost no deviation has been observed for progressive nucleation that occurs when the glue has been added in the electrolyte solution. However, on both of measurements of the GCE and Cu electrode, the proposed curves deviated slightly for the electrolytes without glue content. Even though the deviation is negligibly tiny, this phenomenon was predicted relating the small presence of kinetics controlled growth, or it is due to more negative cathodic potential that leads to the shift of the curve to the intermediate trend between the models [42, 52]. Step potential was taken between -0.2 V and +0.4 V for all measurements regardless electrode type, except on GCE potentials between -0.1 V and +0.4 V were stepped. Therefore, the deviation may resulted from the fact that reduction potential differs based on the different electrode.

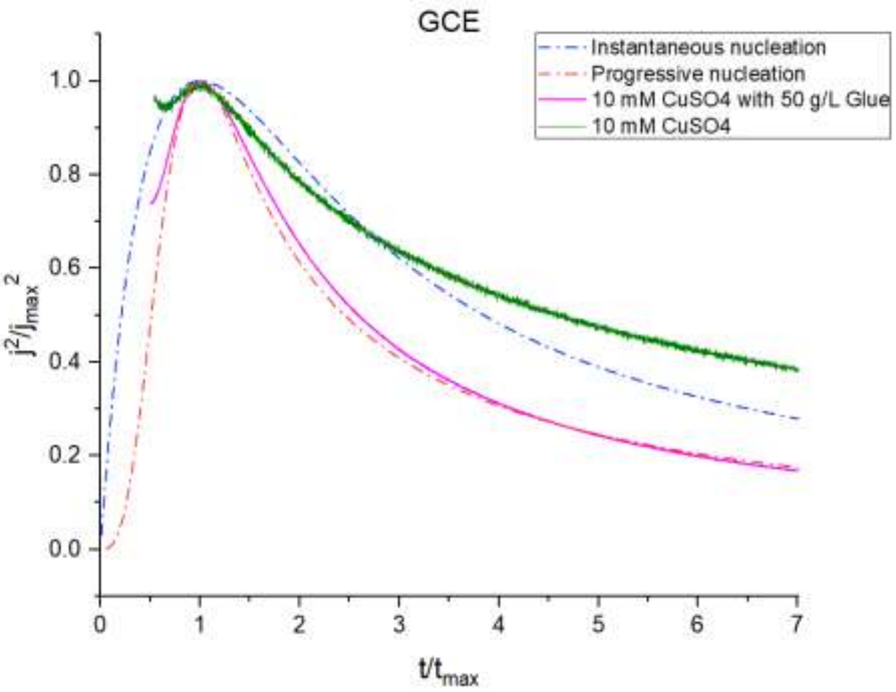

Figure 18 Chronoamperometry results of the copper electrolytes, Glassy Carbon as a working electrode

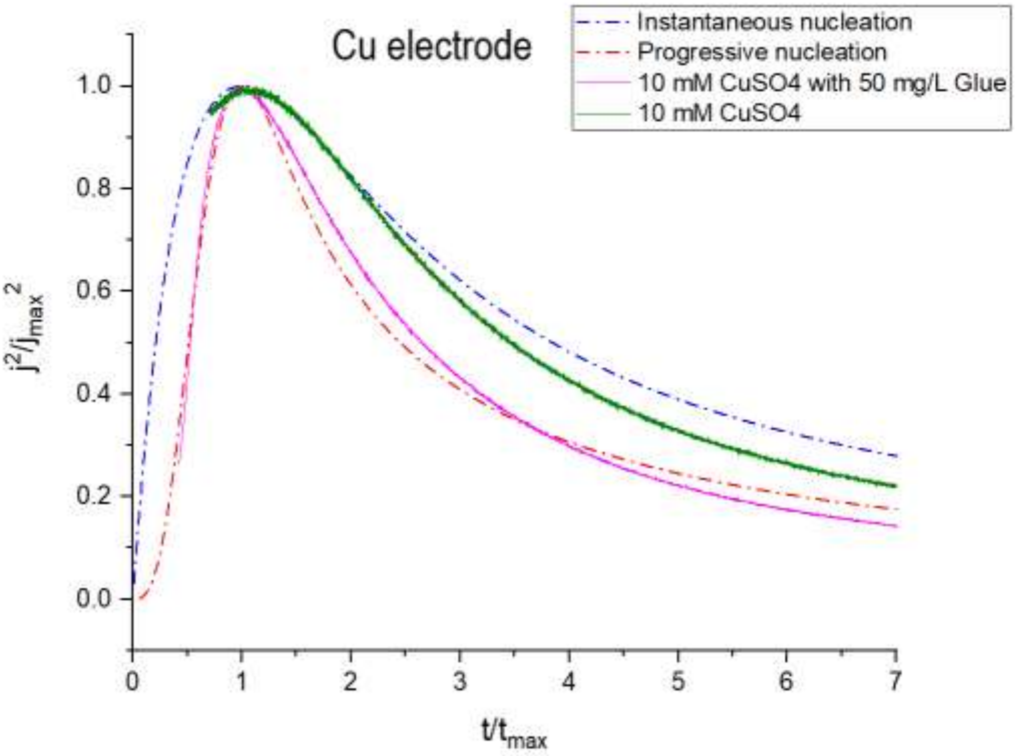

Figure 19 Chronoamperometry results of the copper electrolytes, Cu as a working electrode

From the results, glue changes the nucleation mechanism from instantaneous to progressive nucleation. It suggests that glue makes the diffusion controlled growth of nuclei faster. And the measurements have been made on chronoamperometry technique proves the glue behavior in electrorefining, at which glue makes the surface of copper more smooth by changing nucleation mechanism. Glue is measured conventionally using overpotential. All current transient shows the current peak. From chronoamperometry measurements, time required to reach the maximum current (t_{max}) is influenced by overpotential. The current transient shape usually does not depend on the applied overpotential, but the t_{max} strongly depends on overpotential. When the first step potential is more negative, the peak current is found to be larger and more resolved while t_{max} occurs earlier as shown in Figure 21. Therefore, a shift of maximum time to the left is related to the content of the glue.

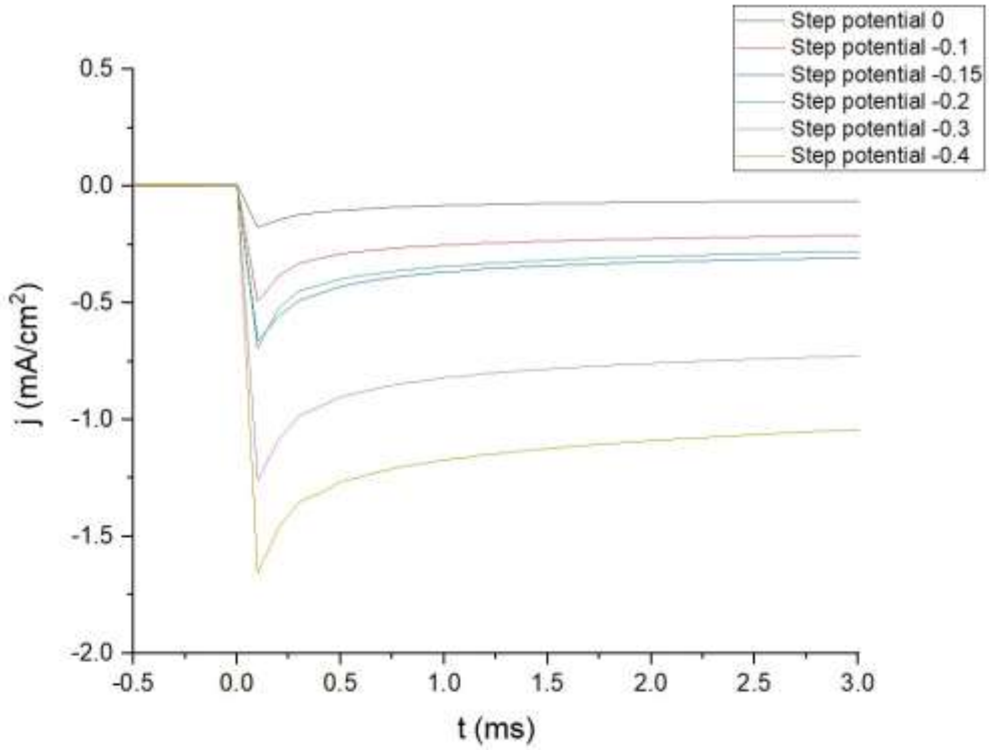

Figure 20 Chronoamperometry measurement of 10 mM $CuSO_4$ on Cu electrode when the step potential was stepped between +0.4 V and various step potentials.

To conclude, glue changes the reduction potential to shift to more cathodic side according to cyclic voltammetry measurement. As graphical illustrations of the models shown in the result, chronoamperometry technique can tell us whether the glue is in present based on the change of nucleation mechanism. The measurements on copper electrode were easier to determine the nucleation since it is same material which is being electrodeposited. Less deviation from the mathematical model occurred as shown in Figure 23. This technique is suitable for identification of glue in the electrolyte and for qualitative analysis of glue. However, deviations of the curve can occur with following reason. More cathodic potential causes shifts of the curve in between progressive and instantaneous nucleation [42].

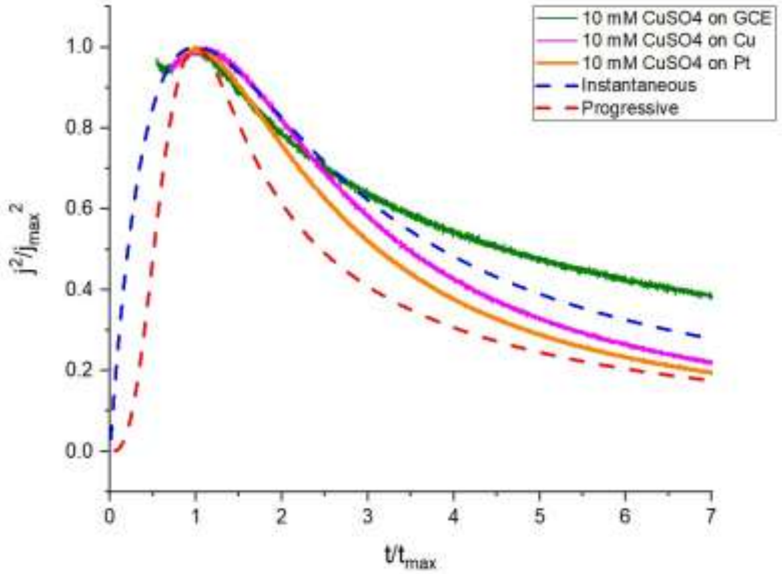

Figure 21 Chronoamperometry results of 10 mM CuSO4 on various electrode when the potential is stepped between +0.4 V and -0.2 V

4.4 Diffusion coefficients

Nuclear number density, nucleation rate constant and diffusion coefficients can be found using current maxima. Diffusion coefficient, D, can be calculated using different methods. One way to find diffusion coefficient would be Randles Sevick equation as described on Equation 16.

Equation 21 Randles Sevick equation

$$j_{max} = 2.687 \times 10^5 c(n^3 vD)^{1/2}$$

j_{max} is maximum current at the peak, n for number of electrons; v, sweep rate (V/s), and c stands for concentration of Cu^{2+} (mol/cm^3).

Cottrell equation is also used for calculating diffusion coefficient after stage 3 as expressed on Equation 4. This method helps to study the diffusion coefficient of the deposition stage on already existing nuclei.

According to Gunawardena *et al.* [53], diffusion coefficient can be determined using maximum current and time based on the nucleation mechanism of the electrodeposition.

Equation 22 Diffusion coefficient correlation to progressive nucleation

$$j_{max}^2 t_{max} = 0.2598\ (nFc)^2 D$$

Equation 23 Diffusion coefficient correlation to instantaneous nucleation

$$j_{max}^2 t_{max} = 0.1629\ (nFc)^2 D$$

Diffusion coefficient, D, is calculated in Table a using theoretical equations.

Table 6 Diffusion coefficients

Electrode	Composition	D (10^{-6} cm^2 s^{-1}) Randles Sevick method	D (10^{-6} cm^2 s^{-1}) Cottrell equation
Pt	10 mM CuSO4	2.22	2.81
	10 mM CuSO4 + 50 mg/L Glue	1.95	2.03
	10 mM CuSO4 + 250 mg/L Glue	0.87	1.05
GCE	10 mM CuSO4	2.21	2.70
	10 mM CuSO4 + 50 mg/L Glue	1.47	1.95
Cu	10 mM CuSO4	1.28	1.55
	10 mM CuSO4 + 50 mg/L Glue	0.49	0.89

Initially diffusion coefficients were determined substituting the data obtained from cyclic voltammetry on Randles Sevick equation. Moreover, chronoamperometry results has been used to calculate diffusion coefficients as a comparison. Both method demonstrates that diffusion coefficient decreases as the amount of glue increases. Since the diffusion relative to the electrode surface correlates to the current going through electrode, glue content influences the current passing the electrode. Moreover, it can be explained that diffusion coefficient has been decreased partly due to increasing viscosity.

5 Conclusion

The study demonstrated electrochemical techniques for determination of nucleation mechanisms of the copper on the electrode surface when the glue is added.

Glue is derived from animal and the chemistry of glue is not completely known. The chemical content of glue varies as it consists of various kinds of long protein molecules. It is important to study the electrodeposition of copper when the glue is added in the system. Glue behavior of changing polarization of electrode in the electrolyte solution enables us to study further about electrochemical techniques.

Cyclic voltammetry technique helped us to understand how the glue changes the electrochemical parameters and provided fundamental electrochemical information to study nucleation mechanisms. The study shows that the higher content of glue results more negative reduction potential of copper ions and small area of negative region. Therefore, peak current density diminishes as the glue concentration increases. For glue quantification, further studies with the electrolytes with distinct glue concentrations must be done in order to fully investigate the feasibility of the method. Based on the change of reduction potential, it is conceivable to use this technique for the glue measurement in practice.

Chronoamperometry technique has been studied for evaluation of the nucleation mechanism of the copper on the electrode. Theoretical mathematics models have been used for evaluation. It suggests that glue changes the nucleation mechanism from instantaneous to progressive. Comprehensively, this study proves and supports the idea of glue on copper electrodeposition by changing slow growth of nuclei that leads to rough surface of the copper. In electrorefining, progressive nucleation is more preferable as progressive nucleation mechanism is described as a fast growing nuclei on the surface to form more flat and dense copper electrodeposition. Content of glue cannot significantly influence the chronoamperometry results. Excessive amount of glue can result the intermediate position between two nucleation mechanisms on the graphical illustration. Therefore, it is suitable method for qualitative analysis of the glue. The results of this technique can tell us the presence of the glue in the electrolyte.

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Statutory Declaration

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Last Name, First Name	Student ID Number

I hereby affirm in lieu of an oath that I provided the submitted bachelor thesis

‘Evaluation of electrochemical techniques for the quantification of glue in copper electrowinning electrolytes’

I did not use any sources other than those stated. In case that the work is additionally submitted on a data medium, I declare that the written and the electronic form are completely identical. The work was not submitted in the same or similar form to any examination authority.

Freiberg, 08.06.2020	
Place, Date	Signature