

Determination of Mass Transfer Coefficient for Copper Electrodeposition by Limiting Current Technique.

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Abstract

An experimental study was conducted to investigate the mass transport behavior for electrochemical reduction of copper in the presence of 0.5M H₂SO₄ as supporting electrolyte by limiting current technique (LCT). The experiments were carried out via rotating cylinder electrode made of copper as cathode. The effects of various operating conditions: rotation rates 100, 200, 300, 400, and 500rpm, electrolyte temperatures 30, 45, and 60°C, and cupric ions concentration 250, 500, and 750 ppm on mass transfer rate were studied. It was observed that mass transfer coefficient based mainly on rotation rates, then temperature and finally cupric ions concentration. The electrodeposition of cupric ions was proved to be a mass control. The mass transfer coefficient for rotating cylinder electrode was correlated with the aid of dimensionless groups as follows:

$$Sh = 0.236 Re^{0.664} Sc^{0.356}$$

And the above correlation is a good agreement with eisenberg equation.

Keywords: Mass transfer coefficient, Electrodeposition of copper, Rotating cylinder electrode (RCE), Cupric ion removal, Limiting current technique (LCT).

1. Introduction

In the recent years, the demand for base and precious metals like copper, zinc, nickel, and chromium is constantly rising because of extending economic development, growing industrialization, and increasing costs of metals production. Simultaneously resources and quality of ores and metals are noticeably decreasing. Wherefore, replacement sources of metals such as industrial waste and exhausted electrolytes should be discovered [1,2].

There are rising economic, social, legal, and environmental compressions to employ the best technology without pollution [3]. The electrochemical technologies can supply worthy cost efficient and environmentally friendly communion to industrial process development

without necessitating addition of chemicals and not creating by-products which would later entail treatment [4]. Some of applications of electrochemical effluent treatment are the removal of heavy metal ions from solutions, destroy of organic pollutants, fuel cell technology, primary and secondary batteries, and electrolysis. The attraction advantages of electrochemical processes are:

- Versatility: direct or indirect oxidation and reduction, phase separation, concentration or dilution, ability to a variety of media and pollutants in gas, liquid, and solids and treatment of small to large volume from microliters to million liters.
- Energy efficiency: lower temperature entailing than non-electrochemical counterparts, like as anodic destruction of organic pollutants instead of thermal incineration. Energy losses caused via disproportionate current distribution, voltage declined, and side reaction can be minimized by obtaining the best cell design.
- Amenability to automation: the system companion variables of electrochemical processes, such as electrode voltage and cell current, convenient for simplifying process automation and control.
- Cost effectiveness: electrochemical cells and equipments are always simple and inexpensive [5].

Copper is the most commonly mined mineral in many countries. Copper manufacturing companies have acknowledged the importance of producing high quality copper in order to suit the market demands and requirements [6]. Electrowinning is used for the recovery of copper from dilute solutions which it is widely used in electronic industry for interconnects, manufacturing printed-circuit boards, as well as making protective and decorative coatings [7,8,9].

Copper is arranged as the third highest consumed metal in the world. The major source of copper is from mine production that about 88%, and 12% comes from recycled scrap metal. Electrowinning of copper is used over 30 years old, 1/5 of the world's copper production comes from electrowinning. Demand for copper was

increased in last years that lead the production to increase. Copper demand is increasing due to global economy [10].

Electrowinning process is able to recovery copper and treatment of wastewater due to all copper compounds are toxic caused by formation of monovalent ions which have the ability to form reactive free radicals that effected on human healthy [11].The electrowinning is achieved by the electrodeposition of copper on the rotating cylinder electrode reactor (RCE) which is effective tool for obtaining high rate of mass transfer and uniform distribution of potential and current, to determine mass transfer coefficient k_m , which characterized the performance of reactor. The main purposes of this work are: to design and construct an electrowinning cell for reduction of cupric ions by using rotating cylinder electrode made of copper as cathode, and compressed graphite as anode. To determine the mass transfer coefficient for reduction of cupric ions by the limiting current technique where effective cell design has been achieved at large mass transfer coefficient, and to study the effect of different parameters on the mass transfer coefficient such as rotational velocity 100, 200, 300, 400, and 500 rpm, electrolyte temperature 30, 45, and 60 °C, and cupric ions concentration 250, 500, and 750 ppm.

2. Theory

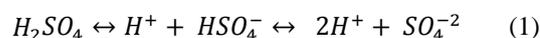
Electrochemistry is the field of the chemistry interested with the relation of electrical and chemical effects. It includes the study of chemical changes in consequence of application of an electric current and the production of electrical energy by chemical reactions [12].

The reaction of atoms using the exchange of electrons is the mystery that resulted in the birth of electrochemistry and electrochemical engineering. The movement of the atom from solution or from one metal to the other, of the same material, without the application of an external voltage is not possible because a cell that is in equilibrium remains in equilibrium forever. The application of external voltage is the basic factor in the deposition of the metal from the anode to the cathode or from solution to the cathode as the case may be [13].

A simple electrowinning system consists of: power supply, electrodes and electrolyte solution. An electrolyte solution provides metal ions to be deposited in low concentrations. It has to be electrically conductive. There are two electrodes necessitated for electrowinning cathode and anode, one of these electrodes works as an electrochemical reactor. An applied electric field across these electrodes supplies the main driving force for the ions motion. The anode was not thawed otherwise electrorefining, where the

electrodes having the same material, the anode liberate the metal cations into solution, afterward deposited on the cathode surface. The needed applied voltage is higher compared to electrorefining [14].

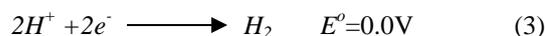
Electrolytic cell solutions used for mass transfer studies always contains a certain concentration of an electroactive species (Cu^{+2}) and large concentration of a supporting electrolyte such as H_2SO_4 , the supporting electrolyte ionizes:



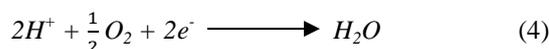
The electron transfer happens at the electrode – electrolyte boundaries (interface), so copper reduced as the major reaction below [14,15]:



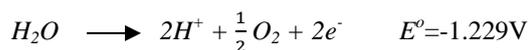
The first side reaction at the cathode is hydrogen evolution:



The second side reaction is a little quantity of oxygen reduction because of remainders of the dissolved gas [14, 16].



At the same time, the oxygen liberated in acidic media at the anode as the following reaction:



The movement of species from the bulk solution to the electrode surface occurs via mass transfer. The mass transfer through migration, convection and diffusion in electrochemical reactors is the result of the applied overvoltage. The mass transfer is described by the Nernst-Plank equation for one dimension as follows:

$$N_j = -D_j \frac{dc_j}{dx} - \frac{D_j C_j z F}{RT} \frac{d\phi}{dx} + C_j U \quad (5)$$

The first term in equation (5) is diffusion term, the second is migration term and third is convection term. Molecular diffusion mass transport is the transfer of matter due to random motion, from high concentration region to low concentration region. Concentration gradient is assumed to give rise to the molecular diffusion, if assumed the process at the electrode surface is the diffusion only [17]. Migration occurs by the movement of charged particles due to the influence of an electric field. It is usually decreased by increasing the conductivity of the electrolyte solution by the addition of high concentration of supporting electrolyte such as H_2SO_4 . There are two kinds of mass transfer by convection: free and forced convection. Free

convection results from a density difference between the solution at the electrode surface and that in the bulk during the accumulation of the metal ions at the cathode surface, this density difference augments a flow of concentrated solution from the bulk to the electrode and then increase the limiting current density [17,18]. Forced convection is occurred by the motion generated by application of an external forces on the solution. It is important factor in the industrial metal deposition which was accelerated the supply of the metal ions to the electrode surface and shows a higher limiting current density. This is attained by rotation, vibration and stirring (agitation) the solution. The most important electrochemical device that employs forced convection is the rotating cylinder electrode (RCE) [18].

For many practical situations the cathodic reaction is under diffusion control, so the current is sentenced by the Fick's first law which connects flux to the concentration gradient:

$$N_j = -D_j \left(\frac{dC_j}{dx} \right)_{x=0} \quad (6)$$

The negative sign in equation (6) indicating the direction of transfer from a high region concentration to one of low concentration.

$$N_j = \frac{i}{zF} = -D_j \left(\frac{dC_j}{dx} \right)_{x=0} \quad (7)$$

$$i = z F D \frac{(C_b - C_s)}{\delta_D} \quad (8)$$

As the applied potential is increased, the current increasing and the reaction rate increased because of a faster depletion of electroactive species at the electrode, give rise to a lower interfacial concentration C_s . Then reaching a constant current called the limiting current or "current plateau", when the C_s approaches zero then increasing the potential does not cause increase the current and at the potential above limiting rate. So the limiting current density defines the maximum rate at which the reaction can take place [19].

$$i_L = z F \frac{D}{\delta_D} C_b \quad (9)$$

$$i_L = z F k_m C_b \quad (10)$$

where k_m is mass transfer coefficient

$$k_m = \frac{D}{\delta_D} \quad (11)$$

Convective mass transfer can be expressed by a dimensionless collection correlation of the following expression.

$$Sh = a Re^b Sc^c \quad (12)$$

For forced convection $c = 0.356$

3. Experimental Work.

3.1 Materials.

In this study the electrolyte solution used are:

- Analar grade sulfuric acid provided by CDH company (purity > 98 wt%, sp.gr. 1.84) is used. Sulfuric acid diluted via distilled water to prepare 0.5M H₂SO₄ solution.
- Sulfuric acid (0.5M H₂SO₄) + copper sulfate petahydrate (CuSO₄.5H₂O) provided by ROMA company used as redox system to give various concentrations of cupric ions 250, 500, and 750ppm.

3.2 Electrowinning Cell and Circuit.

Electrowinning Cell consists of electrolyte solution, working electrode, reference electrode and counter electrode.

The experimental rig which was used for performing the present work is shown in Fig (1). The experimental apparatus was comprised of water bath to get different solution temperatures, digital stirrer to obtain various rotation rates, power supply is used for providing the direct current or applied voltage which is required for reduction of copper, resistance box to control the current flow, digital ammeter to measure the current, digital voltmeter to measure the potential. Rotating cylinder electrode (RCE) used as the working electrode (cathode) made of copper having 25mm outside diameter and 20mm inside diameter and 3.2cm length. The rest of rotating electrode (shaft) was made of teflon.

The counter electrode is a compressed graphite cylindrical bar (insoluble and an electrical conductive material) used for copper electrowinning, which having 28mm diameter and 15cm length. The applied voltage was 6 V and the distance between the electrodes was 3cm for all the experiments. The reference electrode was a saturated calomel electrode (SCE) in order to determine the cathode potential using a Luggin capillary placed midway of the rotating electrode surface at a distance 1-2 mm from it. The electrical connection of cathode was achieved using brush.

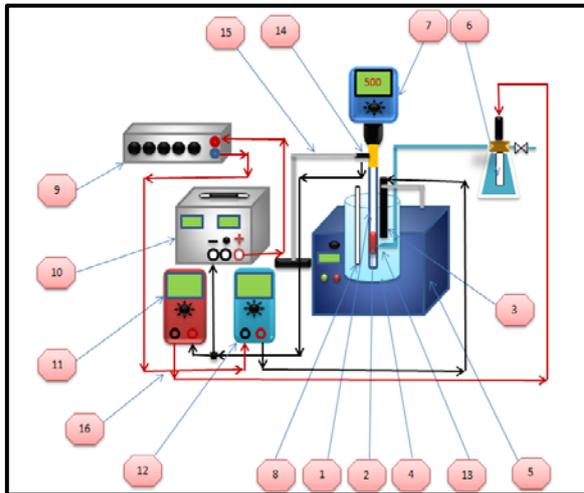


Figure (1): Schematic diagram of experimental setup.

1. Rotating shaft, 2. Working electrode (specimen), 3. Graphite electrode (anode), 4. Beaker, 5. Water bath, 6. Reference electrode (SCE), 7. Digital stirrer, 8. Thermometer, 9. Power supply, 10. Resistance box, 11. Voltmeter, 12. Ammeter, 13. Luggin capillary tip, 14. Brush, 15. Stand, 16. Electric wires.

4. Results and Discussions.

Table (1) demonstrates the calculated mass transfer coefficient (k_m) from polarization data under different operating conditions.

Table (1): The determined k_m via LCT under different operating conditions.

T °C	Rotation Rate (rpm)	$K_m * 10^3$ (cm/s) for 250ppm Cu ⁺²	$K_m * 10^3$ (cm/s) for 500ppm Cu ⁺²	$K_m * 10^3$ (cm/s) for 750 ppm Cu ⁺²
30	100	1.105908	1.048254	1.0639786
	200	1.782033	1.685069	1.6859432
	300	2.290436	2.120095	2.1331986
	400	2.935113	2.625878	2.5909365
	500	4.234949	3.045180	3.0224681
45	100	1.430867	1.692931	1.4727980
	200	2.253747	2.445054	2.3411025
	300	3.081869	3.013732	3.0154798
	400	4.004333	3.852336	3.3194737
	500	4.591356	4.127503	3.6898570
60	100	1.886858	1.986442	2.0598207
	200	3.443517	3.060904	3.3142324
	300	4.014816	4.164192	4.7206410
	400	4.979210	4.913694	5.4142363
	500	6.027465	5.621266	5.6431053

The effect of the Linear Velocity on the rate of metal deposition can be used to know whether the deposition process is diffusion or charge controlled process. Figure (2) gives the relation between the limiting current and the linear

velocity to the power (0.7) at different concentrations and temperatures. Straight lines were gained and the limiting current increases by increasing the linear velocity which denotes that electrodeposition process of copper is diffusion controlled reaction [20,21]. From figure (3) it clear that increasing the rotation rate resulting in rising k_m as shown for a given electrolyte temperature. This can be ascribed to the increase in the transfer rate of cupric ions near to the electrode surface by eddy transport according to the Nernst-Planck equation (5).

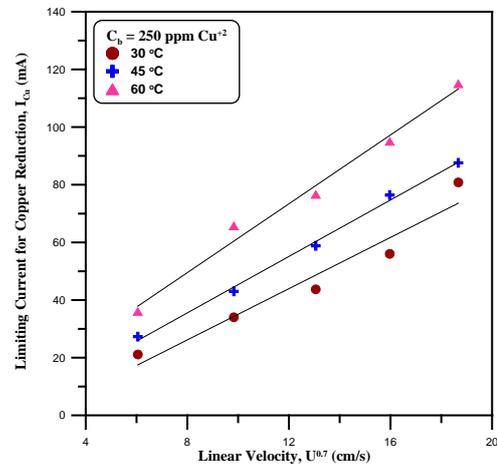


Figure (2): Variation of the limiting current for copper reduction with linear velocity at 250 ppm Cu⁺² and different electrolyte temperatures.

The rate of copper reduction reaction is commonly limited by the speed at which copper can be arrived the surface of the metal.

Increasing velocity leads to increase mass transfer coefficient due to decrease the diffusion layer thickness at the surface, this behavior can be attributed to the eddies penetration the diffusion layer resulting in diminishing its thickness.

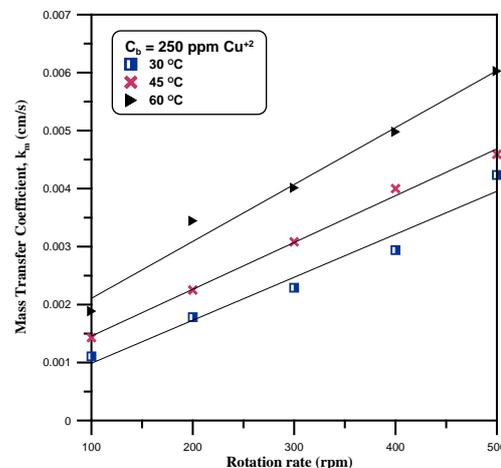


Figure (3): k_m vs. rotating rates at different temperatures for electrolyte containing 250 ppm Cu⁺².

Figure (4) shows that increasing cupric ions concentration leads to an increase the limiting current. This can be ascribed to the truth that by increasing the cupric ions it will resulting to increase the electrical conductivity of solution for flowing the current between electrodes, i.e. this simplify the copper reduction [22].

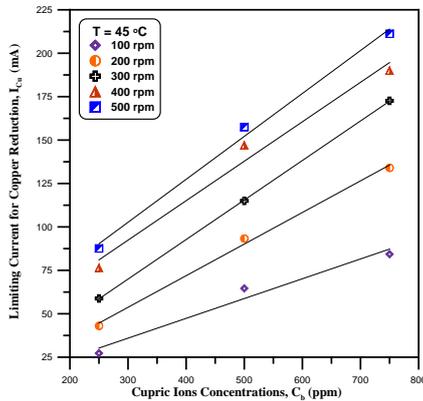


Figure (4): Effect of cupric ions concentrations on the limiting current for copper reduction at 45 °C and different rotation rates.

Figure (5) reveals the experimentally mass transfer coefficient as a function of the temperature of electrolyte at different rotation rates. Increasing the electrolyte temperature gives rise to higher limiting current and hence increase mass transfer coefficient due to the higher internal energy of the particles which can be obtained at elevated electrolyte temperature. This result may be attributed to the increasing temperature will increase the diffusion coefficient of electroactive species (cupric ions), this a good agreement with [23-25], which cause declined the viscosity and hence increase the diffusion rate of cupric ions to the electrode surface [22].

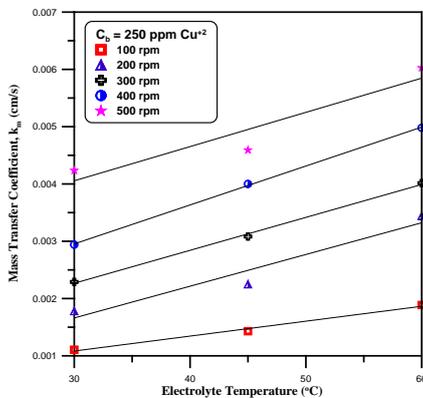


Figure (5): k_m vs. electrolyte temperatures at different rotation rates for electrolyte containing 250 ppm Cu^{+2} .

The analysis of dimensionless groups is a method to express a correlation when the process of reducing the ion is limited by mass transport in

an electrochemical reactor. Figure (6) presents $\log Sh/Sc^{0.356}$ vs. $\log Re$, a straight line was obtained, its slope offered the constant b , while the intercept gives the constant a .

The value of constant a based on the mass transfer coefficient, diffusion coefficient of the relevant specie due to it is the intercept of $Sh/Sc^{0.356}$.

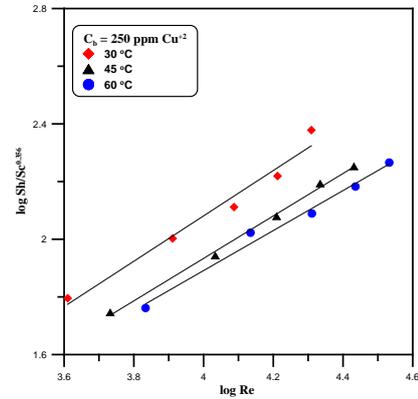


Figure (6): The relation between $\log Sh/Sc^{0.356}$ against $\log Re$ for electrolyte solution contains 250 ppm Cu^{+2} .

From figure 6 a and b were obtained for this technique as presented in the following equation:

$$Sh = 0.236 Re^{0.664} Sc^{0.356} \quad (13)$$

The diffusivities of cupric ions in electrolyte at different temperatures were taken from [26].

Poulson declared that exponent b varies between (0.5-1.0) for most geometries. In the present work the value of b is 0.664 for LCT [27].

Figure (7) shows the calculated k_m vs. Re by LCT, and Eisenberg equation:

$$k_m = 0.079 U^{0.7} d^{-0.3} \nu^{-0.344} D^{0.644} \quad (14)$$

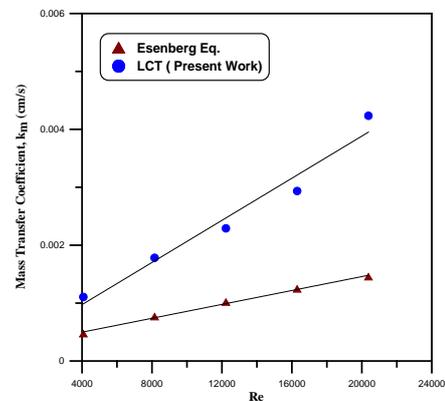


Figure (7): Comparison of k_m values determined by different techniques for electrolyte contains 250 ppm Cu^{+2} .

The line for LCT lies above the Eisenberg correlation line for a smooth cylinder. This suggests that enhanced mass transfer caused by surface roughness could explain the skewing of the data to higher values of the Sherwood number.

5. Conclusions.

- 1) Limiting current technique for determination of mass transfer coefficient for electrodeposition process is a good method.
- 2) RCE proved useful tool for rapid electrolysis studies.
- 3) The most effective parameter on km is the rotation rate and the smallest effective parameter is the cupric ions concentration.
- 4) By using dimensionless group is in a good agreement with Eisenberg study.

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حساب معامل انتقال الكتلة لعملية ترسيب النحاس بواسطة تقنية التيار المحدد.

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الخلاصة:

تم اجراء دراسة تجريبية للتحقيق في سلوك انتقال الكتلة للاختزال الكهروكيمياوي للنحاس بوجود حامض الكبريتيك كمحلول داعم بواسطة تقنية التيار المحدد. لقد اجريت التجارب باستخدام القطب الاسطوانى الدوار المصنوع من النحاس كقطب كاثود. وتم دراسة تأثير ظروف التشغيل المختلفة: معدل دوران 100, 200, 300, 400, و 500 دورة / دقيقة, درجات حرارة المحلول الالكتروليتي 30, 45, و 60 درجة سيليزية, و تركيز ايونات النحاس 250, 500, و 750 على معدل انتقال الكتلة. لوحظ ان معامل انتقال الكتلة تعتمد بشكل اساسي على معدلات الدوران , ثم درجة الحرارة واخيرا تركيز ايونات النحاس. وقد اثبتت التجارب ان الترسيب الكهربائي للنحاس تحت سيطرة الكتلة. تم الحصول على معادلة تربط معامل انتقال الكتلة بمجموعة عديمة الوحدات:

$$Sh = 0.236 Re^{0.664} Sc^{0.356}$$