



## Estimation of Mass Transfer Coefficient for Copper Electrowinning Process

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### ABSTRACT

Mass transfer was examined at a stationary rectangular copper electrode (cathode) by using the reduction of cupric ions as the electrochemical reaction. The influence of electrolyte temperature (25, 45, and 65 °C), and cupric ions concentration (4, 8, and 12 mM) on mass transfer coefficient were investigated by using limiting current technique. The mass transfer coefficient and hence the Sherwood number was correlated as  $Sh = 4.25 \times 10^{-3} (Gr Sc)^{0.486}$

**Key words:** Mass transfer coefficient, copper electrowinning, limiting current, dimension less group.

حساب معامل انتقال الكتلة لعملية استخلاص النحاس

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### الخلاصة

تم اختبار انتقال الكتلة على قطب النحاس الساكن (كاثود) باستخدام الاختزال الكهروكيميائي لأيونات النحاس الثنائية. ومن ثم التحري عن تأثير درجة حرارة المحلول الألكتروليتي (25، 45، و 65 °م) إضافة إلى تركيز أيونات النحاس الثنائية (4، 8، و 12 ملي مولاري) على معامل انتقال الكتلة باستخدام تقنية التيار المحدد. تم الحصول على علاقة تربط بين (Sherwood number) وكل من (Grashof number) و (Schmidt number).

**الكلمات الرئيسية:** معامل انتقال الكتلة، استخلاص النحاس، التيار المحدد.



## 1. INTRODUCTION

An increase world population with growing industrial demands has led to the situation where the protection of the environment has become a major issue and crucial factor for the future development of industrial processes, which will have to meet the requirements of sustainable development, **Juttner K. et al., 2000**. There are increasing economic, social, legal, and environmental pressures to utilize “the best available technology” not entailing excessive cost and to aspire to “performance without pollution”, i.e., “zero pollution processing”. Electrochemical technology has an important role to play as part of an integrated approach to:

- The avoidance of pollution reagents in materials synthesis
- Monitoring of pollution and reagent levels in the gas and liquid phase
- The removal of environmental contaminants, such as metal ions and organics from industrial process streams
- Cleaner processing involved the clean conversion of chemical to electrochemical energy using fuel cell and photovoltaic devices, and modern techniques for electrical energy storage and conversion, **Walsh F.C., 2001**.

The removal (recovery) of metals from aqueous solutions by electrolytic means has been a major factor in extractive technology during the last decades. The source of metal can be an ore as well as waste residue (scrap metals, dusts, sludge's collected from metallurgical operations, etc.), **Soliman H. et al., 2011**. Copper is the most widely mined mineral in many countries though a few other minerals such as gold, cobalt, and silver are also exploited. Copper producing companies have acknowledged the importance of producing high quality copper in order to satisfy the market demands and requirements. There are two methods of electrochemical for production copper: electrorefining is one method that produces high quality copper from 98% to 99.98% copper while electrowinning is used for the recovery of copper from dilute solutions, **Ntengwe F.W, 2008, Fogarasi S. et al. 2015**. One of the aims in studying metal electrowinning is to gain better understanding of the metal electrodeposition. The electrodeposition of copper on foreign substrates is widely used in electronic industry for interconnects, manufacturing printed-circuit boards, as well as making protective and decorative coatings, **Majidi M.R. et al., 2009**.

The objective of the present work is to design and construct a copper electrowinning cell in order to study the effect of different operating parameters (electrolyte temperature and cupric ions concentration) on the mass transfer coefficient.

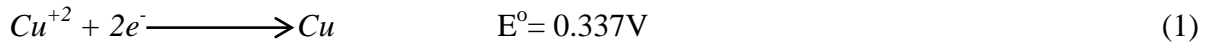
## 2. THEORY

Electrochemistry deals with the study of mutual conversion of chemical and electrical forms of energy. It deals with reactions that proceed at the expense of electrical energy. The application of external voltage is the key factor in the electrodeposition of metal from the anode to the cathode or from solution to the cathode as the case may be. The mass transfer through migration, convection, and diffusion in electrochemical reactors is the result of the applied overvoltage, **Ntengwe F.W, 2008**. The main advantages of the electrochemical technology are:



- ❖ Electrons are clean reagents, this strategy include both the treatment of effluents and waste and development of new processes or products with less harmful effects.
- ❖ Effective control of the electron transfer rate (current density)
- ❖ Measurement of reaction conditions (current density and electrode potential).
- ❖ The process can be turn on and off via the current.
- ❖ Ambient conditions of temperature and pressure can be used, **Walsh F.C., 2001.**

Electrolytic cell solutions used for an electrowinning studies always contains a certain concentration of an electroactive species ( $\text{Cu}^{+2}$ ) and large concentration of an inert electrolyte such as  $\text{H}_2\text{SO}_4$  to supply high solution conductivity and a large number of ions that act as the actual current carriers within the electrolytic solution. Therefore, the transfer of  $\text{Cu}^{+2}$  to the cathode surface by migration is eliminated, so it transferred by diffusion and free convection. When a small potential difference is applied across electrodes, the ions move within the solution toward the oppositely charged electrodes and accumulate near the respective electrodes, current suffer a sudden jump due to exchange of electrons between electrodes and the electroactive ions. Eq. (1) expresses the reduction of  $\text{Cu}^{+2}$ , **Zaki M.M., 2000:**



Due to the discharge of some  $\text{Cu}^{+2}$  ions, the concentration of  $\text{Cu}^{+2}$  ions in the immediate vicinity of the cathode is decreased to  $C_i$  accordingly, the interfacial solution density decreased from  $\rho_b$  to  $\rho_i$  and this density difference gives rise to a buoyancy force,  $g \Delta\rho$ , which causes upward solution flow at the electrode surface. This flow enhances the transfer of  $\text{Cu}^{+2}$  from bulk solution to the edge of the diffusion layer, **Grigin A.P. et al., 2000.** If the cell voltage is sufficiently increased, a state is reached where interfacial concentration becomes zero and the rate of mass transfer becomes maximum. Under this condition, the current reaches a constant value known as the limiting current ( $I_{\text{Lim}}$ ). In the meantime, the cathode potential increases to a high value where hydrogen gas starts to evolve simultaneously with copper deposition according to the reaction shown in Eq. (2):



The flux of  $\text{Cu}^{+2}$  ions ( $N_{\text{Cu}^{+2}}$ ) may be obtained from Eq. (3), **Wiebe S., 2015, Thomas B. D., 1978:**

$$N_{\text{Cu}^{+2}} = \frac{I_{\text{Lim}}}{Z A F} = \frac{D \Delta C}{\delta} = k_m (C_b - C_i) \quad (3)$$

$$\frac{I_{\text{Lim}}}{Z F} = k_m A C_b \quad (\text{when } C_i = 0 \text{ at Limiting current}) \quad (4)$$



$$\text{Or } k_m = \frac{I_{Lim}}{Z F A C_b}$$

For the electrolysis of  $\text{Cu}^{+2}$  in an electrolyte that contains  $\text{H}_2\text{SO}_4$ , under free convection it was found that Sherwood number based on the Grashof number and Schmid number is given in Eq.(5).

$$\text{Sh} = \alpha (\text{Gr Sc})^\beta \quad (5)$$

The Grashof number is given by the following equation since the free convection in the ion transfer is caused by density differences due to concentration change between bulk solution and electrode surface, **Mizushina, T. et al., 1971:**

$$\text{Gr} = \frac{g d^3 (\rho_b - \rho_i)}{\mu^2} \quad (6)$$

### 3. EXPERIMENTAL

#### 3.1 Materials

Annular grade sulfuric acid (1 M  $\text{H}_2\text{SO}_4$ ) (purity > 98.5 wt%) and copper sulfate ( $\text{CuSO}_4$ ) was used as redox system to give various concentrations of cupric ions 4, 8, and 12mM.

#### 3.2 Electrowinning Cell and Circuit

The experimental apparatus which were used for performing the present work is shown in **Fig. 1**.

The cell consisted of beaker with capacity 1.5 liter, the anode was a square graphite sheet (5cm height  $\times$  5cm width), the cathode was a square copper sheet (5cm height  $\times$  5cm width), the distance between electrodes is 2cm. The back of the cathode was coated with epoxy. The electrical circuit consisted of 5V DC power supply was connected in a series with cell and ammeter. A voltmeter was connected in a parallel with the reference electrode and cathode.

The potentiostat technique was used for obtaining the polarization curves at different conditions. The polarization curve (overpotential versus log i) was drawn and the limiting current was measured. The mass transfer coefficient  $k_m$  calculated from the obtained limiting current.

### 4. RESULTS and DISCUSSION

The limiting current  $I_{Lim}$  is obtained from polarization curves (from the clear constant current region which almost start at -100 mV) under the following conditions: cupric ions concentration 4, 8, and 12 mM and electrolyte temperatures 25, 45, and 65 °C in order to determine mass transfer coefficient  $k_m$ .

**Figure 2** shows the polarization curve for electrolyte containing 1 M  $\text{H}_2\text{SO}_4$  only at various electrolyte temperatures, while **Figs. 3 to 5** show the polarization curves for copper

electrodeposition from electrolyte containing 1 M H<sub>2</sub>SO<sub>4</sub> and different concentrations of cupric ions at different electrolyte temperatures. From these figures it is clear that the limiting current is increased with increasing cupric ions concentration, and electrolyte temperature, and this can be attributed to the fact that increasing the reactant concentration will increase the reaction rate ( $I_{lim}$ ), while increasing the temperature will increase the diffusivity of reactant species and decrease the viscosity of electrolyte.

It can be observed from **Fig 6** that increasing cupric ions concentration leads to an increase in the limiting current and hence  $k_m$ . This is a consequence to increase the electrical conductivity of solution i.e. decrease the solution resistivity to the flow of the current between electrodes, **Majidi M.R. et al., 2009**. It is clear from **Figs 7 and 8** that as the temperature increases  $k_m$  increases. This is due to the fact that increasing temperature will increase the rate of copper diffusion to the metal surface and decrease the viscosity of electrolyte which will aid the copper diffusion, **Uhlig H.H., 1985, Theodore L., 2010**.

**Figure 9** shows log Sh against log Gr Sc (the values of dimensionless groups are listed in table 2), straight lines were obtained with a slope equal to the constant  $\beta$  while the intercept gives the other constant  $\alpha$ . And finally the average mass transfer coefficient for a free convection of cupric ions reduction in acidic media was correlated as in the following equation:

$$Sh = 4.25 \times 10^{-3} (Gr Sc)^{0.486} \quad (7)$$

Within an average deviation of  $\pm 4.5\%$  for the following region

$$2.97 \times 10^{12} < Gr Sc < 6.1 \times 10^{12}$$

This proves that the cupric ions reaction results in a movement of ions in the bulk solution guiding to laminar natural convection flow.

## 5. CONCLUSIONS

- The reduction of Cu<sup>+2</sup> ion in acidic media starts at about -100 mV vs. SCE and reaches the maximum at approximately -280 mV vs. SCE.
- Electrolyte temperature is the most significant operating parameters that affects the mass transfer coefficient.
- The electrowinning process of copper is under mass control in the cathodic region (-280 to -550) mV vs. SCE.
- The copper electrowinning process is under laminar natural convection for a stagnant electrolyte.

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## NOMENCLATURE

A = Cathode area, cm<sup>2</sup>

C<sub>b</sub> = bulk concentration of cupric ions, mol/cm<sup>3</sup>

C<sub>i</sub> = interfacial concentration of cupric ions, mol/cm<sup>3</sup>

D = diffusion coefficient, cm<sup>2</sup>/s

F = Faraday's constant (96487)

g = acceleration due to gravity, cm/s<sup>2</sup>

Gr = Grashof number,  $\frac{g l^3 (\rho_b - \rho_i)}{\mu^2}$

I<sub>Lim</sub> = limiting current, A

i<sub>Lim</sub> = limiting current density, A/m<sup>2</sup>

k<sub>m</sub> = mass transfer coefficient, cm/s

l = characteristic length dimension in Sherwood and Grashog numbers, cm

N<sub>Cu+2</sub> = diffusional flux of electroactive species, mol/s.cm<sup>2</sup>

Sh = Sherwood number, k<sub>m</sub> l/D

Sc = Schmidt number, ν/D

T = temperature, °C

Z = number of electrons involved in the reaction

α = constant used in equation 5

β = constant used in equation 5

ΔC = concentration difference between bulk concentration and interfacial concentration, mol/cm<sup>3</sup>

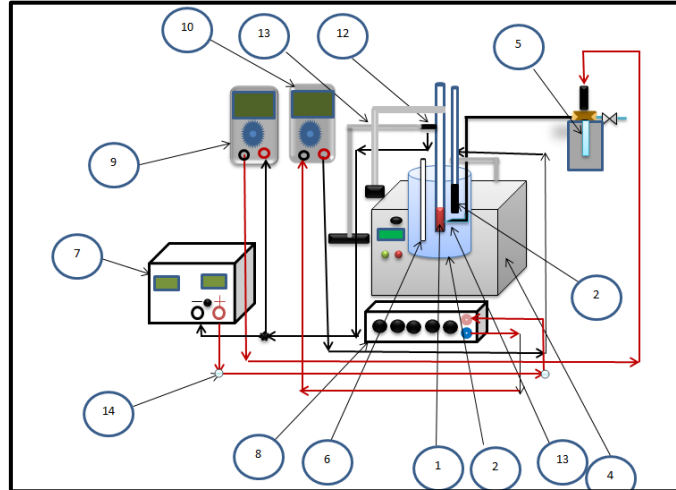
Δρ = density difference between bulk concentration and interfacial concentration, g/cm<sup>3</sup>

μ = dynamic viscosity of cupric ions, g/cm.s

ν = kinematic viscosity of cupric ions, cm<sup>2</sup>/s

ρ<sub>b</sub> = bulk density of cupric ions, g/cm<sup>3</sup>

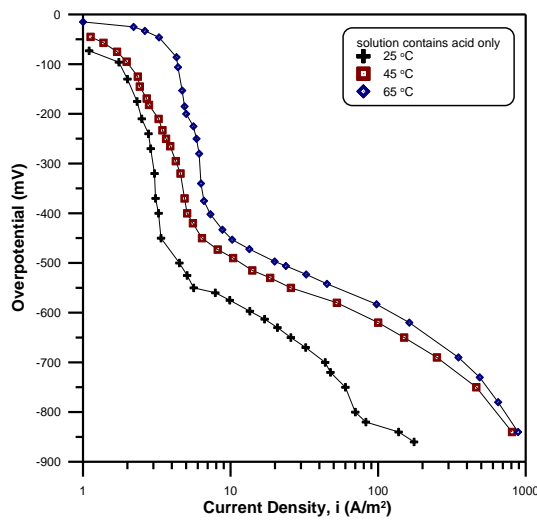
ρ<sub>i</sub> = interfacial density of cupric ions, g/cm<sup>3</sup>



**Figure 1.** Schematic view of equipment setup.

**Table 1.** Experimental Apparatus.

NO.	Item Name	NO.	Item Name
1	Cathode	8	Resistance box
2	Graphite electrode (anode)	9	Voltmeter
3	Beaker	10	Ammeter
4	Water bath	11	Luggin capillary tip
5	Reference electrode (SCE)	12	Brush
6	Thermometer	13	Stand
7	Power supply	14	Electrical wires



**Figure 2.** Effect of temperature on polarization curves for acid only (1 M H<sub>2</sub>SO<sub>4</sub>).



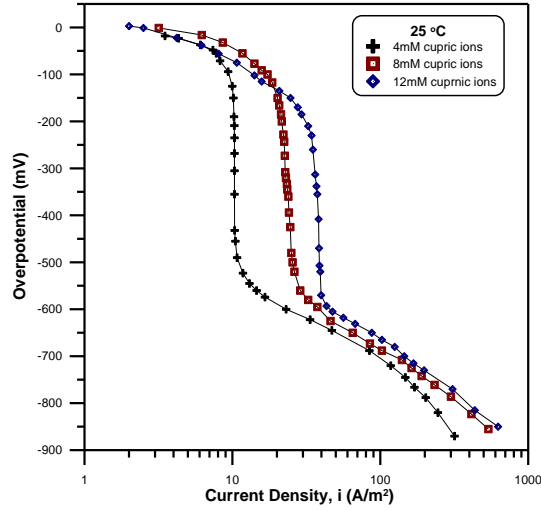


Figure 3. Effect of cupric ions concentration on polarization curves of electrolyte solution at 25 °C.

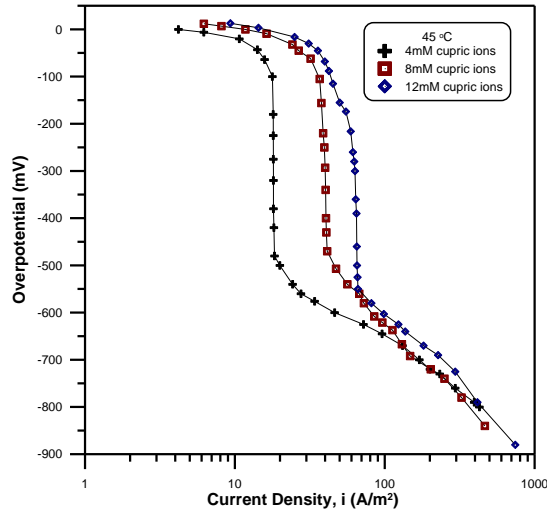
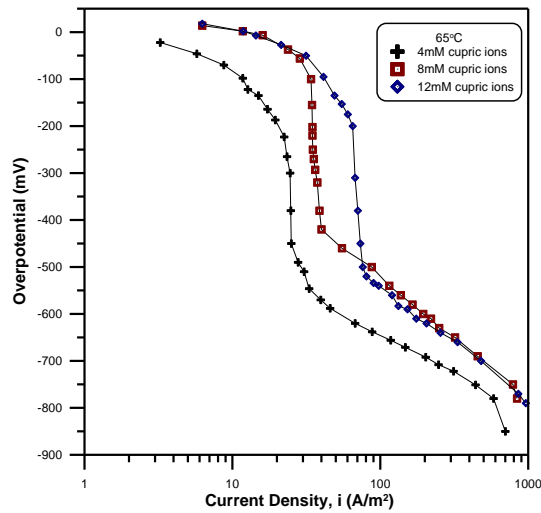
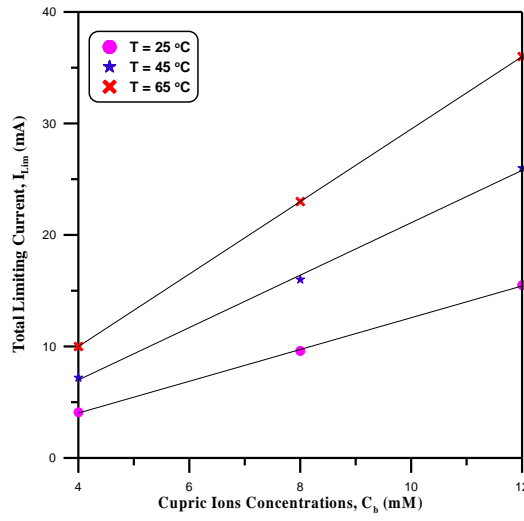


Figure 4. Effect of cupric ions concentration on polarization curves of electrolyte solution at 45 °C.

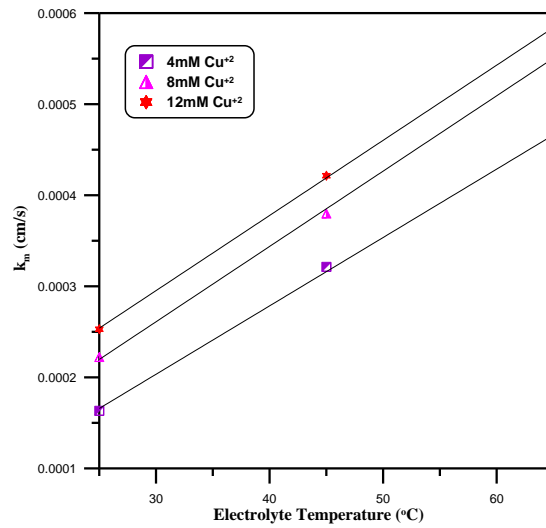




**Figure 5.** Effect of cupric ions concentration on polarization curves of electrolyte solution at 65 °C.



**Figure 6.** Effect of cupric ions concentration on the Limiting current at different temperatures.



**Figure 7.** Mass Transfer coefficients vs. electrolyte temperatures at different cupric ions concentrations.

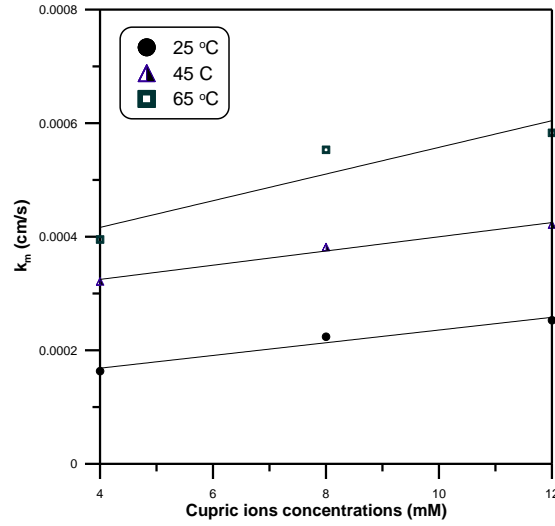


Figure 8. Mass Transfer coefficient vs. cupric ions concentrations at different Temperatures.

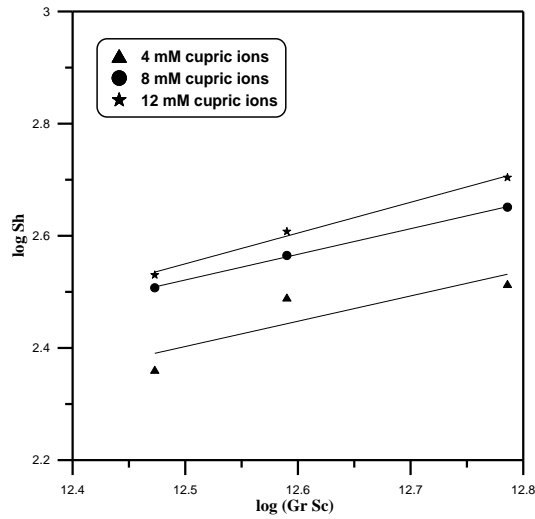


Figure 9. The relationship between Sh vs. Gr\*Sc.

Table 2. Values of dimensionless group (Sh, Gr, and Sc) at different operating conditions.

T °C	Cu <sup>+2</sup> Conc. mM	Sh	Gr × 10 <sup>-9</sup>	Sc
25	4	326.6844	1.9	3212
	8	447.8738		
	12	505.8339		
45	4	309.0531	3.33	1166
	8	367.3173		
	12	405.3156		
65	4	229.7574	5.32	559
	8	321.6603		
	12	339.0198		