

Copper Refining Electrolysis at High Current Densities

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In this study, the possibility of utilizing high current densities in copper refining electrolysis was investigated in relation to the cell design along with the surface characteristics of cathode material, and the changes observed in cell potential depending on the working conditions. Two groups of experiments were conducted. The first series of copper refining electrolyses were carried out without any additives to the bath whereas in the second series, the effect of glue, thiourea, and chloride additions to the bath on cathodic copper was examined. Electrolysis conditions, in accordance with industrial practice, kept constant in both sets of experiments and were as follows: 45 g Cu²⁺/L, 150 g H₂SO₄/L, 55 °C, electrolyte circulation of 15-20 L/min, anode dimensions of 78×74×4.5 mm, copper cathode of 47×85×0.1 mm, current density of 700 A/m², and the aforesaid additives. Lab-scale high current density copper refining electrolysis was carried out in a specially designed cell with a unique electrolyte feeding system and small amount of additives to the bath, resulting in considerably high current efficiencies (≈99%).

Keywords: High current densities, copper refining electrolysis, surface characteristics

1. Introduction

Electronics industry, in particular, has always been highly reliant on for the ultra pure copper, which can be obtained by the electrorefining of copper. The main target aimed by the refining process is twofold: the first is the elimination of conductivity drop caused by the impurities that copper contains, and the second is the recovery of precious metals and other metallic values present in anode slimes, accumulated in the cell during the electrolysis operation [1]. Refined copper production is considerably increased within the last years, both from primary and secondary raw material sources, as a result of the progresses achieved in copper production technologies. These advances aim at lowering the capital costs, while improving plant conditions and cathode quality through enhanced bath designs [2].

Elkington filed the first patent application in copper refining, in 1865 [3, 4]. In 1876, the first copper electrolysis cells became operational by Wohlwill in Hamburg, Germany [4]. Various methods have been tried out ever since, to decrease the cost of operation while increasing the production rate [3]. One of these methods was to increase the current density, giving compact and homogeneously formed copper at the cathode surface [4]. Conditions of the conventional cop-

per refining electrolysis can be summarized as follows: 35–45 g Cu²⁺/L, 150–200 g H₂SO₄/L, electrolyte temperature of 55–65 °C, current density of 160–400 A/m², electrolyte circulation of 15–20 L/min, cell materials of PVC, PbSb6 or pure lead anode [4, 5]. Current density of the refining process depends on the purity of anode copper, plant capacity and the cost of electrical energy. Industrial copper electrolysis plants work at current densities of between 160-400 A/m². Anodic reaction and the surface quality of cathode copper is attempted to be controlled by varying the current density and additives, such as gum arabic, gelatin, thiourea, chloride ion, etc. [4-7].

Forms of multi-crystal metal deposition on cathode surface can be categorized in four groups: [8]

1. Field-oriented isolation type (FI),
2. Matrix-oriented reproduction type (MR),
3. Field-oriented texture type (FT),
4. Un-oriented dispersion type (UD)

All these four types are affected by the circulation of the electrolyte and the current density applied [4]. Increasing current densities cause both FT and UD type of crystals to form, while FI and MR type (dendrite formation) of deposits

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Table 1

Advantages and disadvantages of copper electrolyses carried out at high current densities [4].

Advantages	Disadvantages
<ul style="list-style-type: none"> • relative increase in productivity • decrease in metal stocks • decrease in investment costs • decrease in work/time efficiency • savings in electrolyte heating 	<ul style="list-style-type: none"> • increase in operational costs • increase in energy consumption • decrease in current efficiency • decrease in cathode quality • precious metal losses • danger of passivation • vigorous mixing

Table 2

Composition of the copper anode (in %)

Cu	Ni	Pb	Ag	As	Sb	O
99.1-99.6	0-0.5	0.05-0.1	0.02-0.1	0.02-0.3	0-0.1	0.1-0.3

are generally observed at low current densities [8]. However, working at high current densities brings up the importance of hydrodynamic conditions of cell design. Table 1 summarizes up and downsides of copper electrolysis operations carried out at high current densities. It is possible to reach the optimum conditions by choosing the right parameters on technical and economical basis.

2. Experimental

The optimum conditions for obtaining compact, homogeneous, and smooth-surfaced electrolytic copper metal by the high-density copper refining electrolysis are investigated by the two series of experiments: with and without additives. Composition of the copper anode (78×74×4.5 mm in dimensions) is given in Table 2.

Cathode starting sheet used was an electrolytic copper leaf in 85×45×0.1 mm dimensions. Electrolyte composition of 45 g Cu²⁺/L and 150 g H₂SO₄/L, and electrolyte temperature of 55 °C was kept constant throughout the experimental study. Anode-cathode spacing was 25 mm in the electrolytic cell (5 L volume) where one cathode sheet (surrounded by two anodes) was used. Current density applied was 700 A/m². A peri-

static pump (Multifix) circulated the electrolyte, whereas surface activators were fed to the electrolyte with a dosage pump, continuously. D.C. power supply (Ruhstrat), worked either potentiostatically or galvanostatically, delivered the required power. Anodic and cathodic polarizations were measured with the help of electrolytic copper wires placed in luggin capillaries. Electrolyte temperature was kept constant at a desired value within a precision of ±0.1 °C by circulating it through a series of two heat exchangers. All the acids, salts and surface activators used in the experiments were analytical grade.

Fig. 1 displays the schematic of the experimental setup in which electrolyte was circulated vigorously within the electrolysis cell. Contrary to the conventional electrolysis cell, electrolyte is fed to cell through the holes (1 mm I.D.) of a Plexiglas[®] pipe placed at the bottom of the cell. A scanning electron microscope (JEOL JSM 5410) is utilized to investigate surface characteristics of the copper deposit.

3. Results and Discussion

Experiments carried out in this investigation can be grouped in two categories:

a) the ones which do not provide any additives to the cell, and

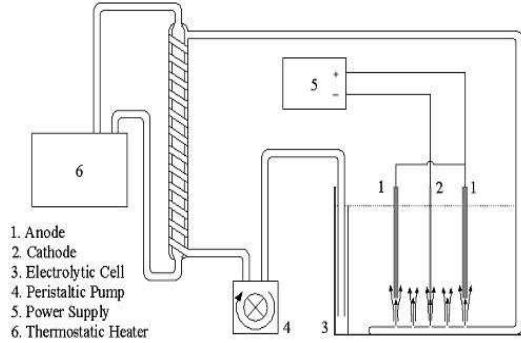


Figure 1. Electrolysis cell used in the experimental study.

b) those with the additives such as, gum arabic, thiourea, and chloride.

3.1. Without the Additives

Polarization curves and cell potential values of the refining electrolysis experiments, run at 700 A/m^2 current density and with no surface activator addition are given in Fig. 2. A field oriented type crystal growth is observed on the cathode surface at the end of 8-hour-electrolysis indicating that the growth mechanism was grain based owing to the insufficient nuclei formation as a result of the low polarization values. A SEM micrograph of copper deposit, showing a smooth and fine grain structure, is seen in Fig. 3.

As seen in Fig. 2, the time-dependent variations in anode and cell potentials are rather small. The peak observed in cathode potential the 180^{th} minute, corresponds to the enlarged distance between the luggin capillary and the cathode surface as a result of the increased electrolyte circulation velocity. The increase detected on anodic polarization however, designates an augmented anode slime thickness, which causes diffusion overvoltage to elevate. Cell potential values, on the other hand, show a rather steady trend.

3.2. With the Additives

Effects of surface activators on polarization curves are seen in Fig. 4, 5, and 6, for 30, 60, and 90 g/t gum arabic and thiourea additions, respectively. Fig. 7, however, displays the re-

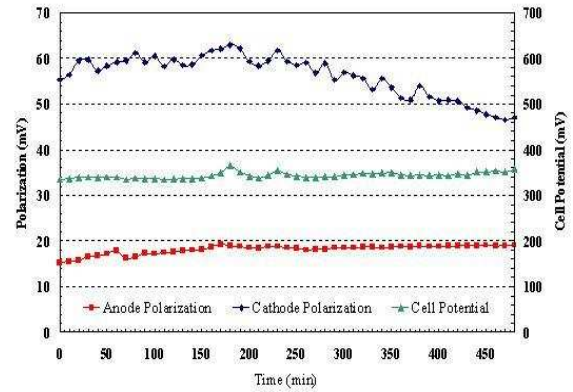


Figure 2. Polarization curves and cell potential values observed in experiments where no additives are used [$45 \text{ g Cu}^{2+}/\text{l}$, $150 \text{ g H}_2\text{SO}_4/\text{l}$, 55° C , 8 h].

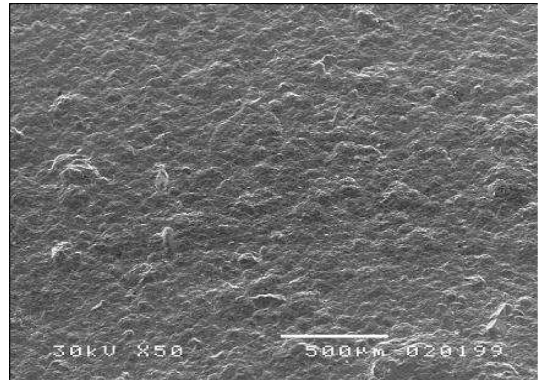


Figure 3. SEM micrograph of copper deposit obtained ($45 \text{ g Cu}^{2+}/\text{l}$, $150 \text{ g H}_2\text{SO}_4/\text{l}$, 55° C , 8 h.)

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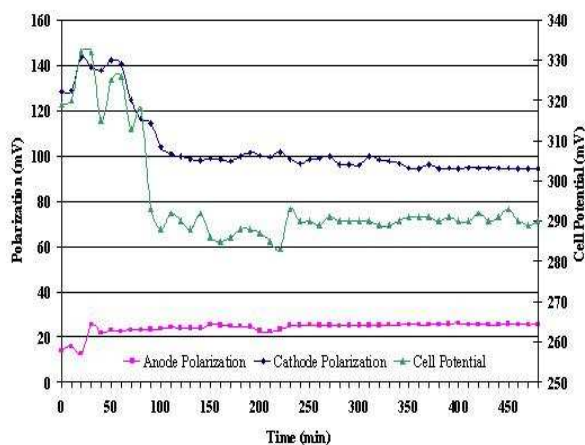


Figure 4. Experiments run with 30 g/t gum arabic and thiourea additions [45 g Cu^{2+} /l, 150 g H_2SO_4 /l, 55 °C, 8 h].

sults of the experiment where 120 g/t gum arabic and thiourea, and 30 mg/l chloride additions were made to the cell. The differences observed between the results of experiments with and without any additions can be summarized as follows:

1. In order to make a comparison, amounts of the additives are selected to be within a close range to the ones practiced in conventional electrolysis. It is recognized that the additives must be used scarcely in higher current density electrolyses.
2. The increase observed in anode polarization curves in Fig. 4 stems from the passivation of anode. No remarkable change is perceived in anode polarization for the later part of the experiment.
3. Cell and cathode potentials increase notably with the increasing amounts of additives, although the same behavior is not observed in anode potential values. Expected improvements on the quality of cathode surface by the additions of gum arabic and thiourea, might as well be attained by the experiments where no addition was made, which implies the dominant effect of forced convection (see Fig. 1).
4. Increases are observed in both cell and cathode potentials, in the range of millivolts,

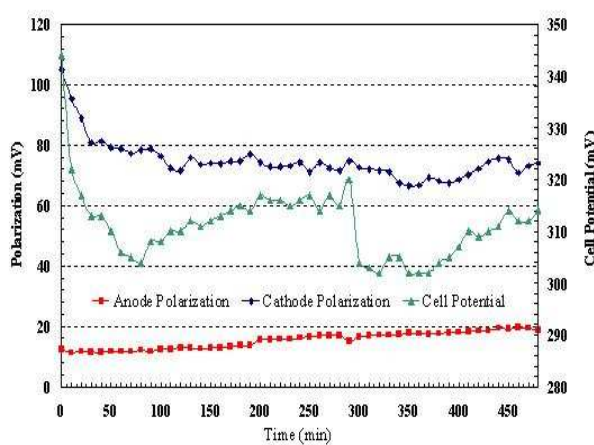


Figure 5. Experiments run with 60 g/t gum arabic and thiourea additions [45 g Cu^{2+} /l, 150 g H_2SO_4 /l, 55 °C, 8 h].

when chloride addition was made, besides gum arabic and thiourea (Fig. 7).

5. It is clearly visible from the results that the amount of additives must be decreased at higher current densities, for the benefit of surface quality of the cathodes.

4. Conclusion

The possibility of applying high current densities in conventional copper refining electrolysis is investigated by the lab-scale experiments. High current efficiencies are attained (99%) through some changes in the design of electrolyte feeding system. Uniform, compact, and smooth cathode surfaces are obtained both with and without additives at the end of 8-hour-electrolysis experiments. In contrast to the anode polarizations of below 20 mV, cell potentials of 350 mV are reached. The power consumption required for this lab-scale copper refining electrolysis experiments was found to be between 285 and 340 kWh/t Cu, expectedly high as a result of applying high current density. Cathode surfaces are examined with naked eye and found out that the quality was decreasing with increasing additive usage. Investigating the surface quality of the cathodes by the semi-pilot-/pilot-scale experiments, for periods of

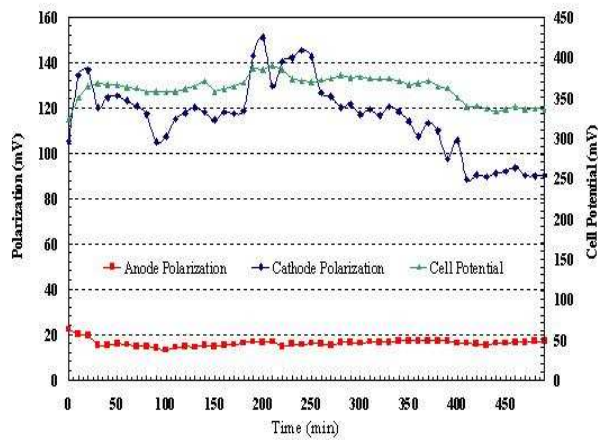


Figure 6. Experiments run with 90 g/t gum arabic and thiourea additions [45 g Cu^{2+} /l, 150 g H_2SO_4 /l, 55 °C, 8 h].

longer than 8-hour and under existing hydrodynamic conditions might prove the good performance of newly developed electrolyte feeding design. There was no contamination of the cathode surface by the flowing of anode slime (rapid circulation), which is described as a disadvantage at high current densities.

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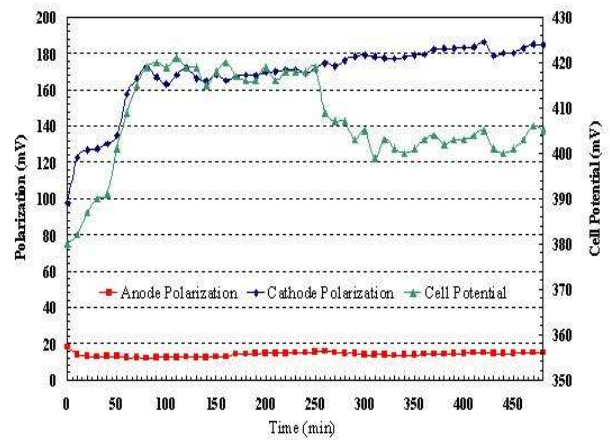


Figure 7. Experiments run with 120 g/t gum arabic, thiourea, and 50 mg/l chloride additions [45 g Cu^{2+} /l, 150 g H_2SO_4 /l, 55 °C, 8 h].

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