

Chronopotentiometric Studies on the Passivation of Industrial Copper Anode at Varying Current Densities and Electrolyte Concentrations

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Received: 28 December 2007 / Accepted: 12 January 2008 / Online published: 20 February 2008

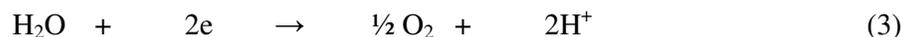
Industrial copper anodes are subjected to chronopotentiometric studies in order to study the passivation effects in the acidic copper sulphate electrolyte solutions. The aim of this investigation is to determine the optimum conditions to recover pure copper from copper alloy scrap by refining electrolysis. The copper anode is actually made from the industrial scrap. The composition of the industrial copper anode is: Cu, 96.66 wt. %, Ag, 2.54 wt. % and Zr, 0.8wt. %. The chronopotentiometric studies are done at current densities of 0.02, 0.04, 0.06 and 0.07 A Acm⁻² and 60, 100, 140 and 180 gl⁻¹copper sulphate solutions. The tendency of the anode to passivate is high in the applied current densities of 0.06 and 0.07 Acm⁻²; 100/ 140 gl⁻¹ copper sulphate concentration in the electrolyte is found to be ideal for copper recovering process.

Keywords: Chronopotentiometry; Industrial copper anodes; Copper recovery; Anode passivation; Acidic copper sulphate electrolytes

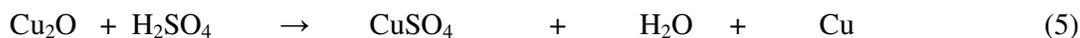
1. INTRODUCTION

Copper refining electrolysis in acidic copper sulfate electrolytes is a well documented process that has been used in commercial scale in industries to recover copper in pure form. The anode is the impure metal and the impurities must be lost during the passage of the metal from the anode to the cathode during electrolysis. Metallic copper is deposited at the cathodes, while the water molecules are decomposed at the anode to produce oxygen. Sulphuric acid is regenerated in the solution, which is recirculated [1, 2]. The electrolysis of copper may be described as follows:





In the production of copper, in order to produce a cast anode that is dimensionally consistent and smooth-surfaced, some oxygen must be present in the molten anode copper. Typically, about 0.1-0.3% oxygen is present, for the most part as cuprous oxide (Cu_2O). During the electrorefining process, contact of the Cu_2O with sulfuric acid in the electrolyte results in its partial dissolution:



Because dissolution is chemical rather than electrochemical, this dissolved copper builds up in the electrolyte. Precipitation of this non-conducting copper sulfite layer on the anode surface due to supersaturation of the electrolyte has been considered as one of the reasons for passivation. Passivation of anodes is affected by the composition of the anode and electrolyte concentration as well as the temperature and electrolyte circulation rate. Impurities such as Se, Te, Bi, As, Sb, S, Ni, Ag and Au also affect the anode passivation even in very low concentrations [3]. Dissolution of anodes decreases or even stops due to passivation phenomenon and subsequently it results in high energy consumption as well as in increments in residue scrap and voltage levels.

Several authors have focused their investigation on the effect of additives on passivation in laboratory scale. Addition of organic compounds such as ethylenediamine tetra-acetic acid (EDTA), diethylene diamine penta-acetic acid (DTPA), triethylene diamine hexa-acetic acid (TTHA), aromatic nitro compounds and miscellaneous additives like glue, thiourea, avitone, percol and chloride ions were also studied as inhibitors to prevent the passivation of copper anodes [4-8]. Using chronopotentiometry, it was shown that thiourea and glue in low concentrations (≤ 2 ppm) and chloride ions in 40 ppm concentration retarded passivation by increasing the passivation time of the anode [9]. These additives form complex with Cu^+ ion so that the concentration of cuprous ion at the double layer decreases so that the following disproportionation reaction may be prevented:



In the absence of additives, copper powder enters the slime; in our copper refining process, we found nearly 10 wt% of copper among the silver slime in the absence of additives in the electrolyte.

According to Faraday's law there are two approaches to enhance the productivity of the electrorefining process; increase in current density and surface area of the electrode. Both aid in increasing productivity. Increasing the surface area necessitates the enlargement of the cell dimensions and therefore an increase in electrolyte volume. On the other hand, increasing current density without increasing electrolyte volume, results in higher production costs, but has some disadvantages such as low purity and undesired morphology of cathode and detrimental phenomenon

of anode passivation [3]. The aim of the present work is to study the passivation of copper alloy anode at various applied current densities and copper sulphate concentrations (constant acid concentration) by using the chronopotentiometric (CP) technique. This research work was undertaken in order to understand the voltage changes (fluctuations) observed during the copper refining electrolysis carried out in our lab. To optimize the conditions, various current densities were selected for a particular concentration and chronopotentiometric studies were done. At a chosen current density, effect of varying copper sulphate concentrations on the passivation of copper anode was also carried out.

2. EXPERIMENTAL PART

All electrochemical experiments were conducted with a PGSTAT 302 Autolab system (Ecochemie, Utrecht, The Netherlands). It was connected to a PC running with Eco-Chemie GPES software. GPES software was used for all electrochemical data analysis. The reference electrode was Ag/AgCl (3M KCl) and the counter electrode was a pure copper sheet. The working electrode was the copper anode (CA). A three electrode cell assembly was used. 1 cm² area of the working electrode was exposed to the electrolyte solutions. The cell design (Flat Cell: Wear and Friction Tech, Chennai, India) is such that only 1 cm² of the working specimen will be exposed to the solution irrespective of the dimension of the electrode.

The following three electrolyte solutions were used for CP measurements: (1) CuSO₄.5H₂O, 180 g l⁻¹ ; Conc. H₂SO₄, 100 ml l⁻¹; (2) CuSO₄.5H₂O, 100 g l⁻¹ ; Conc. H₂SO₄, 100 ml l⁻¹; (3) CuSO₄.5H₂O, 60 g l⁻¹ ; Conc. H₂SO₄, 100 ml l⁻¹. The applied current densities were: 0.02, 0.04, 0.06 and 0.07 A cm⁻². The composition of the industrial copper alloy anode was: Cu, 96.66 wt. %, Ag, 2.54 wt. % and Zr, 0.8wt. %.

3. RESULTS AND DISCUSSION

3.1. Effect of various applied currents densities

Chronopotentiometry has been found to be a useful and sensitive electrochemical technique to screen the additives that inhibit passivation of copper anode during the copper refining electrolysis in acid electrolytes. Application of constant current commences the dissolution of copper anode which results in the first region of the chronopotentiogram. If there is no passivation, then the E-t curve would be a straight line parallel to X-axis under the basic assumption that there are no interferences. However, in reality such a thing seldom happens. Fig. 1 shows the chronopotentiograms recorded under the applied current densities of 0.02 and 0.04 A cm⁻² in the electrolyte of 180 g l⁻¹ CuSO₄ 5H₂O and 100 ml of conc. H₂SO₄. The time required to dissolve 100 mg of copper anode for each applied current was calculated, as per Faraday's law, and fixed as the time limit of electrolysis. For example, the duration of electrolysis was 15060 seconds in the case of 0.02 A and 7540 seconds in the case of 0.04 A and the starting potentials were 0.14 and 0.185 V vs. Ag/AgCl respectively. This potential jump was in response to the overpotentials generated on the application of current. Under these applied currents, passivation of copper anode did not occur and one could consider that these currents can be

safely applied for copper electrolysis in 180 g l^{-1} copper sulphate bath. The chronopotentiograms reveal a gradual and slow increase of potential with time and E-t curve is not a straight line but a bumpy one indicating that the copper concentration at the anode surface varies with time. Mass transfer of copper from the anode predominantly occurs by diffusion because convection is limited in the Nernst boundary layer and migration is hindered by copper's small transport number in these solutions [4].

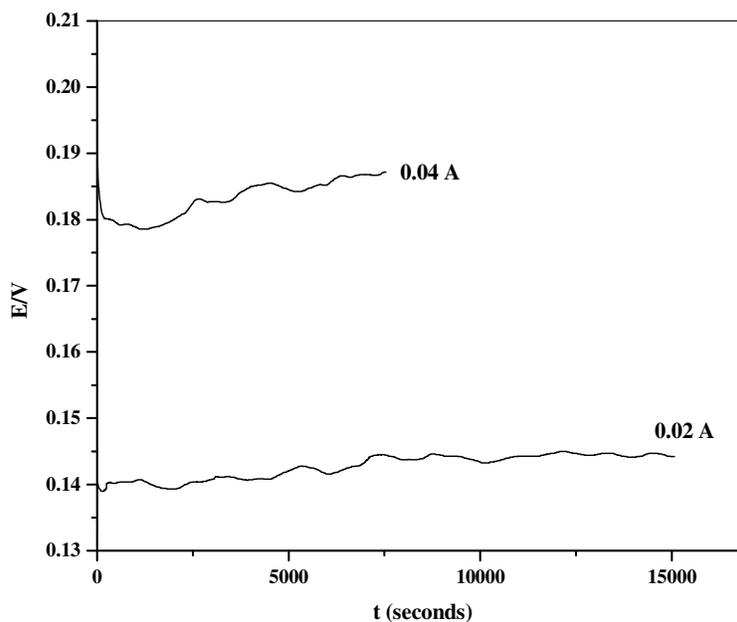


Figure 1. Chronopotentiograms of copper alloy recorded at the constant current densities of 0.02 and 0.04 A cm^{-2} ; Electrolyte concentration: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 180 g l^{-1} ; H_2SO_4 , 100 ml l^{-1} .

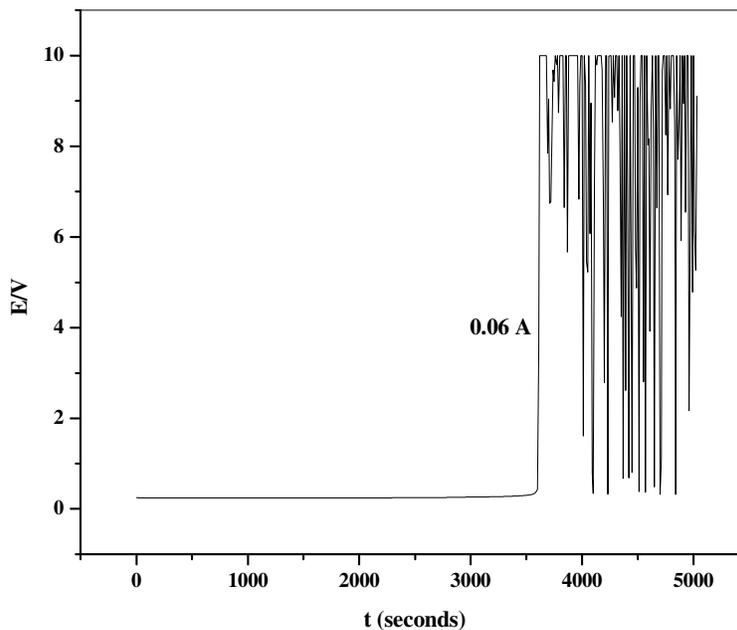


Figure 2. Chronopotentiogram of copper alloy recorded at the constant current density of 0.06 A cm^{-2} ; Electrolyte concentration: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 180 g l^{-1} ; H_2SO_4 , 100 ml l^{-1} .

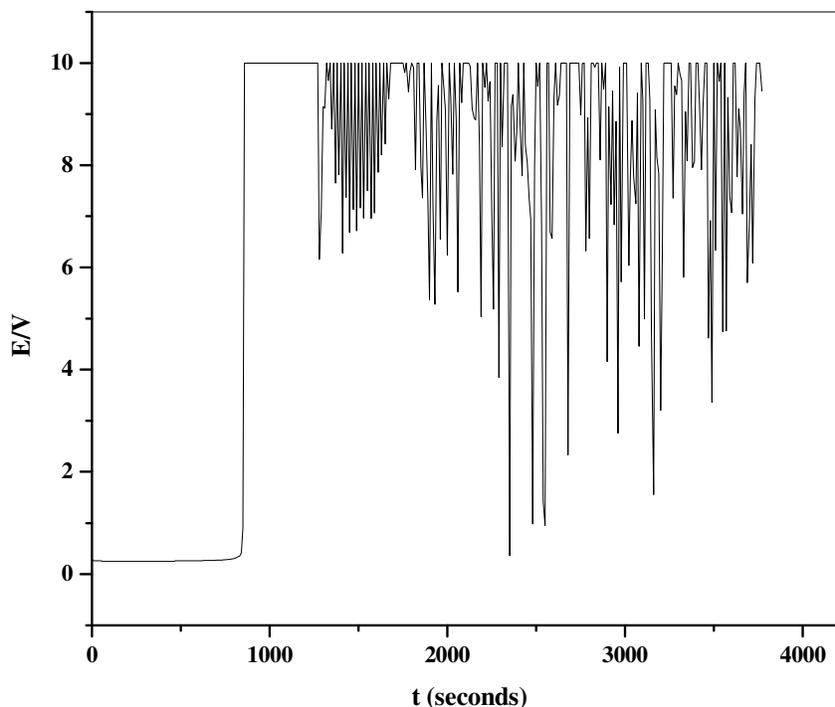


Figure 3. Chronopotentiogram of copper alloy recorded at the constant current density of 0.07 Acm^{-2} ; Electrolyte concentration: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 180 g l^{-1} ; H_2SO_4 , 100 ml l^{-1} .

Figs. 2 and 3 shows the E-t curves at still higher current densities of 0.06 Acm^{-2} and 0.07 Acm^{-2} respectively. In these curves, one could see that the passivation of the anode commences at around 3600 seconds after the passage of 0.06 A while it starts earlier at around 840 seconds at 0.07 A. Passivation of the anode is indicated by the sudden rise in potential followed by large potential anomalies subsequently. At these higher current densities, one expects a higher rate of anodic dissolution which in turn leads to the accumulation of cupric ions at the anode surface. The supersaturation of the electrolyte tends to precipitate non-conducting copper sulphate which forms a layer on the anode surface, thus rendering it passive. The relative decrease in passivation time between 0.06 and 0.07 A currents confirm this point. From these observations, it is obvious that 0.04 A current could be ideal for the copper refining electrolysis.

3.2. Effect of copper sulphate concentrations at constant current

Chronopotentiograms were recorded at four different concentrations of copper sulphate in the electrolyte bath. The current applied was kept constant at 0.04 A and the time window was limited to 7540 seconds for each experiment. Fig.4 shows the chronopotentiogram of CA at $180 \text{ g l}^{-1} \text{ CuSO}_4$ concentration. This was the highest concentration considered. The starting potential was around 0.189 V on the application of current but the potential drops down to 0.184 V within a matter of few seconds. This drop in potential is a sign of commencement of copper dissolution. As the electrolysis prolongs, the potential increases gradually up to 3000 seconds and then it started increasing more steeply around

3500 seconds. Then the rest of time window indicates an array of peaks within the potential range of 0.191 to 0.196 V.

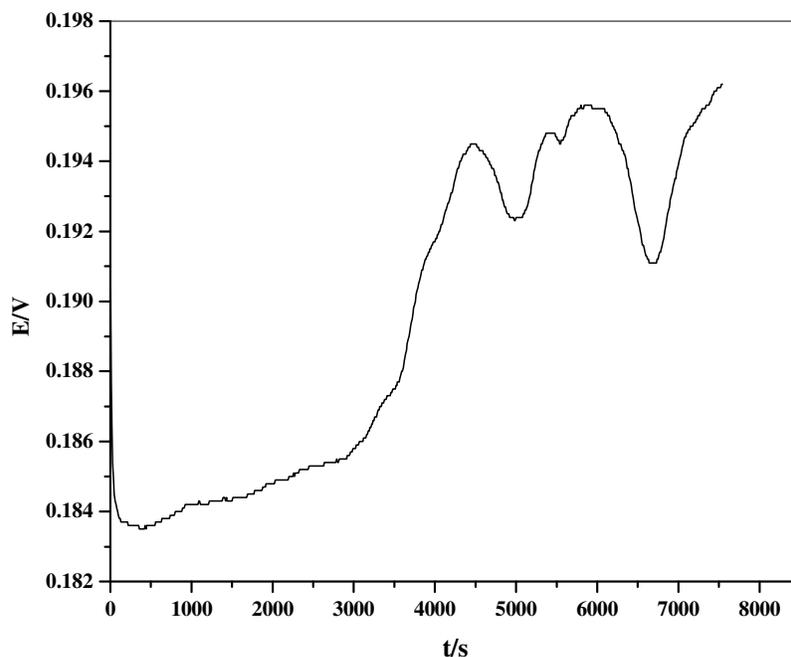


Figure 4. Chronopotentiogram of copper alloy recorded at the constant current density of 0.04 Acm^{-2} ; Electrolyte concentration: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 180 g l^{-1} ; H_2SO_4 , 100 ml l^{-1} .

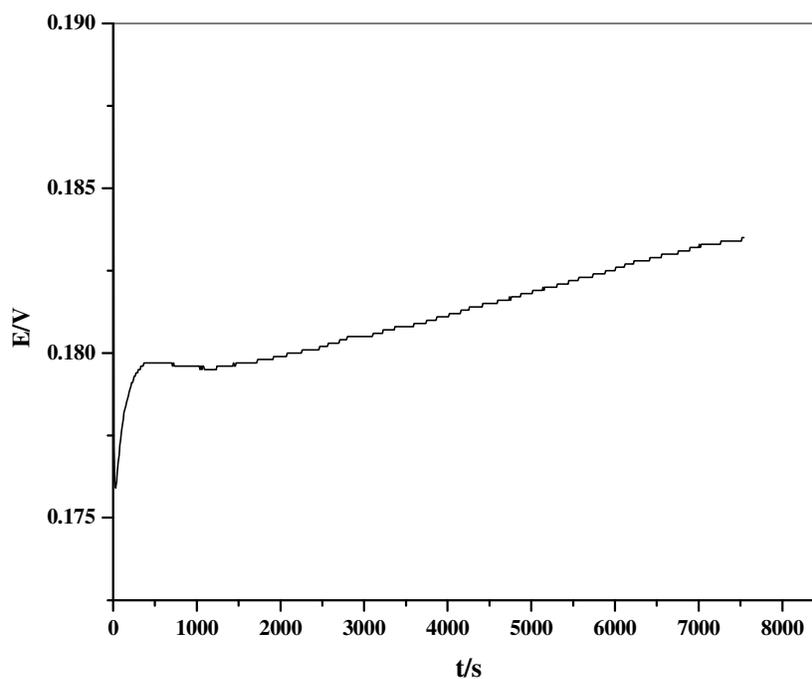


Figure 5. Chronopotentiogram of copper alloy recorded at the constant current density of 0.04 Acm^{-2} ; Electrolyte concentration: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 140 g l^{-1} ; H_2SO_4 , 100 ml l^{-1} .

Fig. 5 shows the chronopotentiogram of CA at 140 g l^{-1} CuSO_4 concentration. The start potential shifted to negative direction with decrease in the concentration of copper sulphate in the bath. It was around 0.176 V . Then the potential started increasing and reached a saturated limit at 500 seconds. The potential jump was ca. 50 mV and around 0.18 V , it remained as a constant value up to 2000 seconds. Again the slope increased gently and continuously.

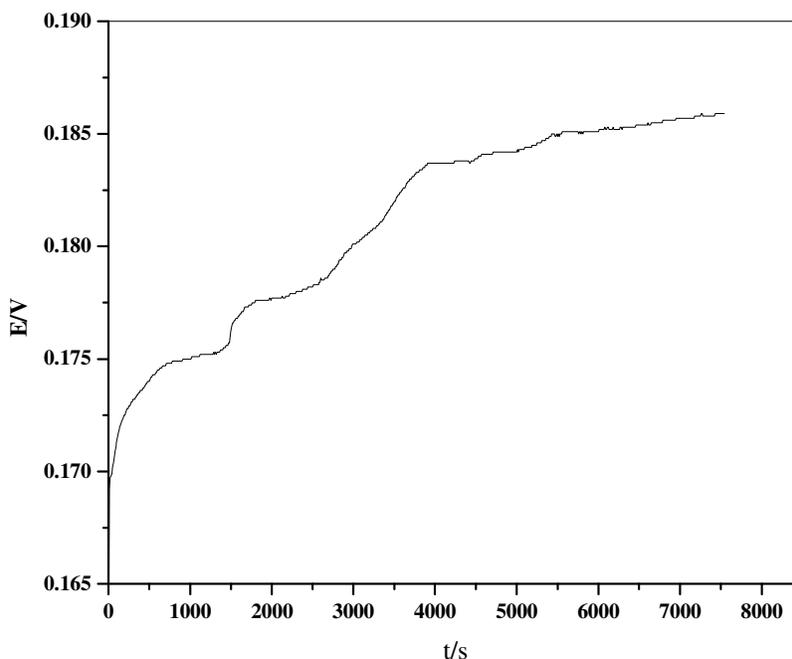


Figure 6. Chronopotentiogram of copper alloy recorded at the constant current density of 0.04 A cm^{-2} ; Electrolyte concentration: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 100 g l^{-1} ; H_2SO_4 , 100 ml l^{-1} .

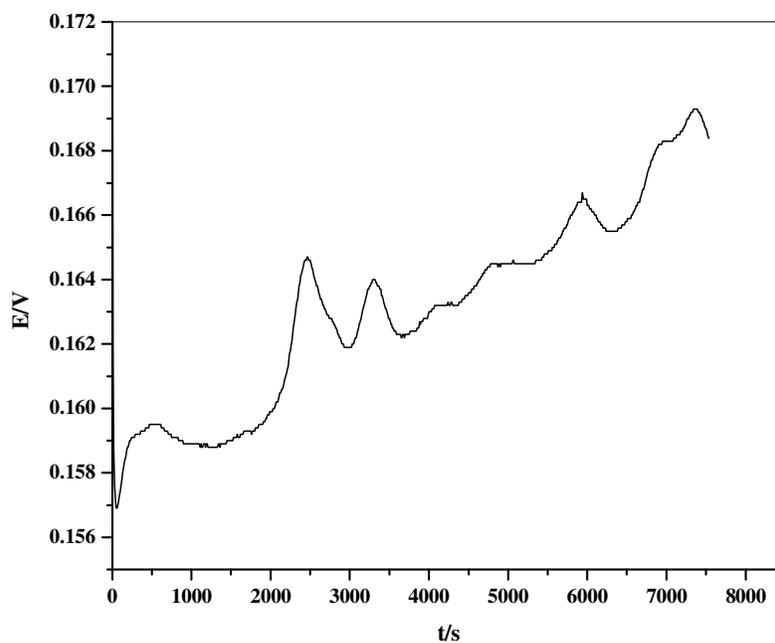


Figure 7. Chronopotentiogram of copper alloy recorded at the constant current density of 0.04 A cm^{-2} ; Electrolyte concentration: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 60 g l^{-1} ; H_2SO_4 , 100 ml l^{-1} .

Fig. 6 shows the chronopotentiogram of CA at $100 \text{ gl}^{-1} \text{ CuSO}_4$ concentration. The starting over potential was about 0.17 V ; this value did not differ much from the value derived from $140 \text{ gl}^{-1} \text{ CuSO}_4$ concentration as shown in Fig. 5. The main difference in behavior was the change in potential with time; while the potential reached a limiting value in the $140 \text{ gl}^{-1} \text{ CuSO}_4$ case within a few seconds, in the diluted solution the limiting value in potential was achieved only after the electrolysis was carried out for 4000 seconds. The potential gradually increased in the positive direction and reached a limiting value.

Fig. 7 shows the chronopotentiogram of CA at $60 \text{ gl}^{-1} \text{ CuSO}_4$ concentration. The E-t curve starts at much more negative potential of 0.157 V and started shifting towards positive potentials with an array of peaks and ends at 0.169 V during the time window of 7540 seconds. In this solution, cupric ion concentration was the lowest of all the solutions considered. More significantly, the curve didn't reach a limiting potential within the allotted time window.

The shift in anode start potential with electrolyte concentration is expected as per Nernst law. The influence of ionic concentration in the electrolyte on electrode potential is well documented. The well-known Nernst law is,

$$E = E^{\circ} + 0.059 \log [\text{Ox}] / [\text{R}]$$

Ignoring E° and for two solutions of ionic activities a and a' , with a corresponding potential of E_1 and E_2 respectively, the shift in electrode potential can be given by the following equation [10],

$$\begin{aligned} E_2 - E_1 (\text{V}) &= 0.059/n (\log a' - \log a) \\ &= 0.059/n \log (a'/a) \end{aligned}$$

Accordingly, for every tenfold decrease in ionic activity or approximately the concentration of the cations, the oxidation potential shifts by a value of $0.05915/n$ in the positive direction i.e the electrode potential becomes more positive. For bivalent cations like cupric ions ($n=2$), the electrode potential changes by 0.0296 V in the positive direction for every 10-fold dilution of concentration. In the case of anions, the dilution of solution concentration shifts the electrode potential towards negative potential. Such interpretations are valid in equilibrium conditions i.e under Nernst conditions where there is no charge transfer is involved. In the present work, starting from 180 gl^{-1} to 60 gl^{-1} copper sulphate concentration in the acidic electrolyte baths, chronopotentiograms recorded for the copper anode in these electrolytes show a negative trend in start potential from 0.189 to 0.157 V . At first sight, this result seem to violate Nernst law as the decrease in cupric ion concentration shifted the anode potential towards the negative direction instead of the expected positive direction. However it is not true in reality. As the acid added in each electrolyte was the same (100 ml^{-1}), pH or the concentration of protons invariably increases proportionally from 180 gl^{-1} to 60 gl^{-1} copper sulfate electrolytes. Such an increase would account for the shift of copper anode start potential in the negative direction.

On the application of constant current, the changes that occur at the Nernst boundary layer is monitored in the form of chronopotentiograms. These E-t curves reflect the functioning of copper

refining process in smaller dimensions. The rate at which copper can transfer across the Nernst boundary layer influences the anode dissolution and cathode deposition characteristics. The three main transport processes that occur during electrorefining are diffusion, convection, and ion migration. While natural convection plays a very important role within the bulk of the electrolyte, hydrodynamics predicts a stagnant layer at the electrode surface. This layer is referred to as the Nernst boundary layer. Transport across the boundary layer typically occurs by diffusion or migration. In the case of copper electrorefining, cupric ion migration is limited. This is indicated by its small transport number of 0.02. Therefore, diffusion is the major component of mass transfer across the boundary layer or double layer [3]. One could see the electrode potential increased in all the cases once the electrolysis started. The current efficiency of this process was almost 99% in all the electrolytes, irrespective of the cupric ion concentrations in the bulk electrolytes; this means that rate of dissolution of copper anode is equal to the rate of deposition of metallic copper at the cathode.

Of the four electrolytes, the electrolytes with 140 and 100 g l^{-1} copper sulphate are better options than the other two electrolytes. Higher concentration of cupric ions may in the prolonged electrolysis form copper sulphate which is undesirable whereas the lower concentration of cupric ions would reduce the diffusivity of cupric ions so that the efficiency of the process would decrease.

4. CONCLUSIONS

Chronopotentiometric studies on industrial copper anode in various applied current densities and copper sulphate concentrations reveal the following:

- Passivation of copper anode gets enhanced at higher current densities; in 180 g l^{-1} copper sulphate electrolyte, the passivation starts around 3600 seconds for 0.06 A cm^{-2} and around 840 seconds for 0.07 A cm^{-2} .
- Passivation did not occur at 0.02 and 0.04 A cm^{-2} in the time window of 15060 seconds in the former case and 7540 seconds in the latter case.
- Anode start potential shifted in the negative direction with decrease in copper sulphate concentration in the electrolytes.
- On the onset of electrolysis (application of current), the copper anode potential shifted in the positive direction in all the electrolytes and current densities.
- Based on the anode tendency to passivate, 100 and 140 g l^{-1} copper sulphate concentration and 0.04 A cm^{-2} current density is found to be ideal for copper recovering process.

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