

Effect of Copper Electrode Geometry on the Electrical Characteristics of Electrolytic Analysis Cell Used for Pure Metal Production

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Abstract

In this work, the effect of geometry of copper electrode employed in electrolytic analysis cell used for metal purification was studied. These effects are apparent when studying the electrical characteristics of such cell as the geometry of the electrode determines the most important parameters of an electrolytic analysis cell; electric field and current density. Three different geometries of the electrodes were considered in this work. To produce mass amount of pure metal, large surface electrodes have to be used at reasonably higher concentrations of hydrochloric acid, while the variation of acetic acid concentration causes little variation in current density and hence produced amount of pure metal. Highly increasing rate of current densities would be achieved but the electrolyte would be changed to undesired or inapplicable form since the conductivity of the electrolyte is very sensitive to the changes in concentration. The electrolytic analysis cells are efficiently used to prepare highly pure metals in electrolyte solutions.

Keywords: Electrolyte analysis; Aqueous solution; Electrode geometry; Metal purification.

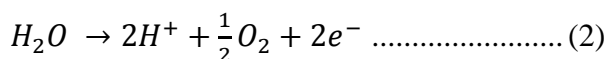
Introduction

Refinement of metals at large and small scale is commercially employing electrolytic processing and methods. Large-scale metals include copper, aluminum, nickel and zinc while small-scale metals include gold and silver nanoparticles. Such methods can be also used for the production of other metals such as titanium and lead [1-3]. However, these methods involve some challenges faced by continuous improvements and innovations. The collection of such methods is referred to as "electrometallurgy", which is made possible by the interactions of metals, electrons and liquids. The acquisition of electrons can be used for the reduction of metals dissolved as ions in liquid media [4]. The reduction reaction can be written in general form as:



A combination of thermodynamics and kinetics represents the fundamental of the metal reduction from the solution. Commercial processes of the electrometallurgy basically include an anode, a cathode and a power source in addition to the substances to be used [5]. As the reaction occurring at the anode represents a source of electrons, a metal reduction process occurs at the cathode making use of the electrons provided by the former reaction at the anode. These electrons

are drifted from anode towards cathode by the electric field applied between the two electrodes from a dc power supply through the aqueous medium – known as electrolyte – containing all provided ions [6]. Obviously, a common reaction occurred at the anode is water electrolysis as:



Oxidation of carbon or chloride mostly provides the electrons required for reduction in molten salt electrometallurgy. The electrons are provided from an impure anode in electrolytic refinement of metals [7]. In order to perform a metal reduction reaction as well as counter reaction, there is a specific voltage or half-cell potential [8].

Low potential metals are contaminated by the existence of higher potential metals, which preferentially accept electrons and deposit in the cathode as impurities. Therefore, careful electrolyte purification is required for lower potential metals to maintain cathode purity [9]. Similarly, reasonable efforts are required to ensure and improve the levels of electrolyte purity. Such requirement is going to be much more important as the levels of impurities increase and their removal becomes difficult [10].

A combination of the mass transport and the shift in potential with respect to half-cell

potential determines the rate of reduction/oxidation reaction whereas the energy required for electrons to move from the anode to the cathode is determined by the difference between the anode and cathode reactions in addition to the shift in potential and potential-related loss in resistance [11-12]. The total requirement of potential by the distance between the electrodes of an electrochemical cell is known as the cell voltage, which is within 0.2-0.4 volts for metal reduction in electrochemical refinement [13]. Deriving from Faraday's law, the energy consumed by an electrochemical cell is given by [14]:

$$\text{Energy} \left(kW \cdot \frac{hr}{ton} \right) = \frac{E_{cell}(n) \times 26800}{A_w \left(\frac{\beta(\%)}{100} \right)} \dots\dots\dots (3)$$

where E_{cell} is the total cell voltage, n is the number of electrons per mole of metal, A_w is the atomic weight (dimensionless) of the metal to be reduced, and β is the percentage of the total applied current, which is used for the reduction reaction of the desired metal. Typically, electrometallurgy requires energies for metal reduction higher than 1500 kW.hr/ton, which is required to be minimized by increasing the efficiency and decreasing the cell voltage [15].

Similar to copper, many nonferrous metals are refined and produced at high purities. Most copper in world markets is refined by electrolytic methods after been recovered by smelting. Different from zinc and nickel, copper recovery by electrolysis is used for almost all refined production because the industrial applications of copper in electrical conductivity purposes requires large-scale high-purity products of copper, which can be produced by electrolysis [16-17]. The large-scale refined production of copper is almost exclusively produced by electrolysis refining after the smelting of sulfide ores. Despite that electrolysis refining is the oldest method, it still dominant to produce copper cathodes [18-19].

In this work, effects of copper electrode geometry on the electrical characteristics of electrolytic analysis cell used for pure metal production were introduced. As well, the effect of acid concentration in the electrolytic solution was introduced in combination with the effect of electrode geometry.

Experiment

Electrolytic analysis cell was a Pyrex pool of 280mm in length, 115mm in width and 70mm in height. The electrolyte solution was prepared by diluting of hydrochloric acid in deionized water at different concentrations. Two electrodes of pure copper were placed inside the solution and fixed to the cover of the cell to prevent them from moving. They were separated by 240mm and connected to the dc power supply, which is regulated source over the range 0-30 volts with a fine step of 1 mV and maximum current of 5 A. The experimental setup is shown schematically in Fig.(1).

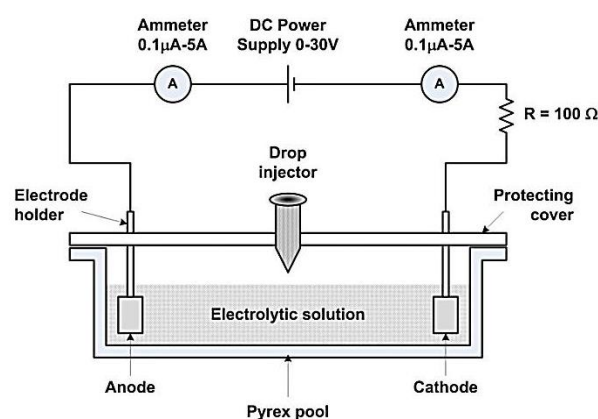


Fig. (1) Experimental setup of this work.

The setup was firstly calibrated by measuring the current in the external circuit in case of using only 500ml of distilled water and no current was measured over the full range of the dc power supply. Three different concentrations of HCl acid (25,50,75ml) were diluted in distilled water to form three different volumetric samples (5,10,15%). Similarly, three different concentrations of acetic acid (50,100,150mL) were diluted in distilled water to form 10, 20 and 30% solutions, respectively. The stock concentrations of hydrochloric and acetic acids were 1.6456 and 1.7468 mol/L, respectively. As well, three pairs of copper electrodes, different in shape and surface area, were used to introduce their effects on the experimental conditions.

Results and Discussion

Fig.(2) shows that increasing of acetic acid concentration in the electrolytic solution caused to shift upward the threshold voltage at which the current started to flow through the

electrochemical cell in case of using polygon copper electrodes. This is mainly attributed to the partial dissolving of acetic acid in water as the major amount of acid still as CH_3COOH molecules while only minority decompose into ions (cations and anions). Therefore, any increase in acetic acid concentration causes to decrease the number of these ions in the solution and hence requires more electric field (voltage over distance) to initiate and force the produced ions to move from an electrode to the other and create a current. Consequently, the maximum current flowing in the electrolytic cell is clearly affected by the concentration of acetic acid and decreased with increasing concentration.

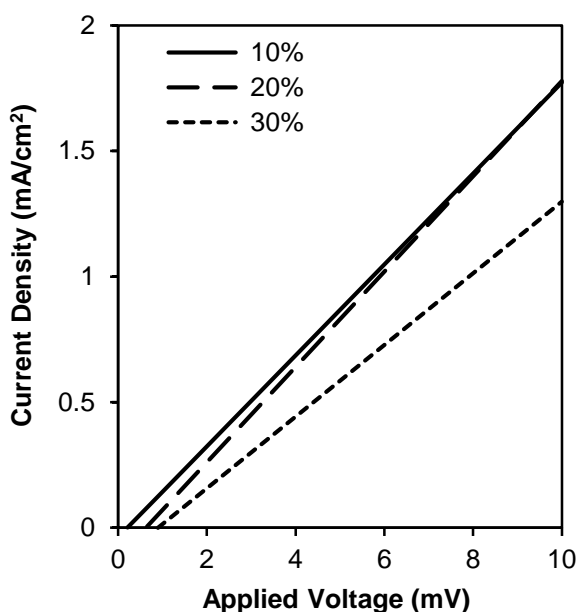


Fig. (2) Variation of measured current density in the electrolytic cell with the applied voltage at three different concentrations of acetic acid in the electrolytic solution.

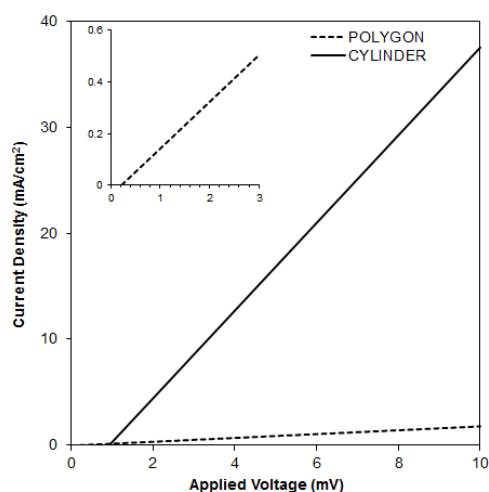
Fig.(3) shows a comparison between two different geometries of copper electrodes in terms of the variation of the measured current density with the applied voltage at different concentrations of acetic acid in the electrolytic solution of the electrochemical cell. As shown, the threshold voltage in case of cylindrical electrodes seems to be constant ($\sim 0.9\text{V}$) with increasing concentration, while it is shifted upward – as shown above – in case of polygon electrodes to be 0.215, 0.65 and 0.895V at concentrations of 10, 20 and 30%, respectively. This may be attributed to the distribution of

electric field between the cylindrical electrodes that decrease the effect of acid concentration in the electrolytic solution as the ions reaching each electrode are distributed symmetrically due to the circular cross section of the electrode.

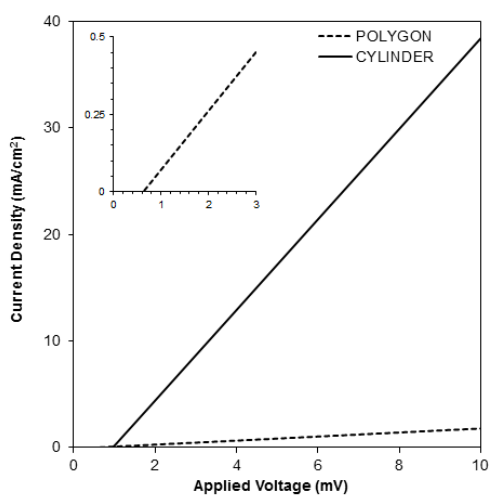
In case of polygon electrodes, the distribution of electric field causes ions reaching each electrode to locate at the vertices of the polygon surface, as shown in Fig.(4). As seen from Fig.(3), the maximum current density in case of cylindrical electrodes is more than 20 times that in case of polygon electrodes. This is due to two reasons; symmetry in distribution and smaller surface area [13].

In Fig.(5), general behavior of linearly increasing current density with increasing applied voltage to a maximum value at 1mV before decreasing exponentially at voltages larger than 1mV. As HCl acid completely dissolves in water, a large amount of ions (cations and anions) is provided to the electrolytic solution as the applied voltage grows from zero to 1mV, where the maximum current density is measured due to the flow of the majority ions. After then, the ions remaining in the solution are depleted exponentially until the minimum value of current density is reached.

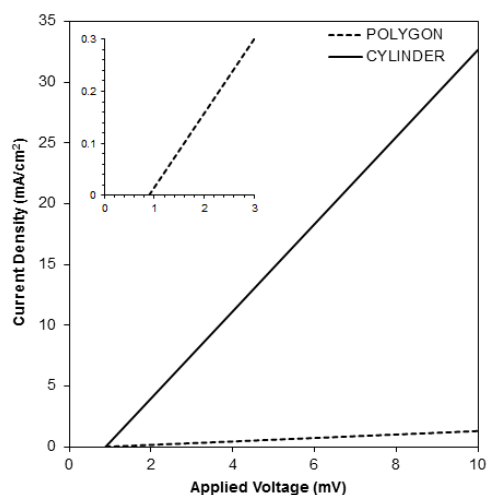
The maximum current density in case of using cylindrical electrodes is slightly affected by the variation of HCl concentration in the electrolytic solution, while a reasonable increase is observed in case of using polygon electrodes with increasing HCl concentration. However, the difference in current densities between two cases (geometries) is clear, which is attributed to the difference in the surface area.



(a)



(b)



(c)

Fig.(3) A comparison between two different geometries of copper electrodes in terms of the variation of the measured current density with the applied voltage at different concentrations of acetic acid in the electrolytic solution of the electrochemical cell (a) 10%, (b) 20% and (c) 30%.

The inset figures of the polygon electrodes shows that the current density is increased by 220% and 189% as the HCl concentration varied from 5% to 10% and from 10% to 15%, respectively, while much lower increases are observed in case of cylindrical electrodes. This can also be attributed to the geometry of the electrodes and the distribution of ions reaching them.

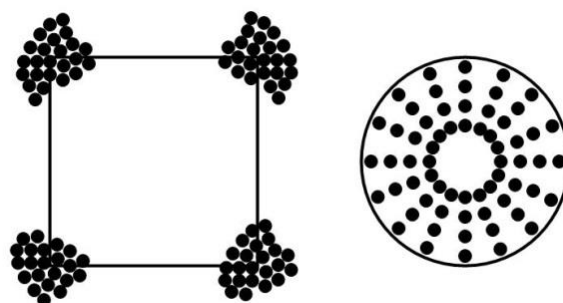
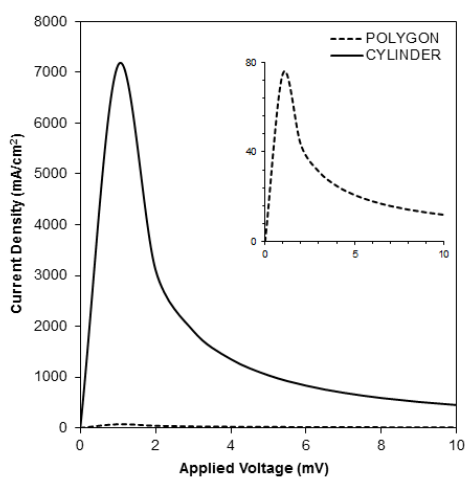
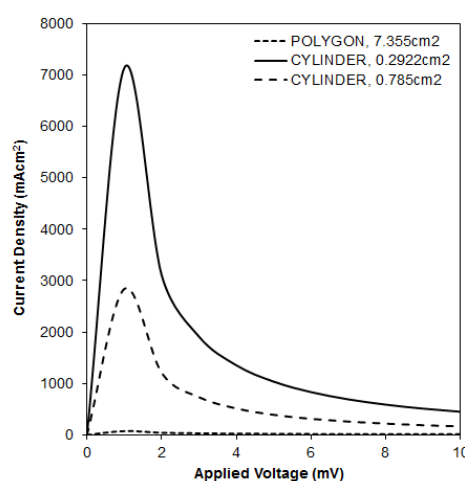


Fig.(4) Distribution of charged ions according to the geometry of electrode surface: polygon (left) and cylindrical (right).

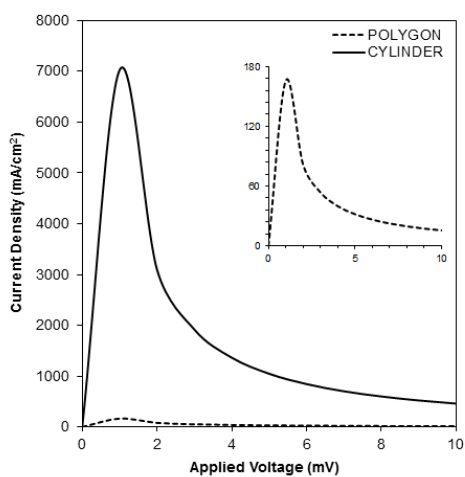
Fig.(6) represents the variation of measured current densities with applied voltage for three different geometries of copper electrodes in the electrochemical cell at different concentrations of HCl acid in the electrolytic solution. Obviously, the electrodes with smaller section area show higher current densities and lower sensitivity to the increase of HCl concentration. Both shape and geometry play the main role in raising the number of ions collected by the surface of electrode. Therefore, designing to obtain as much as possible current density imposes to use small surface area but at the expense of the pure metal production. On other hand, to produce mass amount of pure metal, large surface electrodes have to be used at reasonably higher concentrations of HCl acid. Here, highly increasing rate of current densities would be achieved but the electrolyte would be changed to undesired or inapplicable form since the conductivity of the electrolyte is very sensitive to the changes in concentration.



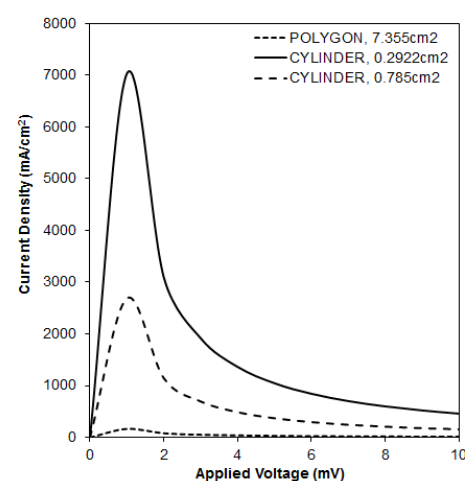
(a)



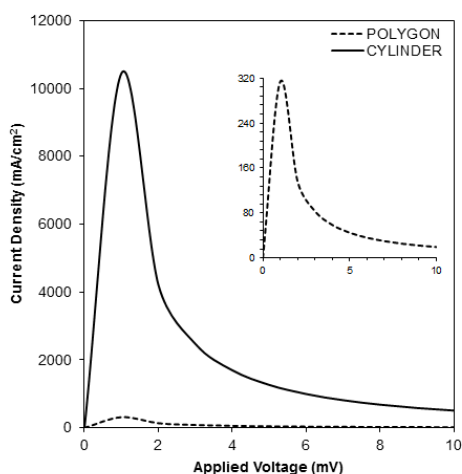
(a)



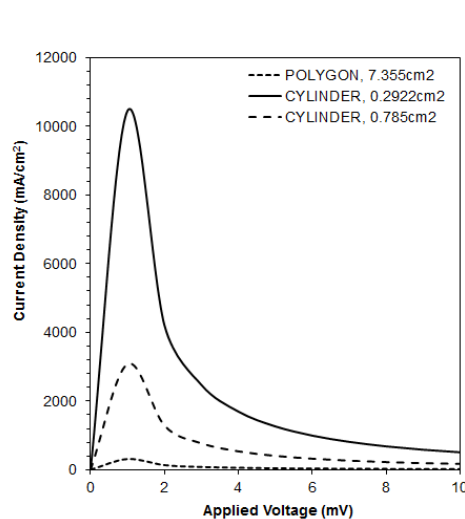
(b)



(b)



(c)



(c)

Fig.(5) A comparison between two different geometries of copper electrodes in terms of the variation of the measured current density with the applied voltage at different concentrations of hydrochloric acid in the electrolytic solution of the electrochemical cell (a) 5%, (b) 10% and (c) 15%.

Fig.(6) Variation of measured current densities with applied voltage for three different geometries of copper electrodes in the electrochemical cell at different concentrations of HCl acid in the electrolytic solution (a) 5%, (b) 10% and (c) 15%.

Conclusion

As can be concluded from the results presented in this work, threshold voltage at which the current started to flow through the electrochemical cell was shifted upward in case of using polygon copper electrodes due to the partial dissolving of acetic acid in water. However, threshold voltage was nearly constant with increasing concentration in case of cylindrical electrodes. The difference in current densities between two cases (geometries) is mainly attributed to the difference in the surface area. Both shape and geometry play the main role in raising the number of ions collected by the surface of electrode. Therefore, designing to obtain as much as possible current density imposes to use small surface area but at the expense of the pure metal production. To produce mass amount of pure metal, large surface electrodes have to be used at reasonably higher concentrations of HCl acid. Highly increasing rate of current densities would be achieved but the electrolyte would be changed to undesired or inapplicable form since the conductivity of the electrolyte is very sensitive to the changes in concentration.

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الخلاصة

في هذا البحث، جرى دراسة تأثير الشكل الهندسي لقطب النحاس المستخدم في خلية التحليل الإلكتروليتي المستخدمة في تنقية المعادن. وقد ظهرت هذه التأثيرات جلية من خلال دراسة الخصائص الكهربية لمثل هذه الخلايا إذ أن الشكل الهندسي للقطب يحدد المعاملات الأكثر أهمية لخلية التحليل الإلكتروليتي وهما المجال الكهربائي وكثافة التيار، وقد تم استخدام ثلاثة أشكال هندسية مختلفة لأقطاب النحاس. أظهرت النتائج ضرورة استخدام أقطاب ذات مساحة سطحية كبيرة بتركيز عالية لحامض الهيدروكلوريك لغرض إنتاج مقادير كبيرة من المعدن النقي. يمكن بلوغ معدلات زيادة عالية لقيم كثافة التيار المار عبر الخلية ولكن على حساب التغير غير المرغوب بالإلكتروليت بسبب الحساسية العالية للتوصيلية الكهربية للإلكتروليت للتغير بالتركيز. لقد بدأ مؤخراً استخدام خلايا التحليل الإلكتروليتي بكفاءة عالية لتحضير وإنتاج المعادن عالية النقاوة في المحاليل الإلكتروليتية.