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Effects of Electrode Geometry on Energy Transfer Characteristics of Electrolytic Cells Used for Production of Metallic Nanostructures

Abstract- *In this work, the effects of geometries of stainless steel electrodes used in electrolytic analysis cells were studied. These cells are used for preparation of metallic nanostructures. These effects can be observed by studying energy transfer characteristics of electrolytic cell as the electric field and current density are determined by its electrode geometry. Four electrode geometries were used in this work.*

Keywords- *Electrical physics; Electrolytic cells; Metallic nanostructures; Energy transfer*

1. Introduction

Commercially, electrolytic processing and methods are employed in the refinement of metals at large (e.g., copper, aluminum, nickel and zinc) and small (e.g., gold and silver nanoparticles) scale. In addition, the production of other metals such as titanium and lead can be performed using such methods [1-3] but involving some challenges faced by continuous improvements and innovations. These methods are collectively known as "electrometallurgy", which becomes applicable 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]. In general, the reduction reaction can be written as:

$$M^{2+} + 2e^- \rightarrow M \qquad (1)$$
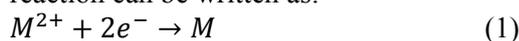
Principally, the fundamental of the solution-based metal reduction is a correlative process of kinetics and thermodynamics.

The commercial processes of the electrometallurgy include an anode, a cathode and a power source in addition to the substances to be used [5]. A metal reduction process occurs at the cathode making use of the electrons provided by a former reaction at the anode, which represents a source of electrons those are drifted from anode towards cathode by the electric field applied between the two electrodes from a dc power supply through the aqueous medium. This medium is known as electrolyte and contains all provided ions [6]. A common reaction occurred at the anode is obviously water electrolysis as:

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \qquad (2)$$
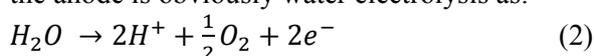
The electrons required for reduction in molten salt electrometallurgy are mostly provided by the oxidation of carbon or chloride while they are provided from an impure anode in electrolytic refinement of metals [7]. There is a specific voltage or half-cell potential should be used in order to perform a metal reduction reaction as well as counter reaction [8].

The higher potential metals can impose contaminations for low potential as they receive electrons and deposit in the cathode in form of impurities. Accordingly, the lower potential metals in the electrolyte must be carefully purified to maintain cathode purity [9]. In similar manner, the levels of electrolyte purity must be ensured and improved by additional efforts during the experimental work. Such requirement is going to be much more important as the levels of impurities increase and their removal becomes difficult [10].

The mass transport combined with the shift in potential with respect to half-cell potential determines the rate of reduction/oxidation reaction. While electrons may leave the anode and move to the cathode due to the effect of energy, which is determined by the difference between the anode and cathode reactions. In addition, this motion from anode to cathode may be attributed to the shift in potential and potential-related loss in resistance [11-12]. The total requirement of potential by the distance between the cell electrodes is known as 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]:

$$\text{Energy} \left(\text{kW.}\frac{\text{hr}}{\text{kg}}\right) = 26.8 \times \frac{E_{cell}(n)}{A_w\left(\frac{\beta}{100}\right)} \qquad (3)$$

where E_{cell} is the total cell voltage, n is the molar density of electrons in metal, A_w is the atomic weight of the reduced metal (dimensionless), and β is the percentage of the total applied current used for the reduction reaction. Typically, electrometallurgy requires energies for metal reduction higher than 1500 kW.hr/ton. In order to minimize these energies, the efficiency is increased while the cell voltage is decreased [15]. In this work, geometrical effects of stainless steel electrode on the electrical energy characteristics of electrolytic analysis cell are introduced. As well, the effect of acid concentration in the electrolytic solution was introduced in combination with the effect of electrode geometry.

2. Experiment

Electrolytic analysis cell was a Pyrex pool of 280 mm 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. Four groups of pure stainless steel (St. St. 316L) electrodes were placed inside the solution and fixed to the cover of the cell to prevent them from moving. These surfaces of electrodes were grinded and polished down using 50 μm grinding paper. These four groups are explained in the Table 1. 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 5A. The experimental set-up is shown schematically in Figure 1.

Table1: The geometry of 316L stainless steel electrodes used in this work

Sample	Shape	Surface area (cm^2)
S1	Polygon	2.712
S2	Big disc	4.047
S3	Small disc	1.53
S4	Rod	0.282
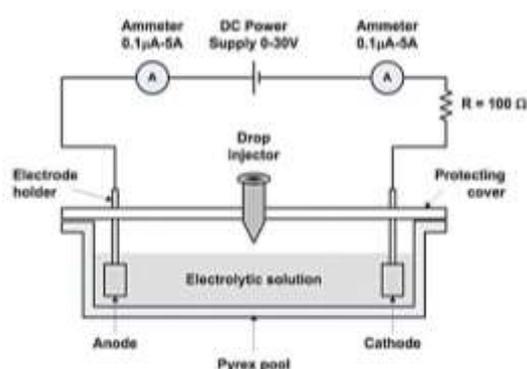
Figure 1: Experimental setup of this work

The set-up was firstly calibrated by measuring the current in the external circuit in case of using only500 ml of distilled water and no current was measured over the full range of the dc power supply. Three different amounts of HCl acid (25, 50, 75ml) were diluted in distilled water to form three solution samples with 5, 10 and 15% HCl acid, respectively. Similarly, three different amounts of acetic acid (50,100, 150 mL) were diluted in distilled water to form three solution samples with 10, 20 and 30% acetic acid, 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.

Accurate electrical measurements at room temperature were carried out using a dc power supply (ATTEN PPS3005S 30V 5A), two digital multimeters (DT9208A) and a resistor to measure the current through an external circuit. Other accessories to control the experimental parameters include pH meter and thermometer. Each point presented herein is an average of few data obtained from the experimental work.

3. Results and Discussion

Figure 2 shows the effect of stainless steel electrode geometry on the measured current through the electrolytic analysis cell using acetic acid at three different volumetric percentages (10, 20 and 30%). As shown, the electrode of larger surface area (S2) can measure higher current in the external circuit at low concentrations of the used acid (10 and 20%). This may be attributed to the effectively of larger surface area to collect more ions (anions and cations) existing in the solution and hence pass them to the external circuit as a current.
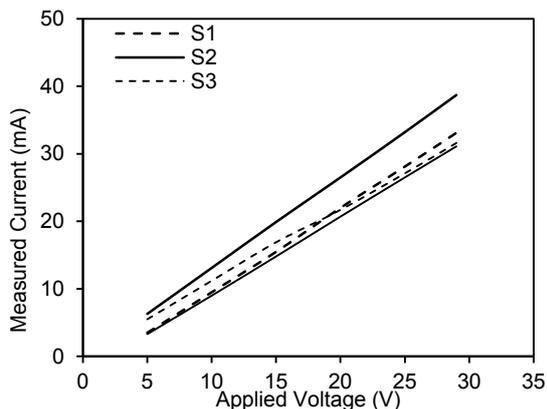
(a)
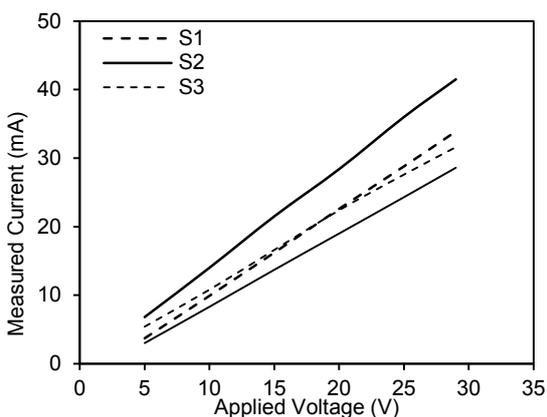
(b)
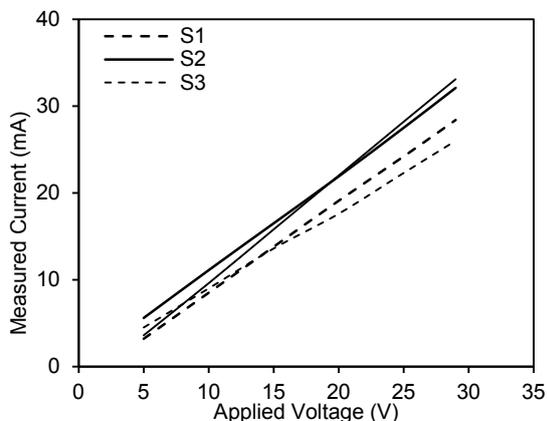
(c)

Figure2: Variation of measured current with applied voltage in an electrolytic analysis cell using acetic acid at different concentration (a)10%, (b) 20% and (c) 30% for four different geometries of 316L stainless steel electrodes

It can be noted that most ions generating the current are crossing the distance between the surfaces of the electrodes along which the voltage is applied. In other words, the electrical potential governing the motion of ions causing the current flow is simply the voltage applied along the distance between the two electrodes. As well, the electrodes of comparable surface areas show approximately equal values of the measured

current at the low concentrations (10 and 20%).

In case of sample with higher acid content (30%), the values of the measured current approach more to each other because the higher concentration of the acid reduces the disintegration of acid molecules and the production of ions causing current flow. Therefore, the effect of electrode geometry can be neglected at the low values of ion concentration resulted from the lower disintegration of the acid.

Figure 3 shows the effect of stainless steel electrode geometry on the measured current through the electrolytic analysis cell using hydrochloric acid at three different percentage contents (5,10 and 15%). As shown, comparable currents are measured at the low contents (5 and 10%) and approximately coincide at higher applied voltages. This can be attributed to the complete disintegration of hydrochloric molecules in aqueous solution, which results in large amount of ions generating current flow in this solution. Consequently, these ions are highly condensed along the distance between the electrodes and hence the effect of electrode surface area to trap the ions is reduced.

At acid percentage amount of 15%, the polygon electrode (S1) shows higher values of measured current that exceed twice those measured by other electrodes as this geometry contains of right angles and spire ends while the other geometries are circular. Obviously, the electric field intensity is uniformly distributed over the circular and spherical surfaces. On the other hand, the electric field intensity is focused on such spire ends of conductors and attracts the electric charges from the near surrounding. This causes to increase the number of charges crossing the electrode per unit time and hence the value of measured current.
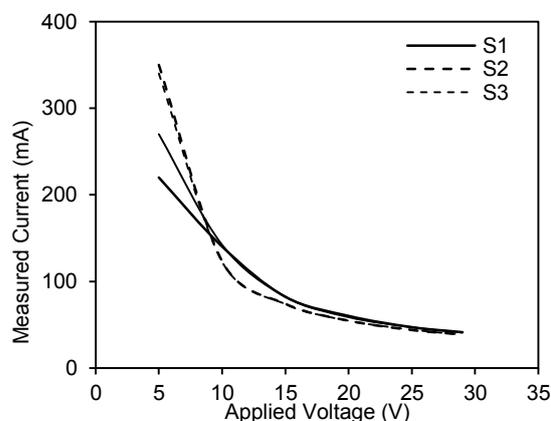
(a)
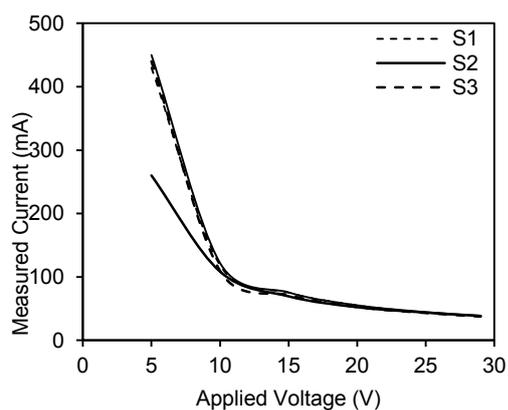
(b)
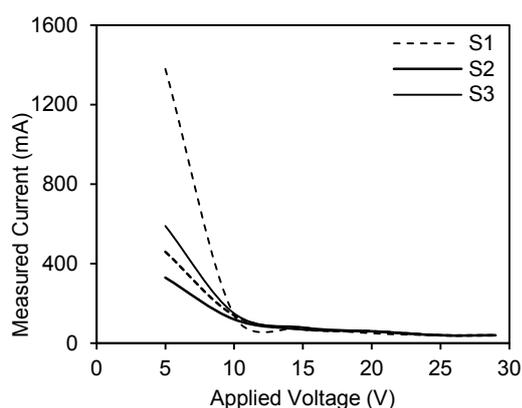
(c)

Figure3: Variation of measured current with applied voltage in an electrolytic analysis cell using hydrochloric acid at different concentration (a) 5%, (b) 10% and (c)15% for four different geometries of 316L stainless steel electrodes

4. Conclusions

From the results presented in this work, one can conclude that threshold voltage at which the current started to flow through the electrochemical cell was shifted upward in case of using polygon electrodes due to the partial dissolving of acetic acid in water. However, threshold voltage was nearly constant with increasing concentration in case of rod-shape electrodes. The difference in current densities between two cases (geometries) is mainly attributed to the difference in the surface area. Both geometry and dimensions play the main role in raising the number of ions collected by the surface of electrode. Therefore, design to obtain as much as possible current density imposes to use small surface area. Large-surface electrodes with sufficiently highconcentration of HCl acid are used for commercial production of pure metal. The design and performance parameters of these cells can be optimized to satisfy certain purposes and applications, such as the production of highly-pure metallic nanostructures.

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