Effect of Angle of Rotation on the Rate of Electropolishing

HOWAIDA M. EL-KASHLAN[1,*] and A.M. AHMED[2]

[1]Department of Physics and Chemistry, Faculty of Education, Alexandria University, Alexandria, Egypt
[2]Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

*Corresponding author: E-mail: helkashlan@hotmail.com

The effect of angle of inclination on the rate of mass transfer was studied by measuring the limiting current of polishing of copper in phosphoric acid using parallel plate cell. Different factors were studied as phosphoric acid concentration, different angles of inclination and temperatures. Five concentrations of phosphoric acid were used, namely, 6, 8, 10, 12 and 14 M. Temperature was 23 ± 1 ºC. Different angle of rotations were used as 15º, 30º, 45º, 60º, 75º, 90º, 105º, 120º, 135º, 150º. The limiting current was found to increases by increasing angle of rotation in divided and undivided cell and limiting current decreases by increasing H_3PO_4 concentration. A comparison between the limiting current measured in divided and undivided cells shows that in undivided cells cathodic H_2 evolution increases the anodic limiting current by an amount ranging from 4.8 to 42 % depending on acid concentration and angle of inclination.

Key Words: Electropolishing, Limiting current, Mass transfer, Phosphoric acid.

INTRODUCTION

Electropolishing of metals is widely practiced in industry to improve the state of their surface phosphoric acid-based electrolytes are commonly employed for electropolishing of such materials. But no general guidelines are available to determine the optimal operating conditions.

The processes of anodic metal surface treatment are carried out in conditions of partial passive and transport limitations[1]. This makes possible the predominant dissolution of metal from micro convexities of the surface and thus the leveling of the surface[2].

Electropolishing of metals is a diffusion controlled process which takes place at the limiting current of the anodic dissolution of the metal[3]. The magnitude of the limiting current is determined by the rate of removal of the anodic dissolution products away from the anode surface according to the equation:

$$\frac{I_1}{ZF} = \left(\frac{D}{\delta}\right)C_s$$

In unstirred solutions, removal of anodic dissolution products takes place by diffusion and downward natural convection arising from the density difference between the light bulk solution and the heavy interfacial solution. As such the rate of electropolishing is determined by the geometry of the work piece, physical properties of the solution stirring. Previous studies on the kinetics of polishing have dealt with geometries such as vertical[2] and horizontal cylinders[4] horizontal plate[5],

vertical[6] and horizontal tube[7] spheres[8] and cavities[8]. Although inclined surfaces are encountered frequently in industry either alone or as an integral part of a more complex work piece, no work has been done on the effect of inclination on the rate of electropolishing of metal plates. The object of this work is to study: (i) The effect of plate inclination on the rate of polishing. (ii) The effect of cathodic H_2 bubbles on the rate of polishing of inclined metal plates; H_2 bubbles which collide with the anode could either destroy the anodic diffusion layer or thin it.

If H_2 bubbles leads to diffusion layer destruction no polishing would take place since mechanistic studies[1] of electropolishing have shown that the presence of the anodic diffusion layer is a prerequisite to polishing. On the other hand if the collision of H_2 bubbles with the anode reduces the diffusion layer thickness the rate of polishing will be enhanced.

Rates of electropolishing were determined by measuring the limiting current of anodic dissolution of copper plates in phosphoric acid, divided and undivided cell were used to test the effect of cathodic H_2 on the rate of electropolishing at different anode inclinations.

EXPERIMENTAL

The cell consisted of a rectangular plastic container having the dimensions (5.1 cm × 5.0 cm × 10.0 cm) with electrodes filling the whole cross section area, the cathode and anode were rectangular copper sheets of 10 cm height and 5 cm width, electrode separation was 5 cm. A PVC porous diaphragm was

used to divide the cell, placed in between the anode and cathode.

The cell was placed in 3 L glass container filled with the electrolyte to ensure that the cell is filled with the electrolyte at different angles of inclination. The cathode-anode distance was 5 cm, the anode height was 10 cm for inclined wax bases were used to hold anode. The inclination of bases beginning 15, 30, 45, 60 and 70°. Cell inclination in the glass container was secured by means of plastic supports. The electrical circuit consists of 6 V dc power supply connected in series with the cell and with multirange ammeter. A voltmeter is connected in parallel with the cell to measure the voltage. Polarization curves, from which the limiting current was determined, were constructed by increasing the current stepwise and measuring the steady state anode potential against a copper reference electrode placed in the cup of Luggin tube containing phosphoric acid of the same concentration as that in the cell. The tip of the Luggin tube was placed at about 1 mm from the anode surface. Before electrolysis the cathode and anode were isolated from their backs and sides with epoxy resin. Five concentrations of phosphoric acid were used, namely, 6, 8, 10, 12 and 14 M prepared from AR orthophosphoric acid. Temperature was 23 ± 1 °C. Each experiment was repeated using a fresh solution (Fig. 1).
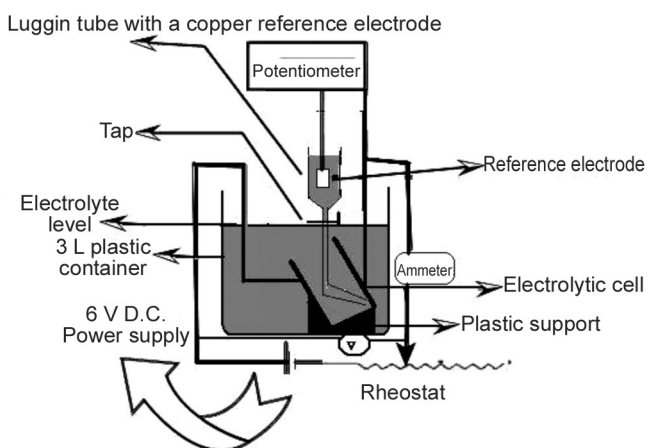

Fig. 1. Electrolytic cell and the electrical circuit

RESULTS AND DISCUSSION

Figs. 2 and 3 showed a set of potential curves obtained at different degrees of anode inclination. It is obvious that the limiting current increases by increasing angles of rotation and in undivided cell than in divided cell. The limiting current was obtained from these curves and plotted against the angle of anode inclination with the horizontal axis in divided and undivided cells as shown in Figs. 4 and 5, respectively. Fig. 4 shows that the limiting current and rate of polishing of a downward and upward facing anode increase with decreasing the angle of inclination with the horizontal position *i.e.*, the rate of polishing is maximum for a downward facing horizontal surface and minimum for low angle of rotation. This is consistent with the fact that at vertical plates, the downward natural convection is laminar[9] while at a downward facing surface the flow is turbulent[5] the degree of turbulent decreases at the angle of inclination with the horizontal axis increases. Turbulent at
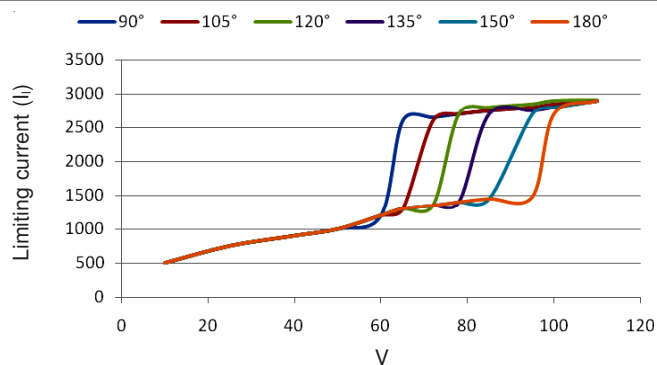

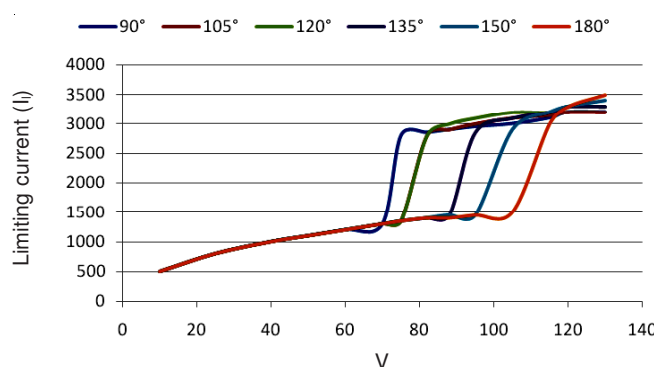Fig. 2. Typical polarization curves obtained for different degrees of anode inclination in undivided cell in 6 M H_3PO_4

Fig. 3. Typical polarization curves obtained for different degrees of anode inclination in undivided cell in 6 M H_3PO_4
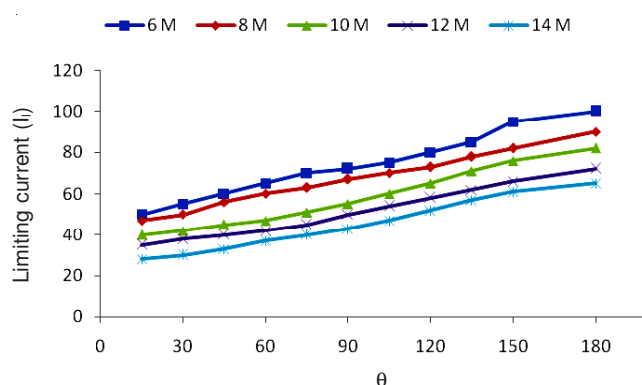

Fig. 4. Effect of anode inclination on the limiting current in undivided cell
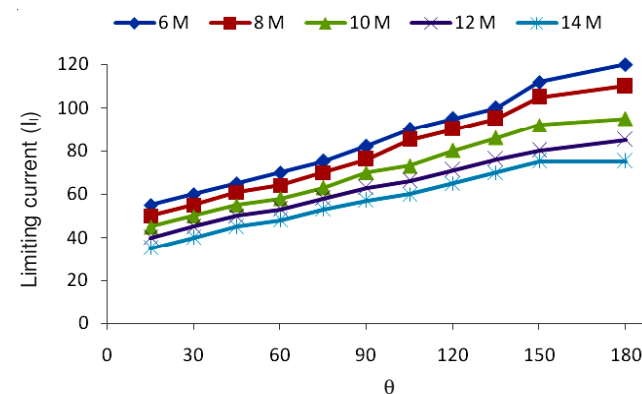

Fig. 5. Effect of anode inclination on the limiting current in divided cell

inclined downward facing plates arises as a result of boundary layer separation from the electrode surface[10]. Fig. 5 shows that

change of anode angle of inclination with the horizontal position also change the limiting current in undivided cells. A comparison between the limiting current measured in divided and undivided cells shows that in undivided cells cathodic H_2 evolution increases the anodic limiting current by an amount ranging from 4.8-42 % depending on acid concentration and angle of inclination as shown in Table-1.

TABLE-1
EFFECT OF ANODE ANGLE OF INCLINATION
ON THE PERCENTAGE INCREASE IN THE LIMITING
CURRENT OVER THE NATURAL CONVECTION
VALUE DUE TO CATHODIC GAS STIRRING

H_3PO_4 (M)	θ										
	15	30	45	60	75	90	105	120	135	150	180
	Increases in the limiting current (%)										
6	4.8	5.1	5.8	6.3	7.0	7.3	7.8	8.0	8.7	9.0	9.7
8	8.1	9.0	9.5	10.0	10.5	11.1	11.9	13.3	14.1	13.9	14.5
10	18.1	19.1	20.1	21.0	22.0	23.5	25.7	27.8	28.9	30.0	30.7
12	23.0	23.6	24.3	25.3	26.1	27.0	27.8	29.0	30.0	31.5	33.3
14	30.6	30.7	31.5	33.0	34.0	35.3	37.0	39.6	39.6	40.8	42.0

Fig. 6 shows that effect of anode angle of inclination on the percentage increases in the limiting current and angle of inclination at different H_3PO_4 concentration.
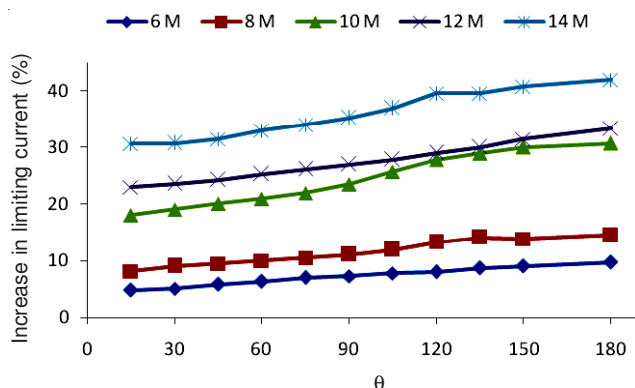

Fig. 6.　Relation between the percentage increases in the limiting current and angle of inclination at different H_3PO_4 concentration

This increase in the anodic limiting current is attributed in part to the fact that the uprising H_2 bubbles includes a radial momentum transfer[11] which enhances the rate of mass transfer at anode. The percentage increase in the limiting current increases as the anode approaches the horizontal position because more H_2 bubbles bump into the anode surface and disrupt the diffusion layer, then these bubbles move along the anode surface where they induce a solution flow along the inclined anode leading to a further enhancement in the rate of mass transfer and the limiting current. Table-2 shows that electrode inclination increases the cell voltage at the limiting current in case of undivided cell which is usually in practice. This can be explained as follows: Electrode inclination affects the cell voltage in two ways: (i) The increase in the limiting current resulting from anode inclination increases the IR drop in the cell. (ii) On the order hand, Bohm[12] found that inclination of the gas evolving electrode (the cathode in present work) decreases the adverse bubble effect on the cell conductivity and the IR drop probably because of the dispersion of gas

TABLE 2
EFFECT OF ANGLE OF INCLINATION ON
THE CELL VOLTAGE AT THE LIMITING CURRENT
IN A CELL STIRRED BY CATHODIC H_2

H_3PO_4 (M)	θ										
	15	30	45	60	75	90	105	120	135	150	180
	Cell voltage (V) at different angle of inclination										
6	1.75	1.80	1.85	1.90	2.00	2.05	2.10	2.16	2.19	2.30	2.35
8	1.80	1.85	1.90	2.00	2.05	2.10	2.15	2.20	2.30	2.35	2.40
10	1.85	1.90	2.00	2.05	2.10	2.15	2.20	2.30	2.35	2.40	2.45
12	1.90	2.00	2.05	2.10	2.20	2.30	2.35	2.40	2.40	2.45	2.50
14	2.00	2.05	2.10	2.15	2.25	2.30	2.30	2.35	2.45	2.50	2.55

bubble in the solution bulk with a consequent decrease in the void fraction and resistance of the bubble layer adjacent to the gas evolving electrode surface[13-15]; under the present conditions it seems that the first effect is predominating. Table-2, also shows that the cell voltage at the limiting current decreases with increasing phosphoric acid concentration probably because of the decrease in the limiting current with increasing phosphoric acid concentration owing to the decrease in the saturation solubility of copper phosphate in concentrated phosphoric acid[5]. The decrease in the limiting current leads to a corresponding decrease in the IR drop. Besides the rate of H_2 discharge at the cathode decreases with a consequent decrease in the adverse effect of H_2 bubbles on the IR drop.

Fig. 7(a-b) shows that the limiting current decreases with H_3PO_4 concentration within the range studied (6-14 M). This is in agreement with the finding of other authors who worked within the same range of concentration using other anode geometries[3-6].
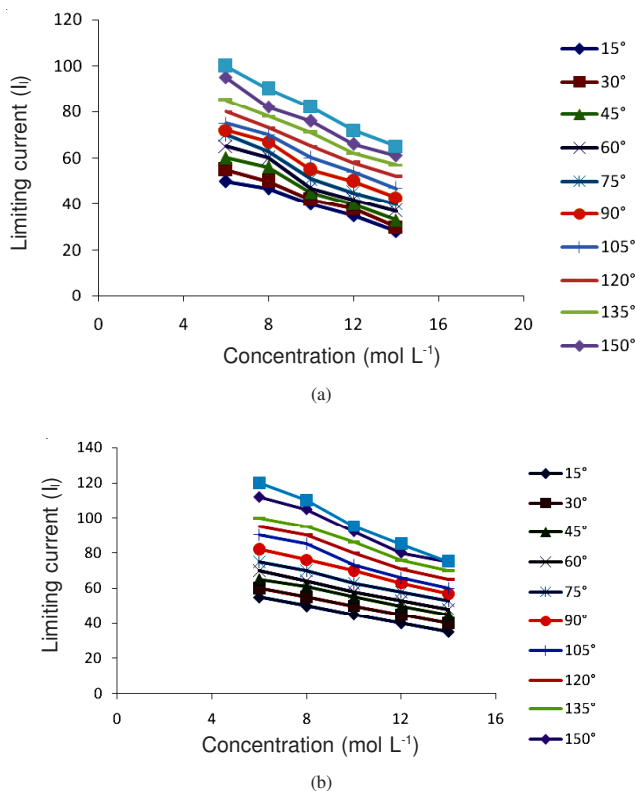

(a)

(b)

Fig. 7.　(a) Effect of H_3PO_4 concentration at the limiting current in undivided cell (b) Effect of H_3PO_4 concentration at the limiting current in divided cell

The decrease in the limiting current with H_3PO_4 concentration is attributed to two effects, first, the solubility of the dissolved copper phosphate in H_3PO_4 which marks the onset of the limiting current, decreases with increasing H_3PO_4 concentration as seen in Table-1.

Second, the viscosity of the solution increases with increasing H_3PO_4 concentration with a consequent decrease in the diffusivity of Cu^{2+} according to the Stokes-Einstein equation:

$$\frac{D\mu}{T} = \text{Const.}$$

Also, the increase in solution viscosity with increasing H_3PO_4 concentration results in an increase in the diffusion layer thickness which represents the resistance to the rate of mass transfer of Cu^{2+}. The limiting current decreases by increase angle of inclination (θ).

Conclusion

The rate of electropolishing is increased by increasing angle of inclination in all concentrations used. The rate of electropolishing at the same angle of rotation were decreased by increasing concentrations. The rate of electropolishing decreases when we used divided cells than undivided one.

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