

The role of natural convection mass transfer in the kinetics of electropolishing of horizontal surfaces

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Limiting currents were measured for the electropolishing of horizontal copper electrodes facing downwards in phosphoric acid solution under natural convection conditions. The electrode diameter was varied from 1-6 cm and the phosphoric acid concentration between 8-12 M. The limiting current was found initially to decrease with electrode diameter and then to remain constant with further increase. Within the concentration range of phosphoric acid used, the limiting current was found to decrease with phosphoric acid concentration. Mass transfer data was found to agree closely with the equation

$$(Sh) = 0.18[(Sc)(Gr)]^{0.33} \text{ for } 1.1 \times 10^9 < (Sc)(Gr) < 2.46 \times 10^{11}.$$

Nomenclature

- I_L limiting current density ($A\text{ cm}^{-2}$)
 K mass transfer coefficient (cm s^{-1})
 z number of electrons involved in the reaction
 F the Faraday number, 96 500 (Coulomb mol^{-1})
 $C_{\text{Cu}^{2+}}$ saturation solubility of Cu^{2+} (produced by copper phosphate) in H_3PO_4 acid (mol cm^{-3})
 (Sh) Sherwood Number $= Kd/D$
 (Sc) Schmidt Number $= \nu_{\text{ave}}/D$
 (Gr) Grashof Number $= \frac{gd^3(\rho_i - \rho_b)}{\nu_{\text{ave}}^2 \rho_i}$
 d electrode diameter (cm)
 D diffusivity of Cu^{2+} ($\text{cm}^2 \text{s}^{-1}$)
 ν_b viscosity in the bulk liquid ($\text{g cm}^{-1} \text{s}^{-1}$)
 ν_i viscosity at the interface ($\text{g cm}^{-1} \text{s}^{-1}$)
 ρ_i density at the interface (g cm^{-3})
 ρ_b density in the bulk liquid (g cm^{-3})
 g acceleration due to gravity (cm s^{-2})
 ν_{ave} average kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$)
 ω angular velocity (rad s^{-1})

1. Introduction

Much work has been done on the phenomenon of electropolishing since it was discovered by Jaquet [1, 2]. Most of this work was directed towards the elucidation of the polishing mechanism as well as establishing conditions for polishing of different metals and alloys. Studies on the polishing mechanism have revealed that electropolishing is a diffusion-controlled process [2, 3] which takes place at the limiting current and electropolishing can therefore be treated quantitatively using the theory of mass transfer in an analogous manner to the application of the theory of mass transfer to the cathodic deposition of metal and metal powders [4]. Some work has been done on the study of electropolishing under forced convection mass transfer conditions [5-9]. A notable recent investigation involving copper and copper-based alloys in a stirred cell is due to Gabe [10] and strongly suggests a diffusion limited mechanism at

low temperature. Fouad *et al.* [11] studied mass transfer under free convection in the electropolishing of vertical copper electrodes in phosphoric acid. The object of the present work is to study the role of mass transfer in the kinetics of electropolishing of horizontal flat surfaces facing downwards under natural convection conditions where the dissolved Cu^{2+} is transferred away from the electrode surface by diffusion and natural convection arising from the density difference between the bulk and the anode surface.

Fenech and Tobias [12] studied natural convection mass transfer at horizontal electrodes facing upwards by measuring the limiting current of the cathodic deposition of copper from an acidified solution of copper sulphate. They correlated their data by the equation

$$(Sh) = 0.19[(Sc)(Gr)]^{0.33}$$

for $10^8 < (Sc)(Gr) < 1.4 \times 10^{12}$. (1)

Using the same system, Wragg and Loomba [13] obtained the following equation for mass transfer at horizontal surfaces facing upwards

$$(Sh) = 0.18[(Sc)(Gr)]^{0.33}$$

for $3 \times 10^7 < (Sc)(Gr) < 10^{12}$. (2)

2. Experimental technique

Fig. 1 shows the cell and electrical circuit used in the present work. The cell consisted of a cylindrical glass container of diameter 11 cm and height

15 cm divided into two compartments by a cylindrical porous PVC diaphragm of diameter 9 cm. This diaphragm served to prevent stirring by the hydrogen bubbles evolved at the cathode interfering with the natural convection process at the anode. The cathode consisted of cylindrical copper sheet of diameter 10 cm and height 14 cm placed in the outer compartment of the cell and it also acted as a reference electrode by virtue of its high surface area compared to that of the anode. The anodes were horizontal discs ranging in diameter from 1–6 cm made of electrolytic pure copper. The electrical circuit consisted of a 6 volt d.c. power supply, a variable resistance and a multirange ammeter connected in series with the cell. A high impedance voltmeter was connected in parallel with the cell to measure its potential. Three concentrations of H_3PO_4 were used: 8, 10, 12 M; all were prepared from AR grade H_3PO_4 .

Polarization curves, from which the limiting current was determined, were plotted by increasing the applied current step-wise and measuring the corresponding steady-state potential. Two minutes were allowed for reaching the steady-state potential. Before each run, the back of the disc anode was insulated with polystyrene lacquer, and the active surface of the disc was polished with fine emery paper, degreased with trichloroethylene, washed with alcohol and finally rinsed in distilled water. The anode was positioned halfway between the top and bottom of the electrolyte. An insu-

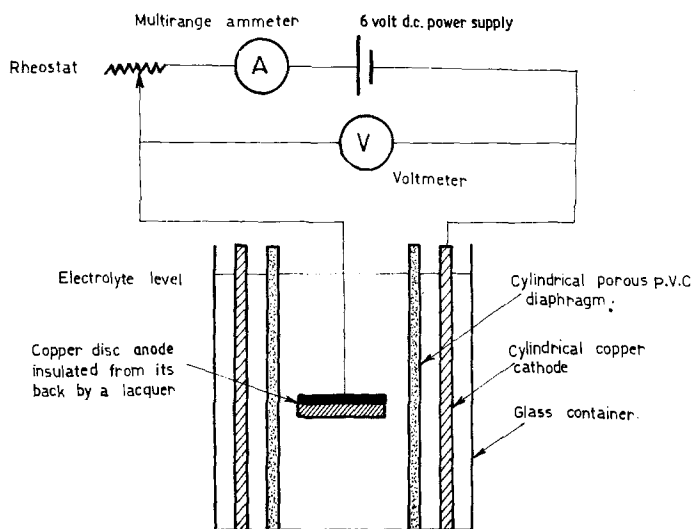


Fig. 1. Cell and electrical circuit.

lated copper wire (2 mm diameter) brazed to the disc acted to hold the anode in position and to feed it with current. The temperature was regulated by placing the cell in a thermostat.

The physical properties of the solution (ρ , u , D) needed to correlate the data were determined experimentally using standard techniques. The diffusivity of Cu^{2+} in different H_3PO_4 concentrations was determined by measuring the limiting current of the anodic dissolution of a copper rotating disc in H_3PO_4 and applying the Levich equation [14]

$$I_L = 0.62 zF \nu^{-1/6} D^{2/3} \omega^{1/2} C_{\text{Cu}^{2+}}. \quad (3)$$

The saturation solubility of copper phosphate in different H_3PO_4 concentrations was determined by iodometry [15].

3. Results and discussions

Fig. 2 shows typical polarization curves with a well-defined limiting current plateau obtained at three H_3PO_4 concentrations. Limiting current decreases with increasing H_3PO_4 concentration owing to the decrease of copper phosphate solubility with H_3PO_4 concentration as seen in Table 1. The mass transfer coefficient was calculated from the limiting current using the equation

$$\frac{I_L}{zF} = K C_{\text{Cu}^{2+}}. \quad (4)$$

Fig. 3 shows the effect of electrode diameter on the mass transfer coefficient; the mass transfer coefficient decreases at first with diameter and then remains almost constant with further increase in electrode diameter thus denoting a turbulent-flow mass transfer mechanism at the electrode surface. The data were correlated using the dimensionless groups (Sh), (Sc) and (Gr) as shown in Table 1 which also lists the values of the physical properties used in their calculation. Fig. 4 shows that the present data compare very favourably with the equations obtained by Fenech and Tobias, and Wragg and Loomba for natural convection at horizontal surfaces. Therefore, these equations can be used in practice to predict the limiting current required to polish horizontal copper surfaces in H_3PO_4 .

The agreement of the present data with the established mass transfer correlations may lend support to the mechanism of electropolishing of copper in H_3PO_4 upon which the present work was based [2, 3, 7, 8] namely: (a) that electropolishing is controlled by the diffusion of Cu^{2+} from the anode surface and not by the diffusion of PO_4^{3-} to the anode surface as suggested by some

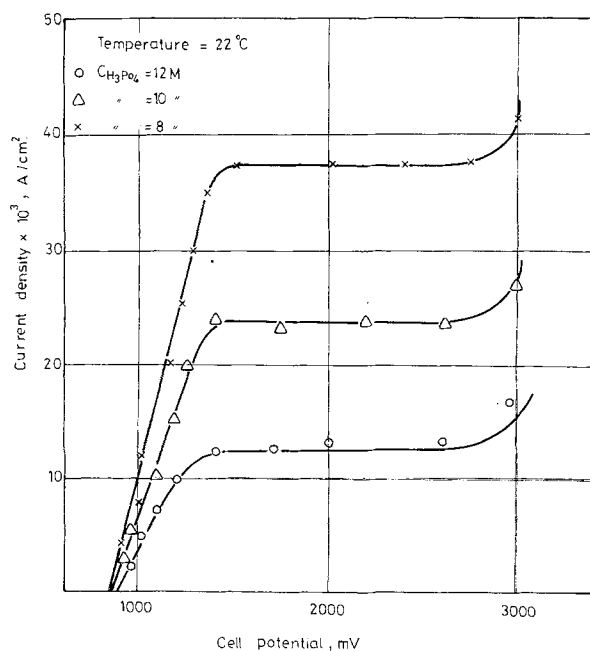


Fig. 2. Typical current-potential curves obtained for three H_3PO_4 concentrations.

Table 1. Physical properties and dimensionless groups used in data correlation. Temperature = 22°C

d (cm)	Cu^{2+} (mol cm ⁻³)	D (cm ² s ⁻¹)	K (cm s ⁻¹)	ρ_b (g cm ⁻³)	ρ_i (g cm ⁻³)	$\Delta\rho$ (g cm ⁻³)	u_b (g cm ⁻¹ s ⁻¹)	u_i (g cm ⁻¹ s ⁻¹)	(Gr)	(Sc)	(Sc)(Gr)	(Sh)
8 M H ₃ PO ₄	1	1.076 × 10 ⁻³	237 × 10 ⁻⁶	1.402	1.545	0.143	0.077 14	0.164	1.35 × 10 ⁴	8.128 × 10 ⁴	1.1 × 10 ⁹	237
	2	1.076 × 10 ⁻³	1.01 × 10 ⁻⁶	1.402	1.545	0.143	0.077 14	0.164	1.08 × 10 ⁵	8.128 × 10 ⁵	8.78 × 10 ⁹	406
	3	1.076 × 10 ⁻³	1.01 × 10 ⁻⁶	1.402	1.545	0.143	0.077 14	0.164	3.65 × 10 ⁵	8.128 × 10 ⁵	2.97 × 10 ¹⁰	570
	4	1.076 × 10 ⁻³	1.01 × 10 ⁻⁶	1.402	1.545	0.143	0.077 14	0.164	8.64 × 10 ⁵	8.128 × 10 ⁵	7.02 × 10 ¹⁰	836
	5	1.076 × 10 ⁻³	1.01 × 10 ⁻⁶	1.402	1.545	0.143	0.077 14	0.164	1.68 × 10 ⁶	8.128 × 10 ⁵	1.37 × 10 ¹¹	1025
	6	1.076 × 10 ⁻³	1.01 × 10 ⁻⁶	1.402	1.545	0.143	0.077 14	0.164	2.92 × 10 ⁶	8.128 × 10 ⁵	2.37 × 10 ¹¹	1170
10 M H ₃ PO ₄	1	0.9384 × 10 ⁻³	0.66 × 10 ⁻⁶	1.476	1.608	0.132	0.1182	0.2256	6.51 × 10 ³	1.68 × 10 ⁵	1.09 × 10 ⁹	265
	2	0.9384 × 10 ⁻³	0.66 × 10 ⁻⁶	1.476	1.608	0.132	0.1182	0.2256	5.21 × 10 ⁴	1.68 × 10 ⁵	8.75 × 10 ⁹	400
	3	0.9384 × 10 ⁻³	0.66 × 10 ⁻⁶	1.476	1.608	0.132	0.1182	0.2256	1.76 × 10 ⁵	1.68 × 10 ⁵	2.96 × 10 ¹⁰	570
	4	0.9384 × 10 ⁻³	0.66 × 10 ⁻⁶	1.476	1.608	0.132	0.1182	0.2256	4.17 × 10 ⁵	1.68 × 10 ⁵	7.01 × 10 ¹⁰	727
	5	0.9384 × 10 ⁻³	0.66 × 10 ⁻⁶	1.476	1.608	0.132	0.1182	0.2256	8.13 × 10 ⁵	1.68 × 10 ⁵	1.36 × 10 ¹¹	917
	6	0.9384 × 10 ⁻³	0.66 × 10 ⁻⁶	1.476	1.608	0.132	0.1182	0.2256	1.41 × 10 ⁶	1.68 × 10 ⁵	2.37 × 10 ¹¹	1218
12 M H ₃ PO ₄	1	0.78 × 10 ⁻³	0.40 × 10 ⁻⁶	1.560	1.671	0.111	0.1936	0.2707	3.17 × 10 ³	3.59 × 10 ⁵	1.14 × 10 ⁹	306
	2	0.78 × 10 ⁻³	0.40 × 10 ⁻⁶	1.560	1.671	0.111	0.1936	0.2707	2.54 × 10 ⁴	3.59 × 10 ⁵	9.12 × 10 ⁹	448
	3	0.78 × 10 ⁻³	0.40 × 10 ⁻⁶	1.560	1.671	0.111	0.1936	0.2707	8.56 × 10 ⁴	3.59 × 10 ⁵	3.07 × 10 ¹⁰	627
	4	0.78 × 10 ⁻³	0.40 × 10 ⁻⁶	1.560	1.671	0.111	0.1936	0.2707	2.03 × 10 ⁵	3.59 × 10 ⁵	7.29 × 10 ¹⁰	746
	5	0.78 × 10 ⁻³	0.40 × 10 ⁻⁶	1.560	1.671	0.111	0.1936	0.2707	3.96 × 10 ⁵	3.59 × 10 ⁵	1.42 × 10 ¹¹	1026
	6	0.78 × 10 ⁻³	0.40 × 10 ⁻⁶	1.560	1.671	0.111	0.1936	0.2707	6.85 × 10 ⁵	3.59 × 10 ⁵	2.46 × 10 ¹¹	1268

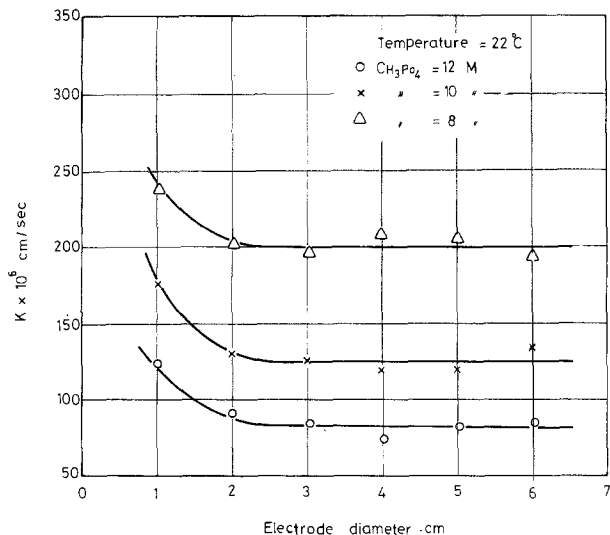


Fig. 3. Variation of mass transfer coefficient (K) with electrode diameter at three H_3PO_4 concentrations.

investigators [16–18], and (b) that limiting current is attained when the diffusion layer becomes saturated with copper phosphate and not phosphate hydroxide complexes as suggested by Kantzner [19].

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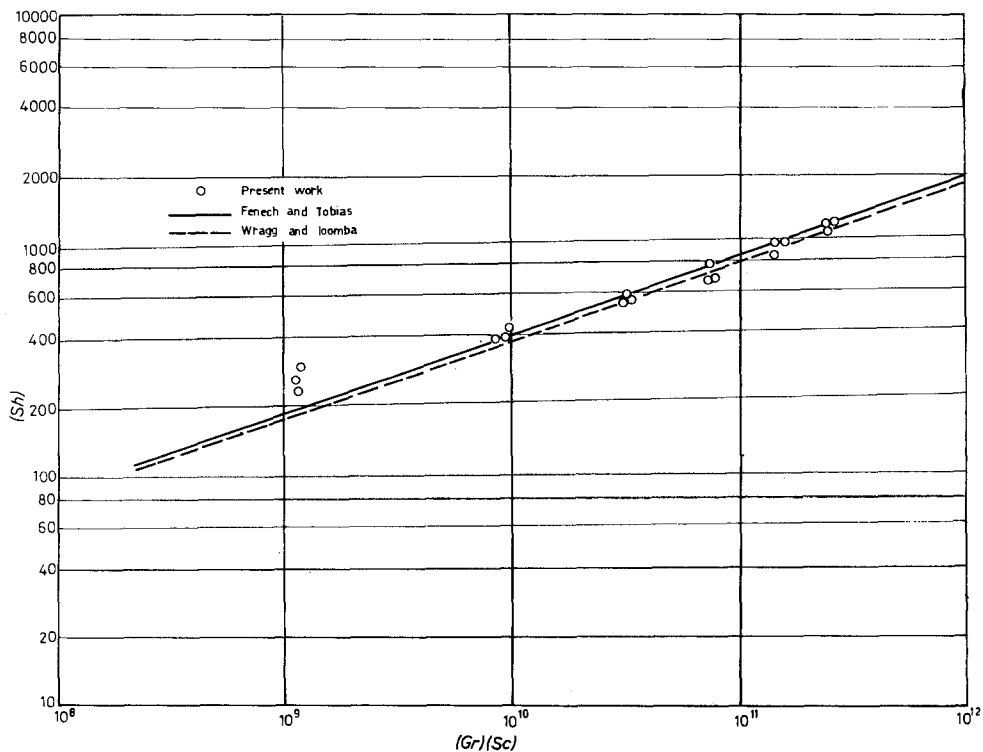


Fig. 4. Plot of the Sherwood number (Sh) against $(Sc)(Gr)$.

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