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The role of mass transfer in the kinetics of anodic dissolution of gas-evolving metallic surfaces

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The rate of anodic dissolution of copper in phosphoric acid above the potential where oxygen evolution takes place was studied. Variables investigated were oxygen discharge rate, phosphoric acid concentration and electrode position. The mass transfer coefficient of the anodic dissolution of copper in phosphoric acid was related to the oxygen discharge rate and the physical properties of the solution by the equations

for a vertical electrode: $k = aV^{0.2}(\rho/u)^{0.93}$

for a horizontal electrode: $k = aV^{0.21}(\rho/u)^{0.93}$

List of symbols

k	mass transfer coefficient (cm s^{-1})
V	oxygen discharge rate, ($\text{cm}^3\,\text{cm}^{-2}\,\text{min}^{-1}$)
a	constant
I	current consumed in copper dissolution (A cm^{-2})
Z	number of electrons involved in the reaction
F	Faraday's constant
C	Solubility of copper phosphate in H_3PO_4, (mol cm^{-3})
N	rate of copper dissolution, ($\text{g-ion cm}^{-2}\,\text{s}^{-1}$)
δ	diffusion layer thickness (cm)
r	bubble radius (cm)
g	acceleration of gravity (cm s^{-2})
$\bar{V}$	rise velocity of O_2 bubble (cm s^{-1})
u	viscosity (poise)
ρ	density (g cm^{-3})

1. Introduction

Mass transfer at gas-generating electrodes has been studied intensively during the last decade owing to the theoretical and practical importance of the subject in the design and operation of gas-evolving electrochemical reactors. Although considerable progress has been made towards the elucidation of the mass transfer mechanism at gas-evolving electrodes [1–8], no general correlation could be obtained owing to the complexity of the mechanism. Previous studies on mass transfer at gas-evolving electrodes have dealt mainly with redox systems. Little has been done on the effect of gas evolution on the rate of mass transfer during anodic dissolution of metals despite the importance of the subject to some technical electrochemical processes such as electropolishing and electrochemical machining. The object of the present work is to study the effect of oxygen discharge on the mass transfer coefficient of the anodic dissolution of copper in orthophosphoric acid under diffusion controlled conditions. In this system H_3PO_4 is present in a large excess so that it can be safely assumed that copper ions are transferred from the anode surface by diffusion and convection without interference from electrical migration [9].

2. Experimental technique

The circuit used in the present work (Fig. 1) consisted of 6 V d.c. power supply with a voltage regulator and a multirange ammeter connected in series with the cell. Two cells were used in the present study, the first cell was a rectangular plexiglass container of 8 cm height and a cross-section of 6.5 × 3.5 cm. The cell was divided into two compartments by a tight porous PVC diaphragm. The second cell was a plexiglass cylindrical container of diameter

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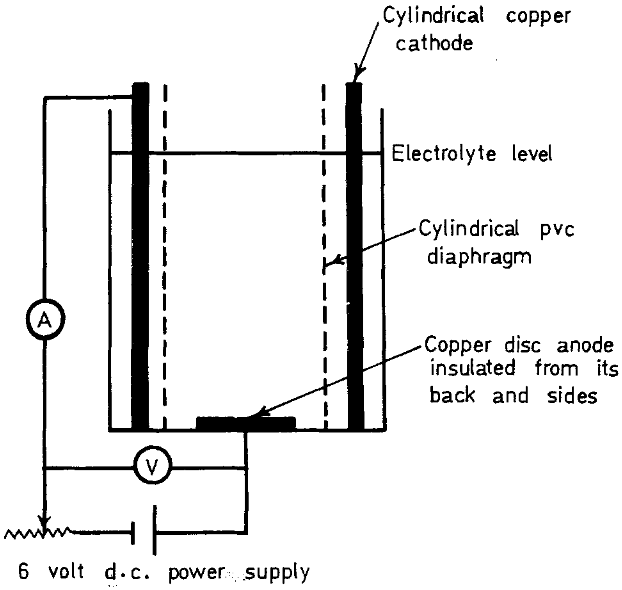

Fig. 1. The cell and electrical circuit used for the horizontal electrode.

11.5 cm and height 14 cm. The cell was divided into two compartments by a cylindrical porous PVC diaphragm of diameter 8 cm. The inner compartment formed the anode compartment while the outer compartment formed the cathode compartment. The object of using a diaphragm in both cells is to prevent the cathodic H_2 bubbles from reaching the anode where they can affect the rate of mass transfer at the anode surface. Rectangular copper sheets of 5 cm height and 3.5 cm width were used as electrodes for the first cell, each electrode exactly fitting in the cell; the distance between the electrodes was 6.2 cm. The back of the anode was insulated with polystyrene lacquer. The second cell contained in its outer compartment a cylindrical copper sheet of 11 cm diameter and 15 cm height which acted as the cathode. The anode was made of a copper disc of diameter 3.7 cm, with its bottom insulated by polystyrene lacquer, and placed in the inner compartment of the cell. Three concentrations of H_3PO_4 were used in this study, all were prepared from AR grade phosphoric acid. Before conducting an electrolysis with oxygen evolution at the anode, the limiting current for the anodic dissolution of copper in H_3PO_4 was first determined for a given set of conditions to determine the minimum current density at which oxygen starts to evolve. The limiting current determination was carried out by the traditional method [10]. Electrolysis above the limiting current was carried out only for a short time in order to avoid the build-up of Cu^{2+} in the anode compartment which affects the rate of mass transfer and also to avoid heating of the solution, especially at high current densities. After each run the amount of copper dissolved was determined by the loss in weight method and checked by iodometric determination of Cu^{2+} in the solution [11]. The rate of copper dissolution was used to calculate the mass transfer coefficient from the equation:

$$N = \frac{I}{ZF} = kC$$

The solubility of Cu^{2+} in H_3PO_4 (C) was determined analytically [11] and the oxygen discharge rate was calculated using Faraday's law. The current corresponding to oxygen discharge is the difference between the current passing through the cell and the current corresponding to the amount of copper dissolved. The temperature was kept constant at 25° C during electrolysis.

3. Results and discussions

Figs. 2 and 3 show that the effect of the oxygen discharge rate on the mass transfer coefficient of copper dissolution at vertical and horizontal electrodes can be represented by the equations
For a vertical electrode:

$$\log k = a + 0.2 \log V$$

For a horizontal electrode:

$$\log k = a + 0.21 \log V$$

The $\log k/\log V$ slopes obtained in this work are less than those reported by other authors who used redox systems to study the effect of oxygen discharge on the rate of mass transfer at oxygen-evolving electrodes. In acid solutions Janssen *et al.* [5] obtained a slope of 0.25 for a vertical oxygen-evolving electrode within the current density range 7–100 mA cm^{-2}. At higher current densities the slope increases because of bubble coalescence. For a horizontal oxygen evolving electrode, Janssen *et al.* [3] obtained a slope of 0.57 and 0.87 in acid and alkaline solutions respectively, for current densities higher than 30 mA cm^{-2}, while for current densities lower than 30 mA cm^{-2} the slope was 0.33 in alkaline solution. Fouad *et al.* [8] obtained a slope of 0.4 for a horizontal oxygen-evolving electrode in alkaline solution for a current density range of 17–105 mA cm^{-2}. According to Ibl's penetration model [2], the slope should be 0.5 for vertical and horizontal electrodes. Weder [12] obtained a slope of 0.31 for horizontal electrodes. The discrepancy between the slopes obtained in the present work and those obtained in previous studies may be ascribed to the special nature of the dissolving surface where copper dissolves through a thin porous copper oxide film covering the anode as revealed by mechanistic studies of copper electropolishing [13, 14].

According to Janssen [6], the nature of the electrode surface can affect the $\log k/\log V$ slope since electrode material influences the tendency of bubbles to coalesce. In view of the relatively low slopes obtained in the present work, it seems that the oxide film covering the copper anode does not favour oxygen bubble coalescence.

The fact that the slope obtained for the horizontal electrode is slightly higher than that obtained for the vertical electrode may be ascribed to the fact that at the vertical electrode the upward gas-solution stream is resisted by a downward natural convection stream arising from the density difference between the metal–solution interface and the solution bulk, while at the horizontal electrode natural convection is absent because copper dissolution takes place at the surface of an upward facing electrode.

Figs. 2 and 3 show that the mass transfer coefficient decreases with increasing phosphoric acid concentration. This is attributed to the decrease in copper ion diffusivity and the rise velocity of oxygen bubbles. According to Stokes law

$$6\pi \bar{V} u r = \tfrac{4}{3}\pi r^3 g(\rho - \rho_{O_2})$$

the rise velocity of oxygen bubbles is proportional to ρ/u. Table 1 shows that ρ/u decreases with phosphoric acid concentration. Figs. 4 and 5 show

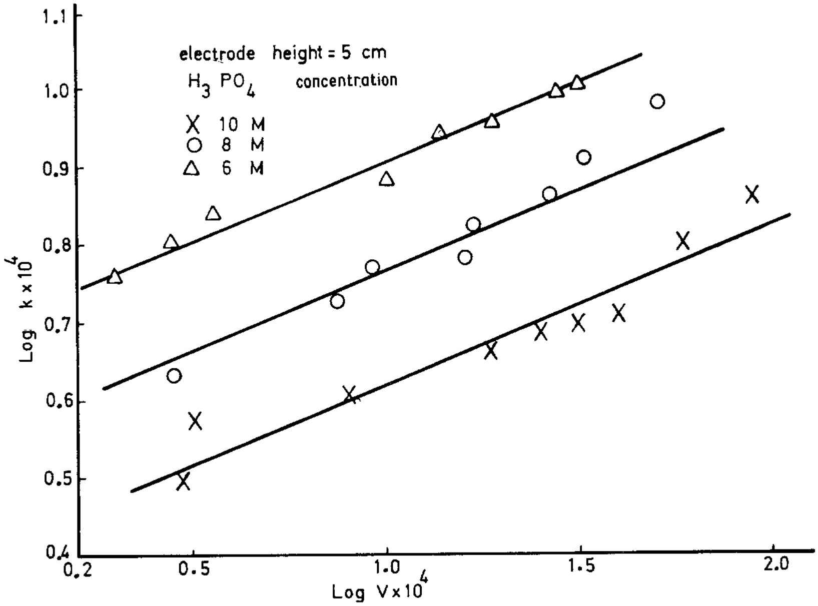

Fig. 2. The effect of oxygen discharge rate on the mass transfer coefficient.

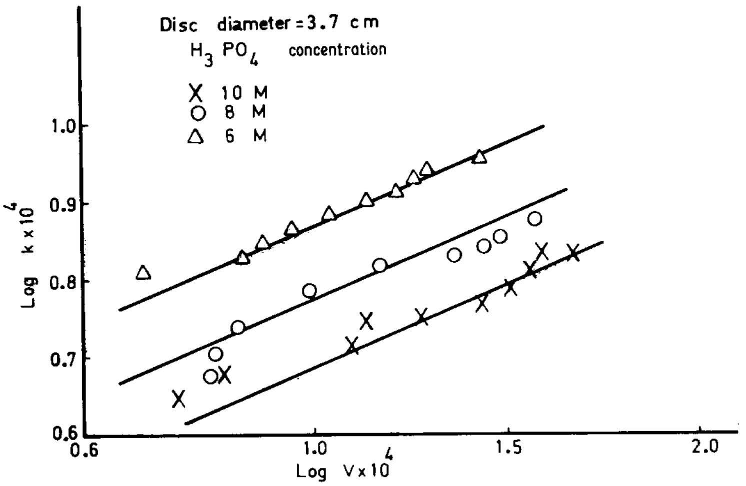

Fig. 3. The effect of the oxygen discharge rate on the mass transfer coefficient at the horizontal electrode.

Table 1. Physical properties of H_3PO_4 solutions. Temperature = 25° C

H_3PO_4 concentration (M)	ρ (gm cm^{-3})	$u \times 10^2$ (poise)	ρ/u
6	1.342	4.65	28.86
8	1.422	7.75	18.48
10	1.510	10.30	14.66

that the mass transfer coefficient can be related to ρ/u by the equation

$$k = a(\rho/u)^{0.93}$$

In an attempt to test the effect of the physical properties of the electrolyte on the mass transfer behaviour of a gas-evolving electrode, Janssen [6] studied the effect of the supporting electrolyte concentration (KOH) on the log δ–log V relation for the reduction of $K_3Fe(CN)_6$ and the oxidation of $K_4Fe(CN)_6$ where H_2 and O_2 evolved, respectively. He found that the rate of mass transfer at the H_2-evolving electrode increases with increasing KOH concentration while at the oxygen-evolving electrode, the rate of mass transfer was unaffected by increasing KOH concentration; Janssen gave no explanation for this finding. Fouad *et al.* [8] found that increasing the concentration of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ leads to a decrease in the mass transfer coefficient at H_2- and O_2-evolving electrodes. Ibl *et al.* [1] found that the addition of glycerol to the electrolyte leads to a decrease in the rate of mass transfer at H_2-evolving electrodes.

In conclusion the mass transfer coefficient of

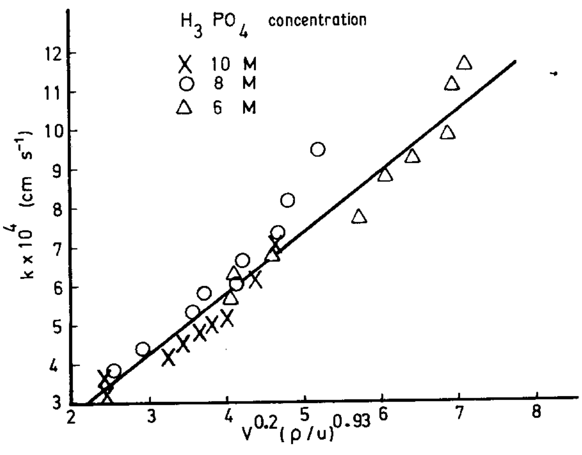

Fig. 4. k versus $V^{0.2}(\rho/u)^{0.93}$ for a vertical electrode.

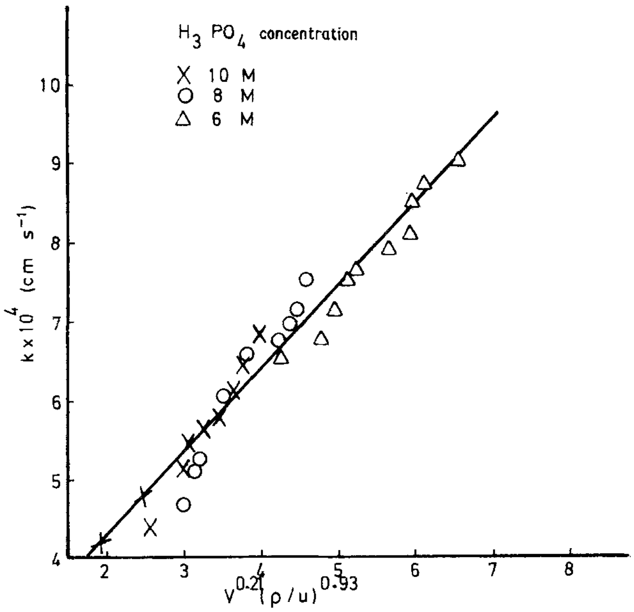

Fig. 5. k versus $V^{0.21}$ $(\rho/u)^{0.93}$ for a horizontal electrode.

copper dissolution in phosphoric acid above the limiting current can be related to oxygen discharge rate and the physical properties of the solution by the equations

For a vertical electrode:

$$k = aV^{0.2}(\rho/u)^{0.93}$$

For a horizontal electrode:

$$k = aV^{0.21}(\rho/u)^{0.93}.$$

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