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Mass transfer at vertical cylinders under forced convection induced by the counter electrode gases

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Mass transfer coefficients were measured for the deposition of copper from acidified copper sulphate solution at a vertical cylinder cathode stirred by oxygen evolved at a horizontal lead anode placed below the cylinder. Variables studied were: oxygen discharge rate, electrolyte concentration and cylinder height. The mass transfer coefficient was found to increase by a factor of 1.8–2.6 depending on oxygen discharge rate and cylinder height. The mass transfer coefficient was related to oxygen discharge rate and cylinder height by the equation:

$$K = 65.8 \times 10^{-4} \frac{V^{0.358}}{h^{0.29}}$$

List of symbols

K mass transfer coefficient (cm s^{-1})
V oxygen discharge rate (cm^3 cm^{-2} s^{-1})
I limiting current (A cm^{-2})
i anodic current density (A cm^{-2})
Z number of electrons involved in the reaction
F Faraday's constant
h electrode height (cm)
R gas constant
T temperature (K)
A anode area (cm^2)
P oxygen pressure (atm)

1. Introduction

Recently there has been interest in the study of the effects of gas evolution on electrode reactions, e.g. the effect of bubble formation on the ohmic drop [1, 2], heat and mass transfer rates in electrochemical reactors [3–22]. Such studies are essential for the rational design and operation of gas-evolving cells. Most of the previous mass transfer studies in gas-evolving cells have concentrated on the effect of gas bubbles on the rate of mass transfer at the gas-evolving electrode [4–16]. In a recent development, the counter electrode gases which evolve in processes such as electrowinning of metals and electrosynthesis have been thought of as a means for enhancing the rate of mass transfer at the working electrode. Ettel *et al.* measured the ability of anodic oxygen to enhance the rate of mass transfer in the electrodeposition of copper in a parallel plate cell; enhancement of mass transfer took place only at the upper half of the working electrode [20–22]. In an attempt to increase the current enhancement by the counter electrode gases as well as to improve current distribution, Sedahmed and Shemilt [18] studied the effect of anodic oxygen on the rate of mass transfer at a vertical plate cathode placed downstream from the anode and flush with it. These authors [19] also studied rates of mass transfer at horizontal cylinders stirred with oxygen evolved at a horizontal counter electrode placed below the cylinder. To combine the advantage of high mass transfer coefficient with high surface area Sedahmed [17] measured rates of mass transfer at an array of closely packed screens stirred with anodic oxygen evolved at an anode placed below the array. The above studies have shown that the degree of mass transfer enhancement depends among other factors on the geometry of the working electrode. The present work deals with the cylindrical geometry in a vertical position where mass transfer is enhanced by oxygen evolving at an anode placed below the vertical cylinder. Mass transfer coefficients were determined by measur-

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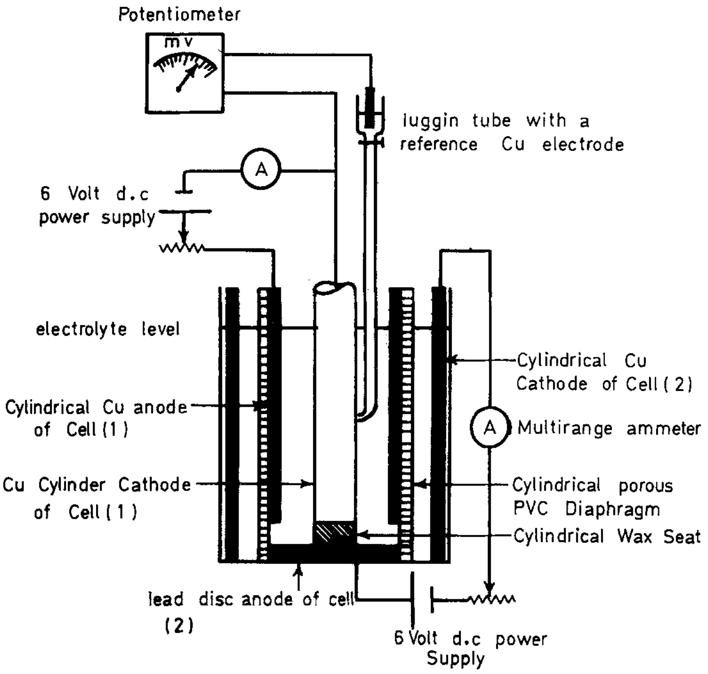

Fig. 1. Cell and electrical circuit.

ing the limiting current for the deposition of copper from acidified copper sulphate and using the equation:

$$\frac{I}{ZF} = KC \qquad (1)$$

2. Experimental technique

The apparatus (Fig. 1) consisted of two separate cells placed in the same container. Each cell was fed with current from a different d.c. source. One of the two cells (cell 2) served to generate oxygen which stirred the solution at the cathode of the other cell (cell 1) where copper was deposited from acidified $CuSO_4$ solution. The container was a 1 ℓ glass beaker of 10.5 cm diameter and 14.5 cm height and it was divided into two compartments by a tight PVC cylindrical porous diaphragm of 6 cm diameter. The inner compartment contained cell 1 and the anode of the oxygen generating cell. The outer compartment contained the cathode of the oxygen generating cell. The oxygen generating cell consisted of a circular lead disc anode of 6 cm diameter placed horizontally at the bottom of the inner compartment and a cylindrical sheet of copper cathode placed in the outer compartment. The other cell (cell1) consisted of a vertical copper cylinder of 2.2 cm diameter cathode and a cylindrical copper sheet of 6 cm diameter anode. The cylinder cathode of cell 1 was positioned in the centre of the inner compartment above the lead anode of cell 2. A wax seat made flush with the cylinder cathode separated it from the lead anode and also served to hold the cathode in position and isolate the flat end of the cathode. The use of the diaphragm and a copper anode for cell 1 ensured the constancy of copper ion concentration in the inner compartment during the experiment. The electrical circuit connected to each cell was composed of a multirange ammeter and 6 V d.c. power supply with a voltage regulator. Mutual electrical interference between the two cells was found to be negligible and each cell behaved independently. Before each run, the surface of the cylinder cathode was polished with fine emery paper, degreased with trichloroethylene and washed with alcohol and distilled water, respectively. Before each run, the container was filled with 800 cm^3 of fresh solution and the cathode height was adjusted to the required value by insulating the inactive part with polystyrene lacquer. The rate of oxygen discharge was controlled by adjusting the current passing through the oxygen generating cell. The limiting current for copper deposition at the cylinder cathode was

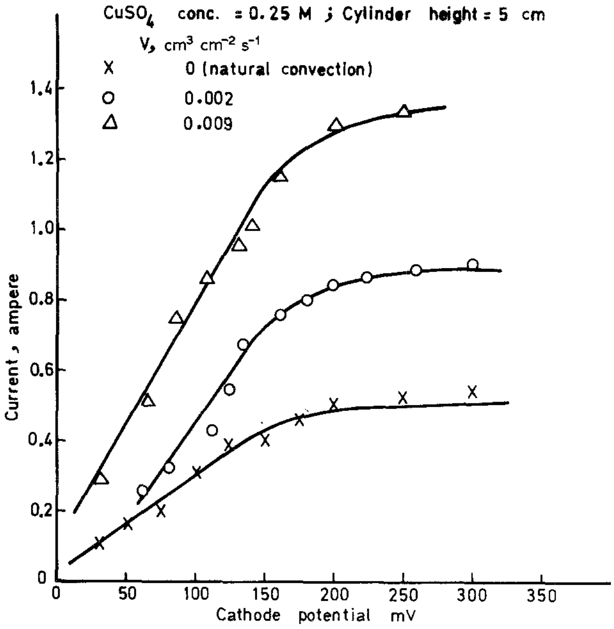

Fig. 2. Current–potential curves at different oxygen discharge rates.

determined at a certain oxygen discharge rate from the polarization curve which was constructed by increasing the applied current step-wise and measuring the corresponding steady state cathode potential. The cathode potential was measured against a reference copper electrode placed in the cup of a luggin tube with a potentiometer; the capillary tip of the luggin tube was position 0.5–1 mm from the cathode surface. The electrolyte used was 1.5 M H_2SO_4 + $CuSO_4$ (0.05–0.25 M). The temperature was kept constant at 25° C by placing the cell in a water bath.

3. Results and discussions

Fig. 2 represents typical current-potential curves obtained at different oxygen discharge rates, the figure shows that oxygen evolution can increase the limiting current by as much as 260% at a oxygen discharge rate of 0.009 cm^3 cm^{-2} s^{-1}. At higher oxygen discharge rates, an ill-defined limiting current plateau was obtained, so the present study was limited to a maximum oxygen discharge rate of 0.009 cm^3 cm^{-2} s^{-1}.

Fig. 3 shows the effect of oxygen discharge

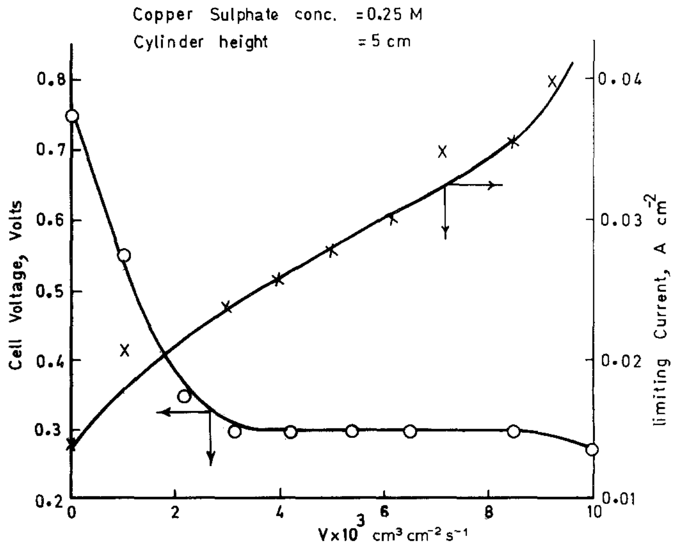

Fig. 3. Effect of oxygen discharge rate on the cell voltage (cell 1) and the limiting current.

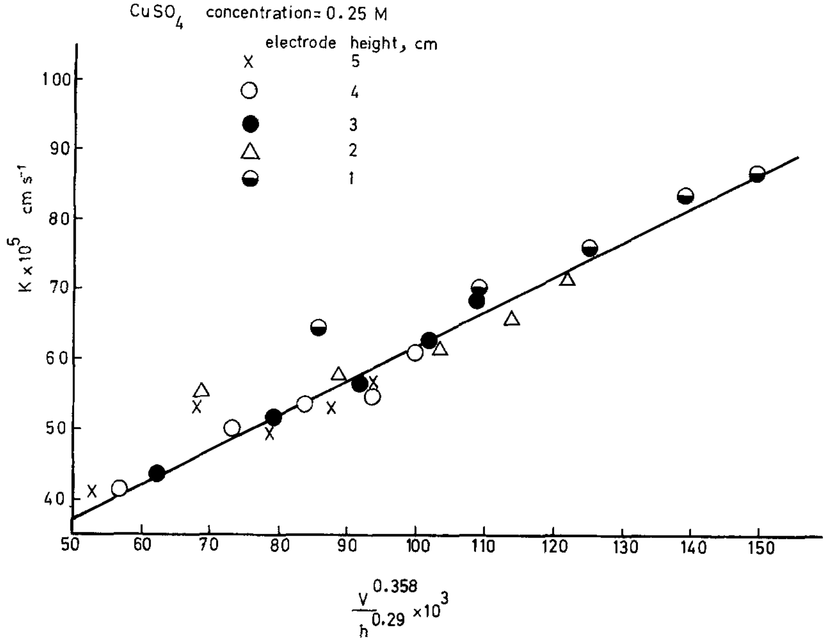

Fig. 4. Effect of oxygen discharge rate and electrode height on the mass transfer coefficient.

rate on the limiting current and the cell voltage (of cell 1); within the range of oxygen discharge rate used in the present study, the cell voltage dropped sharply at low oxygen discharge rates and then remained almost constant with further increase in oxygen discharge rate. It seems that the decrease in cathodic and anodic concentration polarization resulting from oxygen stirring outweighs the increase in the ohmic drop caused by the presence of oxygen bubbles. The increase in limiting current and the decrease in cell voltage caused by oxygen stirring justify the economic feasibility of using counter electrode gases to enhance the rate of mass transfer in electrochemical reactors [17].

Fig. 4 shows the effect of oxygen discharge rate and cylinder height on the mass transfer coefficient, the data fits the equation:

$$K = 65.8 \times 10^{-4} \frac{V^{0.358}}{h^{0.29}} \qquad (2)$$

with an average deviation of ± 8.5%. Equation 2 can be written in terms of the anodic current density which is related to oxygen discharge rate (V) by the equation:

$$V = \frac{i}{4F} \frac{RTA}{P} \qquad (3)$$

Therefore

$$K = \text{constant} \times \frac{i^{0.358}}{h^{0.29}} \qquad (4)$$

The exponent of oxygen discharge rate (0.358) is in agreement with the value obtained in the case of horizontal cylinders [19] (0.37) and packed screens [17] (0.377) stirred by anodic oxygen. The value is also in agreement with the value reported by Ibl [5] (0.36) who studied the effect of nitrogen bubbles forced through a porous frit on the rate of mass transfer. The value compares favourably with the value obtained by McMullin *et al.* [3] (0.34) who studied the effect of cathodically evolved hydrogen on the rate of heat transfer. The value is at variance with that obtained with a vertical plate [18] (0.269) stirred by anodic oxygen. On comparing the magnitude of the mass transfer coefficient of a vertical cylinder with that of other geometries under similar conditions, it will be found that the value is higher than that of a vertical plate but less than that of a horizontal screen; the value is similar in magnitude to that of a horizontal cylinder of a diameter equal to the height of the vertical cylinder.

The decrease of the mass transfer coefficient with cylinder height as shown in Fig. 4 is quali-

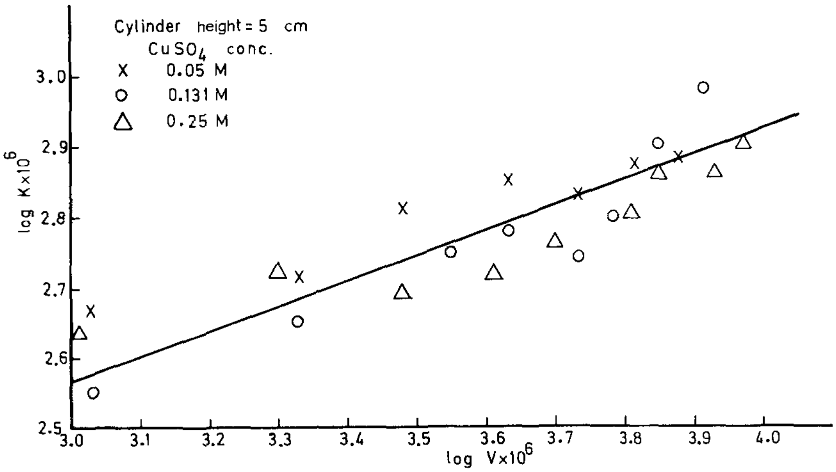

Fig. 5. Effect of oxygen discharge rate on the mass transfer coefficient at different $CuSO_4$ concentrations.

tatively in agreement with the hydrodynamic boundary layer theory and reveals a laminar flow mechanism. However, the height exponent (− 0.29) given by Equation 2 is at variance with the prediction of the hydrodynamic boundary layer theory for single phase mass transfer where the mass transfer coefficient is inversely proportional to the square root of the height [23]. This discrepancy may be accounted for by the fact that in the present case fluid flow is induced by oxygen bubbles whose terminal velocities increase along the electrode height because of the increase in the size of these bubbles. Bubbles grow in size as they rise in the solution because of coalescence [7] and a decrease of hydrostatic pressure.

Fig. 5 confirms the relationship between the mass transfer coefficient and oxygen discharge rate at different $CuSO_4$ concentrations; the data show little dependence on $CuSO_4$ concentration probably because the three concentrations used do not differ significantly in their physical properties [24].

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