

Mass transfer characteristics of a novel gas-evolving electrochemical reactor

G. H. SEDAHMED[†], L. W. SHEMILT*Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada*

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Mass transfer coefficients were measured for the deposition of copper from acidified copper sulphate solution at a vertical-plate cathode stirred by the oxygen evolved at a coplanar, vertical-plate lead anode placed upstream from the cathode. The variables studied were: oxygen discharge rate, electrolyte concentration and height of the cathode. The cathodic mass transfer coefficient was increased by a factor of the order of 2 to 5 over the natural convection value depending on the rate of oxygen discharge at the lead anode. The relationship between the mass transfer coefficient and the oxygen discharge rate was found to be

$$\log K = a + 0.296 \log V.$$

The mass transfer coefficient was found to decrease initially with increasing electrode height, but then reached a constant value independent of further change in electrode height. A new, modified parallel-plate reactor stirred by the counter electrode gases is described. The advantage of the design is that it offers more efficient stirring with no added power consumption. Details of the design are discussed.

Nomenclature

| | |
|-------|---|
| C | concentration of CuSO_4 (mol cm^{-3}) |
| F | Faraday's constant |
| h | electrode height (cm) |
| K | mass transfer coefficient (cm s^{-1}) |
| I_L | limiting current density (A cm^{-2}) |
| V | gas discharge rate (cm s^{-1}) |
| z | number of electrons involved in the reaction |

current densities, air being injected into the cell through a series of fine orifices in a tube located at the bottom of the cathode. Using a similar design, Ettl *et al.* [2, 3] studied the effect of air sparging on the mass transfer coefficient and the mass transfer coefficient distribution on the cathode. Ibl *et al.* [4] considered mass transport enhancement caused by bubbles forced from a fine glass frit or through the walls of a porous metal electrode. Their data could be correlated by the equation:

$$K = aV^{0.36}. \quad (1)$$

1. Introduction

The performance characteristics of industrial electrochemical reactors can be improved by increasing the surface area per unit volume of the reactor and/or enhancing the rate of mass transfer in the reactor. Gas stirring is one of the methods for enhancement of the rate of mass transfer in industrial cells, and recent work has been aimed at measuring the effects of gas stirring. Harvey *et al.* [1] used air agitation to electrowin copper at high

More recently Ibl [5] and Sigrist *et al.* [6] measured mass transfer rates at vertical, gas-sparged electrodes with and without superimposed electrolyte flow. These authors found strong similarity between gas sparging and turbulent-free convection. They represented their results by an analogous correlation in which the Grashof number characteristic for free convection was replaced by a modified Archimedes number. Ibl

[†] On leave from the Department of Chemical Engineering, Faculty of Engineering, Alexandria University, Alexandria, Egypt.

et al. [4] and Gendron and Ettel [3] compared stirring by electrolyte circulation and gas sparging and reached the conclusion that the latter was more economical.

In the aforementioned studies the stirring gas was forced into the reactor from an outside source; in the present work the gas evolved at the counter electrode is used as the stirring agent at the working electrode. This has the potential advantage of reducing operating costs through elimination of an external gas supply system and the power consumed in forcing the gas into the reactor. Some investigations have been carried out on the degree of enhancement of heat and mass transfer rates in electrochemical processes through the evolution of gases at the counter electrode. Ettel *et al.* [7] studied the effect of oxygen evolution at the anode on the rate of mass transfer at the cathode in a parallel-plate, large-scale copper electrowinning cell. They found that the rate of mass transfer was enhanced at the upper parts of the cathode while that at the lower parts was unaffected by the stirring action of the anodic oxygen. Mohanta and Fahidy [8], using a parallel-plate, laboratory-scale copper electrowinning cell measured the effect of the anodically generated oxygen bubbles on the rate of mass transfer at the vertical cell cathode. They correlated their data quantitatively and found that the enhancing effect of anodic oxygen bubbles on the rate of mass transfer at the cathode is modest and does not exceed 20%. Fouad *et al.* [9] studied the effect of cathodic hydrogen bubbles on the rate of mass transfer at a copper anode dissolving in phosphoric acid in a vertical parallel-plate cell and reported an increase in the rate of mass transfer due to the hydrogen bubbles. MacMullin and Ruehlen [10] studied the effect of cathodically evolved hydrogen on the rate of heat transfer from a cooler placed in the cell in an attempt to remove the heat generated during electrolysis. They found that the heat transfer coefficient increased with hydrogen discharge rate according to the relation

$$h = aV^{0.344} \quad (2)$$

Fouad and Sedahmed [11] measured the mass transfer coefficient for the deposition of copper from acidified copper sulphate solution at a horizontal screen-array cathode stirred by oxygen evolved at a horizontal anode placed below the

cathode. They related the mass transfer coefficient to the oxygen discharge rate by the equation

$$K = aV^{0.29} \quad (3)$$

Sedahmed [12] measured the effect of oxygen bubbles evolving from a horizontal lead anode on the rate of mass transfer of copper deposition at a horizontal screen cathode placed above the anode. He correlated his data with the equation

$$K = aV^{0.377} \quad (4)$$

For a similar study [13] using a vertical cylinder cathode placed above an oxygen-generating anode made of a horizontal lead disc, Sedahmed correlated his data with the equation:

$$K = 65.8 \times 10^{-4} V^{0.358} / h^{0.29} \quad (5)$$

He found that the rate of mass transfer for the electrodeposition of copper increased by as much as 260% over the natural convection value. Sedahmed and Shemilt [14] studied, in a similar manner, the effect of anodically evolved oxygen on the rate of mass transfer at a horizontal cylinder cathode, the mass transfer coefficient being related to the oxygen discharge rate by the equation:

$$K = aV^{0.37} \quad (6)$$

The object of the present work is to seek a modification of the traditional parallel-plate cell design that will make efficient use of the gases evolved at the counter electrode as a stirring agent. In the design investigated, the cathode and the oxygen-evolving anode are positioned to be coplanar, with their edges separated by a plastic insulator, and with the cathode placed downstream from the anode. The stirring efficiency was determined by measuring the limiting current for the deposition of copper from acidified copper sulphate at a vertical-plate cathode using a vertical-plate lead anode.

2. Experimental technique

The apparatus (Fig. 1) consisted to two cells placed in the same container (a glass beaker, $d = 10.5$ cm, $h = 14.5$ cm), each cell drawing current from a different d.c. source. One cell served to generate oxygen which stirred the solution in the immediate vicinity of the cathode of the other cell, where copper was deposited. The oxygen-

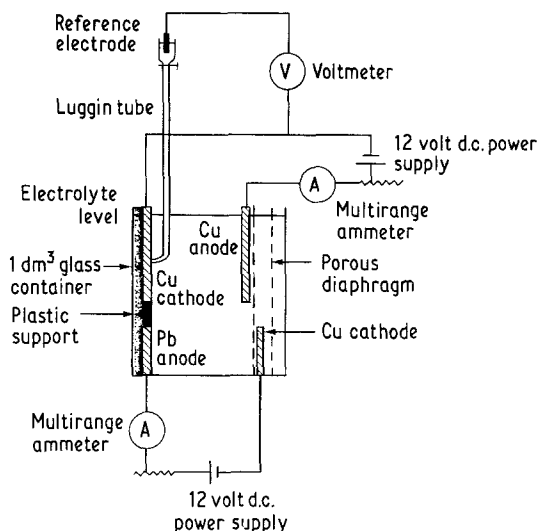


Fig. 1. Experimental apparatus.

generating cell occupied the lower part of the container with the copper deposition cell above. The upper cell consisted of two copper electrodes, each with a height of 10 cm and a width of 3 cm, placed 4 cm apart. The lower cell consisted of a lead oxide (PbO_2) coated lead anode and a copper cathode, each with a height of 4 cm and a width of 3 cm, and also placed 4.2 cm apart. The cathode of the upper cell and the anode of the lower cell were fixed vertically on a plastic support with separation of their edges achieved through a plastic insulator (0.5 cm height and 3 cm width), and with their surfaces flush with the plastic insulator so that the three surfaces formed a continuous surface free of irregularities. To keep the bulk concentration of copper sulphate constant during the experiment, the cathode of the lower cell was placed in a close-fitting cylindrical diaphragm made of synthetic fabric. Copper deposited from the solution at the cathode of the upper cell was compensated by that dissolved from the anode of the upper cell. The electrical circuit connected to each cell included a multirange ammeter and a 12 V d.c. power supply with a voltage regulator.

Mutual electrical interference between the two cells was tested by allowing current to pass in one cell and observing the ammeter of the other cell; it was found that there was no electrical interference between the two cells and each cell behaved independently. Before each run, the cathode surface of the upper cell was polished

with fine emery paper, degreased with trichloroethylene and washed with alcohol and distilled water, successively. The rate of oxygen discharge was controlled by adjusting the current passing through the lower cell. The limiting current for copper deposition at the cathode of the upper cell was determined at the established oxygen discharge rate from the polarization curve. Polarization curves were constructed by increasing the applied current stepwise and measuring the corresponding steady-state cathode potential, two minutes being allowed to achieve steady-state potential. The cathode potential was measured against a reference copper electrode placed in the cup of a Luggin tube with a voltmeter, the capillary tip of the Luggin tube being positioned 0.5–1 mm from the cathode surface. A fresh solution was used in each run and the temperature was kept constant at 25°C . Three concentrations of CuSO_4 were used: 0.05, 0.131 and 0.25 M, in all cases with 1.5 M H_2SO_4 as a supporting electrolyte.

3. Results and discussion

The effect of oxygen discharge at the lead anode of the lower cell on the limiting current deposition at the cathode of the upper cell is shown in Fig. 2. The mass transfer coefficient for copper deposition at the cathode of the upper cell was obtained from the limiting current using the equation

$$K = i_L / zFC. \quad (7)$$

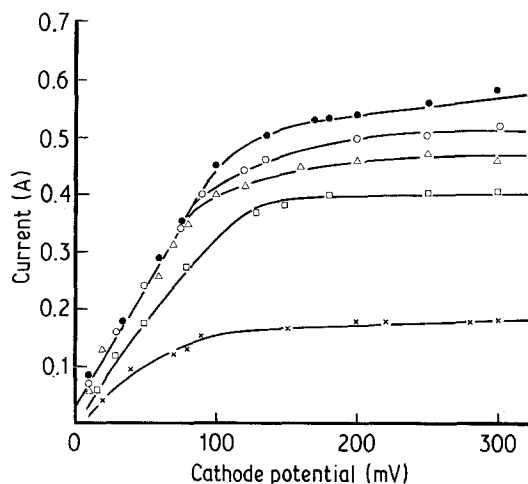


Fig. 2. Polarization curves at different oxygen discharge rates (V). $V(\text{cm s}^{-1}) = \times$, 0 (natural convection); \square , 0.001319; \triangle , 0.002638; \circ , 0.005275; \bullet , 0.010551.

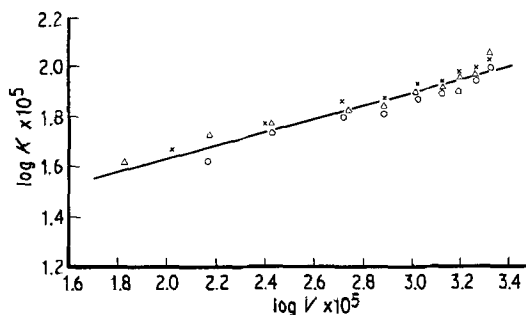


Fig. 3. Effect of oxygen discharge rate on the mass transfer coefficient. Cathode height = 10 cm. Concentration of CuSO_4 : X, 0.25 M; Δ , 0.131 M; \circ , 0.05 M.

Fig. 3 shows the effect of oxygen discharge rate on the mass transfer coefficient at different CuSO_4 concentrations, with the relationship represented by the equation

$$\log K = a + 0.269 \log V. \quad (8)$$

The $\log K/\log V$ slope is less than the values reported by other authors (Equations 1–6), who used gas sparging or counter electrode gases to enhance the rate of mass transfer at the working electrode. This difference may be attributed to the difference in gas-bubble distribution in the cell used here and in cells used by other authors. In the present work oxygen bubbles evolving from the vertical lead anode flow in the form of a thin curtain at the cathode surface. Other investigators [4, 10–14] used cells where the gas bubbles are almost uniformly distributed in the cross-section of the interelectrode gap.

Dynamic studies of bubble swarms have shown that bubbles interact among each other to affect the rising bubble velocity in two different ways [15], namely, (a) a chimney effect can develop in which massive upward current appears at the axis of the bubble stream leading to increased net bubble velocity, (b) the proximity of the bubbles to one another can result in a hindered settling condition, leading to reduced average bulk velocity.

In view of these effects it seems that the present electrode configuration, where the stirring gas bubbles are confined to a relatively thin curtain, favours hindered settling, while other cell geometries where gas bubbles fill the interelectrode gap favour the enhancing chimney effect. In addition, the upward velocity of the bubbles comprising the curtain may be further reduced

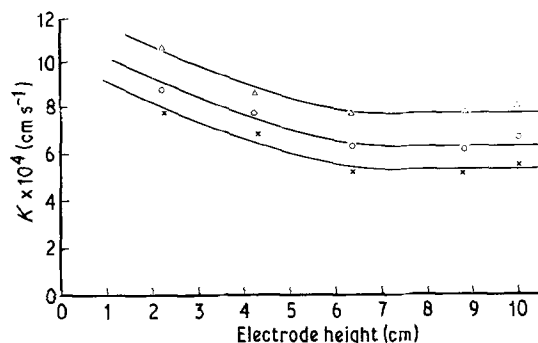


Fig. 4. Effect of electrode height on the mass transfer coefficient. $C = 0.131 \text{ M}$; $V(\text{cm s}^{-1}) = \text{X}, 0.002638$; $\circ, 0.005275$; $\Delta, 0.010551$.

by the wall effect [16] induced by the proximity of the bubbles to the cell electrodes.

Fig. 4 shows the effect of electrode height on the mass transfer coefficient at different O_2 discharge rates. For relatively short electrodes the mass transfer coefficients decrease with electrode height owing to the increase of the thickness of the boundary and diffusion layers with height. With further increase in electrode height, the mass transfer coefficients essentially reach a constant value. This behaviour is probably due to the conversion of the flow from a laminar to a turbulent regime beyond a certain electrode height, in a manner similar to natural convection [17]. This is consistent with the findings of Ibl [5] and Sigrist *et al.* [6] that a turbulent-flow, mass transfer mechanism prevails in gas-sparged electrolytic cells.

4. Practical application

In order to apply the idea of using gases evolved at the counter electrode as a means of stirring at the working electrode, a modification of the experimental reactor is proposed. This modified reactor would consist of a number of parallel vertical plates placed in a tank (Fig. 5), each plate being composed of a number of coplanar positive and negative electrodes arranged alternately. Within each plate, positive and negative electrodes would be separated by a plastic insulator which would form a continuous surface with the electrodes (Fig. 6). Every two parallel plates in the tank would contain a number of cells arranged vertically one above the other, each cell being

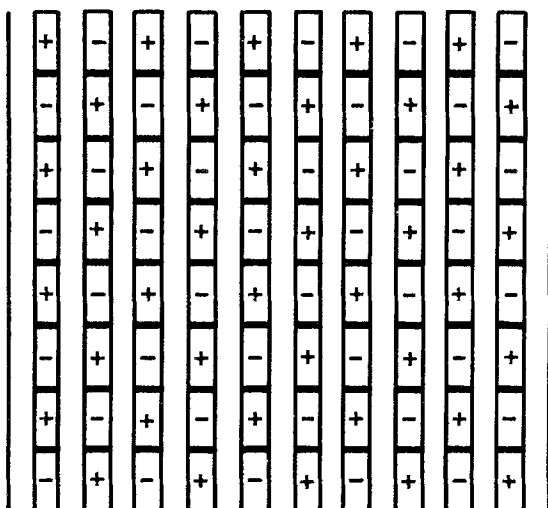


Fig. 5. Front view of the proposed electrochemical reactor.

composed of two separated parallel electrodes, and the cathode of each cell being preceded by the anode of another cell. Cells would be electrically connected in parallel to one d.c. power supply (Fig. 7).

One of the special operational aspects of the reactor would be that the mass transfer coefficient and the limiting current would increase from the leading edge of each plate because of the increase in the amount of oxygen with plate height (this assumes that the mass transfer coefficient is not affected by electrode height at a certain oxygen discharge rate). To illustrate the distribution of the limiting current along the plate height, calculations were made for two parallel plates, assum-

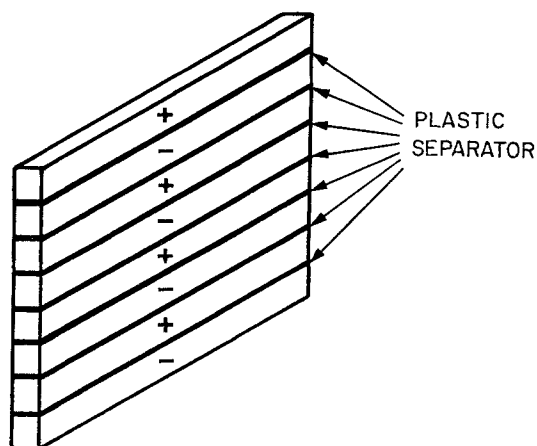


Fig. 6. A multi-electrode plate.

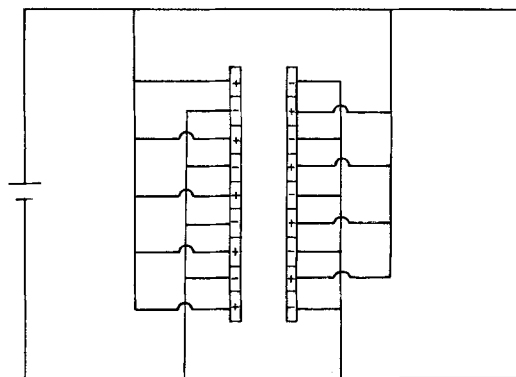


Fig. 7. Electrical connection of cells in two multi-electrode plates to a power supply.

ing that the voltage applied to the cells corresponds to the limiting current value and that each plate is composed of 10 electrodes, i.e., the two plates are composed of 10 cells connected electrically in parallel. Each electrode has a height of 10 cm so that each plate has a height of 100 cm. Upon applying voltage, the first cell (at the bottom of the two plates) will operate at a limiting current corresponding to the natural convection value; oxygen coming from the anode of the first cell will stir the solution at the cathode of the second cell and increase the limiting current over the natural convection value; oxygen coming from the anode of the first cell plus oxygen coming from the anode of the third cell will stir the solution at the cathode of the fourth cell and increase the limiting current to a value higher than that of the second cell, etc. Fig. 8 shows the results of these calculations. The average limiting current is almost double the natural convection value.

The apparent advantage of this reactor is that it eliminates the use of external energy to enhance the rate of mass transfer, thus reducing the operating costs of electrochemical processes. A further advantage is that the reactor can be extended vertically, saving floor space and capital cost. The main disadvantage of this reactor is that the mass transfer and limiting current distribution will not be uniform along each plate. Nonetheless, the reactor could be applied to the electrowinning of metals, the production of metal powders, and organic and inorganic electrosynthesis involving gas evolution at the counter electrode provided that the reaction products are not affected by the gas evolved at the counter electrode.

| | | |
|---|---------------------|---|
| - | $I_{L10} = 0.01325$ | + |
| | $V_{10} = 0.00027$ | |
| + | $I_{L9} = 0.0127$ | - |
| | $V_9 = 0.0002307$ | |
| - | $I_{L8} = 0.0125$ | + |
| | $V_8 = 0.0002027$ | |
| + | $I_{L7} = 0.01163$ | - |
| | $V_7 = 0.000165$ | |
| - | $I_{L6} = 0.0115$ | + |
| | $V_6 = 0.0001413$ | |
| + | $I_{L5} = 0.011$ | - |
| | $V_5 = 0.000104$ | |
| - | $I_{L4} = 0.0105$ | + |
| | $V_4 = 0.0000833$ | |
| + | $I_{L3} = 0.010$ | - |
| | $V_3 = 0.0000487$ | |
| - | $I_{L2} = 0.00925$ | + |
| | $V_2 = 0.0000305$ | |
| + | $I_{L1} = 0.0058$ | - |
| | $V_1 = 0$ | |

Fig. 8. Distribution of the limiting current and the amount of oxygen passing any cathode along two parallel plates.

Acknowledgement

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