Mass transfer enhancement by the counter-electrode gases in a new cell design involving a three-dimensional gauze electrode

G. H. SEDAHMED

Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt

Limiting currents and mass transfer coefficients were measured for the electrodeposition of copper from an acidified solution of copper sulphate at an array of closely packed screens stirred by oxygen. The oxygen evolved at a horizontal lead anode placed below the screen array. Variables studied were: oxygen discharge rate, electrolyte concentration and number of screens per array. For a single-screen electrode, oxygen discharge was found to increase the mass transfer coefficient according to the equation

$$\log K = a + 0{\cdot}377 \log V.$$

The mass transfer coefficient was found to decrease slightly with increasing number of screens per array, the decrease becoming pronounced when the number of screens per array reached six. A new cell design involving an array of closely packed screens as a working electrode stirred by the counter-electrode gases is described and its merits and disadvantages are pointed out.

List of symbols

a constant
I limiting current (A)
Z number of electrons involved in the reaction
F the Faraday (96 500 C)
K mass transfer coefficient ($cm\,s^{-1}$)
C concentration of copper sulphate ($mol\,l^{-1}$)
V oxygen discharge rate ($cm^3\,cm^{-2}\,s^{-1}$)

1. Introduction

The last decade has witnessed a revolutionary change in the design of electrochemical reactors with the advent of the three-dimensional electrodes, namely, the packed- and fluidized-bed electrodes [1–18]. The advantages of these electrodes over the traditional parallel-plate electrolysers are that their specific areas and mass transfer coefficients are exceptionally high; these advantages give rise to a considerable decrease in the capital and operating costs of electrochemical processes and open new possibilities such as the application of electro-chemical methods to electro-organic synthesis on a commercial scale and the recovery of precious metals from extremely dilute waste streams.

Fluidized- and packed-bed electrodes are usually operated by mechanically forcing the electrolyte through the electrode; this involves a consumption of some energy which is required to overcome the friction between the flowing electrolyte and the three-dimensional electrode. The present work seeks to eliminate the external pumping energy by utilizing the gases evolved at the counter electrode as a means of enhancing the rate of mass transfer at the working electrode which is composed of an array of closely packed screens.

The mass transfer characteristics of an array of closely packed screens have been studied under forced convection conditions by Alkire and Gracon [11], Sioda [2, 3], and Blaedel and Boyer [19]. The exploitation of gases evolved at the counter electrode as a means of enhancing the rate of mass transfer at the counter electrode has been initiated by Fouad and Sedahmed [20] who used an array of separated screens as a working electrode. Sedahmed and Shemilt [21] studied rates of mass

transfer for the electrodeposition of copper at a vertical cathode stirred by oxygen evolved at a vertical anode positioned upstream from the cathode and coplanar with it; they found that the mass transfer coefficient is related to the oxygen discharge rate by the equation

$$K = aV^{0.269}. \tag{1}$$

Also, Sedahmed and Shemilt [22] measured the limiting current for the electrodeposition of copper on a horizontal cylinder stirred by oxygen evolved at a lead anode placed below the cylinder. The relationship between the mass transfer coefficient and oxygen discharge rate was found to be

$$K = aV^{0.37}. \tag{2}$$

The present study was carried out by measuring the limiting current for the deposition of copper from an acidified solution of copper sulphate con-

taining a large excess of sulphuric acid to eliminate the transfer of copper ions to the electrode surface by electrical migration.

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 1) served to generate oxygen which stirred the solution at the cathode of the other cell (Cell 2) where copper was deposited. The container was made of plastic and had a diameter of 10 cm and a height of 15 cm. It was divided into two compartments by a tight cylindrical porous PVC diaphragm of 4·7 cm diameter. The inner compartment contained Cell 2 and the anode of the oxygen-generating cell (Cell 1); the outer compartment contained the cathode of the oxygen-generating cell. The oxygen-generating cell
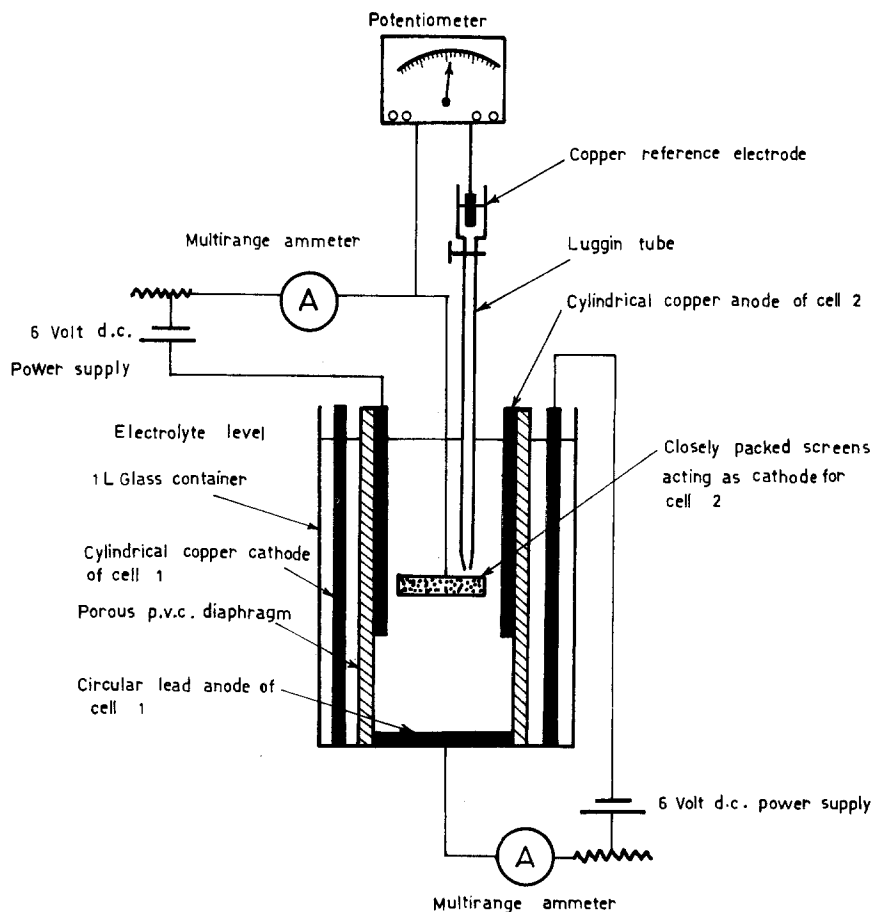

Fig. 1. Cell and electrical circuit.

consisted of a lead disc anode of 4·5 cm diameter placed at the bottom of the inner compartment and a cylindrical copper sheet of diameter 8 cm, acting as a cathode, placed in the outer compartment. The other cell (Cell 2) consisted of an array of closely packed screens as a cathode (1–7 screens); each screen was made of copper and had a mesh number of 8 square apertures per cm linearly, a wire diameter of 0·37 mm, a porosity of 0·75 and a diameter of 3·7 cm. The screens were held in position by a vertical copper wire passing through the centre of the screens. The wire acted at the same time as a current feeder and was electrically insulated except at the contact with the screens. A cylindrical sheet of copper of 4·6 cm diameter formed the anode. The use of a diaphragm and copper anode for cell 2 ensured the constancy of copper sulphate bulk concentration in the inner compartment.

The electrical circuit connected to each cell was composed of a multirange ammeter and 12 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. The rate of oxygen discharge was controlled by adjusting the current passing through the oxygen-generating cell (Cell 1). The limiting current of copper deposition at the screen cathode was determined at a certain oxygen discharge rate from the polarization curve which was constructed by increasing the applied current stepwise and measuring the corresponding steady-state potential against a reference copper electrode placed in the cup of a luggin tube with a high impedence voltmeter. The capillary tip of the luggin tube was 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 copper sulphate concentrations were used: 0·05, 0·131 and 0·25 M. In the three cases 1·5 M H_2SO_4 was used as a supporting electrolyte.

3. Results and discussion

Fig. 2 shows some typical polarization curves for copper deposition at a single horizontal screen obtained at different oxygen discharge rates. Limiting currents were determined from polarization curves and the mass transfer coefficients
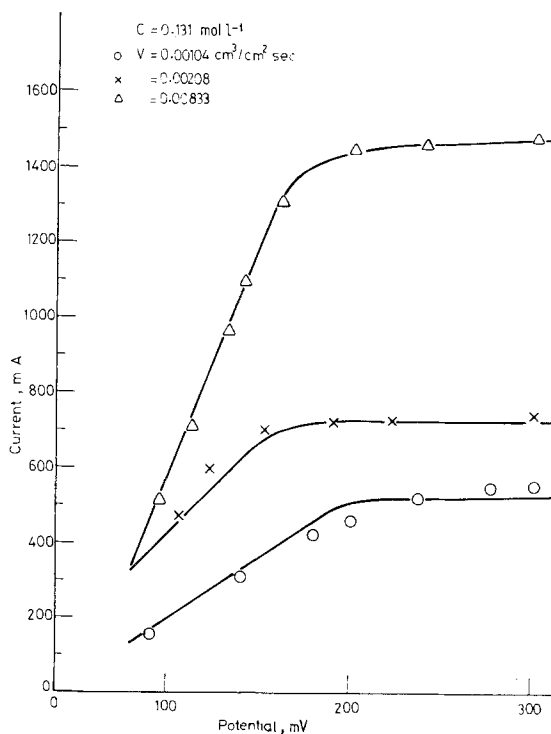
Fig. 2. Typical polarization curves for copper deposition obtained at different oxygen discharge rates.

were calculated using the equation

$$\frac{I}{ZFA} = KC. \qquad (3)$$

The area of the screen, A was calculated using the method of Armor and Cannon [23] from the number of apertures per cm linearly, and the wire diameter.

Fig. 3, shows the effect of the oxygen discharge rate on the mass transfer coefficient for a single-screen electrode; the data can be represented by the equation

$$\log K = a + 0.377 \log V. \qquad (4)$$

Table 1 shows that the ($\log K / \log V$) slope obtained in this work is in agreement with the slopes reported by most authors who used gases to enhance heat or mass transfer in electrochemical processes.

It would be interesting, for the purposes of cell design, to compare the mass transfer characteristics of different electrode geometries stirred by oxygen evolved at the counter electrode. Table 2 shows a comparison of the mass transfer coefficients at

Fig. 3. Effect of oxygen discharge rate on the mass transfer coefficient of copper deposition using a single-screen electrode.

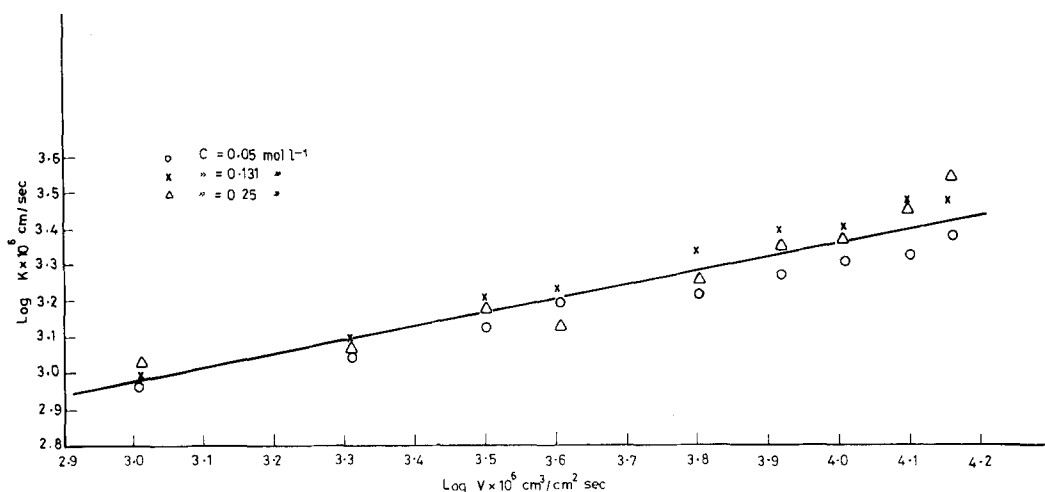Table 1. Comparison of (log K/log V) slopes obtained by different authors who used gasses to enhance the rate of transfer

Case	Reference	log K/ log V slope
Enhancement of mass transfer by forcing N_2 through a glass frit	[24]	0·36
Enhancement of heat transfer by cathodic H_2	[25]	0·344
Enhancement of mass transfer at a vertical cathode by anodic O_2	[21]	0·269
Enhancement of mass transfer at a horizontal cylinder cathode by anodic O_2	[22]	0·37
Enhancement of mass transfer at an array of separated screens by anodic O_2	[20]	0·29
Present work		0·377

different oxygen discharge rates for the electrodeposition of copper on vertical plates [21], horizontal cylinders [22] and a single screen (the present work). It is seen that for the same oxygen discharge rate the screen electrode has the highest mass transfer coefficient among the three electrode geometries; this may be attributed to the ability of the screens to induce a high local solution velocity.

It is noteworthy that the (log K/log V) slope obtained in this work compares favourably with the values obtained by different investigators who studied the mass transfer behaviour of screen electrodes stirred by mechanical circulation of the electrolyte. Sioda [2, 3] obtained a slope of 0·36, Alkire and Garcon [11] obtained a slope of 0·37 while Blaedel and Boyer [19] obtained a slope of 0·321.

Fig. 4 shows the effect of the number of

Table 2. Mass transfer characteristics of single screens in comparison with vertical plates and horizontal cylinders stirred by anodic oxygen

V ($\times 10^{-3}$) (cm^3 cm^{-2} s^{-1})	K ($\times 10^{-4}$)(cm s^{-1}) vertical plate [21]	K ($\times 10^{-4}$)(cm s^{-1}) horizontal cylinder [22]	K ($\times 10^{-3}$)(cm s^{-1}) single screen
0·959	4·266	4·726	0·9842
1·918	5·012	6·228	1·260
2·877	5·623	7·785	1·413
3·836	6·026	9·008	1·585
4·795	6·457	9·342	1·778
5·754	6·761	10·565	1·995
7·183	7·244	11·678	2·239

Fig. 4. Effect of the number of screens per bed on the mass transfer coefficient.

screens per array on the mass transfer coefficient; the mass transfer coefficient decreases slightly with increasing the number of screens per array, the decrease becoming pronounced when the number of screens reaches six. This can be explained by the fact that increasing the number of screens per array leads to an increase in the resistance of the array to the flow of the gas–electrolyte system with a corresponding decrease in the mass transfer coefficient. Fig. 5 shows a proposed design of an electrochemical reactor based on the idea of using an array of closely packed screens as the working electrode stirred by the counter-electrode gases. The proposed reactor is composed of a vertical column in which the working electrodes are arranged alternately with the counter electrodes, i.e. each working electrode is placed between two counter electrodes, which ensures a uniform current distribution on the working electrodes. While the working electrode is composed of an array of closely packed screens, the counter electrode is composed of a single screen.

The apparent advantage of this reactor is the appreciable enhancement of the rate of mass transfer without any consumption of external stirring energy. This should lead to a decrease in the operating costs of electrochemical processes.

The apparent disadvantage of this reactor is that the limiting current and concentration polarization are not the same at different arrays owing to the difference in the amount of gas passing each array; the higher the position of the array, the lower the concentration polarization and the higher the limiting current. Another disadvantage is that the resistance of the cell, particularly of the upper part, may increase due to the presence of the gas bubbles. However, this problem can be alleviated by choosing a high conductivity electrolyte and by decreasing the electrode separation.

The reactor may find applications in the

Fig. 5. Proposed industrial electrochemical reactor.

electrowinning of metals and in the electrolytic production of metal powders, where the anodic reaction is oxygen evolution. It can also be used in electro-organic and inorganic syntheses where the counter-electrode reaction is gas evolution, provided that the gas does not interfer with the main reaction taking place at the working electrode. In view of the high area per unit volume of the reactor, it can be used in the recovery of precious metals from waste streams. The reactor can be operated batchwise or continuously by feeding in the electrolyte slowly at the bottom of the reactor and withdrawing it from the top, fully reacted.

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