Effect of anodically evolved gas bubbles on the rate of cathodic mass transfer in a vertical cylinder cell

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Mass transfer coefficients were measured for the deposition of a copper from acidified copper sulphate solution at a vertical cylinder cathode stirred by oxygen evolved at a coaxial vertical cylinder lead anode placed upstream from the cathode and flush with it. The cathodic mass transfer coefficient was increased by a factor of 2.75–6.7 over the natural convection value depending on the rate of oxygen discharge at the lead anode and height of the cathode. The data were correlated by the equation:

$$J = 0.66(F_r R_e)^{-0.21}$$

An electrochemical reactor built of a series of vertical coaxial annular cells stirred by the counter electrode gases is proposed as offering an efficient way of stirring with no external stirring power consumption.

Nomenclature

a, b, c	constants	u	solution viscosity, poise
C	concentration of copper sulphate, mol cm^{-3}	V	oxygen discharge rate as defined by Equation 9, cm^3 cm^{-2} s^{-1} or cm s^{-1}
d	cylinder diameter, cm	Z	number of electrons involved in the reaction
D	diffusivity, cm^2 s^{-1}	J	mass transfer J factor ($S_t S_c^{0.66}$)
F	Faraday's constant	S_t	Stanton number (K/V)
g	acceleration due to gravity, cm^2 s^{-1}	S_c	Schmidt number (ν/D)
h	electrode height, cm	S_h	Sherwood number (Kh/D)
i	current density at the oxygen generating anode, A cm^{-2}	R_e	Reynold's number ($\rho Vh/u$)
		F_r	Froude number (V^2/hg)
I_L	limiting current density, A cm^{-2}	G_r	Grashof number [$gh^3\epsilon/\nu^2 (1-\epsilon)$]
K	mass transfer coefficient, cm s^{-1}	ρ	density of the solution, g cm^{-3}
P	gas pressure, atm	ν	kinematic viscosity, cm^2 s^{-1}
R	gas constant, atm cm^3 mol^{-1} K^{-1}	ϵ	void fraction of the gas in the liquid–gas dispersion
T	temperature, K		

1. Introduction

In many electrochemical processes, e.g. electrowinning of metals and electrosynthesis, a considerable portion of the electrical energy provided to the cell is consumed in conducting a useless counter electrode reaction, namely, gas evolution. Recently the idea of utilizing counter electrode gases as a means of enhancing the rate of mass

transfer at the working electrode has been conceived with a view to improving the economy of electrochemical reactors by dispensing with external stirring. Measurement of the effect of counter electrode gases on the rate of mass transfer at the working electrode using traditional parallel plate cells showed that the increase in the rate of mass transfer was modest and nonuniform [1–5]. This led to the idea of modifying the cell

design so as to make a more efficient use of the counter electrode gases. Designs based on a flat plate working electrode preceded by a co-planar gas-evolving counter electrode [6], an array of horizontal screens [7] and an array of horizontal cylinders [8] placed above a horizontal gas evolving electrode were tested for the increase in the rate of mass transfer and found to be more efficient than the traditional parallel plate reactor with gas evolving counter electrode. The object of the present work is to measure the rate of mass transfer at a vertical cylinder cathode placed downstream of a vertical oxygen evolving cylinder anode coaxial with the cathode and flush with it. In an earlier report [9], rates of mass transfer at a vertical cylinder cathode, below which was a horizontal oxygen evolving disc anode, were measured; using a horizontal disc anode provides a uniform distribution of gas in the interelectrode gap while, in the present case, oxygen is evolved in the form of a thin curtain surrounding the cathode. In addition, the present work contributes to the understanding of the mechanism of mass transfer at gas evolving electrodes [10] where mass is transferred by combined micro and macro convection; the present work sheds some light on the role played by macroconvection in enhancing the rate of mass transfer at gas-evolving electrodes.

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 made of plastic and had a volume of 4 dm^3 and a diameter of 18 cm. It was divided into two compartments by a tight cylindrical porous diaphragm of 14 cm diameter made of synthetic fabric. The oxygen generating cell consisted of a lead cylinder anode of 2.1 cm diameter and 5 cm height placed in the centre of the inner compartment and a cylindrical sheet of copper cathode placed in the outer compartment. The other cell (Cell 1) consisted of a vertical copper cathode cylinder of 2.1 cm diameter and a cylindrical copper anode sheet of 14 cm diameter and 10 cm height. The cylinder cathode of Cell 1 was positioned in the centre of the inner compartment above the lead anode of Cell 2 and flush with it, these electrodes were separated by a 0.5 cm cylindrical layer of wax. The active height of the cathode of Cell 1 ranged from 1.6 to 10 cm. The use of the porous diaphragm and a copper
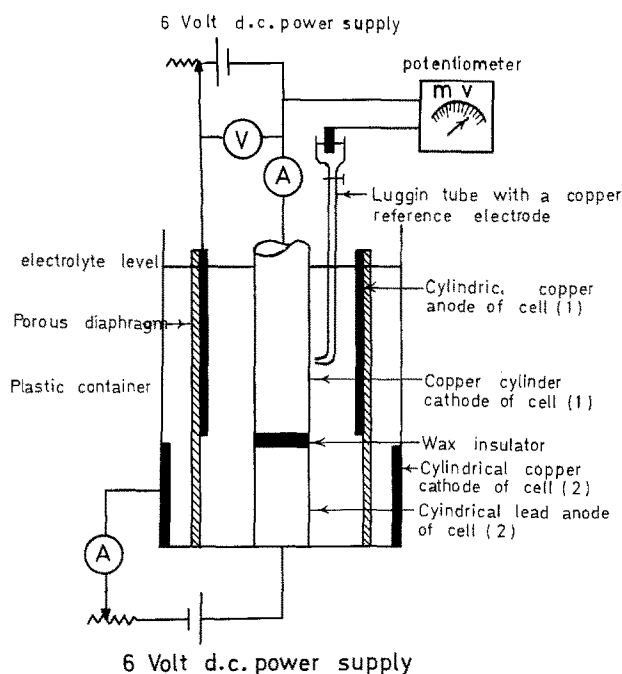

6 Volt d.c. power supply

Fig. 1. Cell and electrical current.

anode for Cell 1 ensured the constancy of copper ion concentration in the inner compartment during electrolysis. Mutual electrical interference between the two cells was found to be negligible and each cell behaved independently during electrolysis. Before each run, the surface of the cylinder cathode of Cell 1 was polished with fine emergy paper, degreased with trichloroethylene, and washed with alcohol and distilled water, respectively. 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 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 cathode potential. The cathode potential was measured against a reference copper electrode placed in the cup of a Luggin tube by means of a potentiometer. The capillary tip of the Luggin tube was positioned 0.5–1 mm from the cathode surface. The solution used was 1.5M H_2SO_4 + $CuSO_4$ (0.027–0.131 M). Cell temperature was kept constant at 20° C. In all experiments the bottom of the lead cylinder anode of Cell 2

was isolated with epoxy resin. A fresh solution was used in each experiment; copper sulphate concentration was checked by iodometry [11]. Each experiment was repeated two or three times.

3. Results and discussion

Fig. 2 shows typical polarization curves with a well defined limiting current plateau at different oxygen discharge rates. These curves were used to obtain the limiting current from which the mass transfer coefficient was calculated from the equation:

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

Fig. 3 shows the effect of oxygen discharge rate on the mass transfer coefficient; the data fit the equation

$$K = aV^{0.37} \qquad (2)$$

The exponent 0.37 is in agreement with the values obtained with other geometries such as horizontal (0.37) [8], vertical cylinders stirred by counter electrode oxygen uniformly distributed in the
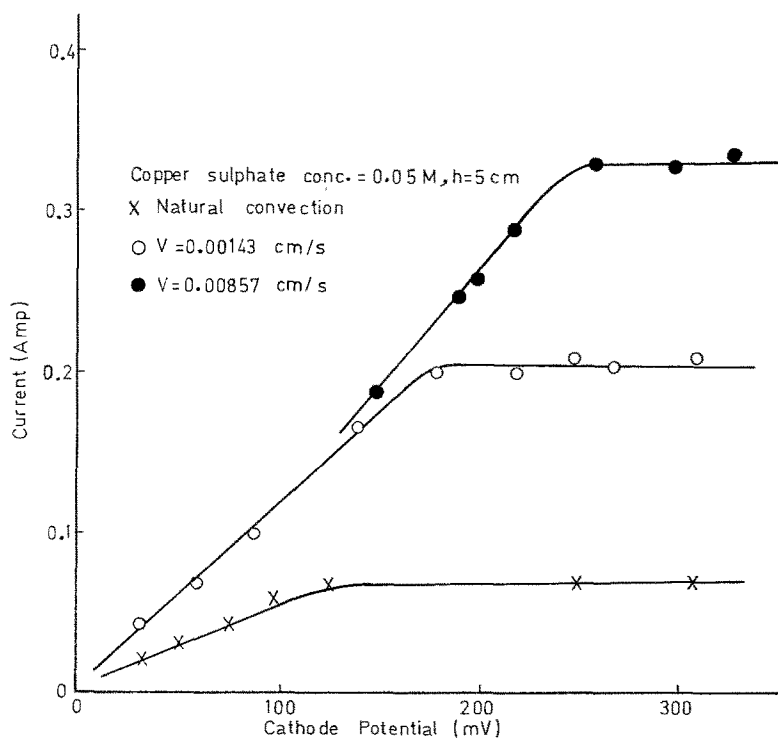
Fig. 2. Typical polarization curves obtained at different oxygen discharge rates. Copper sulphate concentration = 0.05 M; h = 5 cm; x – natural convection, ○ – V = 0.001 43 cm s^{-1}, ● – V = 0.008 57 cm s^{-1}
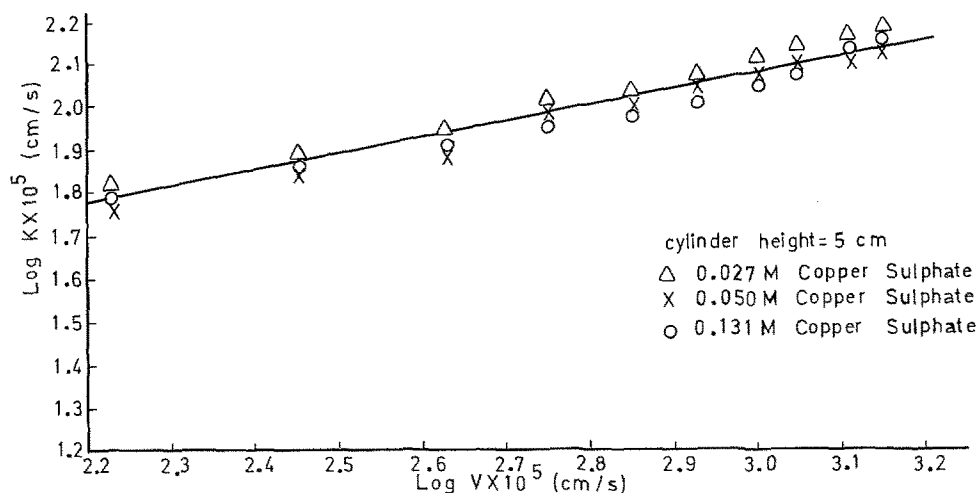
Fig. 3. Log K vs log V for different copper sulphate concentrations. Cylinder height = 5 cm. △ – 0.027 M, X – 0.05 M ○ – 0.131 M copper sulphate.

interelectrode gap (0.358) [9] and horizontal screens (0.377) [7]. The present exponent is at variance with the value obtained for a vertical plate electrode stirred by oxygen evolved at an upstream vertical anode flush with the cathode (0.269) [6]. This discrepancy was unexpected in view of the fact that the two situations are similar in that oxygen is evolved in the form of a thin curtain at the working electrode; no satisfactory explanation could be found. The present exponent also agrees with the value 0.344 reported by MacMullin *et al.* [12] who studied the effect of electrolytic hydrogen

evolution on the rate of heat transfer. The exponent is also close to the value 0.36 obtained by Ibl *et al.* [13] who studied the effect of nitrogen bubbles forced into the solution through a fine glass frit on the rate of mass transfer.

Fig. 4 shows the effect of cylinder height on the mass transfer coefficient at different oxygen discharge rates. The mass transfer coefficient decreases with cylinder height up to a certain limit and then remains constant with further increase in cylinder height probably because of the attainment of fully developed mass transfer. A similar behaviour was observed in studying
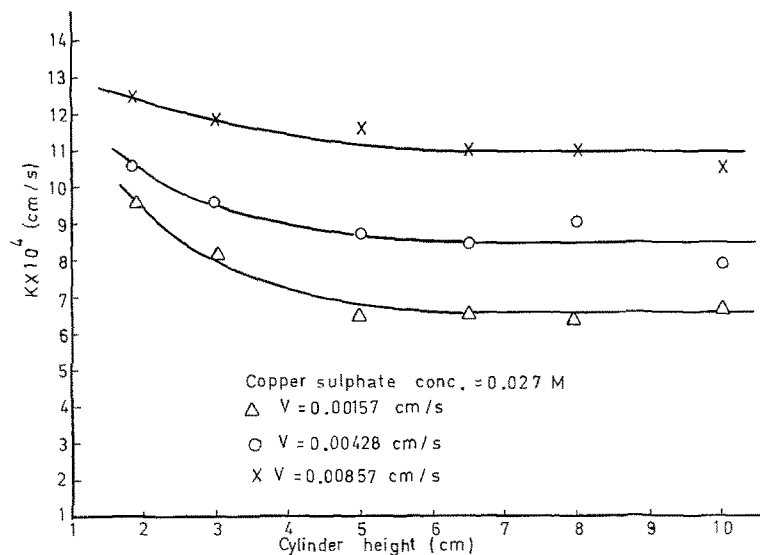

Fig. 4. Effect of cylinder height on the mass transfer coefficient. Copper sulphate concentration = 0.027 M: △ – V = 0.001 57 cm s^{-1}, ○ – V = 0.004 28 cm s^{-1}, x – V = 0.008 57 cm s^{-1}.
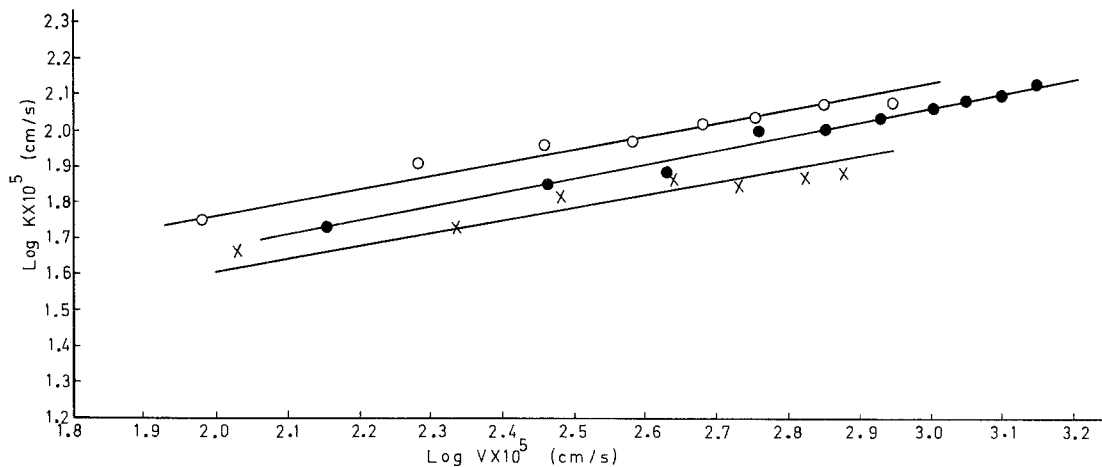
Fig. 5. Log K vs log V for different electrode orientations. Copper sulphate concentration = 0.05 M: x – vertical cylinder (h = 5 cm), O_2 bubbles are uniformly distributed in the solution [7]; ○ – horizontal cylinder (d = 1.4 cm), O_2 bubbles are uniformly distributed in the solution [8]; ● – vertical cylinder (h = 5 cm), O_2 bubbles form a curtain around the cylinder (present work).

the effect of vertical electrode height and cylinder diameter on the mass transfer coefficient at different oxygen discharge rates. Ibl *et al.* [13] and Ettel *et al.* [1, 4] who studied the effect of gas sparging on the rate of mass transfer using electrodes of heights > 20 cm found that electrode height has no effect on the mass transfer coefficient at different superficial gas velocities. In a recent study on the effect of gas sparging on the rate of heat transfer from vertical and horizontal cylinders, Lewis *et al.* [14] found that, for a given gas velocity, the heat transfer coefficient decreased with an increase in the vertical dimension (length in the case of the vertical cylinders and diameter in the case of the horizontal cylinders) to a certain point and remained constant with further increase in the vertical dimension. This agrees with the present finding. The present finding concerning the effect of electrode height on the rate of mass transfer is similar to that observed in the case of natural convection [15].

A comparison has been made between the present case, where oxygen is evolved in the form of a thin curtain surrounding the cathode and two other cases, namely, a vertical cylinder cathode and a horizontal cylinder stirred by oxygen uniformly distributed in the interelectrode gap. Fig. 5 shows that for the same rate of oxygen discharge, the mass transfer rate is highest at horizontal cylinders followed by vertical cylinders stirred

by a curtain of oxygen bubbles, and oxygen bubbles uniformly distributed in the inter-electrode gap, respectively. The higher mass transfer rates at the horizontal cylinder may be attributed to the impingement of gas bubbles on the cylinder surface thus distributing the diffusion layer. There is also the possibility of boundary layer separation and edddy formation in the wake of the horizontal cylinder.

4. Data correlation

An overall correlation was envisaged using the method of dimensional analysis, for the present case:

$$K = f(V, \rho, u, h, g, D) \qquad (3)$$

Writing Equation 3 in terms of dimensionless groups:

$$\left(\frac{K}{V}\right)\left(\frac{u}{\rho D}\right)^a = b\left(\frac{V^3\rho}{ug}\right)^c \qquad (4)$$

Assuming $a = 0.66$, Equation 4 can be written in the form:

$$J = b\left(\frac{V^3\rho}{ug}\right)^c \qquad (5)$$

or,

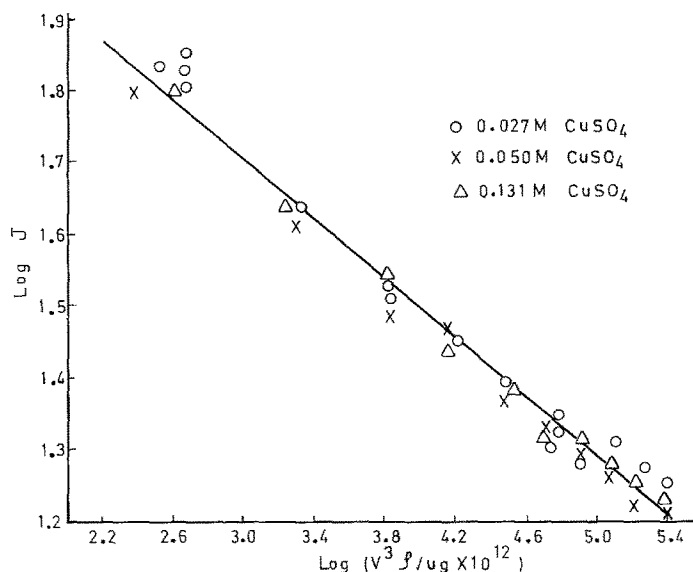$$J = b\left(\frac{V^2}{hg}\right)^c \left(\frac{\rho Vh}{u}\right)^c \qquad (6)$$

Fig. 6. Overall mass transfer correlation: ○ – 0.027 M, x – 0.05 M, △ – 0.131 M copper sulphate.

By applying Equation 5 to the experimental results the following correlation was obtained which fits the data with an average deviation of ± 4.9% (Fig. 6):

$$J = 0.66(V^3 \rho/ug)^{-0.21} \tag{7}$$

or,

$$J = 0.66(F_r R_e)^{-0.21} \tag{8}$$

The physical properties of the solution used in calculating J, F_r and R_e were obtained from the literature [15, 16].

The oxygen discharge rate (V) used in obtaining Equation 7 was calculated from the oxygen generating anode current density (i) using Faraday's law and the gas law, namely,

$$V = \frac{iRT}{4FP} \tag{9}$$

Ibl [17] and Ibl et al. [18] who measured mass transfer rates at a vertical gas sparged electrode correlated their data in a manner similar to that used in natural convection, they obtained the equation:

$$S_h = 0.19(S_c G_r)^{0.33} \tag{10}$$

The disadvantage of Equation 10 compared to Equation 7 is that it needs a priori measurement of the void fraction of the gas in the solution to calculate the value of the Grashof number [$gh^3 \epsilon/$

$v^2 (1 - \epsilon)$]. Sedahmed and Shemilt [8] who measured rates of mass transfer at a horizontal cylinder stirred by the counter electrode oxygen correlated their data with the equation:

$$J = 25 R_e^{-0.53} \tag{11}$$

Although the above equation fits the experimental data quite well it cannot be used generally because the Froude number is ignored.

In the area of heat transfer, Hart [19] correlated heat transfer in bubble agitated systems by the equation:

$$J = 0.125(F_r R_e)^{-0.25} \tag{12}$$

The discrepancy between Equation 12 and Equation 8 may be attributed among other things to the fact that the range of $(F_r R_e)$ used by Hart is much higher than that used in the present work.

Fig. 7 shows the effect of gas discharge rate on the limiting current and cell voltage. Within the range of oxygen discharge rates studied, the limiting current increases by a factor ranging from 2.75 to 6.7 over the natural convection value.

Fig. 7 also shows that, within the present range of oxygen discharge rates, the cell voltage decreases with increasing oxygen discharge rate; it seems that under the present conditions the decrease in concentration polarization outweighs the increase in ohmic drop caused by the presence
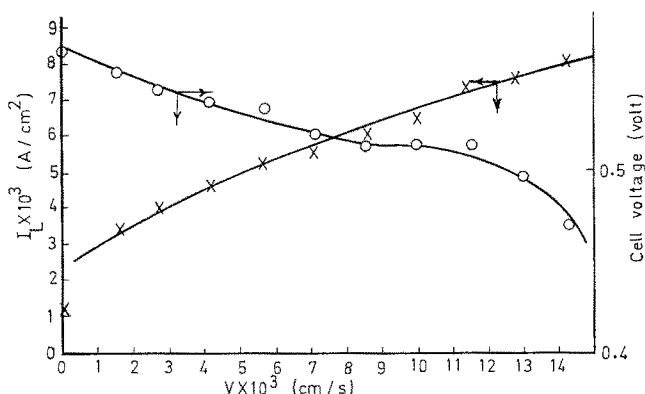
Fig. 7. Effect of oxygen discharge rate on the limiting current and cell voltage. Copper sulphate concentration = 0.027 M, cylinder height = 5 cm: x – I_L vs V, o – cell voltage vs V.

of oxygen bubbles. A similar behaviour was reported in the case of vertical and horizontal cylinders stirred by counter electrode oxygen bubbles uniformly distributed in the interelectrode gap [8, 9]. The increase in the limiting current and the decrease in cell voltage suggest the use of counter electrode gases to enhance the rate of mass transfer in electrochemical reactors.

5. Practical applications

Fig. 8 shows a possible reactor design which utilizes the counter electrode gases to enhance the rate of mass transfer at the working electrode. Electrodes are arranged in such a way that the working electrode of the upper cell lies downstream of the gas-evolving electrode of the lower cell. The advantage of the reactor is the possible

increase in the rate of mass transfer without any consumption of external stirring energy. This type of reactor could possibly find application in electrosynthesis where the counter electrode reaction is gas evolution provided that the gas does not react with the product. Recent studies show that the use of undivided cells in electrosynthesis without the loss of product at the counter electrode has made progress through the choice of electrode material [20, 21] and the use of inhibitors [22–24]. The implication of the present work to gas-sparged reactors (using external gas) proposed for electrowinning and electrorefining of metals [25–27] is that the gas distributor should be designed in such a way so as to produce a thin curtain in the immediate vicinity of the cathode.
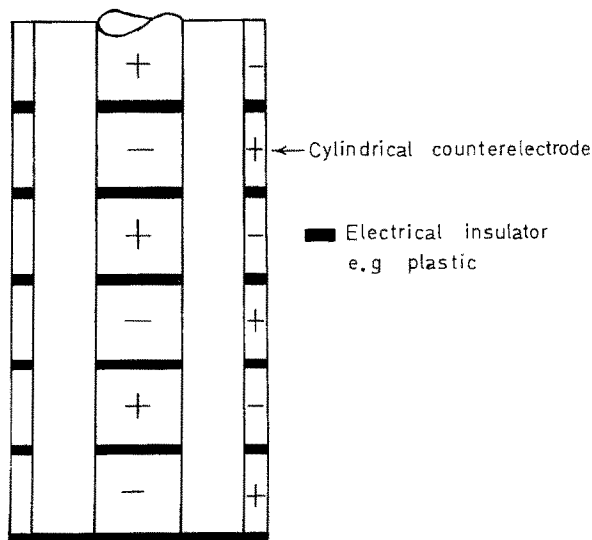

Fig. 8. Proposed electrochemical reactor.

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