JOURNAL OF APPLIED ELECTROCHEMISTRY 19 (1989) 736–743

Mass transfer to percolated porous materials in a small-scale cell operating by self-pumping

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Received 4 October 1988; revised 13 January 1989

The paper deals with an experimental electrochemical study of mass transfer to porous nickel materials (felt, foams) in a small-scale laboratory cell functioning in a self-pumping mode. The liquid flow through a disc of the porous material is induced by the rotation of a solid circular disc. The cell is simple and is useful for laboratory studies of materials for porous electrodes and also for small-scale synthesis using such materials. The work examines separately the mass transfer to the rotating disc and to the porous disc. Empirical correlations of the experimental data are given.

Nomenclature

a_e	specific surface area (per unit of total volume of electrode) (m^{-1})
C_0	entering concentration of ferricyanide ions ($mol\,m^{-3}$)
D	molecular diffusion coefficient of ferricyanide ($m^2\,s^{-1}$)
e	thickness of the sheet of material (m)
F	Faraday number ($C\,mol^{-1}$)
g	acceleration due to gravity ($m\,s^{-2}$)
h	distance between the discs (m)
I_L	limiting current (A)
$\bar{k}_d$	mean mass transfer coefficient ($m\,s^{-1}$)
N	rotating velocity ($rev\,min^{-1}$)
Q_v	volumetric electrolyte flow rate ($m^3\,s^{-1}$)
R	radius of the solid disc (m)
R_c	inner radius of the cell (m)
R_i	radius of the porous disc (m)
Re_h	Reynolds number based on h ($= \omega h^2/\nu$)
Re_R	Reynolds number based on R ($= \omega R^2/\nu$)
Sc	Schmidt number
Sh_h	Sherwood number based on h ($= \bar{k}_d h/D$)
Sh_r	Sherwood number based on R ($= \bar{k}_d R/D$)
$\bar{u}$	mean electrolyte velocity ($m\,s^{-1}$)
V	electrode volume (m^3)
X	conversion
ϱ	electrolyte density ($kg\,m^{-3}$)
ν_e	number of electrons in the electrochemical reaction
ν	kinematic viscosity ($m^2\,s^{-1}$)
ω	angular velocity (s^{-1})
ω_0	minimum angular velocity (s^{-1})

1. Introduction

The present work deals with an original laboratory cell and is based on the fact that the rotation of a planar circular disc generates an axial flow towards this disc, as for the rotating disc electrode [1]. Such a pumping effect can be applied for the study of materials for flow-through porous electrodes, in a small-scale cell with total recycling and designed as in Figs 1a and 1b. In this cell the disc of porous material is installed upstream from the rotating disc. The pumped flow rate, Q_v, towards the rotating disc circulates through the porous disc which may thus be used as a flow-through porous electrode.

The flow between parallel circular discs, one of which is non-porous and the other porous or perforated, has been studied by several authors [2–4] mainly focusing on fluid dynamic aspects. The pumping effect towards a rotating circular disc was applied in the pump cell [4–8]; as in Fig. 1c, a disc of radius R rotates at a distance h from a fixed annular disc of external radius R and internal radius R_i. The rotation of the disc induces flow of the electrolyte through the hole of radius R_i. Such a cell was proposed principally for electro-organic synthesis owing to the different hydrodynamic situations near the two discs; the corresponding layers of liquid situated near the discs (electrodes) would be poorly mixed, a situation favourable to many electro-organic reactions. It is not known if such a cell is actually used.

The present work was undertaken as part of a general study of nickel foam porous electrodes. Its aim was to study the electrochemical mass transfer at the rotating circular disc and at the porous disc disposed as shown in Fig. 1; obtaining quantitative data, allowing the performance of a small laboratory-scale cell constructed as in Fig. 1a to be determined, was the final objective of the work.

2. Experimental details

2.1. *Cell*

The cell used (Fig. 2a) was made of Altuglas (Plexiglass); it is cylindrical (6 cm inner diameter) and composed of five parts. The lower part, A, supported two

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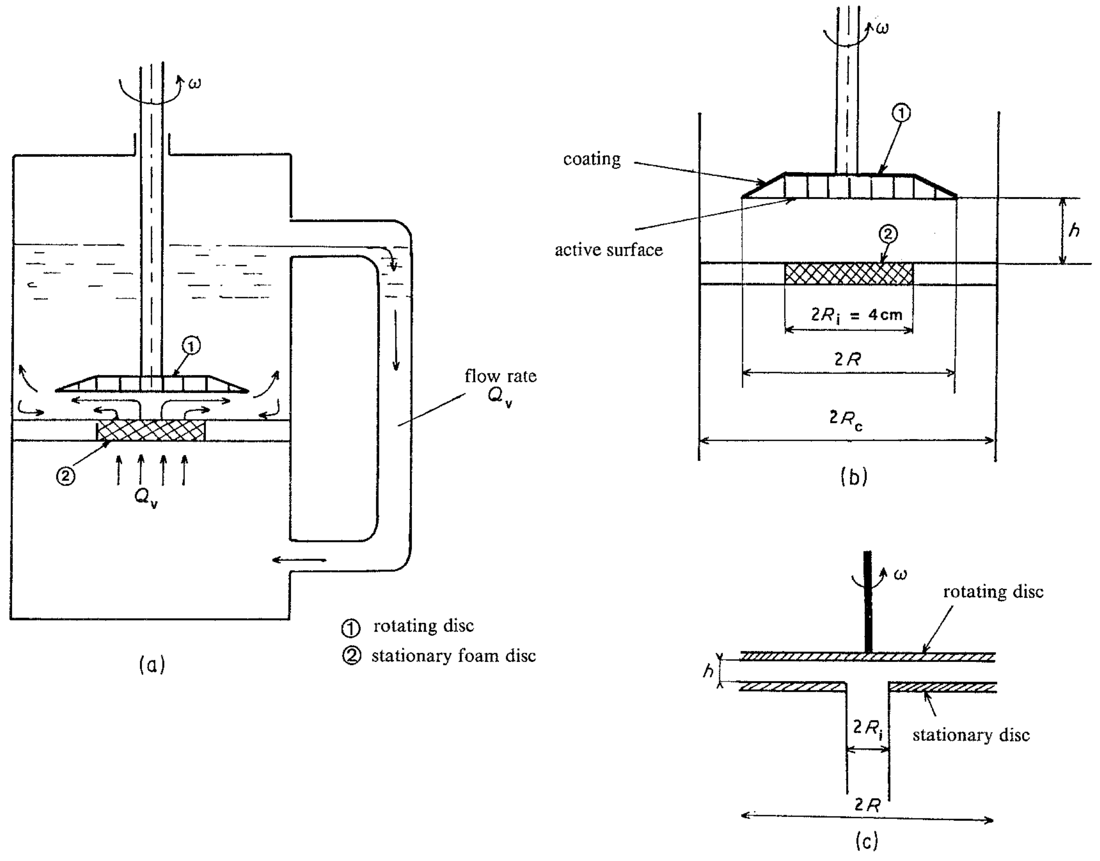

Fig. 1. Schematic views: (a, b) of the projected cell; (c) of the pump cell.

circular rings (part E) made of Altuglas. The disc of porous material studied was held in the circular opening provided by the rings E, as shown. A disc of nickel foam at the bottom of part A acted as the counter-electrode. The central part B contained the rotating disc which was mounted on a Tacussel-EDI system supported by part D which can be moved vertically by screwing it through the cover C. The vertical motion of part D allowed the distance, *h*, between the rotating disc and the porous disc (Fig. 1b) to be adjusted with a precision of 0.2 mm. The lower part of the annular cylinder D was perforated in such a manner that the vortex generated by the rotation of the cylindrical support of the disc was nearly suppressed. A nickel felt of apparent surface area 21 cm^2 was placed on the inner lateral wall of B and was also used as a counter-electrode. The electrolyte left the cell by overflow. The Tacussel-EDI system was connected to a Tacussel-

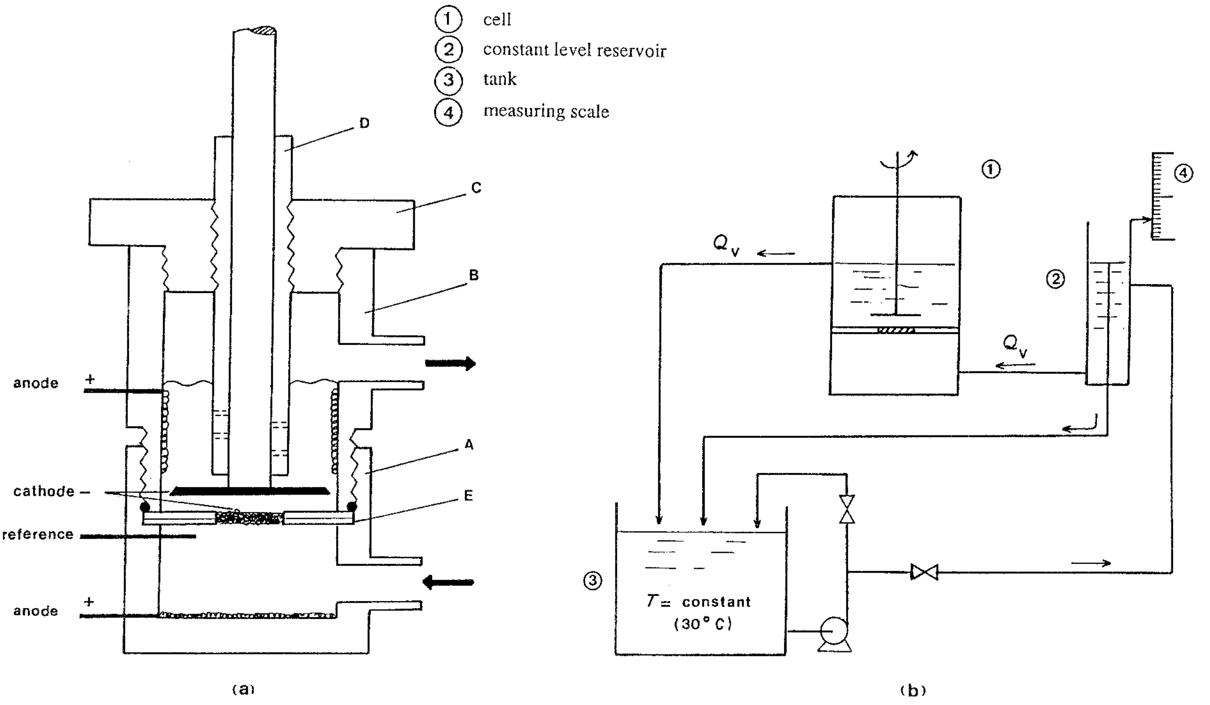

Fig. 2. Cell used (a) and hydraulic circuit (b).

Table 1. Electrolyte composition and properties

Composition:	NaOH	0.5 N
	$Fe(CN)_6K_4$	0.05 M
	$Fe(CN)_6K_3$	0.005 M

Temperature: 30° C
Density: $\varrho = 0.00105\,kg\,m^{-3}$
Kinematic viscosity: $\nu = 0.94 \times 10^{-6}\,m^2\,s^{-1}$
Diffusion coefficient of ferricyanide: $D = 0.88 \times 10^{-9}\,m^2\,s^{-1}$
Schmidt number: $Sc = \nu/D = 1070$

Controvit control unit which allowed the rotation of the disc to be varied between 100 and 5000 rev min^{-1}.

2.2. *Hydraulic circuit*

As indicated in Fig. 2b, the electrolyte was contained in a reservoir (3) (4 litres) where its temperature was maintained at 30° C. A magnetic centrifugal pump directed the electrolyte towards a constant level reservoir (2). When the disc was rotated, the level in (2) was the same as in (1); the rotation of the disc induced the electrolyte flow through the porous disc. When the disc was stationary the flow through (1) was obtained by increasing the height of (2) with respect to (1). In both cases, the flow rate Q_v through the cell was measured by weighing.

2.3. *Electrical circuit – electrodes*

The mass transfer coefficient, $\bar{k}_d$, was measured at the rotating disc and at the porous disc by the usual electrochemical method which uses the reduction of ferricyanide ions in a sodium hydroxide medium. The ferricyanide concentration was known by amperometric titration with a cobalt salt using a platinum rotating disc electrode. The electrolyte composition and properties at 30° C are given in Table 1.

The rotating disc, of diameter R, was made of nickel and was polished with diamond paste. Its upper part was isolated by painting with M-coat D (Vischay-Micromesures); the lower surface of the disc was the only metallic surface of the rotating system in contact with the electrolyte. Four discs, with diameters of 2, 2.5, 3 and 4 cm were used.

The porous discs were made from commercially available [9] nickel felt or foam. The characteristics of these materials were previously determined in our laboratory [10, 11]; they are given in Table 2. One felt and three foams (grade 45, 60 and 100) were used. Each foam is designated by its grade number which represents the number of pores per inch (or ppi).

Each porous disc was made from a circular disc of diameter 3 cm, the rim of which was compressed leaving an uncompressed porous disc of diameter 2 cm. A thin electrical wire was soldered to the compressed rim which was then covered with M-Coat D. As previously indicated in Section 2.1 the compressed rim of the disc was sandwiched between two rings of Altuglas which were held in position between parts A and B of the cell (Fig. 2a).

Depending on the experiments either the rotating disc or the porous disc was made the cathode, while two anodes, respectively located in parts A and B (see Section 2.1) were used. Using the maximum value of the limiting current, I_L, a calculation showed that the variation of the ferricyanide concentration during the flow through compartment A was negligible. The reference electrode was a nickel wire of diameter 1 mm, situated as indicated in Fig. 2a.

3. Results and discussion

The variable parameters of the experimental study were the distance, h, between the two discs, the radius, R, of the rotating disc, the material of the porous disc and the angular velocity, ω, of the rotating solid disc. The radii, R_i, of the porous disc and, R_c, of parts A and B were constant ($R_i = 2\,cm$; $R_c = 3\,cm$).

3.1. *Results concerning the hydrodynamics*

The rotation only generates (by suction) a flow rate through the porous disc above speeds such that the kinetic energy transmitted to the liquid situated between the two discs becomes higher than the hydrostatic pressure energy corresponding to the height of liquid, z, above the disc. Indeed, as a first approximation, the minimum speed of rotation, ω_0, from which Q_v is different from zero would be such that

$$\varrho g z = 0.5 \varrho \omega_0^2 R^2 \tag{1}$$

where ϱ is the liquid density and g the specific gravity.

Figures 3–5 give the experimental variations of Q_v with the number of revolutions per minute, N, which is varied between 500 and 3000. Figure 3 corresponds to foam of grade 45 and shows the influence of h for $R = 0.02\,m$. For a given speed of rotation, the smaller

Table 2. Characteristics of electrode materials

	Felt	*Foam G 100*	*Foam G 60*	*Foam G 45*
Thickness e (m)	0.0013	0.0021	0.0025	0.0027
Specific surface area (BET) (m^{-1})	500 000	41 000	30 000	19 000
Mean porosity	0.95	0.975	0.975	0.975
Permeability to water (m^2)	–	0.315×10^{-8}	0.825×10^{-8}	0.215×10^{-7}

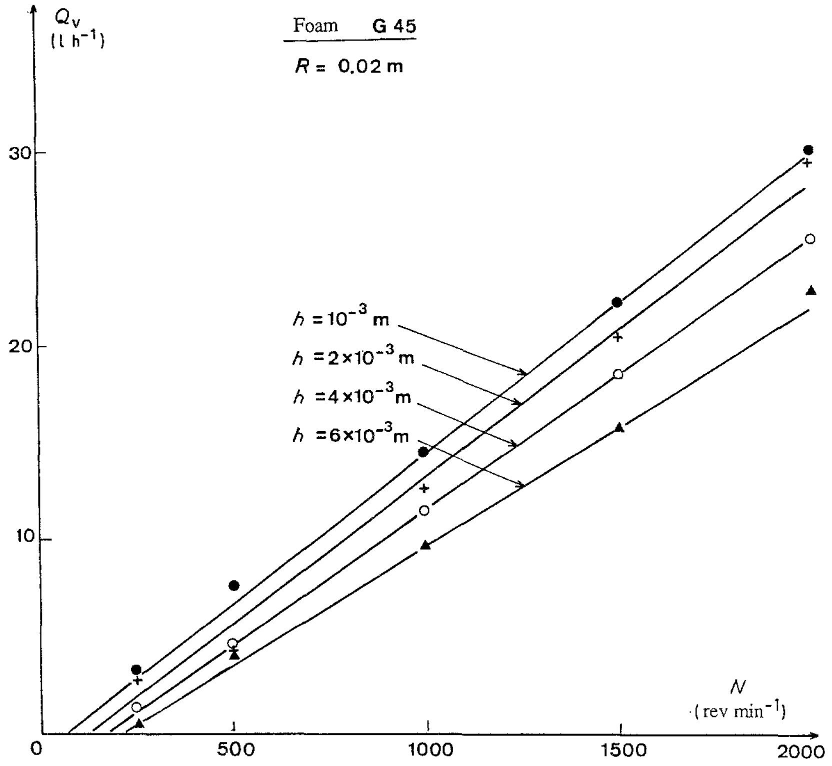

Fig. 3. Variations of the self-pumped flow rate Q_v with the number of revolutions per minute, N: influence of h (foam G45).

the value of h, the higher that of Q_v; indeed, as h is reduced, the energy is transferred to a smaller volume of electrolyte between the two discs. Although not very clearly defined, minimum speeds are necessary to produce flow out of the cell.

Figure 4 shows the influence of the disc radius R for $h = 0.003$ m. For a given speed of rotation, Q_v increases with R. Also, the smaller the value of R, the higher is the minimum speed, ω_0, which is in accordance with Equation 1.

Figure 5 compares the variations of Q_v with N for various materials, all other parameters being constant. It is evident that the suction flow rate, Q_v, depends on the material permeability.

The experimental results show that, for each porous material considered, Q_v is proportional to N, i.e. can be expressed by

$$Q_v = f(h, R)[\omega - \omega_0(h, R)] \qquad (2)$$

Thus, a calibration would allow Q_v to be known from ω. Also it was observed that Q_v was proportional to ω in the case of a pump cell such as that of Fig. 1c, but having two corotating solid circular discs [12].

In the experimentally varied range of ω, Q_v is such

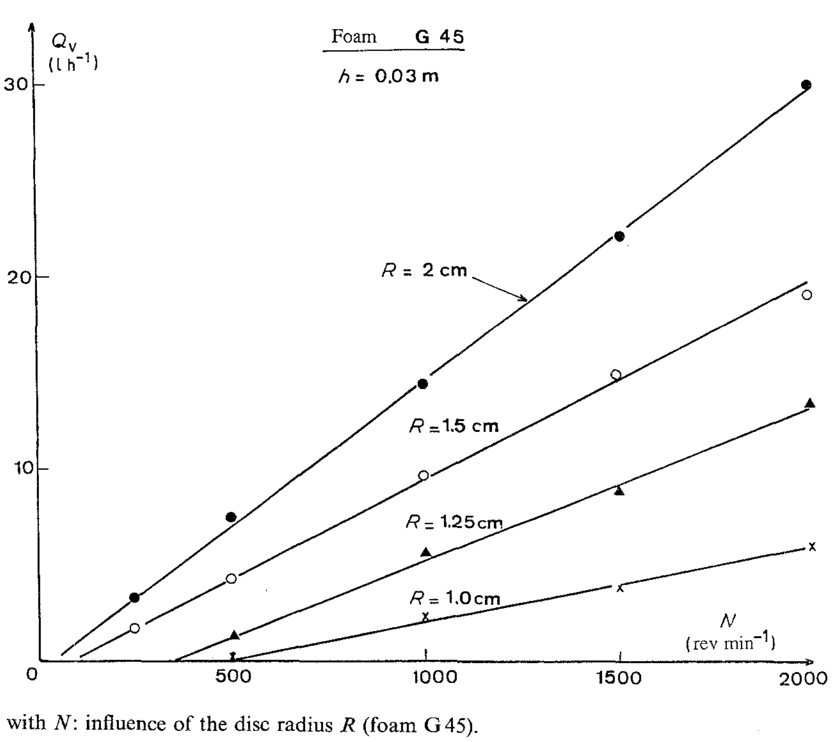

Fig. 4. Variations of Q_v with N: influence of the disc radius R (foam G45).

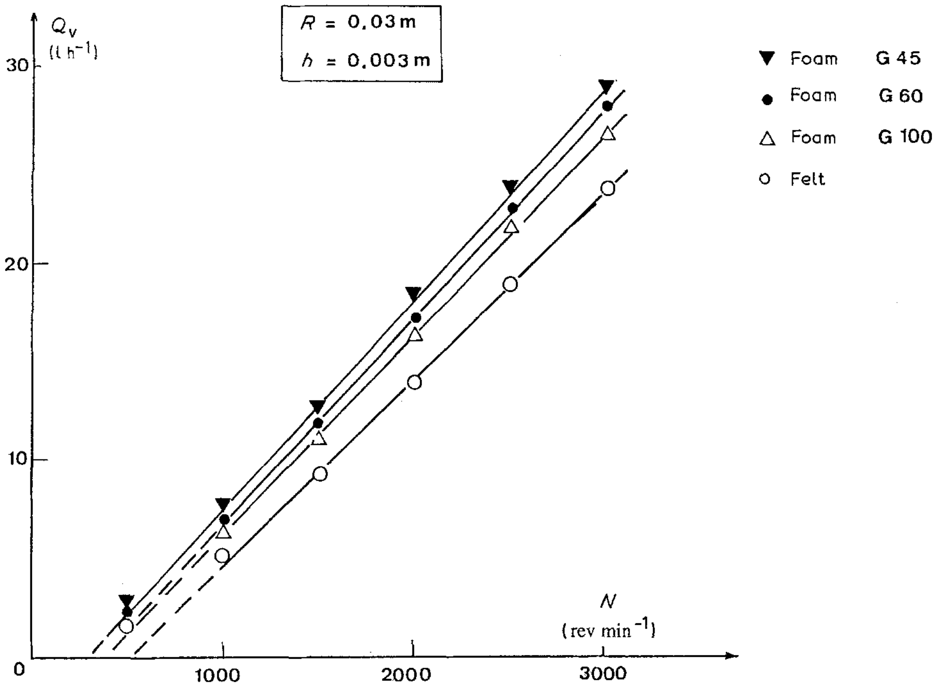

Fig. 5. Variations of Q_v with N: comparison of the different materials.

that the mean liquid velocity towards the porous discs varies approximately between 0.1 and 2 cm s^{-1}.

3.2. *Discussion of the hydrodynamical aspects*

The present work did not consider the flow structure in the inter-disc space itself, unlike other works related to rotating systems with two discs [4, 7, 13–18]. The flow in an infinite medium situated between a rotating disc and a fixed porous disc, through which fluid is blown, was studied by Pecheux [15]. The numerical solution of such a complex problem shows that the flow structure depends on the blowing velocity and on the inter-disc distance. The system used in the present work corresponds to the particular case of [15] where the blown flow rate into the inter-disc space is equal to the suction flow rate, Q_v, induced by the rotating disc.

In the cell of Fig. 1b, the disc is rotating in a space more confined than an infinite medium, and the wall of the cylindrical cell probably influences the flow between the two discs. Tomlan and Hudson [16], Lehmkull and Hudson [17] and Litt and Serad [18] studied the mass transfer at a disc rotating in a closed and confined cylinder (see Fig. 6a). They examined the influence of the distance, h, between the rotating disc and the bottom of the cylinder, and the influence of the ratio R/R_c between the disc radius, R, and the cylinder radius, R_c. In fact the rotating and axial fluid

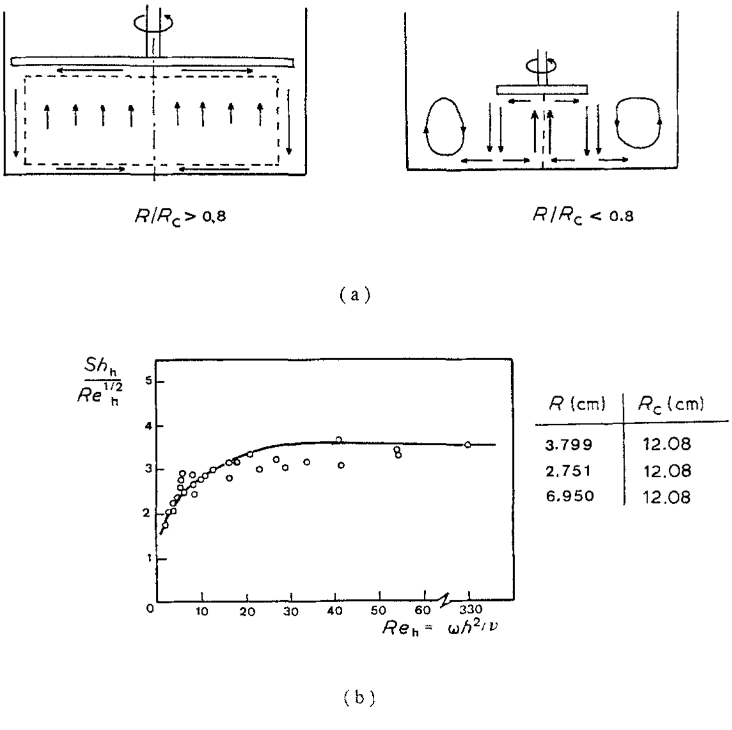

Fig. 6. Figures reproduced from [17]. (a) General flow structure below a disc rotating in a closed cylinder; (b) results for mass transfer at the rotating disc.

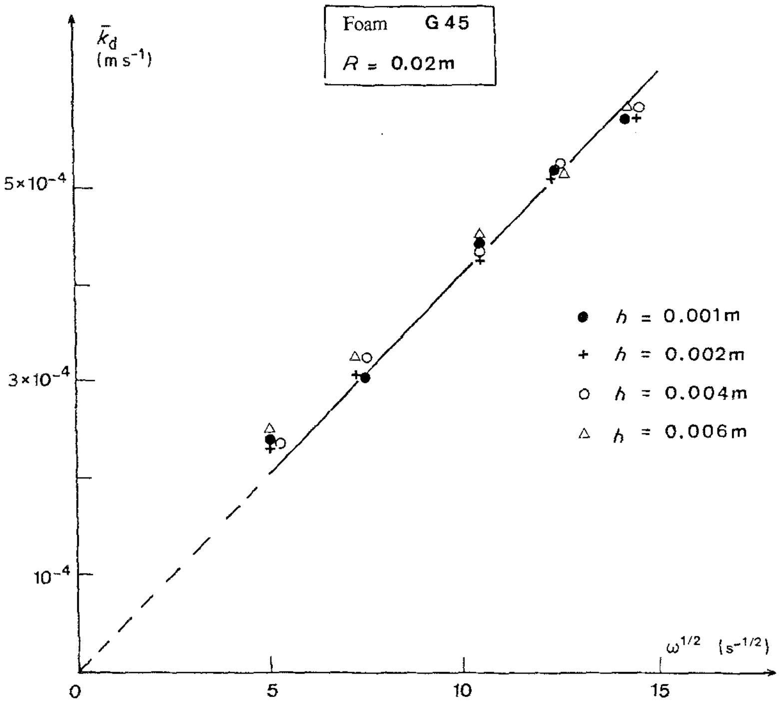

Fig. 7. Mass transfer at the rotating disc. Variations of $\bar{k}_d$ with $\omega^{1/2}$.

velocities in the space between the rotating disc and the bottom of the cylinder depend not only on h and R/R_c, but also on the height of liquid above the rotating disc. Two types of flow structure, depending on the value taken by R/R_c with respect to 0.8, are given in Fig. 6a. According to [16, 17], the flow structure and the mass transfer to the rotating disc are controlled by the development of boundary layers on the walls of the cell.

3.3. *Mass transfer at the rotating disc*

The variations with ω of the mass transfer coefficient, $\bar{k}_d$, were determined for several distances, h, with each of the four rotating discs, the porous disc being made of foam G 45. The value of $\bar{k}_d$ at the disc of area πR^2 was deduced from the limiting current, I_L, using the expression

$$\bar{k}_d = \frac{I_L}{\nu_e F C_0 \pi R^2} \tag{3}$$

where C_0 is the ferricyanide concentration, ν_e ($\nu_e = 1$) the number of electrons in the cathodic reaction and F the Faraday number.

Figure 7 gives the variations of $\bar{k}_d$ with $\omega^{1/2}$ for the disc of radius $R = 2$ cm. It appears that h has no measurable effect, a result also obtained for the other rotating discs. Figure 8 summarizes all the results and

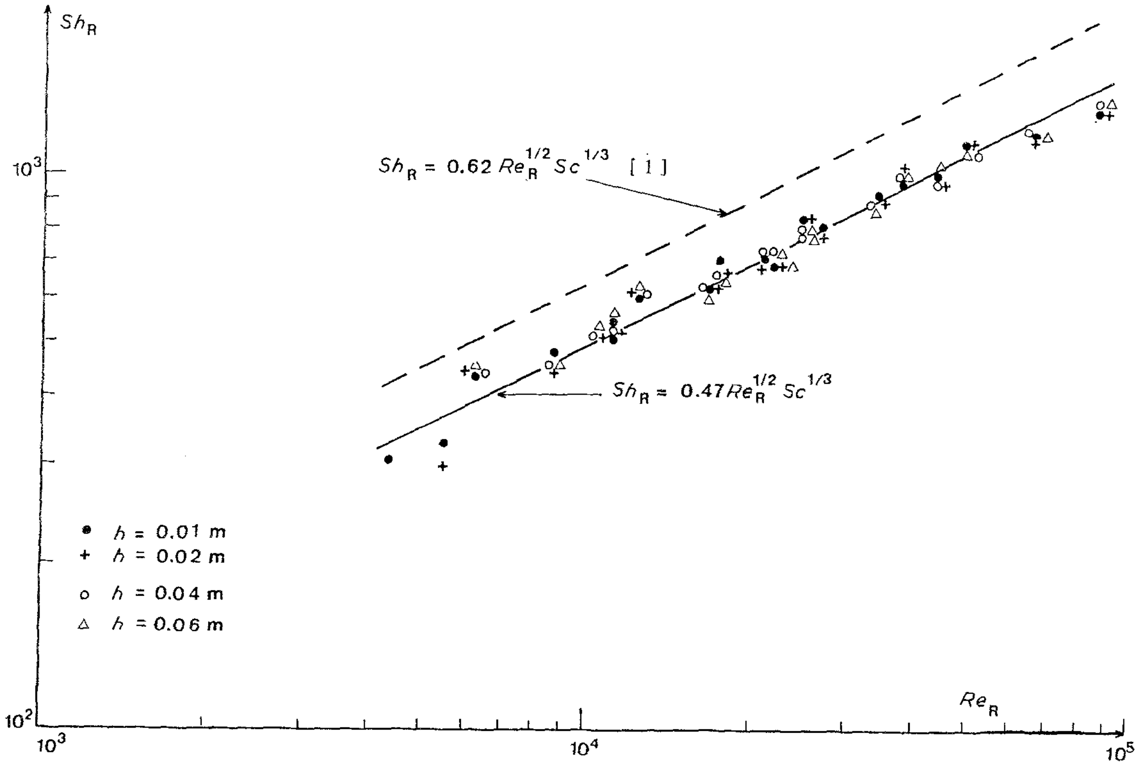

Fig. 8. Mass transfer at the rotating disc. Empirical correlation of the results and comparison with the Levich equation.

shows that they can be described by the following empirical correlation

$$Sh_R = 0.47 Re_R^{1/2} Sc^{1/3} \qquad (4)$$

where $Sh_R = \bar{k}_d R/D$ is the Sherwood number, $Re_R = \omega R^2/\nu$ is the rotation Reynolds number and $Sc = \nu/D$ is the Schmidt number. Expression 4, in which R is the geometrical characteristic dimension of the system, shows that $\bar{k}_d$ is independent of R. In Fig. 8 the Levich correlation for diffusional mass transfer at a disc rotating in permanent laminar flow conditions in an infinite medium has been plotted.

It is interesting to compare the present results with those of Lehmkuhl and Hudson [17] obtained for mass transfer at a disc rotating in a cylindrical cavity (Fig. 6a); these results (Fig. 6b) give the variations of $Sh_h/Re_h^{1/2}$ as a function of Re_h, the distance h being the characteristic dimension. For values of Re_h greater than 50, $Sh_h/Re_h^{1/2}$ is constant and, thus, independent of h, a result which agrees with the present work. As the Schmidt number was $Sc = 600$, the results of Lehmkuhl lead to:

$$Sh_h = 0.43 Re_h^{1/2} Sc^{1/3} \quad \text{for} \quad Re_h > 50 \qquad (5)$$

In agreement with other studies [19], the results of Lehmkuhl also show that $\bar{k}_d$ at the rotating disc does not depend on the radius, R, of that disc. Thus Equation 5 remains valid if R is taken as the characteristic dimension, and it can be seen that it is nearly identical to Equation 4.

Figure 8 shows that Equation 4 deviates from the Levich equation. Lehmkuhl and Hudson [17] explain the corresponding deviation of their results from that equation by the rotation of the liquid itself contained in the confined space; such a rotation of the liquid far from the vicinity of the disc attenuates the axial flow towards that disc and thus the mass transfer coefficient to it [17, 18]. Concerning the pump cell with corotating discs, the spatial distributions of the local mass transfer coefficients show that the electrodes are not uniformly accessible [5, 8, 14]. The results of Jansson and Marshall [8] obtained with a cell similar to that of Fig. 1c shows that the mean mass transfer coefficient at the rotating disc does not depend on h; their correlation establishes that Sh_R is proportional to $Re_R^{0.565}$. Other work on the pump cell [6] shows that the value of R_i influences the mass transfer coefficient at the rotating discs. In the present work, it is probable that the coefficient 0.47 in Equation 4 is a function of the radius R_i of the porous disc.

The constancy of the ratio $Sh/Re^{1/2}$ is to be noted. This means that the suction flow rate, Q_v, has a negligible influence on the mass transfer to the disc.

3.4. *Mass transfer at the porous discs*

It is known that for plug flow through a porous electrode of volume V, the product $\bar{k}_d a_e$ of the mass transfer coefficient by the electrode specific surface area, a_e, is related to the flow rate, Q_v, and to the conversion, X, in the following manner

$$\bar{k}_d a_e = -\frac{Q_v}{V} \ln(1 - X) \qquad (6)$$

The conversion X of the electrolyte entering the electrode at concentration C_0 is calculated from the limiting current I_L using

$$X = \frac{I_L}{\nu_e F C_0 Q_v} \qquad (7)$$

which assumes a faradaic yield of 1.

In previous work concerning mass transfer to porous electrodes of nickel foam [10, 11] it was pointed out that, as the design calculations use the product $\bar{k}_d a_e$, it is not necessary to know $\bar{k}_d$ and a_e separately. This is important because the really active electrochemical specific surface area, a_e, which differs from the geometrical and from the measured specific surface areas, does not have to be known. However, the specific surface areas of the porous materials used were determined by the BET method [10, 11]. The values obtained, which are shown in Table 2, only give an indication as to the specific surface area. The felt appears to have the better performance.

In the mass transfer experiments only the rotating disc of $R = 0.015$ m was used; the distance h was maintained constant and equal to 0.003 m.

Figure 9 gives the variations of $\bar{k}_d a_e$ versus the mean superficial electrolyte velocity, $\bar{u}$, in the circular section of radius R_i; $\bar{u}$ was varied between 0.002 and 0.03 m s^{-1} by changing ω. The empirical correlations given in Fig. 9 were obtained by logarithmic regression, with a correlation coefficient of 0.99. The following general empirical correlations were obtained for the three foams, respectively using $\bar{u}$ and ω and introducing the grade

$$\bar{k}_d a_e = (1.95 \pm 0.1) \times 10^{-4} [\text{grade}]^{1.9} (\bar{u})^{0.32} \qquad (8)$$

$$\bar{k}_d a_e = (2.2 \pm 0.1) \times 10^{-6} [\text{grade}]^{2.1} \omega^{0.43} \qquad (9)$$

In Equations 8 and 9, $\bar{k}_d a_e$ is expressed in s^{-1}, $\bar{u}$ is in m s^{-1} and ω in rad s^{-1}. The difference between the exponents of $\bar{u}$ and ω in these two expressions is due to the existence of a minimum rotating velocity ω_0.

Similar experiments were made without using the hydraulic circuit of Fig. 2b, but only connecting the entrance to the exit of the cell as in Fig. 1a. The new empirical correlations obtained [12, 13] were very nearly identical to those of Fig. 9, which proves that the circuits of Fig. 1a and Fig. 2b were equivalent.

On the other hand, it was of interest to learn what difference there could be between the values of the mass transfer coefficient at the porous disc or when the flow was forced towards the disc at the same mean velocity, $\bar{u}$, and with no rotation of this disc. With the disc kept stationary, the electrolyte flow was forced by lowering the constant level reservoir of Fig. 2b. The results obtained [13] do not differ from those of Fig. 9; it thus appears that the system is such that the rotation of the disc essentially generates an axial velocity through the porous disc; in other words,

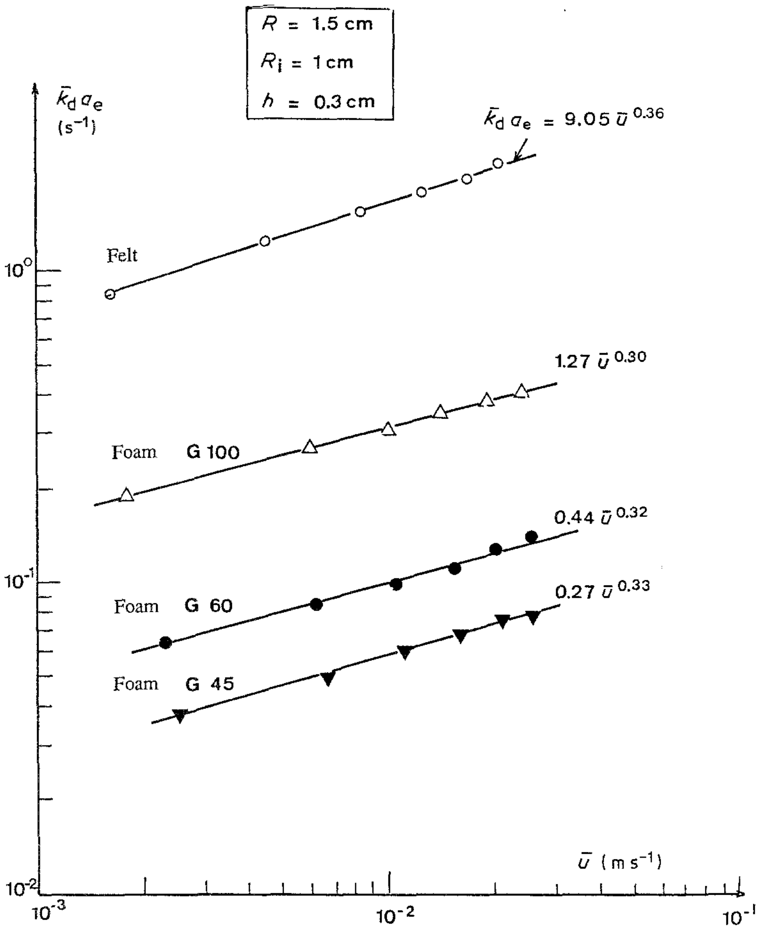

Fig. 9. Mass transfer at the porous discs. Variations of $\bar{k}_d a_e$ with $\bar{u}$.

within this disc there is no evident radial velocity component induced by the rotation.

The mass transfer correlations deduced in the present work were compared with those obtained in previous studies of flow through porous electrodes made of the same materials (nickel felt or foam) [10, 11]. It was seen [13] that the present results are from 1.5 to 3 times those obtained using stacks of porous discs as flow-through porous electrodes. Similar differences in performance were observed [12] between the cases of one disc and of a stack of discs in the flow-through porous electrode configuration.

4. Conclusions

The rotation of a circular disc submerged in a liquid and facing a porous disc generates a forced flow of liquid through the latter. This can be used in a small-scale laboratory cell for the study of porous materials for porous electrodes, without the need to construct an external hydraulic circuit. The cell operates by self-pumping. The empirical correlations for mass transfer at the rotating disc and at the porous disc clearly show the determining influence of the speed of rotation on the suction flow rate through the porous disc.

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