Study of the effectiveness of fixed flow-through electrodes

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This paper presents a theoretical and experimental study of the effectiveness of fixed flow-through electrodes working at very low local overpotentials. An analogy is established between such systems and gas–solid catalytic reactors; a generalisation which extends the treatment to high overpotential operating conditions is also presented. The study establishes the pertinent parameters of the electrode and outlines the conditions for its 3-dimensional behaviour.

1. Introduction

The fixed unconsolidated flow-through electrode is a fixed bed of conducting grains in contact with a current feeder; an electrolyte flows through the system. The main advantage of this type of electrode is its high specific area which makes it suitable for the treatment of dilute solutions that need low current densities.

Bennion and Newman [1] first proposed the use of the fixed granular electrode — which is a limiting case of the fluidised bed electrode — for the concentration of dilute solutions. More recently it has been studied by Chu [2, 3] and by Kuhn [4] also for metal recovery.

The behaviour of fixed flow-through electrodes operating in limiting current conditions has been investigated by Coeuret [5]; the aim was to study the variations of recovery efficiencies and to obtain the mass transfer coefficients between the electrolyte and the particles of the bed. A similar study has been published by Sioda [6]. Metal – solution potentials have also been investigated by Coeuret [7] but a more complete investigation is to be published later [8].

The object of the present paper is to study fixed flow-through electrodes when they are working near equilibrium i.e. at low local overpotentials. The main purpose is to determine, from local overpotential measurements, the conditions in which the electrode is working as a 2 or 3-dimensional electrode and to compare the results with the theory.

2. Theoretical

2.1. Distribution of the overpotential

Fig. 1 shows a cathodic electrode of fixed grains. The bed porosity is ϵ, the specific area of the grains is a_g ($a_g = 6/d_g$ for spherical grains whose diameter is d_g), the cross-sectional area of the column is Ω, the bed height is L and the electrolyte has an electrical conductivity of γ_0. The flow of the electrolyte entering the bed is considered as uniform. The electrical current flowing through the cell corresponds to the current density i_t defined relative to Ω.

For very low values of the electrode overpotential η, the current density i is given by the linear expression:

$$i = i_0 \times \frac{zF}{RT} \times \eta \qquad (1)$$

where i_0 is the exchange current density.

When the electrode is operating in such conditions, the concentration of the reacting species, and consequently the equilibrium potential E_{eq}, remains nearly constant over the whole bed. The local overpotential at the reduced height $X = x/L$ above the bed support is:

$$\eta(X) = E(X) - E_{eq}.$$

The density of the current flowing in the bed through the electrolyte is $i_S(X)$ relative to Ω; it satisfies the limiting conditions:
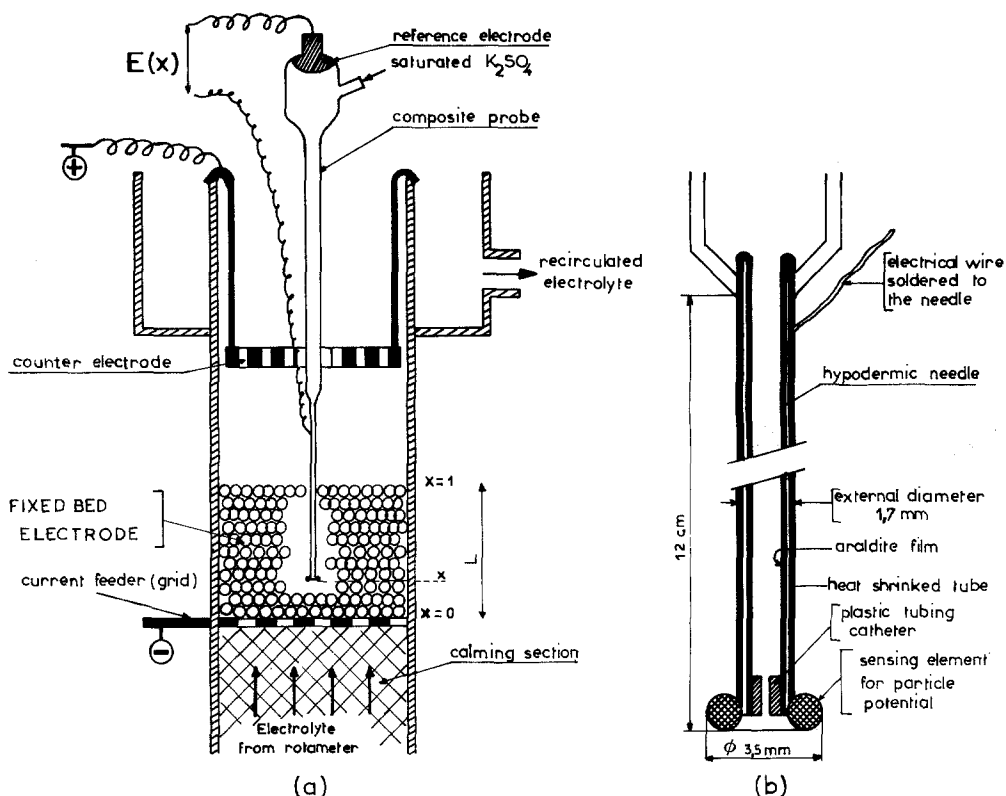
Fig. 1. The cell including the fixed bed electrode and the composite probe.

$$i_S(0) = 0, \qquad i_S(1) = i_t.$$

If we accept that the dispersed phase is equipotential, all the potential drop takes place in the electrolyte and, as a consequence, the variation of the local overpotential can be written:

$$\frac{d\eta(X)}{dX} = \frac{dE(X)}{dX} = -\frac{d\phi_S(X)}{dX} = \frac{L}{\gamma} \times i_S(X)$$

$$(2)$$

in which $\phi_S(X)$ is the local solution potential.

The last expression is Ohm's law applied to the electrical conduction through the pores of the bed. The electrical conductivity γ introduced is the electrolyte conductivity in the bed; it depends on γ_0 and on the tortuosity of the current lines around the grains considered as non-conducting material. Neale [9] has shown that the theoretical expression:

$$\frac{\gamma}{\gamma_0} = \frac{2\epsilon}{3 - \epsilon} \qquad (3)$$

is satisfactory for fixed beds of non-conducting spherical particles.

In a differential element of the bed, the variation of $i_S(X)$ is due to metal–solution mass transfer and is given by:

$$\frac{di_S(X)}{dX} = i_0 \times \frac{zF}{RT} \times (1 - \epsilon) \times a_g \times L \times \eta(X).$$

$$(4)$$

By combining expressions (2) and (4) we have the differential equation:

$$\frac{d^2\eta(X)}{dX^2} - K^2 \times \eta(X) = 0 \qquad (5)$$

with

$$K^2 = i_0 \times \frac{zF}{RT} (1 - \epsilon) \times a_g \times \frac{L^2}{\gamma} \qquad (6)$$

and for spherical grains:

$$K^2 = i_0 \times \frac{zF}{RT} \times \frac{(1 - \epsilon)(3 - \epsilon)}{\epsilon} \times \frac{3}{d_g} \times \frac{L^2}{\gamma_0} \quad (7)$$

By integrating (5) we obtain the following expressions for the overpotentials:

$$\eta(0) = \frac{i_t \times L}{\gamma \times K \times \text{sh}\, K} \qquad (8)$$

$$\frac{\eta(X)}{\eta(0)} = \text{ch}\,(K \times X) \qquad (9)$$

and the adimensional relationship:

$$\frac{\eta(X) - \eta(0)}{\eta(1) - \eta(0)} = \frac{\text{ch}\,(KX) - 1}{\text{ch}\,K - 1} \,. \qquad (10)$$

These expressions could have been deduced as a special case from the work of Euler [10] but here they have been obtained in a more logical fashion by means of the overpotential and not by considering the metal and solution potentials separately as in Euler's work.

2.2. Effectiveness of the electrode

K is a dimensionless number analogous to the Thiele modulus used in the competition between chemical reaction and diffusion in porous reactive solids [11]. The present problem of the fixed flow-through electrode has a mathematical formulation similar to that already known for a first order chemical reaction taking place in a catalytic porous bed. Here the overpotential η plays the same role as the concentration of the gaseous reactant.

The physical meaning of K may be demonstrated by writing (6) in the following manner:

$$K^2 = \frac{i_0 \times \dfrac{zF}{RT} \times (1 - \epsilon) \times a_g \times L \times \eta(1)}{\dfrac{\gamma}{L} \times \eta(1)}$$

$$= \frac{\left\{\dfrac{\mathrm{d}i_S(X)}{\mathrm{d}X}\right\}_{X=1}}{\dfrac{\gamma}{L} \times \eta(1)} \qquad (11)$$

which allows K^2 to be interpreted as:

$$K^2 = \frac{\text{electrochemical reaction rate at } X = 1}{\text{flux of electrical conduction in the electrolyte}}$$

From Equation 9 we see that the 2 or 3 dimensional behaviour of the electrode only depends on the modulus K. This is shown on Fig. 2 which presents the relation (10) for several values of K:

(i) when K is very small, the overpotential is practically constant (Equation 9): the whole volume of the bed is active because the conduction is sufficiently good to bring the reactive ions to
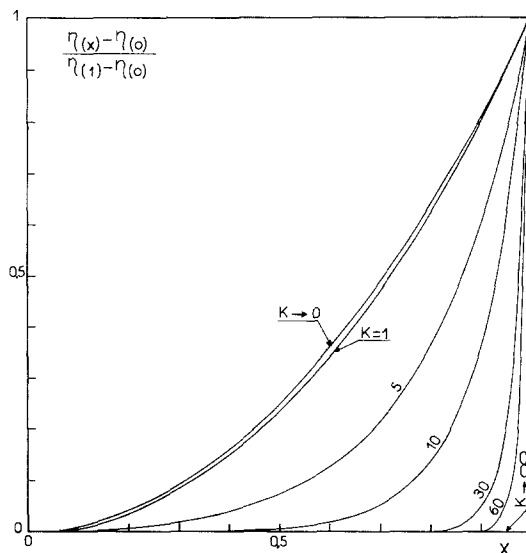

Fig. 2. Some theoretical distributions of the overpotential.

the reaction surfaces (the conducting grains). The bed acts then as a 3-dimensional electrode.

(ii) when K is very high, the reaction takes place only at the top of the bed which behaves then as a 2-dimensional electrode.

(iii) for intermediate values of K, the reaction occurs in a slab whose thickness decreases with increasing values of K.

The effectiveness ξ of the electrode, or its coefficient of utilisation can be defined by the ratio:

$$\xi = \frac{\text{measured electrolytic current}}{\begin{array}{c}\text{current obtained with an electrode whose}\\ \text{overpotential is the same at every point}\end{array}}$$

or

$$\xi = \frac{i_t \times \Omega}{i_0 \times \dfrac{zF}{RT}(1 - \epsilon) \times a_g \times \Omega \times L \times \eta(1)} = \frac{\text{th}\,K}{K}\,. \qquad (12)$$

This effectiveness represents the fraction of the height which is electrochemically reactive in the electrode.

3. Experimental

The hydraulic circuit is identical to that described in [7] except for the column which is shown on Fig. 1a. The column is made of altuglass, is cylindrical with an internal diameter of 4 cm and has a calming section of glass microspheres at the base. The cathodic current feeder which supports the

bed is a metallic grid; the anode is a horizontal perforated disc.

The local electrode potential within the bed is obtained using a probe introduced at the top of the column. The probe is composite; the lower part, which is immersed in the bed, consists of a hypodermic needle modified in order to have access to the local grain-solution potential (Fig. 1b). The sensing element of the probe is a small ring made of 0·5 mm or 1 mm diameter wire depending on the grain diameter of the bed; its position in the axis of the bed can be measured with precision (1/10 mm). The composite probe includes a saturated potassium sulphate reference electrode. Grains with two kinds of external surface have been used depending on the electrochemical reaction employed:

(1) spherical grains of copper or coppered graphite in the case of copper deposition from copper sulphate in sulphuric acid solutions. The anode, the cathode and the sensing element are also made of copper;

(2) spherical grains of bronze electrochemically plated with nickel and gold in the case of cathodic reduction of potassium ferricyanide. The anode, the cathode and the sensing element are also electrochemically plated with nickel and gold respectively.

The inventory of the grains (indicated as A, B, C, D) and of the electrolytes (indicated as 1 to 6) is given in Table 1. The bed porosity ϵ is kept constant and equal to 0·42.

The exchange current densities i_0 have been determined in the same conditions as the experiments ($T = 30°$ C) in an adjoining apparatus. These determinations were made with Equation (1) and also allowed the ranges of linearity of the function $i = f(\eta)$ to be delineated:

$|\eta| \leqslant 40$ mV for cathodic reduction of ferricyanide

$|\eta| < 10$ mV for copper deposition. (A range half as wide has been recommended in the literature [12]).

The values obtained for i_0 are given in Table 1.

The electrical conductivities γ_0 of the electrolytes have been obtained from measurements in the column itself by determining the solution potential gradients between the anode and the top of the bed. The method uses the composite probe as a Luggin capillary. The values of γ_0 are also given in Table 1.

A Tacussel PRT 20-2 potentiostat working as an amperostat, a numerical ammeter and a Schlumberger numerical voltmeter were used to investigate the electrode and obtain the values of i_0 and γ_0.

4. Results

As relatively high values of K were investigated, Equation 10 is the most useful form with which to represent the results.

Two examples of results are presented:

Table 1. Characteristics of electrolytes and conducting grains

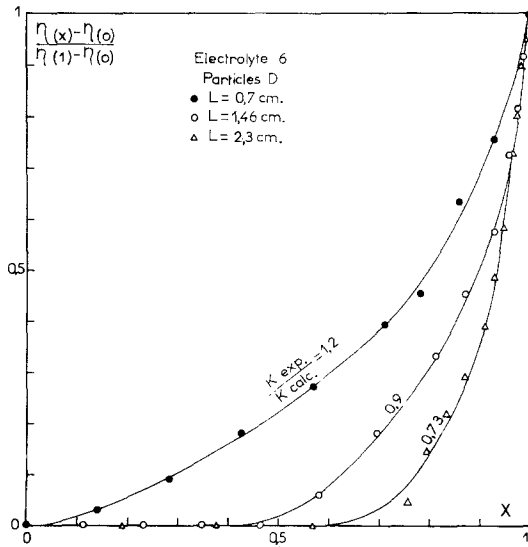| Electrolytes			i_0 [A cm^{-2}]	γ_0 [ohm^{-1} cm^{-1}]	Spherical Grains	
1	CuSO$_4$ H$_2$SO$_4$	0·01 M 1 N	$9\cdot0 \times 10^{-5}$	0·19	electrolytically copper plated graphite	
2	CuSO$_4$ H$_2$SO$_4$	0·1 M 1 N	$2\cdot2 \times 10^{-4}$	0·2	$d_g = 3$ mm	A
3	CuSO$_4$ H$_2$SO$_4$	1 M 1 N	$3\cdot9 \times 10^{-4}$	0·16	$d_g = 1\cdot5$ mm copper 710 $\mu < d_g < 900\ \mu$	B C
4	K$_3$Fe(CN)$_6$ K$_4$Fe(CN)$_6$ NaOH	0.001 M 0·001 M 0·5 N	$5\cdot3 \times 10^{-4}$	0·098		
5	K$_3$Fe(CN)$_6$ K$_4$Fe(CN)$_6$ NaOH	0·005 M 0·005 M 0·5 N	1×10^{-3}	0·1	electrolytically nickel and gold plated bronze $d_g = 825\ \mu$	D
6	K$_3$Fe(CN)$_6$ K$_4$Fe(CN)$_6$ NaOH	0·005 M 0·005 M 5 N	5.26×10^{-4}	0·21		

Fig. 3. Experimental distributions of η for the cathodic reduction of ferricyanide.
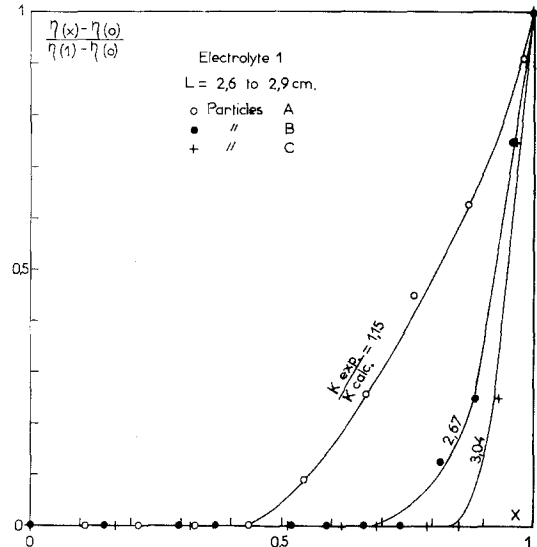

Fig. 4. Experimental distributions of η for copper deposition.

(i) Fig. 3 relates to the cathodic reduction of ferricyanide and shows the influence of L.

(ii) Fig. 4 corresponds to the copper desposition and shows the influence of the grain diameter for a given height L.

Both figures are typical and show well the variation of effectiveness with bed height and grain diameter. It is necessary to mention that the zero values of the ordinate, which correspond to zero values of the difference $\eta(X) - \eta(0)$, correspond also to zero values of $\eta(X)$. In other words, the extent of the range where the ordinate is zero

defines the fraction of the height where there is no electrochemical reaction.

All the results are presented in Table 2. This presentation is due to the high values reached by K and to the presence of exponentials in the theoretical solutions.

As $\eta(0)$ is always very small and the product KX high, in the majority of the cases where a deviation from equilibrium can be measured, Equation 10 takes the simplified form:

$$\frac{\eta(X)}{\eta(1)} \approx \exp\left[K(X - 1)\right]. \qquad (13)$$

Table 2. Calculated and experimental values of K

| Electrolyte	Grains	L [cm]	K_{exp}	K_{calc} (7)	$\dfrac{K_{exp}}{K_{calc}}$	L [cm]	K_{exp}	K_{calc} (7)	$\dfrac{K_{exp}}{K_{calc}}$	L [cm]	K_{exp}	K_{calc} (7)	$\dfrac{K_{exp}}{K_{calc}}$	L [cm]	K_{exp}	K_{calc} (7)	$\dfrac{K_{exp}}{K_{calc}}$
1	A	2·75	3·57	3·13	1·15	3·75	5·1	4·2	1·2	4·75	7·7	5·4	1·42				
1	B	1·65	3·1	2·65	1·17	2·25	4·5	3·6	1·25	2·7	11·5	4·3	2·67	3·15	21	5	4·2
1	C	1·0	6·9	2·2	3·14	1·7	15	3·7	4·05	2·9	19·5	6·4	3·04	3·65	37	8	4·62
2	A	3·2	9	5·6	1·6	4·8	13·7	8·4	1·63								
2	B	1·35	4·4	3·3	1·3	2·4	5	5·9	0·85	3·3	11	8·1	1·35				
2	C	0·8	4·4	2·7	1·63	2·0	5	6·8	0·74	3·15	11	10·6	1·04				
3	A	2·5	6·4	6·4	1	4·9	12·5	12·7	0·98								
3	B	1·2	3·9	4·4	0·88	2·5	8·2	9·1	0·9	3·1	10·5	11·3	0·93				
3	C	0·9	4	4·5	0·88	1·9	9·2	9·5	0·97	3·25	16	16·3	0·98				
4	D	0·86	4·2	4·5	0·93	1·54	5·8	8	0·73	2·74	8·7	14·2	0·61				
5	D	0·7	3·1	4·9	0·63	1·72	6·1	12·1	0·5	2·64	9·6	18·6	0·52				
6	D	0·7	3	2·5	1·2	1·46	4·6	5·1	0·9	2·3	5·9	8·1	0·73				
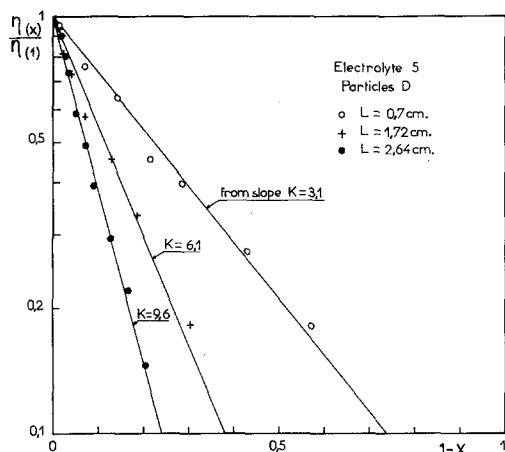
Fig. 5. Example of determination of K_{exp}.

By using semi-logarithmic paper, the value of K_{exp} can be deduced from the slope of the straight line describing the experimental results and can be compared to the value K_{calc} calculable from Equation 7. Fig. 5 shows an example of such a deduction of K_{exp}. Table 2 gives the comparison between K_{exp} and K_{calc} and also gives the values of the ratio K_{exp}/K_{calc}. This ratio is indicated on the curves of Figs. 3 and 4.

5. Discussion of the results

It can be seen from Figs. 3 and 4 that for a given electrolyte the effectiveness of the fixed bed electrode:

decreases with increasing L

increases with the diameter d_g of the conducting grains which is in agreement with the theory.

The influence of i_0, γ_0, d_g, L separately on K_{exp} can be found from Table 2 and it can be observed that the form of this influence agrees with Equation 7. However, except in some cases, there is no agreement as regards the quantitative influence of each parameter. As an example, it can be seen that, in the runs 3/B and 3/C, K_{exp} is proportional to L which is not always true for the other results.

The deviation from the theory also appears in the values of K_{exp}/K_{calc}. This ratio was rarely close to one and sometimes it reached values close to five.

This discrepancy is probably due to the discontinuous nature of the metallic phase of the elec-

trode: the theoretical considerations and the method of metal–solution potential determination ignore this discontinuous nature. The real texture of the bed and the exponential variations of the overpotential with X can explain the discrepancies between theory and experiment.

All the data used in the work have been determined experimentally in order to avoid the significant uncertainties which may appear by using data from the literature, especially for i_0.

It has to be specified that the range of variations of η is very small, particularly for the experiments with copper. Certainly this is an important cause of uncertainty in $\eta(X)$.

The agreement with the theory is satisfactory if the complexity of the system studied and the experimental difficulties are taken into account.

6. Generalisation of the theory

The mathematical aspects of Section 2 have shown that the fixed flow-through electrode can be treated similarly to a gas–solid catalytic reactor. The effectiveness has the same mathematical form in both cases.

Though from a practical point of view, it would not be economical to operate an electrode at very low overpotentials, it was necessary to carry out the present study given the simplicity of the kinetic equation. It is now possible to generalize the calculations in order to see what could happen at higher overpotentials, that is in conditions of practical operation. For that, let us suppose that the kinetic equation can be expressed as a power function of η:

$$i = \alpha \times i_0 \times \eta^n \qquad (14)$$

in which n is an exponent lower than one and α a multiplicative and dimensional coefficient.

The problem is now analogous to that of a gas–solid catalytic reactor with an nth order chemical reaction. When the overpotential $\eta(0)$ at the current feeder is taken to be zero (equilibrium), it can be easily shown that the effectiveness ξ is given by the expression:

$$\xi = \left(\frac{2}{n+1} \times \frac{1}{\alpha} \times \frac{zF}{RT} \right)^{1/2} \times \frac{[\eta(1)]^{(1-n)/2}}{K} \tag{15}$$

where K is still given by Equation 6.

7. Consequences for the practical fixed flow-through electrode – conclusions

The preceding generalisation confirms the influence of the criterion K on the effectiveness of a fixed flow-through electrode. In order to obtain a 3-dimensional electrode, it would be necessary to reduce K in the following manner:

(i) by choosing large conducting particles;

(ii) by using a small bed depth in the direction parallel to current flow;

(iii) by using electrolytes with a good conductivity γ_0;

(iv) by having low exchange current densities i_0.

In the electrolytic treatment of given dilute solutions (recovery of metal or concentration of ions), it would be convenient to act on the parameters d_g, L and γ_0. Equation 15 contains $\eta(1)$ as a positive power. Consequently it is important to make the overpotential at the limit of the bed close to the counter-electrode sufficiently high.

This paper shows that the whole large interfacial metal–solution area within a fixed flow-through electrode is electrochemically reactive only if the criterion of effectiveness achieves sufficiently low values. Otherwise the system may behave as a 2-dimensionnal electrode; this does not bring any advantage over a classical planar electrode. Consequently, in design, care must be taken concerning the value of K.

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