JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 143–149

The characterization of three-dimensional electrodes using an electrochemical tracer method

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Received 21 November 1977; and in revised form 25 May 1979

A new approach is suggested for the characterization of electrochemical reactors and is applied to three-dimensional electrodes. This approach permits the investigation of the fluid flow pattern through heterogeneous media and the overall reactivity of the bed. The fluid flow patterns have been derived by adapting the tracer method (well-known in chemical reaction engineering) for measurements on electrochemical reactors: auxiliary electrodes have been used both for the production and detection of concentration pulses. Experiments have been carried out on beds of glass beads, the size of the beads, height of the beds and flow rates being varied. The results are expressed as *(Pe)*–*(Re)* relationships. The reactivity of the beds has been determined using a new method, the mathematical background of which is due to be published. This method has been tested on electrochemically active beds of glass beads coated with copper and silver, the particle size and flow rates again being varied. The results are expressed as $k = Sk_m (= SD/\delta)$ relationships.

List of symbols

C	concentration (mol cm^{-3})
$\bar{D}$	dispersion coefficient (cm^2 s^{-1})
D	diffusion coefficient (cm^2 s^{-1})
δ	diffusion layer thickness (cm)
d_p	particle diameter (cm)
$I(t)$	function defined by Equation 5
K	overall reactivity constant of the bed (s^{-1})
k_m	mass transfer coefficient (cm s^{-1})
l	distance along the length of the electrode (cm)
$M_{1,2}$	first and second moment of the distribution of residence times
μ	fluid viscosity (g s^{-1} cm^{-1})
(Pe)	Peclét number = UL/D
r	electrochemical reaction rate (mol cm^{-3} s^{-1})
(Re)	Reynolds number = $\rho U d_p/\mu$
ρ	fluid density (g cm^{-3})
S	specific surface area of the electrode (total surface/total volume) (cm^{-1})
t	time (s)
τ	average residence time of the species entering the electrode (s)
U	interstitial fluid velocity (cm s^{-1})
v	volumetric flow rate (cm^3 s^{-1})
V	free volume (cm^3)
X	the degree of a conversion
$y_1(t)$	response of the three-dimensional electrode when the current is switched off
$y_2(t)$	response of the three-dimensional electrode in the limiting current regime

1. Introduction

Three-dimensional electrodes [1] have received considerable attention over the last few years. The flow through these heterogeneous media as well as the non-uniformity of the potential distribution within the bed causes these systems to have a complex structure in comparison to conventional electrochemical cells. In view of this complexity new parameters are required to characterize their performance in addition to those (such as the potential distribution) which have already been measured.

In this work the emphasis will be put on

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lumped parameters relevant to mass balance considerations within the electrode. For a one-dimensional axial flow through a reactor in the steady state the model is described by

$$\frac{\partial C}{\partial t} = \bar{D}\frac{\partial^2 C}{\partial l^2} - U\frac{\partial C}{\partial l} - r \qquad (1)$$

where $\bar{D}$ is the dispersion coefficient which describes the degree of turbulent mixing superimposed on plug flow and r is the electrochemical reaction rate. However, instead of $\bar{D}$, the results will be given as (Pe) values, (Pe) being the Peclét number ($= UL/\bar{D}$) which characterizes the amount of axial dispersion in a more general form.

2. Fluid flow characterization: mixing history

2.1. *Technique*

It is well known that fluid flow through heterogeneous media exhibits certain irregularities in comparison with uniform plug flow. In other words, the residence times will differ for all species entering the bed electrode. Information on the distribution of residence times is of great importance in the evaluation of the performance of such reactors, particularly if these are to be used for complex organic syntheses.

Similar problems have been elegantly solved in chemical engineering practice using a method introduced by Danckwerts [2]. The method relies on the perturbation of the reactor by means of a tracer substance (which does not react in the reactor) and on recording the time dependent concentration at the exit. The system response thus obtained enables one to define the mixing history in the vessel by applying a proper mathematical treatment. Perturbations can be of any type but the majority of experimental and theoretical work has been done using impulse functions.

For the purposes of this study, a special technique has been developed for the generation and detection of the tracer substance so as to permit the characterization of three-dimensional electrodes. The method relies on electrochemical devices, both for the generation of the input perturbation and for the monitoring of the system response. It has the advantages of providing very reproducible signals as well as allowing the instantaneous and sensitive detection of the concentration–time response at the output of the bed or at any point within it.

The circuit used is shown in Fig. 1. The perturbation, or signal, is formed when a short anodic pulse (0.1 s or less) is applied to a copper grid F at the inlet of the reactor. The narrow concentration plug of copper ions flows upwards, driven by the electrolyte flow, exhibiting axial dispersion in the bed and leaves the bed at the position B where another grid electrode (maintained potentiostatically at the limiting current plateau for copper ion deposition) detects the average copper concentration in that cross-section of space. The corresponding schematic representation of the cell and measuring device only are given in Fig. 2. In this series of experiments the bed consisted of glass particles, i.e. the system was electrochemically inactive.

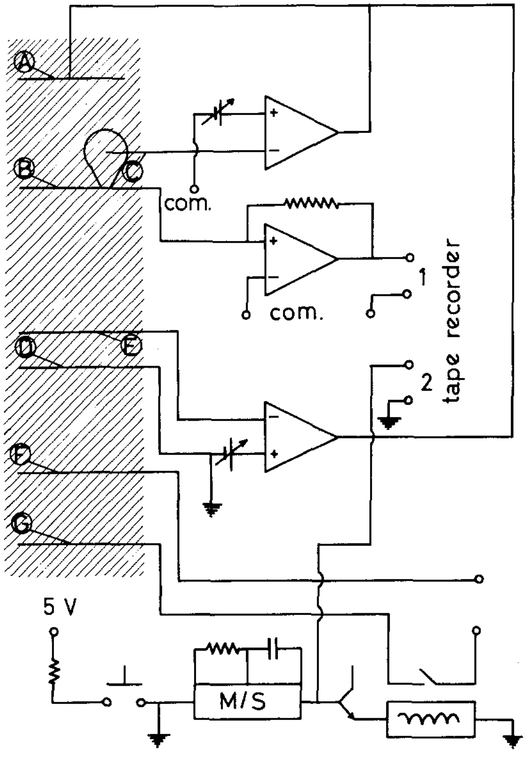

Fig. 1. Schematic representation of the electric circuit used for the determination of the mixing history and overall reactivity of the system. A, counter electrode; B, detector electrode; C and E, Luggin capillaries; D, bed feeder electrode; F, tracer source; G, counter electrode. Electrodes A, B, F and G were used for the inactive system; electrodes D and E were used in addition for measurements on active systems.

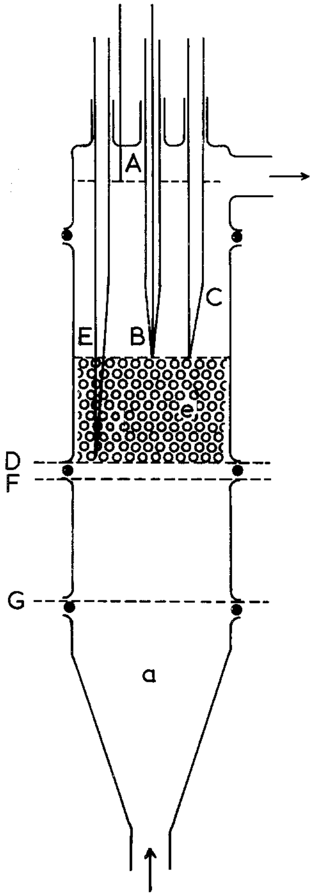

Fig. 2. Schematic representation of the cell and measuring device: a, flow distributer; G, counter electrode; F, tracer source; D, bed feeder; e, bed; E, Luggin capillary for feeder potential control; B, detector electrode; C, Luggin capillary for detector electrode potential control; A, counter electrode.

2.2. *Results*

The responses of the system, i.e. the variations in the current measured by the detector electrode, were recorded continuously. Each curve was then digitalized and statistical and hydrodynamic analyses were carried out. As the system response is the distribution of the residence time in real units for the particular conditions of the experiment, the statistical analysis consisted of the determination of the moments of the distribution.

$$m_0 = \int_0^\infty C_L \mathrm{d}t \qquad (2)$$

$$M_1 = \frac{1}{m_0}\int_0^\infty t C_L \mathrm{d}t \qquad (3)$$

$$M_2 = \frac{1}{m_0}\int_0^\infty t^2 C_L \mathrm{d}t. \qquad (4)$$

The evaluation of the dispersion coefficient (or Peclét number) and residence time must be made in terms of a model. Appropriate initial and boundary conditions may be applied for example to the axial flow through the model described by Equation 1. For simple models it is particularly convenient to deduce and use the Laplace transform of the concentration at the outlet of the reactor, $\bar{C}_L$, since

$$M_1 = -\frac{1}{m_0}\left(\frac{\mathrm{d}\bar{C}_L}{\mathrm{d}s}\right)_{s=0} \qquad (5)$$

and

$$M_2 = \frac{1}{m_0}\left(\frac{\mathrm{d}^2\bar{C}_L}{\mathrm{d}s^2}\right)_{s=0} \qquad (6)$$

i.e. it is not necessary to obtain the inverse of the transform. For the finite 'closed channel' model it is predicted that

$$M_1 = \tau = V/v \qquad (7)$$

where V is the free volume of the bed and v the volumetric flow rate. Comparison of the first moment M_1 and τ however showed discrepancies which indicated that the system should be described as an 'open vessel', according to Levenspiel [3]. Following the suggestion that it is more correct to determine τ and (Pe) from the variance and the first moment [3], the appropriate values were calculated from:

$$\frac{M_1}{\tau} = 1 + \frac{1}{(Pe)} \qquad (8)$$

$$\frac{M_2}{\tau^2} - \left(\frac{M_1}{\tau}\right)^2 = \frac{1}{(Pe)^2}\,[2(Pe)+3]. \qquad (9)$$

Equations 8 and 9 are valid for the so-called semi-infinite channel model [3].

The effect of variations in the parameters of the bed on the mixing history was investigated. Particle size, bed height and flow rate were varied. The variations in the flow rate caused the bed to change from a packed to a fluidized state. Figs. 3–5 illustrate some data for different particle diameters, bed heights and flow rates. The data indicate comparatively reproducible behaviour of the fluid flow. At low values of the Reynolds number,

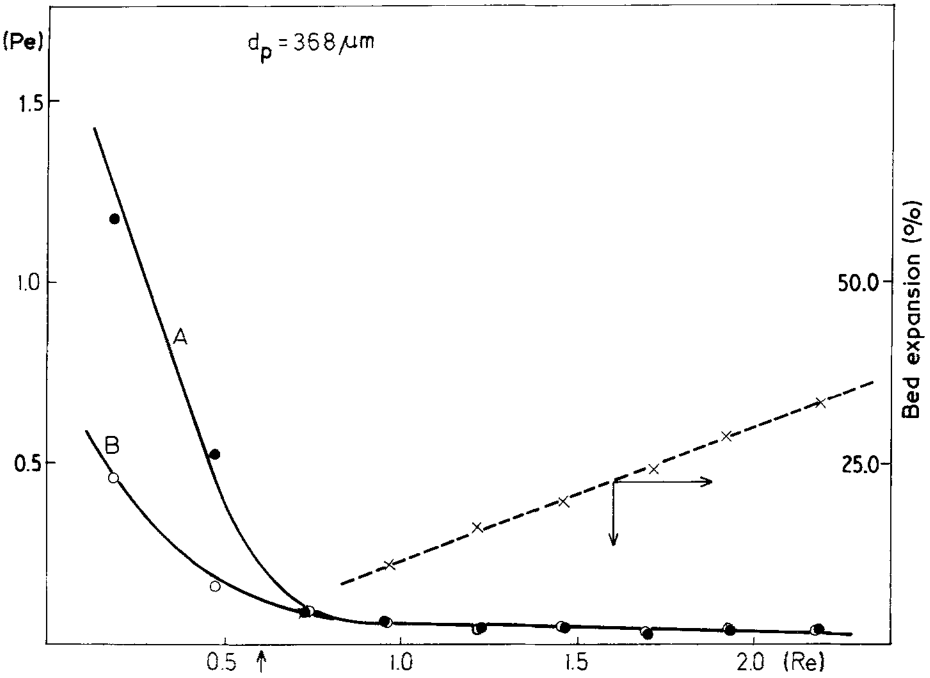

Fig. 3. (*Pe*) versus (*Re*) relationship obtained in bed with particles of 368 μm in diameter: A, initial height of the bed = 50 mm; B, initial height of the bed = 69 mm. The arrow indicates the onset of fluidization.

in the packed bed region, (*Pe*) is relatively high (i.e. $\bar{D}$ is small and mixing is not particularly well developed). At the onset of fluidization, the system tends to reach very small (*Pe*) values (stronger mixing). In the case of particle sizes of 480 and 820 μm, (*Pe*) again rises after the fluidized regime has developed. This behaviour is summarized for three different particle sizes and similar bed heights in Fig. 6.

It is clear that mixing varies in a complex manner with bed height and particle diameter and at this stage we have not found a single dimensionless correlation.

In conclusion it should be noted that mixing in three-dimensional electrodes is so strong that flow models must include the dispersion operator, in addition to the convective term. The dispersion term is, in fact, five to six orders of magnitude

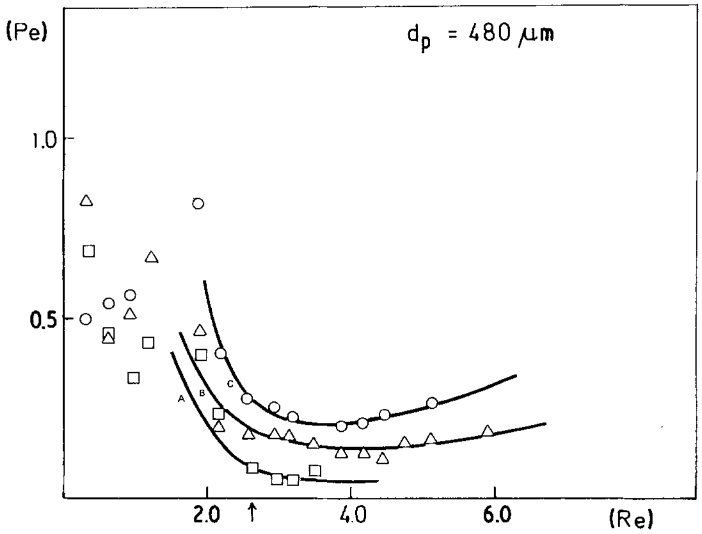

Fig. 4. (*Pe*) versus (*Re*) relationship obtained in bed with particles of 480 μm in diameter: A, initial height of the bed = 24 mm; B, initial height of the bed = 45 mm; C, initial height of the bed = 70 mm. The arrow indicates the onset of fluidization.

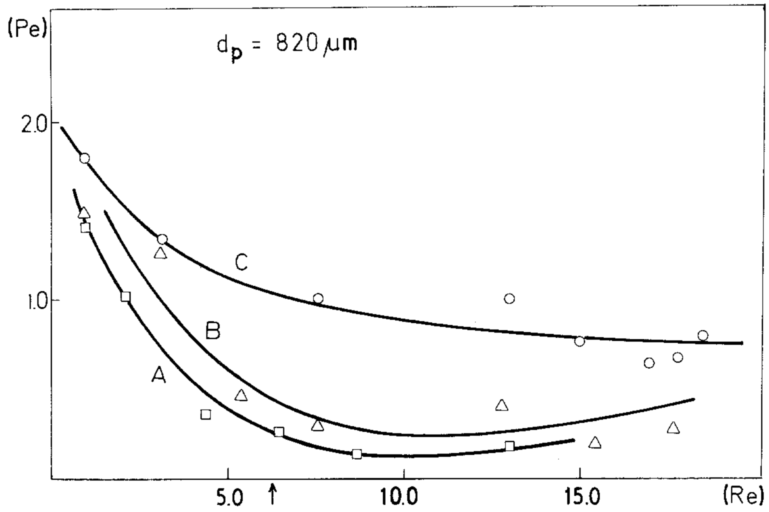

Fig. 5. *(Pe)* versus *(Re)* relationship obtained in bed with particles of 820 μm in diameter: A, initial height of the bed = 67 mm; B, initial height of the bed = 49 mm; C, initial height of the bed = 18 mm. The arrow indicates the onset of fluidization.

higher than the diffusion coefficient so that the effects of dispersion and convection will be comparable for the dimensions of reactors normally used. The effects of dispersion will become particularly evident in systems with long average residence times as well as those where complex reaction mechanisms are under consideration.

The technique permits the rapid and reproducible measurement of the mixing history for every kind of flow system and the modifications for the simultaneous measurement of radial dispersion are straightforward.

3. Characterization of the overall kinetics

3.1. *Method and technique*

It has recently been suggested that the kinetics of the reaction in a flowthrough system can be characterized by means of a new method [4–8] based on the tracer technique. At this stage the interpretation of the experiments rests on the assumption that the reaction rate is a linear function of the concentration:

$$r = KC. \tag{10}$$

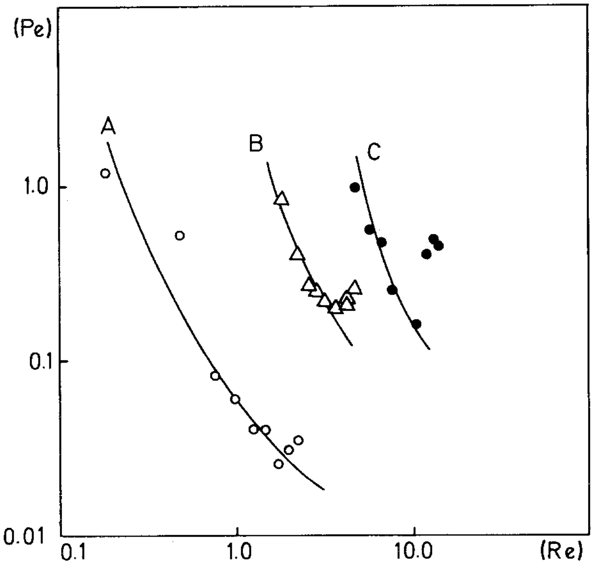

Fig. 6. *(Pe)* versus *(Re)* relationship: A, d_p = 368 μm, H_0 = 50 mm; B, d_p = 480 μm, H_0 = 45 mm; C, d_p = 718 μm; H_0 = 52 mm.

From the point of view of electrochemical reactions this may represent the situation where most of the active electrode surface is in the limiting current regime. In that case, the method allows one to obtain

$$K = Sk_{\mathrm{m}}\left(= \frac{SD}{\delta}\right)$$

i.e. the mass transfer coefficient multiplied by the specific surface area of the electrode. It is interesting to note that, when K fluctuates randomly in space and time around some average value K, the method measures the average K as has been proved theoretically [8].

Experimentally the method consists of perturbing the system twice using an impulse of the reactant concentration. The first response, $y_1(t)$, is obtained when no reaction takes place (current in the bed reactor is switched off) and the second one, $y_2(t)$, is obtained under normal operating conditions. From these two responses one forms a function $I(t)$

$$I(t) = \frac{y_1(t) - y_2(t)}{y_1(t)}. \qquad (11)$$

It is found [4] that the plot of $-\ln[1 - I(t)]$ versus t is a straight line with the same slope as the plot of $-\ln(1 - X)$ versus t for the first order chemical reaction characterized by K (s^{-1}). Therefore by plotting $-\ln[1 - I(t)]$ versus time, one can obtain K the reaction rate operator in Equation 1, i.e. one can extract the desired value of K for the flow through the system which additionally has one first order and one second order differential operator superimposed on K, these operators also being measurable.

The circuit used in these experiments (Fig. 1) is the same as that used in mixing history investigations except that the electrode (which consisted of metal-coated glass beads) was kept under potentiostatic control at a comparatively high overpotential (− 150 mV at the feeder). Under these conditions most of the particles were working in the diffusion-limiting regime.

3.2. *Results*

Different flow rates were applied to beds of glass particles coated with copper (Fig. 7, curve A) and silver (Fig. 7, curves B and C).

Increasing flow rates [increasing (Re)] led to the expected increase in K. The initial parts of

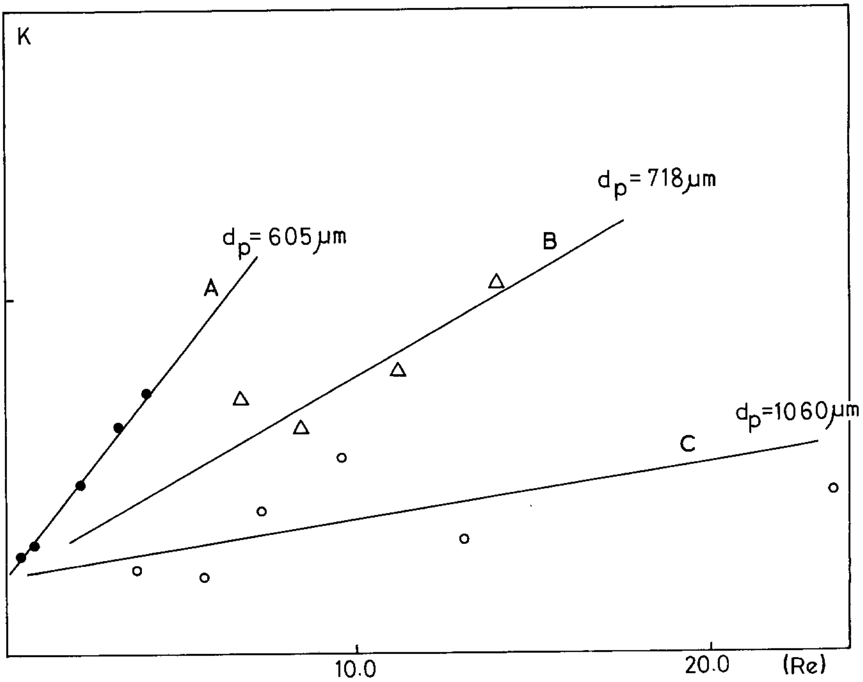

Fig. 7. Overall reactivity of the system, $K = Sk_{\mathrm{m}}$, for different particle sizes. A, copper deposition experiment, $d_{\mathrm{p}} = 605\,\mu\mathrm{m}$; B, silver deposition experiment, $d_{\mathrm{p}} = 718\,\mu\mathrm{m}$; C, silver deposition experiment, $d_{\mathrm{p}} = 1060\,\mu\mathrm{m}$.

all three curves represent the packed bed regime (low flow rates) while the data for the rest of the curves are for the fluidized bed case. Recalling that $K = Sk_m$ and dividing the plotted K values by S, one obtains mass transfer coefficients k_m of the expected order of magnitude [9] (1×10^{-3}–1×10^{-2} cm^2 s^{-1}).

4. Conclusions

A new approach suitable for the characterization of three-dimensional electrodes has been demonstrated. Analysis of the mass balance within the electrode enables one to describe fundamental parameters of the system: (Pe), τ and overall reactivity K. Further work is in progress to increase the applicability of the method to the investigation of active systems, in particular so as to permit the analysis of non-uniform distributions of K along the bed, the situation which normally arises when such an electrode operates with activation control of the electrode reaction.

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