

The performance of porous and gauze electrodes in electrolysis with parabolic velocity distribution

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An approximate numerical method for the estimation of the velocity exponent in (small-scale) flow-through porous and gauze electrodes is presented. The method can also be employed to determine if a plug-flow or a parabolic-flow model offers a more reliable representation of the experimental behaviour of the electrode.

Nomenclature

a	cross sectional area of the electrode	L	length of the electrode
B	integration parameter (Equations 7 and 8)	n	number of electrons involved in the electrode reaction
c	exit active ion concentration, \bar{c} its mean measured value in the case of parabolic flow, c_0 its inlet value; c_m its mean value; \bar{c}_m its mean calculated value in the case of parabolic flow; c^* dimensionless concentration, equal to c/c_0 ; \bar{c}^* mean dimensionless concentration, equal to \bar{c}/c_0	N	ionic flux
F	Faraday's constant	r	radial coordinate
i_L	mean limiting current density (geometric-area base)	R_E	geometric radius
j	proportionality factor (Equation 1)	R	limiting degree of conversion
k_m	mass transport coefficient, \bar{k}_m its mean value	s	specific surface area of the electrode (surface per volume)
		u	linear solution velocity; u_0 its maximum (centre-line) value; \bar{u} its mean value ($\bar{u} = u_0/2$)
		v	volumetric flow rate; \bar{v} its mean value
		x	transform variable for z
		z	dimensionless radial distance
		α	velocity exponent for mass transport (Equation 1)

1. Introduction

Flow-through porous electrodes (FTPE) have become important during recent years [1, 2] in various areas of applied electrochemistry. Specifically, an earlier design [3] consisting of a stack of fine platinum screens (SFPS) was followed by a reticulated vitreous carbon (RVC) system [4], but a large variety of porous electrodes has been employed by various researchers in studying mass transport and kinetic behaviour, e.g., [5, 6] in a three-dimensional configuration, characteristic of such electrodes. Their practical use is primarily in metal recovery from dilute waste solutions, energy-storage systems and to a smaller extent, in electro-organic syntheses (e.g., in the production of nitroso compounds, [7]), but new applications, e.g., in molten carbonate fuel cells [8] and slurry zinc-air cells [9] have also been foreseen. Certain applications in analytical chemistry have been described [10, 11] and various technical aspects of FTPE operation have been discussed [12-15]. SFPS operation has also been analysed in detail [16]; an interesting paper by Ateya

[17] portrays the importance of radial diffusion on the performance efficiency of porous-flow electrodes.

RVC and SFPS electrodes are characterized by high void volumes (80% and higher), resulting in a velocity distribution which approximates parabolic behaviour flow more closely than plug-flow behaviour assumed in an earlier modelling of the FTPE [18]. The purpose of this paper is to analyse FTPE performance in terms of parabolic hydrodynamics and to indicate specifically an experimental determination of the apparent velocity exponent for mass transport on the basis of the chosen performance mode which may also be used for rapid model discrimination.

2. Theory

In conformity with earlier formulations, the mass transport flux is expressed as

$$N = ju^\alpha c = k_m \Delta c \quad (1)$$

where j is a proportionality constant and α is the mass transport velocity exponent. Although this

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formulation is dimensionally awkward due to the dependence of the j dimension on α , this fact has no particular significance in the treatment since the numerical evaluation of j is not necessary (and is, indeed, avoided). The numerical value of α has been shown [18] to be $\frac{1}{3}$ for wire electrodes, but it can be as high as $\frac{1}{2}$, depending on the shape of the electrode. If $\Delta c \simeq c$, i.e. the active ion concentration at the electrode surface is much smaller than in the electrolyte bulk, then

$$k_m = ju^z \quad \text{and} \quad \bar{k}_m \simeq j\bar{u}^z \quad (2)$$

If the velocity distribution is parabolic, i.e.

$$u = u_0(1 - z^2), \quad z = r/R_E \quad (3)$$

Equation 1 may be expressed as

$$N = ju_0^z(1 - z)^z c \quad (4)$$

Let the mean velocity and the mean volumetric flow rate be related by an *a priori* indeterminate coefficient k ; then, since

$$\bar{u} = k\bar{v} = u_0/2 \quad (5)$$

N may be expressed in terms of \bar{v} , a measurable quantity.

The performance of the electrode is related to the ratio of the exit concentration of the active ion to its inlet concentration (or equivalently to the conversion), which can be obtained by integrating the exit concentration over the cross-sectional area of the electrode. The relationship for the exit concentration is obtained in a manner similar to that described earlier [18], except that the velocity is no longer a constant across the cross section. In terms of dimensionless quantities, the concentration ratio is given by

$$\begin{aligned} \bar{c}^* &= \frac{4}{u_0} \int_0^1 uc^*(z)dz = 4 \int_0^1 z(1 - z^2) \\ &\times \exp[-2^{\alpha-1} B(\alpha)(1 - z^2)^{\alpha-1}] dz \quad (6) \end{aligned}$$

where

$$B(\alpha) = (js)Lk^{\alpha-1}\bar{v}^{\alpha-1} \quad (7)$$

is a parameter depending on the physical properties and the geometry of the electrode. Equation 6 may be simplified by the substitution $x = 2(1 - z^2)$ yielding the final form

$$\bar{c}^* = \frac{1}{2} \int_0^2 x \exp[-B(\alpha)x^{\alpha-1}] dx \quad (8)$$

Equation 8 may be regarded as a quantitative measure of performance. Figure 1 portrays the dependence of \bar{c}^* on α for selected values of B ; numerical integration of Equation 8 was carried out on a microcomputer using Romberg's quadrature method [19].

3. An approximate experimental determination of the velocity exponent α

The *a priori* computation of the parameter B via Equation 7 would require the knowledge of the $(jk^{\alpha-1})$ term for a specific porous electrode, whose

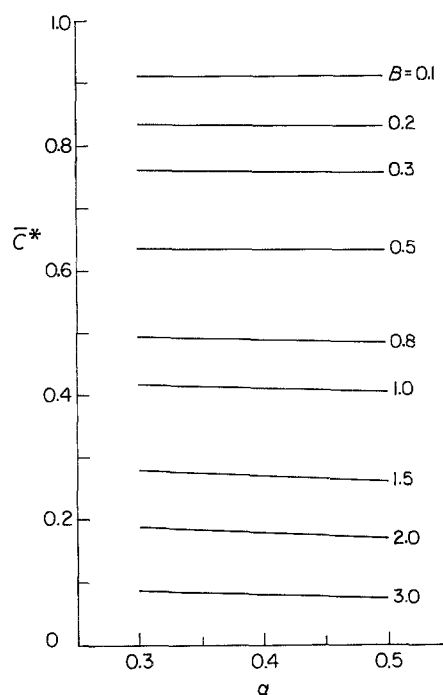


Fig. 1. The variation of \bar{c}^* (Equation 8) with the velocity exponent α at various values of the integration parameter B .

computation may be rather cumbersome. The problem may be circumvented, however, by computing B from measured limiting currents and employing the concept of the mean mass transport coefficient

$$B = \frac{sLa}{\bar{v}} \bar{k}_m, \quad \bar{k}_m = \frac{i_L}{nFc_m} \quad (9)$$

Since \bar{c}^* can be obtained experimentally, the numerical value of α may be found from Fig. 1 once the numerical values of \bar{c}^* and B have been determined; alternatively, Equation 8 may be solved iteratively with assumed values of α until the experimentally determined value of \bar{c}^* has been attained. The computation of \bar{c}_m as an arithmetic mean

$$\bar{c}_m = \frac{1}{2}(c_0 + \bar{c}) \quad \text{small conversion} \quad (10a)$$

or as a logarithmic mean

$$\bar{c}_m = \frac{c_0 - \bar{c}}{\ln(c_0/\bar{c})} \quad (10b)$$

is itself approximate, but a rigorous determination of \bar{c}_m would require exact axial and radial concentration profiles. Owing to this fact, and since the geometric area of the electrode may not be determined very accurately, the computed value of α is approximate, although of acceptable accuracy for the purpose of analysis and design. Appendix I illustrates the approach with a numerical example.

4. Comparison with plug flow analysis: model discrimination

If a uniform velocity profile at any (arbitrary) cross section of the electrode is taken, Equation 8 is replaced by the simpler equation

$$\bar{c}^* = \exp(-B) \quad (11)$$

and no numerical integration is necessary. As shown earlier [18, 20], the numerical value of α in this instance can be computed from the slope of the $\log \log [1/(1 - R)]$ plotted against $\log \bar{v}$ line, where R is the limiting degree of conversion. Since the numerical value of α depends on the model assumed, it is possible to ascertain which of the two models fits more faithfully the experimental data without recourse to a more involved statistical regression and model discrimination analysis. As shown in Appendix II, the absurdity of the α value associated with one model necessitates its rejection. If the numerical values of α are comparable, the true electrode behaviour is between plug flow and parabolic flow and both models offer essentially the same degree of approximateness. In such an instance a statistical analysis of data (on a larger data set) including e.g., a dispersion model [20] may be warranted.

5. Limitations of the approach

In FTPE systems of large dimensions, parts of the electrode may well be under activation control rather than mass transport control, depending on the potential distribution in the bed [21]. Then, the use of a mean mass transport coefficient computed from the limiting current would be hazardous. One possible approach would be to map the portions of the electrode under activation control, compute local values of the $(k_m \lambda)$ product, where λ is the fractional concentration coefficient allowing for non-zero active-ion concentration at the electrode surface [22, 23], and obtain a volume-average value of $(\bar{k}_m \lambda)$ to be employed in Equation 9. Calculations of this kind are becoming increasingly feasible with graphics-supported microcomputer programs, but this aspect is beyond the scope of the current communication.

6. Concluding remarks

The major attractiveness of the approach presented here lies in the minimal number of physical parameters needed for a relatively rapid reliability test for the plug-flow and parabolic-flow models. The method allows at least a preliminary design of a (small-scale) porous or gauze electrode system without a thorough understanding of microscopic electrode properties.

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Appendix I: A numerical illustration for the estimation of the velocity exponent

A highly porous electrode of $L = 0.29$ cm active

length has a specific area of $s = 85$ cm⁻¹ and an effective cross sectional area of $a = 0.75$ cm². The electrode reaction involves a monovalent ionic species ($n = 1$) whose inlet concentration of $c_0 = 0.02$ mol l⁻¹ is reduced to $\bar{c} = 0.0146$ mol l⁻¹ at a volumetric flow rate of $\bar{v} = 0.162$ cm³ s⁻¹ and limiting current density of $i_L = 5.0$ mA cm⁻². Using Equations 9 and 10

$$\begin{aligned} \bar{k}_m &= \frac{(5.0)(10)(2)}{(96487)(1000)(0.02 + 0.0146)} 100 \\ &= 2.995 \times 10^{-3} \text{ cm s}^{-1} \end{aligned}$$

and

$$B = (85)(0.29)(0.75)(2.995 \times 10^{-3})/0.162 = 0.341$$

are computed. Consequently, Equation 8 may be written as

$$\frac{1}{2} \int_0^2 x \exp(-Bx^{\alpha-1}) dx = 0.0146/0.02 = 0.73$$

Numerical integration yields 0.73000 when $\alpha = 0.45944$; hence the velocity exponent in this electrode is taken as $\alpha \approx 0.459$.

Appendix II: A numerical illustration for model discrimination

The experimental data obtained in a porous electrode containing 16 parallel platinum screens [3] are taken as basis for calculation; here, $L = 0.345$ cm, $s = 102$ cm⁻¹, $a = 0.90$ cm², $c_0 = 2$ mmol l⁻¹, $n = 1$ and $R = 0.679$ (corresponding to an exit concentration of 0.642 mmol l⁻¹). The mean mass transport coefficient obtained from the experimental current density at a volumetric flow rate of $\bar{v} = 0.1$ cm³ s⁻¹ is $\bar{k}_m = 3.7 \times 10^{-3}$ cm s⁻¹ ([3] Table 3). Using Fig. 1 [3], the slope of the uppermost straight line of the $\log \log [1/(1 - R)]$ against $\log \bar{v}$ plot yields $\alpha = 0.4$ in the case of the plug-flow model.

If the periodic-flow model is taken, Equation 9 yields

$$B = (102)(0.345)(0.90)(3.7 \times 10^{-3})/0.1 = 1.171$$

Due to the relatively large conversion, the logarithmic mean is taken

$$\bar{c}^* = [(2 - 0.642)/\ln(2/0.642)]/2 = 0.5979$$

rather than the arithmetic mean of $[(2 + 0.642)/2] = 0.6605$. A quick glance at Fig. 1 indicates that no realistic value of α can satisfy these conditions, since the $B = 1.171$ line would not intercept the $\bar{c}^* = 0.5975$ line. It follows that this porous electrode cannot be reliably represented by a parabolic-flow model.

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