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The rôle of diffusion on the performance of porous electrodes

K. SCOTT

Department of Chemical Engineering, Teesside Polytechnic, Borough Road, Middlesborough, Cleveland, TS1 3BA, England

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An approximate method is presented for the analysis of the conservation equations used to describe the effect of a variation of electrolyte concentration and electrode potential on electrochemical reactions in porous electrodes. Asymptotic solutions are obtained for reaction following Tafel kinetic behaviour or a Butler–Volmer approximation and linear approximations are used to define the limits of the asymptotic solutions. Porous electrode behaviour is characterized in terms of effectiveness.

Nomenclature

a	specific area of particulate electrode ($\mathrm{m^{-1}}$)
c_b	bulk electrolyte concentration ($\mathrm{mol\,m^{-3}}$)
c_i	concentration of species i ($\mathrm{mol\,m^{-3}}$)
c_0	reference concentration at $x = 0$ ($\mathrm{mol\,m^{-3}}$)
c_s	surface concentration ($\mathrm{mol\,m^{-3}}$)
D_i	diffusivity of species i ($\mathrm{m^2\,s^{-1}}$)
E	effectiveness (dimensionless)
F	Faraday constant (Coulombs $\mathrm{mol^{-1}}$)
i	local current density or reaction rate ($\mathrm{A\,m^{-2}}$)
i_0	exchange current density ($\mathrm{A\,m^{-2}}$)
i_T	total current density based on cross-sectional area of the electrode ($\mathrm{A\,m^{-2}}$)
I	dimensionless current density $= i_T/ai_0L$
k_m	average mass transfer coefficient ($\mathrm{ms^{-1}}$)
L	bed height in the direction of current flow (m)
n	number of electrons involved in reaction
N_i	flux of species i ($\mathrm{mol\,cm^{-2}\,s^{-1}}$)
R	gas constant ($\mathrm{cal\,mol^{-1}\,K^{-1}}$)
s	dimensionless parameter
T	temperature (K)
x	distance in the direction of current flow (m)
y	dimensionless distances in the direction of current flow $= x/L$
α	charge transfer coefficient (dimensionless)
β	nF/RT ($\mathrm{V^{-1}}$)
δ	dimensionless parameter $= Li\beta/\kappa$
δ'	dimensionless parameter $= \alpha\delta$ or $(1-\alpha)\delta$
η	overpotential $= \phi_m - \phi_s$
κ	effective conductivity of electrolyte phase ($(\Omega\mathrm{m})^{-1}$)
ν^2	dimensionless parameter $= ai_0L^2\beta/\kappa$
ϕ	dimensionless potential $= \beta\eta$

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ϕ_0 value of ϕ at $y = 0$
ϕ_1 value of ϕ at $y = 1$
Φ_0 electrochemical Thiele modulus

1. Introduction

There are many examples of the industrial use of porous electrodes especially where intimate contact of electrode material with solution and possibly a gas is essential. Batteries, fuel cells and similar devices are probably the main areas of application with specific requirements such as compactness and large interfacial area [1]. Another potential area of application is in the treatment of waste streams and in electro-organic synthesis [1]. Then flow-through porous-electrodes are used where electrolyte is continuously circulated through the cell whereas in the case of say fuel cell electrodes, diffusion is the main contributor to mass transport. This paper is concerned with a theoretical one-dimensional analysis of electrodes of the latter type in which reaction rates are distributed unevenly due to diffusion as well as a variation in electrode potential. Flow-through porous-electrodes can be considered as a limiting case of this analysis.

The treatment of the problem of a simultaneous variation in electrolyte concentration and potential distribution in the electrode is treated in an analogous manner to that of non-isothermal chemical reactions in porous catalysts [2]. Approximate asymptotic solutions are obtained for reactions following Tafel kinetics and a Butler–Volmer approximation and which are either first or second order with respect to reactant concentration. The results of the analysis are presented in terms of the engineering concept of effectiveness and it is shown that four dimensionless groups or numbers control the electrode behaviour. The strength of this approach to the problem is that it allows a quick assessment of the proportion of a porous electrode used in practice or of the likely performance of the electrode given relevant kinetic, physical and structural parameters. Primarily we are interested in determining when a porous electrode is not effectively used and hence the region of concern is where the asymptotic approximation gives a reasonable representation of 'actual' behaviour.

One of the main failures of the model is that transient behaviour is not considered, however this analysis should serve as a useful starting point at which specific time varying parameters may be later incorporated.

2. Analysis

In the mathematical modelling of porous or particulate bed electrodes a one-dimensional analysis has frequently proved satisfactory and as such is adopted in this treatment [1]. An inherent part of any model is the adoption of certain simplifying assumptions which minimize mathematical complexity while maintaining practical significance. Assumptions adopted in this analysis are therefore as follows:

1. The porous electrode is one dimensional and both solid and electrolyte phases are continuous media with uniform effective conductivities.*
2. Isothermal and steady state conditions apply.
3. The electrical potential of the dispersed (solid) phase is constant.
4. Ohm's Law is applicable to electrical conduction in the electrolyte phase.
5. Ionic migration of the reacting species is neglectied.*
6. The electrode is characterized by a uniform specific area, a.
7. The flux of reacting species (N_i) is given by Fick's Law

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* For a binary electrolyte variation in electrolyte conductivity and the influence of migration of reacting species can be accounted for. The governing equations are similar to those considered in this analysis but the dimensionless groups which control the electrode behaviour are modified slightly [3].

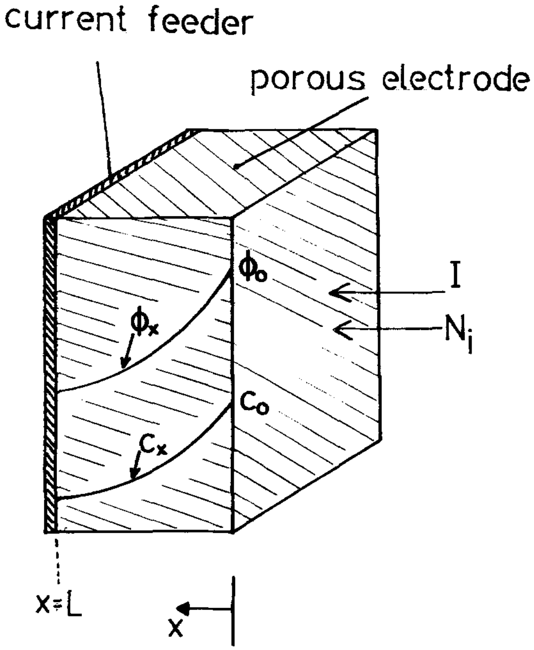

Fig. 1. The one-dimensionless porous electrode.

$$N_i = -D_i \frac{dc_i}{dx} \tag{1}$$

where the diffusion coefficient D_i of species i is uniform throughout the structure.
With the above assumptions the mathematical model can be established for the system in Fig. 1 by considering charge and material balance in the structure. By applying Ohm's Law to electrical conduction in the electrode, a charge balance on the differential element of thickness, dx, leads to the following differential equation:

$$\frac{d^2\eta}{dx^2} = \frac{ai}{\kappa} \tag{2}$$

where η is the local overpotential in the structure, κ, the effective conductivity of the electrolyte phase and i is the local reaction rate at the solid, liquid interface. The analysis considers a variety of kinetic expressions for i but the influence of limiting current behaviour is not included.

A material balance on a differential element, dx, of the electrode structure leads to the following diffusion equation:

$$D\frac{d^2c}{dx^2} = \frac{a}{nF}i \tag{3}$$

where c is the reactant concentration. Boundary conditions which apply to this equation are at

$$x = 0, \quad c = c_0, \quad \eta = \eta_0$$

and

$$x = L, \quad \frac{dc}{dx} = 0, \quad \frac{d\eta}{dx} = 0.$$

The measurable or total current density based on the cross-sectional area of the electrode is given by:

$$i_T = -nFD\left(\frac{dc}{dx}\right)_{x=0} \tag{4}$$

or

$$i_T = -\kappa \left(\frac{d\eta}{dx}\right)_{x=0} \tag{5}$$

It is convenient at this stage in the analysis to introduce dimensionless parameters which characterize the electrode and its performance and to consider specific electrochemical kinetics.

3. Tafel polarization

The equation for Tafel kinetics is of the form:

$$i = i_0 \frac{c}{c_0} \exp\left(\alpha \frac{nF}{RT} \eta\right) \tag{6}$$

where i_0 is the exchange current density and α the charge transfer coefficient. The concentration dependency of the reaction is 1st order. On substituting in Equations 2 and 3 and introducing the following dimensionless parameters:

$$y = \frac{x}{L} \qquad \phi = \beta\eta$$

$$\nu^2 = \frac{a i_0 L^2 \beta}{\kappa} \qquad \beta = \frac{nF}{RT}$$

$$s = L^2 \frac{a i_0}{nFDc_0} \qquad C = \frac{c}{c_0}$$

we obtain:

$$\frac{d^2\phi}{dy^2} = C\nu^2 \exp(\alpha\phi) \tag{7}$$

$$\frac{d^2C}{dy^2} = Cs \exp(\alpha\phi). \tag{8}$$

To assist in the solution of these differential equations we can obtain a relationship between C and ϕ by combining Equations 7 and 8 to give:

$$\frac{d^2\phi}{dy^2} = \frac{\nu^2}{s} \frac{d^2C}{dy^2} \tag{9}$$

which on integration results in:

$$(\phi - \phi_0) = \frac{\nu^2}{s}(C - 1). \tag{10}$$

Hence the potential and concentration drops across the electrode structure are related by the two parameters ν^2 and s.

Combining Equations 7 and 10 gives:

$$\frac{d^2\phi}{dy^2} = \nu^2 \left(1 + \frac{s}{\nu^2}(\phi - \phi_0)\right) \exp(\alpha\phi) \tag{11}$$

the exact solution of which requires numerical techniques. However the problem in hand is not concerned specifically with either the potential distribution or concentration distribution but with a more global view of a porous electrode performance by way of its effectiveness, E, which is defined in the following manner:

$$E = \frac{\text{Actual reaction rate (or current density)}}{\begin{array}{c}\text{Reaction rate (or current density) without mass}\\ \text{transport and ohmic drop limitations}\end{array}}\,.$$

In other words we are interested in the utilization of the electrode in relation to its maximum theoretical performance. As such, we are more concerned with the estimation of an electrode's performance (effectiveness) at conditions other than near the maximum theoretical values and hence approximate solution techniques are adopted. The main approximation is that of obtaining asymptotic solutions as follows. These have been applied quite successfully to the analogous case of non-isothermal effectiveness factors in porous catalysts [2] and to porous electrodes without diffusion limitations [4].

4. Results and discussion

4.1. *Asymptotic solution* ($\phi_1 \to 0$)

For an asymptotic solution the electrode is assumed to be semi-infinite and the boundary condition at $y = 1$ is $\phi_1 = 0$. On first integration of Equation 11 we obtain:

$$\frac{1}{2}\left[\left(\frac{\mathrm{d}\phi}{\mathrm{d}y}\right)_{y=0}\right]^2 - \frac{1}{2}\left[\left(\frac{\mathrm{d}\phi}{\mathrm{d}y}\right)_{y=1}\right]^2 = \nu^2 \int_0^{\phi_0} \left(1 + \frac{s}{\nu^2}(\phi - \phi_0)\right) \exp(\alpha\phi)\,\mathrm{d}\phi$$

$$= \nu^2 \left[\frac{\exp(\alpha\phi_0)}{\alpha}\left(1 - \frac{s}{\nu^2\alpha}\right) - \frac{1}{\alpha}\left(1 - \frac{s}{\nu^2}\phi_0 - \frac{s}{\nu^2\alpha}\right)\right]. \tag{12}$$

The boundary condition at $y = 0$, Equation 5 in dimensionless form becomes:

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}y}\right)_{y=0} = -\nu^2 I \tag{13}$$

where $I = i_{\mathrm{T}}/(ai_0L)$, a dimensionless total current density. Combining Equations 12 and 13 results in the polarization equation of the porous electrode as:

$$I = \left\{\frac{2}{\nu^2}\left[\frac{\exp(\alpha\phi_0)}{\alpha}\left(1 - \frac{s}{\nu^2\alpha}\right) - \frac{1}{\alpha}\left(1 - \frac{s}{\nu^2}\phi_0 - \frac{s}{\nu^2\alpha}\right)\right]\right\}^{0.5} \tag{14}$$

and the effectiveness is given by:

$$E = \frac{I}{\exp(\alpha\phi_0)}. \tag{15}$$

Typical effectiveness data is presented in Fig. 2 as a function of I for a transfer coefficient $\alpha = 1/2$. Increasing the parameter s is seen to decrease the effectiveness at fixed I values due to a relative decrease in the diffusivity which enhances reactant depletion in the electrode. The dimensionless group s can be considered to be an electrochemical Thiele modulus. At sufficiently low values of s the data approaches limiting lines for specific ν^2 values because reactant depletion is not significant. The data in this case is essentially that of a zero order reaction and is therefore given by the corresponding constant concentration analysis [5] and is correlated at high I in terms of a dimensionless parameter $\delta = \nu^2 I$ using the expression:

$$E = \frac{2}{\delta'} \tag{16}$$

where $\delta' = (1 - \alpha)\delta$ or $\alpha\delta$ depending on whether the reaction is cathodic or anodic. Exact data for the zero order reaction is shown as dotted lines for $\nu^2 = 1$ and 3. For $\nu^2 > 10$ agreement between the exact and asymptotic solutions is very good for the zero order reaction.

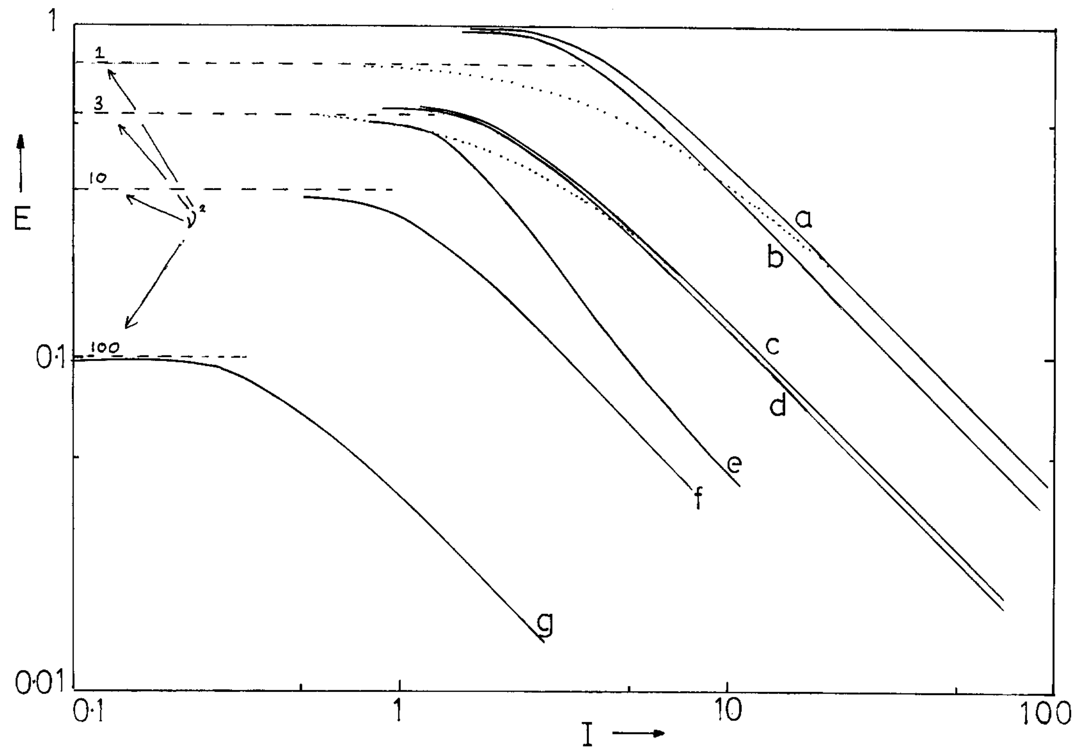

Fig. 2. The variation of effectiveness with total current I for the asymptotic solution $\phi_1 = 0$. ($\alpha = 0.5$).
Curve a: $\nu^2 = 1, s = 0.01$ and 0.001; Curve b: $\nu^2 = 1, s = 0.01$; Curve c: $\nu^2 = 3, s = 0.001$; Curve d: $\nu^2 = 3, s = 0.1$; Curve e: $\nu^2 = 3, s = 1$; Curve f: $\nu^2 = 10, s = 1$; Curve g: $\nu^2 = 100, s = 1$.
.... exact solution $s \to 0$. ——— linear polarization 'asymptotes' from Equation 17 (values of ν^2 indicated).

At high values of ν^2 where effectiveness is generally low the influence of s is not too significant, especially at low values of I where the data should tend towards limiting values given by a similar constant concentration analysis [6] using the linear approximation of the more general Butler–Volmer equation. This is because at low potentials and currents (where the asymptotic analysis generally over-predicts E) reaction rate and hence reactant consumption is low and from Equation 10 concentration will be quite uniform. An upper bound can then be stipulated for effectiveness [6] which is dependent on the value of ν^2, i.e.

$$E = \frac{\tanh(\nu)}{\nu}. \tag{17}$$

A more precise approach is to treat the analysis as described by Equations 2 and 3, using linear polarization kinetics, the solution of which can be obtained in terms of Elliptic Integrals.

The form of the asymptotic solution Equation 13 considered suggests that when the ratio s/ν^2 becomes $\gg 1$ the analysis breaks down. This is confirmed further from Equation 10 which when $\phi_1 = 0$ becomes:

$$C_1 = 1 - \frac{s}{\nu^2}\phi_0$$

implying negative values of concentration C_1 at moderate values of ϕ_0. Hence an alternative asymptotic analysis is preferred in which the concentration at $y = 1$ approaches zero.

4.2. *Asymptotic analysis* ($C_1 = 0$)

In this analysis the depletion of reactant is of greater consequence than the potential drop over the electrode which from Equation 10 is equal to ν^2/s and hence is small for large values of s/ν^2. The asymptotic solution is obtained by first combining Equations 8 and 10 which gives:

$$\frac{\mathrm{d}^2C}{\mathrm{d}y^2} = sC \exp \alpha \left(\frac{\nu^2}{s}(C-1) + \phi_0\right) \tag{18}$$

and on first integration gives:

$$\frac{1}{2}\left[\left(\frac{\mathrm{d}C}{\mathrm{d}y}\right)_{y=0}\right]^2 = \left\{ s \exp\left[\alpha\left(\phi_0 - \frac{\nu^2}{s}\right)\right] \frac{\exp\left(\frac{\alpha\nu^2}{s}C\right)}{\beta\frac{\nu^2}{s}} \left(C - \frac{s}{\alpha\nu^2}\right)\right\}_0^1 \tag{19}$$

From Equation 4 the boundary condition at $y = 0$ in dimensionless form becomes:

$$\frac{\mathrm{d}C}{\mathrm{d}y} = -sI \tag{20}$$

and hence Equation 19 becomes:

$$I = \left\{\frac{2}{s}\exp\left[\alpha\left(\phi_0 - \frac{\nu^2}{s}\right)\right]\left[\exp\left(\frac{\alpha\nu^2}{s}\right)\left[\frac{s}{\alpha\nu^2} - \left(\frac{s}{\alpha\nu^2}\right)^2\right] + \left(\frac{s}{\alpha\nu^2}\right)^2\right]\right\}^{0.5} \tag{21}$$

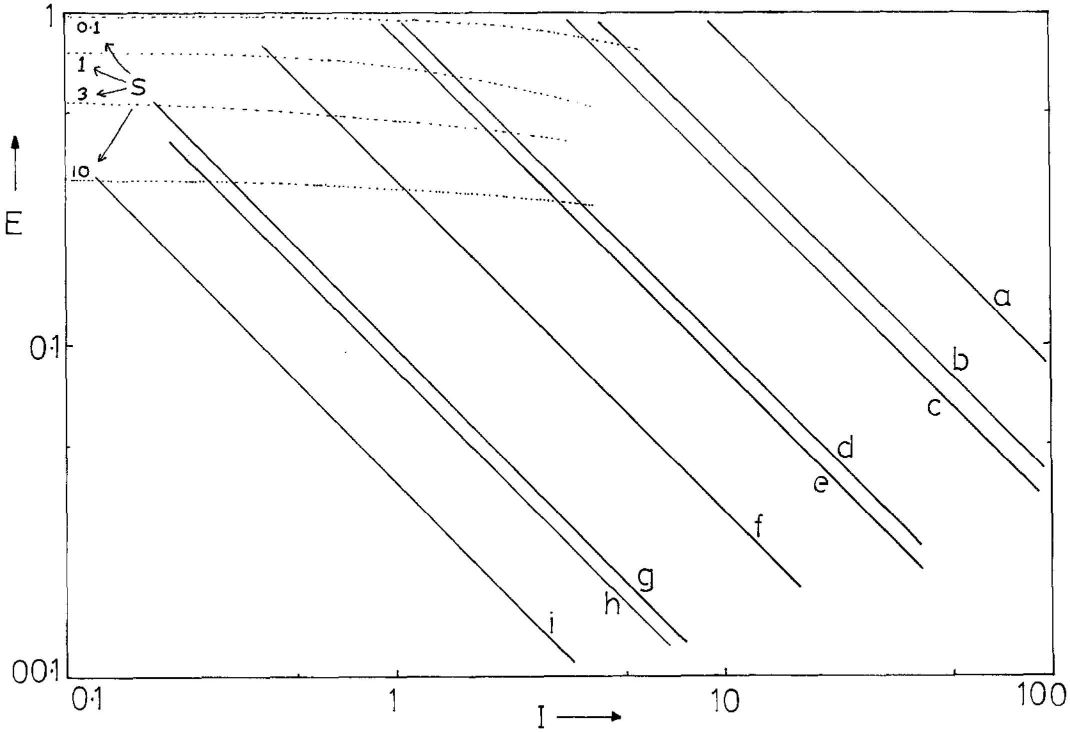

Fig. 3. The variation of effectiveness with total current I for the asymptotic solution $C_1 = 0$. ($\alpha = 0.5$).

s	0.001	0.01	0.1	1.0	10	0.1	1.0	10	1.0	10	1
ν^2	1.0	1.0	1.0	1.0	1.0	0.1	0.1	0.1	10	10	100
Curve	a	b	c	e	g	a	d	g	f	h	i

.... first order reaction at constant potential (values of s indicated).

which describes the polarization characteristics of the porous electrode. The effectiveness is again given by Equation 15. Typical effectiveness data is presented in Fig. 3 as a function of I for various values of ν^2 and s ($\alpha = 1/2$).

Unlike the former asymptotic case, data in all cases is represented by a particular straight line depending on ν^2 and s. At fixed values of ν^2, effectiveness decreases with increasing values of s as expected. At high values of I data from both asymptotic analyses agree at corresponding ν^2 and s.

At low values of ϕ_0 the variation of potential for reactions with low diffusivity or low reactant concentration (say in gas diffusion electrodes) will be of the order of a few mV and hence the system approaches a constant electrode potential and the solution of Equation 18 can be written in terms of the well known expression for effectiveness of a first order chemical reaction in a porous catalyst, i.e.

$$E = \frac{\tanh \Phi}{\Phi} \tag{22}$$

where for an electro-chemical reaction of the Tafel type the Thiele modulus $\Phi = [s \exp(\alpha\phi_0)]^{1/2}$. This expression can assist in defining the range of usefulness of this asymptotic solution as it stipulates a maximum value of E which can be achieved for a particular value of s. From this linear analysis the polarization equation is given by:

$$I = \frac{\tanh(\Phi_0)}{\Phi_0} \tag{23}$$

from which we can compute the effectiveness as a function of the total current density I. This data is

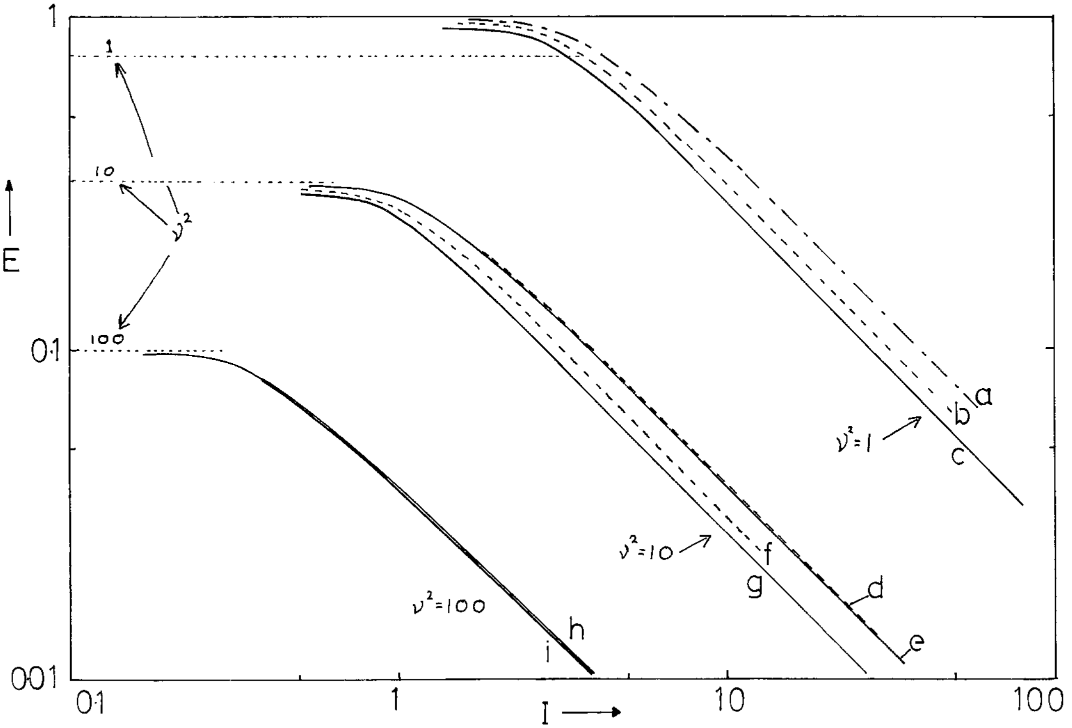

Fig. 4. Effectiveness data for a second order reaction asymptotic solution ϕ_0 comparison with first and zero order reactions.

$\nu^2 = 1, s = 0.1$ Curve a: zero order, Curve b: 1st order, Curve c: 2nd order
$\nu^2 = 10, s = 0.1$ Curve d: zero order and 1st order, Curve e: 2nd order
$\nu^2 = 10, s = 1$ Curve f: 1st order, Curve g: 2nd order.

Curve h: $\nu^2 = 100$, $s = 0.01$ 2nd order; Curve i: $\nu^2 = 100, s = 1$, 2nd order dotted lines = linear polarization constant concentration 'asymptote'.

presented in Fig. 3 (dotted lines) where, as expected, higher values of s produce lower effectiveness which decreases only slightly with I in comparison to the asymptotic solution.

4.3. *Second order reactions*

In general the concentration dependency of a reaction is determined experimentally and as such can be of order greater than or less than unity. We have previously considered a 1st order reaction and indirectly a zero order reaction ($s \to 0$) and it is therefore useful to extend the analysis to a second order reaction. The theoretical development of the asymptotic expressions to predict the polarization behaviour is similar to the first order case and as such is presented in the Appendix. Typical effectiveness data predicted by the analysis is presented in Fig. 4 (asymptotic solution $\Phi_1 = 0$) and in Fig. 5 (asymptotic solution $C_1 = 0$) as a function of the total current I. Overall the trend in the data is similar to the first order case except that because of the higher order of reaction the depletion of reactant is more significant. Hence for the same values of ν^2 and s, E values are lower for the 2nd order reaction, as seen in Fig. 4. The influence of reaction order at fixed ν^2 becomes less significant as s decreases (see Fig. 5) so much so that when $s = 0.01$ ($\nu^2 = 1$) there is little difference in effectiveness for second, first or zero order reactions. The behaviour of the 1st and 2nd order (and zero order) reactions at high values of ν^2 and very low values of s is identical.

In the asymptotic solution for $\phi_1 = 0$ and at low values of I or ϕ_0 when the kinetic behaviour can be represented by a linear approximation of the Butler–Volmer equation, the data should approach the

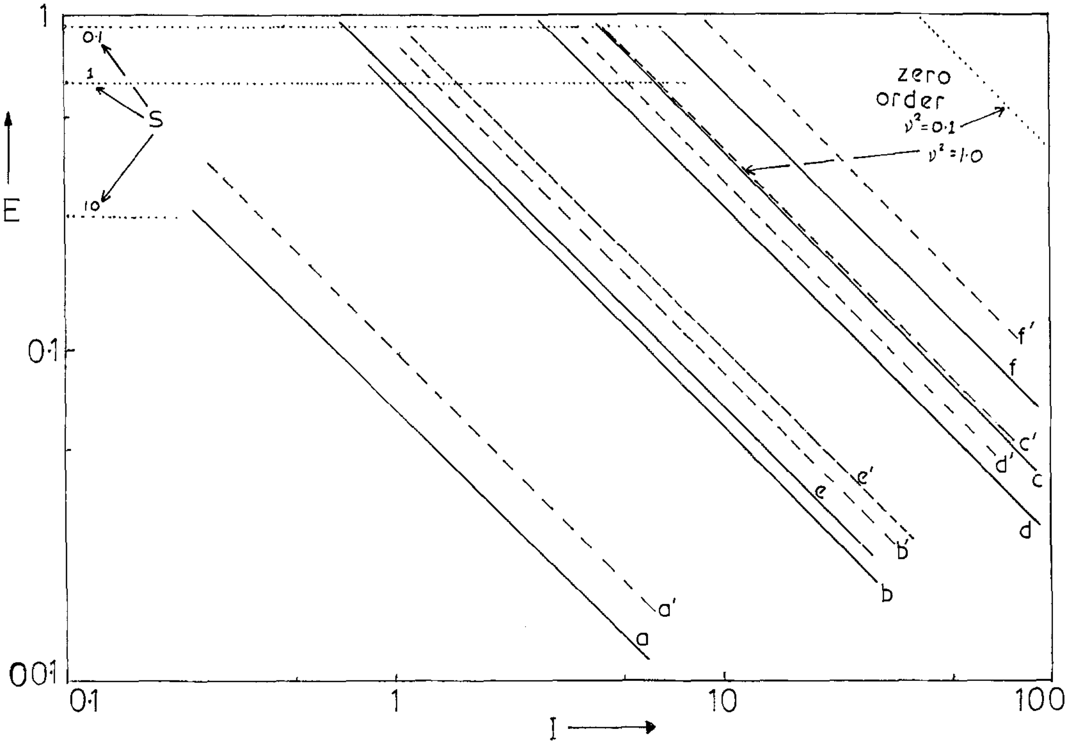

Fig. 5. Effectiveness data for a second order reaction asymptotic solution $C_1 = 0$.
Curve a: $\nu^2 = 1, s = 10$; Curve a': 1st order reaction (dashed lines)
Curve b: $\nu^2 = 1, s = 1$; Curve b': 1st order reaction (dashed lines)
Curve c: $\nu^2 = 1, s = 0.01$; Curve c': 1st order reaction (dashed lines)
Curve d: $\nu^2 = 1, s = 0.1$; Curve d': 1st order reaction (dashed lines)
Curve e: $\nu^2 = 1, s = 1$; Curve e': 1st order reaction (dashed lines)
Curve f: $\nu^2 = 1, s = 0.1$; Curve f': 1st order reaction (dashed lines)
Dotted lines = constant potential, 2nd order reaction 'asymptote'

limiting values given by this analysis for the 1st order reaction. This again allows us to determine limits of applicability of the asymptotic solution.

In the alternative asymptotic solution (when $C_1 = 0$), the limiting case of a constant potential electrode operating at low potentials, i.e. a second order reaction has been solved for the analogous treatment in porous catalysts [7]. The results of this limiting case which define a useful range of applicability of the asymptotic solution are indicated in Fig. 5, (dotted lines).

5. Alternative electrode kinetics – Butler–Volmer approximation

Classical electro-chemical kinetic theory treats the general electrode reaction as reversible and leads to the Butler–Volmer equation which for a first order reaction can be written as:

$$i = i_0 \left\{ \frac{c}{c_0} \exp(\alpha\phi) - \frac{c_R}{c_{R0}} \exp\left[-(1-\alpha)\phi\right] \right\} \tag{24}$$

where c_R and c_{R0} are the concentrations of product species in the bulk and at the electrode surface.

The approximation of this equation considered here treats the reaction as irreversible, i.e. dependent only on the reactant concentration while maintaining the general characteristics of the Butler–Volmer equation by including the second exponential term in Equation 24. The equation then becomes:

$$i = i_0 \frac{c}{c_0} \{\exp(\alpha\phi) - \exp[-(1-\alpha)\phi]\}. \tag{25}$$

Comparing Equations 24 and 25: at low potentials the surface concentrations do not differ much from their bulk solution values so both equations reduce to the same form and at high potentials the second exponential term in both equations approach zero so again the equations are identical.

The asymptotic solutions to Equations 2 and 3 using kinetics described by Equation 25 are derived in similar ways to those for Tafel kinetics and result in the following polarization equations:

For $\phi_1 = 0$

$$I = \left(\frac{2}{\nu^2}\left\{\frac{\exp(\alpha\phi_0)}{\alpha}\left(1 - \frac{s}{\nu^2\alpha}\right) + \frac{\exp[-(1-\alpha)\phi_0]}{(1-\alpha)}\left(1 - \frac{s}{\nu^2(1-\alpha)}\right) - \frac{1}{\alpha}\left[1 - \frac{s}{\nu^2}\left(\phi_0 + \frac{1}{\alpha}\right)\right] - \frac{1}{(1-\alpha)}\left[1 - \frac{s}{\nu^2}\left(\frac{1}{(1-\alpha)} - \phi_0\right)\right]\right\}\right)^{0.5} \tag{26}$$

For $C_1 = 0$

$$I = \left(\frac{2}{s}\left\{\frac{s\exp(\alpha\phi_0)}{\alpha\nu^2}\left(1 - \frac{s}{\alpha\nu^2}\right) + \frac{s\exp[-(1-\alpha)\phi_0]}{(1-\alpha)\nu^2}\left(1 + \frac{s}{\nu^2(1-\alpha)}\right) + \frac{s^2\exp[\alpha(\phi_0 - \nu^2/s)]}{(\alpha\nu^2)^2} - \frac{s^2\exp[(1-\alpha)(\nu^2/s - \phi_0)]}{(1-\alpha)^2(\nu^2)^2}\right\}\right)^{0.5}. \tag{27}$$

Typical effectiveness values predicted from these equations are presented in Fig. 6 ($\phi_1 = 0$) and Fig. 7 ($C_1 = 0$) as a function of I and are compared to the corresponding predictions from the Tafel analysis. The general behaviour of the data is similar to the Tafel analysis with respect to the effect of the parameters ν^2, s and I.

Considering Fig. 6, at high I the data for both kinetic expressions converge and at low I data approaches limiting values. At large values of ν^2 these values are given by the linear approximation to the Butler–Volmer equation. The important difference between the Butler–Volmer and Tafel analysis is apparent in the intermediate regions of I where both the asymptotic and linear approximations tend to overpredict effectiveness. Here values as predicted by the Butler–Volmer analysis are lower and are in good agreement with data for exact solutions (dotted lines $s \to 0$) when $\nu^2 \geqslant 3$. Even at lower ν^2 reason-

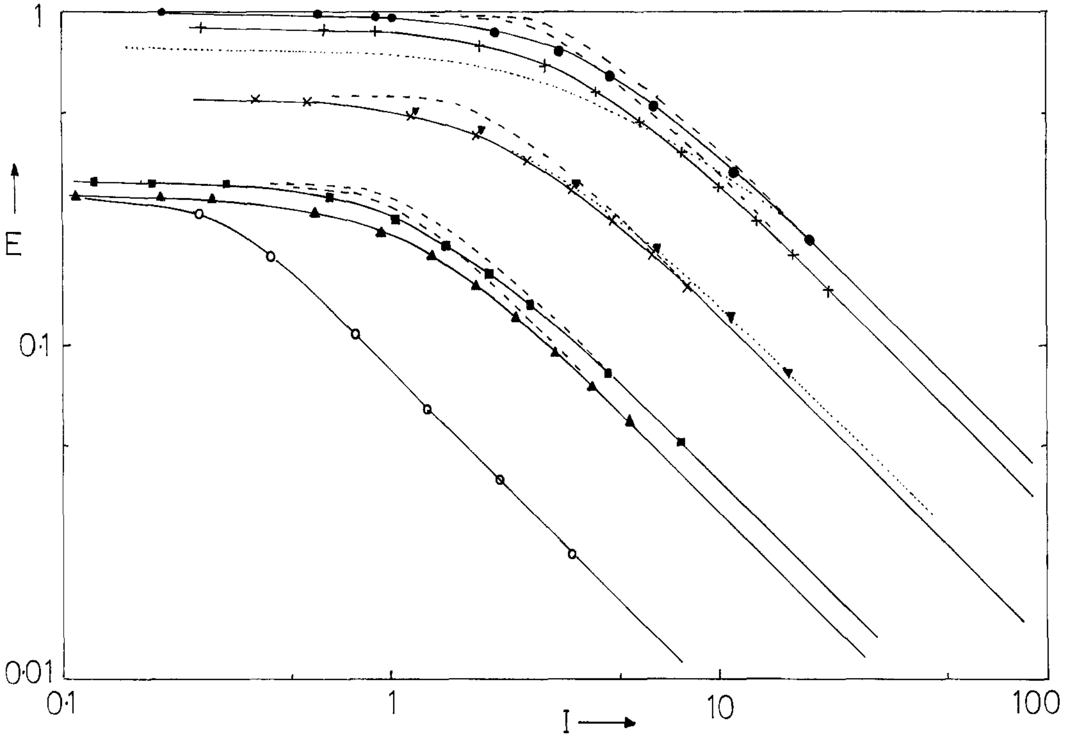

Fig. 6. Comparison of effectiveness for the Butler–Volmer approximation and the Tafel equation. Asymptotic solutions $\phi_1 = 0$.

•: $\nu^2 = 1, s = 0.01$ and 0.001; +: $\nu^2 = 1, s = 0.1$; ×: $\nu^2 = 3, s = 0.1$, ▼: $\nu^2 = 3, s = 0.001$, ■: $\nu^2 = 10$, $s = 0.1$; ▲: $\nu^2 = 10, s = 1$; ○: $\nu^2 = 10, s = 10$.

Solid lines are Butler–Volmer data. Dashed lines are corresponding Tafel data. Dotted lines exact solutions when $s \to 0$ (zero order reaction).

able agreement between the Butler–Volmer approximation and exact solutions is achieved. Therefore the Butler–Volmer approximation gives a better estimate of effectiveness than the Tafel analysis especially when reaction kinetic behaviour diverges from Tafel behaviour. Comparing the effectiveness data in Fig. 7 ($C_1 = 0$) it can be seen that at relatively low values of I the Butler–Volmer curves diverge from the Tafel lines and predict lower effectiveness values.

6. Polarization behaviour

Typical polarization curves for the semi-infinite porous electrode as predicted by the asymptotic solutions are presented in Figs. 8 and 9 for $\alpha = 0.5$. Data for the Tafel analysis, Butler–Volmer approximation and linear polarization are presented. As both the resistance parameter ν^2 and diffusion parameter s increase the potential and current distributions become increasingly non-uniform at constant total current density I. At high potentials all the data exhibit the characteristic linear relationship between ϕ and $\ln I$, the slope of which is twice that for a planar electrode. The polarization curve for Tafel kinetics of a porous electrode with a uniform reaction distribution is drawn in Figs. 8 and 9 and is identical to the polarization curve of a planar electrode with the same area.

Comparing the Tafel behaviour and Butler–Volmer behaviour in Fig. 8, at high potentials the polarization behaviour is identical while at lower potentials the polarization data differ significantly, especially at lower ν^2 and high s values, with the Butler–Volmer currents at constant ϕ_0 the lower of the two. At low ϕ_0 the Butler–Volmer behaviour is comparable to the linear polarization constant concentration situation. A similar polarization behaviour is observed with the other asymptotic solution in Fig. 9. By

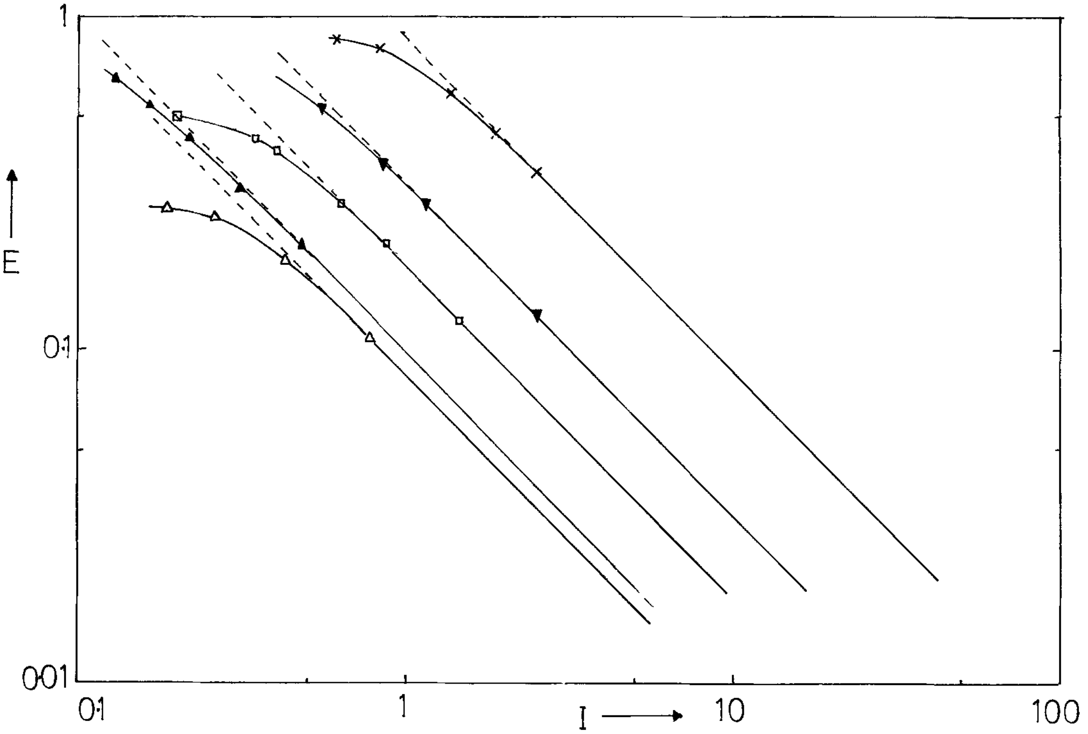

Fig. 7. Comparison of effectiveness for the Butler–Volmer approximation and the Tafel equation, asymptotic solution $C_1 = 0$.

×: $\nu^2 = 1, s = 1$; ▼: $\nu^2 = 1, s = 3$, □: $\nu^2 = 3, s = 5$; ▲: $\nu^2 = 1, s = 10$; △: $\nu^2 = 10, s = 10$.

Solid lines are Butler–Volmer data, dashed lines are corresponding Tafel data.

combining the polarization characteristics of porous electrodes with effectiveness data it is a simple task to assess the effect of electrode potential on effectiveness.

7. Generalization of the analysis

7.1. *Implication to gas diffusion electrodes*

In operation gas diffusion electrodes and similar devices as well as being subjected to potential and concentration distributions in the electrode/electrolyte structure are also influenced by the rate of gas transport (through a porous structure) to the gas/liquid interface. Under these conditions the global rate of reaction is given by an expression describing external mass transfer:

$$i = nFk_{\mathrm{m}}[c_{\mathrm{b}} - c_0] \tag{28}$$

where k_{m} is the external gas phase mass transfer coefficient based on the cross-sectional area of the electrode. The reaction rate is also given by:

$$i = Ec_0\left(\frac{i_0}{c_0}\right)\exp(\alpha\phi_0). \tag{29}$$

Combining both expressions to eliminate c_0 gives:

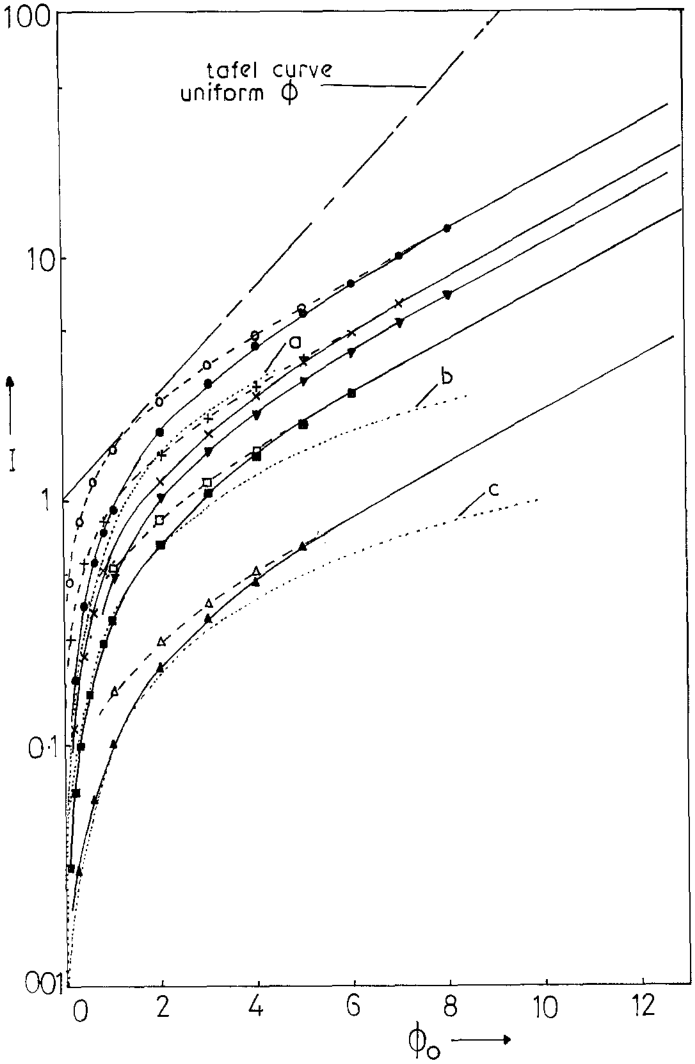

Fig. 8. Typical polarization curves for the asymptotic solution $\phi_1 = 0$ for Tafel kinetics and the Butler–Volmer approximation.

Butler–Volmer curves (solid lines) ●: $\nu^2 = 1, s = 0.1$; ×: $\nu^2 = 3, s = 0.1$; ▼: $\nu^2 = 3, s = 0.5$; ■: $\nu^2 = 10, s = 0.1$; ▲: $\nu^2 = 100, s = 1$. Tafel curves (dashed lines) ○: $\nu^2 = 1, s = 0.1$; +: $\nu^2 = 3$, $s = 0.1$; □: $\nu^2 = 10, s = 0.1$; △: $\nu^2 = 100$, $s = 1$.

Dotted lines – linear polarization constant concentration, curve a: $\nu^2 = 1$; curve b: $\nu^2 = 10$; curve c: $\nu^2 = 100$.

$$i = \frac{c_b}{\dfrac{1}{nFK_m} \quad \dfrac{1}{E\left(\dfrac{i_0}{c_0}\right)\exp(\alpha\phi_0)}} \tag{30}$$

a general expression for determining the overall current density the electrode can support. Situations may arise where this equation reduces to one of two limiting forms, for example in partially immersed gas diffusion electrodes [8] mass transport in the gas phase may tend to control the reaction rate.

7.2. *Influence of mass transfer in the liquid phase*

In porous electrodes operating with sparingly soluble reactants, such as lead–lead sulphate negative electrodes, the active species dissolve and are transported by diffusion to an electro-chemically active site. An effective diffusion path can be assumed for each species which represents a typical distance between a storage site and an active site where reaction takes place. The material is transported by diffusion over this distance and hence we can define a mass transfer coefficient for this step which controls the flux of active material to the site. This mass flux is defined in a similar manner to Equation 28.

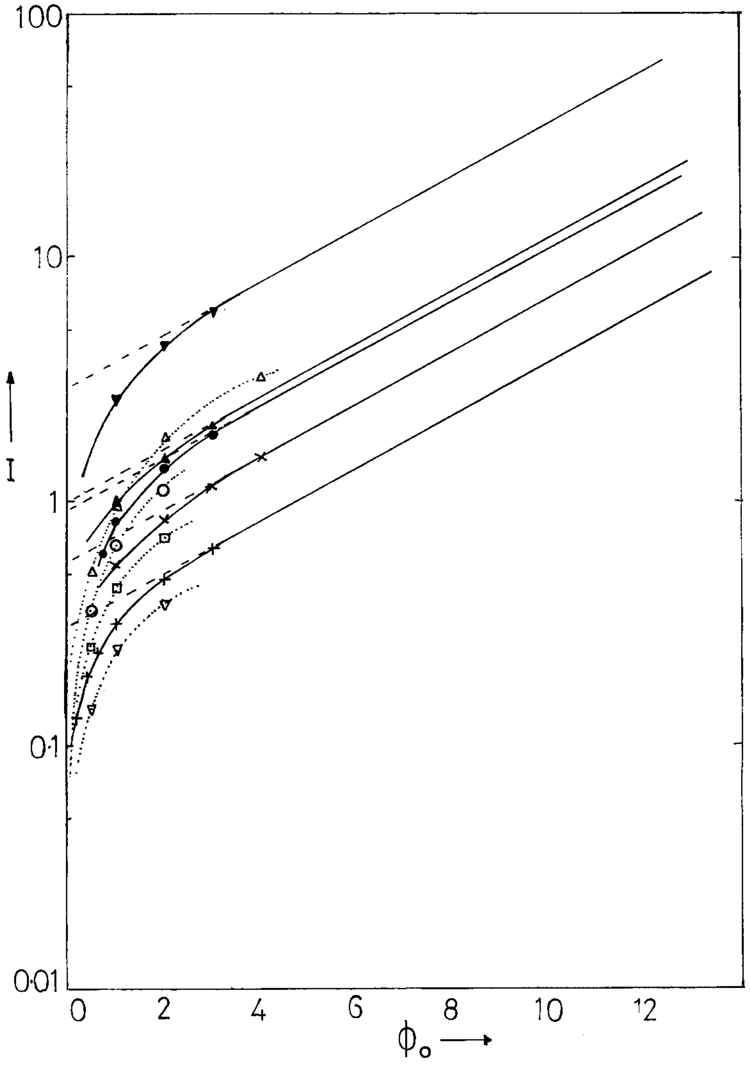

Fig. 9. Typical polarization curves for the asymptotic solution $C_1 = 0$ for Tafel kinetics and the Butler–Volmer approximation.

Butler–Volmer curves (solid lines) ▼: $\nu^2 = 0.1, s = 0.1$; ▲: $\nu^2 = 0.1, s = 1$; ●: $\nu^2 = 1, s = 1$; ×: $\nu^2 = 1, s = 3$; +: $\nu^2 = 1, s = 10$.

Dashed lines are corresponding Tafel data. Dotted lines are for linear analysis using Equation 23. △: $s = 0.1$; ○: $s = 1$; □: $s = 3$; ▽: $s = 10$.

This represents a rather special case [9] as transport of species to and from the bulk solution is not considered and hence no concentration distribution essentially exists within the bulk electrolyte. This problem has been treated by a previous analysis [4] for relatively high overpotentials. A characteristic of electrode performance observed from this analysis is that at low values of $k_m c_b$ a mass transport limitation may occur in batteries which limits obtainable power densities.

A more general treatment of porous electrode behaviour would incorporate limitations in mass transport of reactants and products from bulk electrolyte to electrode surface (as described by Equation 28) with a reaction kinetic equation of the general Butler–Volmer type and then subsequently solving the conservation equations. In this way observed limiting current behaviour, for example with porous Pt electrocatalysts during hydrogen oxidation [10] may be described.

8. Conclusions

By applying relatively simple approximations to the solution of the conservation equations describing porous electrode behaviour the influence of the various system parameters on performance can be quantitatively assessed easily and with reasonable accuracy. The approximations place no reliance on numerical computer techniques which generate data accurately but tend to obscure the physics of the system. It has been shown that the performance of a porous electrode under activation control is essentially governed by two dimensionless parameters ν^2 and s, both of which impose maximum values of effectiveness. The electrochemical Thiele modulus (diffusion parameters) s, which governs reactant concentration distribution in the electrode, specifies by way of Equation 22 the maximum value of effectiveness for a uniform electrode potential distribution. When the electrode potential distribution becomes increasingly non-uniform (i.e. when ν^2 increases) effectiveness decreases below this maximum due to limitations in electrolyte conductivity.

The assumption that the porous solid phase is isopotential may not always be reasonable and hence current flow through this structure should be considered in a more general analysis. If the electrolyte resistivity is at least equal to or greater than that of the solid then the electrode should be more effective than in the isopotential situation as current can penetrate further into the structure and hence reaction rates are more uniform. This situation will be the subject of a more general analysis in relation to the performance of fluidized bed electrodes.

Appendix

Asymptotic solutions for a second order reaction

The equations describing the potential and concentration variation in porous electrodes are:

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}y^2} = C^2\nu^2 \exp(\alpha\phi) \tag{A1}$$

$$\frac{\mathrm{d}^2C}{\mathrm{d}y^2} = C^2 s \exp(\alpha\phi) \tag{A2}$$

$$\phi - \phi_0 = \frac{\nu^2}{s}(C-1). \tag{A3}$$

The asymptotic solution when $\phi_1 = 0$ is obtained by combining Equations A1 and A3 to give:

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}y^2} = \nu^2\left[1 + \frac{s}{\nu^2}(\phi-\phi_0)\right]^2 \exp(\alpha\phi) \tag{A4}$$

and on first integration yields:

$$\begin{aligned}\frac{1}{2}\left(\frac{\mathrm{d}\phi}{\mathrm{d}y}\right)^2 \int_0^{-\nu^2 I} &= \nu^2 \int_0^{\phi_0}\left[1+\frac{s}{\nu^2}(\phi-\phi_0)\right]^2 \exp(\alpha\phi)\,\mathrm{d}\phi \\ &= \left\{\frac{\nu^2\exp(\alpha\phi)}{\alpha}\left[\left(1-\frac{s}{\nu^2}\phi_0\right)^2 + 2\left(1-\frac{s}{\nu^2}\phi_0\right)\frac{s}{\nu^2}\left(\phi-\frac{1}{\alpha}\right)\right.\right. \\ &\quad \left.\left. + \left(\frac{s}{\nu^2}\right)^2\left(\phi^2 - \frac{2\phi}{\alpha} + \frac{2}{\alpha^2}\right)\right]\right\}_0^{\phi_0}\end{aligned} \tag{A5}$$

which then gives an expression for the polarization characteristics as:

$$\begin{aligned}I^2 = \frac{2}{\nu^2}\frac{\exp(\alpha\phi_0)}{\alpha}&\left[\left(1-\frac{s}{\nu^2}\phi_0\right)^2 + 2\left(1-\frac{s}{\nu^2}\phi_0\right)\frac{s}{\nu^2}\left(\phi-\frac{1}{\alpha}\right)\right. \\ &\left. + \left(\frac{s}{\nu^2}\right)^2\left(\phi_0^2 - \frac{2\phi_0}{\alpha} + \frac{2}{\alpha^2}\right)\right] - \frac{2}{\nu^2\alpha}\left[\left(1-\frac{s}{\nu^2}\phi_0\right)^2 - \frac{2}{\alpha}\left(1-\frac{s}{\nu^2}\phi_0\right)\frac{s}{\nu^2} + \left(\frac{s^2}{\nu^2}\right)\frac{2}{\alpha^2}\right].\end{aligned} \tag{A6}$$

The effectiveness is given by:

$$E = \frac{I}{\exp(\alpha\phi_0)}. \tag{A7}$$

The asymptotic solution when $C_1 \to 0$ is obtained in a similar manner to above. Combining Equations A2 and A3 gives:

$$\frac{\mathrm{d}^2C}{\mathrm{d}y^2} = s\exp[\alpha(\phi_0 - \nu^2/s)]\,C^2\exp(c\alpha\nu^2/s) \tag{A8}$$

which on integration gives:

$$\frac{1}{2}(s^2I^2) = \left[s\exp\left[\alpha\left(\phi_0 - \frac{\nu^2}{s}\right)\right] \frac{\exp\left(\frac{\alpha\nu^2}{s}\right)C}{\alpha\frac{\nu^2}{s}} \left(C^2 - \frac{2Cs}{\alpha\nu^2} + \frac{2s^2}{(\alpha\nu^2)^2}\right)\right]_0^1 \tag{A9}$$

which gives the polarization characteristics as:

$$I = \left\{ \frac{2\exp(\alpha\phi_0)}{\alpha\nu^2}\left[\left(1 - \frac{2}{\alpha} + \frac{2}{\alpha^2}\right) - \frac{2\exp(-\alpha\nu^2/s)}{\alpha^2}\right]\right\}^{0.5} \tag{A10}$$

and the effectiveness is again given by Equation A7.

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