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Effect of radial diffusion on the polarization at porous flow-through electrodes

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The effect of radial diffusion on the polarization of porous flow-through electrodes has been investigated with the aid of a mathematical model. The proposed model takes into consideration the rates of mass transfer in the axial direction by convection and in the radial direction by diffusion as well as charge transport in the pore electrolyte and electron transfer kinetics at the electrode–electrolyte interface. Normalization of the variables gave rise to dimensionless groups pertinent to the kinetic, ohmic and radial diffusion effects. These are respectively, I the reversibility index, Δ the parameter of ohmic effect and ψ the parameter of radial diffusion. The latter ($\psi = 2\phi/Sh$) is the ratio of two other dimensionless groups. With this formulation, larger values of ψ correspond to more predominant control of the electrode behaviour by radial diffusion. The same is also true for the parameter of ohmic effect Δ. Solutions have been obtained for two limiting cases: negligible and significant potential drop in the pore electrolyte. In both cases, equations have been derived which give the quantitative (highly non-linear) effect of ψ on the current–polarization relations. In the case of a significant ohmic potential drop in the pore electrolyte, it was found that the controlling parameter is the product $\Delta\psi$. The two variables seem to give a synergistic effect since, at large Δ values a certain change in ψ has a more pronounced effect on the polarization than the corresponding change at lower Δ values. Qualitative and quantitative tests of some aspects of the model are reported using the electrochemical reduction of copper ions from acid copper sulphate solutions at a packed bed of copper particles. Satisfactory agreement was obtained.

Nomenclature

b	RT/F (V) = 25.6 mV at 25° C
R_b	Feed reactant concentration, (mol cm^{-3})
R_s	Reactant concentration at the electrode surface
$R_m(x)$	Reactant concentration at the median of the pore
$R_w(x)$	Reactant concentrations at the wall of the pore
d	Equivalent pore diameter (cm), Equation 1
D	Diffusion coefficient of reactant (cm^2 s^{-1})
$i(x)$	Normalized current density at distance X
i_L	Maximum obtainable limiting current, (A cm^{-2}) Equation 10a
i	Total normalized current density resulting from the electrode (see Equations 15, 20 and 21)
i_0	Exchange current density based on feed concentration, R_b
I	Normalized exchange current density, i_0SL/i_L
k	Mass transfer coefficient (cm s^{-1})
L	Electrode thickness (cm)
Pe	Peclet number, $Pe = V/SD$
q	Tortuosity factor, dimensionless
R	Equivalent pore radius (cm)
Re	Reynolds number $Re = V/S\mu$
S	Specific surface area of the porous medium (cm^{-1})
Sh	Sherwood number Kd/D
V	Superficial flow speed (cm s^{-1})
x	Distance, see Fig. 1
α	Transfer coefficient

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$\eta(x)$	Polarization at distance x
θ	Porosity
ϕ	Dimensionless group, see Equation 7b
μ	Kinematic viscosity (cm^2 s^{-1})
Δ	Parameter of ohmic effect, Equation 11
ψ	Parameter of radial diffusion, Equation 7b
ρ_{free}	Bulk electrolyte resistivity (ohm cm)
ρ_{eff}	Effective electrolyte resistivity, $\rho_{\text{eff}} = \rho_{\text{free}}q/\theta$ (ohm cm)

1. Introduction

Porous flow-through electrodes are currently attracting considerable attention. They have been suggested for use in a variety of applications, e.g., in removing cyanide and heavy metal ions from industrial waste water streams and in electrically rechargeable redox batteries for load-levelling applications. Adequate listing of relevant references are available elsewhere [1, 2]. Such electrodes consist of porous beds of highly interconnected pores, the internal surfaces of which have a complicated geometry. The behaviour of these electrodes depends critically on the mechanism and rate of both mass transfer through the electrolyte-filled pores and electron transfer across the electrolyte–electrode interface. An understanding of the behaviour of this electrode system requires a knowledge of the distribution of current, concentration and potential within the porous electrode. This, in turn, requires simultaneous solution of the differential equations of three-dimensional mass and charge transport through the pore electrolyte. The electron transfer reaction takes place at the pore surface; its rate depends on the local reactant concentration (at the pore surface) which in turn depends on the rate of diffusion in the radial direction of the pore. The equations of this type become rather cumbersome and invariably require numerical solutions. There have been some simplifying approaches which led to calculations of the distribution of current, concentration and potential within the electrode. Some authors have presented one-dimensional models [3–8] where variations in concentration, current and potential were calculated in the axial direction, assuming the corresponding variations in the radial direction to be negligible. Alternatively, several other authors [1, 2, 9–12] have presented modified one-dimensional models where basically a one-dimensional model has been postulated and the mass transfer in the radial direction accounted for by adding an extra transport equation in the radial direction.

In a previous report [2], we have defined the conditions under which concentration variations in the radial direction become negligible and truly one-dimensional transport prevails. The criterion for this condition is

$$I\psi \exp(\alpha\eta) \ll 1$$

where the variables are dimensionless (see below). In all the above models, potential variations were calculated only in the axial direction.

Slow radial diffusion has two related effects on the behaviour of porous flow-through electrodes. It causes the reactant concentration at the pore wall, $R_w(x)$, to be less than that at the centre of the pore, $R_m(x)$. The difference between $R_m(x)$ and $R_w(x)$ determines the extent of radial diffusion control and the magnitude of concentration polarization. Furthermore, it may limit the conversion (or collection) efficiency of the electrode. The latter is defined as the relative decrease in reactant concentration when the electrolyte is passed once through the electrode under conditions of limiting current, i.e., when $R_w(x)$ is kept at zero. This effect had been treated in detail before [2].

The purpose of this paper is to evaluate the effect of radial diffusion on the current-polarization relations of porous flow-through electrodes. Specifically to develop and solve the equations which show the effects of the structural, transport and kinetic parameters of the electrode-electrolyte system on the current-polarization relations. This is given below in the form of analytical solutions, which extend over the entire range of currents. It is noteworthy that previous related models were solved numerically and the results confined to the limiting current. Analytical solutions for this system were obtained before only for fast (reversible) reaction kinetics [7, 9, 11] where activation polarization was assumed negligible.

2. Model, equations and solutions

The porous electrode is assumed to be a uniform highly interconnected porous matrix of good electrical conductivity. The specific surface area of this matrix is S in units of cm^{-1} (cm^2/cm^3). The equivalent pore diameter of this matrix is related to the porosity and the specific surface area by [2, 13]:

$$d = 4\theta/S. \tag{1}$$

The electrolyte concentration is assumed to be high so that mass transfer of the electroactive species by ionic migration is negligible.

A porous flow-through electrode can operate in three different modes [1], counter, parallel and perpendicular flow where current and electrolyte flow directions are respectively, opposite, similar and perpendicular. We treat below the case of counter flow. The corresponding treatment for parallel flow is quite similar; the main difference is in the boundary conditions [8]. The case of perpendicular flow is considerably more complex.

Let us assume a simple one-electron transfer reaction,

$$R \rightarrow P + e. \tag{2}$$

The rate of this reaction is given by the Tafel equation modified by the concentration effect. Thus

$$i = i_0(R_s/R_b)\exp(\alpha\eta/b). \tag{3}$$

Where i is the current per cm^2 of true surface area, i_0 is the exchange current density based on bulk reactant concentration R_b; R_s is the reactant concentration at the electrode surface, α is the transfer coefficient, η is the polarization and $b = RT/F$.

Performing a mass balance on a volume element, dx, of unit geometrical cross-sectional area, Fig. 1, one obtains:

$$di(x) = -nFVdR_m(x) \tag{4}$$

Axial diffusion is assumed negligible with respect to axial convection [7]. This current increment $di(x)$ is supported by radial diffusion, the rate of which per cm^2 of pore surface area is

$$\text{rate of radial diffusion} = k[R_m(x) - R_w(x)] \tag{5}$$

where k is the mass transfer coefficient in the radial direction in cm s^{-1} and is related to the Sherwood number (Sh) by

$$k = Sh \times D/d. \tag{6}$$

The amount of current generated in this volume element is given by:

$$di(x) = nFkS\,[R_m(x) - R_w(x)]\,dx. \tag{7}$$

The rate of electron transfer at the pore surface in this volume element is given by

$$di(x) = i_0S(R_w(x)/R_b)\exp(\alpha\eta(x)/b)\,dx. \tag{8}$$

The flow of current generates a polarization gradient in the pore electrolyte, given by Ohm's law

$$i(x) = (1/\rho_{\text{eff}})d\eta(x)/dx. \tag{9}$$

The variables in the above equations are to be normalized, thus: $\bar{x} = X/L$

$$\bar{R}_w(\bar{x}) = R_w(x)/R_b;\ \bar{R}_m(\bar{x}) = R_m(x)/R_b;$$
$$-\bar{\eta}(\bar{x}) = \eta(x)/b.$$

The currents are to be normalized relative to the maximum obtainable limiting current given by

$$i_L = nFVR_b. \tag{10a}$$

This is the limiting current obtainable when all the reactant is consumed in one pass, i.e., at a conversion efficiency of unity. Thus

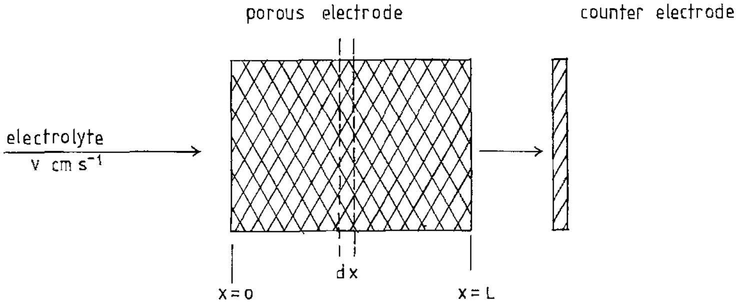

Fig. 1. Illustration of a porous flow-through electrode with counter electrolyte and current flow.

$$I = i_0SL/i_L \tag{10b}$$

$$\bar{i}(x) = i(x)/i_L. \tag{10c}$$

The normalized exchange current density I is frequently called the reversibility index since it relates the effective exchange current density of the electrode i_0SL to the limiting current (see Equation 10a). If $I \gg 1$, the system follows reversible electrode kinetics (7).

Substituting these dimensionless variables in Equations 4, 7–9 and dropping the overbars for convenience, it follows that:

$$\mathrm{d}i(x) = -\,\mathrm{d}R_m(x) \tag{4a}$$

$$\mathrm{d}i(x) = (kSL/V)\,[R_m(x) - R_w(x)]\,\mathrm{d}x \tag{7a}$$

$$\mathrm{d}i(x) = IR_w(x)\exp(\alpha\eta(x))\mathrm{d}x \tag{8a}$$

$$i(x) = (1/\Delta)\mathrm{d}\eta(x)/\mathrm{d}x. \tag{9a}$$

The normalization of Equation 9 results in an important parameter

$$\Delta = i_L L \rho_{\mathrm{eff}}/b. \tag{11}$$

The parameter Δ is the index of ohmic effect [5, 7] which is the maximum possible potential drop in the pore electrolyte in units of b, i.e. it is the difference between the potentials at the entrance and exit faces of the electrode if all the reaction occurs in an infinitesimal region at the entrance face and the generated current travels through the entire thickness of the electrode. Its value depends on the effective resistivity of the pore electrolyte and thickness of the electrode as well as on the limiting current. The latter depends on reactant concentration and electrolyte flow rate, (Equation 10a). Thus Δ combines a number of important variables, a variation in any of which can change Δ without changing the others.

Taking $S = 4\theta/d$, $d = 2R$ and substituting in Equation 7a one gets

$$\mathrm{d}i(x) = (Sh/2\phi)\,[R_m(x) - R_w(x)]\,\mathrm{d}x \tag{7b}$$

where ϕ is a dimensionless group given by

$$\phi = VR^2/2DL\theta$$

Since ϕ and Sh are dimensionless, another dimensionless group ψ can be defined such that

$$\psi = 2\phi/Sh$$

Hence

$$\mathrm{d}i(x) = (1/\psi)\,[R_m(x) - R_w(x)]\,\mathrm{d}x \tag{7b}$$

The initial and boundary conditions are

$$\text{at } x = 0, \quad R_m(x) = 1 \tag{12a}$$

$$\eta = \eta_0 \quad \mathrm{d}\eta(x)/\mathrm{d}x = 0 \tag{12b}$$

$$\text{at } x = 1, \quad \eta = \eta(L) \tag{12c}$$

A similar system of equations has been solved numerically by Alkire *et al.* [10] for conditions of limiting current and parallel flow. In this paper exact analytical solutions are presented for the counter-flow case over the entire range of current–polarization relations. Solutions for the parallel flow case can be obtained following the same procedure.

3. Current–polarization relations

3.1. *Negligible ohmic potential drop in the pore electrolyte*

This is a limiting case which applies when there is no significant ohmic potential drop in the pore electrolyte such that the polarizations at the entrance and exit faces are about equal, i.e., $\eta_0 \simeq \eta(x) \simeq \eta(L)$. This is obtainable for small values of Δ, i.e., for electrolytes of high conductivity, low limiting currents and/or thin electrodes. Under this condition, the behaviour of the electrode is governed by Equations 4b, 7a and 8a since the polarization is independent of distance.

Equation 8a is substituted in Equation 7b, the result is combined with Equation 4a and rearranged to give:

$$-\int \frac{\mathrm{d}R_m(x)}{R_m(x)} = \frac{I\exp(\alpha\eta)}{1 + I\psi\exp(\alpha\eta)}\int \mathrm{d}x$$

In integrating the right hand side of the above equation, it is assumed that η, ϕ and Sh are constants independent of position inside the electrode. The conditions for constant η are mentioned above. A constant value for Sh is obtainable only in 'deep beds' (cf., under significance of ϕ, Sh and ψ).

Integrating the above equation using boundary condition 12a and rearranging, one gets

$$R_m(x) = \exp\left[-\frac{I\exp(\alpha\eta)}{1 + I\psi\exp(\alpha\eta)}\,x\right] \tag{13}$$

The relation between the local current and $R_m(x)$ can be obtained by integrating Equation 4a using Equation 12a. Thus

$$i(x) = 1 - R_m(x)$$
$$= 1 - \exp\left[\frac{I\exp(\alpha\eta)}{1 + I\psi\exp(\alpha\eta)}x\right] \qquad (14)$$

The total current produced by the electrode is obtained by substituting Equation 13 in Equation 14 at $x = 1$

$$i = 1 - \exp\left[-\frac{I\exp(\alpha\eta)}{1 + I\psi\exp(\alpha\eta)}\right] \qquad (15)$$

Under conditions of negligible radial diffusion control, i.e., $I\psi\exp(\alpha\eta) \ll 1$, Equation 15 reduces to an equation previously derived by Austin *et al.* [5] assuming one-dimensional transport in the axial direction.

Equation 15 shows that the current depends on ψ, I and $\alpha\eta$ rather non-linearly. Fig. 2 illustrates this dependence for $I = 0.1$ and different values of $\alpha\eta$. At the same level of polarization, an increase in ψ decreases the dimensionless current exponentially.

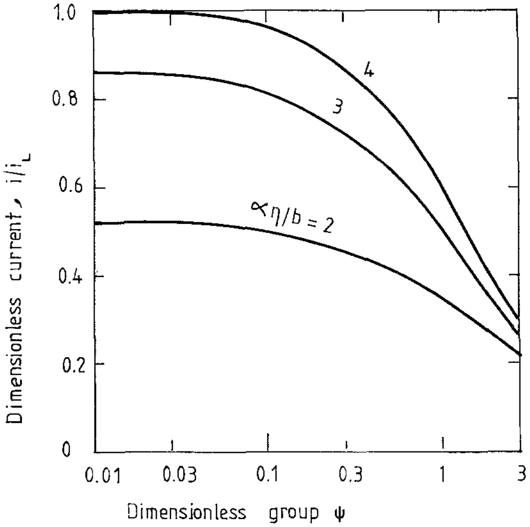

Fig. 2. Effect of the dimensionless group ψ on the dimensionless current at $I = 0.1$ on various values of $\alpha\eta/b$.

The increase in ψ can be brought about by an increase in flow speed or pore radius and/or decrease in electrode thickness, reactant diffusion coefficient or Sherwood number. It appears that the value of $\psi = 0.1$ is of particular significance regarding the extent of radial diffusion control for the conditions of Fig. 2. At $\psi > 0.1$, i/i_L decreases rapidly as ψ increases whereas at $\psi < 0.1$, i/i_L increases only slightly with further decrease in ψ becoming almost independent of ψ at $\psi < 0.03$. A value of $\psi = 0.1$ results from large values of V and R and/or small values of D, L and Sh. These are the conditions which cause significant radial diffusion control, under which $R_w(x) < R_m(x)$. We have previously [2] derived the following relation between the ratio of $R_w(x)$ to $R_m(x)$ and the relevant variables and parameters of the system:

$$\frac{R_w(x)}{R_m(x)} = \frac{1}{1 + I\psi\exp(\alpha\eta)} \qquad (16)$$

For $I = 0.1$ and $\psi = 0.1$, this ratio is 0.93, 0.83 and 0.65 for $\alpha\eta = 2$, 3 and 4, respectively. While the first value indicates no radial diffusion effects, the second and the third correspond, respectively, to slight and moderate radial diffusion control. At $\psi = 0.03$, the corresponding values of the ratio are greater being 0.98, 0.94 and 0.83 while still higher values are obtained at $\psi < 0.03$ indicating that the concentration is rather uniform across the pore. Under these conditions radial diffusion has little or no effect on the behaviour of the electrode. Therefore, the concentration varies only in the axial direction and true one-dimensional transport prevails. On the other hand, as ψ increases ($\psi > 0.1$), the concentration ratio decreases progressively causing a more pronounced decrease in the dimensionless current due to a more actute radial diffusion control, e.g., at $\psi = 0.3$ the ratio is 0.82, 0.62 and 0.38 for $\alpha\eta = 2$, 3 and 4, respectively.

Note that the above ratio depends not only on ψ, which has structural and mass transport significance, but also on the polarization η, transfer coefficient α and reversibility index I which have kinetic significance. Therefore, the extent of radial diffusion control depends on the level of polarization and on the kinetic parameters of the electrode reaction in as much as it depends on the structural and transport properties of the electrode-electrolyte system. Thus, an electrochemical reaction can be under radial diffusion control at high, but not at low, polarizations provided I and ψ have appropriate values. In the light of these conclusions, the belief that radial diffusion can be neglected in electrodes of fine pores or of large thickness seems to be an underestimation of the relevant factors.

The significance of $\psi = 0.1$ in Fig. 2 extends to optimization and design considerations. Any decrease in ψ below 0.1 causes only a slight increase in i/i_L at the same $\alpha\eta$, i.e., further decrease in ψ is not justified. This is because a decrease in ψ can be achieved by increasing electrode thickness, decreasing flow rate or pore radius. These are complex options, e.g., an increase in electrode thickness requires more electrode material and a decrease in pore radius calls for an electrode material of a different structure which, in addition, requires more power for pumping the electrolyte through the electrode. A decrease in flow speed causes a decrease in the actual current, even though the dimensionless current i/i_L remains constant. This is because as V decreases i_L also decreases and, since i/i_L remains constant i decreases.

Figure 3 shows the effect of ψ on the current–polarization relations for $I = 0.1$. As $\alpha\eta$ increases the current increases reaching, at large ψ values, a limiting value $i/i_L < 1$ dependent on ψ. At sufficiently large ψ values ($\psi > 0.2$) radial diffusion controls the conversion efficiency, i.e., the obtainable limiting current is less than that given by Equation 10a. The dependence of conversion efficiency on ψ has been treated in detail before [2].

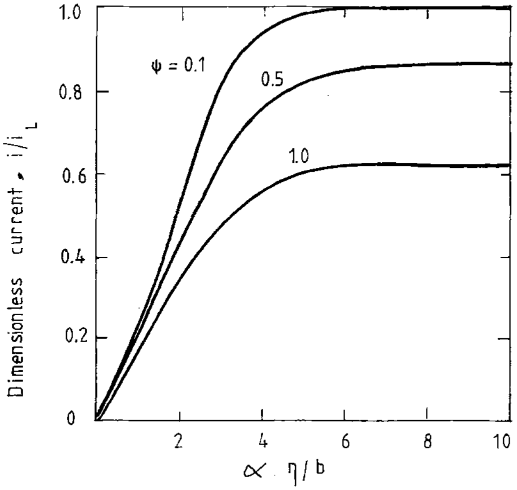

Fig. 3. Effect of dimensionless polarization η/b on the dimensionless current i/i_L at $I = 0.1$ and various values of ψ.

3.2. *Significant ohmic potential drop in the pore electrolyte*

This case is obtainable with large values of the ohmic effect parameter Δ, i.e., large values of reaction rates, electrolyte resistance or electrode thickness. Under these conditions, the polarization varies through the electrode; varying sharply with distance as Δ increases [7, 8]. We have shown above that the polarization affects the extent of radial diffusion control (see Equation 16). Therefore, in presence of significant ohmic potential drop in the pore electrolyte, the extent of radial diffusion control varies from one position to another inside the electrode. This effect is reflected on the current–polarization relations.

The equations to be solved simultaneously for this case are 4a, 7b, 8a, and 9a. Equation 8a is rearranged to give $R_w(x) = [di(x)/dx] \times [1/I \exp(\alpha\eta)]$. Substituting in Equation 7b, solving for $di(x)/dx$ and then combining with Equation 9a one obtains

$$\frac{1}{\Delta}\frac{d^2\eta(x)}{dx^2}\left[1+\frac{1}{I\psi}\exp(-\alpha\eta(x))\right] = \frac{1}{\psi}\left[1-\frac{1}{\Delta}\frac{d\eta(x)}{dx}\right] \qquad (17)$$

There is no general analytical solution to this equation in its present form. However, it can be integrated once to give the polarization gradient, and hence the current, using the following substitution:

$$d\eta(x)/dx = Y$$

thus

$$\frac{d^2\eta(x)}{dx^2} = Y\frac{dy}{d\eta(x)}$$

Substituting in Equation 17 and rearranging, one obtains:

$$\int Y\frac{dy}{1-Y/\Delta} = \frac{\Delta}{\psi}\int\frac{\exp(\alpha\eta(x))}{(1/I\psi)+\exp(\alpha\eta(x))}\,d\eta(x)$$

From tabulated integrals

$$-\Delta Y - \Delta^2 \ln(1 - Y/\Delta) = \frac{\Delta}{\alpha\psi}\ln\left\{\frac{1}{I\psi} + \exp\left[\alpha\eta(x)\right]\right\} + \text{constant}$$

Substituting by boundary conditions 12a, b in the above equation, rearranging and substituting for $y = \mathrm{d}\eta(x)/\mathrm{d}x$, one obtains

$$-\Delta\frac{\mathrm{d}\eta(x)}{\mathrm{d}x} - \Delta^2\ln\left(1 - \frac{1}{\Delta}\frac{\mathrm{d}\eta(x)}{\mathrm{d}x}\right) = \frac{\Delta}{\alpha\psi}\ln\left[\frac{1 + I\psi\exp(\alpha\eta(x))}{1 + I\psi\exp(\alpha\eta_0)}\right] \tag{18}$$

A complete solution of the problem requires further integration of Equation 18 to obtain the polarization distribution, from which the distribution of current and concentration can be calculated. This has been done before [7] for the simpler case of fast electrode kinetics under conditions of one-dimensional transport. However, the relations of practical interest, i.e., the dependence of current-polarization relations on the system variables (e.g. I, Δ and ψ) can be obtained from Equation 18 in its present form. Dividing both sides of Equation 18 by Δ^2, and using Equation 9a, one obtains:

$$-i(x) - \ln(1 - i(x)) = \frac{1}{\alpha\Delta\psi}\ln\left[\frac{1 + I\psi\exp(\alpha\eta(x))}{1 + I\psi\exp(\alpha\eta_0)}\right] \tag{19}$$

At $x = 1$, $i(x) = i$. Thus

$$-i - \ln(1 - i) = \frac{1}{\alpha\Delta\psi}\ln\left[\frac{1 + I\psi\exp(\alpha\eta(L))}{1 + I\psi\exp(\alpha\eta_0)}\right] \tag{20}$$

Equation 20 relates i to η_0 and $\eta(L)$ through α, Δ and ψ. At constant values of α, Δ and ψ there is a fixed value for each of η_0 and $\eta(L)$ for any value of i. The relation between η_0 and $\eta(L)$ can be obtained from the polarization distribution which results from integrating Equation 18. In presence of an ohmic potential drop in the pore electrolyte, there is a large difference between $\eta(L)$ and η_0. Furthermore as Δ increases, $\eta(L)$ increases while η_0 decreases [7, 8]. Taking the limit of large Δ values, and assuming $I\psi\exp(\alpha\eta_0) < 1$, Equation 20 reduces to

$$-i - \ln(1 - i) = \frac{1}{\alpha\Delta\psi}\ln\left\{1 + I\psi\exp\left[\alpha\eta(L)\right]\right\} \tag{21}$$

Equation 21 can be rearranged and presented in the form of a Tafel equation

$$\eta(L) = (1/\alpha)\ln\left[\frac{\exp(-\alpha\Delta\psi i)}{(1 - i)^{\alpha\Delta\psi}} - 1\right] - \ln(I\psi) \tag{22}$$

Equation 22 relates the front face polarization $\eta(L)$ to the current through the dimensionless variables α, Δ, ψ and I at relatively large Δ values such that $\eta(L) \gg \eta_0$. Figures 4–6 illustrate these relations. The effect of the radial diffusion parameter ψ on the current–polarization relations is shown in Fig. 4 at $\Delta = 20$ which is only a moderately large value. At appreciable values of current, i.e., $i/i_L \gtrsim 0.5$, the increase in ψ decreases the current at the same polarization. This is attributed to the depletion of reactant concentration at the pore wall, see Equation 16. Figure 5 shows a stronger effect of variations in ψ at $\Delta = 60$. At $i/i_L < 0.5$, i.e., in the absence of significant concentration changes through the electrode, ψ has no effect on the current–polarization relations. It is also noteworthy that the increase in ψ at values above $\psi = 0.1$ has a more significant effect than a corresponding increase at values below 0.1 (refer also to Fig. 2). Figure 6 illustrates the effect of the ohmic effect parameter Δ on the current–polarization relations at a constant value of ψ. The increase in Δ, at

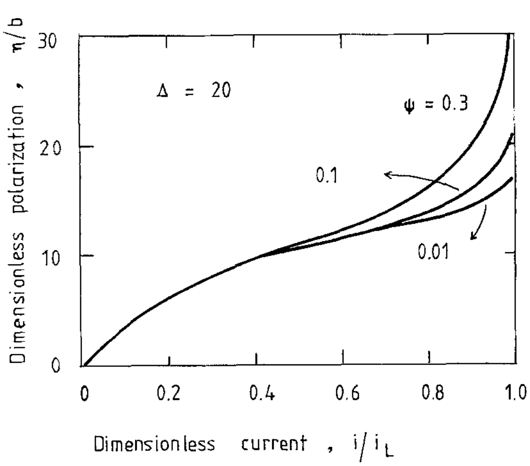

Fig. 4. Effect of the dimensionless group ψ on the current–polarization relations at $\Delta = 20$ and $I = 0.01$.

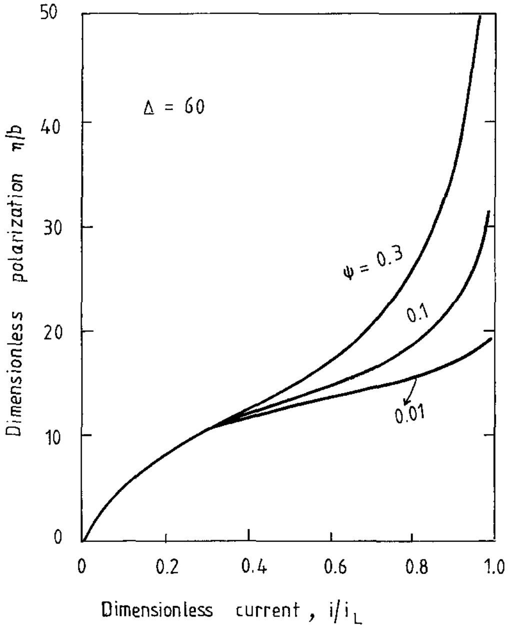

Fig. 5. Effect of the dimensionless group ψ on the current–polarization relations at $\Delta = 60$ and $I = 0.01$.

the same current i/i_L, increases the polarization. This increase in polarization is due to the ohmic potential drop in the pore electrolyte resulting from increase in current, pore electrolyte resistance or electrode thickness.

A comparison of Figs. 4–6 reveals that Δ and ψ have similar effects on the current–polarization relations. This is understandable as the increase in Δ increases the ohmic potential drop in the pore electrolyte whereas an increase in ψ decreases $R_w(x)$ and hence increases the magnitude of concentration polarization. There seems to be a synergistic effect of Δ and ψ on the current–polarization relations. This is borne out by the larger increases in $\eta(L)$ caused by increasing ψ at $\Delta = 60$ as compared to the corresponding increases at $\Delta = 20$.

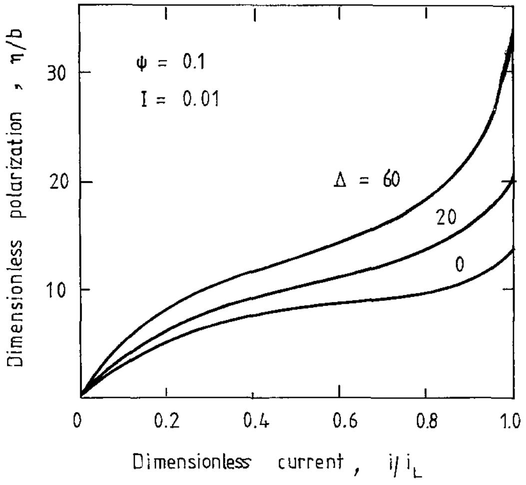

Fig. 6. Effect of the ohmic parameter Δ on the current–polarization relations at constant $I = 0.01$ and $\psi = 0.1$.

The effect of the reversibility index I on the current–polarization relations has been treated before [5, 8]. As I decreases, the current–polarization relations shift bodily to higher polarizations by $(2.3\ b/\alpha)$ V per decade of I.

4. Significance of ϕ, Sh and ψ

In treating the effects of radial diffusion on the conversion efficiency of porous flow-through electrodes, the dimensionless group ϕ was found to influence the efficiency [2].

$$\phi = VR^2/2DL\theta$$
$$= 2V\theta/DLS^2 \qquad (23)$$

This group combines the structural properties of the porous electrode (R, L, θ and S) and the transport properties of the electrolyte (V and D). The significance of ϕ has been discussed in detail before [14, 15] with reference to diffusional entrance effects and residence time through the electrode. This group is also related to the other hydrodynamic dimensionless group commonly used in mass transfer studies, namely Reynolds (Re), Schmidt (Sc) and Peclet (Pe) numbers. From the definitions of these groups

$$\phi = Re\,Sc\,R/L$$
$$= Pe\,R/L \qquad (24)$$

Thus ϕ increases with increase of V and R or decrease of D, L and θ. These variations are comparable to increases in Re, Sc and Pe numbers. Note that whereas Re (being the relation between convective and viscous forces) determines the flow regime, i.e., whether the flow is laminar or turbulent, Sc is a measure of the viscous to diffusional effects and Pe relates convective to diffusional effects.

The rate of mass transfer between the flowing liquid and the surface of the solid is expressed in terms of the Sherwood number *Sh* (referred to also as Nusselt number *Nu*); hence it is a measure of the speed of radial diffusion

$$Sh = kd/D = \frac{4k\theta}{SD} \tag{25}$$

The dependence of *Sh* on *Re* and *Pe* cannot be solved analytically for porous media of irregularly shaped particles; similar solutions are available for straight tubes [13] and for carefully packed spheres [16]. In these cases, the *Sh* number decreases with decreasing *Re* ($Sh \propto Re^{1/3}$) approaching asymptotically a limiting value at sufficiently low *Re*, in the so called 'deep bed' region, i.e., when the concentration profile is fully developed. For randomly packed beds of various packings there have been several empirical correlations of *Sh* to *Re* of the form [17]

$$Sh = a\, Re^{B} \tag{26}$$

where a and B are constants; B is less than unity often ranging from 0.33–0.66. Therefore the parameter of radial diffusion $\psi = 2\phi/Sh \propto V^{(1-B)}$, i.e., it is proportional to $V^{(1-B)}$.

5. Comparison with experimental results

The complexity of the present system is well illustrated by the form of Equation 20. Although Equation 22 is somewhat simpler than Equation 20, the important variables α, Δ and ψ in either equation cannot be easily separated. Thus for experimental testing of the effects of these variables, we used an electrochemical reaction of known value of α on a particular electrode and measured the effects of variations in flow speed (and hence in I, Δ and ψ) on the current–polarization relations. We now test whether the observed effects can be interpreted in terms of the resulting variations in I, Δ and ψ. Measurements were obtained on the electrochemical reduction of copper ions from solutions of copper sulphate in 0.5 mol dm^{-3} H_2SO_4 at 25 ± 2° C. Details of the cell, flow system, circuitry and experimental procedure are available elsewhere [15]. The packed bed electrode was made of small copper wirelets. It had the following specifications: cross sectional area, 3.14 cm^2; length, 2.1 cm; θ, 0.47; S, 177 cm^{-1}; R, 53 μm and ρ_{eff}, 20.1 Ω cm.

Figure 7 shows the effect of flow speed on the current–polarization relations for the reduction of 0.001 mol dm^{-3} Cu^{2+}. The values of Δ are indicated on the figure. Note that the front (exit) face polarization $\eta(L)$ increases with V whereas the rear (entrance) face polarization η_0 has essentially the same low value for the four runs regardless of the value of V. Note also that an increase in V results in an increase in both Δ ($\Delta \propto V$) and ψ (see under significance of ϕ, Sh and ψ) and a decrease in I ($I \propto 1/V$). Thus the effect of flow speed observed in Fig. 7 is the sum of the above variations in I, Δ and ψ. These effects are in the direction predicted by the model, i.e., $\eta(L)$ increases with increase in Δ and ψ or with decrease in I.

A more quantitative test of the validity of the present model can be achieved by applying Equation 22 to the experimental results of Fig. 7 (where $\eta(L) \gg \eta_0$). If the above model simulates the behaviour of the system, then a

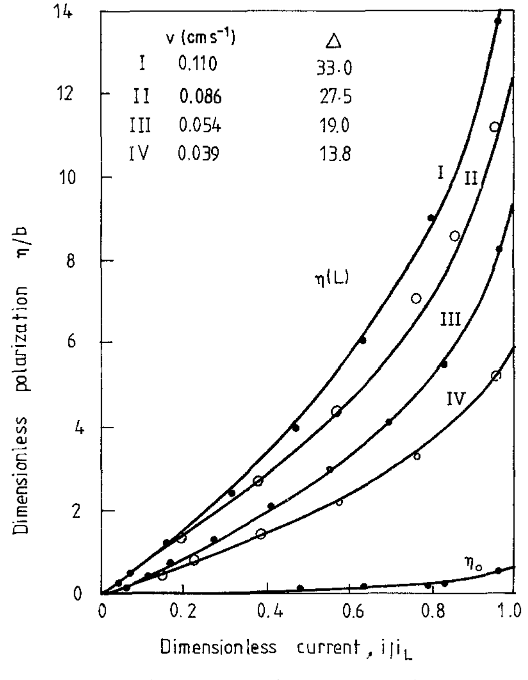

Fig. 7. Effect of electrolyte flow speed on the measured current–polarization relation at large Δ values (see text).

plot of the dimensional polarization $[\eta(L)/b]$ versus the first logarithmic term on the rhs of Equation 22 should give a straight line with a slope of $(1/\alpha)$ and an intercept of $\ln(I\psi)$. Note that Δ and ψ exist also in the first term. From the intercept of the plot one can calculate I and hence i_0. The value of α calculated from the slope must be equal to that used in the calculation. The calculation of I and Δ is direct and simple; the only difficulty is in calculating Sh and hence ψ (cf., significance of ϕ, Sh and ψ). In calculating Sh for a packed bed, use is often made of Equation 26. However, the values of a and B vary widely [17] depending on the system and type of flow. In fact different values have been reported for similar systems, under comparable flow conditions [17].

Note that the transfer coefficient is known rather accurately ($\alpha = 0.5$) and the parameter of ohmic effect Δ is calculated from i_L and ρ_{eff} which can also be measured accurately. The only uncertainty is in calculating Sh and hence ψ. Therefore ψ is regarded as an optimization parameter, the proper value of which satisfies Equation 22. We have tested this equation with some experimental results (cf., Fig. 8) using different values of Sh. In each case a straight line was obtained; the slope (and hence α) and the intercept of which being dependent on the particular value of Sh. It was found that an increase in ψ (decrease in Sh), at fixed values of $\alpha\Delta$, results in a decrease of the slope, i.e., in an increase in α. Fig. 8 shows plots of the experimentally measured polarization (converted to dimensionless) $\eta(L)/b$ versus the first logarithmic term on the right-hand-side of Equation 22 for two runs I and II. The measured and calculated values for runs, I and II, are respectively: D, 7.5×10^{-6} cm^2 s^{-1} [2]; V, 0.11, 0.086 cm s^{-1}; i_L, 20.0 16.7 mA cm^{-2}; Δ, 33.0, 27.5; α, 0.5; ϕ, 0.208, 0.163; Re, 0.062, 0.049; Pe, 82.8, 64.8; Sh, 7.49, 6.96 and ψ, 0.101 and 0.085 (corresponding to Sh = 4.12 and 3.84, respectively). It is noteworthy that these Sh values are only slightly greater than the asymptotic limiting value of 3.66 which was obtained analytically for laminar (Poiseuille) flow in tubes [13]; the value for turbulent (plug) flow being 5.78. The present results are well in the region of laminar flow ($Re = 0.062$ and 0.049) since the onset of turbulent flow in porous media starts at $Re = 1$–10 [18]. The results of the two runs fit one satisfactory straight line over a wide range of polarizations with a slope of 1.86 which corresponds to a value of $\alpha = 0.54$. This value is in good agreement with the value of 0.50 which was used in calculating the rhs of Equation 22. The intercept gives a value of $I\psi = 0.03$ from which the reversibility index $I = 0.297$ and 0.353, respectively. The exchange current density of the reaction, i_0, calculated from these values is 1.6×10^{-5} A cm^{-2} corresponding to a value of 0.016 A cm^{-2} mol^{-1}, which is comparable to the values reported by Hurlin [19]. Similar results were obtained at values of $\Delta = 19.0$ and 13.8 (see Fig. 7). This good agreement between the predictions of the model and the behaviour of the system is taken as a support of the validity of this model with its assumptions and solutions.

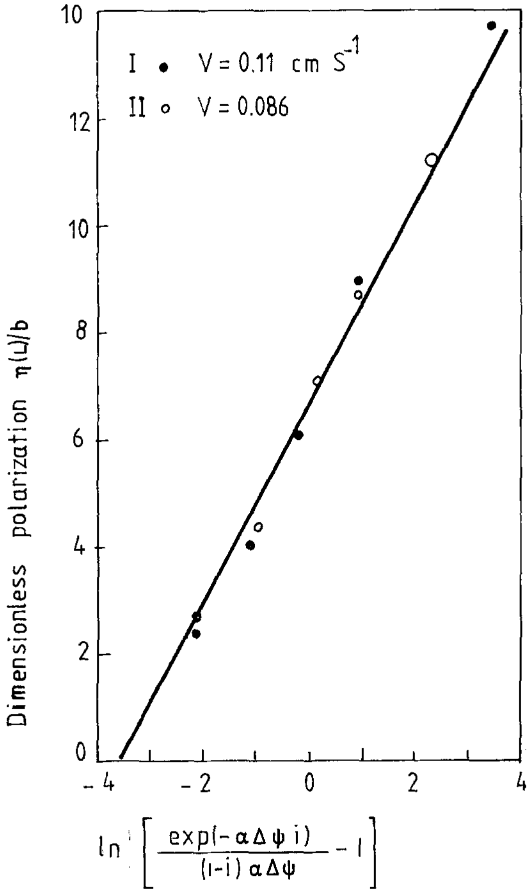

Fig. 8. Plot of the experimental results according to Equation 22 (see text).

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