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THE PENNSYLVANIA STATE UNIVERSITY

Report No. 3
**THE MODE OF OPERATION OF POROUS DIFFUSION ELECTRODES
FOR FUEL CELLS**

by

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The Mode of Operation of Porous Diffusion Electrodes
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ABSTRACT

A number of simple models of diffusion electrodes are examined theoretically. The results are expressed in forms whereby it should be possible to test the models experimentally, and make predictions regarding the effects of variation of the pertinent parameters.

It is not expected that the theories will completely explain operating data on complex electrode structures. It should be possible to test them, however, on experimental equipment designed to approximate to the models chosen.

(1) INTRODUCTION

Although primary and secondary cells have employed porous electrodes for many years, there appears to have been little work on describing the exact influence of the porosity. Presumably this is due to the complex nature of the electrochemical reactions in such cells and the difficulty of describing paste electrodes. The recent surge of interest in fuel cells has led to increased study of porous electrodes, with some hopes of applying reasonably exact mathematical treatments. Fuel cell electrodes are usually hard and solid and retain their configuration during operation, since they serve to provide catalytic reaction surface rather than to provide storage of reactant. Justi et al. (1) have presented a limited analysis of porous fuel cell electrodes. A similar analysis was performed independently by Austin (2). This analysis is incorporated into this report since it forms the basis for more detailed treatments. Stender and Ksenzhak (3) have discussed the limiting case where polarization is due solely to ohmic effects within the electrolyte, in the pores of the electrode and no depletion of reactant occurs in the electrolyte. We will show that this case is only rarely applicable. The transient case, which is difficult to analyze when appreciable amounts of reactant are adsorbed on the surface, has been crudely treated by Uhrbach (4). A number of other workers (5-12) have presented studies of various porous systems, but since the work is as yet available only in abstract form, it is not possible to critically analyze their findings (although reference to their presentations will be made in this report).

One of the difficulties in describing the mode of operation of diffusion electrodes is that the complexity of the systems leads to final solutions which contain several parameters in "awkward" algebraic forms. Thus it is conceivable that by suitable selection of the values of the parameters, several different theories can be made to fit a given set of experimental results. In order to test certain assumptions, it is valuable to consider simple redox reactions at porous electrodes; the reactions have fairly well defined kinetics and a two phase

system results. Theories can be relatively easily checked for such cases. The concepts can then be extended to three phase gas diffusion electrodes with more certainty after they have been proved correct for the simpler systems.

In general, we are looking for a model (or models) of a porous electrode which will satisfy two requirements. It must be sufficiently rigorous to explain quantitatively experimental results from a simple system, for example, a single pore of known radius and length. In addition, it must be general enough to explain qualitatively the behaviour of complex systems such as sintered, double layer structure, Raney electrodes (13) or carbon electrodes. It is, of course, possible to write differential equations covering every conceivable factor affecting the results. It is also possible, in theory, to solve the equations numerically using a digital computer. But we are likely to end up with solutions which have so many unknown parameters that they can be used to fit any set of experimental results. It is my opinion that the better way to approach the problem is to start with the simplest possible models, solve the equations, and perform experimental work specifically aimed at testing the models. By examining the problem at several simplified limiting conditions, it is often possible to show that a particular effect is usually negligible. It is also my opinion that fairly lengthy explanations of the methods of setting up the differential equations are not superfluous. The equations and their solutions may be valuable to people who have not had much experience in writing down these equations, and the extra space used in describing the meaning of the equations is not wasted.

(2) PHYSICAL DESCRIPTION OF ELECTRODES

Several simplifying assumptions must be made about the structure of porous electrodes before it is possible to apply simple equations. These assumptions may not be completely true, but they are necessary to form a model amenable to treatment. For example, it is not generally possible to get a porous electrode which is perfectly homogenous in pore size. A

small pore will have a greater surface area to cross-sectional area ratio than a larger pore. If both pores are held at the same polarization so that current per unit area is the same, and reactant allowed to diffuse in at one end of the pore, the smaller pore must diffuse in a proportionally greater amount of reactant per unit cross-sectional area than the large pore. Consequently, the concentration of reactant will fall off more rapidly with distance from the entrance mouth for the small pore. A bundle of parallel tubes of varying diameter could be used as a porous electrode. Theoretical equations for current density versus polarization for each pore could be obtained and using the common boundary conditions of uniform concentration and polarization at the pore mouths, the sum effect could be found, providing the size/number distribution was known. Ohmic potential gradients and concentration gradients (within the electrolyte in the pores) would vary with each pore. However, if one examines a porous carbon or sintered metal electrode under a microscope it is apparent that this model is not adequate. These structures are spongelike, with the pore spaces interlinked in many directions. Any variation of concentration gradient, or electrolyte potential gradient, existing along two different size pores will tend to even out by lateral mass transport through the inter-linking connections of the pores. This discussion leads to the first assumption. It will be assumed that the pores are so highly inter-linked that the potential and concentration at any given penetration into the electrode are constant. This is probably a good approximation for well constructed electrodes. An electrode with a crack (or large pin-holes) through it, on the other hand, will behave somewhere in between the extremes of completely interlinked pores and discrete tube bundles.

Another assumption is that, in general, a porous electrode has a macroporosity and a microporosity. The macroporosity is the space between particles or material which can be observed under an optical microscope. Microporosity is very fine porosity existing within or on the surface of the large material. For example, in a baked porous electrode carbon, the microporosity is made up of inter-crystallite voids in the filler and fine channels or bubbles in the

carbonized binder. For a platinized platinum electrode, the voids between the base platinum particles form macroporosity, while the fine surface porosity of the platinized layer is the microporosity. In Raney metal electrodes, the microporosity is the fine pore structure within the particles, produced by dissolution of the soluble alloying component. The macroporosity can be considered as having a definite cross-sectional area and geometric perimeter at any cross-section of the electrode. Normally, the microporosity represents only a few per cent or less of the total empty volume and we may equate macroporosity to ϵ , the total porosity. The total perimeter area of the macroporosity represents the area through which mass transport to the reacting surfaces can occur, and may be denoted by A cm^2 per cm^3 of electrode. The total area for reaction, S cm^2 per cm^3 say, can be considered as A times a roughness factor f ,

$$S = Af \text{ cm}^2 \text{ cm}^{-3} \quad (1)$$

f is all the area associated with unit geometric macroporous area A . For completely smooth particles (or tubes), with no microporosity, $f = 1$. For a particle with highly developed interior or surface area, f will be large.

Another assumption made is that the conductivity of the electrode material is large compared to the conductivity in the electrolyte. For small experimental electrodes, ohmic effects within the electrode material will be neglected.

It will also be assumed that the electrodes investigated will be plane electrodes, with uniform current density in the external electrolyte and negligible edge effects.

(3) REDOX SYSTEMS (TWO PHASE SYSTEMS)

3.1. General Discussion

In the consideration of redox reactions at a porous electrode the problem is simplified since we need consider only transport in the electrolyte phase. It is assumed that any surface intermediate is present in small quantities ($\theta \rightarrow 0$, where θ is the fractional surface coverage). The activity of bare surface, $1-\theta$, is, therefore, close to 1 and can be taken as constant over a wide voltage range. The rate equation can be expressed as

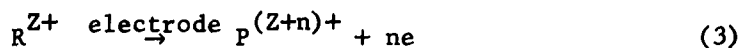
(14),

$$i = i_o \left(\frac{R}{R_1} e^{\frac{\alpha n_1 F \eta}{RT}} - \frac{P}{P_1} e^{\frac{-(1-\alpha) n_1 F \eta}{RT}} \right) \quad (2)$$

i is current density, i_o is the exchange current density for concentrations (activities) of reactant and product of R_1 , P_1 , respectively. η is the difference between the ideal reversible double layer potential for concentrations R_1 , P_1 and the actual double layer potential, therefore it represents the sum effect of activation and concentration polarization. Even for redox reactions, equation 2 is not the only form of rate equation which may be applicable (see 4.5 later), but it forms a good starting point in the lack of definite knowledge of a particular reaction. It assumes that the solutions considered are concentrated enough to render diffuse double layer effects small and that R and P are the actual reactant and product for the slow step in the reaction (or have a simple equilibrium relation with the actual reactant and product).

3.2 Rates of Mass Transport

Let us consider a simple anodic redox system such as



Associated with the cations will be the corresponding anions, and at steady state, the law of neutrality requires that each step in equation 3 must be accompanied by n charge transfer in the electrolyte between the electrodes. Each cation charge in the electrolyte must be balanced by a corresponding anion charge. For a steady state condition in which R is being linearly transported to the electrode and equimolar amounts of P are being transported away, the mass transport equations for a stationary system can be approximated as follows. Let D be diffusion coefficient, V voltage in the electrolyte and x distance from the electrode face. Let R be concentration of reactant, P be concentration of product and let A be the concentration of anion with a valence charge of Z_A . If the mass transport effects are

such that different parts of the electrolyte contain different totals of R, P and A then clearly the amount of water present per unit volume is different.* A water diffusion gradient exists and at steady state this must be balanced by an equal but opposite flow of water, that is

$$D_{H_2O} dC/dx = Cv \quad (4)$$

C is the concentration of water and v is the bulk flow velocity in the opposite direction to the diffusional effect. This bulk flow will also carry R, P and A with it. Whether or not this bulk flow significantly affects the transport of the other constituents, R for example, depends on the relative magnitudes of $D dR/dx$ and Rv . The magnitude of $D dR/dx$ will be roughly equal to that of $D_{H_2O} dC/dx$, therefore, from equation 4 the effect depends on the relative magnitudes of R and C. It will be assumed that R (and P, A) are so small compared to C that the bulk flow of water carries only a small fraction of the total mass transport of the constituents other than water. This will be a fairly good approximation even up to concentration changes of several moles per litre.

It will also be assumed, since the redox ions R and P are identical except for the different charge, that D_R and D_P are equal and the ionic mobilities (velocity of migration in unit potential gradient) are proportional to the valence charge. Then, at steady state, rate of transport of R towards electrode (gm. moles per sq. cm. per sec.)

0 :

*The relation is $X_R + X_P + X_A + X_{H_2O} = 1$ litre, where the X values are the effective partial volumes of the constituents, in litres. These volumes are functions of the concentrations. For example, the value of $X_R = \int_0^R \bar{X}_R dR$, where $\bar{X}_R$ is the partial molar volume of R (15) in litres per gm. mole per litre, R being in gm. moles per litre. The functional relation of $\bar{X}_R$ to R, P, A, C is complex and $\bar{X}_R$ can vary from the molar volume of the pure state to zero or even negative values.

$$= D \, dR/dx + RZu \, dV/dx$$

where u is the mobility per unit charge. For the anodic case, dR/dx will be positive and dV/dx negative. Thus,

$$i/nF = D \, dR/dx + RZu \, dV/dx \quad (5)$$

Also, considering the mass transport of product away from the electrode,

$$i/nF = -(D \, dP/dx + P(Z+n)u \, dV/dx) \quad (6)$$

At steady state the total transfer of the non-discharging anion is zero and

$$0 = D_A \, dA/dx + AZ_A u_A \, dV/dx \quad (7)$$

D_A , u_A are the diffusion coefficient and ionic mobility per unit charge respectively of A. Z_A is the algebraic charge, e.g., for Cl^1 , Z_A would be -1. The final equation, that of electrical neutrality at any point in the electrolyte is

$$ZR + (Z+n)P = Z_A A \quad (8)$$

From equation 8,

$$ZdR/dx + (Z+n)dP/dx = Z_A \, dA/dx \quad (8a)$$

Subtracting equation 6 from equation 5,

$$(D/u)d(R+P)/dx + (RZ + P(Z+n))dV/dx = 0$$

From equation 8,

$$(D/u) \, d(R+P)/dx + Z_A A dV/dx = 0$$

From equation 7,

$$(D/\mu)d(R+P)/dx - (D_A/\mu_A)dA/dx = 0$$

Substituting for dA/dx from equation 8a,

$$(D/u)(dR + dP) - (D_A/u_A)[(Z/Z_A)dR + ((Z+n)/Z_A)dP] = 0$$

$$[(D/u) - (D_A/u_A)(Z/Z_A)]dR + [(D/u) - (D_A/u_A)(Z+n)/Z_A]dP = 0$$

or

$$k_1 dR + k_2 dP = 0 \quad (9)$$

The boundary conditions are $R = R_b$, the bulk concentration (unaffected by mass transport) when $P = P_b$, therefore

$$k_1 (R - R_b) + k_2 (P - P_b) = 0 \quad (10)$$

Equation 10 represents the relation between P and R at any point in the electrolyte. Eliminating dV/dx between 5 and 6,

$$(i/nF - D dR/dx)(1/RZ) = (-i/nF - D dP/dx)(1/P(Z+n))$$

Substituting for dP/dx and P from equations 9 and 10 gives

$$(i/nF - D dR/dx)(1/RZ) = (-i/nF + D(k_1/k_2)dR/dx)(1/[(k_1/k_2)(R_b - R) + P_b](Z+n))$$

Collecting terms in i

$$i = (nFD dR/dx) (k_2 + k_1 k_3) / (k_2 + k_2 k_3) \quad (11)$$

where

$$k_3 = RZ / [(k_1/k_2)(R_b - R) + P_b](Z+n) \quad (11a)$$

Clearly the complete form of equation 11 is too complex to be of much use. In general, however, k_3 will be some value between 0 and ∞ and

$$i = (nFD dR/dx) (1 \text{ to } k_1/k_2) \quad (12)$$

Now

$$k_1/k_2 = [(D/u) - (D_A/u_A)(Z/Z_A)] / [(D/u) - (D_A/u_A)(Z+n)/Z_A]$$

But (16)

$$D/u = kT/e = D_A/u_A \quad (13)$$

Therefore,

$$k_1/k_2 = (Z_A - Z)/(Z_A - (Z+n)) \quad (14)$$

Note that Z_A is always of opposite sign to Z and therefore zero cannot occur in the denominator or numerator. For example, for $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, with SO_4 anion, $k_1/k_2 = (-4)/(-5) = 0.8$. For $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$ with Cl^- anion, $k_1/k_2 = (-3)/(-5) = 0.6$. Thus k_1/k_2 is not widely different from 1. The above equations have been derived assuming that Fick's law applies with a constant diffusion coefficient and that mobilities are constant. These assumptions are not likely to be exactly true, therefore it appears that a reasonable simplification of equation 11 is

$$i = nF\bar{D} \, dR/dx \quad (15)$$

where $\bar{D}$ is nearly constant with varying i and is of the same order of magnitude as the true diffusion coefficient. Equation 15 may be compared with the often used (17) equation

$$i = (nFD/(1-n_+)) \, dR/dx \quad (15a)$$

n_+ being the transport number of the reactant. It can readily be shown that this equation follows from equation 11 when k_3 is large ($Z+n = 0$, for example), $Z = -Z_A$, and $D = D_A$. However, if equation 13 is taken to be precisely correct, $D = D_A$ means that $u = u_A$ and therefore the transfer number is one-half. Equation 15a must be an approximation since it has no term in the diffusion coefficient of the anion.

When a supporting non-discharging electrolyte is present a precise treatment requires the writing of additional equations of the form of equation 7 and the simultaneous solution of the equations as before. However, it is readily seen that a supporting electrolyte will have the effect

of reducing k_3 towards zero, giving $i = nFD \, dR/dx$.

For diffusion in a porous medium of porosity ϵ and tortuosity factor q (18), the mass transport based on the total area is given by

$$i = nFD_{\text{eff}} dR/dx \quad (16)$$

where $D_{\text{eff}} = D\epsilon/q \quad (16a)$

3.3 Redox Reactions at a Porous Electrode: Ohmic Effects Neglected

3.3.1 Reaction Within Electrode

The system considered is illustrated in Figure 1. It will be assumed that electrolytic current and mass transfer occur through one plane face, with negligible edge effects and negligible non-uniformity of current density in the electrolyte. The system is, therefore, one dimensional and we can consider a unit area of face. Let the concentration of reactant and product in the bulk of the electrolyte be R_b , P_b respectively. Let the thickness of the electrode be t . Equation 2 can be written as

$$i = i_o \left((R/R_b) e^{\alpha n F \eta / RT} - (P/P_b) e^{-(1-\alpha) n F \eta / RT} \right)$$

or

$$i = i_o \left((R/R_b) e^{\alpha \eta / b} - (P/P_b) e^{-(1-\alpha) \eta / b} \right) \quad (17)$$

For electrodes of reasonable thickness and pore size, the macro-pore size will be at least two orders of magnitude less than the thickness (10 microns and 1 mm, for example) and we can assume that mass transfer effects across the radius of a pore are negligible compared to mass transport effects along the axis of the pore.

Consider a differential element dx as shown in Figure 1. The reacting area is Sdx and the current, di , from the element is

$$di = i_o \left((R/R_b) e^{\alpha \eta / b} - (P/P_b) e^{-(1-\alpha) \eta / b} \right) Sdx$$

The amount of reactant diffused out of the element at the plane x is $D \cdot dr/dx$ (where D is understood to be the D_{eff} of equation 16). The amount diffused in through the plane at $x + dx$ is equal to $D(dR/dx + d(dR/dx))$. In the usual way, therefore, at steady state,

$$di = nFD(d^2R/dx^2)dx$$

and

$$d^2R/dx^2 = (i_0 S/nFD) [(R/R_b)e^{\alpha\eta/b} - (P/P_b)e^{-(1-\alpha)\eta/b}] \quad (18)$$

If ohmic effects are neglected, η is constant through the electrode. For a redox reaction with supporting electrolyte the effective diffusion coefficients of R and P are nearly equal and little error is introduced by letting the diffusion coefficients be equal. Then, for equi-molar counter-current diffusion

$$R + P = R_b + P_b \quad (19)$$

Substituting for P into equation 18

$$\begin{aligned} d^2R/dx^2 &= (i_0 S/nFD) [(e^{\alpha\eta/b}/R_b) + (e^{-(1-\alpha)\eta/b}/P_b)]R \\ &\quad - (i_0 S/nFD)(R_b + P_b)(e^{-(1-\alpha)\eta/b}/P_b) = K_1 R - K_2 \quad (20) \end{aligned}$$

The boundary conditions are $dR/dx = 0$ at $x = 0$, since no mass transport occurs beyond the left hand face, and $R = R_s$ at $x = t$, R_s being the concentration at the right hand face. The solution of equation 20 for these boundary conditions is

$$\frac{K_1 R - K_2}{K_1 R_s - K_2} = \frac{e^{\sqrt{K_1}x} + e^{-\sqrt{K_1}x}}{e^{\sqrt{K_1}t} + e^{-\sqrt{K_1}t}}$$

The total steady state current from reaction in the interior of the electrode is

$$i = nFD(dR/dx)_{x=t}$$

Now

$$K_1 dR/dx = \frac{(K_1 R_s - K_2)}{(e^{\sqrt{K_1}t} + e^{-\sqrt{K_1}t})} (\sqrt{K_1} e^{\sqrt{K_1}x} - \sqrt{K_1} e^{-\sqrt{K_1}x})$$

therefore

$$\begin{aligned} i &= nFD \frac{(K_1 R_s - K_2)(\sqrt{K_1}) (e^{\sqrt{K_1}t} - e^{-\sqrt{K_1}t})}{(K_1) (e^{\sqrt{K_1}t} + e^{-\sqrt{K_1}t})} \\ &= nFD(K_1 R_s - K_2)(1/\sqrt{K_1}) \tanh(t\sqrt{K_1}) \end{aligned}$$

But since the RHS of equation 20 equals the RHS of equation 18, $K_1 R_s - K_2$ can be replaced and

$$i = (i_0 S t) [(R_s/R_b) e^{\alpha\eta/b} - (P_s/P_b) e^{-(1-\alpha)\eta/b}] (1/t\sqrt{K_1}) \tanh(t\sqrt{K_1}) \quad (21)$$

Thus we arrive at the usual form of rate equation but modified by a factor $(1/t\sqrt{K_1}) \tanh(t\sqrt{K_1})$.

Several limiting cases can be described.

(i) Low exchange current, low to moderate polarization. From equation 20,

$$K_1 = (i_0 S / nFD) [(e^{\alpha\eta/b} / R_b) + (e^{-(1-\alpha)\eta/b} / P_b)] \quad (22)$$

If $i_0 S$ is low and polarization not too high, $t\sqrt{K_1}$ is small. Then $(1/t\sqrt{K_1}) \tanh t\sqrt{K_1}$ is near 1,* and

$$i = (i_0 S t) [(R_s/R_b) e^{\alpha\eta/b} - (P_s/P_b) e^{-(1-\alpha)\eta/b}] \quad (23)$$

Thus, if there is negligible concentration drop from the bulk electrolyte to the electrode surface (as would be expected at low currents), $R_s = R_b$, $P_s = P_b$

*For example, $(\tanh x)/(x) = 0.97$ at $x = 0.3$.

and we obtain the usual form for a low exchange current reaction with the whole of the interior surface area (St) of the electrode being utilized. If $i_0 St$ is so small that $t\sqrt{K_1}$ is small for polarizations above 50 millivolts or so, then equation 23 reduces to the normal Tafel form, with a slope of $2.3 RT/\alpha nF$.

(ii) Low or moderate exchange current, high polarization.

From equation 22 it is seen that as η goes up (or as $i_0 S$ is higher), $t\sqrt{K_1}$ goes up. Eventually the situation is reached where $t\sqrt{K_1} > 2$. Then $\tanh(t\sqrt{K_1})$ is equal to one and equation 21 goes to

$$i = i_0 S \frac{[(R_s/R_b) e^{\alpha\eta/b} - (P_s/P_b) e^{-(1-\alpha)\eta/b}]}{\sqrt{(i_0 S/nFD)[(e^{\alpha\eta/b}/R_b) - e^{-(1-\alpha)\eta/b}/P_b]}} \quad (24)$$

The thickness of the electrode disappears from the equation since the concentration of reactant in the interior reaches zero at some penetration less than the thickness. When η is great enough for $e^{-(1-\alpha)\eta/b}$ to be negligible,

$$i = (i_0 S n F D R_b)^{1/2} (R_s/R_b) e^{\alpha\eta/2b} \quad (25)$$

For negligible concentration gradient outside of the electrode $R_s/R_b = 1$ and equation 25 is a Tafel form equation, with a slope, however, of twice the expected normal value. The apparent exchange current is $\sqrt{i_0 S n F D R_b}$.

(iii) High exchange current; pure concentration polarization.

For very high exchange currents, that is, $i/i_0 St$ small, we get the normal form

$$\eta = 2.3b \log (R_b P_s / R_s P_b) \quad (26)$$

The physical meaning here is that the current can be supplied from an infinitesimal layer at the electrode surface. This layer is so thin that the concentration gradient which is diffusing reactant from the surface into this reaction zone is virtually zero. The interior of the electrode is at $R_s - \delta R$ and $P_s + \delta P$; where δR and δP are small quantities which bring

the interior of the electrode to equilibrium conditions. In the infinitesimal surface reaction layer where R goes from $R_s - \delta R$ to R_s , the slight deviation from equilibrium is sufficient to supply the current being drawn.

3.3.2 Reaction at Surface of Electrode

The treatment in the previous section describes the current-voltage relation for current produced from the interior of the electrode. In addition, however, the exposed face of the electrode will support current. Although the geometric external area considered is unit area, the external reacting area which is freely available without mass transport restrictions in the interior porous system can be considered as f sq. cm. per sq. cm. of geometric area (see discussion of equation 1). Therefore, a more complete equation for current density is

$$\begin{aligned} i &= i_{\text{interior}} + i_{\text{exterior}} \\ &= (i_o t S) [(R_s/R_b) e^{\alpha \eta/b} - (P_s/P_b) e^{-(1-\alpha)\eta/b}] (1/t \sqrt{K_1}) \tanh(t \sqrt{K_1}) \\ &\quad + i_o f (1-\epsilon) [(R_s/R_b) e^{\alpha \eta/b} - (P_s/P_b) e^{-(1-\alpha)\eta/b}] \end{aligned}$$

$1-\epsilon$ is the area of the exterior allowing for open pore mouths. Thus,

$$i = [(i_o t S) (1/t \sqrt{K_1}) (\tanh t \sqrt{K_1}) + i_o f (1-\epsilon)] [(R_s/R_b) e^{\alpha \eta/b} - (P_s/P_b) e^{-(1-\alpha)\eta/b}] \quad (27)$$

The relative importance of the two currents is described by

$$i_{\text{interior}}/i_{\text{exterior}} = t(S/f(1-\epsilon))(1/t \sqrt{K_1}) \tanh(t \sqrt{K_1})$$

From equation 1,

$$i_{\text{int}}/i_{\text{ext}} = [(t(1-\epsilon)A)(1/t \sqrt{K_1}) \tanh(t \sqrt{K_1})] \quad (28)$$

A is the internal perimeter area. For example, an electrode of 30% porosity and a pore diameter of 10 microns has $A = 4 \epsilon/d = (4)(0.3)10^3 \approx 1000$ sq. cm. per cubic cm. For $t \sqrt{K_1}$ small (< 0.3),

$$i_{int}/i_{ext} = tA(1-\epsilon) \quad (28a)$$

For a thickness of 0.1 cms. and $A = 1000 \text{ cm.}^{-1}$, the ratio of interior to exterior current is then about 100, and the exterior current is negligible. For $t\sqrt{K_1} > 2$,

$$\begin{aligned} i_{int}/i_{ext} &= A(1-\epsilon)/\sqrt{K_1} \\ &= A(1-\epsilon)/\sqrt{(i_0 S/nFD)} [(e^{\alpha\eta/b}/R_b) + (e^{-(1-\alpha)\eta/b}/P_b)]^{1/2} \end{aligned} \quad (28b)$$

For $e^{-(1-\alpha)\eta/b}/P_b$ negligible

$$i_{int}/i_{ext} = A(1-\epsilon)/\sqrt{(i_0 S/nFDR_b)} e^{\alpha\eta/2b}$$

From equation (25),

$$i_{int}/i_{ext} = (A(1-\epsilon)/i_{int}) \sqrt{nFDR_b} (R_s/R_b) \quad (28c)$$

For example, for $n = 1$, $R_b = 0.1 \text{ gm. mole/litre}$, $D = 10^{-6} \text{ cm.}^2/\text{sec.}$, (allowing for porosity and tortuosity), $R_s/R_b = 1$,

$$i_{int}/i_{ext} = (A/i_{int})(2)(10^{-3})$$

For i_{int} in millamps/sq. cm. and $A = 1000 \text{ cm.}^{-1}$,

$$i_{int}/i_{ext} \approx 2000/i_{int}$$

Thus the exterior current would still be a small fraction of the total current at 100 mamps/sq. cm., providing the electrode was not near the limiting current, of course.

3.3.3 Effect of External Mass Transport

Assuming a simple "stagnant film" (14) concept to be sufficiently accurate, the effect of mass transport outside of the electrode can be expressed (14) by

$$R_s/R_b = 1 - i/i_L \quad (29)$$

$$P_s/P_b = 1 + \gamma i/i_L$$

As before it is assumed that the effective mass transport coefficients of R and P are equal. γ is the ratio R_b/P_b . Substituting in equation 21,

$$i = (i_0 tS)(1/\sqrt{K_1}) \tanh(t\sqrt{K_1}) [(1-i/i_L)e^{\alpha\eta/b} - (1 + \gamma i/i_L)e^{-(1-\alpha)\eta/b}]$$

Rearranging,

$$i/i_L = \frac{(i_0 tS/i_L) (e^{\alpha\eta/b} - e^{-(1-\alpha)\eta/b})}{(t\sqrt{K_1}/\tanh(t\sqrt{K_1}) + (i_0 tS/i_L)(e^{\alpha\eta/b} + \gamma e^{-(1-\alpha)\eta/b})} \quad (30)$$

A somewhat more convenient form can be obtained as follows. From equation 22

$$K_1 = (i_0 tS/\tanh(t\sqrt{K_1})) [e^{\alpha\eta/b} + \gamma e^{-(1-\alpha)\eta/b}]$$

The limiting current is given by

$$i_L = nFDR_b q/\delta\epsilon \quad (31)$$

δ is the effective thickness of the "stagnant film" at the exterior of the electrode. q and ϵ are present to convert the effective diffusion coefficient in the porous electrode to that in the free electrolyte outside. Let

$$\psi = qt/\delta\epsilon = \frac{\text{ease of mass transport at exterior}}{\text{ease of mass transport in interior}} \quad (32)$$

Also let $i_0 tS = \bar{i}_0$ ($\bar{i}_0$ is the exchange current density for complete utilization of the electrode.) Then,

$$t^2 K_1 = (\bar{i}_0/i_L) \psi [e^{\alpha\eta/b} + \gamma e^{-(1-\alpha)\eta/b}]$$

Equation 30 now goes to

$$\frac{i}{i_L} = \frac{(\bar{i}_o/i_L)(e^{\alpha\eta/b} - e^{-(1-\alpha)\eta/b})}{\sqrt{\psi(\bar{i}_o/i_L)[e^{\alpha\eta/b} + \gamma e^{-(1-\alpha)\eta/b}] + (\bar{i}_o/i_L)[e^{\alpha\eta/b} + \gamma e^{-(1-\alpha)\eta/b}]} \tanh \frac{\sqrt{\psi(\bar{i}_o/i_L)[e^{\alpha\eta/b} + \gamma e^{-(1-\alpha)\eta/b}]}}{\sqrt{\psi(\bar{i}_o/i_L)[e^{\alpha\eta/b} + \gamma e^{-(1-\alpha)\eta/b}]}} \quad (33)$$

Equation 33 represents the complete form up to the limiting current. When i is not near i_L it reduces to the previous forms, with $R_s/R_b = 1$.

For high exchange current reactions, that is, $\bar{i}_o/i_L$ large, $i/\bar{i}_o \rightarrow 0$, equation 33 reduces to

$$i/i_L = (e^{\alpha\eta/b} - e^{-(1-\alpha)\eta/b}) / (e^{\alpha\eta/b} + \gamma e^{-(1-\alpha)\eta/b})$$

Rearranging,

$$\eta = 2.3b \log [(1 + \gamma i/i_L) / (1 - i/i_L)] \quad (34)$$

This is the expected equation for pure concentration polarization.

3.3.4 Calculation of Equations

Equation 33 contains the parameters $\bar{i}_o/i_L$, ψ , γ , α , b . For irreversible conditions, γ disappears and α , b can be combined as α/b . It will be noted that for irreversible conditions $(\bar{i}_o/i_L)$ and $e^{\alpha\eta/b}$ always occur together as $(\bar{i}_o/i_L)e^{\alpha\eta/b}$. Thus as $(\bar{i}_o/i_L)$ varies, the shape of the curve $\log (i/i_L)$ versus $\alpha\eta/b$ will be the same, but displaced by a definite increment of $\alpha\eta/b$. If we know the shape at $(\bar{i}_o/i_L)_1$ and if $\Delta\eta$ represents the bodily shift at $(\bar{i}_o/i_L)_2$,

$$(\bar{i}_o/i_L)_1 e^{\alpha\eta_1/b} = (\bar{i}_o/i_L)_2 e^{(\alpha\eta_1/b) + (\alpha\Delta\eta/b)}$$

$$\text{or} \quad \Delta\eta = (2.3)(b/\alpha) \log[(i_o/i_L)_1 / (i_o/i_L)_2] \quad (35)$$

It is convenient to compute the results in terms of i/i_L and $\alpha\eta/b = \bar{\eta}$. Then,

$$-(1-\alpha)\eta/b = \bar{\eta}[(1-\alpha)-1]$$

Reasonable values of ψ can be derived, as follows. δ is normally about 0.05 cms for unstirred electrolytes and may be 10 times lower for vigorous rates of flow past the electrode (17). q/ϵ is normally in the range 5 to 10, t may be from about 0.01 cms (a lower value may mean that the external surface reaction cannot be neglected) to say, 1 cm. Therefore

$$\psi = qt/\delta\epsilon = (5)(0.01)/(.05) = 1 \text{ minimum}$$

$$\text{or} \quad \quad \quad = 10/(.005) \quad \quad = 2000$$

For unstirred electrolytes, $q/\epsilon = 5$ and a thickness of 0.1 cm., a value of $\psi = 10$ seems reasonable. Therefore results were computed for $\psi = 1, 10, 100$. For near reversible conditions, γ was taken as 1, α as 1/2. The results are shown in Figure 2.

[Note that $\psi = 0$ means $t = 0$. When $t = 0$, the term for reaction at the external surface must be included and current from the interior neglected. Therefore $\psi = 0$ represents a solid electrode with a surface exchange current density of $\bar{i}_0$.] It can be seen from Figure 2D that as ψ becomes greater, a Tafel section is obtained with double the normal slope and this section increases in length as ψ becomes greater. However, it should be noted that when the reaction is irreversible, not near the limiting current and completely in the internal mass transport affected region ($\sqrt{K_1}$ large), equation 33 (or equation 25) reduces to

$$i/i_L = \sqrt{(\bar{i}_0/i_L)/\psi} e^{\alpha\eta/2b}$$

Since $\bar{i}_0$ and ψ are both proportional to t , it is not possible to force the system into a longer Tafel region by increasing t . If the basic exchange current is so high that no clear Tafel region exists, then increasing t will not produce a Tafel region. The apparent exchange current of this region is $i_L \sqrt{(\bar{i}_0/i_L)/\psi}$. For the case plotted in Figure 2D, when $\psi = 100$ this equals $i_L/100$, which agrees with the value obtained by extrapolation of the linear part of the curve to zero polarization.

3.4 Redox Reactions at a Porous Electrode: Ohmic Effects Included.

3.4.1 Basic Equations.

The treatment given in section 3.3 is only a limiting case of the general current-polarization relation, since it neglects the effect of ohmic voltage gradient in the pore electrolyte. The effect of potential gradient in the electrolyte within the pores of the electrode depends on the relative magnitudes of the conductivity of the electrolyte and the diffusion coefficient and concentration of the reactant. For a high concentration of supporting electrolyte (and consequently high conductivity) and a low concentration of reactant, the limiting current will be low and the polarization is controlled mainly by activation and mass transport. For a weakly conducting electrolyte and a high concentration of reactant, the activation and the ohmic effects within the pores will be the controlling factors.

Let us consider the case where the conductivity of the electrolyte is reasonably constant, even though reactant ions are being changed into product ions. This is a good assumption for a strongly supported electrolyte. Let ρ be the specific resistance of the electrolyte in the pores. Then, as before,

$$\rho = \rho^1 \epsilon / q \quad (36)$$

where ρ^1 is the free specific resistance. Ohm's law gives

$$i = (1/\rho) dV/dx \quad (37)$$

When current is being drawn from the electrode, the current is supported by ionic flow in the electrolyte in the pores. Just as in the case of mass transport, all of the current-carrying ions must pass through the external face, while only a few may be required to reach the left hand face. The voltage gradient is highest, therefore, at the external face. Unlike ohmic loss in the electrolyte away from the electrode, the voltage change in the pore electrolyte has a direct effect on the speed of the electrochemical reaction, since the pore electrolyte potential is the potential from which ions are discharging to the surface. In the equation

$$i = i_o \left((R/R_b) e^{\alpha\eta/b} - (P/P_b) e^{-(1-\alpha)\eta/b} \right)$$

the polarization must be measured between the pore electrolyte and the electrode. η will vary along the pore, being greatest at the external face, and $dV/dx = d\eta/dx$.

The equations to be solved are now

$$di = i_o S \left((R/R_b) e^{\alpha\eta/b} - (P/P_b) e^{-(1-\alpha)\eta/b} \right) dx$$

$$di = nFD(d^2R/dx^2) dx$$

$$i = (1/\rho) d\eta/dx .$$

The boundary conditions are

$$dR/dx = 0 \text{ at } x = 0$$

$$R = R_s \text{ at } x = t$$

$$\eta = \eta_s \text{ at } x = t$$

$$\eta = \eta_o \text{ at } x = 0.$$

The total interior current is given by

$$i = D(dR/dx)_{x=t} = (1/\rho) (d\eta/dx)_{x=t}.$$

As before, we can assume the mass transport factors of R and P to be equal and constant and

$$R + P = R_b + P_b$$

$$\text{or} \quad P/P_b = (\gamma + 1) - R/P_b$$

Combining the ohmic and mass transport equations

$$(1/\rho) d\eta/dx = nFD \int_0^x (d^2R/dx^2) dx$$

Since $dR/dx = 0$ at $x = 0$,

$$\int d\eta = \rho n F D \int dR$$

$$\eta_s - \eta = \rho n F D (R_s - R) \quad (38)$$

We are now in a position to compare the relative effects of mass transport and internal ohmic voltage gradient. For example, if $R = 0$ at $x = 0$, $R_s = 10^{-3}$ gm. mole/cm.³, $\rho = 50$ ohm cm., $n = 1$, $D = 10^{-6}$ cm.²/sec., then $\eta_s - \eta_0 \simeq 0.5$ millivolts. Such a small change in voltage will not produce much effect compared to the corresponding depletion of reactant in the interior of the electrode. As current density is increased, the penetration into the electrode at which R becomes nearly zero becomes smaller and due to this mass transport effect the reaction is concentrated in the region towards the right hand face of the electrode. Then the mean path through which ions have to travel becomes less and although i becomes greater and hence $d\eta/dx$ becomes greater, this is accomplished by x being smaller and not by η becoming greater; $\eta_s - \eta$ remains the same.

$\eta_s - \eta$ becomes greater as ρ and R_s become greater. However, if R_s is an ion it is not possible to make the specific resistance ρ greater while increasing or maintaining R_s . To make the internal voltage effect outweigh the mass transport effect it would appear to be necessary to use low conductivity solutions with a high concentration of a non-conducting reactant.

The complete equations can be written as follows. From equation 38

$$R = R_s - (\eta_s - \eta) / \rho n F D \quad (39)$$

Combining the kinetic and ohmic equations gives

$$\begin{aligned} (1/\rho) d^2 \eta / dx^2 &= i_0 S \left((R/R_b) e^{\alpha \eta / b} - (P/P_b) e^{-(1-\alpha) \eta / b} \right) \\ &= i_0 S \left[(e^{\alpha \eta / b} / R_b) + (e^{-(1-\alpha) \eta / b} / P_b) \right] R \\ &\quad - i_0 S (\gamma + 1) e^{-(1-\alpha) \eta / b} \end{aligned}$$

Substituting for R from equation 39

$$(1/\rho i_0 S) d^2 \eta / dx^2 = [(e^{\alpha \eta / b} / R_b) + (e^{-(1-\alpha) \eta / b} / P_b)] [R_s - (\eta_s - \eta) / \rho n F D] - (\gamma + 1) e^{-(1-\alpha) \eta / b} \quad (40)$$

Equation 40 is the equation relating polarization to distance through the electrode.

3.4.2 Limiting Cases.

Case 1. Low resistance, low current density, R small.

This would apply for a low concentration of reactant and a high concentration of supporting electrolyte. Under these circumstances, the mass transport limited currents would be low; the limit at which ohmic effects are negligible is the case which has been dealt with in section 3.3. Mathematically, from equation 38 this limit is given by $\eta_s - \eta$ being small, for low values of ρ and R_s . This case is probably the most widely applicable.

Case 2. High exchange current: pure concentration polarization.

For very high exchange currents, a slight deviation from the reversible potential will give a large current. Therefore, as discussed in section 3.3.1, the reaction will be accomplished in a thin layer at the outside of the electrode. As this layer tends to zero thickness, that is $dx \rightarrow 0$, both dr and $d\eta$ tend to zero and the electrolyte in the interior of the electrode is at almost the same concentration and potential as at the surface. Equations 26 and 34 then apply at this limit.

Case 3. Very low conductivity, high reactant concentration, high current.

This case applies when the currents being drawn are great enough compared to the conductivity and small enough compared to the mass transport that ohmic polarization is large without the values of R being much changed. Mathematically, from equation 38, $\eta_s - \eta$ must be large for $R_s - R$ small. For example, a change of R from R_s to $0.9R_s$ will not produce much change in rate or polarization. The change in polarization through the electrode is then

$$\eta_s - \eta \simeq \rho n F D (R_s / 10)$$

For $\rho = 10000$ ohm cm., $R_s = 2N = 2(10^{-3})$ gm. moles/cm.³, $D = 10^{-6}$ cm.² sec.⁻¹, $\eta_s - \eta$ would be 0.2 volts. Such a voltage change would completely outweigh the effect of change in R. The equation to be solved is then

$$d^2\eta/dx^2 = \rho i_0 S [(R_s/R_b) e^{\alpha\eta/b} - (P_s/P_b) e^{-(1-\alpha)\eta/b}] \quad (41)$$

The physical picture is as follows. At the left hand face of the electrode, with a polarization η_0 , the current being produced is very small. However, this small current produces a small ohmic gradient which increases η as we proceed from left to right. The larger η produces a larger current increment and, since the total current is additive, the ohmic effect becomes greater and greater. The exponential nature of the current increment versus polarization means that at some cumulative polarization the current will increase extremely rapidly and most of the reaction occurs towards the right hand face of the electrode. It is clear that very small changes in η_0 will produce very large changes in η_s and the final current. Thus we may cover several orders of magnitude of current with an almost constant value of η_0 . The value of η_0 for a given order of magnitude of current will depend on Si_0 . Again, two limiting cases can be considered.

Case 3A. Low exchange current.

Let us consider the case where the effective exchange current Si_0 is so low that η_0 must be fairly large before appreciable current is obtained. For this irreversible condition, the negative exponential term in equation 41 can be neglected and

$$d^2\eta/dx^2 = \rho i_0 S (R_s/R_b) e^{\alpha\eta/b} \quad (42)$$

Letting $\eta = \eta_0 + \Delta\eta$,

$$d^2(\Delta\eta)/dx^2 = \rho i_0 S (R_s/R_b) e^{\alpha\eta_0/b} e^{\alpha\Delta\eta/b} \quad (42a)$$

The boundary conditions are now $\Delta\eta = 0$ at $x = 0$, $d(\Delta\eta)/dx = 0$ at $x = 0$. For

very low values of $\rho i_0 S (R_s/R_b) e^{\alpha \eta_0/b}$, the current is small, ohmic effects are negligible and $d^2 \Delta \eta / dx^2 \rightarrow 0$. Equation 42a can be put as

$$d(\Delta \eta / dx) = \rho i_0 S (R_s/R_b) e^{\alpha \eta_0/b} \int_0^x e^{\alpha \Delta \eta / b} dx.$$

When $d^2 \Delta \eta / dx^2 \rightarrow 0$, $\Delta \eta \rightarrow 0$,

$$= \rho i_0 S (R_s/R_b) e^{\alpha \eta_0/b} x$$

Since $i = (1/\rho) (d\eta/dx)_{x=t}$,

$$i = i_0 S t (R_s/R_b) e^{\alpha \eta_0/b}$$

This, of course, is the required Tafel form with uniform utilization of the electrode. The more interesting case is when $\rho i_0 S e^{\alpha \eta_0/b}$ is high enough to make $\Delta \eta$ appreciable, so that the bulk of the reaction occurs in a layer near the external face. Putting $\rho i_0 S (R_s/R_b) e^{\alpha \eta_0/b} = k$ and $\alpha/b = a$, the equation is

$$d^2(\Delta \eta) / dx^2 = k e^{a \Delta \eta}$$

Let $y = d(\Delta \eta) / dx$ then $d^2 \Delta \eta / dx^2 = dy/dx = (dy/d\Delta \eta) y$.

Then

$$y dy / d(\Delta \eta) = k e^{a \Delta \eta}$$

$$\text{and } y^2 / 2 = (k/a) e^{a \Delta \eta} + C$$

$$\text{or } d\Delta \eta / dx = [(2k/a) e^{a \Delta \eta} + C]^{1/2}$$

When $x = 0$, $\Delta \eta = 0$ and $d(\Delta \eta) / dx = 0$, therefore $C = -(2k/a)$ and

$$d(\Delta \eta) / dx = [(2k/a) e^{a \Delta \eta} - (2k/a)]^{1/2} \quad (43)$$

Thus the total current is

$$\begin{aligned} i &= (1/\rho) [d(\Delta \eta) / dx]_{x=t} \\ &= (1/\rho) \sqrt{(2k/a)} (e^{a(\eta_s - \eta_0)} - 1)^{1/2} \\ &= (1/\rho) \sqrt{2 \rho i_0 S (R_s/R_b) e^{\alpha \eta_0/b} b / \alpha} (e^{\alpha(\eta_s/\eta_0)/b} - 1)^{1/2} \end{aligned}$$

(44)

When $\exp[\alpha(\eta_s - \eta_0)/b]$ is large enough for the 1 to be negligible,

$$i = \sqrt{\frac{2i_0 S(R_s/R_b)b}{\alpha \rho}} e^{\alpha\eta_s/2b} \quad (45)$$

For $R_s/R_b = 1$, the plot of $\log i$ versus η_s is a Tafel form with double the usual slope. The apparent "exchange current" is dependent on ρ .

Case 3B. High exchange current.

Letting $R_s/R_b = 1$, $P_s/P_b = 1$, equation 41 can be written as

$$d^2\eta/dx^2 = 2\rho i_0 S \sinh(\alpha\eta/b) \quad (46)$$

This has been solved by Stender and Ksenzhak (3). (See also Section 4.2).

For the boundary condition of $\eta_0 \rightarrow 0$, (that is, high exchange current and thick electrodes)

$$i = \sqrt{\frac{2i_0 S b}{\alpha \rho}} (e^{\alpha\eta/2b} - e^{-(1-\alpha)\eta/2b}) \quad (47)$$

We will not discuss equations 45 or 47 at this point, because the conditions under which they apply will be very rarely met in the type of system considered here. In this respect we disagree with Stender and Ksenzhak, who calculated results at $\rho = 50$ ohm-cm, assuming uniform concentration of reactant throughout the electrode. Equation 38 shows that $\eta_s - \eta_0$ would be only a fraction of a millivolt, with complete internal mass transport control of the process for such a resistance and a feasible reactant concentration. For the same reasons, we will not compute equation 40 since it is felt that the ohmic effect will be small.

Another interesting case is that where no supporting electrolyte is present and the product is non-ionic. The specific resistance is then given by

$$\rho = \rho_s (R_s/R) \quad (48)$$

where ρ_s is the resistance at concentration R_s . For 1 N solution, $R_s = 10^{-3}$

moles/cm³ and ρ_s is about 50 ohm cm maximum. (allowing for porosity, tortuosity factors). The ohmic and mass transport equations now combine to give

$$d\eta/dx = \rho_s n F D R_s (1/R) \int_0^x (d^2 R/dx^2) dx$$

Since $dR/dx = 0$ at $x = 0$,

$$\int d\eta = \rho_s n F D R_s \int (1/R) dR$$

$$\eta_s - \eta = \rho_s n F D R_s 2.3 \log(R_s/R) \quad (49)$$

Since $\rho_s R_s$ is about $5(10^{-2})$, D is about 10^{-6} ,

$$\eta_s - \eta \simeq (1/100) \log(R_s/R)$$

$$\sim 10 \log(R_s/R) \text{ millivolts.}$$

A value of R_s/R of 100 would represent large mass transport effects in the pore electrolyte, but $\eta_s - \eta$ would be only 20 millivolts. Therefore, although the ohmic effect is much greater in this case, it may not cause a very pronounced deviation from the treatment of section 3.3. It should be noted that at a given current density, the treatment of section 3.3 gives a value of η which lies between η_o and η_s . Therefore, the deviation of η from η_s is some fraction of $\eta_s - \eta_o$, not the total amount. The complete equations can be set up as follows. The combined mass transport-electrochemical equation is equation 18

$$d^2 R/dx^2 = (i_o S/nFD) [(R/R_b) e^{\alpha\eta/b} - (P/P_b) e^{-(1-\alpha)\eta/b}]$$

The measured polarization is that at the surface, η_s and from equation 49,

$$e^{\alpha\eta/b} = (R/R_s)^{\alpha\rho_s n F D R_s/b} e^{\alpha\eta_s/b}$$

Substitution of this into the preceding equation gives the final form. The effect of ohmic voltage gradient is given by the factor

$$(R/R_s)^{\alpha \rho_s b F D R_s / b}$$

For $\alpha = 1/2$, $b = 0.026$ at room temperature and $\rho_s n F D R_s \sim 5/1000$ we get

$$(R/R_s)^{\alpha \rho_s n F D R_s / b} \simeq (R/R_s)^{1/10}$$

At $R/R_s = 10^{-3}$, the factor is $10^{-0.015} = 0.93$, therefore, the deviation from 1 is not great and the solution of equation 18 as before can be used. Although $\eta_s - \eta_o$ may be appreciable, η_s lies close to, but a bit greater than, the value of η calculated from equation 33. The physical meaning here is that the ohmic effect is small until R/R_s is small, that is, well within the electrode. But most of the reaction occurs towards the outer face of the electrode so that $\eta_s \approx \eta$ effective. η_o may be markedly different to η_s , but very little reaction occurs at η_o conditions due to the low value of R .

3.5 Effect of Double Electrode Structure

The previous treatments have assumed that the electrode is homogeneous with penetration and that the polarization is measured adjacent to the exposed face of the electrode. If a double layer structure is employed, as shown in Figure 3, the mass transfer coefficient in the outer layer is different to that in the free electrolyte. Let us suppose that the inner layer is the active electrode material, while the outer layer is inert electrochemically. The polarization, and the value of R_s , to be used in the previous equations are those at t , whereas the polarization is measured at L .

If ϵ/q is the porosity-tortuosity factor for the coarse layer, and δ is the effective "film thickness" in the free electrolyte,

$$i = n F D (R_b - R_s) 1 / [(Lq/\epsilon) + \delta]$$

$$i_L = n F D R_b / [(Lq/\epsilon) + \delta] \quad (50)$$

and

$$R_s/R_b = 1 - i/i_L$$

This is the result used previously, except that i_L now depends on the values

of L , q and ϵ of the outer layer.

For example, if L is 0.05 cms and q/ϵ is 5 (a reasonable figure), the term Lq/ϵ is 0.25 cms. This is five times the effective δ of 0.05 cm. for unstirred electrolytes, therefore i_L will be only 1/6 of the usual limiting current.

The ohmic voltage drop in the coarse layer is

$$\Delta\eta = i\rho'Lq/\epsilon \quad (51)$$

The measured polarization must be corrected for this $\Delta\eta$ before experimental results are compared to theoretical expectations. For a large conductivity, $\rho'q/\epsilon \simeq 10$ ohm cm and for $L = 0.05$ cm, $i = 100$ mamps/cm², $\Delta\eta = 50$ millivolts.

It is apparent that the use of a double layer structure is a big disadvantage where the limiting factor is the mass transport of reactant from the bulk of the electrolyte to the reacting electrode.

(4) GAS DIFFUSION ELECTRODES (THREE PHASE SYSTEMS)

4.1 General Introduction

The mode of operation of a gas diffusion electrode is, in general, more difficult to describe mathematically than a simple redox system. The principal difficulty is that the processes occurring at the three phase boundary are not known with any degree of certainty. It is necessary to choose a simplified model of what we think is happening. If an attempt is made to allow for every possible factor, the model becomes so complex that extensive computation is required. It would appear to be more reasonable to start with the simplest models, determine how these would behave, and compare the theory to experimental values. For example, a simple model which might be applicable under certain conditions is shown in Figure 4. In this model it is assumed that the bulk of the electrolyte is stabilized in the macro-pore system of the electrode, but that a thin film of electrolyte covers, and penetrates into, the micropore system. Reaction occurs by diffusion of gas through the film, followed by adsorption and reaction on the active surface. The current must be supported by movement of ions through the thin film of

electrolyte, parallel to the active surface. If the "film" is so thick that it fills the pore, then gas will not be able to diffuse to the active surface fast enough to support much current. On the other hand, if the film is very thin, the horizontal ionic mass transport and conductivity in the film will be too low to support much current. Thus this model can only apply if the film thickness is considerably less than the macropore size (10 microns, say), but much thicker than a few molecules.

The treatment of such systems may sometimes reduce to similar forms to those considered before, but it might be expected that fresh formulae will have to be derived in some cases.

4.2. Thin Film Model: Hydrogen Fuel in Acid Electrolyte.

The case of hydrogen fuel used at a porous diffusion electrode in acid electrolyte is exceptional for two reasons. Firstly, there is no ionic reactant from the electrolyte. Unlike redox systems, the system does not have equimolar counter-current mass transport of reactant and product ions. Mass transport limitations occur for dissolved hydrogen diffusing through the film thickness W , and for H^+H_2O diffusing horizontally away from the area of reaction. (However, H_2O can be considered as a reactant.) Secondly, hydrogen ion has a high mobility compared to other ions. For these reasons, we have to consider anew the problem of mass transport polarization versus ohmic potential gradient.

Let us consider the mass transport of product hydrogen ion, with concentration denoted by P . Consider a differential element dx through the electrode. At steady state, the mass transport of P along the film (assumed linear) is related to current by

$$i = -nFD_p(dP/dx)(AW/q) \quad (52)$$

A is the macropore perimeter (per sq. cm. of electrode face) and W is the mean thickness of the film, therefore the cross-sectional area for horizontal mass transport is AW ; q is the tortuosity factor. This neglects geometric effects, but the geometry of the pores of an actual electrode is likely to be

complex, and the linear approximation is probably as valid as assuming some other geometry, e.g., a cylindrical geometry. The ohmic effect, again taking a linear approximation, is

$$i = (1/\rho')(d\eta/dx)(AW/q) \quad (53)$$

Combining and integrating equations 52 and 53

$$\eta_s - \eta = \rho' n F D_p (P - P_s) \quad (54)$$

where η_s , P_s refer to the polarization and concentration at the junction of the thin film and the bulk pore electrolyte. As the current density becomes greater, hydrogen ion builds up in the film and the specific resistance goes down. The minimum specific resistance is about 2 ohm cm and ρ' will normally be higher than this; D for hydrogen ion is about 10^{-4} , therefore,

$$\eta_s - \eta > 20(P - P_s)$$

P can easily increase from 1 N to 10 N, giving an ohmic voltage change of at least 200 millivolts. Thus, in this case, the large effective diffusion coefficient of hydrogen ion combined with the large possible concentrations make ohmic effects appreciable compared to mass transport effects.

Since there is no counter-current flow of reactant product ions, the outward mass transport of hydrogen ion leads to, at steady state, a diffusive inflow of water. Since water is not discharged, this must be matched by an outward bulk flow of electrolyte. As before (see section 3.2), when P is not very high the outward flow of water will not much increase the effective diffusion coefficient of P . We will assume as a first approximation that the activity of water remains 1. We will also assume that the specific resistance of the film is constant.

Case 1. Reversible Electrochemical Reaction.

For a good surface catalyst such as highly active platinum it is possible that the electrochemical reaction remains close to reversible at all current densities. Then the polarization at any point x in the thin

film is related to the concentration of dissolved hydrogen at the active surface, H say, and the concentration of P , such that

$$\eta = (RT/F) \ln[(H_b/H)^{1/2}(P/P_b)]$$

H_b is dissolved H_2 concentration corresponding to saturation at the pressure of the gas in the pore. Or

$$e^{-2\eta/b} = (H/H_b)(P/P_b)^2$$

Let us assume, again as a first approximation, that for concentrated acid solutions the variation of P/P_b along the film can be neglected. Also we will assume that mass transport of dissolved hydrogen occurs across W , that is, it is a linear process perpendicular to the active surface. It is also assumed that mass transport resistance in the gas phase is negligible. Then, since $A dx$ is cross section for vertical mass transport,

$$di = (2FD/W)(H_b - H)A dx$$

$$\text{or } H/H_b = 1 - (W/2FDH_b) di/dx \quad (55)$$

Substituting into the previous equation for polarization,

$$e^{-2\eta/b} = 1 - (W/2FDH_b) di/dx$$

But from equation 53

$$di/dx = (AW/q\rho') d^2\eta/dx^2,$$

therefore,

$$d^2\eta/dx^2 = k(1 - e^{-2\eta/b}) \quad (56)$$

where

$$1/k = W^2/2FDH_b q\rho' \quad (57)$$

The total current density is given by

$$i = (AW/\rho'q) (d\eta/dx)_{x=t} \quad (58)$$

t is the length of the thin film up to the bulk pore electrolyte.

The partial solution of equation 56 can be obtained as follows. Let $d\eta/dx = y$, then

$$d^2\eta/dx^2 = \frac{dy}{dx} = \frac{d\eta}{dx} \frac{dy}{d\eta} = y dy/d\eta$$

Thus equation 56 goes to

$$y dy/d\eta = k(1 - e^{-2\eta/b})$$

Separating and integrating,

$$y^2/2 = k\eta + (bk/2)e^{-2\eta/b} + C$$

or

$$d\eta/dx = (2k\eta + (4bk)e^{-2\eta/b} + C)^{1/2}$$

From the boundary condition that $d\eta/dx = 0$ at $x = 0$ (since $i = 0$ at $x = 0$), $C = -(2k\eta_0 + 4bke^{-2\eta_0/b})$ and

$$d\eta/dx = \sqrt{2k} [(\eta - \eta_0) + (b/2)(e^{-2\eta/b} - e^{-2\eta_0/b})]^{1/2} \quad (59)$$

This, of course, is only a partial solution since η_0 is unknown.

Let us consider low polarization conditions where η is low. Then, using the exponential expansion and neglecting higher power terms than η^2 ,

$$\begin{aligned} d\eta/dx &= \sqrt{2k} (\eta - \eta_0 + \frac{b}{2} - \eta + \frac{\eta^2}{b} - \frac{b}{2} + \eta_0 - \frac{\eta_0^2}{b})^{1/2} \\ &= (\eta^2 - \eta_0^2) (2k/b)^{1/2} \end{aligned}$$

Separating and integrating,

$$\ln[(\eta + \sqrt{\eta^2 - \eta_0^2})/C] = \sqrt{2k/b} x$$

When $x = 0$, $\eta = \eta_0$, therefore $C = \eta_0$ and

$$\eta + \sqrt{\eta^2 - \eta_0^2} = \eta_0 e^{\sqrt{2k/b} x}$$

and

$$\eta^2 - \eta_0^2 = \eta_0^2 e^{2\sqrt{2k/b} x} + \eta^2 - 2\eta_0\eta e^{\sqrt{2k/b} x}$$

or

$$\eta = (1/2)\eta_0 (e^{\sqrt{2k/b} x} + e^{-\sqrt{2k/b} x})$$

At $x = t$, $\eta = \eta_s$; therefore

$$\eta/\eta_s = (e^{\sqrt{2k/b} x} + e^{-\sqrt{2k/b} x}) / (e^{\sqrt{2k/b} t} + e^{-\sqrt{2k/b} t}) \quad (60)$$

Therefore, from equation 58

$$i = (AW/\rho'q)\eta_s \sqrt{2k/b} \tanh(\sqrt{2k/b} t) \quad (61)$$

The result obtained is that i is directly proportional to η_s , which is the measured polarization (allowing, of course, for ohmic drop in the bulk of the electrolyte). The slope is

$$\begin{aligned} & (AW/\rho'q) \sqrt{\frac{4FDH_b q \rho'}{W^2 b}} \tanh \sqrt{\left(\frac{4FDH_b q \rho'}{b}\right) \left(\frac{t}{W}\right)^2} \\ & = \sqrt{(2AFDH_b)(A/\rho'q)(2/b)} \tanh \sqrt{(2FDH_b)(2q\rho'/b)(t/W)^2} \end{aligned} \quad (61a)$$

Good estimates can be made of all of these terms except t/W . t/W can be replaced by a measurable quantity by expressing it in terms of the limiting current density i_L .

The limiting current is obtained when $H \rightarrow 0$ along all of the thin film, therefore from equation 55,

$$i_L = (t/W) 2FDAH_b \quad (62)$$

For example, $2FDH_b$ at room temperature and 1 atmosphere of H_2 is about 10^{-6} . For a value of A of $10^3 \text{ cm}^2/\text{cm}^3$

$$\begin{aligned} i_L &= (t/W) 10^{-3} \text{ amps/sq. cm.} \\ &= (t/W) \text{ milliams/sq. cm.} \end{aligned}$$

Thus, values of t/W of the order of 100 appear reasonable, assuming that the limiting currents observed experimentally are due to the physical model discussed above.

When the term $\sqrt{(8FDH_b)(q\rho'/b)(t/W)^2}$ is small (< 0.1) the tanh term reduces in the form $\tanh x = x$. Then

$$i = 2(2AFDH_b/b)(t/W) \eta_s \quad (61a)$$

$$\text{or} \quad i/i_L = 2\eta_s/b$$

The slope is now independent of the specific resistance of the electrolyte. This is the case of pure concentration polarization with negligible ohmic effect. When the tanh term reduces in the form $\tanh x = 1$, ($x > 2$)

$$i = \sqrt{(2AFDH_b)(A/\rho'/q)(2/b)} \eta_s \quad (62a)$$

The apparent conductivity is now proportional to the square root of the true specific conductivity.

Returning to equation 59 to consider the full form of the equation, it can be seen that it does not have a convenient general solution. However, physical reasoning tells us that if the ohmic effect through the thin film is large, then η_o will be small. In fact, at any given current density the value of η_o is less than η_c which is less than η_s , where η_c is the polarization which would be obtained from simple concentration polarization (of the hydrogen through the thin film). η_c is given by

$$\eta_c = (2.3)(b/2) \log\left(\frac{1}{i - i/i_L}\right)$$

Thus η_c is not large until i approaches i_L . Since η_o is much less than η_c when the ohmic effect is large (that is, t/W is large) then η_o will approach zero except for conditions near the limiting current. Therefore, equation 59 can be put in the form

$$d\eta/dx = \sqrt{2k} \left[\eta_s - \frac{b}{2}(1 - e^{-2\eta_s/b}) \right]^{1/2}$$

From equation 58, then,

$$i = (AW/\rho'q) \sqrt{\frac{4FDH_b q\rho'}{W^2}} \left[\eta_s - \frac{b}{2}(1 - e^{-2\eta_s/b}) \right]^{1/2}$$

$$= \sqrt{(2AFDH_B)(2A/q\rho') [\eta_s - \frac{b}{2}(1-e^{-2\eta_s/b})]^{1/2}}$$

As expected, this reduces to equation 62a when η_s is small. The equation can be put into a form suitable for computation by noting that $2AFDH_B t/W = i_L$ and $q\rho' t/AW = \bar{\rho}$, the resistance of the electrolyte (for 1 sq. cm. of electrode) in the thin film of cross-section AW and length t. Then equation 63 can be put as

$$i = \sqrt{(i_L/\bar{\rho})(b/2)} [(2\eta_s/b) - (1-e^{-2\eta_s/b})]^{1/2}$$

Letting $2\bar{\rho}/b = r$, $\eta_s/b = \bar{\eta}$

$$i = \sqrt{i_L/r} [(2\bar{\eta}) - (1-e^{-2\bar{\eta}})]^{1/2} \quad (63a)$$

For a given system i_L , r are constants while $\bar{\eta}$ is the polarization as multiples of $b(=RT/F = 0.025$ volt at room temperature). The form of the equation is shown in Figure 5. It must be remembered that the equation is not valid at the limiting current, therefore, Figure 5 does not show any limiting current. For values of $2\bar{\eta}$ greater than about 2

$$i \propto \sqrt{(2\eta/b) - 1} \quad (63a)$$

Thus i^2 versus η is a straight line.

Figure 6 shows the very pronounced effect which r has for a given limiting current. However, it is unlikely that a process will have a high limiting current ($\propto t/W$) with a low value of r ($\propto t/W$). Referring to equation 63, it will be seen that parameters which decrease polarization at a given current are A and H_B . However, if A is made too large, the free gas space will become small and gas transport restrictions will occur. H_B can be increased by increasing pressure, according to a Henry's law relation.

Case 2. Low Exchange Current Reaction.

In the case considered previously, the ohmic effect along the thin film of electrolyte came into balance with the mass transport of hydrogen through the thin film. For low exchange current reactions, the ohmic effect

can also come into balance with the kinetic polarization. For long thin films, it is possible that mass transport through the film is rapid even at fairly high currents and ohmic voltage gradients in the film. Then, providing the current is not of the same order of magnitude as the limiting current, we may set H/H_b constant. The situation now corresponds to that discussed in Case 3, section 3.4.2. Case 3B, that of high exchange currents, will clearly tend to the reversible condition treated above as Case 1, section 4.2. Therefore, we would not expect it to be possible to consider it without allowing for mass transport of hydrogen through the thin film. However, for Case 3A, that of low exchange current, we may be able to neglect mass transport effects providing we are well away from the limiting current. Then

$$di/dx = i_o S e^{\alpha\eta/b}$$

and

$$di/dx = (AW/q\rho') d^2\eta/dx^2$$

Therefore,

$$d^2\eta/dx^2 = (q\rho' i_o S/AW) e^{\alpha\eta/b} \quad (64)$$

The assumption implicit in equation 64 is that the exchange current is so low that the polarization at $x = 0$, η_o say, must be large (large enough for $e^{-(1-\alpha)\eta_o RT}$ to be negligible) before enough current is produced to give an appreciable ohmic effect. As before, we can derive an equivalent equation to equation 43,

$$d(\Delta\eta)/dx = [(2kb/\alpha) e^{\alpha\Delta\eta/b} - (2kb/\alpha)]^{1/2}$$

where k is now

$$k = (q\rho' i_o S/AW) e^{\alpha\eta_o/b} \quad (64a)$$

Let $e^{\alpha\Delta\eta/b} = y$, $dy/d\Delta\eta = (\alpha/b) e^{\alpha\Delta\eta/b} = (\alpha/b)y$. Then, separating and integrating,

$$\begin{aligned}
 \sqrt{2kb/\alpha} x &= \int_0^x \frac{d(\Delta\eta)}{\sqrt{e^{\alpha\Delta\eta/b} - 1}} \\
 &= \int_0^x \frac{dy}{(\alpha/b)y \sqrt{y-1}} \\
 &= (b/\alpha) 2 \tan^{-1}(\sqrt{y-1}) + C \\
 &= (2b/\alpha) \tan^{-1}(e^{\alpha\Delta\eta/b} - 1)^{1/2} + C
 \end{aligned}$$

When $x = 0$, $\Delta\eta = 0$, therefore $C = 0$ and

$$e^{\alpha\Delta\eta/b} - 1 = (\tan x \sqrt{k\alpha/2b})^2$$

or

$$(\alpha/b)(\eta_s - \eta_o) = \ln[(\tan t \sqrt{k\alpha/2b})^2 + 1] \quad (65)$$

Differentiating with respect to x ,

$$(\alpha/b) d\eta/dx = 2 \sqrt{k\alpha/2b} \tan(x \sqrt{k\alpha/2b})$$

Since $i = (AW/q\rho')(d\eta/dx)_{x=t}$

$$\begin{aligned}
 i &= (AW/q\rho') \sqrt{2kb/\alpha} \tan(t \sqrt{k\alpha/2b}) \\
 &= \sqrt{(AW i_o S / q\rho') (2b/\alpha)} e^{\alpha\eta_o/2b} \tan(\sqrt{q\rho' i_o S / AW} (\alpha/2b) t e^{\alpha\eta_o/2b}) \quad (66)
 \end{aligned}$$

This is the explicit relation between i and η_o , while equation 65 allows η_s to be calculated. They can be expressed in convenient parameters by noting that the total exchange current density of the electrode is $\bar{i}_o = i_o S t$, while the resistance of the thin film of electrolyte (for 1 sq. cm. of electrode face) is $q\rho' t / AW = \bar{\rho}$ say, then

$$i = \sqrt{(\bar{i}_o / \bar{\rho}) (2b/\alpha)} e^{\alpha\eta_o/2b} \tan(\sqrt{(\bar{i}_o / \bar{\rho}) (\alpha/2b)} e^{\alpha\eta_o/2b}) \quad (66a)$$

For low values of the $\tan$, that is, low values of $e^{\alpha\eta_o/2b}$ (and current), $\tan x = x$, therefore

$$i = \bar{i}_o e^{\alpha\eta_o/b}$$

and $\eta_s = \eta_o$. This is the required logical result, since we assumed an irreversible Tafel form as our basic equation. As the tangent becomes large, from equation 65, neglecting the 1, $\tan = \exp[(\alpha/2b)(\eta_s - \eta_o)]$ and

$$i = \sqrt{(\bar{i}_o/\bar{\rho})(2b/\alpha)} e^{\alpha\eta_s/2b}$$

This is the corresponding form to equation 45. The full form of the equation can be computed considering as parameters $\bar{\rho}\alpha/2b = r$ say, $\alpha\eta/b = \bar{\eta}$, then

$$i = \sqrt{\bar{i}_o/r} e^{\bar{\eta}_o/2} \tan(\sqrt{\bar{i}_o r} e^{\bar{\eta}_o/2})$$

$$\bar{\eta}_s - \bar{\eta}_o = \ln[(\tan \sqrt{\bar{i}_o r} e^{\bar{\eta}_o/2})^2 + 1]$$

or

$$i/i_o = (1/A) e^{\bar{\eta}_o/2} \tan(Ae^{\bar{\eta}_o/2})$$

$$\bar{\eta}_s - \bar{\eta}_o = 2.3 \log[(\tan(Ae^{\bar{\eta}_o/2}))^2 + 1]$$

$$\text{where } A = \sqrt{\bar{i}_o r} \text{ (dimensionless)}$$

When $\sqrt{\bar{i}_o r} e^{\bar{\eta}_o/2} = \pi/2$, the tangent is infinity and $\bar{\eta}_s$ is infinity. Therefore the maximum value of $\bar{\eta}_o$ for a given system is given by

$$(\bar{\eta}_o)_{\max} = 2 \ln(\pi/2 \sqrt{\bar{i}_o r}) \quad (67)$$

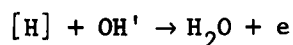
$(\bar{\eta}_o)_{\max}$ cannot be small, since we have assumed an irreversible reaction, therefore equation 67 only applies when $\bar{\eta}_o$ is greater than about 2.

The forms of the results are shown in Figure 7, where i/i_o is plotted versus $\bar{\eta}_o$, $\bar{\eta}_s$ for various values of $\bar{i}_o r$. [The order of magnitude of r can be decided by taking $q\rho'$ as of the order of 10, A as of the order of 10^3 , t/W as in the range 10 to 1000 and $\alpha/2b$ as approximately 10. Then r would be expected

to range from 1 to 100.] As expected, for a given value of i_0 , a decrease in the value of r gives a lower polarization at high current densities and a more extended true Tafel line. The current density at which the double Tafel slope line takes over is higher. Alternatively, for a given value of r a bigger exchange current has the same effect.

4.3. Thin Film Model: Hydrogen Fuel in Alkaline Electrolyte

In strongly alkaline electrolyte the reaction probably involves hydroxyl (14), as follows,



In this case we do have an ionic reactant from the electrolyte and therefore we would expect mass transport of OH' in the thin film to be a critical factor. As in the case of redox reactions, the concentration of the hydroxyl ion will tend to zero at $x = 0$ and equation 33 (and its reduced forms) may apply. It should be noted that the thin film of electrolyte may have a low conductivity due to its narrow cross-section. However, the effective mass transport of ion in the thin film will also be low, by exactly the same ratio. Therefore, what was said before about the relative effects of mass transport to ohmic effects will still apply (see section 3.4.1). The ohmic effect should be considered as a disturbance of the basic relation of equation 33, and it will give somewhat higher total polarizations than predicted by equation 33. The effect will be most marked at high current densities, therefore it leads to a more gradual approach to the limiting current than expected.

The relative ease of mass transport at the exterior to that in the interior, ψ , is given for the thin film model, by

$$\psi = qt/\delta AW \quad (68)$$

Comparing with equation 32, it is seen that ϵ is replaced with AW . AW cannot be greater than ϵ . For $A = 10^3$, $W = 1$ micron, AW is $1/10$. This compares with a value of ϵ of about $1/3$. Of course, W might be considerably

less than 1 micron.

4.4. Non Thin-film Model: Saturated Electrode

Another physical model which might be applicable under certain conditions is one where no extended thin film exists. This would apply to a fully saturated electrode. In this case the reactant gas has to diffuse into the electrolyte in the macropores. When current is drawn, the reactant gas in the interior will be rapidly used up and the reaction will be concentrated at the gas-electrolyte face. Ohmic polarization increases from this face towards the bulk electrolyte and this will have the effect of speeding up internal reaction, giving rise to low internal dissolved gas concentrations, which again means that the reaction is concentrated towards the gas entry face. This is opposite to the ionic mass transport case, in which the concentration of reactant ion decreases from the free electrolyte face back into the electrode. For the ionic case, reaction is concentrated at the electrode-bulk electrolyte face and consequently the path of the current-carrying ions does not penetrate deeply into the electrode. For the dissolved gas case, the current-carrying ions have to travel right through the pores of the electrode to (or from) the reaction site and, therefore, ohmic effects within the pore electrolyte are much greater than for the ionic case.

Let us consider the case where the electrochemical reaction is reversible, where the principal mass transport effect is that of dissolved reactant gas and where the dissolved gas has to diffuse linearly along the axis of the pore. If the concentration of dissolved gas is R , and the equilibrium concentration at the gas pressure used is R_b ,

$$\eta = (RT/nF) \ln(R_b/R)$$

If D is the effective diffusion coefficient of dissolved gas,

$$di/dx = nFD(d^2R/dx^2) \quad (69)$$

Also

$$i = (1/\rho) d\eta/dx$$

The boundary conditions are $i = 0$ at $x = 0$, $R = R_o$ at $x = 0$ and $i_t = -nFD(dR/dx)_{x=0}$, where i_t is the final current density. Integrating equation 69 from $x = 0$ to $x = x$,

$$i = nFD(dR/dx) - nFD(dR/dx)_{x=0} = i_t + nFD dR/dx$$

Therefore,

$$d\eta = \rho i_t x + \rho nFD dR$$

Integrating from $x = 0$, $\eta = \eta_o$ to $x = t$, $\eta = \eta$

$$\eta - \eta_o = \rho nFD(R - R_o) + i_t \rho x$$

or

$$R/R_o = 1 - (i_t x / nFDR_o) + (\eta - \eta_o) / (\rho nFDR_o) \quad (70)$$

The measured polarization, at the electrolyte face of the electrode, is at $x = t$, therefore

$$\begin{aligned} e^{-n\eta/b} &= (R_o/R_b)(R/R_o) \\ &= (R_o/R_b)[1 - (i_t / nFDR_o) + (\eta - \eta_o) / (\rho nFDR_o)] \end{aligned}$$

or

$$i = (nFDR_b/t)[(R_o/R_b)e^{-n\eta/b} - 1] + (\eta - \eta_o)/t\rho \quad (71)$$

If there is no gas mass transport limitation to $x = 0$ then $R_o/R_b = 1$ and $\eta_o = 0$. Then

$$i = (nFDR_b/t)(1 - e^{-n\eta/b}) + \eta/t\rho \quad (71a)$$

When η is small,

$$\begin{aligned} i &= \eta[(1/t\rho) + (n^2FDR_b/bt)] \\ &= (1/t\rho)\eta[1 + (\rho n^2FDR_b/b)] \end{aligned} \quad (71b)$$

Thus η is linearly dependent on i . $t\rho$ is the ohmic resistance of the electrolyte in the pores, therefore the effective resistance is less as the mass transport of dissolved gas is greater. For strongly conducting electrolytes the factor $\rho n F D R_b / b$ is of the order of $10^{-2} M$, where M is the molar concentration of dissolved gas. Since M is low, the term containing R_b is normally negligible. The physical meaning of this is that the dissolved gas mass transport is so slow that the reaction occurs in a thin layer near $x = 0$. Then all the current has to traverse the complete thickness of the electrode and the ohmic voltage drop is the maximum possible.

When η is large, equation 71 goes to

$$i = (n F D R_o / t) + (\eta - \eta_o) / t\rho$$

For dissolved gases and strongly conducting electrolytes the term in R_o is negligible and

$$i(t\rho) = \eta - \eta_o \quad (72)$$

This, of course, is the expected Ohm's law relation. The total polarization is made up of an ohmic part, $\eta - \eta_o$, and a mass transport part η_o . The mass transport part may consist of diffusion through a thin film of electrolyte to reach reaction surface at $x = 0$. If so, the limiting current will be small. If no thin film exists, then electrolyte at $x = 0$ is in equilibrium with the reactant gas pressure at the electrolyte surface and the mass transport limitation will be that of gas transport to the surface. However, since the reaction is concentrated more and more into a thin layer at $x = 0$ as ohmic polarization increases, the true current density becomes high and activation polarization may be encountered.

4.5. Surface Effects.

When a catalyst is impregnated or plated onto the internal surface of a porous electrode, its principal effect is to increase the exchange current of the reaction involved, which forces the system towards

a pure mass transport-ohmic polarization condition. This condition represents the best possible performance obtainable with the given electrode structure. Once this condition is reached, improved catalysis of the reaction will have no further benefit. Electrode performance can then be improved by making the electrode thinner and more open, thereby reducing internal mass transport and ohmic limitations. But, by doing this the effective catalytic area is reduced so that activation polarization may again come into play. For the thin film model of a gas diffusion electrode, reducing the thickness of the electrode beyond a certain limit may reduce t , the length of the thin film. Polarization at low currents is then reduced, but the limiting current becomes less. Clearly, design of the optimum electrode requires the balancing of a number of different factors. At present, the theories described above have not been sufficiently investigated experimentally to show if they are correct. Also, the important parameters, such as t/W , have not been determined.

When a catalytic surface is micro-roughened, the principal effect is again that of increasing the effective exchange current. A secondary effect may be that the roughened surface holds electrolyte, thus giving a greater cross section of electrolyte for ionic mass transport and ionic conduction. The gas diffusion limiting current would still be determined by t/W , but ionic mass transport and ohmic polarization effects would be smaller. If this were true, it might be possible for W to be very thin, giving large limiting currents, without the ohmic resistance, for example, tending to large values. This would appear to be a more refined model well worth investigating.

Several surface chemistry effects can disturb some of the analysis described. Firstly, some of the work is based on the applicability of a simple Tafel equation for the reaction studied. If several steps in the over-all reaction proceed at comparable rate, then the rate equation is more complex and the form of the rate equation may change with current density. However, it is often found that the Tafel equation applies over wide ranges of current density. Secondly, the Tafel equation does not

always take into account the variation of the amount of surface complex with conditions. Since the electrode reactions are surface reactions, the activities of covered surface and bare surface should appear in the rate equations. Where gas adsorption-desorption is involved, the change in surface coverage can lead to limiting currents of chemisorption or desorption. Since the Tafel equation is found so often, it might be postulated that the complex, for redox and gas reactions, has a Temkin isotherm for its surface coverage versus heat of reaction relation. In this case, large changes in current density can occur with only small changes in surface coverage (14)..

(5) UNSTEADY STATE REDOX SYSTEMS.

5.1. Introduction.

The unsteady state relations for porous electrodes have not received much study. It would appear reasonable to obtain experimental confirmation of the simpler steady state relations before spending much time on the unsteady state theory. For a redox system, as in Figure 1, we can assume as a first approximation that ohmic gradients within the pore electrolyte are small.

Considering an element dx , the rate of build-up of reactant is $\epsilon(\partial R/\partial t)dx$ (t being time). The sum rate of diffusion of reactant into the element is $D(\partial^2 R/\partial x^2)dx$, where D is understood to be an effective mass transport factor. The rate of conversion of R to P in the element is given by

$$di_f/nF = (i_o S/nF) [(R/R_b)e^{\alpha\eta/b} - (P/P_b)e^{-(1-\alpha)\eta/b}] dx$$

i_f is the faradaic current. Then

$$\epsilon \partial R / \partial t = D \partial^2 R / \partial x^2 - (i_o S / nF) [(R/R_b)e^{\alpha\eta/b} - (P/P_b)e^{-(1-\alpha)\eta/b}] \quad (73)$$

The current density at time t is given by

$$i = i_f + i_c$$

$$= \int_0^d di_f + Cd\eta/dt$$

d is the thickness of the electrode, i_c is the capacitative current, C is the capacity. The boundary conditions are $(\partial R/\partial x)_{x=0} = 0$ at all values of t , and $D(\partial R/\partial x)_{x=d} = D_b(\partial R/\partial y)_{y=0}$, where D_b is the effective mass transport factor in the free electrolyte and y is distance into the electrolyte from the electrode-electrolyte interface.

Clearly, the complete solution of these equations for a number of initial conditions is not easy. However, two simplified cases can be readily examined.

5.2. Large Applied Current

Consider a redox electrode at open circuit with uniform concentrations throughout. Let a large constant current (greater than the limiting current) be applied to the electrode. For short periods of time, the fresh reactant diffused in from the exterior will be small and the current will be supported mainly by the existing reactant in the interior of the electrode. The system is as illustrated in Figure 8. Let us assume that the concentration of reactant in the interior is constant with x and thus goes down as a horizontal line in Figure 8. Assuming negligible reactant transfer into the electrode from the outside,

$$i = Cd\eta/dt + i_f = \text{constant applied current}$$

$$\epsilon dR/dt = -(i_0 S/nF) [(R/R_b)e^{\alpha\eta/b} - (P/P_b)e^{-(1-\alpha)\eta/b}]$$

$$i_f = i_0 Sd [(R/R_b)e^{\alpha\eta/b} - (P/P_b)e^{-(1-\alpha)\eta/b}]$$

Then,

$$dR/dt = -(i - Cd\eta/dt)/\epsilon n F d \quad (74)$$

Integrating from $t = 0$, $R = R_b$, $\eta = 0$ to $t = t$, $R = R$, $\eta = \eta$,

$$R_b - R = (it/denF) - (C\eta/denF) \quad (75)$$

or

$$R/R_b = 1 - it/denFR_b + C\eta/denFR_b \quad (75a)$$

Polarization becomes large when $R/R_b \ll 1$ and a "transition time" τ can be defined by this condition. Then

$$\tau = (denFR_b/i) + (C\eta/i) \quad (76)$$

$$\text{Then } R/R_b = (i/d \cdot nFR_b)(\tau - t) \quad (75b)$$

For example, consider $d = 0.1$ cm., $\epsilon = 1/3$, $n = 1$, $R_b = 0.1$ M,

$$\tau \simeq 0.3/i + C\eta/i$$

For a charge current density of 0.1 amps per sq. cm. and a capacity of $10^4 \mu F$ per sq. cm. ($= 10^5 \mu F$ per cubic cm. in this case), and assuming that the transition time is reached by the time $\eta = 1/2$ volt,

$$\tau \simeq 3 + 1/20 \text{ secs.}$$

Under these conditions the effect of double layer capacity on the transition time is negligible. In 3 seconds, mass transport from outside the electrode will be fairly small.

The voltage-time relation is obtained by substituting for R/R_b from equation 75a to give

$$i = Cd\eta/dt + i_0 Sd[(i/denFR_b)(\tau - t)e^{\alpha\eta/b} - (P/P_b)e^{-(1-\alpha)\eta/b}] \quad (77)$$

This cannot be usefully integrated over the entire range. However, some limiting cases can be considered.

Case 1. Low Exchange Current Reaction, Irreversible Conditions.

Consider the period of time when the capacitative current is small and $Cd\eta/dt$ is small. This applies when the faradaic current is small until a fair amount of polarization is present: the initial current is then mainly capacitative until this polarization is reached. When the reverse reaction

term is negligible,

$$i \simeq i_0 S d [(i/denFR_b)(\tau-t)] e^{\alpha\eta/b}$$

Replacing $denFR_b/i$ by τ (when $C\eta/i$ is negligible near the transition time)

$$-\eta \simeq (b/\alpha) \ln(i_0 S d/i) + (b/\alpha) \ln(1-t/\tau) \quad (78)$$

Thus a plot of η versus $\log(1-t/\tau)$ is a straight line and αn can be obtained from the slope and $i_0 S d$ from the intercept. [If C is known, t can be corrected for $C\eta$ and i for $Cd\eta/dt$.]

As t approaches the transition time and the polarization becomes large, reaction on the external surface will start to carry current. This in turn will have a transition time, defined in the usual way by

$$\tau = (R_b/2i)^2 (nF)^2 D/\pi$$

Under the conditions used before, that is, $R_b = 0.1 M$, $i = 0.1$ amps/cm.², and assuming D to be about 10^{-5} cm.²/sec., $\tau \approx 0.075$ seconds. Thus the extension of the total transition time due to the external current is small under these circumstances. However, the second transition time is proportional to $(R_b/i)^2$, whereas the first is proportional to R_b/i . If R_b/i is made too large, then the disturbance of the transition time of equation 76 by the external face current may be excessive. It can be made negligible if d , the thickness of the electrode, can be varied to suit our purposes.

An estimate of the effect of mass transport into the interior can be made as follows. Consider, as before, that the concentration R in the porous electrode is constant up to the face. Then the rate of mass transport into the interior is, in the usual manner [†] (19), given by

$$dQ/dt = (R_b - R) (D/\pi)^{1/2} / t^{1/2} \quad \frac{\text{gm. moles}}{\text{cm.}^2 \text{ sec.}} \quad (79)$$

Q is the total amount transported in time t . The total mass transport in time τ is

[†]This corresponds to the linear, semi-infinite heat transfer case of a block of material initially at uniform temperature R_b , with a fixed temperature of R applied to one face.

$$Q = 2(R_b - R)(D/\pi)^{1/2} \tau^{1/2} \quad (80)$$

But R is changing with time as given approximately by equation 75 and applying the principle of superposition,

$$Q = \int_0^{\tau} 2(D/\pi)^{1/2} (\tau-t)^{1/2} d(R_b - R) \quad (81)$$

Substituting for $R_b - R$ from equation 75 (neglecting the capacity term)

$$\begin{aligned} Q &= \int_0^{\tau} 2(D/\pi)^{1/2} (\tau-t)^{1/2} (i/denF) dt \\ &= (4/3)(D/\pi)^{1/2} (i/denF) \tau^{3/2} \end{aligned} \quad (82)$$

The total charge corresponding to Q is nFQ , while the charge corresponding to i is $i\tau$. Therefore,

$$nFQ/i\tau = (4/3)(D/\pi)^{1/2} (1/d\epsilon) \tau^{1/2} \quad (83)$$

Taking D as 10^{-5} , d as 0.1 cm., ϵ as 1/3 and τ as 3 seconds,

$$nFQ/i\tau \simeq 12\%.$$

Thus a nominal transition time of 3 seconds would actually give rise to a transition time about 10% in excess of three seconds. This predicted disturbance is probably too high, since in practice part of the concentration gradient occurs within the solid rather than within the free electrolyte, and the effective diffusion coefficient within the solid is 1/5 to 1/10 of the free value.

Case 2. Reversible Reaction.

For a reversible reaction the voltage-concentration relation is

$$\eta = (b) \ln[(R_b/R)(P/P_b)]$$

Since we are assuming negligible diffusion in or out of the electrode $R + P = R_b + P_b$ and

$$\eta = (b) \ln[(R_b/R)(R_b + P_b - R)/P_b]$$

or, if $R_b/P_b = \gamma$,

$$-\eta = (b) \ln[(R/R_b)/(1 + \gamma - \gamma R/R_b)]$$

Substituting from equation 75b, assuming the capacity term in equation 76 is small,

$$-\eta = (b) \ln[(1-t/\tau)/(1 + \gamma - \gamma (1-t/\tau))] \quad (84)$$

For γ not large and $t \rightarrow \tau$,

$$-\eta \simeq (b) \ln[(1-t/\tau)/(1 + \gamma)] \quad (84a)$$

Again, a plot of $\log(1-t/\tau)$ versus η should be a straight line. In this case t is zero where η is nearly zero, whereas in equation 78, the extrapolation to $t = 0$ does not give a value of η near zero.

5.3. Current Interruption.

Consider a redox electrode operating at a steady current, with negligible internal ohmic polarization. When the current is shut off suddenly, the electrochemical reaction will continue and will charge (or discharge) the electrical double layer until reversible conditions are obtained. The relations are now

$$i_c + i_f = 0$$

$$i_c = C(d\eta/dt)$$

Case 1. Irreversible Reaction.

The relation of faradaic current to polarization is, as before,

$$di_f = i_o S[(R/R_b)e^{\alpha\eta/b}]dx$$

For negligible internal ohmic effects, this can be written as

$$i_f = i_o S e^{\alpha\eta/b} \int_0^d (R/R_b) dx$$

For a short period of time after current shut-off, the values of R/R_b will be essentially constant due to the slowness of mass transport. Then,

$$C \partial \eta / \partial t + i_o S e^{\alpha\eta/b} \int (R/R_b) dx = 0$$

Separating and integrating, with η_s for the steady current polarization,

$$(i_o S \int (R/R_b) dx \alpha / Cb) t e^{\alpha\eta_s/b} = e^{\alpha(\eta_s - \eta)/b} - 1 \quad (85)$$

When $\eta_s - \eta$ is large,

$$-\eta = (b/\alpha) \ln t + (b/\alpha) \ln [(\alpha/Cb) i_o S \int (R/R_b) dx] \quad (86)$$

A plot of η versus $\log t$ is a straight line. If no concentration gradients exist then equation 86 is the usual equation (14), with $i_o S d$ as the exchange current. If R/R_b does vary, then it is convenient to introduce the pre-interruption current i ,

$$i = i_o S e^{\alpha\eta_s/b} \int_0^d (R/R_b) dx$$

Then

$$\eta_s - \eta = (b/\alpha) \ln t + (b/\alpha) \ln [(\alpha/Cb) i] \quad (86a)$$

The extrapolation to $\eta_s - \eta = 0$ gives

$$t_o = Cb/\alpha i \quad (87)$$

C can be estimated if $n\alpha$ is known.

The equations can only apply at short times, before appreciable mass transfer occurs, for highly irreversible reactions. It should be noted that any ohmic polarization in the electrolyte decays with time according to the decay of i_f . If $\Delta\eta$ is ohmic polarization, it is readily shown that

$$\ln(\Delta\eta/\Delta\eta_s) = (\alpha/b)(\eta - \eta_s) \quad (88)$$

Figure 9 illustrates the general shape of the curve.

Case 2. Reversible Reaction.

As discussed previously (see section 3), a completely reversible electrochemical reaction with negligible internal ohmic effect has a uniform concentration throughout the solid. When current is shut off, reactant diffuses to the surface and tries to decrease the concentration polarization. But this change in polarization drives product in the interior of the electrode to reactant. An electron balance requires that

$$\begin{aligned} &\text{electrons taken up per second by } P \rightarrow R \text{ in the interior of the} \\ &\text{electrode} - \text{electrons produced per second by } R \rightarrow P \text{ at surface} \\ &\text{of electrode} = Cd\eta/dt. \end{aligned} \quad (89)$$

The situation can be envisaged as in Figure 10. As time progress R increases and P decreases towards the equilibrium bulk concentrations. It is clear from equation 89 that we cannot consider the reaction at the surface to be zero when the current is interrupted.

The mathematical analysis of this situation has not yet been completed.

(6) GAS PHASE TRANSPORT.

6.1. Introduction

For a porous electrode fed with gas at one face, it is always possible that gas concentration gradients exist within the pores of the electrode. Although mass transport of ions or dissolved gases in the electrolyte will normally be slower than gas mass transport, the system may be such that long gas diffusion paths exist compared to short paths in the electrolyte. It is also possible that concentration gradients exist due to gas transport to the face of the electrode, since practical fuel cell assemblies will use thin electrode jackets which will probably put the gas flow in the laminar flow regime. In this section we will be concerned with concentration gradients within the porous electrode, between the gas entry face and the electrolyte at which utilization occurs. Two limiting cases occur, gas diffusion at constant pressure and gas permeability with varying pressure.

6.2 Gas Diffusion.

In the consideration of gas diffusion through porous media, two principal types of diffusion can be distinguished. Firstly, there is normal diffusion in which one gas diffuses through another, with negligible influence of the pore walls on the rate of diffusion. This applies when the mean free path of the molecules is much less than the pore diameter. Secondly, when the mean free path of the molecules is much greater than the pore diameter, Knudsen diffusion occurs. In this case, the resistance to mass transport is due to collisions with the walls and the presence of other gases has little influence on the diffusion of the component considered. Some specific cases are as follows.

Equimolar Counter-Current Normal Diffusion of Reactant and Product, Two Components.

The notation and presentation follows that of McCarty and Mason (20). Let J_1 be the molar flux (moles per sq. cm. per second) of gas 1 and J_2 the molar flux of gas 2 (in the same direction). The equations of diffusion for one dimensional diffusion are

$$\begin{aligned} J_1 &= -D_1(dn_1/dx) + n_1v \\ J_2 &= -D_2(dn_2/dx) + n_2v \end{aligned} \tag{90}$$

n_1, n_2 are the concentrations in moles per cm.³ and v is the velocity of bulk flow. Since the mass of one gas diffusing in one direction does not in general equal the mass diffusing in the other direction, a definite net mass flow in one direction is present. The velocity of flow is the net mass flow divided by the density ($n_1m_1 + n_2m_2$ in this case, where m_1, m_2 are the respective molecular weights). This net flow must, of course, obey the laws of fluid dynamics. The diffusion coefficients in equation 90 are quite arbitrary; they are defined by equation 90, and they may be concentration dependent. $J_1 = -D_1dn_1/dx$ only when $v = 0$, therefore the D values are equi-mass diffusion coefficients. In other words, we can consider a mass flow along the axis, carrying n_1, n_2 with it. If a plane is moved

along with the fluid, at velocity v then the diffusion rates of components 1 and 2 with respect to this plane are given by $-D_1 dn_1/dx$ and $-D_2 dn_2/dx$ respectively.

To proceed further we must consider the fluid dynamics of the mass transfer. For one dimensional transport the equation of motion is (21).

$$\partial p / \partial x + \partial \tau / \partial y + \rho v \partial v / \partial x = 0 \quad (91)$$

p is pressure, τ is viscous force, ρ is density. The pressure term represents the driving force, the viscous term represents the viscous resistance and the density-velocity term represents the bulk momentum term. For low values of ρ and v and negligible viscous force, $\partial p / \partial x$ is small. If we assume this to be true, then $n_1 + n_2 = \text{constant} = N$ say. For steady state conditions, then, $\partial n_1 / \partial x = -\partial n_2 / \partial x$ and equation 90 goes to

$$J_1 = -D_1 dn_1 / dx + n_1 v$$

$$J_2 = D_2 dn_1 / dx + n_2 v$$

For equimolar counter-current mass transfer $J_1 = -J_2$ and

$$0 = -(D_1 - D_2) dn_1 / dx + v(n_1 + n_2)$$

or

$$v = (1/N) (D_1 - D_2) dn_1 / dx$$

Substituting into equation 90,

$$J_1 = -[(n_2/N)D_1 + (n_1/N)D_2] dn_1 / dx \quad (92)$$

or

$$J_1 = -D_{12} dn_1 / dx \quad (93)$$

D_{12} is the conventional equimolar binary diffusion coefficient of kinetic theory and is independent of the partial concentration of the components. We see, therefore, that in this case the mass transport of reactant can be represented by a Fick's law form, equation 93. The effective D_{12} for a

porous electrode, based on unit geometric area, is smaller than the true diffusion coefficient because the effective diffusion area is the porosity. In addition, if dx is linear dimension, the actual path length is qx , where q is a tortuosity factor. Thus, as before,

$$(D_{12})_{\text{effective}} = D_{12} \epsilon/q.$$

For a diffusion path of t from the entry face to the reaction zone, equation 93 can be integrated in the usual way to give

$$n_o - n_t = (1/D_{12})_e (ti/nF)$$

The limiting current is

$$i_L = nFn_o D_{12} e/t \quad (94)$$

Then

$$n_t/n_o = 1 - i/i_L$$

It should be noted that this is an approximation which applies at relatively low rates of mass transfer, since viscous forces have been neglected. Negligible pressure gradient exists in the electrode.

Two Component, Non-Equimolar, Normal Diffusion

Equation 90 can be expressed as

$$J_1 = -D_{12}(dn_1/dx) + (n_1/N)J \quad (95)$$

$J = J_1 + J_2$ = net molar transport. With the same assumption as before, that negligible pressure gradient exists (therefore N = constant) even though net mass transfer is occurring, this equation can be integrated if the flux ratio J_1/J_2 is known. An important case is that of a two component gas mixture in which one component reacts to a non-gaseous product and the other component is inert. Air reacting at an oxygen electrode is an important example. In this case, at $x = 0$ the respective concentrations of reactant and inert are n_{10} and n_{20} , say, J_1 is the rate, while J_2 is zero. Then

$$J_1 = -D_{12} \, dn_1/dx + (n_1/N)J_1$$

or

$$J_1 = -D_{12}(1/(1-n_1/N))dn_1/dx$$

Integrating from $x = 0$ to $x = t$,

$$J_1 = (D_{12}/t)N \ln[(1-n_1/N)/(1-n_{10}/N)]$$

or

$$J_1 = (D_{12}/t)N \ln[(N-n_1)/n_{20}] \quad (96)$$

where n_1 now refers to the concentration at the reaction site. The limiting current is nFJ_1 or

$$i_L = (nFD_{12}/t)N \ln(N/n_{20}) \quad (97)$$

N is in gm. moles per cm.³, and at 1 atmosphere and room temperature it is about $(1/2)10^{-4}$. Equation 97 can be put into a form comparable to a simple Fick's law form modified by a correcting factor,

$$i_L = (nFD_{12}/t)n_{10} \, f \quad (97a)$$

where

$$f = (N/n_{10})^{2.3} \log(N/n_{20})$$

The values of f as a function of the molar fraction of inert present are shown in Table 1.

Table 1. Correction to Fick's Law When Inert Gas is Present.

Molar fraction of inert in bulk gas stream n_{20}/N	Correcting factor f
1.0	0
0.9	0.0105
0.8	0.0446
0.6	0.204
0.4	0.550
0.2	1.285
0.1	2.07
0.01	4.55
0.001	6.91

For air, with a mole fraction of nitrogen of $4/5$, the correction factor is about $1/5$, therefore the limiting gas diffusion rate is $1/5$ of that expected from a simple Fick's law form with $1/5$ partial pressure of oxygen. Oxygen with less than a few% inert impurities would give an f of about 5, therefore, at the same total pressure the oxygen would give a limiting diffusion rate about 125 times larger than air.

As the percentage of inerts is reduced the limiting diffusion rate becomes very large, tending to infinity. However, it is important to note that this is a spurious prediction for flow through porous materials. The case of zero impurity is the same as mass transport of one gas, the reacting gas, with no other component present. This clearly becomes a permeability or bulk flow system when the rate of flow becomes high. Thus an upper limit is set to the applicability of equation 97 by the corresponding permeability limited rate of transport (see 6.4). The breakdown of equation 97 under these conditions is obviously due to the neglect of viscous forces in its derivation.

To estimate values of limiting diffusion rates it is usually sufficiently accurate to remember that $D_{12} \propto 1/P$, P being total pressure; $D_{12} \propto T^{1.75}$, T being absolute temperature; and $D_{12} \propto \sqrt{(1/m_1) + (1/m_2)}$, m_1 , m_2 being the molecular weights. Thus, assuming D_{12} to be about $0.1 \text{ cm}^2/\text{sec.}$, $t = 0.1 \text{ cm.}$, 1 atmosphere and room temperature, $n = 2$, and ϵ/q to be about $1/10$, then $i_L \simeq (n_{10}/N)f \text{ amps./sq. cm.}$ Thus for equi-molar counter current diffusion ($f = 1$) and a molar fraction of reactant near 1, $i_L \sim 1000 \text{ amps./sq. cm.}$ This figure is, of course, very sensitive to t , the thickness of the diffusion path through the electrode. For air at the same conditions, $n = 4$, $n_{10}/N = 1/5$ and $f = 1/5$ therefore $i_L \simeq 80 \text{ amps./sq. cm.}$ An increase in the pressure of air does not produce a proportional increase in the limiting current because although n_{10} increases proportionally (and f remains the same), D_{12} is inversely proportional to total pressure and the pressure increase effect is cancelled out.

Knudsen Diffusion

When the mean free path for the diffusing molecule is greater than the pore radius, collisions with the walls provide most of the resistance to

transport. The presence of other molecules will thus have little effect on the mass transport and we would expect the diffusion coefficient to be independent of total pressure and partial concentration, but dependent on the size of the pores. The steady state of motion is equation 91, that is,

$$\partial p / \partial x + \partial \tau / \partial y + \rho v \partial v / \partial x = 0$$

For Knudsen diffusion where the viscous forces occur at the surface, v is constant with y except at the surface and v is the mean mass velocity defined by $nv = J$, n being the molar concentration, J the molar flux. Usually, the velocities of flow through porous media are low, and the density is low, so that the bulk momentum term (or kinetic energy term) is negligible compared to the viscous force.

The viscous forces are due to the change of momentum of a molecule striking the wall. The loss of momentum, in the direction of flow, per sq. cm. per second gives a force

$$F = (1/4) n \bar{C} m v f$$

where f is the accommodation coefficient. Substituting J/n for v

$$F = (1/4) \bar{C} m J f$$

From the equation of motion, for a tube

$$\pi r^2 dp/dx = -(1/4) J m \bar{C} f 2\pi r$$

$$J = -(2r/m\bar{C}f) dp/dx \quad (98)$$

or

$$J = D_K dn/dx \quad (98a)$$

where

$$D_K \simeq (2/3) r \bar{C}$$

Thus D_K is proportional to r , to $\sqrt{T}$, and to $1/\sqrt{m}$ but independent of pressure and the composition of other gases present. Integrating equation 98a,

$$i_L = (nFD_K/t)n_{10} \quad (99)$$

In this case, an increase of pressure increases n_{10} but does not decrease D_K , therefore the limiting current increases. It should be noted that Knudsen diffusion and Knudsen permeability are the same physical process, when only one component is present.

6.3 Permeability

When a single gas is flowing, in laminar flow, through a tube of diameter d , the relation between flow rate and pressure drop is (18)

$$p_1 u_1 = (d^2/32\eta)(\bar{p})(\Delta p/L) + (8\bar{C}d/3)(\Delta p/L) \quad (100)$$

u_1 is the linear velocity at p_1 , η is the viscosity, $\bar{p}$ is the arithmetic mean pressure over length L , Δp is the pressure drop over length L , δ is a constant close to one and $\bar{C}$ is the mean molecular velocity. The first term in the RHS of the equation derives from Poiseuille's formula, while the second term is the slip flow term. This arises from Knudsen flow within a mean free path of the wall which changes the effective viscosity. As d becomes small the equation reduces to the Knudsen equation, with an appropriate value of δ of δ_0 . As d becomes large, δ changes somewhat from δ_0 but the slip flow term becomes a smaller fraction of the total until a pure Poiseuille's equation is obtained. For non-circular flow paths, the diameter can be replaced by $4Mk$, where M is the mean hydraulic radius and k is a constant for a given shape but varies with different geometries; k is close to 1. Making this substitution and rearranging, equation 100 goes to

$$p_1 u_1 = (M^2/k_0)(\bar{p}/\eta)(\Delta p/L) + (M/k_1)(\bar{C})(\Delta p/L) \quad (100a)$$

k_0 , k_1 are constants. As will be seen later, the constants characterizing the geometry and pore size are not known for flow through porous media and they have to be determined experimentally, therefore we will use the equation in the form

$$p_1 u_1 = B_0(\bar{p}/\eta)(\Delta p/L) + K_0\bar{C}(\Delta p/L) \quad (100b)$$

When the slip flow term is negligible, B_o is the permeability coefficient (in darcies for η in centipoises and p in atmospheres) and replacing $p_1 u_1$ with JRT, p with NRT,

$$J = B_o (\bar{p}/\eta) (\Delta N/L) \quad (100c)$$

As before, J is the net molar flux density, N is the total molar concentration. For a one component system, pure reactant transporting to the reaction site, for example, $J = J_1$ and the limiting current is obtained when $\Delta N = N$. Then $\bar{p} = P/2$, where P is the total entrance pressure and, using t in place of L ,

$$i_L = nF(B_o/\eta)(P/2t)N \quad (101)$$

6.4. Comparison of Diffusion and Permeability Limitations.

We can now compare the predicted limiting currents for an almost pure reactant transporting through an electrode with no gaseous product. The equations are 97 and 101, that is,

$$i_L = (nFD_{12}/t)N \ln(N/n_{20})$$

and

$$i_L = (nFB_o/t\eta)N(P/2)$$

(n_{20} is the percentage of inert in the feed stream.) The smaller of these two limiting currents will be the best approximation to the actual limiting current. Comparing the two values

$$\begin{aligned} i_L \text{ diffusion} / i_L \text{ permeability} \\ = \eta D_{12} \ln(N/n_{20}) / B_o (P/2) \end{aligned} \quad (102)$$

For example, let us consider D_{12} effective to be about $0.01 \text{ cm.}^2/\text{sec.}$, η to be about 100 micropoises, P to be 1 atmosphere and n_{20} to be 1/10 per cent. Then

i_L diffusion/ i_L permeability

$$= (10^{-2})(10^{-2})(2.3)(3)(2)/B_0$$

$$\simeq 10^{-3}/B_0 \quad (102a)$$

Permeability coefficients of 0.1 to 0.40 have been reported (22) for porous carbon electrodes. Thus it is concluded that diffusion will almost certainly be the mass transport limiting mechanism for porous electrodes.

B_0 is related to the viscous area and flow path in a porous solid. In equation 100a, u_1 is the true velocity, whereas the value of J is based on the external face area. The actual open area for transport is ϵ and the actual path length per unit thickness is q , therefore the true rate of flow in the solid is Jq/ϵ . Thus, neglecting slip flow and assuming $k_0 = 2$, equation 100a can be expressed as

$$J = (\epsilon/q^2)(M^2/2)(\bar{p}/\eta)\Delta N/L$$

For η in centipoises, p in atmospheres (1 atmosphere = 10^6 dynes/sq. cm.)

$$B_0 \simeq (\epsilon/q^2)(M^2/2)(10^8) \text{ darcies} \quad (103)$$

M is the effective mean hydraulic radius defined by equation 103. It is constant for a given material. If the pore size of the material does not vary widely, M can be approximated by an overall hydraulic radius defined by total cross-sectional area divided by wetted perimeter = ϵ/A , A being as before, the perimeter area per unit volume of electrode. Thus for $A = 10^3 \text{ cm}^2/\text{cm}^3$, $\epsilon = 1/3$, $q = 2$, $B_0 \simeq 1/2$ darcy. Again, we must conclude that equation 97 is the equation which will be applicable.

In general, then, we may assume that the mass flow associated with net mass transfer can be accomplished with virtually zero total pressure gradient in the electrode and that the equation to be solved for any specific set of conditions is equation 95, or a multicomponent equivalent of this equation (23).

6.5 Combined Normal and Knudsen Diffusion.

Since diffusion is the predominant factor to be considered, and since electrodes containing very fine pores may be used in some circumstances, it is worthwhile to investigate the combined effects of the two types of diffusion. If it is assumed that the pores of different sizes are highly interlinked and randomly arranged, then it can be assumed that the path of any molecule through the solid will involve essentially the same resistances to flow as the path of any other molecule. Over a short element dx we can envisage part of the resistance to flow being caused by Knudsen effects, giving dn_{1k} concentration drop for flow J_1 .

An effective Knudsen diffusion coefficient D_{1k} can be defined by

$$J_1 = -D_{1k} (dn_1/dx)_k$$

Similarly an effective normal diffusion coefficient can be defined by

$$J_1 = -D_{12} (dn_1/dx)_N + (n_1/N)J$$

The total pressure drop over dx is $dn_{1k} + dn_{1N}$ and $dn_1/dx = (dn_{1k} + dn_{1N})/dx$. Therefore

$$-dn_1/dx = J_1 \left(\frac{1}{D_{12}} + \frac{1}{D_{1k}} \right) - (n_1/ND_{12})J$$

Thus,

$$J_1 = -(1/(\frac{1}{D_{12}} + \frac{1}{D_{1k}})) dn_1/dx + (n_1/N)J(1/D_{12}(\frac{1}{D_{12}} + \frac{1}{D_{1k}})) \quad (104)$$

or,

$$J_1 = -D_1 dn_1/dx + (n_1/N)J\delta \quad (104a)$$

For $D_{1k} \gg D_{12}$, $D_1 = D_{12}$ effective, $\delta = 1$. For $D_{12} \gg D_{1k}$, $D_1 = D_{1k}$ effective, $\delta \rightarrow 0$. Thus D_1 , δ will change with the absolute pressure of the system. If the molar flux ratio J_1/J_2 is known, then, since $J = J_1 + J_2$, J can be replaced in terms of J_1 and equation 104 can be integrated as before for a given set of circumstances.

(7) FUTURE WORK.

This report lays the theoretical ground work for a number of interesting investigations. Examination of the derivations of the equations shows the assumptions involved and it is then relatively easy to set up simple experimental systems which approximate as nearly as possible to the conditions required. From a study of such systems it should be possible to extend the work to practical fuel cell electrodes. In practical systems it is inevitable that more complex conditions will exist. For example, the flow of reactant gas across the face of an electrode may lead to concentration profiles across the face, with the exit gas at a lower concentration. Even if the flow is slow enough that free space diffusion will even out this concentration, each cell in a battery of cells will operate with a different feed concentration. Again, it is possible that high output cells will not operate at isothermal conditions.

Some of the equations derived here are being investigated in this department, but not enough experimental results have been obtained to date to warrant their discussion. Will (12) has apparently proved the validity of equation 63 for a partially immersed platinum wire, with hydrogen fuel and sulphuric acid electrolyte. Allowing for what is certainly a misprint in the abstract, the form of equation he quotes is identical to that of equation 63.

It is to be expected that the next few years will see the development of completely adequate theoretical and experimental descriptions of the steady state porous electrode, and at least a partial description of unsteady state situations.

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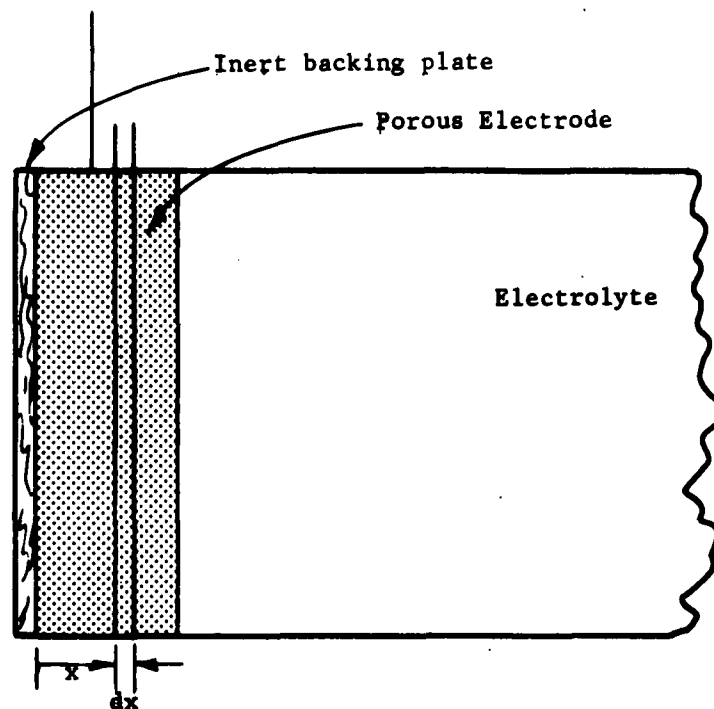


Figure 1. Illustration of Porous Electrode Reacting at One Face.

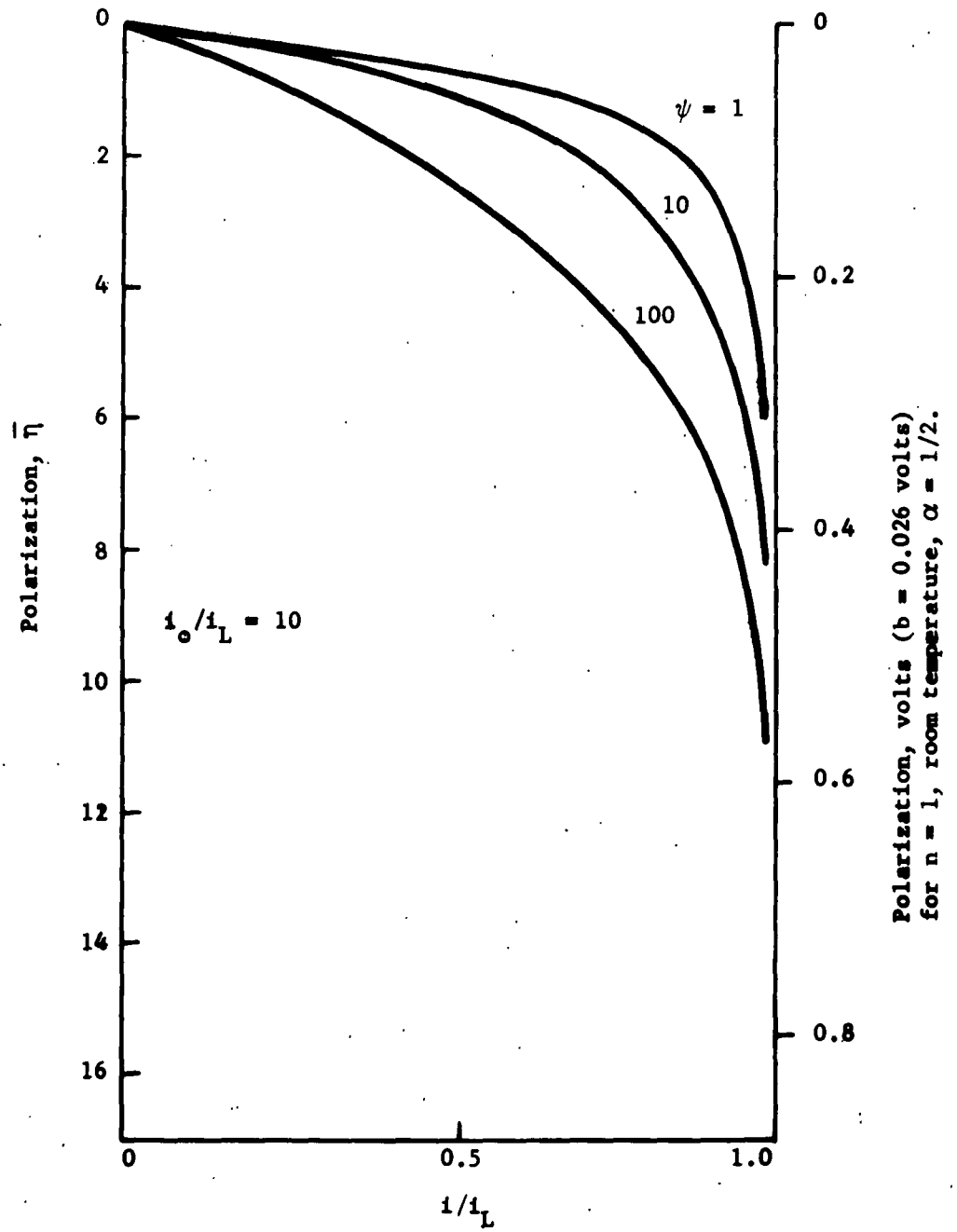


Figure 2A. Polarization-Current Relation for Equation 33.

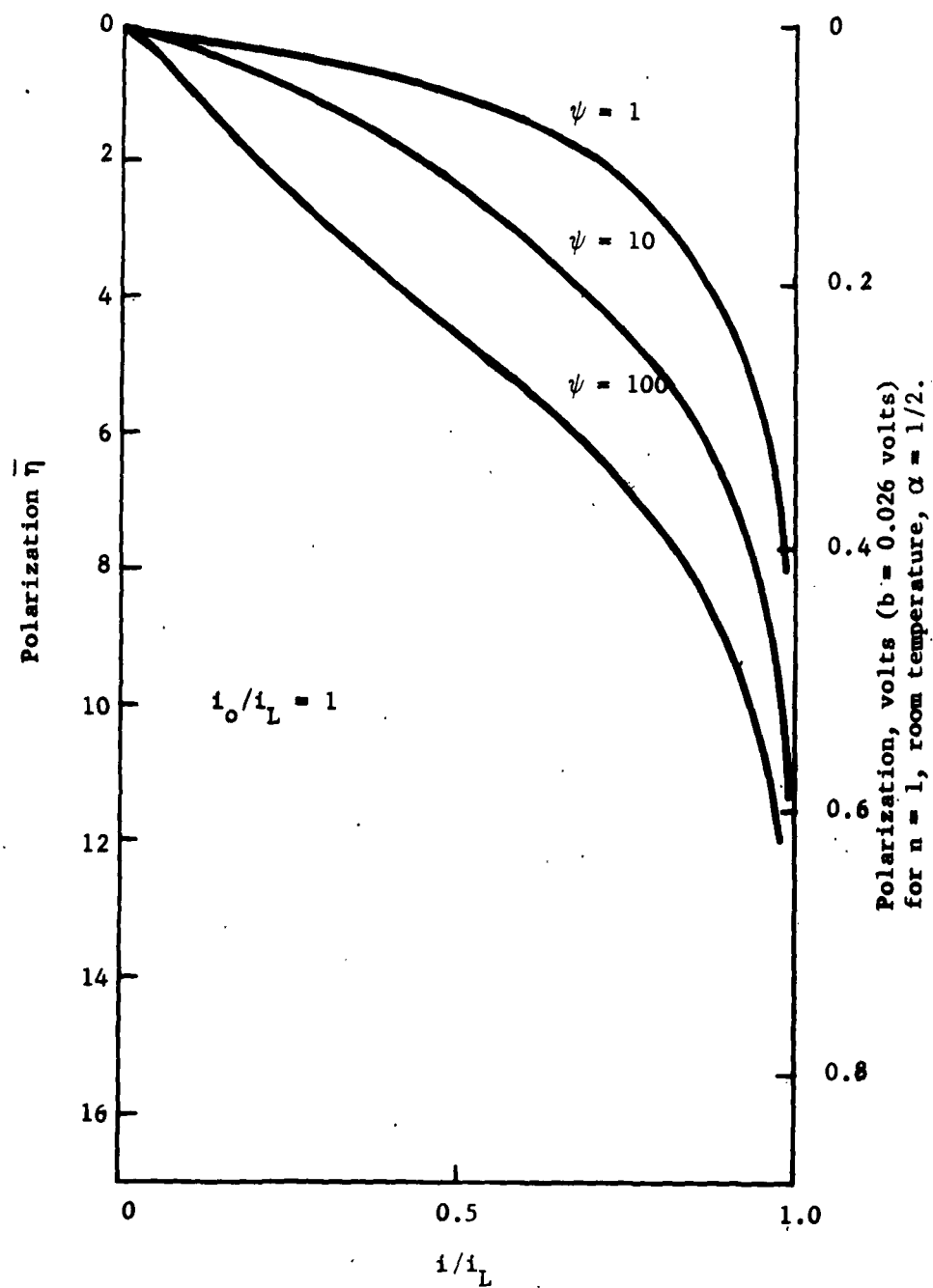


Figure 2B. Polarization-Current Relation for Equation 33.

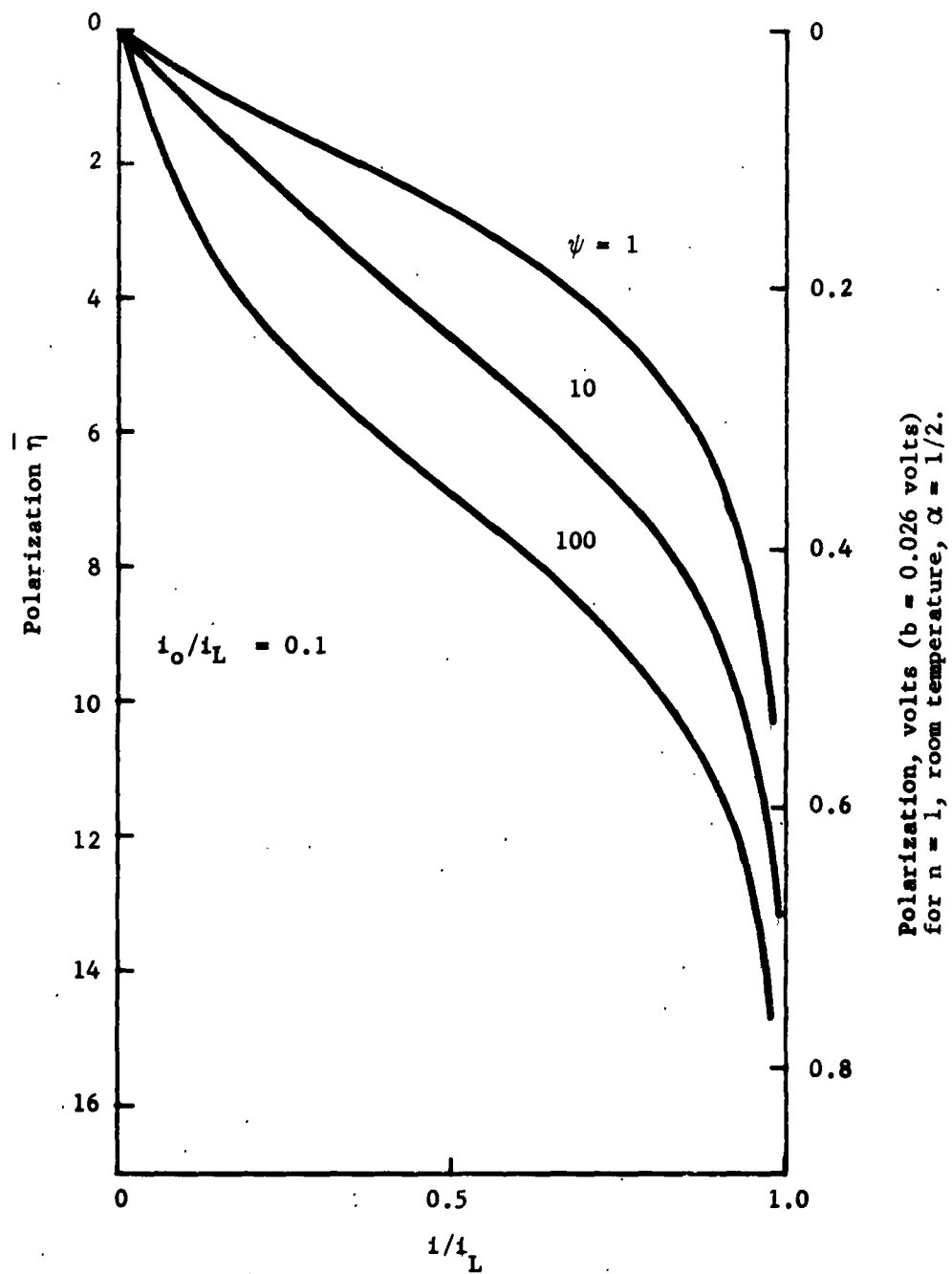


Figure 2C. Polarization-Current Relation for Equation 33.

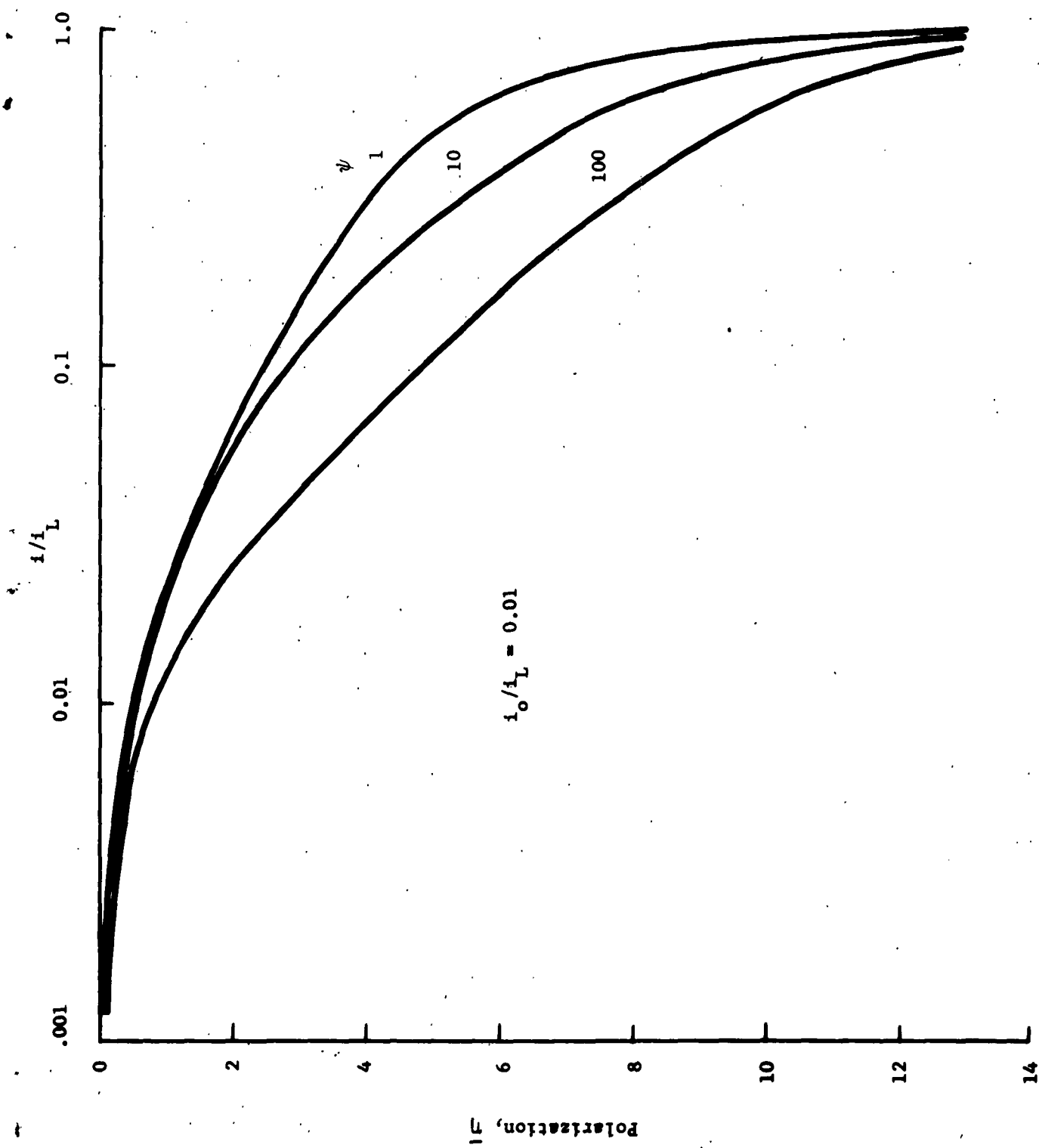


Figure 2D. Polarization-Current Relation for Equation 33.

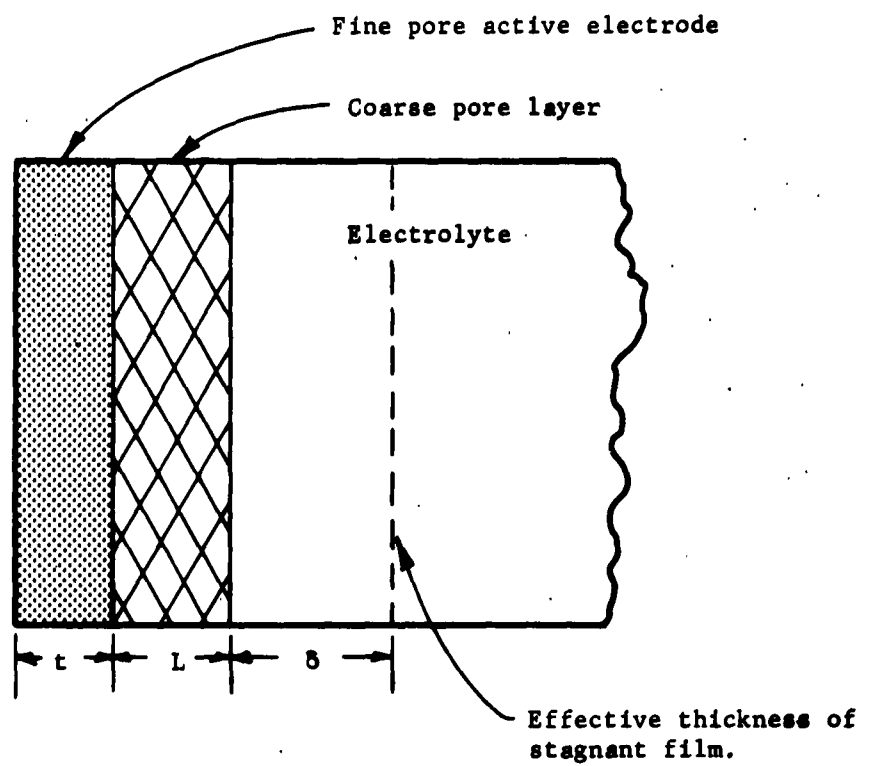


Figure 3. Illustration of Double Layer Electrode Reacting at One Face.

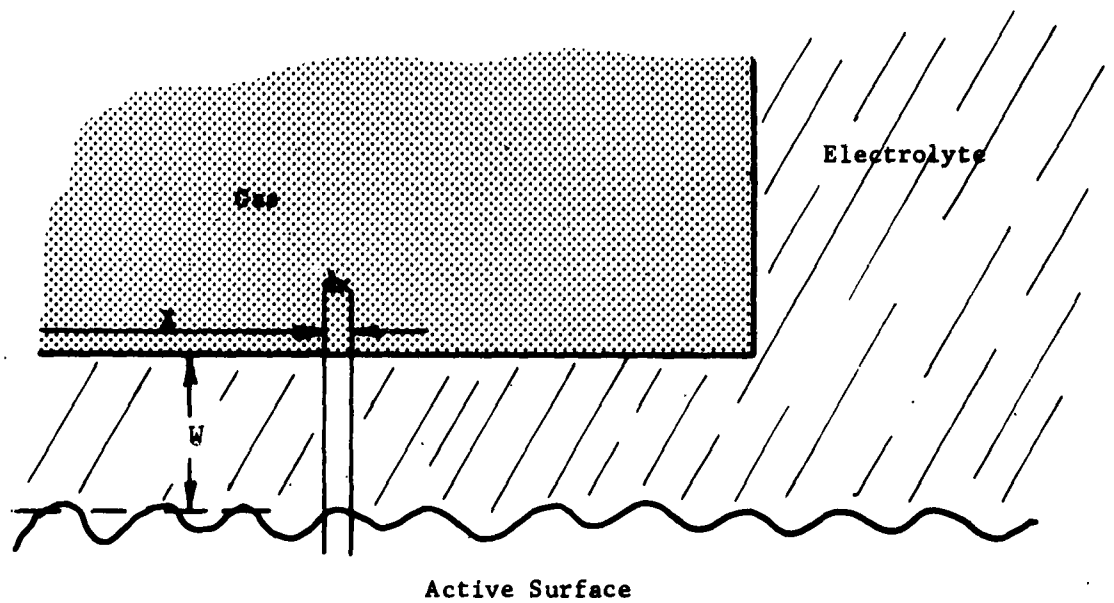


Figure 4. Illustration of "Thin Film" Model of a Gas Diffusion Electrode.

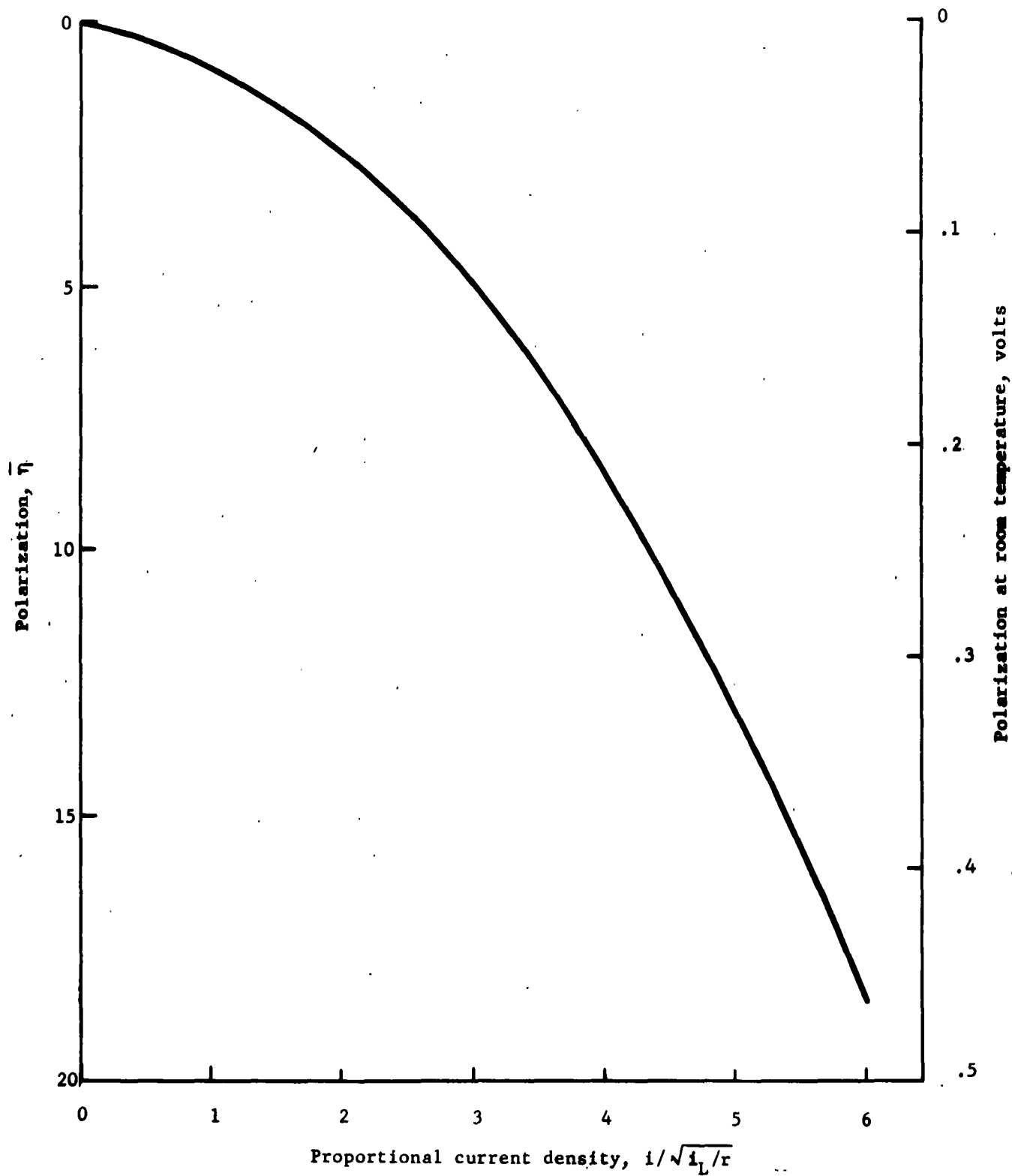


Figure 5. General Shape of Equation 63.

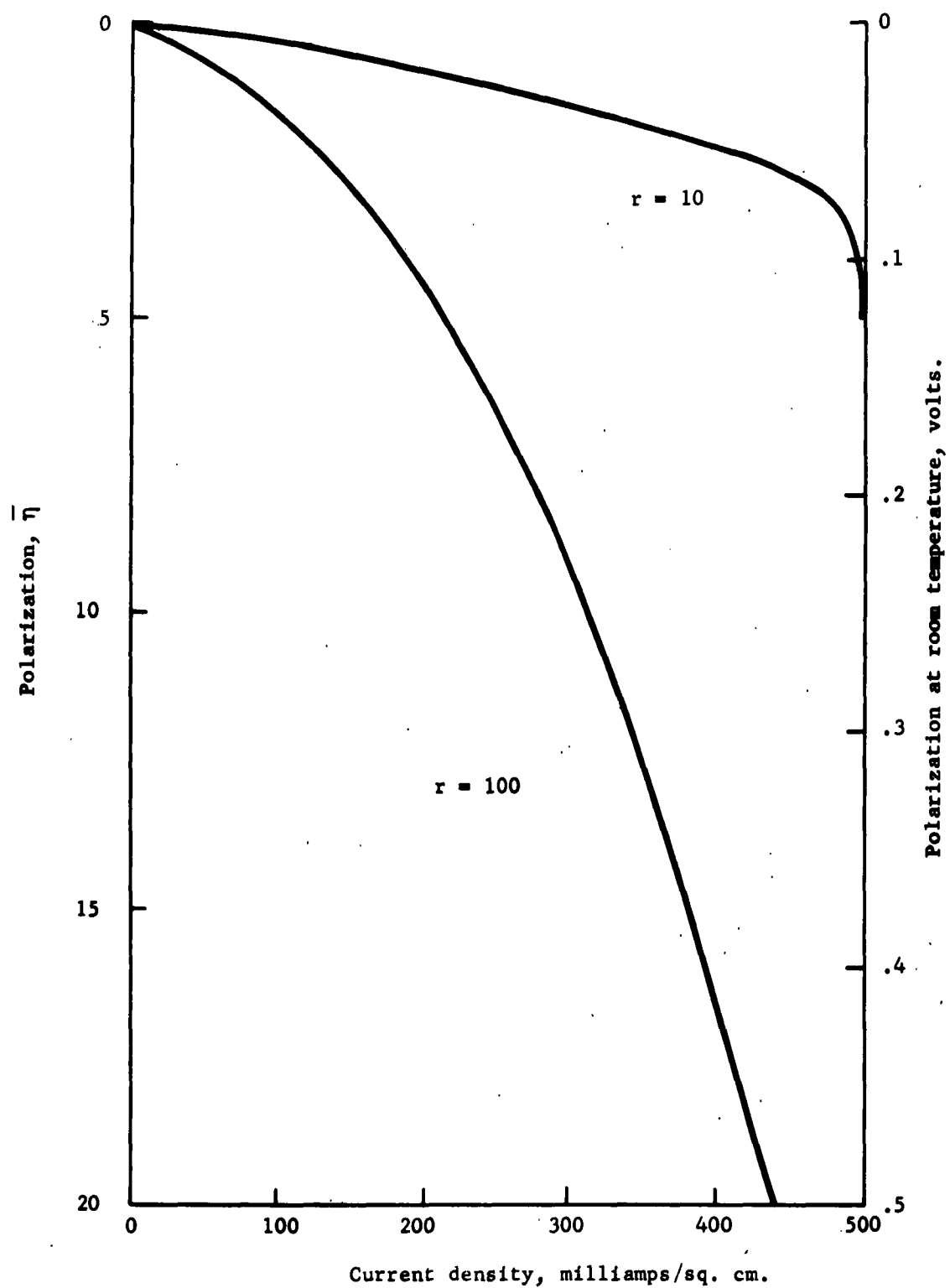


Figure 6. Predicted Polarization V. Current Density, for a Limiting Current Density of 500 ma/cm² (Equation 63).

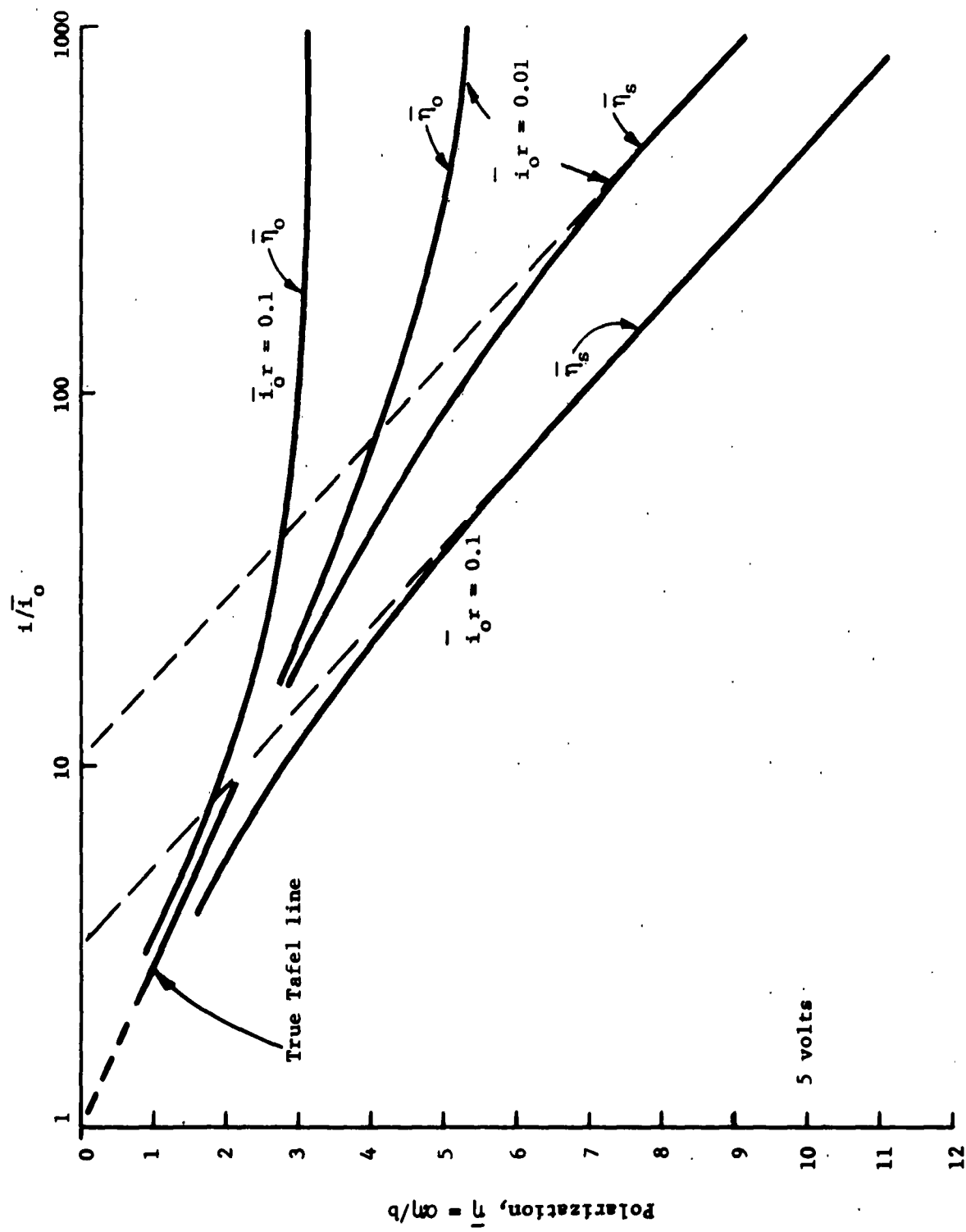


Figure 7. Polarization V. Current Density for Equations 65, 66.

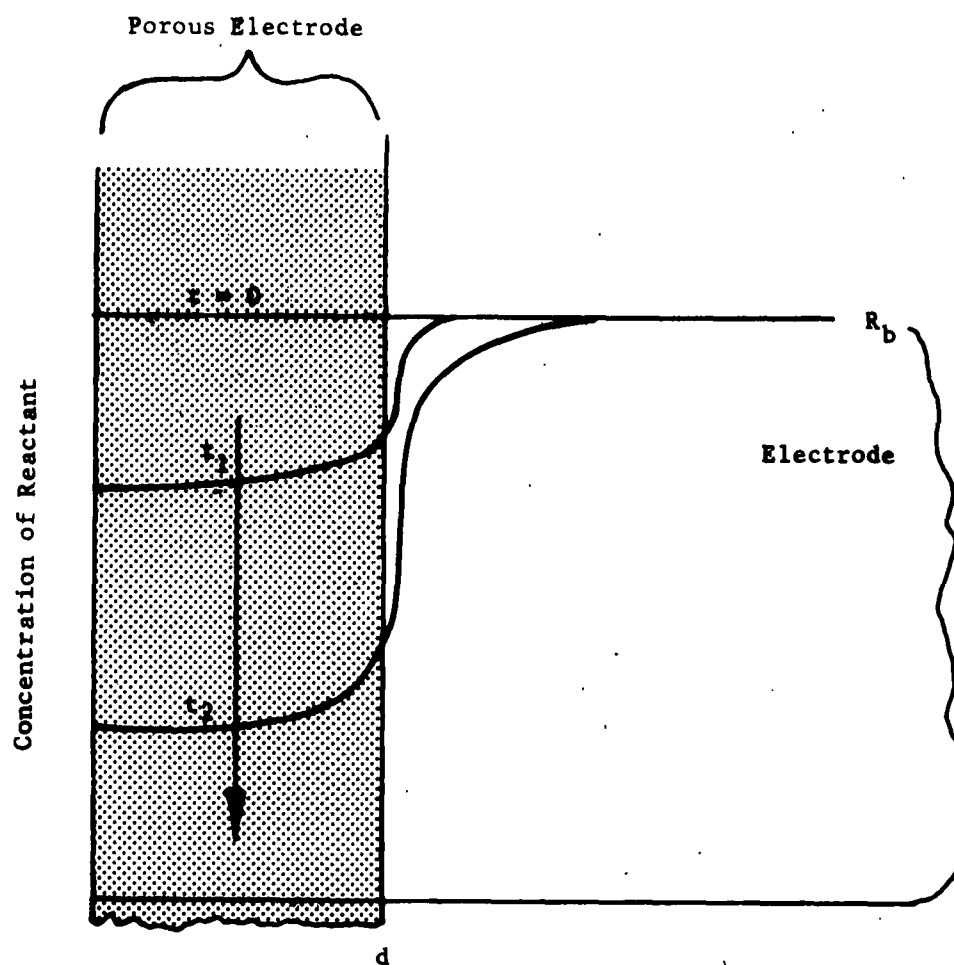


Figure 8. Illustration of Concentration Profiles for Large Applied Current.

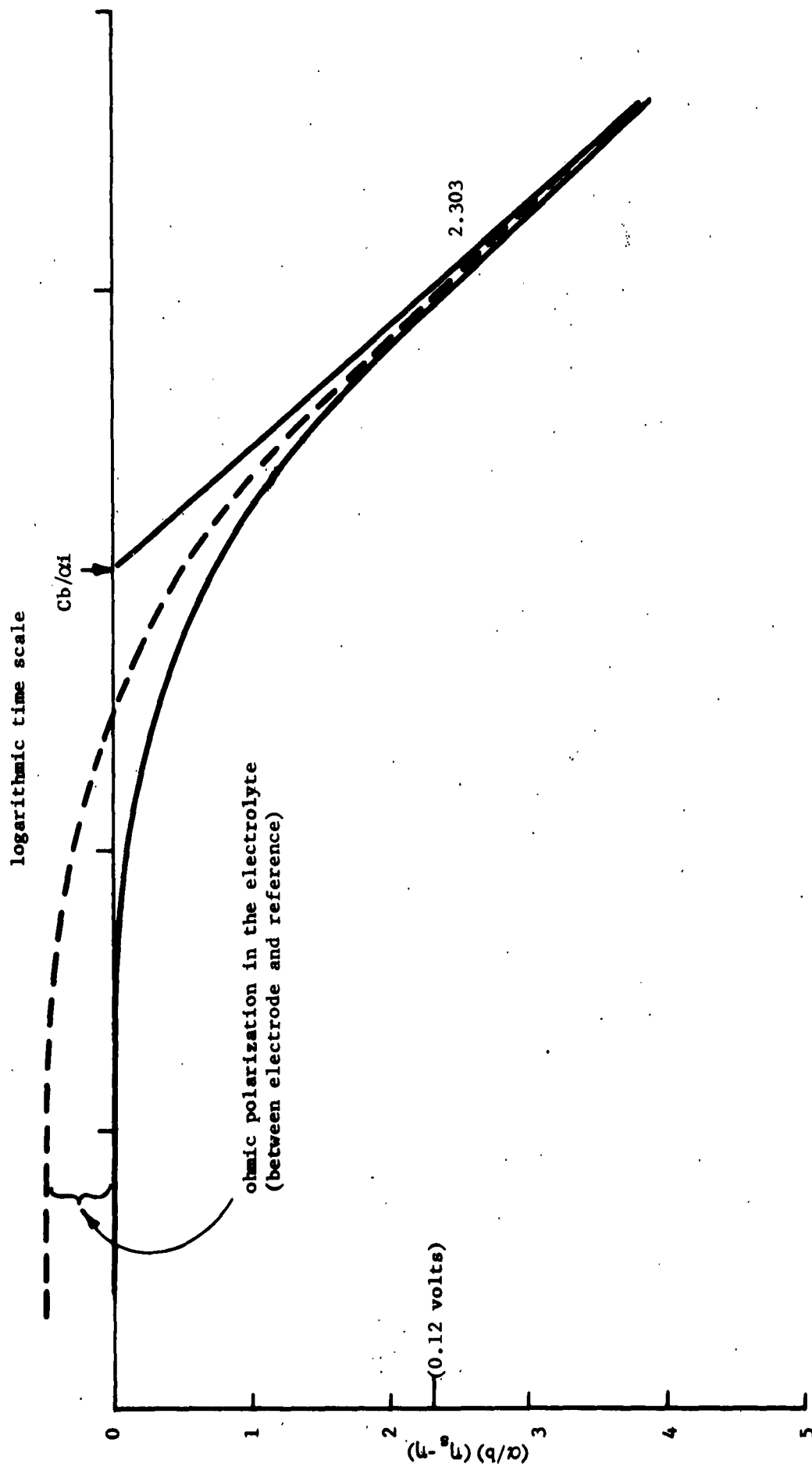


Figure 9. Decrease of Polarization Versus Time after Current Shut-off: Irreversible. (Equations 85, 86, 87, 88)

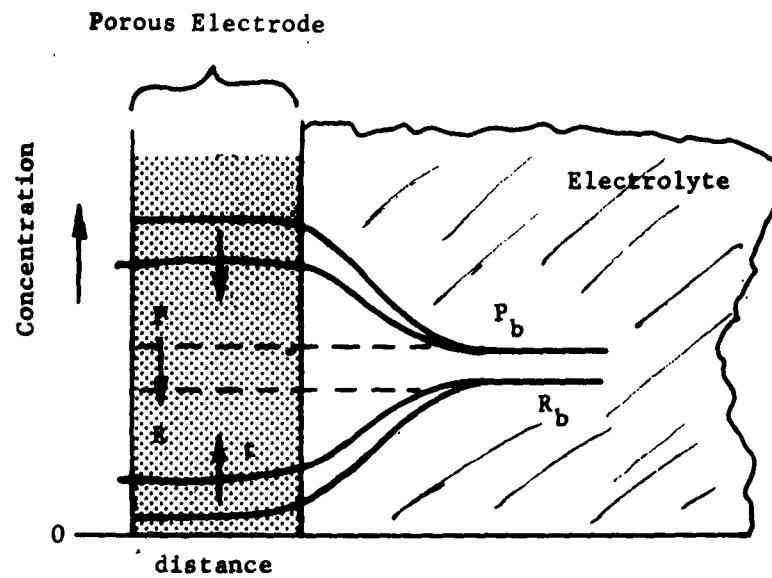


Figure 10. Illustration of Concentration Profiles in Porous Electrode After Current Interruption (Reversible).