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POLARIZATION AT DIFFUSION ELECTRODES

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INTRODUCTION

The theory of electrochemical kinetics at solid electrodes has been well developed and, in particular, the hydrogen evolution reaction has received much study (1). Many fuel cells, however, use porous diffusion electrodes and it is found that the polarization-current curves for fuel cell half-cells do not always correspond to the theory for solid electrodes. Gorin and Recht (2) have considered electrode processes on screen electrodes in molten salts, assuming a well-defined geometry of the metal-gas-electrolyte interface. For low-temperature porous electrodes in aqueous solution, some degree of electrolyte penetration into the porous system is to be expected and concentration gradients in the electrolyte are possible. This paper examines the effect of penetration and also discusses several other relevant features of fuel cell electrode processes.

PROPOSED PHYSICAL MODELS

The general assumption is made that a porous diffusion electrode consists of a highly interlinked porous system. The pores may vary in radius over a wide range but if they are highly interlinked the system can be considered as one pore of very irregular area and cross-section. Consequently, penetration of electrolyte and concentration profiles within the electrode can be considered uniform at a given depth within the electrode (3).

The theory developed below might be expected to apply rather well for a redox system reacting in a porous electrode. In this case the reactant in the electrolyte must diffuse into the electrode and the product, also in the electrolyte, must diffuse back out. Due to mass transport effects, the concentration of reactant within the electrode would fall towards the center of the electrode, while the concentration of product would increase in order to establish sufficient diffusion gradient to remove the product. The theory might also apply for gas evolution on a porous electrode. For example, electrolysis to produce hydrogen would force hydrogen onto the internal surface covered by electrolyte. This hydrogen would diffuse to nucleation sites, probably by diffusion along grain-boundaries and surface irregularities, and be given off as bubbles. Providing the mass transport of gas was not rate restricting and providing the bubbling did not too much disturb the system, the theoretical voltage-current curves developed below might be expected to apply at steady state conditions.

For the case of a gas-diffusion fuel cell electrode it appears unlikely that the electrode would behave exactly like electrolysis in reverse. On the other hand, it is difficult to believe that the reaction area is located only at the conjunction of the gas-solid-liquid meniscus. It seems more reasonable to suppose that gases can diffuse along the surface underneath the bulk of the electrolyte in a pore. A "feeder" system of surface diffusion paths can be visualized, with the geometry of the paths being so small as to maintain gas equilibrium with an appreciable amount of the surface under the electrolyte. The extent of this surface or gas penetration might be small, perhaps being limited to the length of a single crystallite within the metal or carbon. In theory, it should be possible to compare the effective surface utilization during fuel-cell usage with that during electrolysis (gas driven off at the fuel electrode instead of consumed) by comparing the exchange currents for the two cases. In practice, when voltage is applied to a hydrogen fuel cell electrode so that hydrogen is evolved, the current-voltage relation is initially unsteady with time, with appreciable current being passed

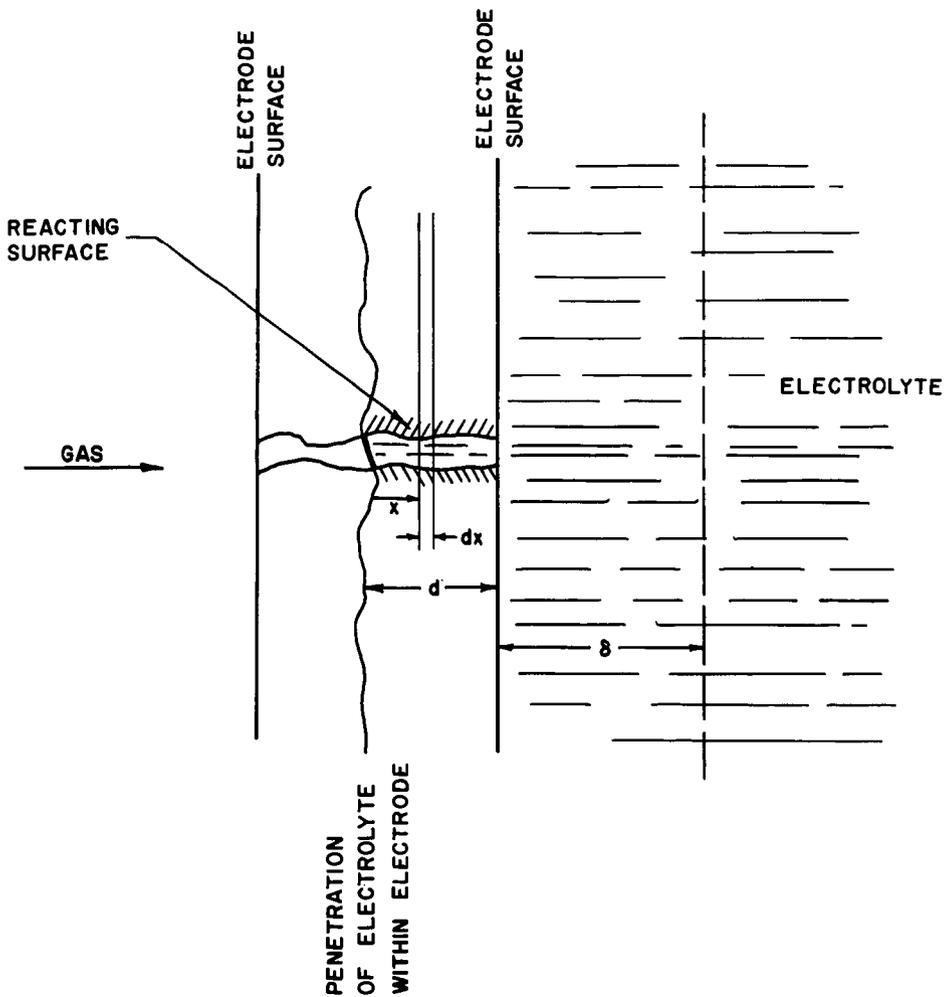


FIGURE 1. ILLUSTRATION OF SYSTEM CONSIDERED.

at overvoltages lower than those expected. Presumably this is due to hydrogen being formed on a greater amount of electrolyte-covered surface. Only when this new reacting surface is saturated with the equilibrium quantity of hydrogen will vigorous hydrogen evolution occur. A stable, normal over-voltage/current curve can then be obtained.

The following theory has been derived on the basis of mass transport in the electrolyte as the factor causing polarization. It is possible that mass transport of gas within the "feeder" system is the polarizing factor. The theory would apply equally well to such a system with gas instead of liquid mass transport factors. For electrolyte concentration polarization the limiting current for a given electrode should be dependent on the concentration of electrolyte and independent of the surface catalyst. For gas concentration polarization the limiting current will be a function of gas pressure and if a "feeder" system exists, different surface catalysts might give widely different mass transport coefficients.

EFFECT OF INTERNAL MASS TRANSPORT

Let us consider a system as illustrated in Figure 1. A reactant molecule or ion A in the electrolyte reacts with the surface to give a product B. A must diffuse into the porous system to reach the surface and B must diffuse out of the porous system. The current density at an electrode potential of V is (4)

$$i = kN_g A_e(a_p) \left(a_r \right)^{\alpha} \frac{1-\alpha}{e} \frac{-\Delta F_o^*}{RT} \frac{\alpha \Delta F_o}{RT} \frac{\alpha n^2 \eta}{RT} \frac{-(1-\alpha)n^2 \eta}{RT} \quad (1)$$

where the symbols have the meaning given in the list of nomenclature. Combining factors which are constant for a given system and putting $\eta = E_r - V$, where E_r is the reversible potential,

$$i = K_1 A_e(B) (A) \left(e \right)^{\alpha} \frac{1-\alpha}{e} \frac{\alpha n^2 (E_r - V)}{RT} \frac{-(1-\alpha)n^2 (E_r - V)}{RT} \quad (2)$$

(A), (B) are the activities of diffusing reactant and product respectively. If (a) is the required function of activities left after removing (A) and (B)

$$K_1 = kN_g(a)e \frac{-\Delta F_o^*}{RT} \frac{\alpha \Delta F_o}{RT} \quad (3)$$

Consider the case where the reverse reaction represented by the right hand term in the parenthesis in equation 2 is negligible (4). Then

$$i = K_1 A_e(B) (A) \left(e \right)^{\alpha} \frac{1-\alpha}{e} \frac{\alpha n^2 (E_r - V)}{RT} \quad (4)$$

Let S be the area per cm^3 of the porous system in the electrode. Then, at a section dx in the electrolyte/electrode corresponding to x (see Figure 1), reaction in element dx, per sq cm of geometric area of electrode

$$\begin{aligned} &= K_1 S(B) (A) \left(e \right)^{\alpha} \frac{1-\alpha}{e} \frac{\alpha n^2 E_r}{RT} \frac{-\alpha n^2 V}{RT} dx \\ &= D(d^2 A / dx^2) dx \end{aligned}$$

for steady state conditions (assuming activity coefficients to be either unity or constant.) Thus

$$d^2 A / dx^2 = K_1 (S/D) e^{-\alpha n^2 V / RT} (B)^{\alpha} (A)^{(1-\alpha)} e^{\alpha n^2 E_r / RT} \quad (5)$$

If the ohmic resistance within the pores and the electrode is neglected, V must be a constant for the electrode. However, E_r will vary with penetration according to

$$E_r = E_o + (RT/n^2) \ln(A/B) \quad (6)$$

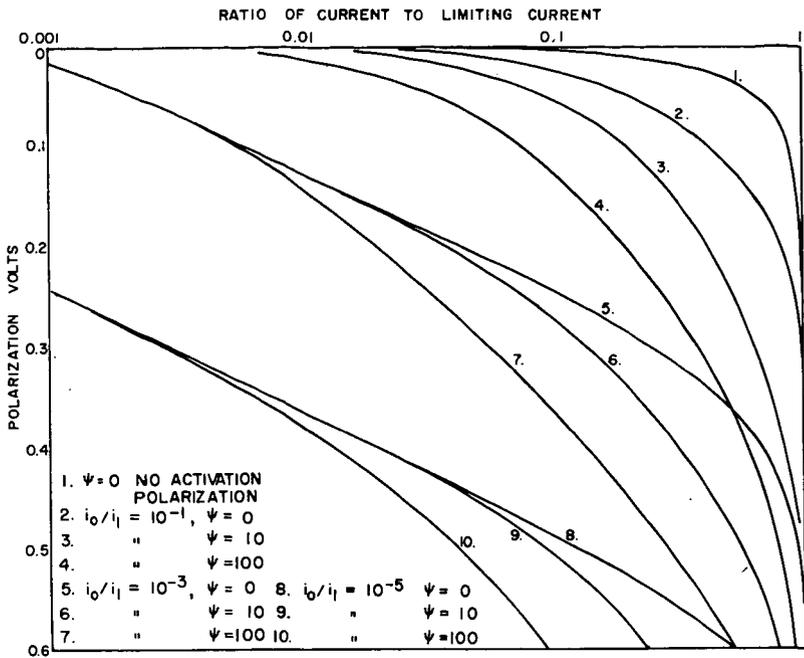


FIGURE 2. RELATION BETWEEN CURRENT, POLARIZATION, EXCHANGE CURRENT, AND ψ .

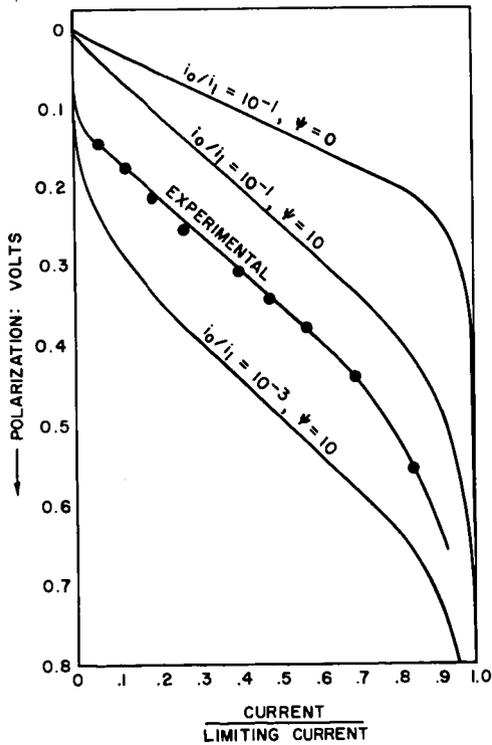


FIGURE 3. COMPARISON OF EXPERIMENTAL AND THEORETICAL POLARIZATION CURVES FOR A POROUS-CARBON H_2 ELECTRODE

Therefore equation (5) can be written as

$$d^2A/dx^2 = K_2(B)^{\alpha} (A)^{1-\alpha} (A)^{\alpha} (B)^{-\alpha} \quad (7)$$

where

$$K_2 = K_1(S/D)e^{-\alpha nFV/RT} e^{\alpha nFE_0/RT} \quad (8)$$

Thus

$$d^2A/dx^2 = K_2(A) \quad (9)$$

The solution of this equation for boundary conditions of $A = A_g$ at $x = d$ and $dA/dx = 0$ at $x = 0$ is

$$A = A_g \left(\frac{e^{\sqrt{K_2}x} - \sqrt{K_2}x}{e^{\sqrt{K_2}d} + e^{-\sqrt{K_2}d}} \right) \quad (10)$$

The steady state current density (based on the geometric area of electrode) is given by

$$i = D(dA/dx)_{x=d} \quad (11)$$

That is

$$i = DA \sqrt{K_2} \tanh(d\sqrt{K_2}) \quad (12)$$

Let

$$d\sqrt{K_2} = \beta \quad (13)$$

Then

$$i = (D/d)A_g\beta \tanh\beta \quad (14)$$

For a fixed system β is a function of V only.

The effect of concentration polarization in the "stagnant film" on the exterior of the electrode is given by (5)

$$i = (\Delta/\delta)(A_b - A_s) \quad (15)$$

where δ , the thickness of the stagnant film, is defined by equation 15* and Δ is the effective diffusion coefficient (in appropriate units) of A in the electrolyte. The interface concentration A_s is, in general, unknown. Eliminating A_s from equations (14) and (15) gives

$$i = (D/d)A_b\beta^2 / (\beta/\tanh\beta + \beta^2/\psi) \quad (16)$$

where

$$\psi = (\Delta/\delta)(d/D) = \frac{\text{ease of mass transport at exterior}}{\text{ease of mass transport in interior}} \quad (17)$$

Now if there were no concentration polarization effects inside or outside of the electrode the current would be the "ideal" current where

$$\begin{aligned} i_{\text{ideal}} &= dSK_1(B_b)^{\alpha} (A_b)^{1-\alpha} e^{\alpha nFE_{rb}-V}/RT \\ &= dSK_1(A_b) e^{\alpha nFE_0/RT} e^{-\alpha nFV/RT} \end{aligned}$$

From equation 8

$$i_{\text{ideal}} = dD K_2(A_b)$$

and from equation 13

$$i_{\text{ideal}} = (D/d)(A_b)\beta^2 \quad (18)$$

Therefore, from equations (16) and (18)

$$i = \frac{i_{\text{ideal}}}{\beta/\tanh\beta + \beta^2/\psi} \quad (19)$$

*The δ concept is retained for convenience as it allows a direct comparison of D with Δ .

In equation (19) the term

$$\frac{1}{\beta/\tanh\beta + \beta^2/\psi} \quad (20)$$

represents an effectiveness factor for the utilization of the electrode. At low currents it will tend to 1, but at currents approaching the limiting current it will tend to zero. The limiting current is given by

$$i_1 = (\Delta/d)(A_b) \quad (21)$$

Therefore

$$(d/DA_b) = \psi/i_1$$

Since $i_{ideal} = i_0 e^{\alpha n f \eta / RT}$ where i_0 is the exchange current per unit geometrical area of electrode

$$\beta^2 = \psi(i_0/i_1) e^{\alpha n f \eta / RT}$$

Thus equation (19) can be expressed as

$$i/i_1 = \frac{(i_0/i_1) e^{\alpha n f \eta / RT}}{\sqrt{\psi(i_0/i_1) e^{\alpha n f \eta / RT}} / \tanh \sqrt{\psi(i_0/i_1) e^{\alpha n f \eta / RT}} + (i_0/i_1) e^{\alpha n f \eta / RT}} \quad (22)$$

FOUR ZONES OF POLARIZATION VERSUS CURRENT

We can now describe four zones in the polarization current relation. Firstly, at low currents where no mass transport polarization exists and the reverse reaction is appreciable, the polarization versus current relation is

$$\text{Zone I} \quad i = i_0 (e^{\alpha n f \eta / RT} - e^{-(1-\alpha) n f \eta / RT}) \quad (23)$$

At higher currents the normal Tafel region is reached. In this case, if concentration polarization is negligible the required relation is

$$\begin{aligned} \text{Zone II} \quad i &= i_0 e^{\alpha n f \eta / RT} \\ \text{or} \quad \eta &= (2.3RT/\alpha n f) \log i - (2.3RT/\alpha n f) \log i_0 \\ &= a + b \log i \end{aligned} \quad (24)$$

The slope of the $\eta/\log i$ curve is b . This can be obtained from equation (19) by noting that at small values of β , $\beta/\tanh\beta$ is one and $\beta^2 \rightarrow 0$.

When concentration polarization within the pores of the electrode comes into force and if ψ is large, equation (19) can be simplified to (since $\beta/\tanh\beta$ for $\beta > 2$ is very nearly β),

$$\begin{aligned} \text{Zone III} \quad i &= i_{ideal}/\beta \\ &= \sqrt{(D/d)(A_b)} i_0 e^{\alpha n f \eta / 2RT} \\ \text{or} \quad \eta &= a^1 + 2b \log i \end{aligned} \quad (25)$$

The slope of the polarization/current curve is now twice the normal Tafel slope.

At higher currents where mass transport in the stagnant film becomes important, $\beta^2/\psi \gg \beta$ and

$$\begin{aligned} \text{Zone IV} \quad i &\rightarrow i_0 e^{\alpha n f \eta / RT} / (i_0 / i_1) e^{\alpha n f \eta / RT} & (26) \\ &\rightarrow i_1 \end{aligned}$$

Calculated Polarization Versus Current Curves

In practice, the four zones will probably not often occur in discrete recognizable form. For instance, if the penetration of the electrolyte into the electrode is zero then Zone III disappears completely. Furthermore, the transition zones between the various may be quite extended, and the zones themselves relatively short. Figure 2 illustrates the effect of ψ on the polarization-current curve. The representative values of ψ were chosen as follows. The theory of diffusion through porous media (6) indicates that

$$D = \Delta \theta / q \quad (27)$$

where θ is the porosity and q is a tortuosity factor. Taking θ as 0.3 and q as $\sqrt{2}$ (6)

$$\psi = 5d/\delta$$

δ is of the order (5) of 0.05 cms for unstirred electrolytes, to 0.001 cms for high rates of flow past the electrode. d is possibly in the range of 0 to 0.1 cms. Therefore ψ can quite reasonably range from zero to 500. For unstirred electrolytes a value of ψ of 10 seems reasonable. Therefore, values of ψ of 0, 10 and 100 were used in the calculations.

It is convenient to plot the current in the form given by equation (22), that is, in the dimensionless form i/i_1 . The unknown variables in the current-voltage relation are then ψ , i_0/i_1 and αn . Figure 2 shows a series of curves, on a logarithmic current basis, calculated from equation (22). The value of αn chosen was 1/2* and the calculations performed for room temperature conditions: the value of b in the Tafel equation is thus approximately 0.12 volts per logarithmic current increment.

Use of Curves

It can be noted from Figure 2 that although there are three adjustable parameters, the curves for values of ψ between 10 and 100 vary in position more than in shape. Change in αn changes the scale of the voltage ordinate, but again the shape of the curves at different values of ψ is fairly definite. Therefore the curves do not represent a theory which can be forced to fit any given set of data.

Figure 3 shows a linear plot of the curves compared with a typical hydrogen half-cell curve for an activated porous carbon electrode (with negligible i_r loss to the reference electrode).

Where only the normal concentration polarization in the exterior "stagnant" film is applicable, that is $\psi = 0$, the straight line portion of the curve has a slope of about 2b. Therefore, the cell behaves as if it had an extra ohmic resistance of

$$r = 2b/i_1 \quad (28a)$$

At values of ψ between 10 and 100, the slope is about 3.9b and

$$r = 3.9b/i_1 \quad (28b)$$

Interfering Factors

A number of factors can change the shape of the polarization-current curve in ways not predicted by the theory. Some of these are as follows.

In solving equation 7 it was assumed that the activity of the reactant occurred in first order form. However, if the equation is solved for zero or second order it is found that the final result is the same as equation 22.

It has been assumed that concentrations giving mass transport are proportional to activity gradients giving polarization. The effects of deviations from this assumption are probably fairly small.

*For different values of αn or b , the voltage scale must be adjusted accordingly.

Where more than one reaction path is possible the total current at a certain voltage is the sum of the reaction currents. One current will normally out-weigh the other in the polarization-current relation. However, if the Tafel b coefficient is higher for the predominating reaction at near open-circuit conditions than for another possible reaction, the second reaction may come to be predominating at higher current drains (7). In addition, when the limiting current for a given reaction is reached it is often observed that another more highly polarized reaction can occur to give extra current. This sometimes has the effect of making the limiting current ill-defined.

When consecutive reactions or processes are involved, the polarization at a given current is the interacting sum of the two polarization effects (7). This is so for an electrochemical reaction in series with a mass transport process, or an electrochemical reaction in series with another reaction such as chemisorption or desorption. At low currents the polarization due to one reaction may be negligible but it may become an added polarization at higher currents.

OPEN-CIRCUIT POLARIZATION

Equation 22 was derived on the assumption that the reactions were far from equilibrium and the reverse current negligible (see equation 4). At low currents when the system is near equilibrium this assumption is clearly not true. However, there are a number of factors which make measurements at or near open circuit conditions difficult to interpret. Consequently, this region is sometimes of less importance than the higher current density regions considered. Some of the factors which affect low current density results are as follows.

At low current densities, the currents produced by secondary reactions due to impurities, electrode corrosion, or depolarization by diffusion or leakage of gas to the opposite electrode may be sufficient to interfere with the reaction under investigation. For example, where these reactions have free energies differing from the basic reaction, all of the reactions cannot be at equilibrium at a certain open-circuit potential. The electrode thus tends to assume a mixed open-circuit potential. For precise electrochemical measurements it is necessary to rigorously purify the components to minimize secondary reactions (8), but this is sometimes impossible or undesirable in practical fuel cells.

For high temperature systems it is possible that oxides form on an electrode faster than they can be reduced by the fuel. In this case, the apparent open-circuit potential will be a potential between that corresponding to the fuel pressure and that corresponding to the hypothetical fuel pressure in equilibrium with the oxide. Again, the fuel may be irreversibly cracked at the electrode and the potential will then correspond to the free energy of the active constituent in the fuel gas and not the total free energy of the fuel.

CONCENTRATION POLARIZATION AT LOW CURRENTS

Under certain circumstances, concentration polarization may occur at low currents. Let us consider concentration polarization at conditions where activation polarization is negligible. If the reversible potential corresponding to the bulk activities of the reactants and products is E_b , the actual reversible potential is, for first order reactions,

$$E_r = E_b - (RT/nF) \ln(R_b P / R P_b)$$

where R, P are the actual activities of reactant and product and R_b, P_b are the bulk activities. Putting

$$\eta = E_b - E_r,$$

$$\eta = (RT/nF) \ln(R_b P / R P_b) \quad (29)$$

Now

$$i = k_1 (R_b - R) = k_2 (P - P_b) \quad (30)$$

where k_1, k_2 are appropriate mass transport factors in units corresponding to current. Combining equations 29 and 30 to eliminate the unknowns R and P,

$$\eta = (RT/nF) \ln \left[\frac{1 + i/P_b k_2}{1 - i/R_b k_1} \right] \quad (31)$$

In normal circumstances R_b, P_b are large quantities and η is negligible at small values of i . However, where a product of reaction is present in only very small bulk concentration, $i/P_b k_2$ may be significant at very low currents. Then

$$i = k_2 P_b (e^{n\eta/RT} - 1) \quad (32)$$

This has the form

$$i = I (e^{\alpha n\eta/RT} - e^{-(1-\alpha)n\eta/RT})$$

with $\alpha = 1$, and I an apparent exchange current. For appreciable values of η

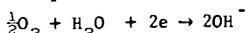
$$i = P_b k_2 e^{n\eta/RT} \quad (33)$$

For example, consider the formation of peroxide ion in oxygen-alkaline half-cells according to $O_2 + H_2O + 2e \rightarrow OH^- + HO_2^-$.

If the value of the activity of HO_2^- is the equilibrium value of $HO_2^- \rightleftharpoons \frac{1}{2}O_2 + OH^-$

then the reversible half-cell voltage corresponds to the reaction $\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$.

However, the equilibrium concentration of peroxide ion in the bulk of the solution is of the order of 10^{-16} gm-ions per liter. The mass transport factor is of the order of 25 milliamps per sq cm per gm-ion per liter for unstirred electrolyte. In order to diffuse away peroxide ion the concentration of peroxide ion at the electrode must increase considerably and, since the equilibrium concentration is so small, the increase produces a large deviation from the expected open-circuit value of the

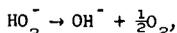


reaction. Substituting values into equation 33 gives

$$i = (25)(10^{-16}) \text{ antilog } (\eta/0.03)$$

This gives a polarization of 0.36 volts at the small current of 2.5 microamps per sq cm and a polarization of 0.51 volts at 250 milliamps per sq cm, for an uncatalyzed electrode.

If a catalyst is added to the surface of the electrode to bring about decomposition of the peroxide according to



then polarization is much reduced. Mass transport polarization effects of the OH^- ion are small due to the large bulk concentration of the ion already present. Let us assume that the catalyst causes a first-order decomposition of peroxide at the electrode surface, of the form

$$\text{rate} = k_3 P \quad (34)$$

where k_3 is a rate constant in amps per sq cm of electrode per gm-ion liter⁻¹ of peroxide. Then

$$i = k_2 (P - P_b) + k_3 P \quad (35)$$

and

$$\eta = (RT/nF) \ln [(i + k_2 P_b) / (k_2 + k_3) P_b]$$

or

$$i = (k_2 + k_3) P_b [e^{n\eta/RT} - k_2 / (k_2 + k_3)] \quad (36)$$

For an appreciable value of η

$$i = (k_2 + k_3) P_b e^{n\eta/RT} \quad (37)$$

Comparing equation (37) with equation (33) it is seen that the effect of the catalyst, which increases k_3 , is to increase the apparent exchange current. Thus a greater current is required to produce a given amount of polarization.

A more general treatment which combines the effects of activation polarization with the mass transport and catalytic decomposition effects given above is as follows.

The following equations are combined:

$$E_r = E_b - (RT/nf) \ln(P/P_b)$$

$$i = k_2(P - P_b) + k_3P$$

$$i = kN_s A_e (R_b)^{1-\alpha} (P)^\alpha (e^{\alpha n f (E_r - V)/RT} e^{-(1-\alpha) n f (E_r - V)/RT})$$

$$= I(P/P_b)^\alpha (e^{\alpha n f (E_r - V)/RT} e^{-(1-\alpha) n f (E_r - V)/RT})$$

$$\eta = E_b - V$$

These give

$$i = I \left\{ e^{\alpha n f \eta / RT} e^{-(1-\alpha) n f \eta / RT} \left[(i + k_2 P_b) / (k_2 + k_3) P_b \right] \right\}$$

Then, if i is appreciable and, if P_b is very small,

$$i/P_b \gg k_2$$

Therefore

$$i = \frac{I e^{\alpha n f \eta / RT}}{1 + (I/k_2 + k_3) P_b} e^{-(1-\alpha) n f \eta / RT} \quad (38)$$

When $I/(k_2 + k_3)P_b$ is large and at moderate values of η , equation 38 reduces to equation 37. At large values of η , the equation reduces to the normal equation

$$i = I e^{\alpha n f \eta / RT}$$

It should be noted that since I contains a term $(P_b)^\alpha$, (see equation 4), then values of I will be about $\sqrt{P_b}$ smaller than the usual exchange currents for unit activities. However, k_3 must still have large values to overcome the influence of the small value of P_b . For any appreciable amount of catalysis k_2 is probably much smaller than k_3 and the equation which is most likely to apply is

$$i = k_3 P_b e^{n f \eta / RT} \quad (39)$$

Of course, many assumptions have been made in the above analysis, but it does serve to show that the current-voltage relation may be almost entirely dependent on the effectiveness of the peroxide decomposing catalyst.

CONCLUSIONS

Very little precise information on the mechanisms and causes of polarization in fuel cells has appeared up to the present. Possibly this is partly due to the previous lack of theories to explain the shape of the polarization-current curves in the range of currents of practical use (9). Stender and Ksenzhek (10) have considered theoretically and experimentally the case where concentration gradients in the electrode are negligible, but appreciable ohmic resistance occurs within the pores. For practical fuel cells, the opposite case considered in this paper is perhaps more generally applicable since high concentrations of strongly conducting electrolytes are used.

Even with the application of the theory developed herein, results of polarization investigations of both gas usage and gas evolution are still sometimes difficult to interpret. For the hydrogen half-cell using porous electrodes, for instance, our experimental work indicates that dual consecutive and simultaneous reaction mechanisms are present with some catalyst materials and electrolytes.

ACKNOWLEDGMENTS

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SYMBOLS

a	Tafel constant ($2.3RT/\alpha nF$) $\log(i/i_0)$.
a^1	Pseudo Tafel constant defined by equation 25.
(a_p)	The product of the activities of reaction products, each raised to the appropriate power necessary to satisfy the Nernst equation for the reaction considered.
(a_r)	As for (a_p) , but for the reactants involved.
A	Activity or concentration of the mass transport limited reactant.
A_b	The value of A in the bulk of the electrolyte (or gas phase).
A_e	The effective reaction area per unit geometric area of the electrode.
A_s	The value of A at the external surface of the electrode.
B	The activity or concentration of the product of reaction.
B_b	The value of B in the bulk of the electrolyte.
d	The thickness of the effective reaction penetration in the electrode (see Figure 1).
D	The effective diffusion coefficient of A in the electrode pores.
E_0	The reversible open-circuit potential at unit activity.
E_r	The reversible potential for the concentrations A, B.
E_{rb}	The reversible potential for the concentrations A_b, B_b .
F	Faraday
ΔF_0^\ddagger	Standard state free energy change.
ΔF_0^\ddagger	Standard state free energy of activation.
i	Current density.
i_1	Limiting current density.
i_0	Exchange current.
I	An apparent exchange current (equation 32) or, the exchange current for unit activity of P (equation 38).
k	Pre-exponential rate constant in units of current density.
k_1	Mass transport factor defined by equation 30.
k_2	Mass transport factor defined by equation 30.
k_3	Decomposition rate defined by equation 34.
K_1	Constant defined by equation 3.
K_2	Constant defined by equation 8.
K_3	Constant defined by equation A4.
n	Number of electrons in the Nernst equation.
N_s	Number of active sites per unit effective area.
P	Activity or concentration of reaction product at low currents.
P_b	The value of P in the bulk of the electrolyte.
q	Tortuosity factor for pores in the electrode.
r	Apparent ohmic resistance.
S	Surface area of electrode per unit volume.
V	Voltage of electrode.
α	The fraction of polarization aiding the reaction in the direction considered.
β	Parameter defined by equation 13.
δ	Effective thickness of stagnant film.
Δ	Effective diffusion coefficient of reactant in electrolyte.
η	Polarization.
ψ	Parameter defined by equation 17.
θ	Effective cross-sectional area, per unit area, of electrode for mass transport \approx porosity.

LITERATURE CITED

- (1) Parsons, R., "Handbook of Electrochemical Constants", p. 95, Academic Press, Inc., New York, 1959.
- (2) Gorin, E., and Recht, H. L., Chapter 8 in "Fuel Cells", Ed. G. Young, Reinhold Pub. Corp., New York, 1960.
- (3) Austin, L. G., "Effect of Mass Transport on the Carbon-Carbon Dioxide Reaction", p. 65, Doctoral Thesis, Pennsylvania State University, 1961.
- (4) Austin, L. G., Chapter 4 in "Fuel Cells", Ed. G. Young, Reinhold Pub. Corp., New York, 1960.
- (5) Kortum, G., and Bockris, J. O'M., "Textbook of Electrochemistry", p. 400, Vol. II, Elsevier Pub. Co., New York, 1951.
- (6) Carman, P. C., "Flow of Gases Through Porous Media", p. 46, Academic Press, Inc., New York, 1956.
- (7) Parsons, R., Trans. Faraday Soc., (London), 54, 1053 (1958).
- (8) Bockris, J. O'M., "Modern Aspects of Electrochemistry", p. 212, Butterworth's Scientific Publications (London), 1954.
- (9) Yeager, E., Technical Report 13, "The Measurement of Polarization", p. 17, Office of Naval Research Contract Nonr 2391(00), Project NR359-277, (1960).
- (10) Stender, V., and Ksenzhek, O., Zhur. priklad. Khim., 32 III, 121 (1957). Quoted in reference 9 above, p. 18.

APPENDIX

DERIVATION OF THE INTERNAL MASS-TRANSPORT-AFFECTED POLARIZATION RELATION FOR NEAR REVERSIBLE CONDITIONS

Instead of making the assumption involved in equation 4, let us use the full equation

$$i = K_1 A e(B) \alpha_{(A)}^{1-\alpha} (e^{\alpha n f (E_r - V) / RT} - e^{-(1-\alpha) n f (E_r - V) / RT}) \quad (A1)$$

Substituting for E_r from

$$E_r = E_o + (RT/nf) \ln(A/B)$$

$$i = K_1 A (A e^{\alpha n f (E_o - V) / RT} - B e^{-(1-\alpha) n f (E_o - V) / RT}) \quad (A2)$$

As before, a differential equation relating concentration and distance is obtained, this time of the form

$$d^2 A / dx^2 = K_1 (S/D) (A e^{\alpha n f (E_o - V) / RT} - B e^{-(1-\alpha) n f (E_o - V) / RT}) \quad (A3)$$

This can be put as

$$d^2 A / dx^2 = K_2 A - K_3 B \quad (A4)$$

where K_2, K_3 are constants. For equimolar counter-diffusion of A and B

$$A + B = A_b + B_b = \text{constant}$$

This assumes that concentration gradients external to the electrode are negligible, that is, we are dealing with the low current range.

Equation A4 can now be expressed as

$$d^2 A / dx^2 = (K_2 + K_3) [A - K_3 (A_b + B_b) / (K_2 + K_3)] \quad (A5)$$

The solution of this equation is similar to that given before, with the end result,

$$\begin{aligned}
 i &= D[A_b - K_3(A_b + B_b)/(K_2 + K_3)] \sqrt{K_2 + K_3} \operatorname{tanh} \sqrt{K_2 + K_3} \\
 &= D[(A_b K_2 - B_b K_3) / \sqrt{K_2 + K_3}] \operatorname{tanh} \sqrt{K_2 + K_3} \quad (A6)
 \end{aligned}$$

Now

$$i_{\text{ideal}} = dSK_1(A_b e^{\alpha n_f(E_0 - V)/RT} - B_b e^{-(1-\alpha)n_f(E_0 - V)/RT}) \quad (A7)$$

Therefore

$$\begin{aligned}
 A_b K_2 - B_b K_3 &= A_b K_1(S/D) e^{\alpha n_f(E_0 - V)/RT} - B_b K_1(S/D) e^{-(1-\alpha)n_f(E_0 - V)/RT} \\
 &= i_{\text{ideal}}/dD
 \end{aligned}$$

and

$$i = \frac{i_{\text{ideal}}}{d \sqrt{K_2 + K_3}} \operatorname{tanh} \sqrt{K_2 + K_3} \quad (A8)$$

When $A_b \simeq B_b$ and if the reaction is near equilibrium, $K_2 \simeq K_3$ and

$$\begin{aligned}
 K_2 + K_3 &\simeq 2K_2 \\
 &\simeq \frac{2 i_0 e^{\alpha n_f \eta / RT}}{dDA} \quad (A9)
 \end{aligned}$$

Since $d/DA_b = \psi/i_1$,

$$i = \frac{i_{\text{ideal}}}{\sqrt{2} \sqrt{\psi A_0 / i_1} e^{\alpha n_f \eta / RT}} \operatorname{tanh}(\sqrt{2} \sqrt{\psi A_0 / i_1} e^{\alpha n_f \eta / RT}) \quad (A10)$$

This is of the same form as obtained before, except for the numerical factor $\sqrt{2}$, but the i_{ideal} is in this case the complete form

$$i_{\text{ideal}} = i_0 (e^{\alpha n_f \eta / RT} - e^{-(1-\alpha)n_f \eta / RT})$$