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The Fundamentals of Electrode Kinetics as They Apply to Low Temperature Hydrogen Oxygen Fuel Cells

L.G. Austin

Fuel Technology Department
The Pennsylvania State University
University Park, Pennsylvania

INTRODUCTION

In a short paper such as this it is impossible to do more than briefly summarize and explain some of the fundamental equations of irreversible electrode kinetics. It is believed, however, that there is a need for such a presentation since many of the workers becoming interested in the field of fuel cells will not be familiar with the terms and concepts involved. The subject is treated with respect to the well known [1] low temperature hydrogen oxygen fuel cell employing porous conducting electrodes.

DISCUSSION

Basic Formulae

The following thermodynamic formulae form the basis of the more specific formulae derived later and are presented for convenience. In any process

$$aA + bB + \cdots\cdots \rightleftharpoons mP + nQ + \cdots\cdots$$

the change in free energy per mole of reaction from left to right is given by

$$\Delta G = -RT \ln K_p + RT \ln \frac{(P)^m (Q)^n \cdots}{(A)^a (B)^b \cdots} \quad (1)$$

a, b, m, n are the number of molecules involved, (A), (B), (P), (Q) are the activities of the reactants and products and K_p is the equilibrium constant of the reaction.

For some arbitrary definition of a standard state where the activities are unity

$$\Delta G_o = -RT \ln K_p \quad (2)$$

where ΔG_o is known as the standard state free energy change. For a substance going from one activity, a_1, to another, a_2, $K_p = 1$, and

$$\Delta G = RT \ln a_2/a_1$$
$$a_2 = a_1 e^{\frac{\Delta G}{RT}} \qquad (3)$$

The rate of an activated chemical reaction in one direction is given by

$$v_1 = k_1 (A)_1^a (B)_1^b (\ ) \cdots (\ ) e^{\frac{-\Delta G_o^*}{RT}} \qquad (4)$$

where v_1 is the rate of reaction, $(A)_1$, $(B)_1$ are the activities of reactant at the reaction condition, ΔG_o^* is the free energy of activation at the standard state used to define the activities and k_1 is a constant for the reaction.

The electrical potential, E, involved for a change of free energy ΔG is given by

$$\Delta G = -nFE \qquad (5)$$

where F is the Faraday and n is the number of electrons involved in the reaction. A consistent system of units must be used.

Open Circuit Potentials

Hydraulic Analogy

At open circuit, when no current is drawn from the cell, the potential obtained from the cell is equal to the corresponding free energy change in transporting reactant to product under these ideal reversible conditions. Figure 1 shows a hydraulic analogy of a fuel cell at open circuit. Since it is impossible to measure the potential of a single electrode it is necessary to have two electrodes, represented by the two U-tubes of the figure. The difference in levels of the liquid in each arm of a U-tube (h_1 say) represents the free energy change between the reactant and the product for a half cell. For a fuel cell in which reactant is supplied continuously to each electrode and product removed continuously, the hydraulic analogy requires infinite reservoirs at the liquid levels; one of these is shown at A for illustration.

It is impossible to measure the voltage corresponding to h_1 but if the right hand U-tube is considered as a reversible standard state hydrogen half cell, h_2 is arbitrarily taken as zero, and Δ_p corresponds to the half cell potential (with respect to the standard hydrogen half cell) of the left hand electrode. With valve V closed, that is, no flow through the system, $\Delta_p \equiv h_1$, and the open circuit potential, E_r (infinite external resistance is comparable to the valve being closed) is equivalent to ΔG. It is clear from this picture that the potential change through the electrode-electrolyte surface is zero at zero current drain; the potential drop, Δ_p, exists across the external electrode to electrolyte connection. In an electrode process at open circuit, at the instant of electrode immersion ions pass into solution across the

electrode-electrolyte interface. The charge remaining on the electrode produces an attractive electric field holding back further dissolution, while the charge of opposite sign produced in the electrolyte also produces an electric field opposing further dissolution. These forces are equivalent to the p_1 (suction) and p_2 (pressure) in the analogy.

Hydrogen half cell with catalyzed porous carbon electrode and alkaline electrolyte

The half cell reaction can be represented as

$$H_2 + \text{active site} \rightleftharpoons 2[H]_{\text{chemisorbed}} \qquad (6)$$

$$[H] + OH' \rightleftharpoons H_2O + e + \text{active site} \qquad (7)$$

At equilibrium let the fraction of the active sites occupied by chemisorbed hydrogen be θ_e. The fraction of unoccupied sites is then $1-\theta_e$ and the chemisorption equilibrium of reaction (6) can be represented (2) by

$$p(1-\theta_e)^2 i = \theta_e^2 j \qquad (8)$$

where i and j are rate constants and p is the pressure of hydrogen. Thus, from equations (1) and (2), the free energy change on chemisorption is

$$(\Delta G)_c = (\Delta G_o)_c + RT \ln \theta/(1-\theta)p^{\frac{1}{2}} \qquad (9)$$

For reaction (7), the free energy change from the chemisorbed state to product, $(\Delta G)_{C-H_2O}$, is given by

$$(\Delta G)_{C-H_2O} = (\Delta G_o)_{C-H_2O} + RT \ln \frac{(H_2O)(1-\theta)}{(\theta)(OH')} \qquad (10)$$

Substituting for $\theta/1-\theta$ from (9)

$$(\Delta G)_{C-H_2O} = (\Delta G_o)_{C-H_2O} + (\Delta G_o)_c - (\Delta G)_c + RT \ln \frac{(H_2O)}{(OH')p^{1/2}}$$

Now at equilibrium in the chemisorption process, equation (1) shows that $(\Delta G)_c$ is zero; further $(\Delta G_o)_{C-H_2O} + (\Delta G_o)_c = (\Delta G_o)_{H_2-H_2O}$, therefore

$$(\Delta G)_{C-H_2O} = (\Delta G_o)_{H_2-H_2O} + RT \ln \frac{(H_2O)}{(OH')p^{1/2}} \qquad (11)$$

where $(\Delta G_o)_{H_2-H_2O}$ is the overall standard state free energy change from hydrogen

to product. From equation (5)

$$nFE_r = nFE_o + RT \ln \frac{(H_2O)}{[OH^-]\,p^{1/2}} \qquad (12)$$

Thus, at open circuit, the reversible potential E_r should be independent of the chemisorption step and hence independent of the surface or catalyst used. Young and Rozelle [3,4] have presented evidence to show that this is not true, and they ascribe the loss of potential on open circuit as being due to loss of free energy on chemisorption. This immediately raises the question as to why, when hydrogen is allowed to stand in contact with the catalyst surface, a normal adsorption equilibrium fitting a Langmuir or Tempkin isotherm is not reached? Equation (8) can be expressed as

$$\theta = \frac{a p^{1/2}}{1 + a p^{1/2}} \qquad (13)$$

where a is a constant at a given temperature. This indicates that the surface is saturated, and hence irreversible, only at infinite pressure. A similar result is obtained by the use of the Tempkin isotherm[5]. The theory of these isotherms states that, providing θ is not continually removed as some other product of reaction, then the gas surface reaction is reversible and will reach an equilibrium state. The modification of the Freundlich adsorption isotherm suggested by Taylor and Halsey[6] gives θ as

$$\theta = (a_o p)^{\frac{RT}{q_m}} \qquad (14)$$

where a_o, q_m are constants. Clearly when $p = 1/a_o$, θ is 1, and hence $1/a_o$ represents a saturation pressure p_s, beyond which further increase in gas pressure (and hence gas free energy) produces no further free energy increase in the surface, and the system is irreversible. The loss of theoretical open circuit voltage, assuming that the Langmuir isotherm (equation 8) has fair numerical agreement with the Freundlich isotherm up to the saturation pressure[7] is approximately

$$E_r - E_{actual} = \frac{RT}{nF} \ln \frac{p}{p_s}, \quad p \not< p_s \qquad (15)$$

Raising the temperature of the cell should bring the cell nearer to reversibility since p_s increases with temperature. Different catalyst surfaces may have different values for p_s.

Young has attempted to correlate the loss of open circuit potential with heats of chemisorption[4]. However, such heats are free energy changes obtained on raising the pressure and consequently have little significance for an equilibrium process. Indeed these heats are often calculated using isotherms derived by assuming that an equilibrium state exists in which the transfer of an infinitesimal quantity of gas to the surface involves no free energy change.

There are other possible explanations for the open circuit voltage loss. It may be that a pseudo equilibrium is reached in which stray currents

are sufficiently large to disturb the equilibrium on a poorly catalyzed surface. Again the attainment of equilibrium may be slow, especially if the activation energy for chemisorption is high and θ_e tends to one. The rate of chemisorption is proportional to $(1-\theta)^2 \exp(-\Delta G_a^*/RT)$.

Under these circumstances it would be expected that the potential of the half cell would increase slowly with time. In general, if such irreversibility exists, it should be difficult to obtain consistent results for open circuit potentials.

Loss of Potential During Current Flow

The polarization or loss of potential during current flow is obviously of prime importance in the design of fuel cells. To obtain good fuel efficiency the cell must be operated at a maximum internal voltage loss of about 20 to 30% of the open circuit voltage. If the current flowing per sq. cm. of electrode area or per pound of cell is small, then the cell will be bulky and uneconomic. The theoretical analysis of polarization is an attempt to show which factors must be varied to obtain optimum conditions.

Activation polarization across the electrode-electrolyte surface

Consider the hydraulic analogy discussed previously. The transfer of ions across the electrode-electrolyte interface, being a chemical reaction, is activated, and the potential energy curve through the surface at open circuit can be visualized as in Figure 2. The energy is composed of the original chemical free energy and the electrical field energies which counterbalance the chemical energy to give zero free energy change across the interface. Stated more precisely, the activities of the reactants and products at the surface change to bring the reaction into dynamic equilibrium. This produces a concentration of electrons in the electrode surface and a concentration of positive ions at the plane of closest approach in the electrolyte; the open circuit potential is due to this double layer. Reducing the external resistance from infinity is comparable to partially opening valve V and allowing flow. Clearly a small flow will increase p_1 slightly and reduce p_2, Δp will decrease, and a pressure gradient is set up across B. In the electrical case this is equivalent to reducing the retaining electric fields and consequently the energy curve on the left in Figure 2 rises and that on the right falls. (See broken curves in Figure 2). The change in free energy through the surface on flow is clearly not available for outside potential and E_r is reduced to E. The rest of the overall free energy change of the reaction is carried through the external circuit by the electrons involved and the reaction can proceed only as fast as the external resistance will allow the current to flow, with Ohm's Law applying.

Let the change in free energy through the surface be $d(\Delta G)$. Then

$$\eta_a = E_r - E = \frac{-d(\Delta G)}{nF} \qquad (16)$$

η_a is called the activation polarization at the given current flow. At short circuit, if there were no other resistances to flow present, then the drop of free energy through the surface would be the total free energy change and $\eta_a = \frac{-\Delta G}{nF} = E_r$ where ΔG is the total free energy change of the reaction.

At open circuit a dynamic equilibrium exists across the interface,

$$[H] + OH' \rightleftharpoons H_2O + e +$$

Let $(a_H)_e$ be the activity of the chemisorbed hydrogen at equilibrium, $(a_{OH})_e$ be that of OH', $(a_{H_2O})_e$ be that of water, and $(a_s)_e$ be activity of active sites. Then from equation (4)

forward reaction rate $\nu_{1e} = k_1 (a_H)_e (a_{OH})_e e^{\frac{-\Delta G^*_{01}}{RT}}$

back reaction rate $\nu_{2e} = k_2 (a_s)_e (a_{H_2O})_e e^{\frac{-\Delta G^*_{02}}{RT}}$

The rate may be expressed as amps per sq. cm. of active area, and at equilibrium $\nu_{1e} = \nu_{2e} = I'$. Under non-equilibrium conditions, from equation (3)

$$(a_H)(a_{OH}) = (a_H)_e (a_{OH})_e e^{\frac{\Delta G_1}{RT}}$$

where ΔG_1 is the free energy change from equilibrium activities to those considered. A similar expression can be written for the back reaction with a free energy change of ΔG_2. Clearly the free energy changes represent the loss in free energy through the surface due to current flow and

$$-\Delta G_1 + \Delta G_2 = d(\Delta G) = -nF\eta_a$$

Let α be the fraction of η_a aiding the reaction from left to right. Then

$$\Delta G_1 = \alpha n F \eta_a$$

The new reaction rate from left to right is

$$\nu_1 = k_1 (a_H)(a_{OH}) e^{\frac{-\Delta G^*_{01}}{RT}}$$

$$= k_1 (a_H)_e (a_{OH})_e e^{\frac{-\Delta G^*_{01}}{RT}} e^{\frac{\Delta G_1}{RT}}$$

$$= I' e^{\frac{\alpha n F \eta_a}{RT}} \qquad (17)$$

I' is the equilibrium current corresponding to rate in either direction at equilibrium. Similarly, $\Delta G_2 = -(1-\alpha) n F \eta_a$ where $1-\alpha$ is the fraction of η_a decreasing the reaction from right to left, and

$$\nu_2 = I' e^{\frac{-(1-\alpha) n F \eta_a}{RT}} \qquad (18)$$

Thus the net current flow from left to right is

$$i' = I' \left(e^{\frac{\alpha n F \eta_a}{RT}} - e^{\frac{-(1-\alpha) n F \eta_a}{RT}} \right) \qquad (19)$$

In general, part of the polarization measured in equation (19) exists through the diffuse part of the double layer [8] extending from the plane of closest approach into the electrolyte. The structure of the double layer can be changed by the presence of salts in the electrolyte, specific adsorption on the electrode surface and electrolyte concentration. Thus I' in equation (19) is changed by these factors. It is easily shown[9] that I' may be represented as

$$I' = (I)_c \, e^{\frac{F\psi}{RT}(\alpha n - z)} \tag{20}$$

where ψ is the potential drop in the double layer and z is the number of electrons involved in transfer through the layer. $(I)_c$ is an equilibrium current which is more nearly characteristic of the reaction, while the term involving ψ can be used to explain the effects of modification of the double layer [10]. For the type of cell considered here the composition of the electrolyte is usually dictated by other considerations and providing specific adsorption is avoided the factor involving ψ is predetermined.

In equation (19), the value of i' was derived per sq. cm. of active site area. Normally, current is expressed per sq. cm. of geometric electrode area and

$$i = (\text{constant}) \quad N_s A_e i' \tag{21}$$

where N_s is the number of sites per unit effective area and A_e is the effective area per unit geometric electrode area. Then

$$\begin{aligned} i &= k N_s A_e I' \left(e^{\frac{\alpha n F}{RT}\eta_a} - e^{-\frac{(1-\alpha) n F}{RT}\eta_a} \right) \\ &= I \left(e^{\frac{\alpha n F}{RT}\eta_a} - e^{-\frac{(1-\alpha) n F}{RT}\eta_a} \right) \end{aligned} \tag{22}$$

I is called the exchange current density as it is the equilibrium forward and reverse currents flowing at open circuit. This term is sometimes reserved for the equilibrium current for standard state conditions, I_o, but it is easy to convert from one to the other knowing the cell pressures and concentrations.

As η_a becomes large in equation (22) (and if α does not alter in value) then the reverse reaction becomes negligible and

$$i = I \, e^{\frac{\alpha n F}{RT}\eta_a} \tag{23}$$

or

$$\begin{aligned} \eta_a &= \frac{2.3RT}{\alpha n F} \log i - \frac{2.3RT}{\alpha n F} \log I \\ &= a + b \log i \end{aligned} \tag{24}$$

where

$$a = \frac{2.3RT}{\alpha n F} \log \frac{1}{I}$$

$$b = \frac{2.3RT}{\alpha n F}$$

This is known as the Tafel equation. It applies when the polarization is greater than about 100 millivolts. For a required current the polarization is small as I is large. Neglecting double layer effect

$$I = k N_s A_e e^{-\frac{\Delta G^*_{01}}{RT}} \quad \text{(terms in equilibrium activities)} \qquad (25)$$

To obtain low polarization it is desirable to have as much effective surface per unit geometrical area as possible. This is accomplished by having a system of small pores with a high surface roughness in contact with the electrolyte. Thus when using porous carbon electrodes it is sometimes necessary to "activate" the carbon by reaction with air or steam. This burns open pores which were closed and increases the surface roughness. Again, since the reaction takes place at an area of contact of gas, solid and liquid, saturation of the surface with electrolyte will greatly increase polarization.

The function of the catalyst impregnated on the surface is to decrease the activation energy ΔG^*_{01} of the reaction. The standard state free energy change during the reaction is illustrated in Figure 3. Considering the chemisorption step,

$$\Delta G^*_{cf} = \Delta H^*_{cf} - T\Delta S^*$$

The desorption step gives

$$\Delta G^*_{cb} = \Delta H^*_{cb} - T\Delta S^*$$

Therefore

$$\Delta G^*_{cb} - \Delta G^*_{cf} = \Delta H^*_{cb} - \Delta H^*_{cf} = q$$

where q is the exothermic standard state heat of chemisorption[11]. When comparing catalysts, the catalyst with the smaller q should have a smaller ΔG^*_{01} and hence less activation polarization at a given current.

Increase in temperature increases I, but it also reduces the other term in equation (22). Normally the polarization is markedly decreased by increase in temperature. The effect of the quantity of catalyst is governed by N_s. As the quantity is increased from zero the polarization is decreased, but a saturation state is reached when the surface is completely covered with the optimum quantity of catalyst.

Increasing the gas pressure on the cell increases the equilibrium activities and should thus decrease polarization.

<u>Activation polarization of chemisorption.</u>

Equation (22) was derived specifically for the reaction

$$[H] + OH' \rightleftharpoons H_2O + e + \text{active site}$$

However, it is possible that the preceding chemisorption of hydrogen is slow during current flow. If this is true, the electrochemical reaction comes into balance with the chemisorption and an additional polarization is introduced, due to free energy changes on chemisorption. Considering the reaction

$$H_2 + \text{active site} \rightleftharpoons 2[H]$$

the activities may be represented as p, $(1-\theta)^2$ and θ^2. In a similar manner to the derivation of equation (22)

$$i = k N_S A_e p (1-\theta_e)^2 e^{-\frac{\Delta G_c^*}{RT}} \left(e^{\frac{\alpha n F \eta_a}{RT}} - e^{-\frac{(1-\alpha) n F \eta_a}{RT}} \right)$$

$$= I \left(e^{\frac{\alpha n F \eta_a}{RT}} - e^{-\frac{(1-\alpha) n F \eta_a}{RT}} \right)$$

where the rate constant, value of activation energy and exchange current are for the chemisorption process. When the cell is supplying current, θ must decrease to allow more chemisorption. If θ is near 1, a small decrease in θ produces much extra chemisorption but virtually no change in the back reaction; therefore the polarization completely aids the reaction from left to right and $\alpha = 1$. Since $n = 2$, the slope b of the Tafel line under these circumstances is

$$b = \frac{2.303RT}{2F} \simeq 0.03 \text{ volts, at room temperature.}$$

If the chemisorption is fast compared to the electrochemical step the value of θ does not change much and the value of (a_H) in equation (17) can be considered constant; α is about 1/2, n is 1 and the slope of the Tafel equation is about 0.12 volts[12]. Thus the slope of the Tafel equation gives a means of determining whether the chemisorption step or the electrochemical step is predominantly rate controlling. For chemisorption rate controlling, the function of the catalyst is to lower the activation energy of chemisorption. Activation and chemisorption activation polarization are considered in more detail by Parsons[13].

At sufficiently large current flows, θ tends to zero, α tends to zero and η_a tends to infinity. This expresses the fact that the reaction cannot proceed faster than chemisorption on to an almost bare surface. Thus the complete polarization versus current curve is as illustrated in Figure 4. If θ is not near 1 at open circuit, the curve will start at E_r but its shape will be that of the right hand portion of Figure 4.

Concentration Polarization

Concentration polarization is the loss of potential during current flow due to mass transport limitations in the cell. During current flow reactant has to be transported to the reaction site and energy is thus used in overcoming the resistance to flow which is always present.

Gas transport polarization

Gas transport through a porous carbon electrode is illustrated in Figure 5. If the reversible potential of the cell is for a pressure of p_1, then as the reaction proceeds and p_2 becomes less than p_1, the cell e.m.f. will fall.

If the fall is η_c at a current of i

$$\eta_c nF = RT \ln \frac{p_1}{p_2} \tag{26}$$

Assuming the carbon has an effective diffusion coefficient D_{eff}, independent of pressure [14] and that the electrode is in the form of a slab

$$\text{Rate} = D_{eff} \frac{(p_1 - p_2)}{\Delta L} \quad \text{per sq. cm.} \tag{27}$$

ΔL is the thickness of the electrode. Equation (27) may be expressed as

$$i = B\,(p_1 - p_2)$$

where B includes a conversion factor. Then

$$\eta_c = \frac{RT}{nF} \ln \frac{p_1 B}{p_1 B - i}$$

Since the maximum value of $p_1 - p_2$ is p_1, Bp_1 represents a limiting current, I_ℓ say, and

$$\eta_c = \frac{RT}{nF} \ln \frac{I_\ell}{I_\ell - i} \tag{28}$$

When i is small compared to I_ℓ, η_c is linearly dependent on i, and as i approaches I_ℓ, polarization becomes very great. Thus it is desirable for I_ℓ to be large. The thickness of the electrode cannot in practice be reduced beyond a certain limit. Due to the inhomogeneous nature of the pore system, reducing the thickness tends to give either gas leakage from the surface or flooding of the pore system by the electrolyte. Thus it is desirable to have an electrode which has a high diffusion coefficient, high internal area or roughness factor and which is as homogenous in pore structure as possible. In operation, since p_2 has to be maintained sufficiently high to prevent electrolyte flooding, p_1 would have to be raised as concentration polarization becomes appreciable.

Electrolyte concentration polarization

In a similar manner to that above the concentration polarization due to mass transfer of ions is

$$\eta_c = \frac{RT}{nF} \ln \frac{i_\ell}{i_\ell - i}$$

where the limiting current i_ℓ is given by

$$i_\ell = \frac{D_i z F a_i}{(1 - t_i)\,\delta} \tag{29}$$

D_i, a_i, t_i are respectively the diffusion coefficient, bulk activity and transport number of the ion and δ is the effective thickness of the diffusion layer adjacent to the electrode surface. This type of polarization is well described by Kortüm and Bockris [15].

The effect of concentration polarization can be introduced into equation (22) by writing

$$\alpha_1 \eta_0 = \alpha \eta_a + \eta_c$$

where η_0 is the overall polarization and η_c is the concentration polarization in the same direction as $\alpha \eta_a$. Considering just this direction

$$\begin{aligned} i &= I\, e^{\frac{\alpha n F \eta_a}{RT}} \\ &= I\, e^{\frac{\alpha_1 n F \eta_0}{RT}}\, e^{\frac{-nF\eta_c}{RT}} \\ &= I\, \frac{C_r}{C_{ro}}\, e^{\frac{\alpha_1 n F \eta_0}{RT}} \end{aligned} \qquad (30)$$

where C_r is the effective activity and C_{ro} is the original bulk activity of the reactants. $C_r/C_{ro} = I_e - i/I_e$ thus i appears on both sides of equation (3). The general form of the equation is similar to that in Figure 4. The introduction of concentration polarization in equation (22) must be made for all of the steps in the reaction which give appreciable concentration polarization.

Ohmic Resistance

In addition to the polarization already described an internal loss of potential, η_r, occurs due to the electrical resistance of the electrolyte. By Ohm's Law

$$\eta_r = i r$$

r is low for high concentration of ions in the electrolyte. It is of interest to note that if penetration of electrolyte into the pore system occurs, then the effective conductivity for ionic conduction is [16]

$$c_{eff} = \frac{\epsilon}{q} c_{free} \qquad (31)$$

where ϵ is the porosity of the carbon and q is a tortuosity factor. For porous carbon electrodes ϵ is of the order of 1/3. q may be very high[17] but is often[18] about 2 to 3 Thus a penetration of 1 mm will usually give as high an electrical resistance as about 1 cm of the free electrolyte between the electrodes.

The Oxygen Alkali Half Cell

If the oxygen half cell reaction were

$$\tfrac{1}{2} O_2 \rightleftharpoons [O] \;,\quad [O] + H_2O + 2e \rightleftharpoons 2\,OH'$$

then the standard state potential of an hydrogen oxygen fuel cell should be about 1.23 volts at room temperature. However, it has been shown[19,20] that the half cell reaction is

$$[O_2] + H_2O + 2e \rightleftharpoons HO_2' + OH'$$

Since the normal cell is not standard with respect to peroxide concentration the open circuit potential is usually not 1.23 volts. It is easily shown that if the peroxide ion is rapidly decomposed to its equilibrium value with respect to oxygen (in the electrode) and hydroxyl then the cell voltage would again be 1.23 volts. Even if peroxide decomposing catalysts are employed it appears that, at room temperatures, the decomposition is not sufficiently rapid for this equilibrium to be reached near the electrode surface and a loss of ideal potential occurs[21].

CONCLUSION

In studying the polarization of the type of fuel cells considered here it is important to determine the contribution of each type of polarization to each half cell. If such determinations are made, they will indicate what can be done to improve the performance of the cell. The various techniques for determining each polarization are described in the literature[12,15,22]. However, even if optimum conditions for minimum polarization are obtained, there are still many mechanical and technological difficulties to overcome in the construction of operating fuel cells.

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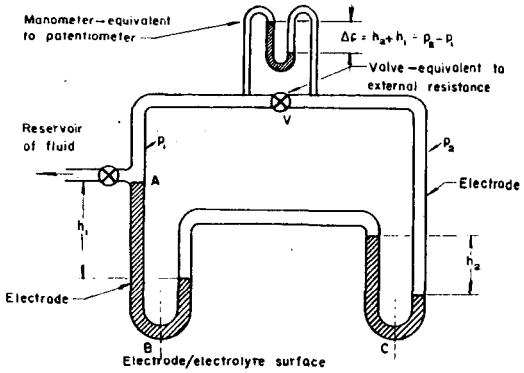

FIG. 1 Hydraulic analogy of a hydrogen – oxygen porous electrode fuel cell.

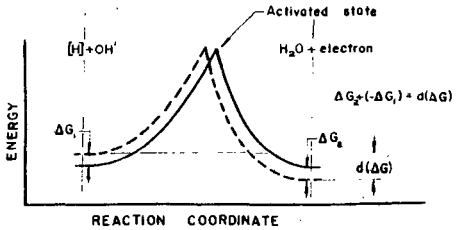

FIG. 2 Representation of energy state of reaction across electrode – electrolyte interface

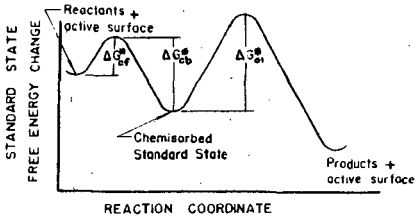

FIG. 3 Illustration of standard state free energy changes during reaction.

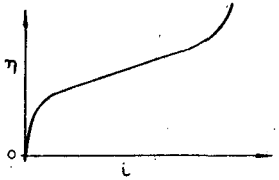

FIG. 4 Illustration of variation of chemisorption polarisation with current flow.

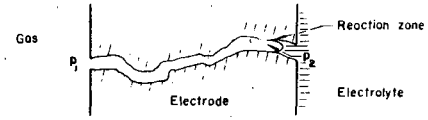

FIG. 5 Illustration of gas transport process in a porous electrode.