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HARRY DIAMOND LABORATORIES

Summary Report Number 7

on

Fuel Cells

ENGINEERING AND INDUSTRIAL EXPERIMENT STATION

College of Engineering

University of Florida

Gainesville

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The Current Density Supportable By Mass Transport at Submerged Electrodes

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Revised Scope of Work - ORDTL-CB-762

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Task 1 - Energy Transformation Systems

Conduct theoretical and experimental investigations to define the mechanism and control parameters of gas diffusion electrodes to fuel cells. Work will include, but not be limited to

1. Establish a mathematical model of the overall diffusion process including terms for contributions of known mechanisms in porous media.

2. Develope expressions for contributing mechanisms which contain the physical properties of the reactants and products, and the physical properties and geometrical parameters of the electrode.

3. Conduct experimental work to verify the mathematical model.

1.0 SUMMARY

A mathematical model is developed for the mass transport of a reacting species through a liquid to an electrode surface. The resistance is considered to be concentrated in a stagnant film of thickness δ. By considering no bulk flow of the non-reacting species the following equation is derived.

$$i_m = \frac{-cnF\ D_{AB} x_A^o}{\delta} \qquad (1)$$

If bulk flow of component B is considered, equation (2) is obtained.

$$i_m = \frac{m}{m+1} \frac{cnF\ D_{AB}}{\delta} \ln(1 - \frac{m+1}{m} x_A^o) \qquad (2)$$

In equations (1) and (2) the symbols have the following significance:

i_m = current density supportable by mass transport

c = concentration of solvent

n = number of g. equivalent per gram mole

F = Faraday

D_{AB} = diffusivity of A in B

x_A^o = concentration of A in bulk

δ = film thickness

m = moles of B produced per mole of A

Calculations are made for the case of oxygen (A) in water (B) under various concentrations and temperatures. For a film thickness of 10^{-3} cm, a temperature of 300^oK, and a partial pressure of oxygen of 1 atm, i_m is equal to 1.03×10^{-2} amps/cm^2.

For the case examined there is no significant difference between equations (1) and (2).

It is found that current densities are highest for low temperatures and high partial pressures of O_2. At constant pressure of O_2, the current density exhibits a minimum at approximately 80°C.

2.0 INTRODUCTION

One possible method of obtaining electrical energy directly from chemical energy is in a fuel cell with submerged electrodes. In this type of cell two compartments, the anode and the cathode compartments, might be filled with aqueous solutions saturated with an oxidizable gas and oxygen respectively. The gas may be bubbled through the solution in a compartment to keep it saturated and well mixed. In this type of cell the rate-controlling step could be the rate of diffusion of the reactants to the electrode surface.

The purpose of this report is to calculate the current density supportable by mass transfer to such submerged electrodes.

3.0 MATHEMATICAL MODEL

Since the processes in each electrode compartment are similar it is only necessary to develope the mathematical expressions for one of them. A solution for the other compartment results when the proper values of the several variables are inserted in the equations.

To develop a model in general terms, consider A diffusing through B. Since the liquid, B, is assumed to be well mixed, the concentration of A at any point in the bulk liquid may be assumed to be constant. We will also assume that all A which reaches the electrode surface will react instantaneously, so that the concentration of A at the electrode surface is zero. Because the concentration difference between the bulk liquid and the electrode surface is the only driving force and the electrode may be thought of as having infinite area as compared to the thickness of liquid through which reactant molecules must diffuse, we are concerned only with one-dimensional transport. This concentration difference may be assumed to exist over a small distance, δ, which may be thought of as a stagnant film. One may derive an expression for the flux, flow per unit time per unit area, of A arriving at the electrode surface by diffusion through this stagnant film. A schematic diagram is shown in Figure 1.

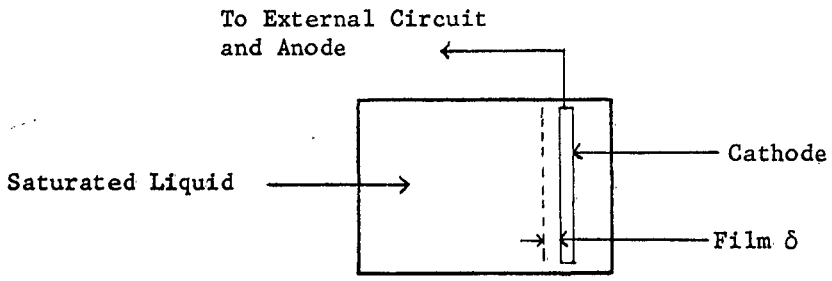

Figure 1

Schematic Diagram of Cathode Compartment

Writing a shell mass balance (1)

$$N_A = -cD_{AB} \frac{dx_A}{dz} + x_A(N_A + N_B) \qquad 3.0\text{-}1$$

In equation 3.0-1 the first term on the right hand side is the flux resulting from diffusion and the second term is the flux resulting from bulk flow. Before this equation can be solved a relation between N_A and N_B must be known.

3.1 No Bulk Flow of Component B

If we assume N_B to be equal to zero, equation 3.0-1 now becomes

$$N_A(1 - x_A) = -cD_{AB} \frac{dx_A}{dz} \qquad 3.1.1$$

Two solutions to this equation are possible. If we assume $x_A \ll 1$ and D_{AB} not a function of concentration we obtain

$$\int_0^{\delta} N_A dz = \int_0^{x_A^o} -cD_{AB} dx_A \qquad 3.1\text{-}2$$

$$N_A = \frac{-cD_{AB}\, x_A^o}{\delta} \qquad 3.1\text{-}3$$

Equation 3.1-3 is the Fick's law equation (2) for steady state diffusion of A through stagnant B.

If $x_A \cong 1$ then the solution to equation 3.1-1 is

$$\int_0^{d} N_A dz = \int_0^{x_A^o} \frac{-cD_{AB}\, dx_A}{1 - x_A} \qquad 3.1\text{-}4$$

$$N_A = \frac{-cD_{AB}}{\delta} \ln \frac{1}{1 - x_A^o} \qquad 3.1\text{-}5$$

3.2 Bulk Flow of Component B

If we consider the bulk flow of B, we take into account the removal of the reaction product, assuming that A reacts to form B, as it would in the case of oxygen and water.

$$A = mB \qquad 3.2\text{-}1$$

$$N_A = + m N_B \qquad 3.2\text{-}2$$

Equation 3.0-1 now becomes

$$N_A \left[1 - \frac{m+1}{m} x_A \right] = -cD_{AB} \frac{dx_A}{dz} \qquad 3.2\text{-}3$$

and integrating with D_{AB} not a function of concentration

$$N_A = \frac{m}{m+1} \frac{cD_{AB}}{\delta} \ln \left(1 - \frac{m+1}{m} x_A^o\right) \qquad 3.2\text{-}4$$

3.3 Numerical Calculations

i_m, the current density supportable by mass transport is directly proportional to the flux.

$$i_m = nFN_A \qquad 3.3\text{-}1$$

$F = 9.65 \times 10^4$ amp sec/gram equivalent

n = number of gram equivalents/gram mole

For investigational purposes we will assume that A is oxygen and B is water.

Applying Henry's law to this situation

$$x_{O_2}^o = \frac{P_{O_2}}{H} \qquad 3.3\text{-}2$$

we obtain for equation 3.1-3 in terms of current density

$$i_m = \frac{nF\ cD_{O_2 - H_2O}}{\delta} \frac{P_{O_2}}{H} \qquad 3.3\text{-}3$$

The c in equation 3.0-1 is the concentration of water (B) in the solution of water and oxygen (A). However since this is a very dilute solution of oxygen, it is taken equal to the concentration of water in water, or 0.0556 moles/cc.

For low concentrations of A in B, Bird (1) reports that the diffusivity is directly related to the absolute temperature.

$$D_{O_2 - H_2O} = D^o_{O_2 - H_2O} \frac{T}{T^o} \qquad 3.3\text{-}4$$

Brown (3) reports the value of $D_{O_2-H_2O}$ at 20°C to be 2.08×10^{-5} cm^2/sec. With 4 gram equivalents of oxygen per mole equation 3.3-3 now becomes

$$i_m = 1.52 \times 10^{-3} \frac{T}{\delta} \frac{P_{O_2}}{H} \qquad 3.3\text{-}5$$

There is very little information on the values of δ in the literature. To show the relationship of i_m with temperature and pressure, let us introduce a new variable $\Phi = (i_m)(\delta)$. Calculations of Φ are then made at various temperatures and pressures. H, the Henry's law constant, is a function of temperature and pressure. Values from Perry's Chemical Engineers Handbook, page 675, Tables 21, and 22 may be used.

A normalizing factor, Φ^o, at 300°K and 1 atmosphere partial pressure of oxygen is used to obtain a normalized current density, $\frac{\Phi}{\Phi^o}$, which values are shown in Table 1, and Figures 2 and 3. This value of Φ^o is 1.03×10^{-5} cm amps/cm^2.

Table 1

NORMALIZED CURRENT DENSITY AT A SUBMERGED ELECTRODE

t°C	T°K \ P_{O_2}, atm	0.1	0.5	1.0	6.0	10.0
7	280	0.138	0.697	1.38	6.70	10.07
17	290	0.116	0.583	1.161	5.874	9.462
27	300	0.1	0.502	1	5.202	8.475
37	310	0.089	0.446	0.892	4.776	7.780
47	320	0.083	0.415	0.830	4.529	7.354
57	330	0.080	0.398	0.798	4.350	7.085
67	340	0.078	0.388	0.776	4.260	6.951
77	350	0.076	0.390	0.761	4.22	6.906
87	360	0.076	0.381	0.762	4.215	6.951
100	373	0.0789	0.394	0.789	4.318	7.085

Some discussion should be made of δ, the effective film thickness. This is perhaps best thought of as a hypothetical layer whose thickness is such that it gives the proper mass transport, as observed experimentally, given a fixed concentration gradient. This film is simply that region where the concentration gradient is at a maximum. It is a calculated quantity, not easily measured experimentally, and therefore, few values exist in the literature. It is reported that 2.5×10^{-2} cm(4) is not an unreasonable figure for this film. Other references (5,6) gives values of 1×10^{-3} cm for stirred solution and 5×10^{-2} cm for unstirred solutions.

Calculating current density at 1 atmosphere oxygen partial pressure and 300°K, with a δ of 10^{-3} cm thick, we obtain a value of 1.03×10^{-2} amps/cm^2. Other values can be obtained, for any δ, by using Φ^o and the figures in Table 1. The thinner this film can be made the higher the current density possible.

Current densities are highest for low temperatures (7°C) and high partial pressures of O_2 because the solubility of O_2 is greater under these circumstances. At constant pressure, the current density exhibits a minimum at approximately 80°C and then shows a slight increase due to the decrease of O_2 solubility and the increase of O_2 diffusivity with increasing temperature.

If we consider the bulk flow of water (B) m, in equation 3.2-2 is equal to -2 and equation 3.2-4 becomes

$$i_m = +2 \frac{nFc}{\delta} D^o_{O_2-H_2O} \ln(1 - \frac{1}{2} x_A) \qquad 3.3\text{-}5$$

For very small y, ln(1 + y) is approximately equal to y, and substituting equation 3.3-2 and 3.3-4

$$i_m = \frac{nFc}{\delta} D^o_{O_2-H_2O} \frac{T}{T^o} \frac{P_{O_2}}{H} \qquad 3.3\text{-}6$$

$$i_m = 1.52 \times 10^{-3} \frac{T}{\delta} \frac{P_{O_2}}{H} \qquad 3.3\text{-}7$$

By considering bulk flow of the solvent as in equation 3.2-4, we find that for the case of O_2 in H_2O the current density is uneffected. An exact calculation without the approximation ln(1 + y) = y would show a decrease in current density for the case of bulk flow of the solvent.

SYMBOLS

c	constant concentration of solvent
$D_{O_2-H_2O}$	diffusivity of oxygen in water
H	Henry's law constant atms/mole
i_m	current density supportable by mass transport
$\mathbb{F}$	conversion factor 9.65×10^4 ampere-seconds/equivalent
N_{O_2}	mass flux of O_2 moles/sec cm^2
P_{O_2}	partial pressure of oxygen in atm
T	absolute temperature, ^oK
x	mole fraction
δ	thickness of film, cm
Φ	current density times film thickness $(\delta)(i_m)(amps/cm^2)(cm)$
n	number of g. equivalent per gram mole
m	moles of B produced per mole of A

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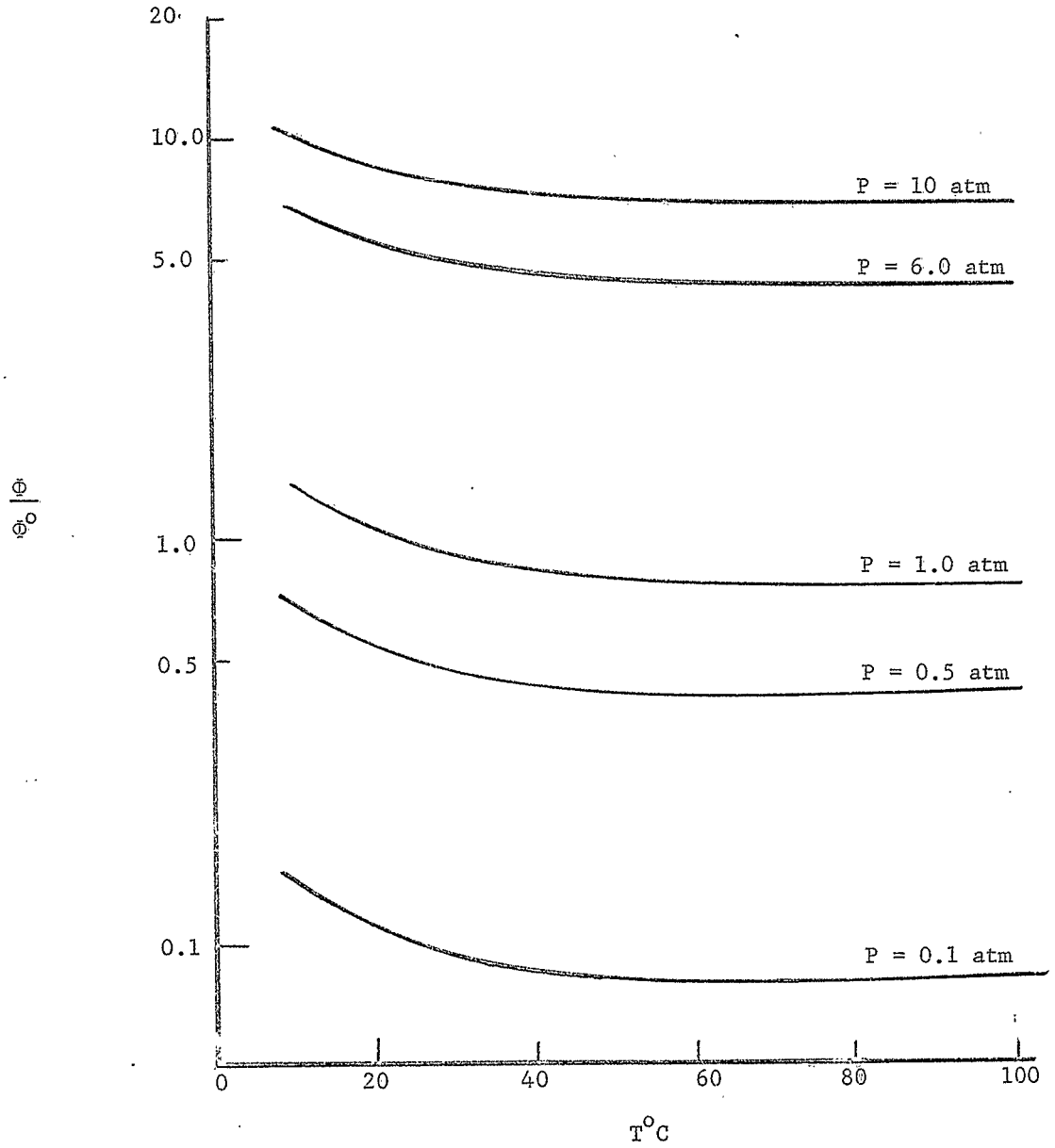
Figure 2

Normalized Current Density at Constant Pressure



$\Phi^o = 1.03 \times 10^{-5} (\frac{amps}{cm^2})(cm)$ @ $T=300^oK$, P=1 atm

Figure 3

Normalized Current Density at Constant Temperature