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APPENDICES

◆ Appendix A: Mathematical Analysis of Hydrogen Diffusion Through Various Materials.

A mathematical analysis has been made for hydrogen diffusion within both bare palladium and palladium-coated material to determine the response time for changes in hydrogen concentration.

A.1 Diffusion of H atom in Pd

A.1.1 Flat Plate Detector System

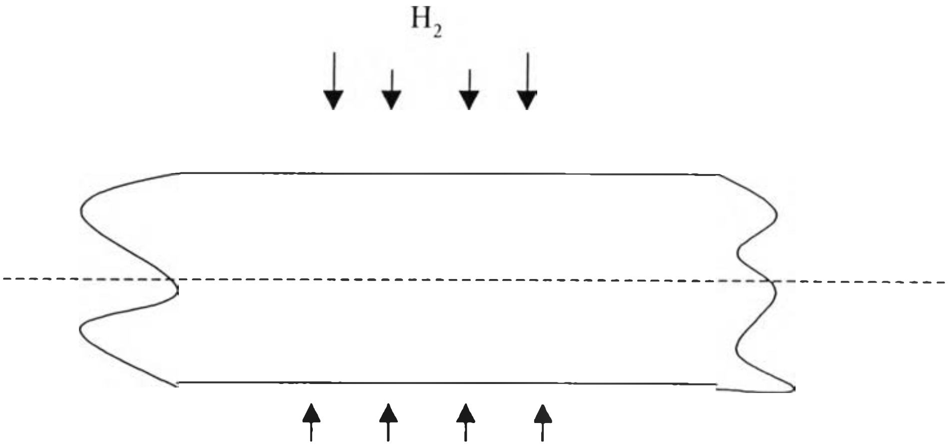

Figure A.1 One-region (Palladium) slab.

Consider the diffusion into a slab. Initially the slab has a uniform concentration, and the surfaces are raised to a new concentration and maintain constant. The solution is based on Fick's Second Law with a constant diffusivity (Geiger and Poirier, 1973). The concentration as a function of time and spare is given by

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (A.1)$$

where c is the concentration.

t is the elapsed time.

D is the diffusion coefficient.

x is the distance along the axis-X.

The initial and boundary concentrations of interest are

$$c(x,0) = C_0 \qquad (A.2)$$

$$\frac{\partial c(0,t)}{\partial x} = 0 \qquad (A.3)$$

and

$$c(L,t) = C_1 \qquad (A.4)$$

where L is the thickness of Palladium film .

The solution to this problem can be determined by separation of variables. It has the form:

$$\theta = X(x).G(t) \qquad (A.5)$$

where θ is C-C$_1$, and all the boundary conditions can be written in a homogeneous form. Therefore,

$$X = C_1 \cos(\lambda x) + C_2 \sin(\lambda x) \qquad (A.6)$$

and

$$G = \exp(-\lambda^2 Dt) \qquad (A.7)$$

The boundary condition (A.2) requires that c_2=0, and applying eq (A.3) $c_1 \cos \alpha L$ =0. This is satisfied by α= $(2n+1)\pi/2L$ where n is any interger from 0 to ∞. Hence

$$\theta = \sum_{n=0}^{\infty} A_n \exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4L^2}\right]\cos\left[\frac{(2n+1)\pi x}{2L}\right] \qquad (A.8)$$

where the A_n's are now the constants involved. Now

$$A_n = \frac{(-1)^n}{(2n+1)}\frac{4}{\pi}\theta_i, \theta_i = 0 - c_1 \qquad (A.9)$$

The solution is given by

$$\frac{\theta}{\theta_i} = \frac{c - c_1}{0 - c_1} = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left[\frac{-(2n+1)^2\pi^2}{4}\frac{Dt}{L^2}\right]\cos\left(\frac{(2n+1)\pi}{2}\frac{x}{L}\right) \qquad (A10)$$

The average concentration C is determined from

$$\bar{c} = \frac{1}{L}\int_{0}^{L} c\,dx \qquad \text{(A11)}$$

Carrying out this operation, one can obtain the relative change in average composition for diffusion into a slab:

$$\frac{\theta}{\theta_i} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2}{4}\frac{Dt}{L^2}\right] \qquad \text{(A.12)}$$

A.1.2 Cylindrical Detector System

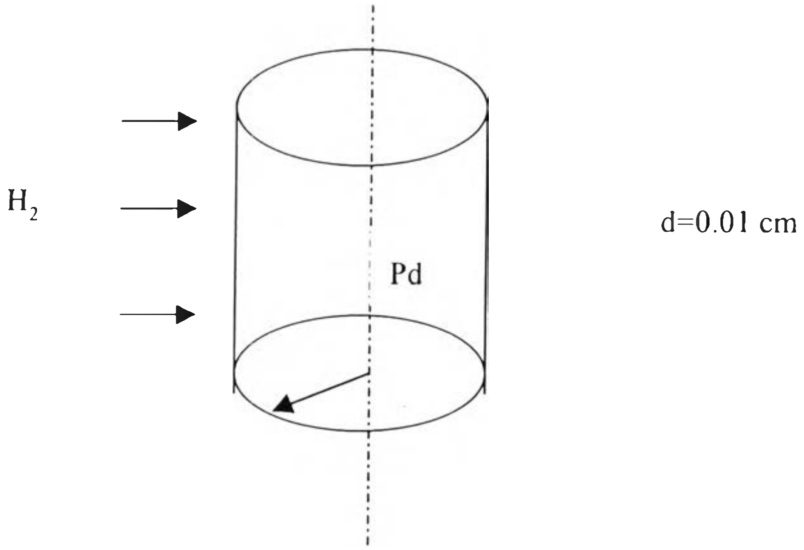

Figure A.2 One-region (palladium) cylinder.

Consider the diffusion into a cylinder. Initially the cylinder has a uniform concentration. Its surface is raised to C_1 and maintained constant. The solution is obtained from Fick's Second Law with a constant diffusivity (Geiger and Poirier, 1973).

$$\frac{\partial c}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)\right]$$

The boundary concentrations are given by

$$c(r,0) = C_0 \tag{A.13}$$

$$\frac{\partial c(0,t)}{\partial r} = 0 \tag{A.14}$$

and

$$c(R,t) = C_1 \tag{A.15}$$

The average concentration C is determined from

$$\bar{c} = \frac{1}{L}\int_0^L c\,dr$$

Carrying out this operation, one obtains the average concentration for diffusion into a cylinder.

The solution is given by

$$\frac{\theta}{\theta_1} = \frac{\bar{c} - c_s}{0 - c_s} = \sum_{n=0}^{\infty} \frac{4}{\xi_n^2} \exp\left(\frac{-\xi_n^2 Dt}{R^2}\right) \tag{A.16}$$

where $\xi_n = 2.405, 5.520, 8.654, 11.792, 14.931$, when n =1,2,3,4,5,etc

ξ_n are the roots of equation $J_0(x) = 0$,where $J_0(x)$ is the Bessel function of zero order.

A.2 Diffusion of H_2 and Cl_2 through composite materials

A.2.1 Flat Plate System

The solution for either H_2 gas or Cl_2 gas is similar to that of A.1.1. However, H_2 and Cl_2 diffuse as H_2 and Cl_2 molecules through certain materials.

A.2.2 Cylindrical System

The solution for either H_2 gas or Cl_2 gas is similar to that of A.1.2. The diffusion of H_2 and Cl_2 are in the form of molecules through certain materials.

A.3 Combination of Palladium with Material coatings

In order to identify the coating materials for the sensor to measure the hydrogen concentration, the mathematical calculation for composite material is investigated for the response time.

A.3.1 Flat Plate System

Applying the orthogonal-expansion technique over the multilayer. Fig.A.3 shows a two-region solid slab ($0 \leq x \leq L$) (Ozisik, 1968).

Consider the diffusion into slab. Let $D_{H\text{-}Pd}$, $D_{H\text{-}derakane}$ be the diffusivity of palladium and Derakane layer respectively. There is no reaction within the solids.

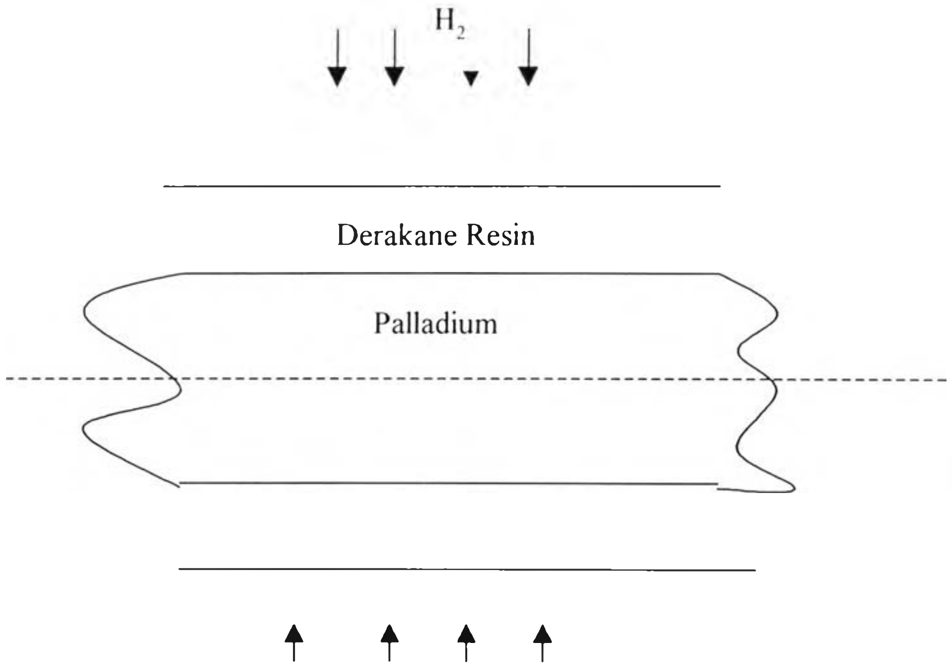

Figure A3 Two-region (palladium –materials) slab.

The mass transfer differential equations to be solved are:

$$\frac{\partial^2 c_{A1}}{\partial x^2} = \frac{1}{D_{H-Pd}} \frac{\partial c_{A1}}{\partial t} \qquad (A.17)$$

$$\frac{\partial^2 c_{A1}}{\partial x^2} = \frac{1}{D_{H-Dreakane}} \frac{\partial c_{A1}}{\partial t} \qquad (A.18)$$

with the boundary condition

$$C_{A1} = kC_{A2}$$ at the interface x =a , t>0 (A.19)

$$D_{H-Pd}\frac{\partial c_{A1}}{\partial x} = D_{H-Derakane}\frac{\partial c_{A2}}{\partial x}$$ at the interface x=a,t>0 (A.20)

$$\frac{\partial c_{A2}}{\partial x} = 0$$ at the inner surface x=b,t>0 (A.21)

where k is the equilibrium constant between hydrogen gas in the material and in palladium.

$$H_2\text{ (material)} \longleftrightarrow 2H(Pd)$$

a is the thickness of coating material.

b is the thickness of palladium film and coating material.

The initial boundary conditions are

$$C_{A1} = C_{A1,0}$$ in $0 \le x \le a$, t=0 (A.22)

$$C_{A2} = C_{A2,0}$$ in $a \le x \le b$, t=0 (A.23)

$$C_{A1,0} = k\,C_{A2,0}$$ r = a , t = 0 (A.24)

The solution of this problem is the form

$$c_j(x,t) = \sum_{n=1}^{\infty} A_n X_{jn}(x).e^{-\alpha_j \beta_{jn}^2 t}$$

in layer j , j=1,2

The eigenfunction $X_{jn}(x)$ for the two-layer problem under consideration is given as:

$$X_{1n}(x) = \sin(\beta_{1n}x) \qquad \text{in layer 1 i.e.,} 0 \leq x \leq a \qquad (A.25)$$

$$X_{2n}(r) = B_n[\sin(\beta_{2n}x) + C_n\cos(\beta_{2n}x)] \quad \text{in layer 2 i.e.,} a \leq r \leq b \qquad (A.26)$$

The $\cos(\beta_{1n}x)$ function is excluded from the solution for region 1 because it includes the origin.

Consider the interface at X_1 between the layers (i-1) and i. Since there is mass storage in the infinitesimal thickness of the interface, the time behavior of the concentration at the interafce X_i should correspond to the equilibrium constant between hydrogen in Derakane Resin and in palladium. This condition is satisfied if we have

$$D_{H\text{-}pd}\beta_{1n}^2 = k.D_{H\text{-}derakane}\beta_{2n}^2$$

The eigenvalues β_{1n} and β_{2n} are related to each other according to the equation:

$$D_{H\text{-}pd}\beta_{1n}^2 = k.D_{H\text{-}derakane}\beta_{2n}^2$$

There are two unknown coefficients B_n, C_n and the eigenvalues β_{1n} (or β_{2n} since they are related) to be determined: three independent relations are needed to determine these unknown quantities. The boundary conditions (A.19)-(A.21) provide the required three independent relations.

C_n is evaluated by applying the condition (A.21),

$$C_n = \tan(\beta_{2n} b) \tag{A.27}$$

B_n is evaluated by applying the condition (A.19)

$$\mathrm{Sin}(\beta_{1n} a) = k.Bn[\cos \beta_{2n} a + \tan \beta_{2n} b . \sin \beta_{2n} a] \tag{A.28}$$

$$B_n = \frac{\sin(\beta_{1n} a)}{k[\cos(\beta_{2n} a) + \tan(\beta_{2n} a).\sin(\beta_{2n} a)]}$$

When the condition (A.20) is applied, the following transcendental equation is obtained for evaluating the eigenvalues

$$D_{H-Pd} \frac{\cos(\beta_{1n} a)}{\beta_{1n}} = D_{H-derakane} B_n \left[\frac{-\sin(\beta_{2n} a)}{\beta_{2n}} + \frac{C_n \cos(\beta_{2n} a)}{\beta_{2n}} \right] \tag{A.29}$$

The eigenvalues β_{1n}(or β_{2n}) are evaluated from the solution of this transcendental equation in which B_n and C_n are given by (A.27) and (A.28) repectively, and β_{1n}, β_{2n} are related to each other by eq (A.25).

The solution (A.24) involves only one unknown coefficient A_n, which can be evaluated according to the relationship given by:

For the slab problem

$W_1^2 = 1 \quad , W_2^2 = 1$

$W = 1$

$Fi = To \quad , i = 1,2$

$X_{1n}(x) = \sin(\beta_{1n}x)$

$X_{2n}(r) = B_n[\sin(\beta_{2n}x) + C_n\cos(\beta_{2n}x)]$

$$A_n = \frac{W_1^2\int_0^a F_1(x).X_{1n}(x).w(x).dx + W_2^2\int_a^b F_2(x).X_{2n}(x).w(x).dx}{W_1^2\int_0^a X_{1n}^2(x).w(x).dx + W_2^2\int_a^b X_{2n}^2(x).w(x).dx}$$

$$= \frac{\int_0^a T_0 \sin(\beta_{1n}x)dx + \int_a^b T_0.B_n\left[\cos(\beta_{2n}x) + C_n \sin(\beta_{2n}x)dx\right]}{\int_0^a \sin^2 \beta_{2n}xdx + \int_a^b B_n^2\left[\cos(\beta_{2n}x) + C_n \sin(\beta_{2n}x)dx\right]^2 dx}$$

$$\frac{A_n}{T_0} = \frac{\int_0^a \sin(\beta_{1n}x)dx + \int_a^b B_n\left[\cos(\beta_{2n}x) + C_n \sin(\beta_{2n}x)\right]dx}{\int_0^a \sin^2 \beta_{2n}xdx + \int_a^b B_n^2\left[\cos(\beta_{2n}x) + C_n \sin(\beta_{2n}x)\right]^2 dx}$$

in which

$$\int_a^b \sin \beta_{1n} x.dx = \frac{1-\cos(\beta_{1n} a)}{\beta_{1n}}$$

$$\int_a^b [\cos(\beta_{2n} x + C_n \sin(\beta_{2n} x)]dx = \frac{1}{\beta_{2n}}[\sin(\beta_{2n} b) - \sin(\beta_{2n} a)] + C_n \left[\frac{\cos(\beta_{2n} a) - \cos(\beta_{2n} b)}{\beta_{2n}}\right]$$

$$\int_a^b \sin^2 \beta_{1n} x dx = \frac{1}{2}\left[a - \frac{\sin(2\beta_{1n} a)}{2\beta_{1n}}\right]$$

$$\int_a^b [\cos(\beta_{2n} x) + C_n \sin(\beta_{2n} x)]^2 dx = \frac{1}{2}\left[(b-a) + \frac{\sin(2\beta_{2n} b) - \sin(2\beta_{2n} a)}{2\beta_{2n}}\right] + C_n \left[\frac{\cos(2\beta_{2n} a) - \cos(2\beta_{2n} b)}{2\beta_{2n}}\right]$$

$$+\frac{C_n^2}{2}\left[(b-a) - \left[\frac{\sin(2\beta_{2n} b) - \sin(2\beta_{2n} a)}{2\beta_{2n}}\right]\right]$$

A.3.2 Cylindrical System

Applying the orthogonal-expansion technique over multilayer (Ozisik, 1968) .Fig A.4 shows a two-region solid cylinder of outer radius r = b with an inner core of radius r = a.

Let $D_{H\text{-}pd}$, $D_{H\text{-}derakane}$ be the diffusivity of the inner and outer regions respectively.

There is no reaction within the solid

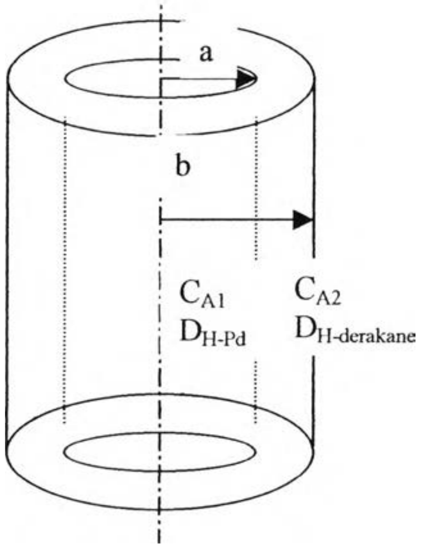

Figure A.4 Two-region solid cylinder.

The boundary-value problem of mass transfer of hydrogen in the Pd-Derakane system is given as:

$$\frac{\partial^2 c_{A1}}{\partial r^2} + \frac{1}{r}\frac{\partial c_{A1}}{\partial r} = \frac{1}{D_{H-Pd}}\frac{\partial c_{A1}}{\partial t} \tag{A.30}$$

$$\frac{\partial^2 c_{A2}}{\partial r^2} + \frac{1}{r}\frac{\partial c_{A2}}{\partial r} = \frac{1}{D_{H-derakane}}\frac{\partial c_{A2}}{\partial t} \tag{A.31}$$

with boundary conditions

$$C_{A1} = kC_{A2}$$ at the interface r=a , t>0 (A.32)

$$D_{H-Pd}\frac{\partial c_{A1}}{\partial r} = D_{H-derakane}\frac{\partial c_{A2}}{\partial r}$$ at the interface r=a , t>0 (A.33)

$$\frac{\partial c_{A2}}{\partial r} = 0$$ at the inner boundary , r=0 , t>0 (A.34)

where k is equilibrium constant between hydrogen gas in coating material and in palladium.

The initial boundary conditions are

$$C_{A1} = C_{A1,0}$$ in $0 \le r \le a$, t=0 (A.35)

$$C_{A2} = C_{A2,0}$$ in $a \le r \le b$, t=0 (A.36)

$$C_{A10} = kC_{A2\,0}$$ $r = a$, t= 0 (A.37)

The solution of this problem is in the form

$$c_j(r,t) = \sum_{n=1}^{\infty} A_n X_{jn}(r).e^{-\alpha_j \beta_{jn}^2 t}$$

in layer j , j=1,2

The eigenfunctions $X_{jn}(r)$ for the two-layer problem under consideration is given as:

$$X_{1n}(r) = Jo(\beta_{1n}r) \quad \text{in layer 1 i.e.,} 0 \le r \le a \tag{A.38}$$

$$X_{2n}(r) = B_n[J_o(\beta_{2n}r) + C_n Y_o(\beta_{2n}r)] \quad \text{in layer 2 i.e.,} a \le r \le b \tag{A.39}$$

The $Y_0(\beta_{1n}r)$ function is excluded from the solution for region 1 because it includes the origin.

Consider the interface at X_1 between the layers (i-1) and i. Since there is mass storage in the infinitesimal thickness of the interface, the time behavior of concentration at the interafce X_i should correspond to the equilibrium constant between hydrogen in derakane resin and in palladium. This condition is satisfied by

$$D_{H\text{-}pd}\beta_{1n}^2 = k.D_{H\text{-}derakane}\beta_{2n}^2$$

The eigenvalues β_{1n} and β_{2n} are related to each other according to the equation as:

$$D_{H\text{-}pd}\beta_{1n}^2 = k.D_{H\text{-}derakane}\beta_{2n}^2$$

There are two unknown coefficients B_n, C_n and the eigenvalues β_{1n}(or β_{2n}). Since they are related this gives three independent relations to determine these unknown quantities. The boundary conditions (A.32)-(A.34) provide the required three independent relations.

C_n is evaluated by applying the condition (A.34), that is

$$C_n = \frac{-J_1(\beta_{2n}b)}{Y_0(\beta_{2n}b)} \tag{A.40}$$

B_n is evaluated by applying the condition (A.32)

$$J_0(\beta_{1n}a) = k.B_n\,[J_0(\beta_{2n}a) + C_nY_0(\beta_{2n}\,a)]$$

$$B_n = \frac{J_0(\beta_{1n}a)}{k[J_0(\beta_{2n}a) + C_nY_0(\beta_{2n}a)]} \qquad \text{(A.41)}$$

When the condition (A.33) is applied, the following transcendental equation is obtained for evaluating the eigenvalues

$$D_{H\text{-}pd}\beta_{1n}J_1(\beta_{1n}a) = D_{H\text{-}derakane}\,\beta_{2n}B_n\,[J_1(\beta_{2n}a)+C_nY_1(\beta_{2n}a)] \qquad \text{(A.42)}$$

The eigenvalues β_{1n} (or β_{2n}) are evaluated from the solution of this transcendental equation in which B_n and C_n are given by (A.40) and (A.41) repectively, and β_{1n}, β_{2n} are related to each other by eq (A.38).

The solution (A.37) now involves only one unknown coefficient A_n, which can be evaluated according to the relationship:

$$\frac{A_n}{T_0} = \frac{\int_0^a J_0(\beta_{2n}r).r.dr + B_n\int_a^b [J_0(\beta_{2n}r) + C_nY_0(\beta_{2n}r)]r.dr}{\int_0^a J_0^2(\beta_{2n}r).r.dr + B_n^2\int_a^b [J_0(\beta_{2n}r) + C_nY_0(\beta_{2n}r)]^2.r.dr} \qquad \text{(A.43)}$$

in which

$$\int_0^a J_0(\beta_{1n} r).r.dr = \frac{aJ_1(\beta_{1n} a)}{\beta_{1n}}$$

$$\int_a^b B_n \left[J_0(\beta_{2n} r) + C_n Y_0(\beta_{2n} r)\right] r.dr$$

$$= \frac{B_n}{\beta_{2n}}\left[b.J_1(\beta_{2n} b) - a.J_1(\beta_{2n} a)\right] + \frac{C_n B_n}{\beta_{2n}}\left[b.Y_1(\beta_{2n} b) - a.Y_1(\beta_{2n} a)\right]$$

$$\int_0^a J_0{}^2(\beta_{1n} r).r.dr = \frac{a^2}{2}\left[J_0{}^2(\beta_{1n} a) + J_1{}^2(\beta_{1n} a)\right]$$

$$\int_a^b \left[J_0(\beta_{2n} r) + C_n Y_0(\beta_{2n} r)\right]^2 .r.dr =$$

$$\frac{1}{2}\left[\begin{array}{l} b^2(\left[J_0(\beta_{2n} b) + C_n Y_0(\beta_{2n} b)\right]^2 + \left[J_1(\beta_{2n} b) + C_n Y_1(\beta_{2n} b)\right]^2) + a^2(\left[J_0(\beta_{2n} a) + C_n Y_0(\beta_{2n} a)\right]^2 \\ + \left[J_1(\beta_{2n} a) + C_n Y_1(\beta_{2n} a)\right]^2) \end{array}\right]$$

Summarizing, the solution of the problem described by eq(A.30)-(A.34) is given

$$c_j(r,t) = \sum_{n=1}^{\infty} A_n X_{jn}(r).e^{-\alpha_j \beta_{jn}^2 t}$$

in layer j , j=1,2

A.4 Response time of Instruments based on Analysis

The response time of hydrogen concentration as a function of time were determined in a number of cases ; palladium , coating material , and combination of palladium and coating materials as shown in Figure A.5-A.10

Table A.1 The response time for a number of cases in palladium and palladium – material systems

	Response Time (sec)		
	Palladium[(a)]	Materials [(b)]	Palladium +Materials[(b)]
Flat Plate System	170	260	60000
Cylindrical System	60	120	40000

(a) Palladium wire 0.01 cm

(b) Derakane Resin 0.01 cm

From the Table A.1, it take a great deal of time for diffusion through coating material on palladium even though diffusion through either palladium or coating materials is quite fast since there is equilibrium between hydrogen concentration in coating material and palladium. For figure A.9 and A.10, the response time for flat plate and cylindrical system are 11.11 and 16.67 hours, respectively.

Table A.2 The response time for a number of cases in palladium and palladium – material systems for various dimension of palladium and coated materials

	Response Time (hr)	
	Flat Plate System	Cylindrical System
Pd 10 micron, Derakane Resin 0.01 cm	1.138	1.38
Pd 10 micron, Derakane Resin 0.05 cm	3.333	2.92
Pd 10 micron, Derakane Resin 0.1 cm	7.639	8.33

From Table A.1 and A.2, the response time was reduced with decreasing the palladium dimension. From Table A.2, the different thickness of derakane resin for 10 micron palladium were determined by the mathematical analysis. The thicker of thickness, the longer response time. Because of small diameter of palladium, the response time for flat plate and cylindrical system are in vicinity.

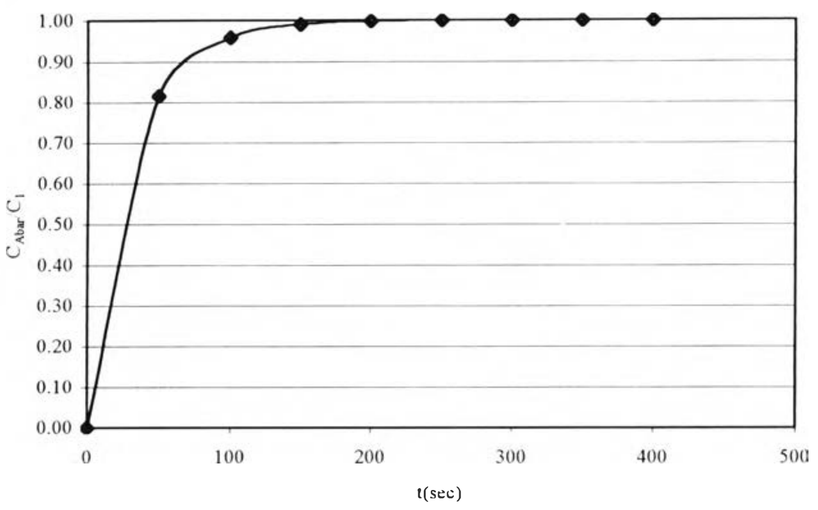

Figure A.5 Response time for palladium-hydrogen in rectangular system when Pd thickness = 0.01 cm.

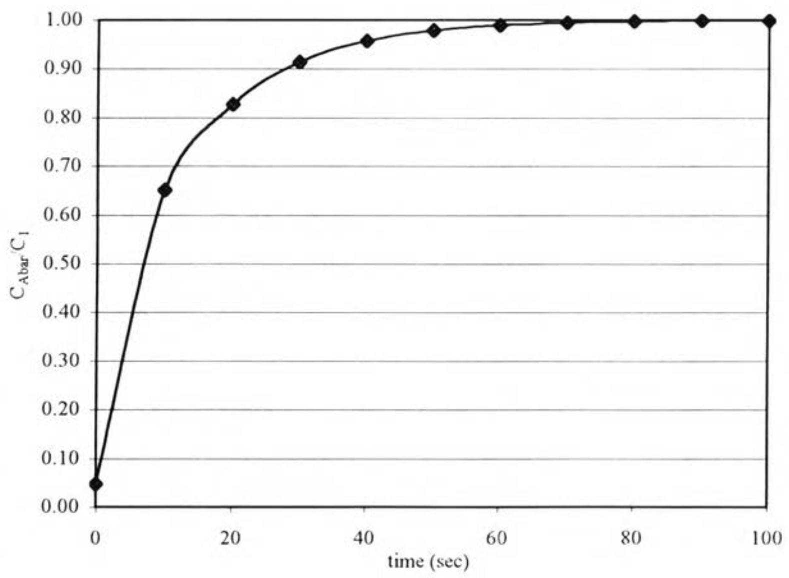

Figure A.6 Response time for palladium-hydrogen in cylindrical syste when Pd diameter = 0.01 cm.

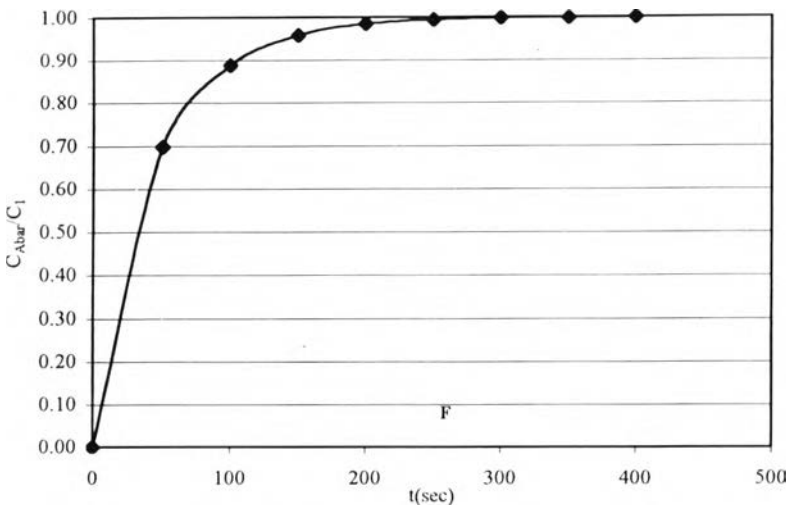

Figure A.7 Response time for hydrogen diffusion through materials in rectangular system when Derakane Resin thickness = 0.01 cm.

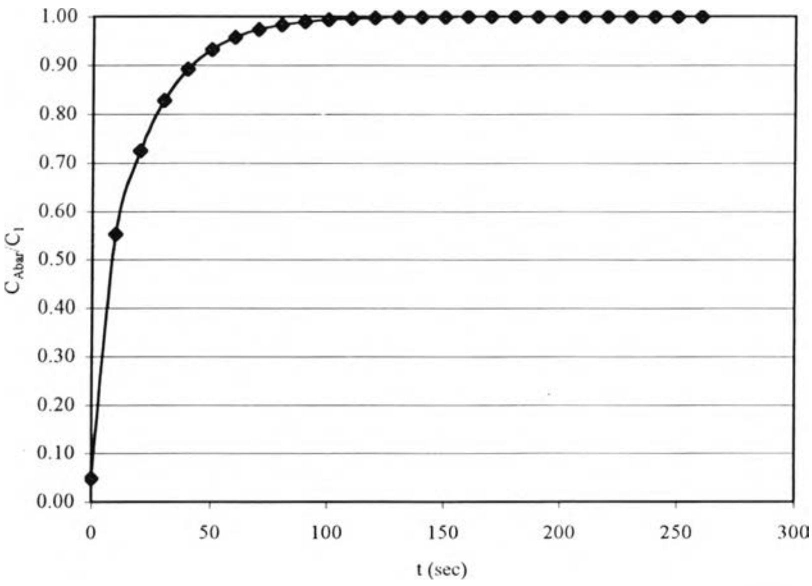

Figure A.8 Response time for hydrogen diffusion through materials in cylindrical system when Derakane Resin thickness = 0.01 cm.

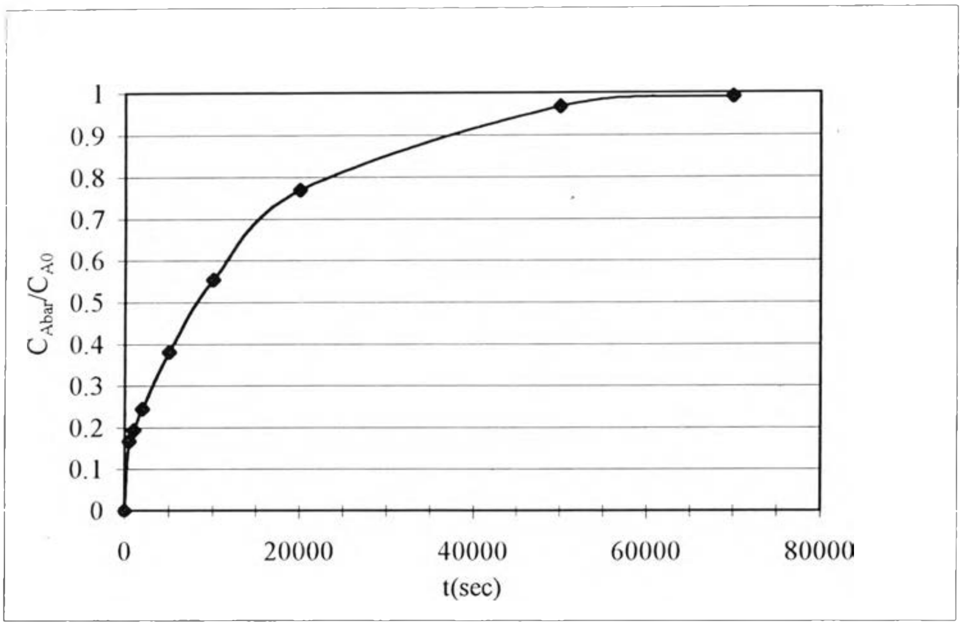

Figure A.9 Response time for Pd-Derakane Resin in rectangular system when Pd film = 0.01 cm and Derakane Resin = 0.01 cm.

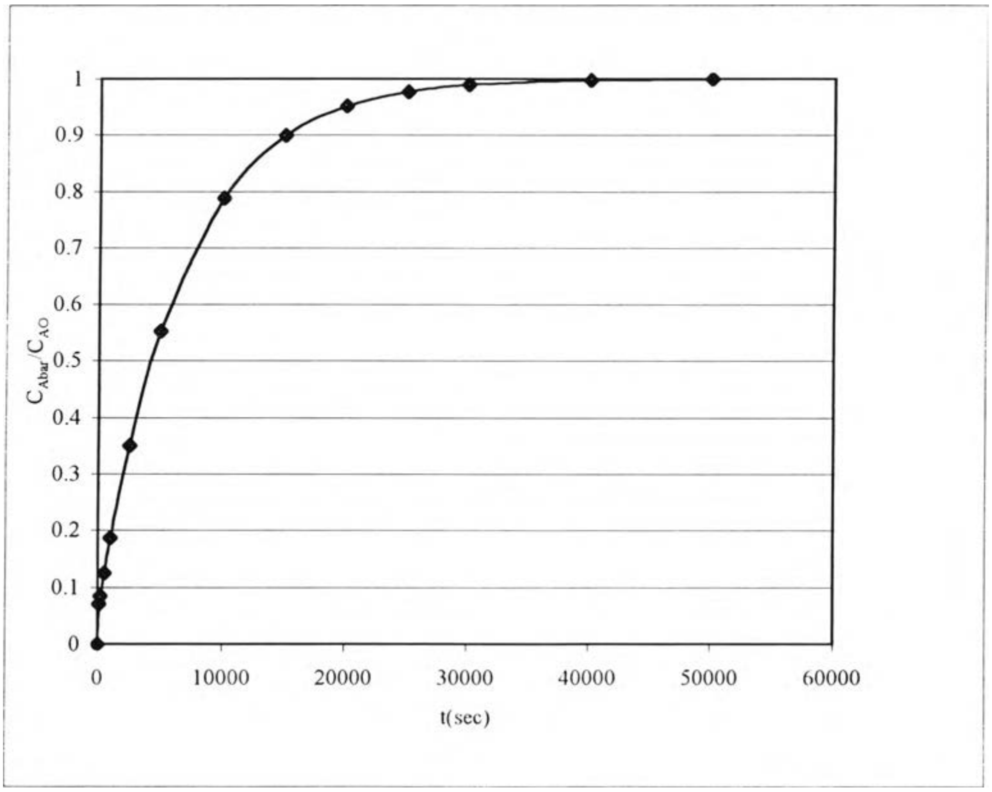

Figure A.10 Response time for Pd-Derakane Resin in rectangular system when Pd diameter = 0.01 cm ,Derakane Resin thickness = 0.01

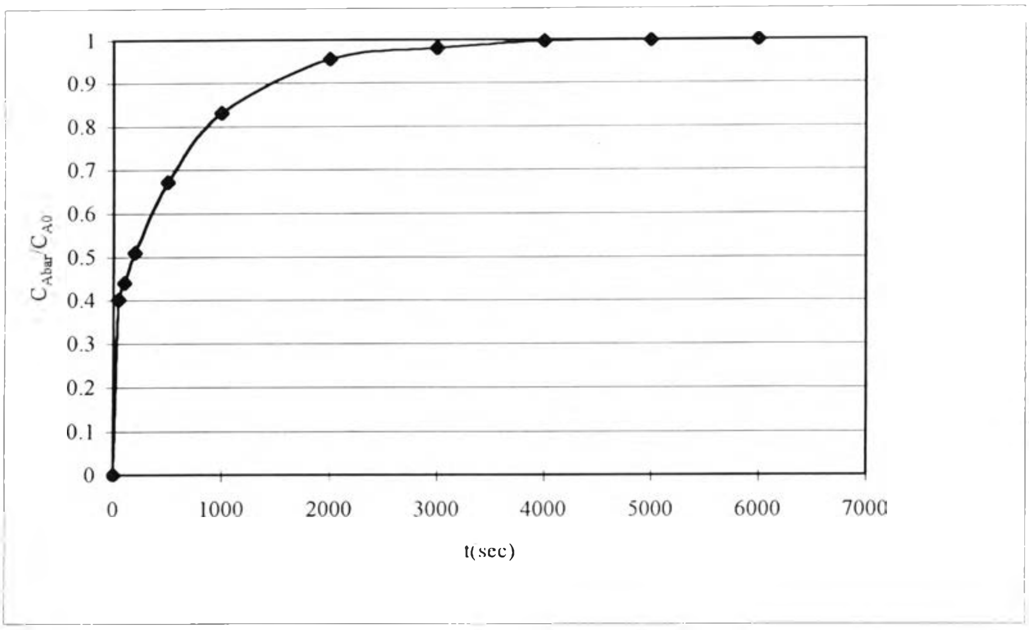

Figure A.11 Response time for Pd-Derakane Resin in rectangular system when Pd diameter = 10 micron , Derakane Resin thickness = 0.01 cm.

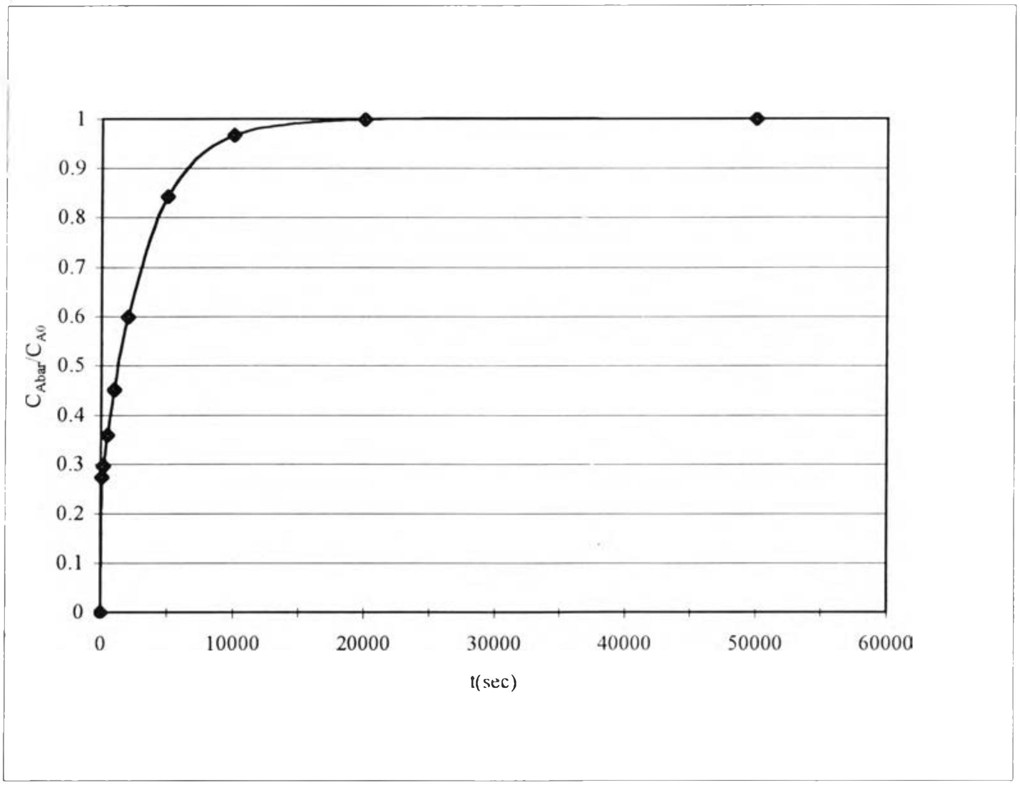

Figure A.12 Response time for Pd-Derakane Resin in rectangular system when Pd diameter = 10 micron , Derakane Resin thickness = 0.05 cm.

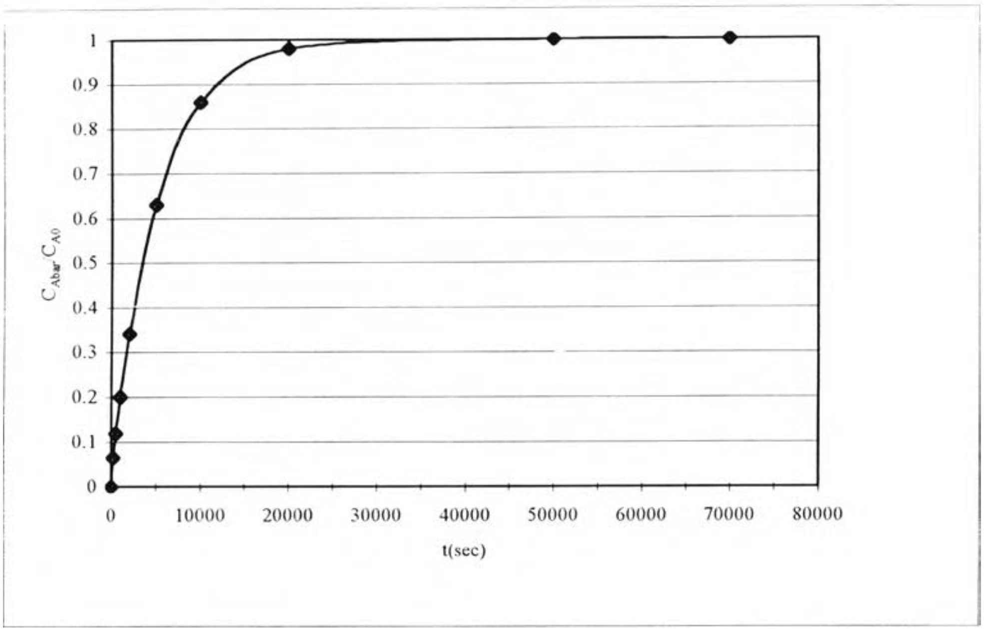

Figure A.13 Response time for Pd-Derakane Resin in rectangular system when Pd diameter = 10 micron , Derakane Resin thickness = 0.1 cm.

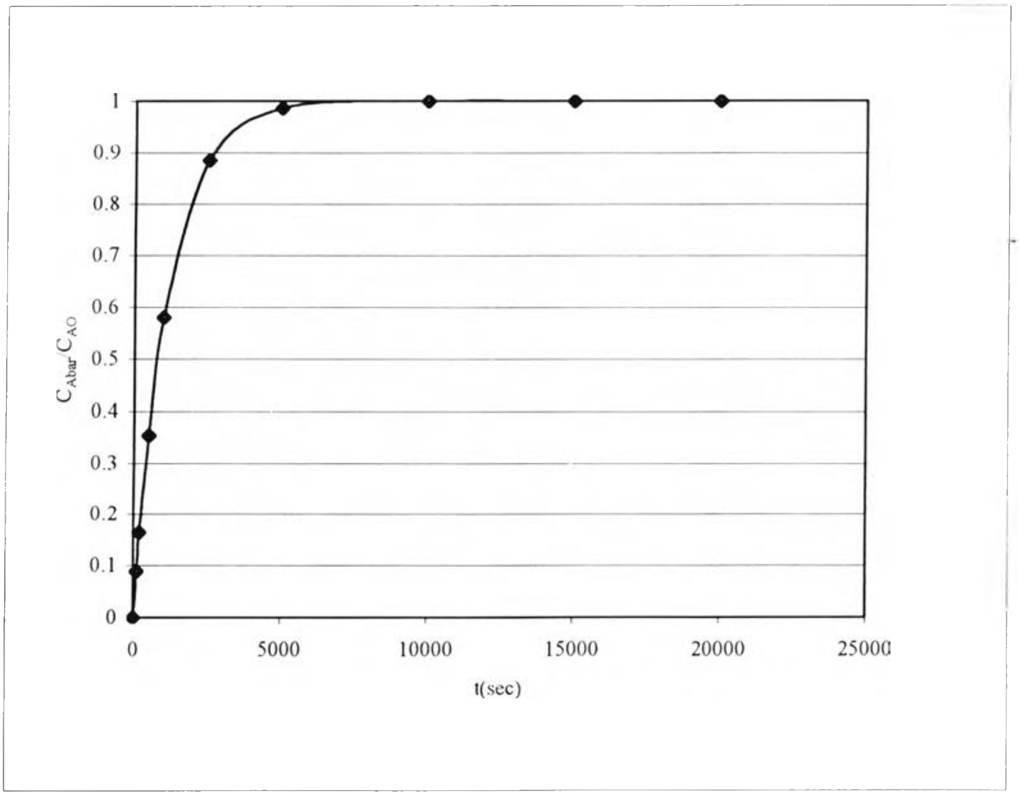

Figure A.14 Response time for Pd-Derakane Resin in cylindrical system when Pd diameter = 10 micron , Derakane Resin thickness = 0.01 cm.

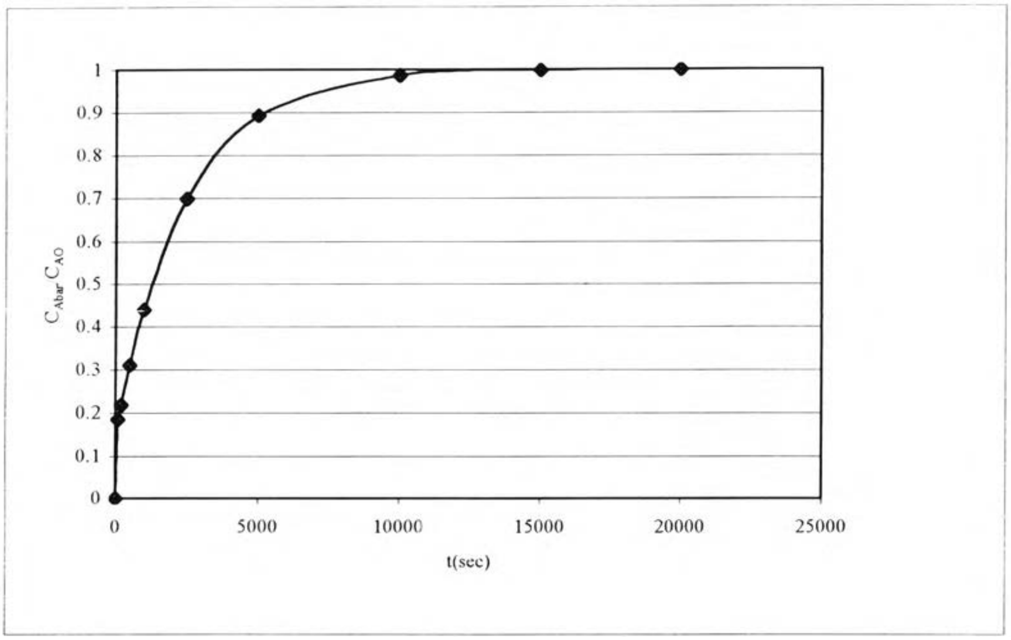

Figure A.15 Response time for Pd-Derakane Resin in cylindrical system when Pd diameter = 10 micron , Derakane Resin thickness = 0.05 cm.

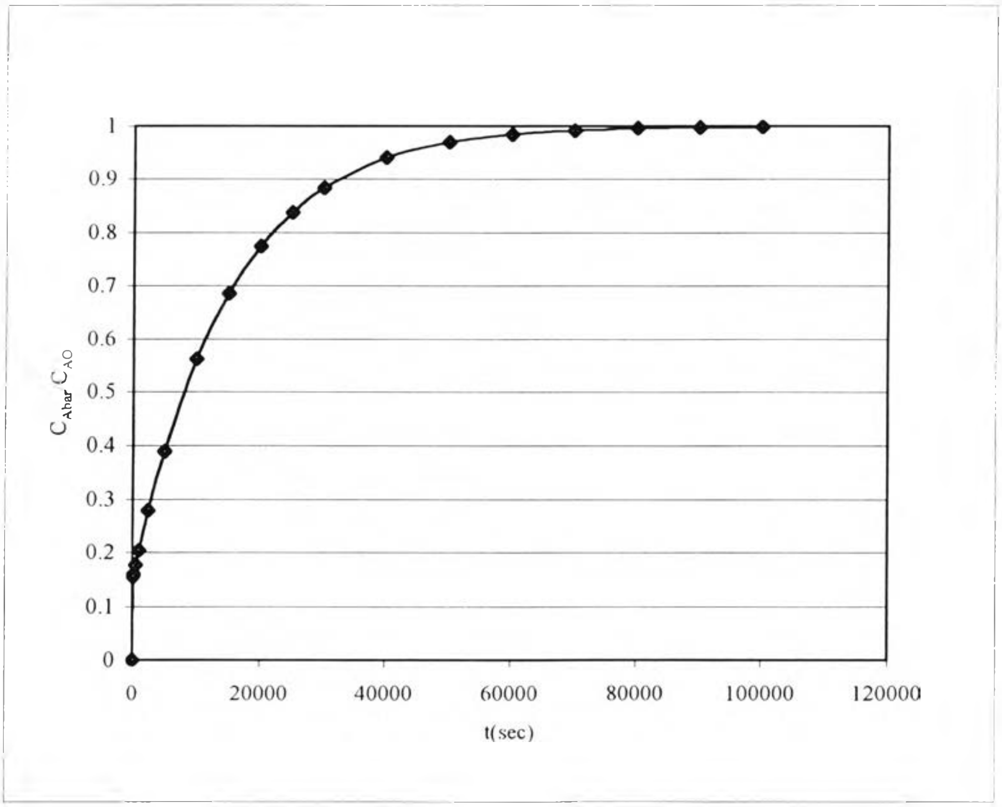

Figure A.16 Response time for Pd-Derakane Resin in cylindrical system when Pd diameter = 10 micron , Derakane Resin thickness = 0.1 cm.

Appendix B Devices for Measuring Hydrogen Concentration from an Electrical Signal

B.1 Palladium Resistance Sensor: Absorption by Palladium (Pd)

The palladium resistance probe is based on the well-known fact that the electrical resistance of a palladium wire is related to hydrogen concentration absorbed in the lattice (Lewis, 1967). Palladium and palladium alloys have been used in a number of hydrogen sensors and related devices since they are able to reversibly absorb hydrogen and to have relatively large coefficients of electrical resistivity with respect to hydrogen concentration in the lattice.

The equilibria between hydrogen gas and hydrogen in palladium at temperature T may be represented as

$$H_{2(g)} \rightleftharpoons 2H_{Pd} \tag{B.1}$$

The equilibrium constant, $K_{g,T}$, is from Sievert's Law (Parken and Gurry, 1953)

$$K_{g,T} = x_H^2/p_{H_2} \tag{B.2}$$

where x_H is the mol fraction of hydrogen atom in palladium and p_{H2} is the partial pressure of hydrogen in the contacting gas.

As a whole, the electrical resistivity of a metal increases linearly with the impurity atom concentration .For the palladium-hydrogen system, the ratio of the resistance R (T,x_H) of a palladium wire containing hydrogen at temperature

T , to the resistance of the pure palladium wire $R(T,x_H = 0)$ is a linear function of the hydrogen concentration x_H only;

$$\rho(x_H) = \frac{R(T,x_H)}{R(T,x_H = 0)} = 1 + kx_H \qquad (B.3)$$

where k is a constant .

For equilibrium between hydrogen gas mixtures with the palladium wire, equation (B.1) and (B.2) become;

$$\rho(x_H) = 1 + kK_g^{1/2} p_{H_2}^{1/2} = 1 + k_g p_{H_2}^{1/2} \qquad (B.4)$$

where $k_g = kK_g^{1/2}$ is a constant at a given temperature.

Hence by measurement of the electrical resistance of a palladium wire, the hydrogen concentration may be determined. This concentration may then be related to the hydrogen concentration in the equilibrating eg.gas phase.A diaphragm of a typical sensor is shown in Fig.B.1.

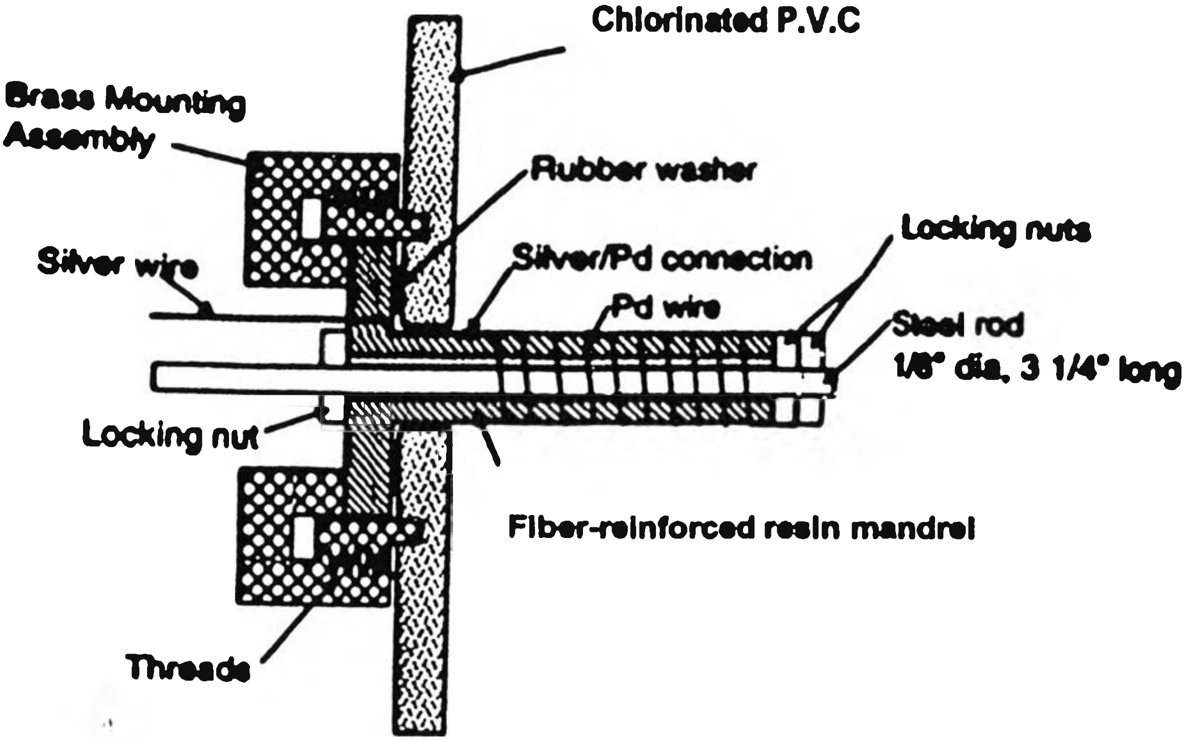

Figure B.1 Cross section of Pd/H electric resistance sensor.

B.2 Potentiometric Sensor : Electrical Cells

The potentiometric hydrogen sensor used in the present work may be represented schematically as following (Wan, 1993);

$$H_2(g), H_2O\,(g), Pt \;\underset{I}{\Big|}\; \text{Nafion} \;\underset{II}{\Big|}\; \text{reference mixture}, C, \text{stainless steel} \qquad (B.5)$$

where g indicates a gas phase .

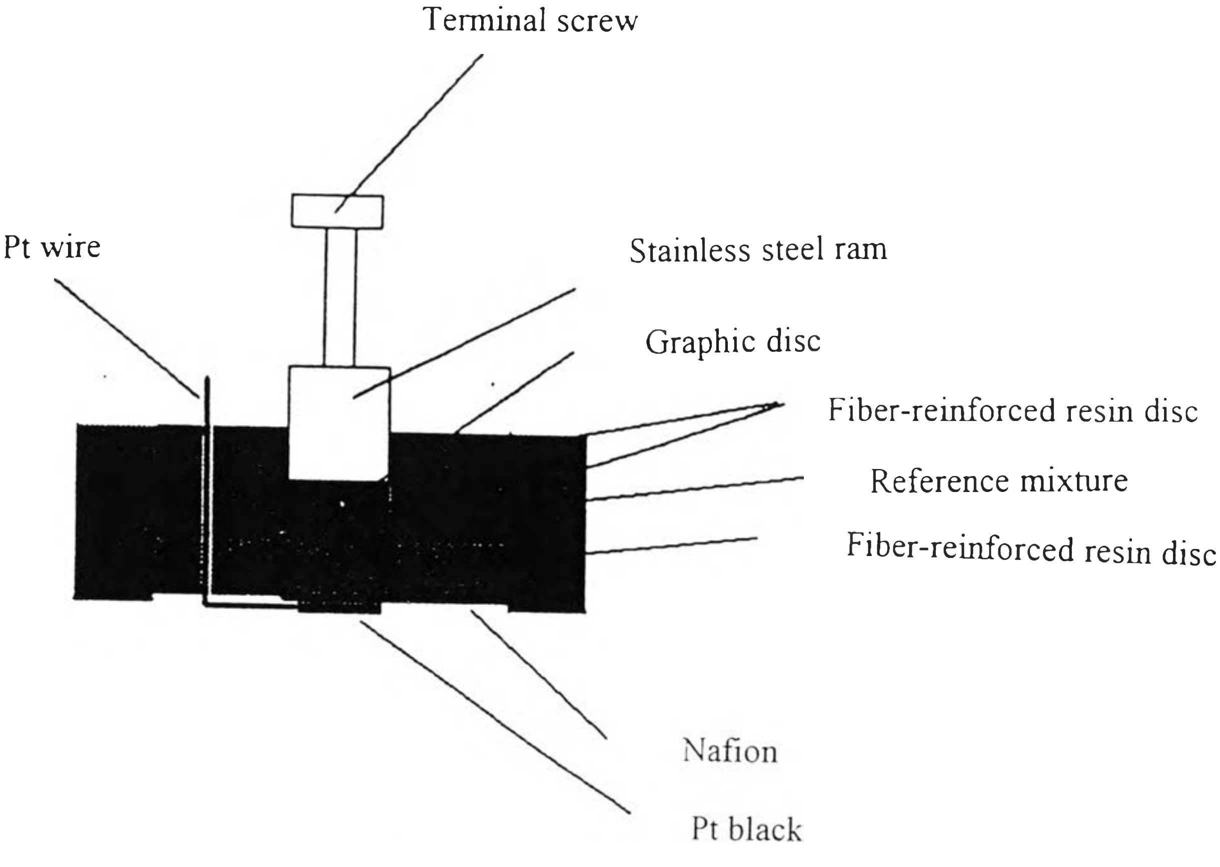

Figure B.2 Cross section of potentiometric sensor.

According to Figure B.2, the polymer electrolyte used was a Nafion (a perfluorinated sulfonic acid, PFSA) conductive to hydrogen ions. In the phase sequence, Pt represented platinum black applied in a slurry to the Nafion disc (Morris and Wan, 1995). The reference mixture consisted of Fe(II) and Fe (III) sulphate hydrates with Nafion powder .C represents a graphite (Gr) disc between the stainless steel (SS) ram and the reference mixture. The equilibria at the interfaces I and II of sensor are postulated to be:

I. Hydrogen gas (H_2) ,

$$H_3O^+_{(Nafion)} + e^-_{(Pt)} \leftrightarrow \frac{1}{2}H_{2(g)} + H_2O_{(g)} \tag{B.6}$$

II. Reference mixture,

$$Fe^{3+}_{(s)} + e^-_{(c)} \leftrightarrow Fe^{2+}_{(s)} \tag{B.7}$$

where s, c is a solid and carbon , respectively.

At interface I, the half cell electrode potential, E_I, is given by the Nerst equation as,

$$E_I = E_I^0 - \frac{RT}{F} \ln \frac{P_{H_2}^{1/2} P_{H_2O}}{a_{H_3O^+}} \tag{B 8}$$

where P_{H2} and P_{H2O} are the ratio of hydrogen partial pressure or water vapor pressure to the standard atmospheric pressure, E_I^0 is the standard electrode potential, a is activity, R is gas constant, F is Faraday constant and T is absolute temperature. The above equation can be also written as:

$$E_I = E_I^0 + \frac{RT}{F}\ln\frac{a_{H_3O^+}}{P_{H_2O}} - \frac{RT}{2F}\ln P_{H_2} \qquad (B.9)$$

The half cell electrode potential at interface II is able to be written as,

$$E_{II} = E_{II}^0 - \frac{RT}{F}\ln\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \qquad (B.10)$$

where E_{II}^0 is standard electrode potential for Fe^{3+}/Fe^{2+} redox reaction.

Consequently, the cell potential E developed by this sensor was the difference of two half cell electrode potentials,

$$E = E_{II} - E_I$$

$$E_I = E_{II}^0 - E_I^0 + \frac{RT}{F}\ln\frac{a_{Fe^{3+}}P_{H_2O}}{a_{Fe^{3+}}a_{H_3O^+}} + \frac{RT}{2F}\ln P_{H_2} \qquad (B.11)$$

Since the reference mixture comprised the pure hydrated sulfates, the ionic activities (a $_{Fe}2+$, $a_{Fe}3+$) were constant, and since also the hydrogen ion concentration in the polymer electrolyte (Nafion) was fixed, a_{H3O^+} was constant. The activity of water in the polymer electrolyte (Nafion) was fixed by saturation of the H_2 mixture with water.

Therefore, the equation (B.11) becomes,

$$E = E_0 + \frac{RT}{2F} \ln P_{H_2} \qquad (B.12)$$

where E_0 is a constant which is determined by calibration of the sensor with pure hydrogen gas at 1 atm.

B.3 Other Methods

Amperometric sensors are based on electrochemical permeation of hydrogen through metal foils and the oxidation of the extracted hydrogen to give a hydrogen oxidation current, from which the hydrogen concentration in the metal foils may be determined. Based on the above concept. The information of an amperometric sensor is obtained from the current-concentration relationship. The chemical transformation which takes place at an electrode during the passage of current is governed by Faraday's Law:

$$J = \frac{I}{zFA} \qquad (B.13)$$

where J is the flux of species ($mol.sec^{-1}.cm^{-2}$).

I is the current (A).

Z is the number of electrons per mol.

F is the Faraday constant.

A is the area of the electrode.

With regard to one dimensional transfer based on Fick's Law, the stationary diffusion current is

$$J = \frac{I}{zFA} = D_i \frac{C_i - C_0}{\delta} \qquad \text{(B.14)}$$

where D_i is the diffusion coefficient of species I

δ is the thickness of the diffusion layer

C_i and C_o are the concentration of the reacting substance remote from the electrode and immediately adjoining its surface, respectively.

If the polarization is strong enough, the concentration Co at the electrode surface can become zero, so that every particle reaching the electrode reacts immediately and the so-called limiting current I_L is reached (Bard and Faulkner, 1980):

$$I_L = \frac{D_i zFA}{\delta} C_i \qquad \text{(B.15)}$$

I_L is linearly related to the concentration C_i .By measuring the steady state I_L, one is able to determine the concentration of the reacting substance.

B.3.1 Amperometric Sensor with Aqueous Electrolyte

An amperometric sensor based on the Clark oxygen sensor for detecting dissolved hydrogen at room temperature, as shown in Figure 2.3., The sensor consists of an Ag/Cl cathode and a Pt/Pt-black anode with 1 M KCl (pH 1.0 with HCl) as the internal electrolyte.

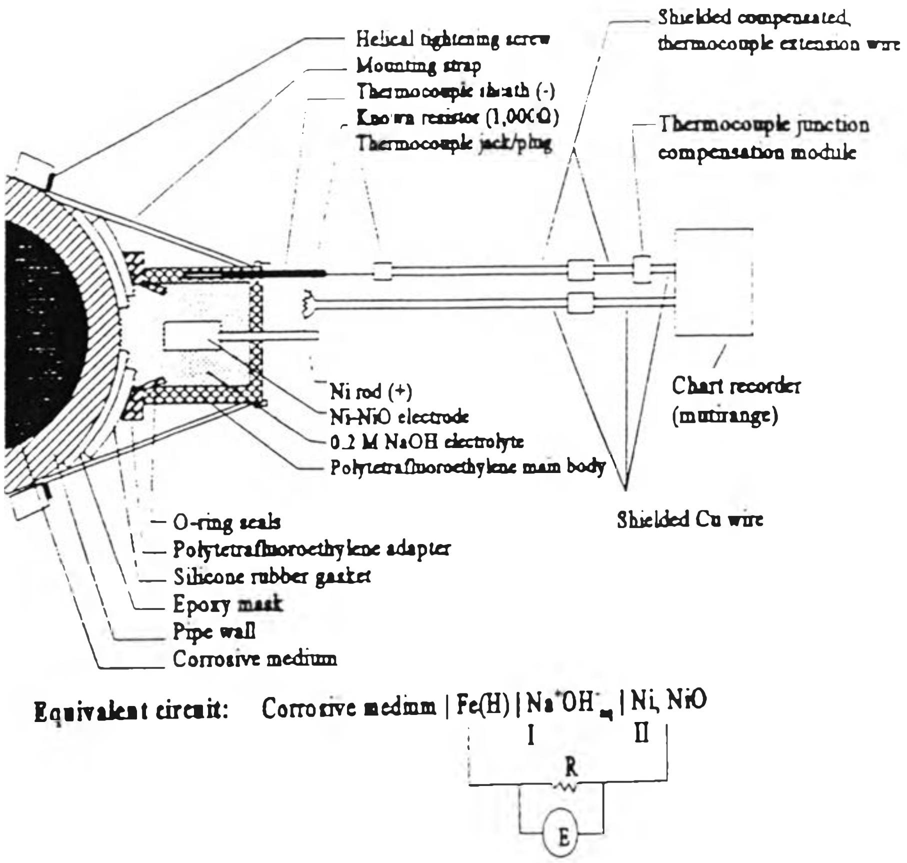

Figure B.3. The Clark-type sensor for dissolved hydrogen.

The reaction at the anode and cathode electrodes may be represented as

Anode : $\frac{1}{2} H_2 \longrightarrow H^+ + e^-$ (B.16)

Cathode : $Ag^+ + e^- \rightarrow Ag$ (B.17)

The current generated by electrons can be determined directly. The experimental results indicated that the current was proportional to dissolved hydrogen partial pressure in distilled water with a slope of 28.4 μA/atm.

The amperometric sensor for monitoring hydrogen in pipeline steels was developed by Hay (1983, 1988). The sensor contained a 0.2 M NaOH electrolyte and a Ni-NiO electrode as shown in Figure 2.4. The metal diaphragm, Fe(H) in the equivalent circuit, was the steel pipeline into which H was introduced by the corrosive medium. The reactions at the interfaces I and II could be written as:

$$\mathrm{I}: \mathrm{H}_{\mathrm{Fe}} \rightarrow \mathrm{H}^{+}_{\mathrm{aq}} + \mathrm{e}^{-} \qquad (\mathrm{B}.18)$$

$$\mathrm{II}: \mathrm{e}^{-}_{\mathrm{II}} + \mathrm{H}^{+}_{\mathrm{aq}} + \tfrac{1}{2}\mathrm{NiO} \rightarrow \tfrac{1}{2}\mathrm{H_2O} + \tfrac{1}{2}\mathrm{Ni} \qquad (\mathrm{B}.19)$$

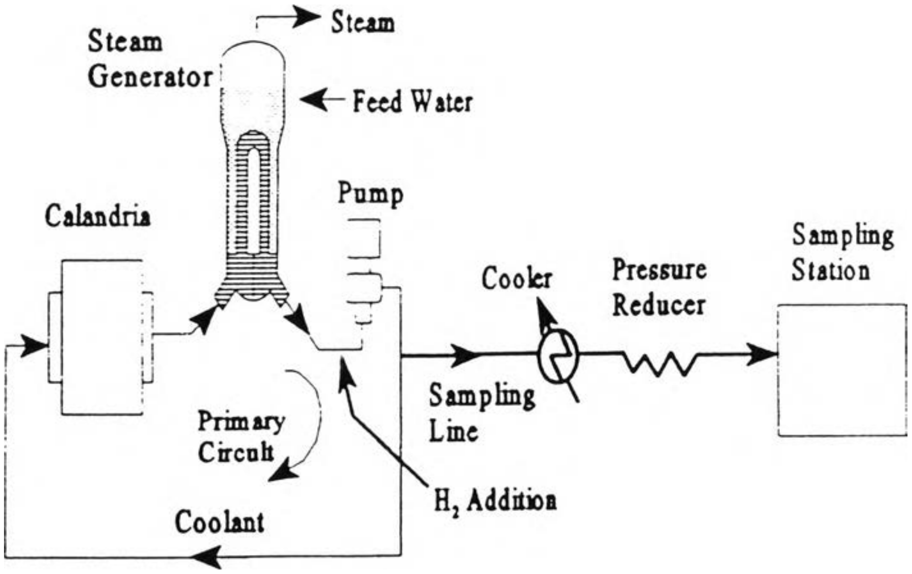

Figure B.4 Sectional view and equivalent circuit of Hay sensor.

The hydrogen concentration at the input surface of the pipeline (C_i) could be determined by:

$$C_i = \frac{L}{FAD_{app}} I \qquad (B.20)$$

where D_{app} is apparent diffusivity

L is the specimen thickness

However, an amperometric sensor based on the conventional aqueous electrolyte have maintenance problems such as leakage and evaporation of electrolytes and corrosion of electrodes. The liquid electrolyte elimination is important for the miniaturization and simplification of the total system. Subsequently, a new amperometric sensor based on solid state electrolytes has been developed and has become increasingly important in many applications.

B.3.2 Amperometric Sensor with Solid Electrolyte

A solid electrolyte used in electrochemical cells must have an adequately large ionic conductivity. Many ion-exchange compounds, such as antimonic acid, Nafion, zirconium phosphate, hydrogen uranyl phosphate (HUP), express relatively high protonic conductivities ($> 1\text{x}10^{-4}$ S/cm) at room temperature.

The mechanism of hydrogen detection by the amperometric sensor is explained as follows (Miura *et.al*, 1988). Under the open circuit condition the proton produced by the electrochemical oxidation is consumed at the sensing electrode by the electrochemical reduction to balance these two reactions. Under the short-circuit condition, the sensing electrode potential is forced to shift to make the cathodic reaction (the consumption of proton) less favorable. The excess proton thus produced on the sensing electrode migrates through the proton conductor disc toward the counter electrode to be consumed there by reaction B.22. At the same time, an equivalent amount of electrons should flow through the external circuit. Since reaction B.21 is still considered to be a diffusion-limited process even under the short-circuit condition, the amount of protons produced by this reaction is proportional to the H_2 concentration in air. Finally, this gives an external current roughly proportional to the H_2 concentration in the gas phase.

$$H_2 \rightarrow 2H^+ + 2e^- \qquad \text{(B.21)}$$

$$(1/2)O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad \text{(B.22)}$$

An amperometric sensor has been described for monitoring hydrogen in high temperature high pressure aqueous solution ($T < 300\ ^0C$) .For a constant cell voltage, the current was found to vary linearly with the square root of the hydrogen concentration in the water. A modification of this sensor was suggested to allow monitoring of hydrogen at temperatures above 300 ^0C (Kriksunov and Macdonald, 1996).

CURRICULUM VITAE

Name: Ms. Punnee Kitjareonvong

Date of Birth: March 27, 1977

Nationality: Thai

University Education:

1994-1997 Bachelor Degree of Science, 2nd honors, in Department of Chemical Technology (Chemical Engineering), Faculty of Science, Chulalongkorn University, Bangkok, Thailand.