CHAPTER 5
HYDROGEN PERMEATION IN METALS

5.1. HYDROGEN EVOLUTION REACTION

Hydrogen evolution is the most thoroughly studied reaction in electrode kinetics. The first step (the transport of the electroactive species to the electrode surface) proceeds almost unhindered. The next step is the discharge of hydrogen ions (or water molecules) with the formation of adsorbed hydrogen atoms.\(^1\, 2\)

It is generally recognized that the overall hydrogen evolution reaction from acid solutions

\[
2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O
\]

proceeds in two successive stages. The first step, which occurs on all metals, consists in discharge of hydrogen ions and leads to the hydrogen atom adsorption on the electrode surface:

\[
H_3O^+ + M + e^- \rightarrow MH_{\text{ads}} + 2H_2O
\]

For steady-state electrolysis conditions to be attained it is necessary that the surface concentration of hydrogen atoms be kept constant. They should be continuously removed from the cathode surface. Thus, the second step of the hydrogen evolution reaction may involve recombination (chemical desorption), electrochemical desorption or emission. In the recombination mechanism hydrogen atoms are recombined into molecules and simultaneously desorbed:

\[
MH_{\text{ads}} + MH_{\text{ads}} \rightarrow H_2 + 2M
\]

the electrode metal serving as the catalyst.
In electrochemical desorption, the hydrogen atoms are removed from the electrode surface as a result of the discharge of hydrogen atoms (or water molecules) on the already adsorbed atoms according to the equations

\[MH_{\text{ads}} + H_2O^+ + e^- \rightarrow H_2 + H_2O + M\]  
(4)

where \(M\) represents the metal substrate; when water is discharged

\[H_2O + H_{\text{ads}} + e^- = H_2 + OH^-\]  
(5)

In the emission mechanism, adsorbed hydrogen atoms evaporate from the electrode surface as free atoms

\[H_{\text{ads}} = H\]  
(6)

which then recombine into hydrogen molecules.

Thus, the cathodic hydrogen-evolution process may be represented by the following scheme:
Any of these four steps may be rate determining and responsible for the appearance of hydrogen overpotential. There is evidence that at high current densities and acid solutions the discharge step is best described with the slow rate of transport of \( \text{H}_3\text{O}^+ \) ions.

In the electrochemical hydrogen-evolution reaction the removal of adsorbed hydrogen atoms can be effected in several ways. If step III in the above scheme is slow, then the rate of the overall process must be determined by the rate of the most effective of the indicated three desorption mechanisms. For example, slow recombination implies that the catalytic formation of hydrogen molecules is more strongly hindered than the discharge or transport step and at the same time proceeds much faster than the electrochemical desorption or emission of hydrogen atoms. Thus, the individual steps may have different rates. The rate of the slowest step controls the overall reaction rate. Following six possible mechanisms have been discussed by Bockris et al.\(^3,4\) according to the rate determining step and the second stage of the H.E.R.:

1. The Volmer-Tafel mechanism corresponds to the case where the discharge step runs slow and the removal of hydrogen atoms is accomplished by recombination.

   \[
   \text{[Slow discharge-fast recombination]:} \quad \text{H}_3\text{O}^+ + e^- \rightarrow \text{M}\text{H}_{\text{ads}} + \text{H}_2\text{O} \quad (7)
   \]
   \[
   \text{M}\text{H}_{\text{ads}} + \text{M}\text{H}_{\text{ads}} \leftrightarrow \text{H}_2 + 2\text{M} \quad (8)
   \]

2. According to the Volmer-Heyrovsky mechanism, the discharge is the slow step, but the hydrogen atoms are removed by electrochemical desorption.

   \[
   \text{[Slow discharge-fast electrochemical desorption]:}
   \]
\[ H_3O^+ + e^- \rightarrow MH_{ads} + H_2O \]  \hspace{1cm} (9)

\[ MH_{ads} + H_3O^+ + e^- \leftrightarrow H_2 + M + H_2O \]  \hspace{1cm} (10)

3. In the Tafel-Horuiti mechanism, the recombination of hydrogen atoms determines the rate of the overall reaction.

[Fast discharge-slow recombination]:

\[ H_3O^+ + e^- \rightarrow MH_{ads} + H_2O \]  \hspace{1cm} (11)

\[ MH_{ads} + MH_{ads} \leftrightarrow H_2 + 2M \]  \hspace{1cm} (12)

4. The Heyrovski-Horuiti mechanism is based on the assumption that the overall rate is determined by the electrochemical desorption mechanism.

[Fast discharge-slow electrochemical desorption]:

\[ H_3O^+ + e^- \rightarrow MH_{ads} + H_2O \]  \hspace{1cm} (13)

\[ MH_{ads} + H_3O^+ + e^- \rightarrow H_2 + M + H_2O \]  \hspace{1cm} (14)

5. Coupled discharge-recombination:

\[ H_3O^+ + e^- \rightarrow MH_{ads} + H_2O \]  \hspace{1cm} (15)

\[ MH_{ads} + MH_{ads} \rightarrow H_2 + 2M \]  \hspace{1cm} (16)

6. Coupled discharge-electrochemical desorption:

\[ H_3O^+ + e^- \rightarrow MH_{ads} + H_2O \]  \hspace{1cm} (17)

\[ MH_{ads} + H_3O^+ + e^- \rightarrow H_2 + M + H_2O \]  \hspace{1cm} (18)

In the case of first four mechanisms, it is assumed that the fast step is at equilibrium. Thus, the rate of the forward reaction equals the rate of the reverse one. In the last two mechanisms, the rates of both the reverse reactions are negligible, whereas the rates of both the forward reactions are equal.
Other kinetic variants of the occurrence of the cathodic hydrogen-evolution reaction are also possible. The actual mechanism of the cathodic hydrogen-evolution reaction on a given metal can be established on the basis of comprehensive experimental investigations.

5.2. DEVANATHAN-STACHURSKI TECHNIQUE

HYDROGEN PERMEATION

On the basis of electrochemical parameters such as the Tafel slope, the hydrogen surface coverage, the exchange current density, the transfer coefficient, or the stochiometric number, it can be established which of the above mechanisms is probable. However, these criteria do not give a unique possible mechanism partially because a part of adsorbed hydrogen, more or less, will absorb and diffuse into the substrate. The hydrogen absorption

\[ MH_{\text{ads}} = MH_{\text{abs}} \]  

occurs on the surface simultaneously with the hydrogen evolution reaction. Investigations on hydrogen absorption and permeation can provide valuable information on the mechanism of the hydrogen evolution reaction. Processes involved in the evolution and ingress of hydrogen into a metal are shown in Figure (1).

To measure experimentally the hydrogen permeation rate through a metallic material, Devanathan-Stachurski permeation method\(^5\) has been widely used. The permeation experiments are carried out in a system with two compartments, separated by a bipolar metal membrane. The current due to hydrogen permeation through the membrane is recorded continuously as a function of time and is measured by keeping the potential on the anodic side of the membrane (the side from which the hydrogen emerges)
positive enough to be oxidized, usually under potentiostatic conditions. The adsorbed hydrogen concentration on the anodic side of the membrane is practically zero. The steel membrane on the cathodic side of the cell is polarized potentiostatically, creating conditions for hydrogen evolution. The details of the permeation cell and the auxiliary equipment are given in Figure (2).

Theoretical Diffusion Solutions

The technique developed by Devanathan and Stachurski was based on the presumption that well-defined conditions are established at each surface of the membrane under potentiostatic control:

1. The surface coverage of adsorbed hydrogen is constant on the input side and zero on the exit side.

2. The kinetics of hydrogen entry are fast enough to maintain equilibrium at the input surface.

3. The hydrogen arriving at the exit surface is immediately oxidized and is maintained at approximately zero.

The concentration profile and a typical anodic transient for potentiostatic control are shown schematically in Figure (3).

It is generally believed that the hydrogen diffusion through metals is the rate determine step among other steps involved. The hydrogen permeation transients through metals have been obtained by solving the Fick's laws of diffusion in one-dimensional form, namely,

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial^2 x}
\]  

(20)
And

\[ J_i = -FD \left( \frac{\partial C}{\partial x} \right)_{x=L} \]  \hspace{1cm} (21)

under different boundary conditions. Where \( C \) is the concentration of hydrogen, \( D \) the diffusion coefficient, \( L \) the thickness of the membrane, \( F \) the Faraday constant, \( J_i \) the diffusional flux. Among various solutions\(^6-8\), two typical solutions were obtained:

(1) For the case where the hydrogen concentration at the entry side of the membrane is constant\(^9\)

\[ \frac{J_i}{J_\infty} = \frac{2}{\sqrt{\pi \tau}} \sum_{n=0}^{\infty} \exp \left\{ -\frac{(2n+1)^2}{4\tau} \right\} \]  \hspace{1cm} (22)

(2) For the case where the flux of the hydrogen entering the membrane is constant\(^6\)

\[ \frac{J_i}{J_\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \left( \frac{-1}{2n+1} \right)^n \exp \left\{ -\frac{(2n+1)^2 \pi^2 \tau}{4} \right\} \]  \hspace{1cm} (23)

where \( \tau = tD/L^2 \) is the dimensionless time. By fitting an experimental permeation transient with the theoretical solution, the hydrogen diffusivity may be evaluated.

**EVALUATION OF DIFFUSIVITY**

Whether obtained potentiostatically or galvanostatically, the transients are typically characterized by four parameters:

(1) Breakthrough time (\( t_b \)).
(2) Inflection point time (\( t_i \)).
(3) Half-rise time (\( t_{1/2} \)).
(4) Time lag (\( t_L \)).
Thus, the diffusivity can also be obtained from four principal time characteristics of the anodic current transient:

(a) Half-Rise Time

A common approach is to measure the time \( t_{1/2} \) required for \( i \) to reach 0.51 \( i_c \) so that \( D \) can be evaluated from:

\[
t_{1/2} = \frac{0.14L^2}{D}
\]  \hspace{1cm} (24)

(b) Inflection Point Time.

The time of the inflection point of the rising transient can be represented by:

\[
t_i = 0.924 \frac{L^2}{\pi^2 D}
\]  \hspace{1cm} (25)

(c) Breakthrough Time.

The breakthrough time \( t_b \) is essentially the time needed for hydrogen to begin arriving at the output side. \( t_b \) is obtained by extrapolation of the tangent at the inflection point to the initial level of the output current, and is related to the diffusivity by

\[
t_b = 0.924 \frac{L^2}{\pi^2 D}
\]  \hspace{1cm} (26)

(d) Time Lag.

The best known of the four characteristics is the time lag \( t_L \). It is related to the time required to obtain a steady-state flow through the sample after charging is begun. The time lag can be evaluated from the charge-time dependence on the anodic side. When the current reaches a steady state, the charge follows a linear dependence, which on extrapolation yields \( t_L \) as the intercept on the time axis.
Under diffusion-controlled conditions, these time characteristics should each be proportional to the square of the thickness, and so the above equations provide a test to verify that the permeation rate is controlled by diffusion rather than surface kinetics.

**Basic Model of Hydrogen Permeation**

A basic mechanistic model of hydrogen permeation was developed by Iyer, Pickering and Zamanzadeh\(^{10,11}\) on the basis of following assumptions:

1) The hydrogen evolution reaction is a coupled discharge-recombination process;
2) \(\eta >> \text{RT}/F\) so that the backward reactions are negligible;
3) The surface coverage is low enough so that Langmuir isotherm is used for the hydrogen coverage;
4) The intermediate hydrogen adsorption-absorption reaction is in local equilibrium;
5) The hydrogen permeation current density through the membrane without trapping is described by a simple diffusion model once the steady state is reached.

From the first three assumptions, one obtains:

\[
\begin{align*}
    i_c &= i_0 (1 - \theta_H) e^{\frac{F\eta}{RT}} \\
    i_r &= Fk_3 \theta_H^2
\end{align*}
\]

where \(i_c\) is the cathodic current density, \(i_r\) is the hydrogen recombination current density, \(F\) is the Faraday constant, \(\alpha\) is the transfer coefficient, \(\eta\) is the overpotential, \(R\) is gas constant, \(T\) is temperature, \(k_3\) is the recombination constant, \(\theta_H\) is the hydrogen surface
coverage, \( i'_e = \frac{i_0}{1 - \theta_e} \), here \( i_0 \) is the exchange current density and \( \theta_e \) equilibrium hydrogen coverage.

Using assumption 5, the steady state permeation current density is given by

\[
j_\infty = \frac{FD}{L} C_s
\]  

(30)

Where D is the diffusivity of hydrogen in the metal, L is the membrane thickness, \( C_s \) is the concentration of hydrogen in metal adjacent to the surface, \( j_\infty \) is the steady state hydrogen permeation current density, and

\[
i_r = i_e - j_\infty
\]  

(31)

Combining above equations, one obtains Equations (32) and (33)

\[
j_\infty = \frac{k''}{b \sqrt{Fk_3}} \sqrt{i_r}
\]  

(32)

Where \( b = \frac{L}{FD} \), and \( k'' = \frac{k_{abs}}{k_{ads} + \frac{D}{L}} \) is the thickness dependent adsorption-absorption constant.

\[
i_e e^{\frac{Faq}{RT}} = -\frac{b i_0}{k''} j_\infty + i_0
\]  

(33)

The atomic hydrogen permeation transients through AISI 4340 membrane as a function of time for different applied potentials in an electrolyte containing 0.5 M HClO\(_4\) and 0.25 M NaClO\(_4\) (pH=0.3) and the comparison of the experimental results with theoretical solutions for two typical theoretical solutions in dimensionless forms are given in Figure (4) and Figure (5), respectively.
This model enables computation of the hydrogen surface coverage and the rate constants using the data obtained from hydrogen permeation experiments. However, this model is only applicable for the case of coupled discharge-recombination H.E.R. and constant hydrogen concentration on the cathodic side of the membrane.
EXPERIMENTAL

REQUIRED EQUIPMENT AND SUPPLIES

AISI 4340 disc electrodes, A=0.5cm².

0.5 M HClO₄.

0.25 M NaClO₄.

0.2 M NaOH

0.3 mm thick steel membrane.

Two PAR Model 273 Potentiostats interconnected to an IBM PS/2.

OBJECTIVES

Determination of Hydrogen Permeation Parameters in AISI 4340 Steel.

The anodic compartment should be washed with deionized water and filled with the anodic solution (0.2 M NaOH). To keep the electrolyte impurities in the lowest possible level, the anodic solution should be pre electrolyzed for at least 24 hours in a separate electrolytic cell before putting it in the permeation cell. The cathodic compartment should be filled with a solution containing 0.5 M HClO₄, 0.25 M NaClO₄, pH=0.3

Membrane Design

It is important to choose an appropriate membrane thickness to carry out permeation experiments. If a permeation transient takes a few days, then the problems of impurity adsorption at the cathode, change in pH of the electrolyte, and background corrosion in the anodic cell would result in inaccurate data. It is, therefore, advised [11] that the time to attain steady state should be well within 24 hours, if possible. On the other hand, if extremely thin membranes are chosen, the grain boundary effects will
become dominant. In such thin membranes, grain boundaries will not only short circuit hydrogen diffusion, but also localize the hydrogen adsorption and absorption processes. This will mean that the hydrogen diffusivity values, evaluated from the transient measurement, and the adsorption and absorption characteristic parameters, evaluated from the steady state permeation, will not represent the bulk material[11]. Besides the thickness, the lateral dimension of the membrane is also an important consideration. In order to avoid edge effects causing significant hydrogen leakage laterally, the membrane thickness to the membrane radius exposed to the catholyte should be less than 0.2 for leakage to be less than 5%[12, 13].

Procedure

Using the Devanathan-Stachurski permeation technique, the rate of hydrogen permeation through steel membrane was measure continuously as a function of time. The permeation rate through a thin membrane was measured by setting the potential on the “diffusion side” of the membrane (the side from which the hydrogen emerges) at a fixed value (-0.3 V vs Hg/HgO). This value corresponds to almost a zero concentration of absorbed hydrogen on the surface. The membrane on the cathodic side of the cell was polarized potentiostatically. Prior to the permeation studies the steel membrane was mechanically polished with 600 grade sand paper and 0.5 micron high purity alumina powder to a mirror finish. The steel membrane was then cleaned in an ultrasonic cleaning bath and saturated with hydrogen in a 0.1 M H₂SO₄ solution maintaining the solution at cathodic current density of 10 mA/cm². Then the membrane was removed from the cell, etched for 20 seconds in a solution containing methyl alcohol and 1% H₂SO₄, rinsed with deionized water, dried in air and fitted into the permeation cell.
To avoid possible passivation, the anodic side of the membrane was electroplated with a thin layer (0.15-0.20 µm) of palladium. The deposition was carried out in an electrolyte containing $2\times10^{-5}$ M Na$_2$Pd(NO$_2$)$_4$ using a current density of 100 $\mu$A/cm$^2$ for two hours. Then, the electrolyte was drained off, and the compartment was washed with deionized water and filled with the anodic solution (0.2 M NaOH). To keep the electrolyte impurities at the lowest possible level, the anodic solution was pre-electrolyzed for at least 24 hours in a separate electrolytic cell before putting it in the permeation cell. In the anodic compartment, the electrolyte was kept at $-0.3$ V vs. Hg/HgO reference electrode until the background current was reduced to below 3 $\mu$A/cm$^2$. Then, the cathodic compartment was filled with a supporting electrolyte containing 0.5 M Na$_2$SO$_4$ and 0.5 M H$_2$SO$_4$. Pre-purified nitrogen was bubbled through both compartments in order to keep the system free of dissolved oxygen. After the membrane was fitted into the Devanthan-Stachurski permeation cell, the anolyte was first introduced into the anodic cell and kept at a sufficiently oxidizing potential. Once the background current decreased to a very low value, then the catholyte was introduced and the permeation experiments were started immediately.

The values of the steady-state hydrogen permeation current $j_\infty$ as a function of the overpotential and hydrogen cathodic current density are given in Table (1).

**Table 1 Kinetic Data for Hydrogen Evolution and Hydrogen Permeation in AISI 4340 Steel**

<table>
<thead>
<tr>
<th>$\eta$ (mV)</th>
<th>$i_c$ ($\mu$ A/cm$^2$)</th>
<th>$j_\infty$ ($\mu$ A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-248</td>
<td>894</td>
<td>22.5</td>
</tr>
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</table>
Calculations

(a) Using the mechanistic model developed by Iyer et al., calculate:

1. Hydrogen diffusivity, $D_{\text{H}}$ (cm$^2$/s) in AISI 4340 steel.
2. Exchange current density, $i_o$ A/cm$^2$.
3. Hydrogen recombination current density, A/cm$^2$.
4. Recombination rate constant, mol (cm$^2$s)$^{-1}$.
5. Hydrogen Evolution Reaction coverage-dependent transfer coefficient, $\alpha$.
6. Hydrogen surface coverage, $\theta_H$.

Construct the following plots:

1. Hydrogen permeation current vs square root of the hydrogen recombination current density, membrane thickness = 0.3 mm. Explain why the permeation current increases with an increase of the hydrogen recombination current and levels off at higher recombination current densities.

2. Plot of $i_e e^{\alpha \eta}$ as a function of hydrogen permeation through an AISI 4340 steel membrane. Explain why the absolute values of this function decrease as the hydrogen permeation through AISI 4340 steel membrane increases.
3. Hydrogen coverage as a function of the overpotential on AISI 4340 steel membrane. Explain why the hydrogen coverage decreases as the overpotential on AISI 4340 steel membrane increases.

*Calculation of Steady-State Hydrogen Overpotential.*

1. Hydrogen evolution reaction for which the exchange current density is $5 \times 10^{-7}$ A/cm$^2$ is proceeding at overpotential $\eta = -0.199$ V under the control of a potentiostat. What is the current density?

Using a fast switch, the potentiostat is disconnected from the electrode and a cathodic current density of $2.05 \times 10^{-4}$ A/cm$^2$ is imposed on the electrode. What is the new steady-state overpotential and approximately how long would it take to attain it? Take the electrode area as 0.1 cm$^2$ and the double layer capacitance $C_{DL}$ as 50 $\mu$F/cm$^2$

Help: $\tau = C_{DL} R_p$, where $\tau$ is the time required for the system to respond to the imposition of a constant current, $R_p$ is the polarization resistance and $C_{DL}$ is the double layer capacitance.