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Hydrogen-Atom Direct-Entry Mechanism into Metal Membranes

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ABSTRACT

The hydrogen-atom direct-entry mechanism is used to explain why the steady-state hydrogen permeation current density through a metal membrane is directly proportional to the cathodic current density, \( i_0 \), and is independent of the membrane thickness when \( i_0 \) is small.

Bagotskaya\(^1\) and later Frumkin\(^2\) postulated that hydrogen atoms enter directly into a metal membrane and do not go through an intermediate adsorbed state. The mechanism they proposed is

\[
\begin{align*}
\text{H}^+ + \text{M} + e^- & \rightarrow \text{MH}_{\text{ads}} \quad [1] \\
\text{H}^+ + \text{M} + e^- & \rightarrow \frac{k_3}{k_{-3}} \text{MH}_{\text{ads}} + \frac{1}{2} \text{H}_2 + \text{M} \quad [2]
\end{align*}
\]

where \( k_1, k_{-1}, k_3, \) and \( k_{-3} \) are rate constants.

Bockris et al.\(^3\) checked this mechanism by considering the following equations

\[
\begin{align*}
J_o &= F \left( k_1 \left(1 - \frac{C_o}{C} \right) e^{-\alpha \eta} - k_{-1} C_o e^{(1-\alpha) \eta} \right) \quad [3] \\
i_0 &= i_0 e^{-\alpha \eta} \quad [4] \\
j_o &= \frac{DF}{L} C_o \quad [5]
\end{align*}
\]

where \( j_o \) is the steady-state hydrogen permeation current density, \( \eta \) is the overpotential, \( a = F/RT \), \( C_o \) is the hydrogen concentration directly beneath the cathode surface, \( C \) is the saturation value of \( C_o \), \( \alpha \) is the transfer coefficient of reaction 1, \( \alpha_2 \) is the transfer coefficient of reaction 2, \( i_0 \) is the cathodic current density, \( D \) is the hydrogen diffusion coefficient, and \( L \) is the membrane thickness. Bockris et al.\(^3\) used Eq. 3 to 5 to claim that the hydrogen permeation current density is proportional to the cathodic current density squared

\[ j_o \propto i_0^2 \quad [6] \]

Since no experimental evidence exists in literature to support Eq. 6, Bockris et al.\(^3\) concluded that the direct entry mechanism does not predict the observed results and is unable to explain the hydrogen permeation through a membrane.

The hydrogen atom direct mechanism\(^1,2\) is used here to explain why the steady-state hydrogen permeation current density \( j_o \) is directly proportional to the cathodic current density \( i_0 \) and is independent of the membrane thickness when \( i_0 \) is small. Assuming that the metal is far from saturation, then \( 1 - C_o/C = 1 \), and if in reaction 1, \( k_{-1} \) is negligible to \( k_1 \), Eq. 3 becomes

\[ j_o = \frac{Fk_1}{i_0} e^{-\alpha \eta} \quad [7] \]

The ratio of Eq. 7 to 4 is

\[ \frac{i_0}{i_e} = \frac{Fk_1}{i_0} e^{-\alpha \eta} \quad [8] \]

and assuming that the overpotential for the electrode (\( \eta \)) applies to both reactions 1 and 2

\[ j_o = i_0 \frac{Fk_1}{i_0} e^{-\alpha \eta} \quad [9] \]

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Experimental

The Devanathan-Stiachurski permeation technique\(^4\) was used to investigate the rate of hydrogen permeation through a HY-130 steel and through palladium membranes with an area of approximately 4 cm\(^2\) with thicknesses of 0.15 and 0.025 mm, respectively. The permeation experiments were carried out in a system with two compartments, separated by a bipolar membrane made of HY-130 steel or palladium.

The electrolyte on the cathodic side of the cell for the HY-130 steel membranes was 1M Na\(_2\)SO\(_4\), 0.4M NaCl, and 1M H\(_3\)BO\(_3\) and for the palladium membrane was 1N H\(_2\)SO\(_4\). Atomic hydrogen permeation transients through a HY-130 steel membrane for different applied cathodic potentials were recorded continuously as a function of time. At the beginning of each experiment, the cathodic side of the steel membrane was held at a constant potential of 0.58 V vs. SCE. Next, the potential was stepped to a more negative value after the hydrogen permeation current density reached a steady-state value. After the permeation stabilized at an applied potential of about 0.87 V vs. SCE, the potential was switched off, and a decay curve was recorded. The palladium alloy membrane on the cathodic side of the cell was polarized galvanostatically using a low cathodic current density in the range of 59.4 to 594.3 \( \mu \)A/cm\(^2\). The electrolyte on the anodic side of the cell for a HY-130 steel membrane was 0.2M NaOH while for the palladium membrane it was 1N H\(_2\)SO\(_4\). To avoid passivation or dissolution, the anodic side of the HY-130 membrane was electropolished with a thin layer (0.15 to 0.20 \( \mu \)m) of palladium. The electrodeposition of palladium was carried out in an electrolyte containing \( 2 \times 10^{-3} \)M Na\(_2\)Pd(NO\(_3\))\(_4\) using a current density of 100 \( \mu \)A/cm\(^2\) for 2 h. After the electrolyte was drained off, the compartment was washed with deionized water and filled with the anodic solution.

The potential on the anodic side for HY-130 steel membranes (the side from which the hydrogen emerges) was set at 0.3 V vs. a Hg/HgO reference electrode placed in the solution in the cell. The permeation rate through a palladium membrane was measured by setting the potential at a fixed value of 0.3 V vs. a SCE. These values of the set potentials correspond to a practically zero concentration of absorbed atomic hydrogen on the anodic surface of the mem-
Atomic hydrogen permeation transients through a HY-130 steel membrane as a function of time for different applied cathodic potentials in a catholyte containing 1M Na₂SO₄, 0.4M NaCl, and 1M H₃BO₃. The thickness of the membrane was \( L = 0.15 \) mm.

**Results and Discussion**

Atomic hydrogen permeation transients through a HY-130 steel membrane as a function of time for different applied potentials are shown in Fig. 1. The plateaux in Fig. 1 represent the \( j \) values for different values of \( E \). The corresponding cathodic current density, \( i_c \), was recorded for each value of \( E \). As expected, the permeation current densities increased as the applied cathodic potentials and the resulting cathodic current densities were increased. Figure 2, a plot of \( j \) vs. \( i_c \), is clearly linear.

Permeation transients through a palladium membrane obtained as function of applied cathodic current densities, as shown in Fig. 3. The plateaux in Fig. 3 represent \( j \) values for the associated set of \( i_c \) values. The permeation current density, \( j \), for palladium also increases linearly with the cathodic current density, as shown in Fig. 4.

![Fig. 1. Atomic hydrogen permeation transients through a HY-130 steel membrane as a function of time for different applied cathodic potentials in a catholyte containing 1M Na₂SO₄, 0.4M NaCl, and 1M H₃BO₃. The thickness of the membrane was \( L = 0.15 \) mm.](image1)

![Fig. 2. The steady-state hydrogen permeation current density (\( j \)) as a function of the cathodic current density (\( i_c \)) through the HY-130 steel membrane.](image2)

![Fig. 3. Hydrogen permeation transients through a Pd membrane obtained at constant cathodic current densities. The thickness of the palladium membrane was \( L = 25 \ \mu m \). The catholyte was 1N H₂SO₄.](image3)

![Fig. 4. The steady-state hydrogen permeation current density (\( j \)) as a function of the cathodic current density (\( i_c \)) through a palladium membrane (\( L = 25 \ \mu m \)).](image4)

**Conclusion**

The direct hydrogen entry mechanism was shown to be correct for HY-130 steel and Pd for small values of \( j \). A simple expression (Eq. 9) was developed that showed that the hydrogen permeation current density, \( j \), is directly proportional to the applied cathodic current density, \( i_c \), and is independent of the thickness of the metal membrane. This expression was shown to be consistent with experimental data presented here and with data from previous workers.

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LIST OF SYMBOLS

- \( a \) = \( F/RT \), V\(^{-1}\)
- \( C_s \) = hydrogen concentration directly beneath the cathode surface, mol cm\(^{-3}\)
- \( C_s^* \) = saturation value of \( C_s \), mol cm\(^{-3}\)
- \( D \) = hydrogen diffusivity, cm\(^2\) s\(^{-1}\)
- \( E_c \) = cathodic potential, V
- \( F \) = Faraday's constant, 96,487 C (eq)
- \( i_c \) = cathodic current density, A cm\(^{-2}\)
- \( i_0 \) = exchange current density, A cm\(^{-2}\)
- \( j_{se} \) = steady-state hydrogen permeation current density, A cm\(^{-2}\)
- \( k_1 \) = absorption constant, mol (cm\(^2\) s\(^{-1}\))
- \( k_2 \) = desorption constant, cm s\(^{-1}\)
- \( k_3 \) = hydrogen recombination rate constant, mol (cm\(^2\) s\(^{-1}\))
- \( L \) = membrane thickness, cm
- \( R \) = gas constant, 8.3143 J/(mol K)
- \( T \) = temperature, K

Greek

- \( \alpha_1 \), \( \alpha_2 \) = transfer coefficients, dimensionless
- \( \eta \) = overpotential, V

REFERENCES