1-1-1995

Hydrogen-Atom Direct-Entry Mechanism into Metal Membranes

G. Zheng
University of South Carolina - Columbia

Branko N. Popov
University of South Carolina - Columbia, popov@engr.sc.edu

Ralph E. White
University of South Carolina - Columbia, white@ece.sc.edu

Follow this and additional works at: http://scholarcommons.sc.edu/eche_facpub

Part of the Chemical Engineering Commons

Publication Info
© The Electrochemical Society, Inc. 1995. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in the Journal of the Electrochemical Society.
http://www.electrochem.org/
DOI: 10.1149/1.2043855
Publisher’s link: http://dx.doi.org/10.1149/1.2043855

This Article is brought to you for free and open access by the Chemical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact SCHOLARC@mailbox.sc.edu.
Hydrogen-Atom Direct-Entry Mechanism into Metal Membranes

G. Zheng,* B. N. Popov,** and R. E. White**
Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208

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, and is independent of the membrane thickness when is small.

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

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

where $k_1$, $k_{-1}$, $k_3$, and $k_3$ are rate constants.

Bockris et al. checked this mechanism by considering the following equations

$$\begin{align*}
J_0 &= F\left[k_1(1 - C_0) e^{-\alpha_2} - k_{-1} C_0 e^{(1-\alpha_2)}\right] \quad [3] \\
i_0 &= i_{\text{cath}} e^{\alpha_2} \quad [4] \\
j_0 &= \frac{DF}{L} C_0 \quad [5]
\end{align*}$$

where $j_0$ is the steady-state permeation current density, $\alpha_2$ is the overpotential, and $C_0$ is the hydrogen concentration directly beneath the cathode surface. $C_0$ is the saturation value of $C_0$, $\alpha_2$ is the transfer coefficient of reaction 1, $\alpha_1$ 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. used Eq. 3 to 5 to claim that the hydrogen permeation current density is proportional to the cathodic current density squared

$$j_0 \propto i_0^2 \quad [6]$$

Since no experimental evidence exists in literature to support Eq. 6, Bockris et al. 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 is used here to explain why the steady-state hydrogen permeation current density ($j_0$) 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 $1 - C_0/C = 1$, and if in reaction 1, $k_{-1}$ is negligible to $k_1$, Eq. 3 becomes

$$j_0 = Fk_1 e^{-\alpha_1} \quad [7]$$

The ratio of Eq. 7 to 4 is

$$\frac{i_0}{i_{\text{cath}}} = \frac{Fk_1 e^{-\alpha_1}}{i_{\text{cath}} e^{\alpha_1}} \quad [8]$$

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

$$j_0 = i_0 \frac{Fk_1}{i_{\text{cath}}} e^{-\alpha_1} \quad [9]$$

If $\alpha_1 = \alpha_2$, Eq. 9 shows that $j_0$ is directly proportional to $i_0$, which is in agreement with previous experiment work that was done under conditions consistent with the development of Eq. 9. For example, Early reported that $j_0$ through palladium membranes is directly proportional to $i_0$ when $i_0$ is less than 20 mA/cm². Heath reported the same for $i_0$ less than 22 mA/cm². Raczynski and Zacroszyński et al. demonstrated that $j_0 \propto i_0$ for low values of $i_0$ for hydrogen permeation through iron. Also Evseev reported that $j_0 \propto i_0$ for iron for values of $i_0$ between 5 and 80 mA/cm².

Note that Eq. 9 shows that $j_0$ does not depend on the thickness of the metal membrane ($L$). This is consistent with results presented by Hoare and Schuldiner and Bowker and Piercy for Pd membranes.

**Experimental**

The Devanathan-Stachurski permeation technique was used to investigate the rate of hydrogen permeation through a HY-130 steel and through palladium membranes with an area of approximately 4 cm² 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 1 M Na₂SO₄, 0.4 M NaCl, and 1 M H₃BO₃ and for the palladium membrane 1 N H₂SO₄. 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 −0.3 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 A/cm².

The electrolyte on the anodic side of the cell for a HY-130 steel membrane was 0.2 M NaOH while for the palladium membrane it was 1 N H₂SO₄. To avoid passivation or dissolution, the anodic side of the HY-130 membrane was electroplated with a thin layer (0.15 to 0.20 μm) of palladium. The electrodeposition of palladium was carried out in an electrolyte containing 2 × 10⁻¹⁷ M Na₃Pd(NO₃)₄, using a current density of 100 μA/cm² 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-
Results and Discussion

Atomic hydrogen permeation transients through a HY-130 steel membrane as a function of time for different applied cathodic potentials are shown in Fig. 1. The plateaux in Fig. 1 represent the \( j_0 \) values for different values of \( E_0 \). The corresponding cathodic current density, \( i_c \), was recorded for each value of \( E_0 \). 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 \( j_0 \) vs. \( i_c \), is clearly linear.

Permeation transients through a palladium membrane were obtained as a function of applied cathodic current densities, as shown in Fig. 3. The plateaux in Fig. 3 represent \( j_0 \) values for the associated set of \( i_c \) values. The permeation current density, \( j_0 \), for palladium also increases linearly with the cathodic current density, as shown in Fig. 4.

Conclusion

The direct hydrogen entry mechanism\(^1\) was shown to be correct for HY-130 steel and Pd for small values of \( j_c \). A simple expression (Eq. 9) was developed that showed that the hydrogen permeation current density, \( j_0 \), 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.

Acknowledgment

Technical assistance and financial support by A. John Sedriks, the Office of Naval Research, under Contracts No. N00014-93-1-0259 and AASERT N00014-93-1-1094 are gratefully acknowledged.

Manuscript submitted Nov. 15, 1993; revised manuscript received Sept. 19, 1994.

The University of South Carolina assisted in meeting the publication costs of this article.
LIST OF SYMBOLS

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

\[ \alpha_\text{a}, \alpha_\text{s} \quad \text{transfer coefficients, dimensionless} \]
\[ \eta \quad \text{overpotential, V} \]

REFERENCES