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# Hydrogen-Atom Direct-Entry Mechanism into Metal Membranes

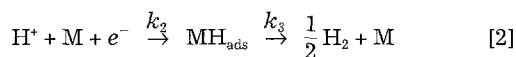
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## ABSTRACT

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

Bagotskaya<sup>1</sup> and later Frumkin<sup>2</sup> postulated that hydrogen atoms enter directly into a metal membrane and do not go through an intermediate adsorbed state. The mechanism they proposed is



where  $k_1$ ,  $k_{-1}$ ,  $k_2$ , and  $k_3$  are rate constants.

Bockris *et al.*<sup>3</sup> checked this mechanism by considering the following equations

$$J_\infty = F \left[ k_1 \left( 1 - \frac{C_o}{C_s} \right) e^{-\alpha_1 a \eta} - k_{-1} C_o e^{(1-\alpha_1) a \eta} \right] \quad [3]$$

$$i_c = i_o e^{-\alpha_2 a \eta} \quad [4]$$

$$j_\infty = \frac{DF}{L} C_o \quad [5]$$

where  $j_\infty$  is the steady-state permeation current density,  $\eta$  is the overpotential,  $a = F/RT$ ,  $C_o$  is the hydrogen concentration directly beneath the cathode surface,  $C_s$  is the saturation value of  $C_o$ ,  $\alpha_1$  is the transfer coefficient of reaction 1,  $\alpha_2$  is the transfer coefficient of reaction 2,  $i_c$  is the cathodic current density,  $D$  is the hydrogen diffusion coefficient, and  $L$  is the membrane thickness. Bockris *et al.*<sup>3</sup> used Eq. 3 to 5 to claim that the hydrogen permeation current density is proportional to the cathodic current density squared

$$j_\infty \propto i_c^2 \quad [6]$$

Since no experimental evidence exists in literature to support Eq. 6, Bockris *et al.*<sup>3</sup> 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<sup>1,2</sup> is used here to explain why the steady-state hydrogen permeation current density ( $j_\infty$ ) is directly proportional to the cathodic current density ( $i_c$ ) and is independent of the membrane thickness when  $i_c$  is small. Assuming that the metal is far from saturation, then  $1 - C_o/C_s \approx 1$ , and if in reaction 1,  $k_{-1}$  is negligible to  $k_1$ , Eq. 3 becomes

$$j_\infty = F k_1 e^{-\alpha_1 a \eta} \quad [7]$$

The ratio of Eq. 7 to 4 is

$$\frac{j_\infty}{i_c} = \frac{F k_1 e^{-\alpha_1 a \eta}}{i_o e^{-\alpha_2 a \eta}} \quad [8]$$

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

$$j_\infty = i_c \frac{F k_1}{i_o} e^{-(\alpha_2 - \alpha_1) a \eta} \quad [9]$$

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If  $\alpha_1 = \alpha_2$ , Eq. 9 shows that  $j_\infty$  is directly proportional to  $i_c$ , which is in agreement with previous experiment work<sup>4-9</sup> that was done under conditions consistent with the development of Eq. 9. For example, Early<sup>4</sup> reported that  $j_\infty$  through palladium membranes is directly proportional to  $i_c$  when  $i_c$  is less than 200  $\mu\text{A}/\text{cm}^2$ . Heath<sup>5</sup> reported the same for  $i_c$  less than 22  $\text{mA}/\text{cm}^2$ . Raczyński<sup>6</sup> and Zaczaryński *et al.*<sup>7</sup> demonstrated that  $j_\infty \propto i_c$  for low values of  $i_c$  for hydrogen permeation through iron. Also Evseev<sup>8</sup> reported that  $j_\infty \propto i_c$  for iron for values of  $i_c$  between 5 and 80  $\text{mA}/\text{cm}^2$ .

Note that Eq. 9 shows that  $j_\infty$  does not depend on the thickness of the metal membrane ( $L$ ). This is consistent with results presented by Hoare and Schuldiner<sup>9,10</sup> and Bowker and Piercy<sup>11</sup> for Pd membranes.

## Experimental

The Devanathan-Stachurski permeation technique<sup>12</sup> was used to investigate the rate of hydrogen permeation through a HY-130 steel and through palladium membranes with an area of approximately 4  $\text{cm}^2$  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  $\text{Na}_2\text{SO}_4$ , 0.4M  $\text{NaCl}$ , and 1M  $\text{H}_3\text{BO}_3$  and for the palladium membrane was 1N  $\text{H}_2\text{SO}_4$ . 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  $-0.58 \text{ V vs. SCE}$ . 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  $-0.87 \text{ V vs. SCE}$ , 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  $\mu\text{A}/\text{cm}^2$ .

The electrolyte on the anodic side of the cell for a HY-130 steel membrane was 0.2M  $\text{NaOH}$  while for the palladium membrane it was 1N  $\text{H}_2\text{SO}_4$ . To avoid passivation or dissolution, the anodic side of the HY-130 membrane was electroplated with a thin layer (0.15 to 0.20  $\mu\text{m}$ ) of palladium. The electrodeposition of palladium was carried out in an electrolyte containing  $2 \times 10^{-5} \text{M Na}_2\text{Pd}(\text{NO}_3)_4$  using a current density of 100  $\mu\text{A}/\text{cm}^2$  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  $-0.3 \text{ V vs. a Hg/HgO reference electrode}$  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 adsorbed atomic hydrogen on the anodic surface of the mem-

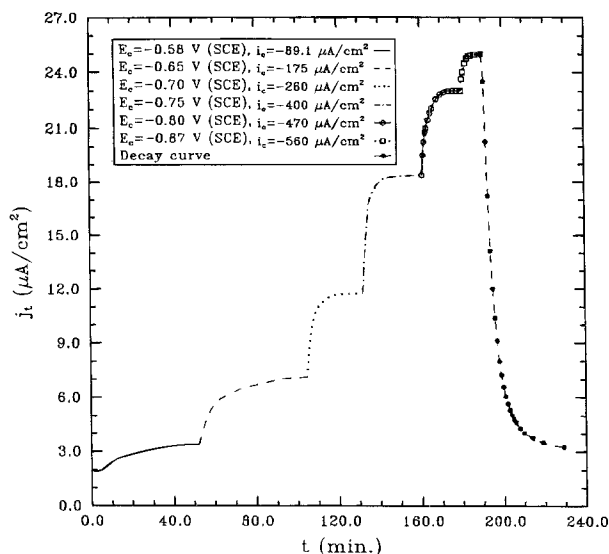


Fig. 1. Atomic hydrogen permeation transients through a HY-130 steel membrane as a function of time for different applied cathodic potentials in a catholyte containing 1M Na<sub>2</sub>SO<sub>4</sub>, 0.4M NaCl, and 1M H<sub>3</sub>BO<sub>3</sub>. The thickness of the membrane was  $L = 0.15$  mm.

brane. Prepurified nitrogen was bubbled through both compartments in order to keep them free from oxygen contamination.

### 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  $j_{\infty}$  values for different values of  $E_c$ . The corresponding cathodic current density,  $i_c$ , was recorded for each value of  $E_c$ . 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  $j_{\infty}$  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  $j_{\infty}$  values for the associated set of  $i_c$  values. The permeation current density,  $j_{\infty}$ , for palladium also increases linearly with the cathodic current density, as shown in Fig. 4.

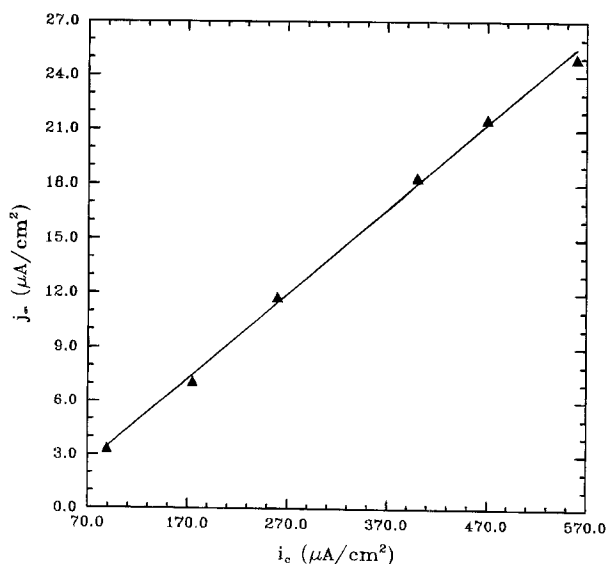


Fig. 2. The steady-state hydrogen permeation current density ( $j_{\infty}$ ) as a function of the cathodic current density ( $i_c$ ) through the HY-130 steel membrane.

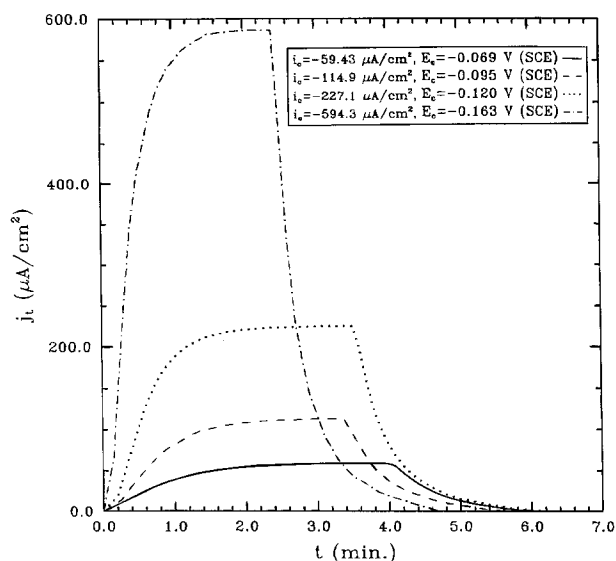


Fig. 3. Hydrogen permeation transients through a Pd membrane obtained at constant cathodic current densities. The thickness of the palladium membrane was  $L = 25$   $\mu$ m. The catholyte was 1N H<sub>2</sub>SO<sub>4</sub>.

### Conclusion

The direct hydrogen entry mechanism<sup>1,2</sup> 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,  $j_{\infty}$ , 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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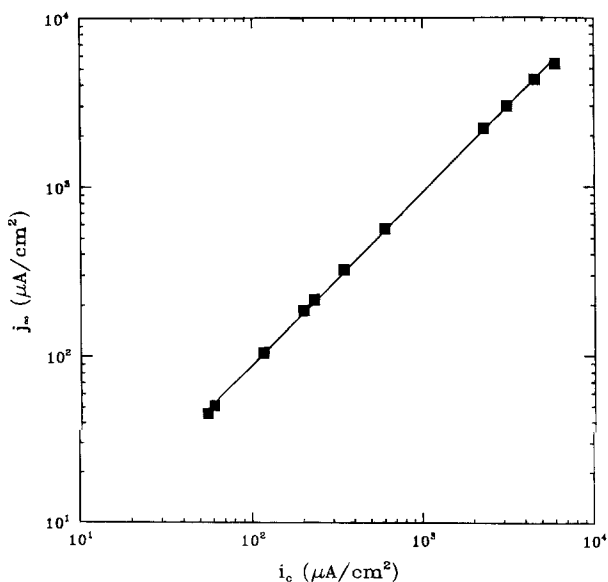


Fig. 4. The steady-state hydrogen permeation current density ( $j_{\infty}$ ) as a function of the cathodic current density ( $i_c$ ) through a palladium membrane ( $L = 25$   $\mu$ m).

## LIST OF SYMBOLS

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

## Greek

$\alpha_1, \alpha_2$	transfer coefficients, dimensionless
$\eta$	overpotential, V

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