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ELECTROCHEMICAL EXCHANGE CURRENT OF α-PHASE PALLADIUM/HYDROGEN ELECTRODE AS A FUNCTION OF HYDROGEN CONTENTS JUST BELOW THE ELECTRODE SURFACE IN ACID AND ALKALINE SOLUTIONS

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Abstract

A three compartments cell, separated by two palladium membranes, was composed (see Fig. 5). By this cell the exchange currents $i_0$ of α-phase Pd/H electrode in acid and in alkaline solutions were observed under the steady condition of 100%-permeation of hydrogen through the membrane without any trace of gaseous evolution. The relations of log $i_0$ vs. log permeation current $i$ in acid and in alkaline solutions were found as that in acid solution log $i_0$ increases linearly as log $i$ increases, whereas that in alkaline solution log $i_0$ decreases as log $i$ increases. In the steady state of permeation of hydrogen, the hydrogen concentration at the outlet side surface can be set at zero, so that $i$ decides the hydrogen concentration just below the surface of inlet side. Considering the adsorption isotherm of Langmuir for the adsorbed species, conclusions were deduced by rate-treatments, respectively for acid and alkaline. The log $i_0$ vs. log $i$ relations deduced are in good accordance with those obtained by experiments.

Introduction

The exchange currents of the palladium hydrogen electrode have been measured by many workers. Holleck and Flanagan measured the exchange currents $i_0$ in acid solution as a function of the hydrogen contents of the electrodes of palladium/hydrogen and gold (18.8%) palladium/hydrogen. The values of $i_0$ were markedly dependent upon the hydrogen contents of the electrodes.

In this paper we report the relations of $i_0$ against the hydrogen contents $C_H$ just below the surface of the α-phase (3.10×10^{-4}~6.2×10^{-4} H/Pd) pal-
ladium hydrogen electrodes in acid and alkaline solutions, with an improved technique, as described later, assuring 100% permeation of electrolytic hydrogen through palladium membrane without any trace of the evolution of hydrogen and oxygen on the electrodes.

**Theoretical**

(A). Analysis for a steady state of 100% permeation of hydrogen

Case (a) Acid solution

Under specified condition of a steady state of 100% permeation of hydrogen by a given current $i$, the dissolved hydrogen in solution should be in equilibrium with the hydrogen atoms on the electrode surface. The mechanism of the steady permeation of hydrogen is composed of steps as follows,

\[ \text{H}^+ + e \rightarrow \text{H}_{\text{ad}}, \]  
\[ \text{H}_{\text{ad}} \rightarrow \text{H}_{\text{diss}}, \]

and

\[ \text{H}_{\text{diss}} \rightarrow \text{diffuses through the membrane electrode}, \]

where $\text{H}_{\text{ad}}$ and $\text{H}_{\text{diss}}$ is the adsorbed and dissolved hydrogen atom, respectively.

Assuming the Langmuir isotherm for the adsorbed hydrogen ($\text{H}_{\text{ad}}$), we have the rate equation for the step (I) as,

\[ i = i_0 \left[ \exp \left( \frac{a_{\text{H}^+} f_{\text{H}}}{b_{\text{H}}} \right) - \exp \left( - \left(1 - a_{\text{H}^+} \right) f_{\text{H}} \right) \right], \]  

and

\[ i_0 = K_1 a_{\text{H}^+}^{(1 - \alpha)} \theta_{\text{H}}^* (1 - \theta_{\text{H}})^{(1 - \alpha)}, \]

where $K_1$ is the standard rate constant of the step (I), $a_{\text{H}^+}$ is the activity of the hydrogen ion in the solution and $\theta_{\text{H}}$ is the coverage of the adsorbed hydrogen atom and $f$ stands for $F/RT$. When step (II) is in equilibrium we have,

\[ \theta_{\text{H}} = K_2 C_{\text{H}}^0 / \left( 1 + K_2 C_{\text{H}}^0 \right), \]

where $K_2$ is the equilibrium constant and $C_{\text{H}}^0$ is the activity of hydrogen just below the surface. Since hydrogen diffuses through the membrane and at the outlet side being oxidized completely to zero concentration by a current $i$, we have from Fick's law,
Exchange Current of α-Pd/H Electrode

\[ C_\text{H}^0 = \beta i l / F D, \]  

(4)

where \( \beta \) is the reducing factor, \( i \) is the permeation current density, \( l \) is the thickness of the membrane, and \( D \) is the diffusion coefficient of hydrogen respectively. From Eqs. (2), (3), and (4), within the same solution \( i.e. \), \( a_{\text{H}^+} \) is constant, we have

\[
i_0 = K_i \left\{ K_2 i / (1 + K_2 \gamma i) \right\}^\alpha (1 + K_2 \gamma i)^{-\alpha} \]

\[ = K_i (K_2 \gamma i)^\alpha / (1 + K_2 \gamma i), \]  

(5)

where \( \gamma \) stands for \( \beta l / F D \). Fig. 1 shows the theoretical relation of \( \log i_0 \) vs. \( \log i \) for several values of \( K_2 \) which decide the inclination of the curve, under the assumption, \( \alpha = 0.5 \).

![Figure 1](image-url)

**Fig. 1.** Theoretical relations of \( \log i_0 \) vs. \( \log i \) for several values of \( K_2 \) in acid. \( C \) is an arbitrary constant.

Curve 1: \( K_2 = 1 \), Curve 2: \( K_2 = 100 \), Curve 3: \( K_2 = 300 \),
Curve 4: \( K_2 = 500 \), Curve 5: \( K_2 = 1000 \).

Case (b) Alkaline solution

As an example we chose potassium hydroxide solution. We assume two preceeding steps for the production of \( \text{H}_\text{ad} \) which support the steady permeation of hydrogen through the palladium membrane as follows,
K⁺ + e → K_ads, \hspace{1cm} (IV)
K_ads + H₂O → K⁺ + OH⁻ + H_ads, \hspace{1cm} (V)
H_ads → H_diss \hspace{1cm} (VI)

and

H_diss → diffuses through the membrane. \hspace{1cm} (VII)

From the rate equations for the steps (IV), (V), (VI), (VII) and assuming that each of the steps (V) and (VI) is in equilibrium, we obtain the rate equations

\[ i_o = K_s a^{(1+n)}_K (1-\theta_H-\theta_K)^{(1-n)}, \] \hspace{1cm} (8)
where \( K_s \) is the standard rate constant of the step (IV), and

\[ \theta_K/(1-\theta_H-\theta_K) = K_4 \theta_H/(1-\theta_H-\theta_K) \] \hspace{1cm} (9)
and

\[ \theta_H/(1-\theta_H-\theta_K) = K_5 C_ii, \] \hspace{1cm} (10)
where \( K_4 \) and \( K_5 \) is the equilibrium constant of the steps (V) and (VI), respectively. Rewriting Eq. (8) with (4), (9) and (10) we have,

\[ i_o = \frac{K_3(K_4K_5) a^{(1+n)}_K C_ii^o}{1+K_4(1+K_5) C_ii^o} = \frac{K_3(K_4K_5)^* a^{(1+n)}_K C_ii^*}{1+K_4(1+K_4) C_ii^*} \]

\[ = \frac{K' a^{(1+n)}_K}{1+K'' a^{(1+n)}_K}, \] \hspace{1cm} (11)

Fig. 2 shows the relation of log \( i_o \) vs. log \( i \), for several values of \( K'' \).

(B). Analysis for a transient state

After a steady permeation was established, the current was cut off. Then we can observe a sudden rise of the electrode potential followed by slow rise, as shown in Fig. 3.

The overpotential is composed of three parts, namely of \( \eta_1 \), \( \eta_2 \) and \( \eta_r \), in which \( \eta_r \) is the ohmic drop and is subtracted from the figure. The sudden rise \( \eta_1 \) and the slow rise \( \eta_2 \) can be attributed to that of discharge step and that of hydrogen diffusion step through membrane, respectively. Time dependent build up of \( \eta_{1,t} \) is deduced as follows,

\[ -C_D \frac{d\eta_{1,t}}{dt} = i_o \left( \exp(\alpha f\eta_{1,t}) - \exp\left\{-\left(1-\alpha\right)f\eta_{1,t}\right\} \right), \] \hspace{1cm} (14)

where \( C_D \) is the double layer capacity and \( \eta_{1,t} \) is the value of \( \eta_1 \) at time \( t \) (\( t=0 \) denotes the instant of interruption of the current). Under the as-
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Fig. 2. Theoretical relations $\log i_0 + C$ vs. $\log i$ for several values of $K''$ in KOH solution. $C$ is an arbitrary constant.
Curve 1: $K'' = 10^6$, Curve 2: $K'' = 10^4$, Curve 3: $K'' = 5 \times 10^3$, Curve 4: $K'' = 2 \times 10^3$, Curve 5: $K'' = 10^3$.

Fig. 3. Typical curve of potential $\phi$ against time, after the moment of interruption of the current.
sumption $\alpha = 1 - \alpha$ (i.e., $\alpha = 0.5$) the solution of Eq. (14) is given below,
\[
\ln \left[ \frac{\exp(\alpha f \eta_{1,0} - 1) \exp(\alpha f \eta_{1,0} + 1)}{\exp(\alpha f \eta_{1,0} - 1) \exp(\alpha f \eta_{1,0} + 1)} \right] = i_0 \frac{f}{C_B} \times t,
\]
where $\eta_{1,0}$ denotes the value of $\eta_1$ at $t = 0$. The plot of the left hand side of Eq. (15) against $t$ should give a straight line, and from the tangent we can calculate the $i_0$ value.

On the other hand, we can derive an equation which shows the relation of $\eta_2$ against time $t$, in solving the diffusion equation of Fick's second law with given conditions.\(^*)\) The solution is given below as,
\[
\eta_2 = \frac{1}{f} \left( \ln \frac{a_{H^+}}{C_{H^+,t=0}} - \ln \frac{a_{H^+}}{C_{H^+,t=0}} \right) = - \frac{1}{f} \ln \left\{ 1 - 2 \left( \frac{D}{\pi t} \right)^{1/2} \right\}
\]
\[
= \frac{2}{f} \left( \frac{D}{\pi t} \right)^{1/2}.
\]
Eq. (17) can be compared with experiments. Using the $D$ value, $D = 3.7 \times 10^{-7}$ cm$^2$/s, the theoretical curve is shown in Fig. 4 by solid line.

\[\text{Fig. 4. } \eta_2 \text{ against } t^{1/2} \text{ relation.}\]
\text{-: theoretical value, } \bigcirc: \text{ experimental value.}\]

**Experimental**

Fig. 5 shows the block diagram of experimental set up with a three compartments cell. Two palladium membrane electrodes, of the thickness 50 \( \mu m \), were baked in an oxidizing flame in air, and then they were subjected to anodic oxidation in acid or in alkaline solution, just before being mounted to the cell. Glass wares (in 3 parts) were immersed in conc. \( \text{HNO}_3 \) solution for a time, and then washed thoroughly by steam. The two palladium membranes were mounted to the cell with O-rings made of teflon rubber at the both sides. After the construction, whole cell were rewashed by steam. Two auxiliary electrodes (1) and (2) were platinum wire or palladium wire, respectively in acid (\( \text{HClO}_4 \)) or alkaline (\( \text{KOH} \)) solution. All

![Diagram of experimental set up.](image)
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chemicals used were of the grade Pro-Analyti of Merck. All measurements were worked at 25±0.1°C in an air-thermostat. The center-compartment of the cell, composed of palladium membrane electrodes Pd-1 and Pd-2, is the working cell. The left hand side of the Pd-1 is kept at a potential by the potentiostat-1 against the reference electrode-1. Supplied hydrogen permeates through the membrane to the other side, and at this surface adsorbed hydrogen H_{ad} is oxidized by a constant current \( i \) to H\(^{+}\), and only a part of H\(_{ad}\) dissolves into the solution as H\(_{2}\). At the cathode Pd-2, charged by a constant current \( i \), most H\(_{ad}\) permeates through the membrane to other side, and there oxidized completely to H\(^{+}\) without evolution of H\(_{2}\) gas, by the aid of potentiostat-2. Only a part of H\(_{ad}\) at the inlet surface of Pd-2 dissolves into the solution as H\(_{2}\). Fig. 6 shows the flows of hydrogen through the working cell in acid solution.

![Diagram of the flows of hydrogen through the working cell.](image)

In the working cell, the solution is moderately stirred by a magnetic stirrer S. After a while, the constant current \( i \) becomes the same with the hydrogen permeation current which is supplied by the potentiostat-2. The 100% efficiency of hydrogen permeation against supply current can be guaranteed down to the current density of 0.25 mA. This high efficiency cannot be attained by a two compartments double cell. Furthermore a great merit is that at the anode of the working cell there is no evolution of oxygen which can disturb the equilibrium balance of hydrogen in the working cell.
Results and Discussion

The values $i_o$, obtained by analysis of stationary states and of transient states, are in good accordance. The theoretical and experimental values of time-dependent change of $\eta_2$ caused by hydrogen diffusion are shown in Fig. 4. The experimental linear line $\eta_2$ vs. $t^{1/2}$, passing through the origin, lies close to the theoretical solid line. The results show clearly that the analysis of transient curve of overpotential $\eta$ of Fig. 3 is appropriate. The potential $E_o$, marked in Fig. 3, is really the equilibrium potential. The figure, $E_o$ vs. log $i$ showing straight line of Nernst's equation, is omitted here.

Fig. 7 shows the results of log $i_o$ vs. log $i$ relations in acid and alkaline solutions. The both linear relations correspond to those theoretically derived linear relations of Fig. 1, in which the magnitude of $K_2$ should be $300 < K_2 < 500$ and those of Fig. 2, in which the magnitude of $K''$ should be $10^6 \sim 10^8$. Our experiment in acid tells that in this circumstance, the coverage of hydrogen atom $\theta_H$ can be estimated as 0.27 and 0.38 at the current density of 1 mA, in the case of $K_2=300$ and $K_2=500$, respectively. While in alkaline solution the value of $1 - \theta_H - \theta_K$ is very small. Although the magnitudes of $\theta_H$ and $\theta_K$ are not determined in this case, it is observed

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{fig7.png}
\caption{Experimental relations between $i_o$ and $i$ in acid and alkaline solutions.}
\end{figure}

$\triangle$: in 2.3 M HClO$_4$, $\circ$: in 0.13 M KOH.
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that some surface active species such as $\Gamma^-$ ion can greatly disturb the linear relation of $\log i_0$ vs. $\log i$. Further works are on the way in our laboratory.

References