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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

By

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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 Flanagan¹⁾ 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^0 just below the surface of the α -phase ($3.10 \times 10^{-4} \sim 6.2 \times 10^{-3}$ H/Pd) pal-

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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

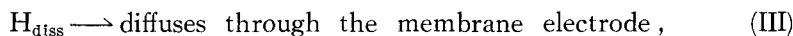
(A). Analysis for a steady state of 100% permeation of hydrogen

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,



and



where H_{ad} and H_{diss} is the adsorbed and dissolved hydrogen atom, respectively.

Assuming the Langmuir isotherm for the adsorbed hydrogen (H_{ad}), we have the rate equation for the step (I) as,

$$i = i_0 [\exp(\alpha f \eta_1) - \exp\{-(1-\alpha) f \eta_1\}], \quad (1)$$

and

$$i_0 = K_1 a_{\text{H}^+}^{(1-\alpha)} \theta_{\text{H}}^{\alpha} (1 - \theta_{\text{H}})^{(1-\alpha)}, \quad (2)$$

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

$$\theta_{\text{H}} = K_2 C_{\text{H}}^0 / (1 + K_2 C_{\text{H}}^0), \quad (3)$$

where K_2 is the equilibrium constant and C_{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,

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$$C_H^0 = \beta i l / FD, \quad (4)$$

where β 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_{H^+} is constant, we have

$$\begin{aligned} i_0 &= K_1' \left\{ K_2 i / (1 + K_2 \gamma i) \right\}^\alpha (1 + K_2 \gamma i)^{-(1-\alpha)} \\ &= K_1' (K_2 \gamma i)^\alpha / (1 + K_2 \gamma i), \end{aligned} \quad (5)$$

where γ stands for $\beta l / FD$. 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, $\alpha = 0.5$.

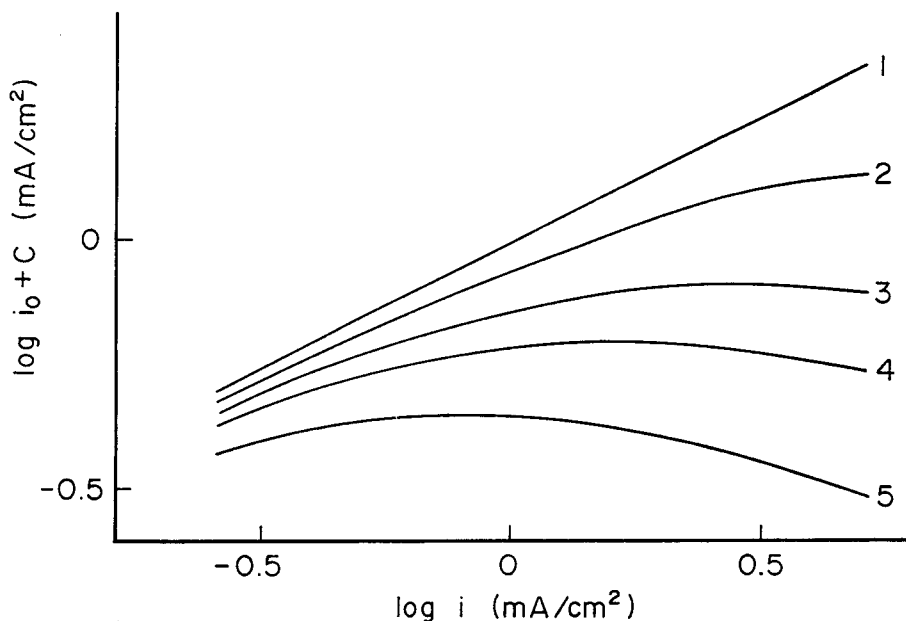


Fig. 1. Theoretical relations of $\log i_0$ vs. $\log i$ for several values of K_2 in acid. C is an arbitrary constant.

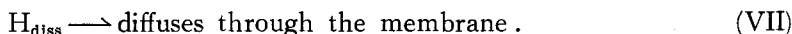
Curve 1: $K_2=1$, Curve 2: $K_2=100$, Curve 3: $K_2=300$,
Curve 4: $K_2=500$, Curve 5: $K_2=1000$.

Case (b) Alkaline solution

As an example we chose potassium hydroxide solution. We assume two preceeding steps for the production of H_{ad} which support the steady permeation of hydrogen through the palladium membrane as follows,

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and



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

$$i_0 = K_3 a_K^{(1-\alpha)} \theta_K^\alpha (1 - \theta_H - \theta_K)^{(1-\alpha)}, \quad (8)$$

where K_3 is the standard rate constant of the step (IV), and

$$\theta_K / (1 - \theta_H - \theta_K) = K_4 \theta_H / (1 - \theta_H - \theta_K) \quad (9)$$

and

$$\theta_H / (1 - \theta_H - \theta_K) = K_5 C_H^0, \quad (10)$$

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,

$$\begin{aligned} i_0 &= \frac{K_3 (K_4 K_5)^\alpha a_H^{(1-\alpha)} C_H^{0\alpha}}{1 + K_5 (1 + K_4) C_H^0} = \frac{K_3 (K_4 K_5)^\alpha a_H^{(1-\alpha)} \gamma^\alpha i^\alpha}{1 + K_5 (1 + K_4) \gamma i} \\ &= \frac{K' \gamma^\alpha i^\alpha}{1 + K'' \gamma i}, \end{aligned} \quad (11)$$

Fig. 2 shows the relation of $\log i_0$ 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 η_1 , η_2 ,²⁾ and η_r , in which η_r is the ohmic drop and is subtracted from the figure. The sudden rise η_1 and the slow rise η_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,

$$-C_D \frac{d\eta_{1,t}}{dt} = i_0 [\exp(\alpha f \eta_{1,t}) - \exp\{-(1-\alpha) f \eta_{1,t}\}], \quad (14)$$

where C_D is the double layer capacity and $\eta_{1,t}$ is the value of η_1 at time t ($t=0$ denotes the instant of interruption of the current). Under the as-

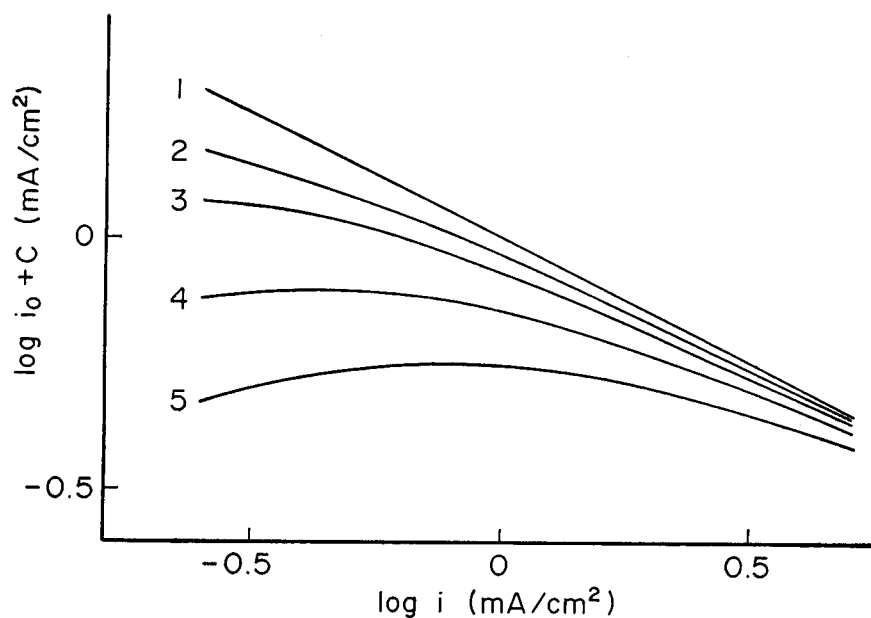
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Fig. 2. Theoretical relations $\log i_0$ vs. $\log i$ for several values of K'' in KOH solution. C is an arbitrary constant. Curve 1: $K''=10^6$, Curve 2: $K''=10^4$, Curve 3: $K''=5 \times 10^3$, Curve 4: $K''=2 \times 10^3$, Curve 5: $K''=10^3$.

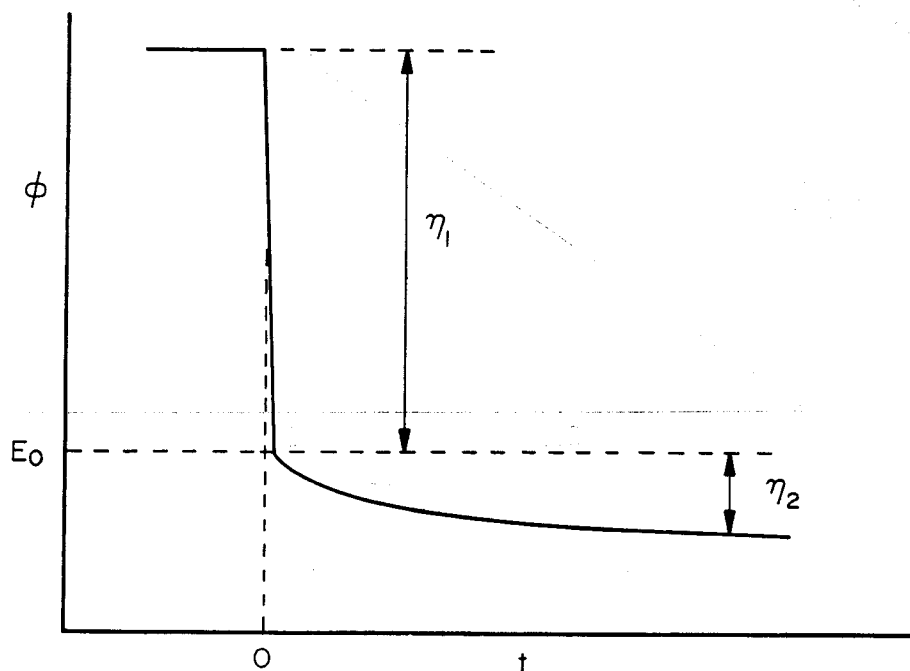


Fig. 3. Typical curve of potential ϕ against time, after the moment of interruption of the current.

sumption $\alpha=1-\alpha$ (*i. e.*, $\alpha=0.5$) the solution of Eq. (14) is given below,

$$\ln \left[\frac{\{\exp(\alpha f \eta_{1,0}) - 1\} \{\exp(\alpha f \eta_{1,t}) + 1\}}{\{\exp(\alpha f \eta_{1,t}) - 1\} \{\exp(\alpha f \eta_{1,0}) + 1\}} \right] = i_0 \frac{f}{C_D} \cdot t, \quad (15)$$

where $\eta_{1,0}$ denotes the value of η_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 η_2 against time t , in solving the diffusion equation of Fick's second law with given conditions.*) The solution is given below as,

$$\begin{aligned} \eta_2 &= \frac{1}{f} \left(\ln \frac{a_{H^+}}{C_{H,t=t}^0} - \ln \frac{a_{H^+}}{C_{H,t=0}^0} \right) \doteq -\frac{1}{f} \ln \left\{ 1 - 2 \left(\frac{D}{\pi l^2} \right)^{\frac{1}{2}} \cdot t^{\frac{1}{2}} \right\} \\ &\doteq \frac{2}{f} \left(\frac{D}{\pi l^2} \right)^{\frac{1}{2}} t^{\frac{1}{2}}. \end{aligned} \quad (17)$$

Eq. (17) can be compared with experiments. Using the D value, $D=3.7 \times 10^{-7} \text{ cm}^2/\text{s}$, the theoretical curve is shown in Fig. 4 by solid line.

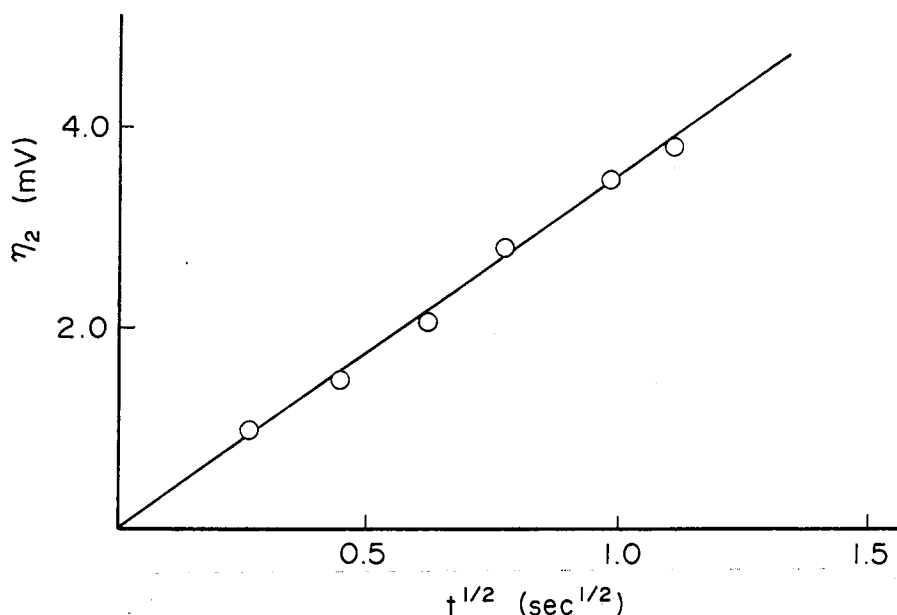


Fig. 4. η_2 against $t^{1/2}$ relation.

—: theoretical value, ○: experimental value.

*) S. Nakamura, Thesis, Rikkyo (St. Paul's) University, Tokyo (1979).

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Experimental

Fig. 5 shows the block diagram of experimental set up with a three compartments cell. Two palladium membrane electrodes, of the thickness $50\ \mu\text{m}$, 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. 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 (HClO_4) or alkaline (KOH) solution. All

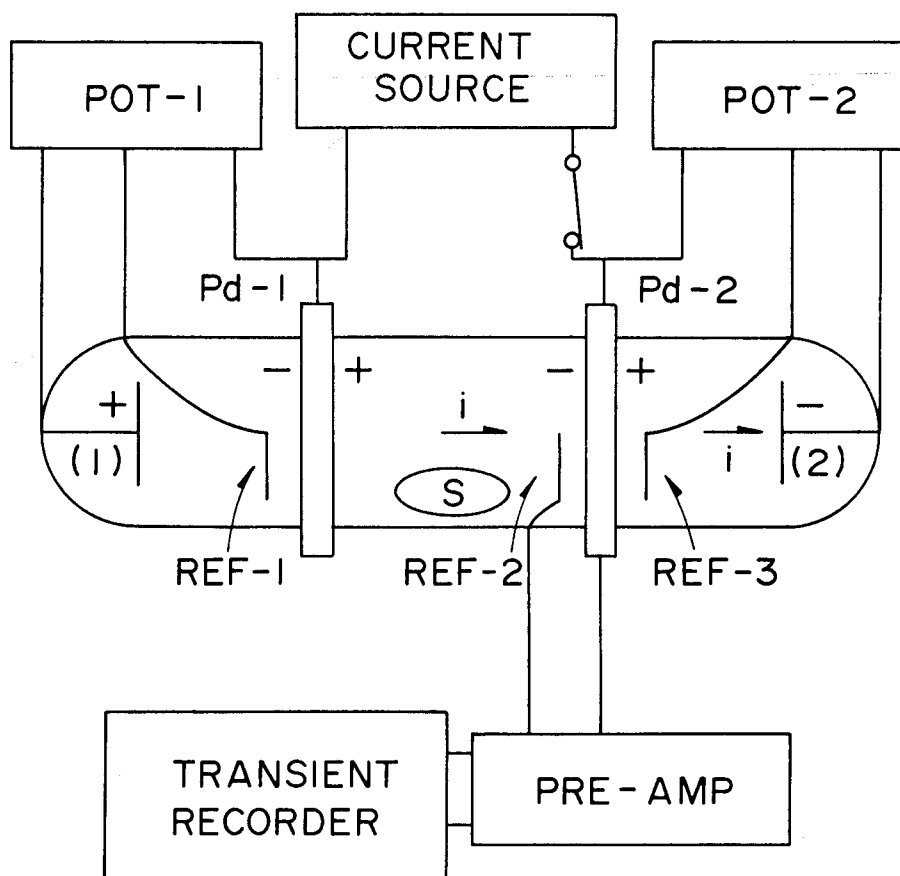


Fig. 5. Diagram of experimental set up.

chemicals used were of the grade Pro-Analysi of Merck. All measurements were worked at $25 \pm 0.1^\circ\text{C}$ 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.

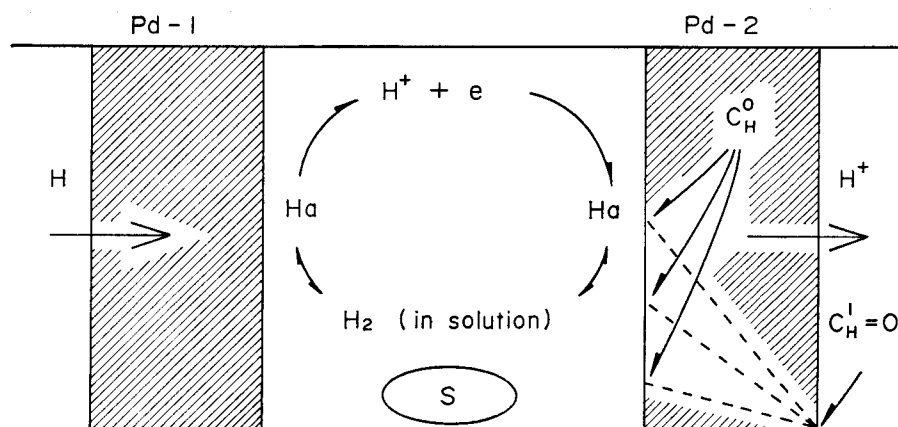


Fig. 6. Diagram of the flows of hydrogen through the working cell.

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.

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Results and Discussion

The values i_0 , obtained by analysis of stationary states and of transient states, are in good accordance. The theoretical and experimental values of time-dependent change of η_2 caused by hydrogen diffusion are shown in Fig. 4. The experimental linear line η_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 η of Fig. 3 is appropriate. The potential E_0 , marked in Fig. 3, is really the equilibrium potential. The figure, E_0 vs. $\log i$ showing straight line of Nernst's equation, is omitted here.

Fig. 7 shows the results of $\log i_0$ 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 $10^5 \sim 10^6$. Our experiment in acid tells that in this circumstance, the coverage of hydrogen atom θ_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 θ_H and θ_K are not determined in this case, it is observed

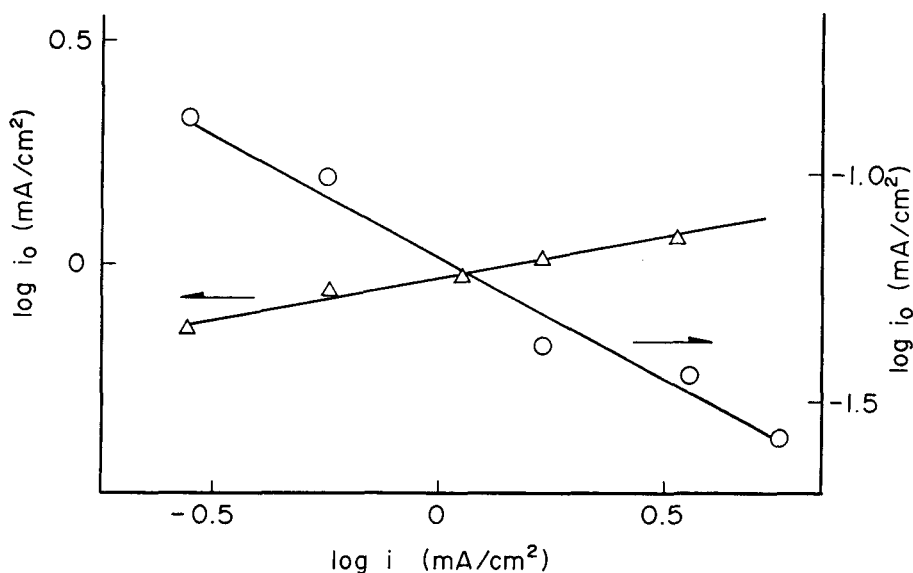


Fig. 7. Experimental relations between i_0 and i in acid and alkaline solutions.

△: in 2.3 M HClO₄, ○: in 0.13 M KOH.

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that some surface active species such as I^- ion can greatly disturb the linear relation of $\log i_0$ vs. $\log i$. Further works are on the way in our laboratory.

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- 2) A. Frumkin and N. Aladjalova, Acta Physicochim., **19**, 1 (1944).