FREQUENCY RESPONSE METHOD FOR DETERMINATION OF
DIFFUSION COEFFICIENT OF HYDROGEN IN METAL

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A new electrochemical method for the study of the diffusion process of hydrogen in metal foils is proposed. In the bielectrode system when hydrogen charging direct current is overlapped with sinusoidal current, there appears a phase lag in permeation current. This phase lag is related mathematically to the diffusion coefficient D of hydrogen in metal. The values of D obtained by this method are in good agreement with those by other methods in α-phase palladium-hydrogen system.

Various electrochemical techniques have been proposed for the determination of the D value of hydrogen in metals[1)-4)]. These are essentially based on the observation of the time dependency of the permeation current or the electrode potential of one side of the metal bielectrode while the other side is cathodically polarized by a constant current or by a constant potential. In this paper a new frequency response method is proposed in the investigation of the diffusion phenomena.

Theoretical   When one side of the palladium foil is cathodically polarized by a cathodic current J_c in an electrolyte solution, hydrogen enters into the foil and permeates to the other side which has previously been anodically polarized by a suitable device, and there it gives a permeation current J_a due to oxidation of hydrogen. In such a case the diffusion equation is expressed by Fick's second law as

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \ , \tag{1}$$

where C is the concentration of hydrogen in the foil at a distance x from the per-
meation side of the foil and t is the time. Under the condition that 1) no hydro-
gen is present in the foil at t = 0, 2) the concentration of hydrogen at the per-
meation side x = 0 is always maintained at zero by a potentiostat, and 3) hydrogen
enters at a rate J_c at the cathodic side x = ℓ for any time, the initial and
boundary conditions are expressed as follows:

$$C = 0 \qquad \text{for } 0 \leqq x \leqq \ell \qquad \text{at } t = 0, \tag{2}$$

$$C = 0 \qquad \text{for } x = 0 \qquad \text{at any time,} \tag{3}$$

$$J_c = DF \left(\frac{\partial c}{\partial x} \right)_{x=\ell} . \tag{4}$$

When J_c is composed of the constant current I_c and the sinusoidal current
$i_c \sin \omega t$, i.e., J_c is $I_c + i_c \sin \omega t$, we obtain equation (5) after a few
operations (to be published elsewhere in the near future). Equation (5)
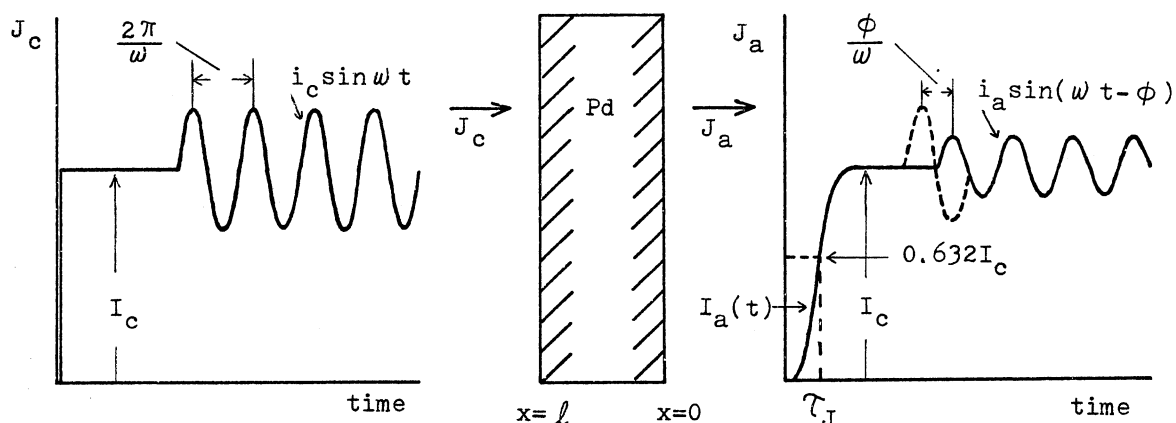describes the permeation current at a sinusoidal steady state $J_{a, t=\infty}$.

Fig.1   Principle of the frequency response method for diffusion
measurement.

$$J_{a, t=\infty} = I_c + i_a \sin(\omega t - \phi), \tag{5}$$

$$i_a = i_c \, (\cosh^2\sqrt{\omega/2D}\,\ell \cdot \cos^2\sqrt{\omega/2D}\,\ell$$
$$+ \sinh^2\sqrt{\omega/2D}\,\ell \cdot \sin^2\sqrt{\omega/2D}\,\ell)^{-1/2} \tag{6}$$

$$\phi = \tan^{-1}(\sinh\sqrt{\omega/2D}\,\ell \cdot \sin\sqrt{\omega/2D}\,\ell \,/\, \cosh\sqrt{\omega/2D}\,\ell \cdot \cos\sqrt{\omega/2D}\,\ell), \tag{7}$$

where ϕ is the phase lag (see Fig.1).

Specifically, when $\sqrt{\omega/2D}\,\ell$ equals π, equations (6) and (7) give the following simple relations:

$$i_a / i_c = 0.0863 \tag{8}$$

$$\phi = \pi, \tag{9}$$

and $\qquad D = \ell^2 f / \pi. \tag{10}$

Equations (6), (7) and (10) are related to the D value and can be used to determine the D value.

In the case when J_c is composed only of a constant current I_c, the time dependency of the permeation current I_a is expressed by

$$I_a = I_c \left\{ 1 + \sum_{n=1}^{\infty} (-1)^n \exp(-Dn^2\pi^2 t/\ell^2) \right\}, \tag{11}$$

and the time when relative permeation current I_a / I_c reaches 0.632 is

$$\tau_J = \ell^2 / 2D, \tag{12}$$

where the time τ_J is termed as the lag time.

Experimental   The cell and the electrical circuit are shown in Fig.2. A palladium foil* of thickness ℓ (ℓ = 20 to 100μm) was mounted between two Pyrex glass compartments as a bielectrode, one of them being the cathodic charging compartment and the other the permeation compartment. Both compartments were filled with 1 M NaOH solution and the electrode potential of the permeation side of the foil was maintained at +0.40 V vs. saturated calomel electrode by a potentiostat.
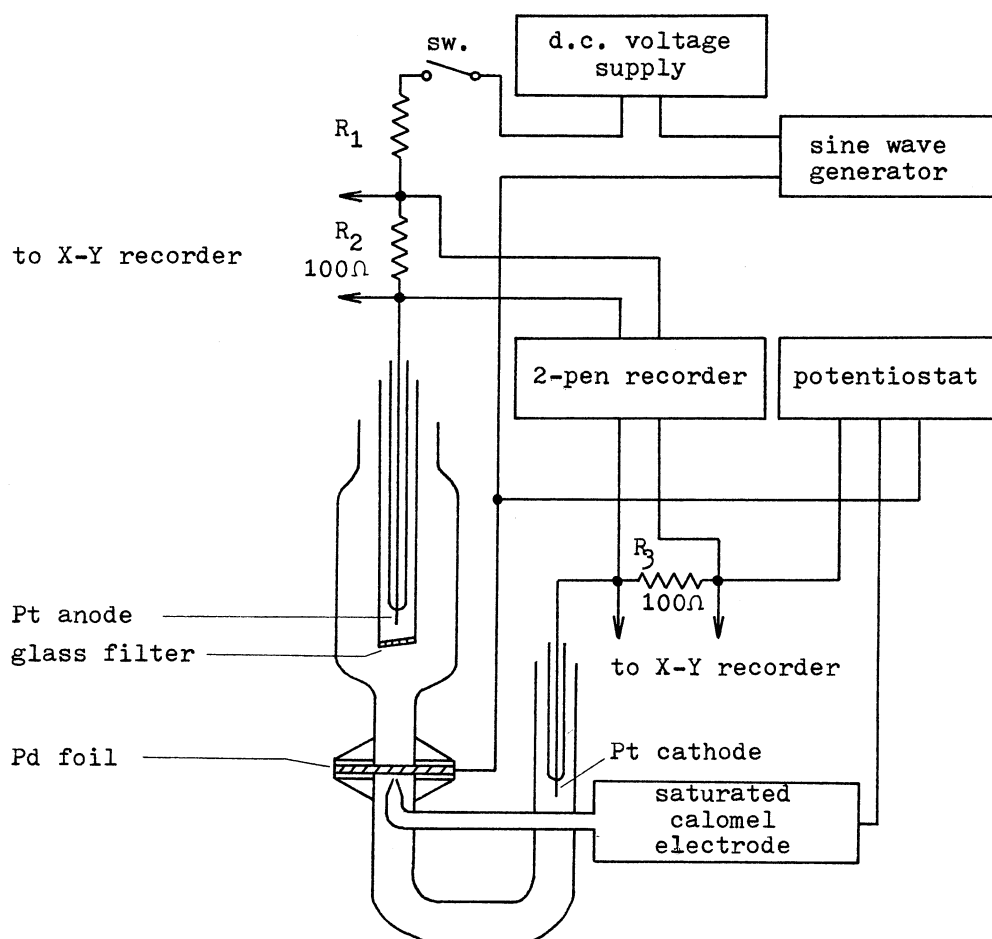
Fig.2.   Measurement circuit and electrolytic cell.

The sinusoidal current with frequency f superimposed on the direct current from the d.c. voltage supply was supplied to the charging side through an appropriate resistance R_1. J_c and J_a were recorded simultaneously by a 2-pen recorder and an X-Y recorder.   The phase lag ϕ is evaluated by analysing the recorder figure on the X-Y chart (an oval or a straight line). The temperature of the cell was maintained at $25° \pm 0.05°$ C.

<u>Results and Discussion</u>   Fig.3 shows the relation between the thickness of the palladium foil l and the frequency f when the phase lag ϕ becomes π (Lissajous's figure on the X-Y recorder becomes a negative straight line at this frequency). These measurements carried out under the condition $C_{x=l}$ lies in the region between 0.0015 to 0.008 (in atomic ratio (H / Pd)). From this relation the value D = **3.71** $\times 10^{-7}$ (cm^2/sec) is obtained as the diffusion coefficient of hydrogen in α-Pd at

Fig.3. Relation between
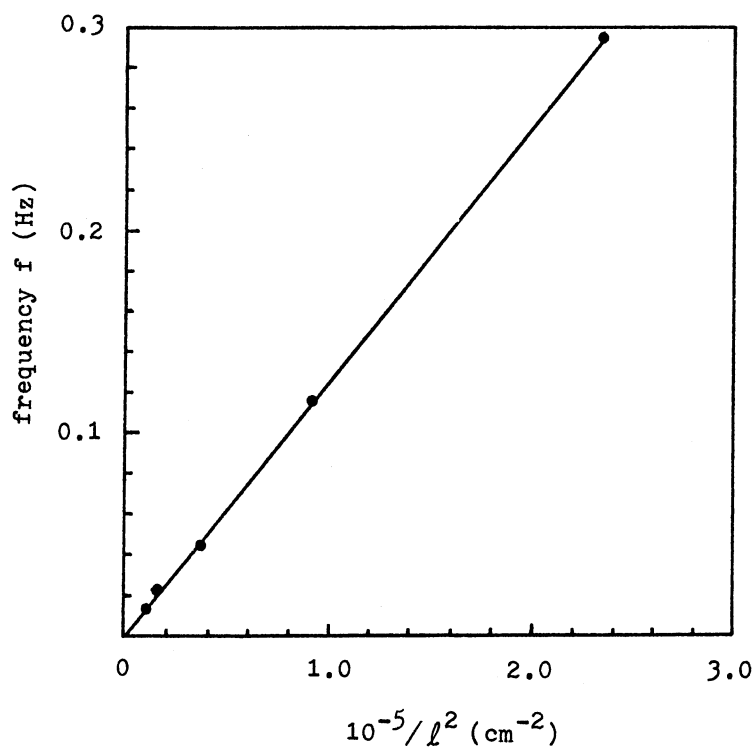the frequency f and the
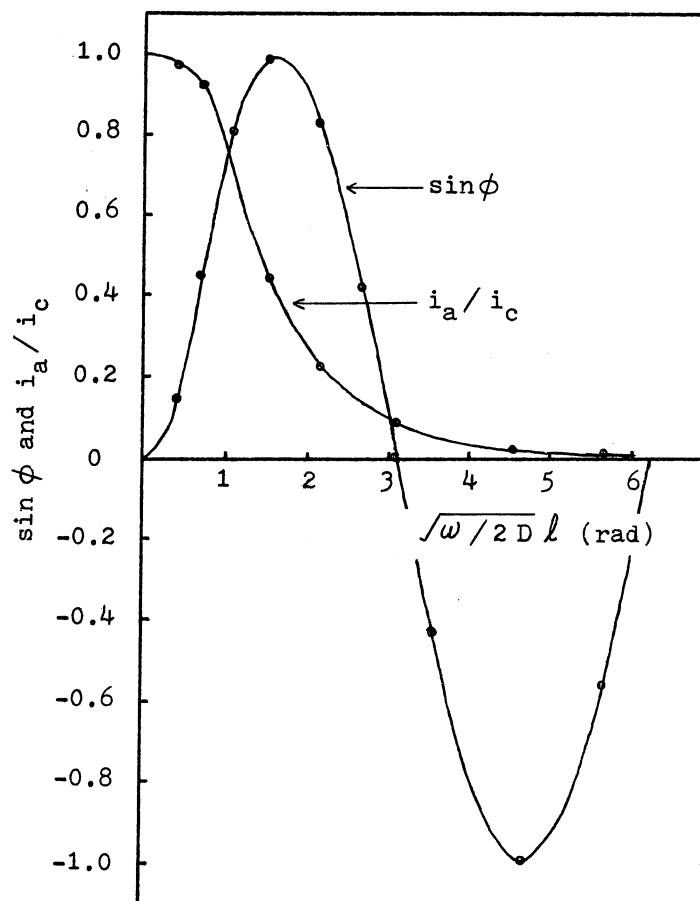thickness of Pd ℓ at
25°C.

Fig. 4. Relations between
the value of $\sin\phi$ and
$\sqrt{\omega/2D}\,\ell$ and between
the intensity ratio i_a/i_c
and $\sqrt{\omega/2D}\,\ell$.

solid line: calculated
from eqs. (6) and (7).
• : observed with
a 32.9μm thick Pd foil
at 25°C.

25°C. This value is in good agreement with the value $D = 3.68 \times 10^{-7}(cm^2/sec)$ obtained by the step response method using equation (12) under the same conditions, and is comparable with the values observed by many authors[1),2),5),6)]. From the temperature dependence of D for the foil of 35μm thick, we obtained the value of D as $D = 2.10 \times 10^{-3} \exp(-5,100/RT)$. Fig.4 shows the calculated and the observed results of $\sin\phi$ and i_a/i_c for various $\sqrt{\omega/2D}\,\ell$ values. These results indicate the validity of this new method for determining the D value of hydrogen in palladium. We hope this method will become one of the useful techniques for investigating diffusion phenomena in various single phase metal-hydrogen system.

* The surfaces of the palladium foil were activated by bringing to bright red heat in a gas flame. Further activation by electrodeposition of Pd black on the surfaces gave the same results.

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