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DETERMINATION OF THE RATE OF HYDROGEN ELECTRODE PROCESS ON MERCURY CATHODE AT HIGHER ELECTRODE POTENTIAL:

By

Juro HORIUTI and Atusi MITUYA

I. Introduction

In the foregoing paper it has been deduced from the electrochemical mechanism of hydrogen electrode process on mercury that,

$$\alpha = - \frac{RT}{F} \frac{\partial \log \bar{I}}{\partial \eta} \quad (1)$$

should be a proper fraction or a proper fraction plus unity according as the electrode potential is sufficiently low or high, where R is gas constant, T the absolute temperature, F the Faraday, \bar{I} the current accompanied by the reaction,



in one direction η the electrode potential referred to the reversible hydrogen electrode at the same condition of hydrogen pressure and hydrogen ion concentration. Observable cathodic current i is related to \bar{I} as that,

$$i = \bar{I} - \bar{I} \quad (3)$$

where \bar{I} is the current in the reverse direction to that of \bar{I} .

The above conclusion is exclusive of that derived from the catalytic mechanism i.e. that $\alpha = 2$, proper fraction or 0 according as η is sufficiently high, intermediate or sufficiently low. This situation affords us a method uniquely to determine the mechanism of the electrode by determining α at different range of η .

It is the purpose of the present research to appeal to the experiment for deciding the alternative mechanism with the mercury electrode.

It is α is a constant proper fraction at 0.52 so far observed: our measurement must inevitably arranged for that at higher electrode potential than ever observed. This accompanies however, the following

difficulties.

(a). We could observe only i but not \bar{I} directly. \bar{I} may safely be replaced by i provided η is sufficiently low \bar{I} in (3) being negligible there but that is not at all assured at higher η especially in the neighbourhood of the reversible potential of hydrogen electrode.

(b). Diffusion of oxygen toward the electrode uncontrollably disturbs the electrode potential as usually observed.

(c). Observed current is generally the sum of that due to hydrogen electrode process and that due to the neutralization of mercury ion. We have to determine the latter separately from the former.

The difficulty (a) may be avoided by virtue of the relation¹⁾ that

$$\bar{I}/I = e^{nF\eta/RT} \quad (4)$$

or according (2) that

$$i = \bar{I} (1 - e^{-nF\eta/RT}) \quad (5)$$

if we know n , the number of the rate-determining step occurring per once the chemical reaction of equation (2).

The n is, however, 2 for the catalytic mechanism whereas 1 for the electrochemical. In view of our standpoint to settle the mechanism independently it is not legitimate to assign a definite value to n . This difficulty is of set provided that, as turned out actually the case, the conclusion derived using the alternative n -value unanimously fits in exclusively with that of the either mechanism.

The difficulty (b) may be avoided by sealing the mercury cathode and a suitable made in vacuum which does not evolve oxygen.

The last one (c) may now be excluded by choosing such an experimental condition that the electrode is in Nernst equilibrium with mercury ion whereas steady with hydrogen electrode process.

We thus arrive at the following experimental method. Platinum electrode of big area is sealed in a vessel together with solution, hydrogen gas by a vacuum process excluding oxygen and kept at the solution-gas interface to facilitate the diffusion of hydrogen gas toward the electrode and hence to assure its reversibility as a hydrogen electrode. The current is now passed through the cell thus obtained from the platinum anode to the mercury cathode, keeping the cathode at a definite polarization, so that hydrogen, being ionized at the anode and

1) HORIUTI and IKUSIMA, Proc. Imp. Akad. Tokio, 15 (1939), 39.

2) HORIUTI and OKAMOTO, Sc. Pap. I.P.C.R. Tokio, 28, (1936), 231.

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neutralized at the cathode, circulates steadily within the vacuum vessel while mercury ion in the solution is gradually attains the concentration at which the mercury ion and mercury electrode is in equilibrium at the fixed polarization contributing no resultant current. The current thus asymptotically attained is now taken that due to the hydrogen electrode process. Materials, procedures of the experiment, the results and the conclusion derived are described in what follows.

II Materials

(1) Pt-anode :—a disc of 2.8 cm diameter formed by folding platinum gauge of 100 cm² area.

(2) Mercury :—Ordinary material was shaken for 7 days with the hydrochloric acid, described on (3), washed sufficiently with re-distilled water and finally distilled in vacuum.

(3) HCl :—KAHLBAUM'S HCl "Zur Analyse" with sp. gr. 1.19. was distilled in vacuum and diluted with re-distilled water to 0.1436 N.

(4) Hydrogen :—Bomb hydrogen was filtered by palladium thimble.

III Experimental Procedures

Fig. 1 shows the vessel of about 20 cm height used for preparing the cell in sight, P_R is reference electrode consisting in a platinum wire wound around a glass rod fixed to the wall, P_A the platinum anode at three point to the vessel of 3cm apparent diameter, B₁ and B₂ are small flasks of about 1.5 cc volume used for distilling mercury into the cell.

The platinum anode was preliminarily treated at room temperature respectively with 3 N. KOH for 10 hr, then with chromic acids mixture for 4 hr, washed and dried. The small flask B₁, containing 0.6 cm³ mercury, was now fused to the vessel at E taking care not to admit expiration, the whole vessel was evacuated through the tap J, down to 10⁻⁴ mm Hg and sealed off at S after admittance of about 1 mm Hg purified hydrogen gas. The mercury in B₁ was now distilled into

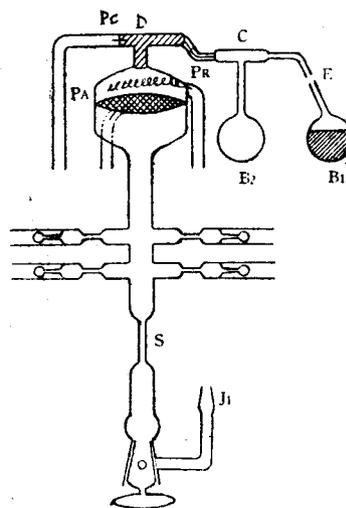


Fig. 1

B₂ by cooling the part C and B₁ sealed off.

The vessel was now carefully upset so as the mercury in B₂ filled the hatched part and electrically connected with outside through a sealed platinum wire, P_C, and then B₂ is sealed off then at the capillary between C and D. The vessel assumed now the form shown in Fig. 2, a. The area of cathode of mercury thus obtained was about 0.25 cm². The vessel just, obtained will be called a.

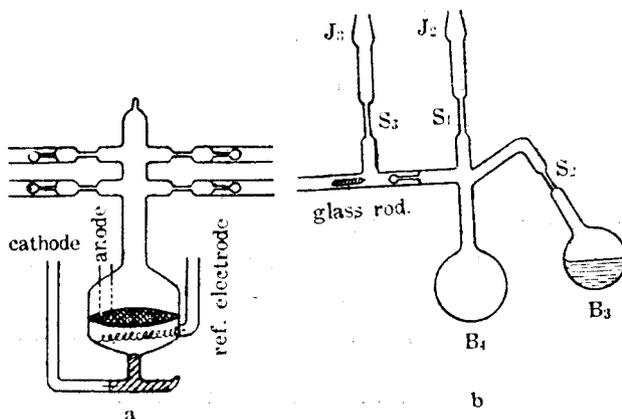


Fig. 2

The cell was now completed by introducing *N*/10 HCl into a by the following procedure. The acid was first introduced into B₃ shown in Fig. 2 b, frozen by liquid air, evacuated through J₂, the vessel b sealed off from the vacuum line at S₁, and then the acid distilled from B₃ into B₄ at S₂. After B₃ was sealed off at S₂ b was attached at its left end to one of breakable joints, a, evacuated through J₃, sealed off from the vacuum line at S₃ the breakable joint was opened by impact of a glass rod inside, 5 cc acid distilled into a until the anode was just immersed in the liquid and then the joint was sealed off.

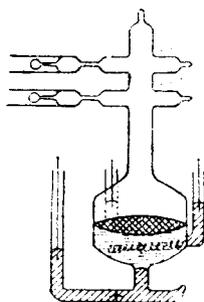


Fig. 3

Purified hydrogen was now admitted to fill about 30 cm³ gas space inside a at 70 cm Hg pressure through another breakable joint and then the latter sealed off to complete the cell as shown in Fig. 3.

The cell was now immersed in melting ice contained in a Dewar vessel, the mercury electrode kept at a definite polarization against the anode and the

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resulting current was measured by a galvanometer of 10^{-10} amp sensitively observing time to time the potential of the anode referred to the reference electrode.

IV Experimental Results and Conclusions

It was found that the potentials of the platinum anode were always less than 5×10^{-4} volts at current densities up to 10^{-8} amp of the present experiment which showed satisfactory reversibility the platinum anode. The current measured at a definite potential of the mercury electrode was found asymptotically decreased or increased to a definite value as expected according as the cathode potential was raised or lowered from the former definite value to the present one the asymptotic current being quite reproducible irrespective of the history.

On the ground of this experimental facts and the above theoretical consideration the asymptotic values thus was taken the current density due to genuine hydrogen electrode reaction, i . \bar{I} was now determined according to (5) putting observed value of i , the corresponding η and $n = 1$ or 2 in it in accordance with the method described in the introduction. The result is shown in Table 1 for each value of n and in Fig. 4. The first column " $-\eta$ volt" shows the measured polarization of the cathode, " i " the asymptotic total current, \bar{I} , $n = 1$ and \bar{I} , $n = 2$

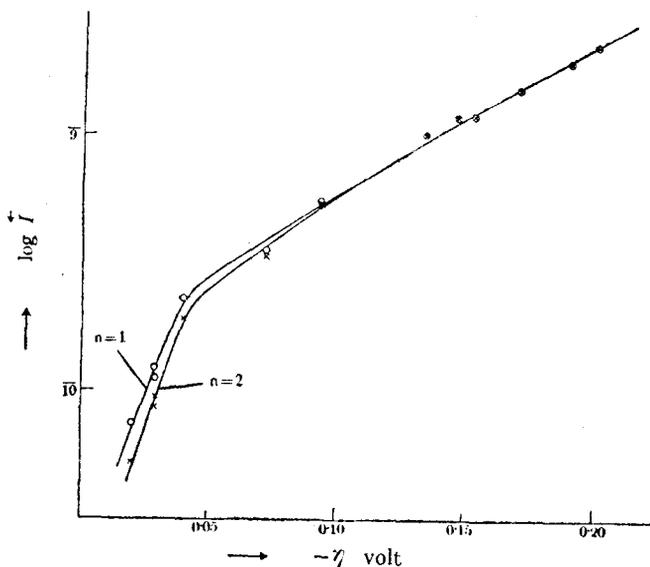


Fig. 4

that obtained for the respective values n . It is seen from Fig. 4 that for both the values of n , $\log \bar{I} - \eta$ curve shows a pronounced knick in the neighbourhood of $\eta = -0.35$ volt, running almost linearly below and above the point.

The α derived from the linear part of $\log \bar{I} - \eta$ curve respectively above and below the knick for both values of n is shown in Table II.

TABLE I. Current due to hydrogen electrode reaction,
Temperature: 0°C
Area of the mercury cathode: -0.25 cm²
Area of the platinum anode: -100 cm²

Electrode Potential - η Volt	i amp	\bar{I} $n = 1$	\bar{I} $n = 2$
0.377 0	1.87×10^{-8}	1.87×10^{-8}	1.87×10^{-8}
0.318 0	9.35×10^{-9}	9.35×10^{-9}	9.35×10^{-9}
0.314 5	9.12×10^{-9}	9.12×10^{-9}	9.12×10^{-9}
0.250 0	4.32×10^{-9}	4.32×10^{-9}	4.32×10^{-9}
0.201 5	2.18×10^{-9}	2.18×10^{-9}	2.18×10^{-9}
0.191 0	1.89×10^{-9}	1.89×10^{-9}	1.89×10^{-9}
0.171 0	1.46×10^{-9}	1.46×10^{-9}	1.46×10^{-9}
0.153 5	1.16×10^{-9}	1.16×10^{-9}	1.16×10^{-9}
0.147 5	1.14×10^{-9}	1.14×10^{-9}	1.14×10^{-9}
0.134 5	9.83×10^{-10}	9.85×10^{-10}	9.83×10^{-10}
0.072 0	3.34×10^{-10}	3.50×10^{-10}	3.34×10^{-10}
0.094 0	5.30×10^{-10}	5.40×10^{-10}	5.30×10^{-10}
0.040 0	1.85×10^{-10}	2.26×10^{-10}	1.92×10^{-10}
0.029 5	7.86×10^{-11}	1.11×10^{-10}	8.59×10^{-11}
0.020 5	4.32×10^{-11}	7.42×10^{-11}	5.24×10^{-11}
0.029 5	8.65×10^{-11}	1.21×10^{-10}	9.42×10^{-11}

TABLE II

n	higher potential	lower potential
1	1.3	0.3
2	1.5	0.3

The result shown in Table II fits unanimously and exclusively the

*) Activity coefficient was not taken into account for the present purpose of estimating the extent of contamination by order of magnitude.

conclusion derived from the electrochemical mechanism.

V Discussion

J. O'M. BOCKRIS²⁾ has recently questioned the present result for the contamination of mercury surface by the anode material i.e. platinum. The present authors might quote here the result of calculation due to КЕИИ of this institute, which shows any contamination effectively disturbing the hydrogen electrode process on mercury is highly im-probable.

The upper limit of the concentration of platinum ion in the solution is that at Nernst equilibrium with the platinum. But since the hydrogen electrode process is at equilibrium as observed we have the relation,

$$C^{Pt^{4+}} = \frac{(C^{H^+})^{-4FE_H/RT}}{(P^{H_2})^2} e \quad (6)$$

where E_H is the standard potential of Pt/Pt^{4+} electrode on hydrogen scale, $C^{Pt^{4+}}$ etc. are concentrations of Pt^{4+} etc, and P^{H_2} the partial pressure of hydrogen prevailing in the cell.

Numerical values of C^{H^+} , P^{H_2} and T are picked up from the above description as that

$$C^{H^+} = 0.14 N, \quad P^{H_2} = \frac{70}{76} \text{ atm. and } T = 273.$$

E_H is unfortunately unknown but we might expect it higher than taking $E_H = 1.36$ V of An/An^{4+} and, hence that the latter value when put in (6) would give the upper limit of $C^{Pt^{4+}}$ i.e.

$$C^{Pt^{4+}} = 4 \times 10^{-103} N.$$

The upper limit of the platinum current may now be derived from the above value according to the usual model that the concentration gradient exists only through the diffusion layer of thickness δ covering the cathode surface, the equilibrium concentration above obtained prevailing homogeneously outside. The rate J of diffusion per cm^2 of the electrode surface is now,

$$J = \frac{D(C^{Pt^{4+}} - C_s)}{\delta},$$

Where D is the diffusion constant and C_s the concentration of Pt^{4+} just at the surface of the electrode. It is known that D is of order of magnitude $10^{-5} cm^2/sec$ and δ ranges from 0.05 to $10^{-3} cm$ depending

2) J. O'M. BOCKRIS, Chem. Rev. 45 (1948), 525.

on the extent of agitation in the solution. The upper limit of J is now calculated by taking the smallest possible values both of C_s and δ i.e. 0 and 10^{-3} on respectively as that,

$$\begin{aligned} J &= \frac{10^{-5} \times 4 \times 10^{-103}}{10^{-3}} \text{ mols/sec} \\ &= \frac{10^{-5} \times 4 \times 10^{-103} \times 6 \times 10^{23}}{10^{-3}} \text{ ions/sec} \\ &= 2.4 \times 10^{-81} \text{ ions/sec.} \end{aligned}$$

This means that it takes $1/2.4 \times 10^{-81} = 4 \times 10^{80}$ sec = 1.3×10^{73} years at least for one atom of platinum to deposit on the cathode surface, which utterly excludes the possibility of any effective contamination.