The Concentration of Molecular Hydrogen on the Platinum Cathode

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It has previously been shown[1] that the concentration of hydrogen, ${}_0C_{H_2}$, in the immediate vicinity of the cathode during the passage of a current could be estimated by analyzing the potential-time curve which had been obtained when the cathodic current polarizing the electrode was abruptly reversed into a steady anodic one.

In the present work, ${}_0C_{H_2}$ was determined as a function of the cathodic current density by the following two different methods:

1) If the diffusion of hydrogen is the rate-determining stage in the anodic ionization process of the molecular hydrogen in the solution, ${}_0C_{H_2}$ can be estimated by the use of Sand's equation[2]:

$$ {}_0C_{H_2}=i_a\tau^{1/2}/\boldsymbol{F}\pi^{1/2}D^{1/2} \tag{1}$$

where τ is the transition time of the horizontal portion of the steady potential appearing at the first stage of that potential-time curve, $\boldsymbol{F}$ is a Faraday, D is the diffusion coefficient of the hydrogen molecule in the solution, and i_a is the anodic polarizing current density.

When, in addition to the diffusion, the spontaneous expellant of hydrogen from the solution as bubbles of gas is also contributable, ${}_0C_{H_2}$ can be written as[1]:

$$ {}_0C_{H_2}=\frac{i_a}{2\boldsymbol{F}D^{1/2}k^{1/2}}\exp(k\tau)\operatorname{erf}(k^{1/2}\tau^{1/2}) \tag{2}$$

where k is a expellant rate constant of the hydrogen from the solution. It is assumed that the rate of expellant is proportional to the supersaturation.

2) The polarization, or departure from the reversible potential, observed during the discharge of hydrogen ions at the electrode is generally considered to be due to the following effects[3,4]: a discharge overpotential of hydrogen ions η_D[5]; a recombination overpotential

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[1] S. Shibata, This Bulletin, **33**, 1635 (1960).

[2] H. J. S. Sand, *Phil. Mag.*, **1**, 45 (1901).

[3] P. M. Bryant and C. E. Coates, *Discussions Faraday Soc.*, **1**, 115 (1947).

[4] R. Clamroth and C. A. Knorr, *Z. Elektrochem.*, **57**, 399 (1953).

[5] M. Breiter and R. Clamroth, ibid., **58**, 493 (1954).

of hydrogen atoms, η_{R}[5-8]; the ohmic fall of resistance between the working electrode and the tip of a fine capillary connecting with the reference electrode, η_{Ω}[4]; a concentration overpotential of hydrogen ions, η_{H^+}[5,9] and a concentration overpotential of hyrogen molecules, η_{H_2}[5,10]. When the current is cut off, the overpotentials η_{D}, η_{R} and η_{Ω} should disappear at once, while η_{H^+} and η_{H_2} decay only slowly[3,11]. Moreover, in the acidic electrolyte the value of η_{H^+} is so small that it can be disregarded except in the cases of very large electrolytic currents[5,9]. The overpotential which is still contributable after the current of a moderate intensity has been cut off may be η_{H_2} only. Clamroth and Knorr[4] attempted to measure the concentration overpotential ${}_0\eta_{\mathrm{H}_2}$ during the passage of current, free from the effect of the other kinds of overpotential, by extrapolating to zero time the decay curve of η_{H_2}, taken after the circuit had been opened. They could also obtain ${}_0\eta_{\mathrm{H}_2}$ by means of extrapolating the $m_{\mathrm{H}_2}-\eta_{\mathrm{H}_2}$ curve to the zero volume of m_{H_2}, where m_{H_2} is the amount of hydrogen gas evolved for the time elapsed since the cut off of the current; it has a linear relation with η_{H_2} observed at the same time. Though their results obtained are reliable for low current experiments, they are not reliable for high current experiments, because the rates of overpotential decay and of H_2 gas evolution are so rapid that their manual potentiometric or microvolumetric technique surely never could follow them. The present author has therefore attempted to obtain a reasonable way of measuring ${}_0\eta_{\mathrm{H}_2}$ at high currents, i_{k}, by means of oscilloscopic observation of the overpotential. The relation of the concentration overpotential, ${}_0\eta_{\mathrm{H}_2}$, and the activity, ${}_0a_{\mathrm{H}_2}$, of the hydrogen is, according to Nernst's equation, as follows:

$${}_0a_{\mathrm{H}_2}=a_{\mathrm{H}_2}{}^0\exp\{-(2\boldsymbol{F}/\boldsymbol{RT})\cdot{}_0\eta_{\mathrm{H}_2}\} \qquad (3)$$

where $a_{\mathrm{H}_2}{}^0$ is the activity of hydrogen in the solution which is in contact with hydrogen gas at 1 atm. pressure. Since the hydrogen behaves ideally even under high pressure[12,13], the activity can be replaced by the concentration.

Experimental

Measurement of the Potential-time Curve.—The electrical circuit used for reversal of the current through the cell, from cathodic to anodic, is shown in Fig. 1. It is fundamentally the same as that used in the previous work[1], except for modification by the addition of an appropriate switching arrangement. Instead of a mechanical switch, a cyratron was used for the sake of a quick raising of the current following the reversal. The change of the working electrode potential against an S. C. E. was recorded with a cathode-ray oscilloscope (Iwasaki Synchroscope, Model SS-5151) synchronized with the reversal of current direction.

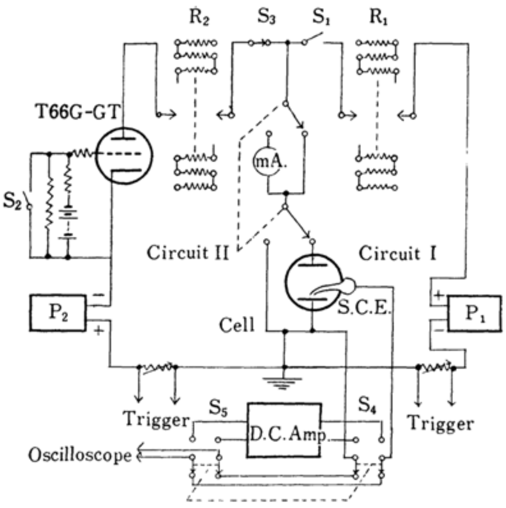

Fig. 1. Circuit diagram.

Measurement of the Decay Curve of η_{H_2}.—In order to measure the decay curves, circuit I was used, circuit II being excluded. A constant cathodic current, i_{k}, was passed through the cell, sufficient time being allowed for the potential to become constant; the circuit was then opened, and the decay curve was photographed with the cathode-ray oscilloscope synchronized with the cut-off of the current. As the amount of the concentration overpotential was too small for direct oscilloscopic measurement, a d. c. vacuum-tube amplifier was used in order to detect it. The value of ${}_0\eta_{\mathrm{H}_2}$ on the cathode was obtained by extrapolating the decay curve to zero time; the constant, k, in Eq. 2 was obtained from the slope of the curve.

The cell used for the experiment is shown in Fig. 2. The working electrode A, bright platinum wire 1 cm. in length and 0.05 cm. in diameter, the end of which had been covered with a small glass ball to prevent edge effect of the discharge, was placed vertically in the solution. B is an auxiliary electrode consisting of a cylindrical platinum foil of a large area, on the center-line of which the working electrode had been fixed in order to ascertain the uniform current density over the surface of the working electrode. A platinized platinum plate C is a hydrogen gas electrode used as a reference electrode immersed in the experimental solution. The difference in potential between A

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6) E. Lange, ibid., **58**, 83 (1954).

7) K. J. Vetter, ibid., **56**, 931 (1952).

8) G. Falk and E. Lange, ibid., **54**, 132 (1950).

9) M. Breiter, ibid., **62**, 161 (1958).

10) L. Kandler, C. A. Knorr and M. Schweitzer, *Z. physik. Chem.*, **180A**, 281 (1937).

11) G. Falk and E. Lange, *Z. Elektrochem.*, **54**, 132 (1950); **55** 396 (1951).

12) W. R. Hainsworth, *Science*, **53**, 578 (1921).

13) G. Tammann and H. Dickmann, *Z. anorg. u. allgem. Chem.*, **150**, 129 (1926).

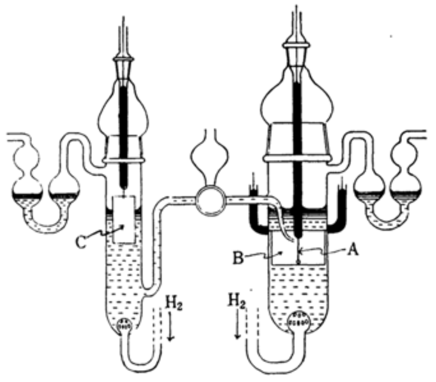

Fig. 2. Electrolysis cell.

and C gives the overpotential directly. The solution was saturated with hydrogen passing through two inlets made at the bottom of each chamber. Prior to use, the working electrode was activated by means of anodic and subsequent cathodic polarizations[14]. The sulfuric acid solution (1 N) used as the electrolyte throughout was prepared with G. R. sulfuric acid and with conductivity water which had been carefully redistilled thrice with a silica still.

All experiments were carried out in a thermostat at a temperature of 25±0.1°C.

Results and Discussion

The Hydrogen Concentration Evaluated from the Transition Time.—Provided that Sand's Eq. 1 is applicable to the anodic process after the reversal of the current, the value of $i_a\tau^{1/2}$ for the given i_k should be constant, independent of i_a. As is seen in Fig. 3, however, the value of $i_a\tau^{1/2}$ was affected considerably by the strength of the anodic polarizing current. Thus, the value of $i_a\tau^{1/2}$ for the given i_a value passed through a maximum at a certain i_k value which is larger because of a higher i_a value. Further, the height of this maximum decreased with the increasing value of i_a untill it vanished when i_a exceeded some definite value. The appearance of such a maximum on the curve may be attributed to the removal of the accumulated hydrogen during τ by the agitation of the solution due to the bubbling of the evolved hydrogen gas. At a low i_k value, the effect of this removal would not be very large, so that the accumulation of deposited hydrogen would be increased with an increasing value of i_k. At a large i_k value, however, the amount of the hydrogen ionized during τ may be rather decreased by increasing stirring. The magnitude of $i_a\tau^{1/2}$ at a given i_k value should grow and finally tend to a limiting value according as the i_a value increases, since the transition time, τ, becomes so short that the effect of stirring is very much diminished during that time. Furthermore, as a cause of the reduction of the transition time, τ, we must call attention to the spontaneous expulsion of hydrogen from the solution due to supersaturation. The curves in Fig. 3 are subject to the influence of both the stirring and the expulsion. For the above-mentioned reason, the correct values of ${}_0C_{H_2}$ at a given i_k value must be evaluated from τ_0, the limiting value of the transition time obtained at a sufficiently large i_a value. Figure 4 shows plots of the concentration of hydrogen, calculated with Eq. 1 and Eq. 2, against i_k for various values of i_a. Since in the range of small i_k values under about 10 mamp./cm² and of large i_a values over about 30 mamp./cm² (cf. Fig. 4.), the value of $i_a\tau^{1/2}$ for a given i_k value is constant, independent of the magnitude of the i_a value, the disturbance, by the expulsion of hydrogen and the agitation, of the solution in relation to the transition time obtained in this range of i_k and i_a values is so small that it can be disregarded. The concentrations calculated with Eq. 2, being little affected by the strength of i_a, may be considered to be the true concentrations of ${}_0C_{H_2}$. These values at higher i_k values were evaluated with a τ_0 value obtained at a large anodic polarization current, i_a=634 mamp./cm².

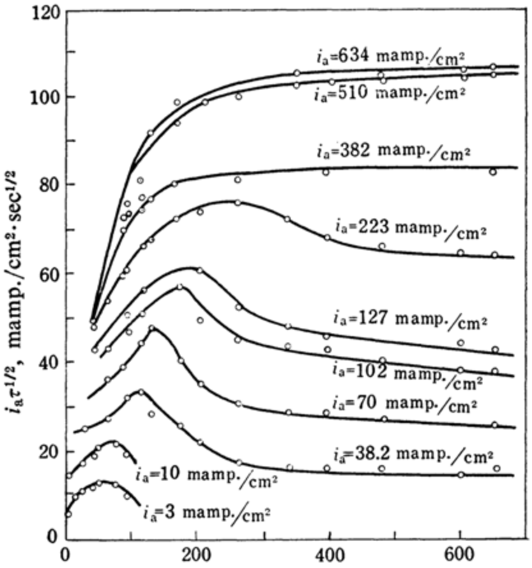

Fig. 3. $i_a\tau^{1/2}$ vs. cathodic current density curves at constant anodic polarizing current densities.

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[14] J. A. V. Butler and G. Armstrong, *J. Chem. Soc.*, **1934**, 743; E. Wiek and B. Webrus, *Z. Elektrochem.*, **56**, 159 (1952); J. O'M. Bockris, I. A. Ammar and A. K. M. S. Huq, *J. Phys. Chem.*, **61**, 879 (1957); T. Erdey-Gruz and M. Volmer, *Z. physik. Chem.*, **A150**, 203 (1930); J. O'M. Bockris and I. A. Azzam, *Trans. Faraday Soc.*, **48**, 154 (1952); E. Yeager, T. S. Oey and F. Hovorka, *J. Phys. Chem.*, **57**, 268 (1953).

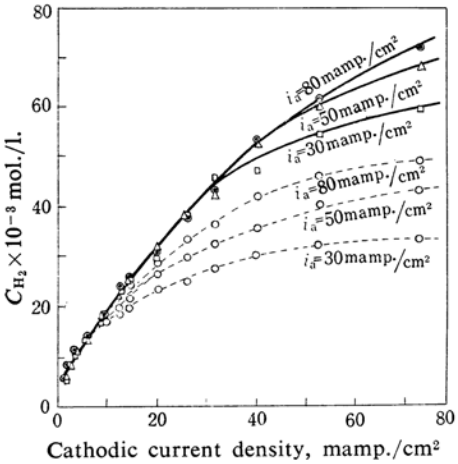

Fig. 4. The hydrogen concentration evaluated with Eq. 1 (dotted line) and with Eq. 2 (solid line).

Relation of the Cathodic Current and the Concentration Overpotential of the Hydrogen.—When, after the cut-off of the cathodic current through the working electrode, the solution in the cell was suddenly stirred with bubbles of hydrogen gas, the overpotential decayed rapidly and settled down on the reversible potential, i. e., on $\eta_{H_2}=0$, as is shown in Fig. 5. This fact is an illustration of how the overpotential is caused by the accumulation of hydrogen and of how the rapid decay, following the bubble agitation, is attributable to the almost complete removal of the accumulated hydrogen. Figures 6 and 7 show oscillograms tracing the decay of η_{H_2} taken after the cut-off of the cathodic current. The potential falls down rapidly at first, but at last tends only slowly to zero. As the initial, short part of the decay curve, as seen in Fig. 7, can be taken to be a straight line, it could be exactly extrapolated to zero time; ${}_0\eta_{H_2}$ was obtained. As may be seen in Fig. 8, ${}_0\eta_{H_2}$ increases linearly with the logarithm of the cathodic current density, but at last tends to a constant value of 64.5±0.5 mV. as the current density exceeds about 300 mamp./cm².

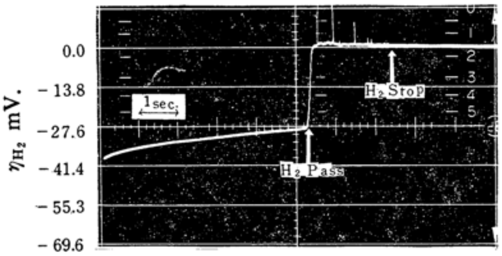

Fig. 5. Oscillogram of the overpotential change when, after the cut off of the cathodic current, i_k=7.0 mamp./cm², the solution was stirred with bubbles of hydrogen gas.

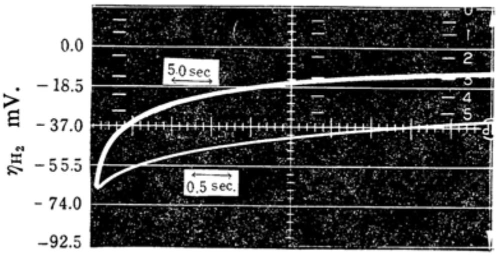

Fig. 6. Oscillograms of the overpotential decaying after the cut off of the cathodic current, i_k=92.4 mamp./cm².

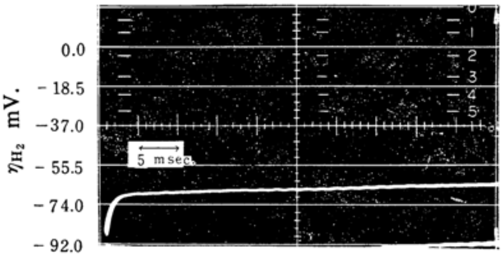

Fig. 7. Oscillogram of the overpotential decaying immediately after the cut off of the cathodic current, i_k=92.4 mamp./cm².

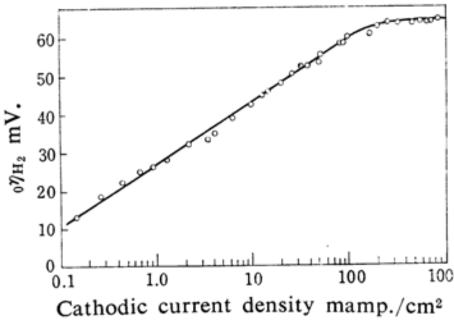

Fig. 8. Relation between the cathodic current density and concentration overpotential of hydrogen.

The concentrations of ${}_0C_{H_2}$ obtained by means of the potential-time curve, together with that obtained from the concentration overpotential, are shown in Fig. 9, the solubility of hydrogen at 1 atm. $C_{H_2}{}^0$ being taken to be 7.24×10^{-4} mol./l.[15] The agreement between the results for ${}_0C_{H_2}$ derived from τ_0 and from ${}_0\eta_{H_2}$ is seen to be satisfactory. The limiting value of ${}_0C_{H_2}$ was 11.6×10^{-2} mol./l. Such a high supersaturation may be ascribed to the fact that the process of the evolution of hydrogen as bubbles of gas may be relatively slow. The rate of the transfer of hydrogen molecules from the solution to the gas phase should be proportional to the product of the

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[15] A. Seidell, "Solubilities of Organic and Inorganic Compounds", Van Nostrand Co., New York (1940), p. 557.

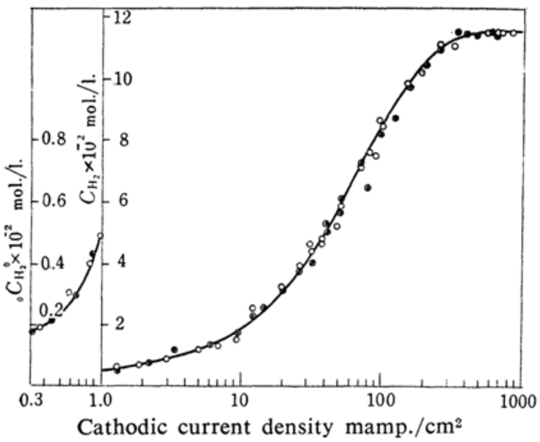

Fig. 9. Relation between the cathodic current density and the concentration of hydrogen in the vicinity of the electrode surface.
—○— from ${}_0\eta_{H_2}$
—⊙— from τ_0

density of the distribution of bubbles and the rate of growth of each bubble. If the rate of the formation of growth nuclei is represented with the equation described by Hook[16] and if the rate of growth is proportional to ${}_0C_{H_2}-C_{H_2}{}^0$, the rate of the transfer of hydrogen, V, may be given by the expression:

$$V=K'C_{H_2}{}^0(\alpha-1)\cdot K''\exp\left[-\frac{16\pi M^2\sigma^3}{3d^2\boldsymbol{R}^3T^3\ln^2\alpha}\right] \tag{4}$$

where α is the supersaturation as a concentration ratio, ${}_0C_{H_2}/C_{H_2}{}^0$; K', a rate constant of the growth; K'', a frequency factor; σ, an interfacial energy between the solution and hydrogen gas; d, the density of the nucleus; M, the molecular weight of hydrogen; $\boldsymbol{R}$, the gas constant, and T, the absolute temperature. This expression demands an almost explosive increase in the rate of nucleation, as α exceeds the denfinite real value. It has been confirmed that a limiting value of the supersaturation calculated with Eq. 4 for water vapor was in good agreement with that one obtained experimentally, i. e., $\alpha=4.2$ at 275.2°K[17]. Since the d of gaseous nucleus is far smaller than that of the liquid or solid nuclei, the supersaturation of the gas in the solution may be much larger than the above value of the water vapor and also than the result obtained in the present work. However, the irregularity of the electrode surface may accelerate the formation of nuclei, and agitation and convection of the solution may prevent the high increase of α near the electrode.

Summary

The concentration of molecular hydrogen in the vicinity of the bright platinum cathode during electrolysis was determined as a function of current density by means of two different methods, the potential-time curve on the reversal of current from cathodic to anodic, and the concentration overpotential obtained by extrapolating the decay curve of the overpotential to zero time, free from other overpotentials. The agreement between the results for the concentration derived from the potential-time curve and from the concentration overpotential was satisfactory. It was found that the concentration of hydrogen increased with the increasing i_k value and approached a limiting value of 11.6×10^{-2} mol./l. for cathodic currents exceeding about $i_k=300$ mamp./cm².

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[16] A. V. Hook, "Crystallization", Reinhold Publishing Co., New York (1961), p. 95.

[17] M. Volmer and H. Flood, *Z. physik. Chem.*, **170A**, 273 (1934); G. M. Pound, *Ind. Eng. Chem.*, **44**, 1278 (1952).