Title	HYDROGEN ELECTRODE REACTION ON EVAPORATED NICKEL FILM IN AQUEOUS SODIUM HYDROXIDE : Part Ⅰ. pH-Effect on Hydrogen Overvoltage
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 10(3), 203-214
Issue Date	1962-12
Doc URL	https://hdl.handle.net/2115/24764
Type	departmental bulletin paper
File Information	10(3)_P203-214.pdf

HYDROGEN ELECTRODE REACTION ON EVAPORATED NICKEL FILM IN AQUEOUS SODIUM HYDROXIDE

Part I. pH-Effect on Hydrogen Overvoltage

By

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(Received December 16, 1962)

Abstract

The pH-effect of the hydrogen overvoltage was studied with evaporated nickel film electrode in aqueous sodium hydroxide over a range of pH from 10.72 to 13.68, which was found of remarkable reproducibility and of quick response. The ohmic overvoltage was determined from the initial vertical jump of the build up curve. It was found that the true hydrogen overvoltage practically remains constant independent of pH in concentrated solutions in accord with the conclusion from the catalytic mechanism.

Introduction

Numbers of workers have studied the hydrogen electrode reaction on nickel with special reference to the pH-effect on overvoltage in acid and alkaline solutions. FRUMKIN *et al.*[1)] have observed that the hydrogen overvoltage on nickel increases with decrease of concentration of aqueous hydrogen chloride and sodium hydroxide and decreases with addition of sodium chloride in sodium hydroxide solution. LUKOWTZEV and LEVINA[2)] have also observed the pH-dependence of overvoltage in sodium hydroxide solution eliminating ohmic resistance of solution by addition of excess potassium chloride. BOCKRIS *et al.*[3)] have found under very pure condition of solution that the hydrogen overvoltage on nickel varies considerably with concentration in aqueous hydrogen chloride, but hardly in aqueous sodium hydroxide. The positive effect of pH or neutral salt on the hydrogen overvoltage is the important reason why these authors maintain the slow discharge mechanism against the catalytic mechanism on nickel.

HORIUTI *et al.*[4)], on the other hand, have observed that the catalysed exchange rate of deuterium between hydrogen and water on the presence of nickel remains practically constant with increase of concentration of potassium hydroxide. This is one of the reasons why HORIUTI *et al.*[5)] attribute the catalytic mechanism to hydrogen electrode reaction on nickel.

These contradictory observations may be due to either or both of impurity and varying texture of electrode depending on the treatment of electrode. The procedure of preparing very pure aqueous electrolyte appears to have been standardized in the method of pre-electrolysis as developed by BOCKRIS *et al.*[6], whereas the same is not the case with preparation of electrode. As a matter of fact, FRUMKIN *et al.* used nickel plate as cathode which was activated by heating it at 300–400°C in a hydrogen stream and BOCKRIS *et al.* used nickel wire fused in a hydrogen or helium stream and sealed in the same medium in glass bulbs to avoid the contamination and oxidation of the electrode. HORIUTI *et al.* treated nickel wire thoroughly in vacuo at 800°C to remove impurity gas occluded in wire.

Horiuti[7] has recently theoretically formulated the dependence of the mechanism of the hydrogen electrode reaction, besides on overvoltage and pH of solution, on the physical properties of electrode materials, *i.e.* work function and energy of adsorbed hydrogen atoms which vary with the electrode material and are sensitive to the treatment. Experimental data are in consequence expected to be useful for elucidating the underlying mechanism only when obtained with electrodes of pure material at a well-defined state in very pure condition.

The studies of adsorption of gas on metals have recently been remarkably developed by using evaporated metal film prepared in vacuo which is in the purest state attainable at present, allowing us to investigate the adsorption in close connection with the physical properties of adsorbent metal such as work function, electric conductivity and lattice constant[8]. It is similarly desirable to observe the hydrogen electrode reaction on electrodes of evaporated metal film. The present work is concerned with the preparation of the electrode of evaporated film at the desired condition and with the observation of the pH-effect in question with the electrode.

I. Experimental

1. 1) Purification of glass apparatus

The electrolytic cell and the purification trains for hydrogen and solution were all made of Halio glass supplied by SHIBATA & Co. Tokyo, which almost equals Pyrex glass in the strain point and the thermal expansion. Glass tubes and vessels used for the construction of the electrolytic cell and the purification trains were boiled in a mixture of concentrated nitric acid and sulfuric acid for 3 hrs, washed with boiled equilibrium water several times, and inserted in a continuous circulation still in which they were washed with hot thrice distilled water in a hydrogen stream.

1.2) Preparation of evaporated nickel film

Fig. 1a shows a glass tubing of 9 mm diameter, 8 cm length with a ground flat surface (A) of 1 cm^2 at its bottom on which nickel is evaporated. The electrode thus finished was prepared as follows. A piece of platinum foil (B) was welded to a tungsten wire (C), which was sealed in the glass wall at the bottom of the tubing with the lower end of the platinum foil just exposed. The bottom surface was now grounded, removing the ejected portion of the platinum foil and the tubing was cleaned by the procedure described in 1.1), put into a small vessel of quartz (H) together with a coil of two turns (G) of Johnson Matthey "pure" nickel wire of 1 mm diameter and enclosed as shown in Fig. 1b in a Halio glass tube (D) which was connected to a vacuum system (E) through a trap (F) immersed in liquid nitrogen. Nickel coil was degassed under high vacuum by heating at 800°C in an induction furnace (I) until a vacuum of 10^{-6} mmHg was attained and then nickel was evaporated on the ground glass surface (A) at about 1100°C. The nickel evaporation was continued until the electric resistance between the tungsten lead and nickel wire contacted at any point on the evaporated film became less than 1 ohm. The true area

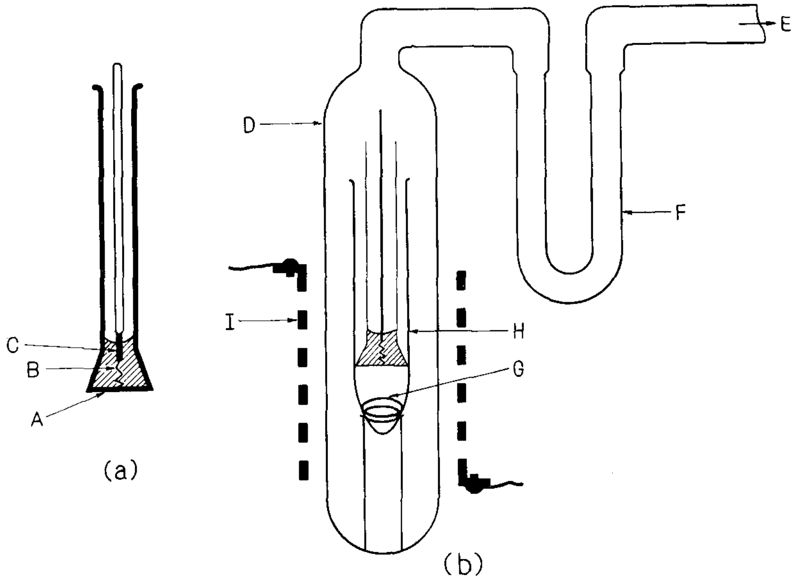

Fig. 1 (a). Evaporated nickel film electrode; (b) Evaporation apparatus.

of the film thus prepared did not much differ from the apparent area, as estimated from the capacity measurements as described in Part II.

1. 3) Preparation of evaporated platinum film electrode

The evaporated platinum film anode and reference electrodes were each of the same geometrical area as the evaporated nickel film cathode. The evaporated platinum film was made similarly as the evaporated nickel film at about 1700°C near the melting point of platinum. The nickel film electrode and the platinum film electrodes thus prepared in vacuo were sealed each in a compartment, *i. e.* the cathode, anode or reference compartment of the electrolytic cell.

1. 4) Purification of hydrogen

Fig. 2 shows the hydrogen purification train. The cylinder hydrogen (A) is passed successively through trap (B), silica gel (C), hopkalite (D), soda lime (E), platinized asbestos (10%) at 400°C (F), silica gel (G) and then trap (H) containing active charcoal to remove trace of oxygen. The hydrogen purification train could be evacuated as a whole. Silica gel and active charcoal were kept respectively at 110°C and 400°C in vacuum for 4 hrs before each run of purification and traps (B), (H), (I) and (J) were immersed in liquid nitrogen in course of purification. The purified hydrogen was supplied through greaseless taps into the electrolytic cell and to the purification train of solution described later.

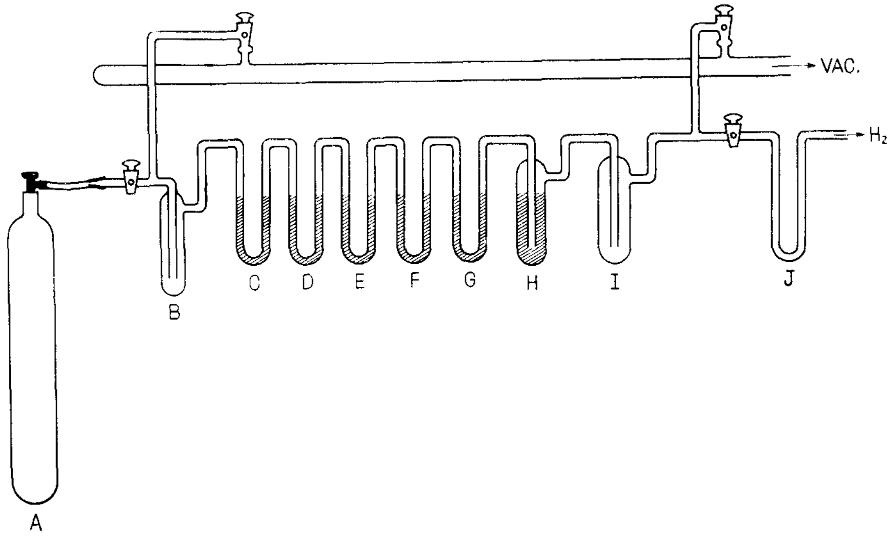

Fig. 2. Hydrogen purification train.

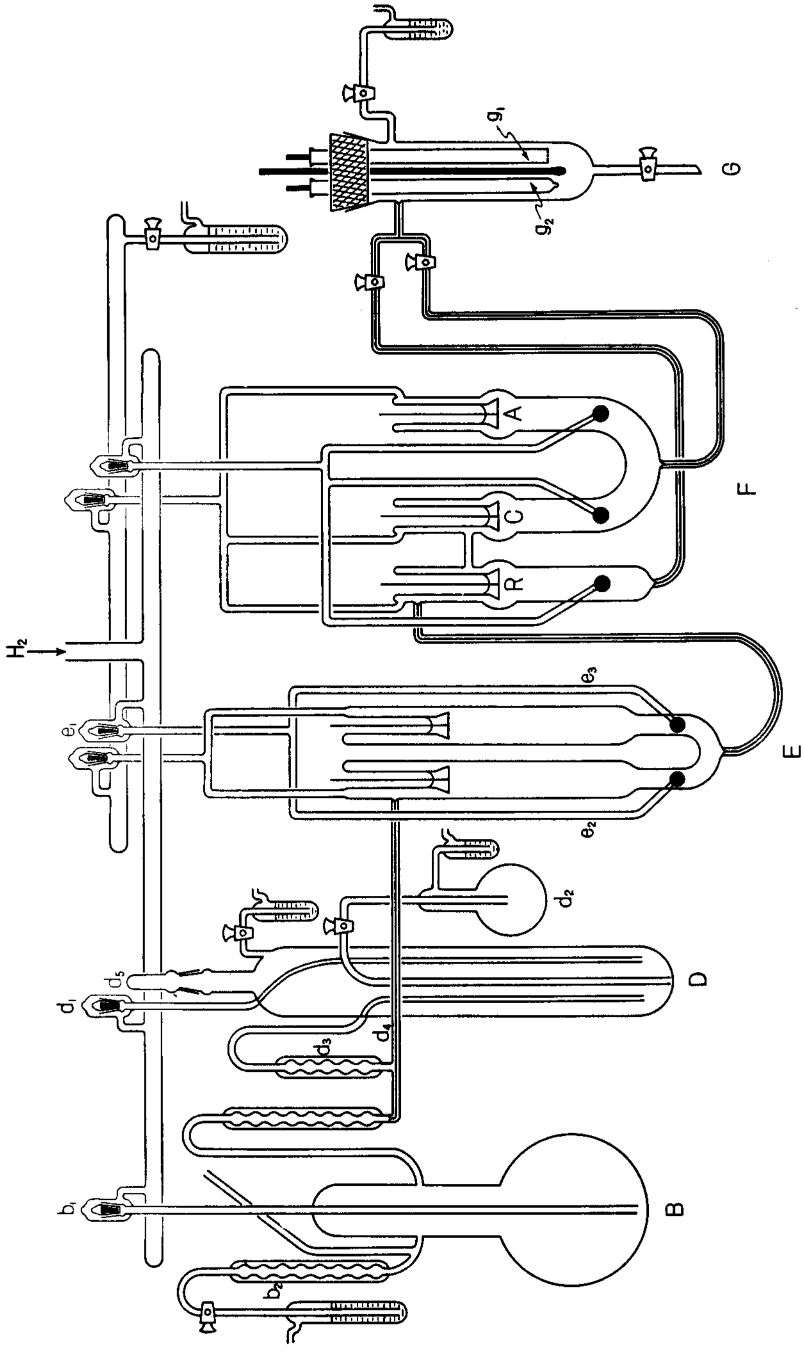

Fig. 3. Arrangements for preparation of the electrolytic cell and for determination of pH.

1. 5) Preparation of electrolytic cell

Fig. 3 shows arrangements for preparing the electrolytic cell (F) for the observation in question. (G) is the cell for pH-determination, (E) the pre-electrolysis cell, and (B) and (D) compose the train for preparing pure aqueous sodium hydroxide. Deionized water of *ca.* 10^7 ohm specific resistance was distilled with addition of alkaline potassium permanganate into a vessel containing barium hydroxide, and then further into a flask (B) with reflux condenser (b_2). The water thus distilled twice was boiled in (B) at least 4 hrs in a stream of hydrogen purified as described in 1. 4) to remove trace of organic substances. The water thus purified was now ready to be distilled into vessel (D) for preparation of alkaline solution or into pre-electrolysis cell (E). (D) is a vessel of *ca.* 200 cc capacity where sodium hydroxide was purified by recrystallization as follows. "Guaranteed reagent" (KANTO Chemical Co. Ltd.) of sodium hydroxide was introduced from the intake (d_5) covered with a ground cap into the vessel in a stream of purified hydrogen, and water purified in (B) was distilled by *ca.* 100 cc into vessel (D) in a stream of the same hydrogen. (D) with the concentrated sodium hydroxide solution thus formed was now immersed for 2 hrs in ethylalcohol bath cooled at −30°C to recrystallize sodium hydroxide. Mother liquor was pushed out into receiver (d_2) with purified hydrogen admitted from greaseless tap (d_1). this procedure of recrystallization was repeated twice or thrice and the resulting crystal of hydrated sodium hydroxide was diluted by distilling *ca.* 100 cc purified water over it from (B) and the resulting solution was transferred into the pre-electrolysis cell (E) through condenser (d_3) and horizontal capillary (d_4) by pushing the solution with hydrogen admitted through (d_1). The solution was finally purified by pre-electrolysis in (E) for 30–50 hrs with 20–30 mA/cm^2 current by means of evaporated platinum film electrodes each of 1 cm^2 apparent area, constantly passing purified hydrogen through the solution. The solution was now transferred into the electrolytic cell (F) similarly as before by hydrogen admitted through greaseless tap (e_1) and two tubes (e_2) and (e_3) with ball glass filter at each end. After each experiment in the electrolytic cell (F) the solution was transferred by hydrogen pressure into a vessel (G) provided with a calomel (g_1) and a glass (g_2) electrodes to determine pH of the solution used. (A), (C) and (R) in the electrolytic cell (F) denote the anode, the cathode and the reference electrode respectively.

2. Results and Discussions

2. 1) Build up curve

Fig. 4 shows the electric circuit for the measurement. The polarizing

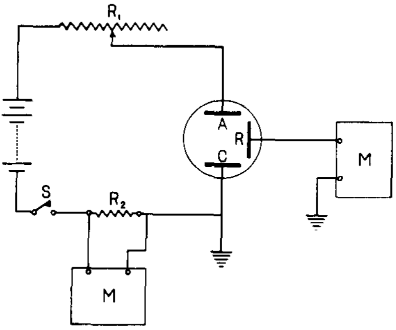

Fig. 4. The electric circuit.

A : anode
R : reference
C : cathode
B : 200 v storage battery
R_1 : variable resistance
R_2 : fixed resistance
S : switch
M : memoscope.

current was supplied from a 200 v battery (B) through a variable high resistance (R_1) and its strength was determined by measuring the potential drop across a fixed resistance (R_2) by means of a memoscope (M) (HUGH's Aircraft Co. Ltd.). The potential difference between each two of the three electrodes (A), (C) and (R) was found coincident within 1–2 mv immediately after immersed in the solution. The polarizing current was now switched on by means of a contact of nickel wire and mercury (S) and the resulting build up of the potential difference E between the test electrode (C) and the reference electrode (R) was traced on the memoscope screen. The LUGGIN capillary was avoided for fear of disturbing the current distribution in the neighbourhood of the cathode and the ohmic drop of the potential included in E was eliminated by identifiing the initial vertical jump η_Ω of the build up curve with the ohmic overvoltage. A typical example of the build up curve is shown in Fig. 5, where the initial vertical jump is clearly distinguishable from the subsequent gradual increase of the overvoltage. Fig. 6 shows η_Ω plotted against the current density i in different solutions. The proportional relation holds between η_Ω and i over the whole range of i and pH of the solution used. The logarithm log r_s

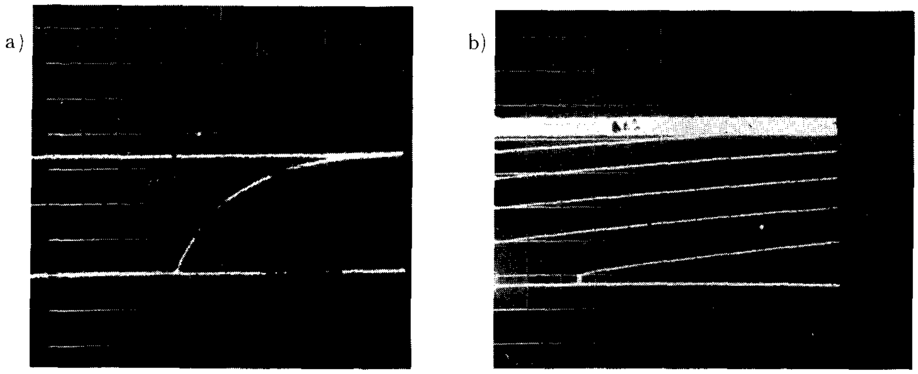

Fig. 5. Build up curve.

a) : 10 mv/div, 1 sec/div, $i=1.9\cdot10^{-5}$ A/cm², 13.10 pH.
b) : 50 mv/div, 500 μ sec/div, $i=8.3\cdot10^{-3}$ A/cm², 13.68 pH.

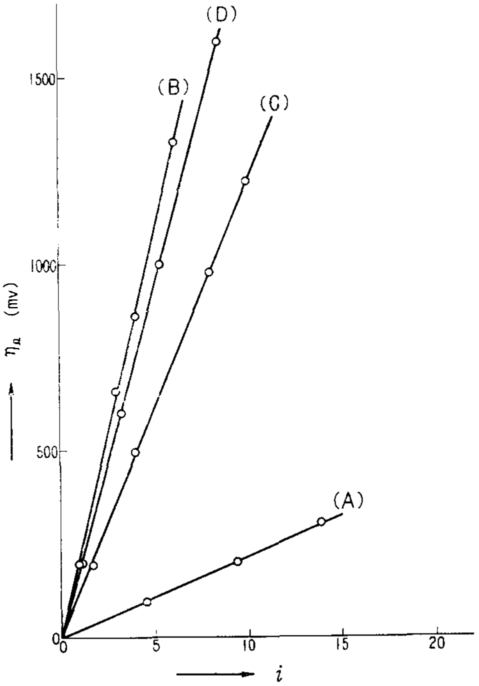

Fig. 6. Ohmic overvoltage η_Ω *vs.* current density *i*.

Line—A, B: 10^{-2} A/cm² unit
line—C: 10^{-3} A/cm² unit
line—D: 10^{-4} A/cm² unit

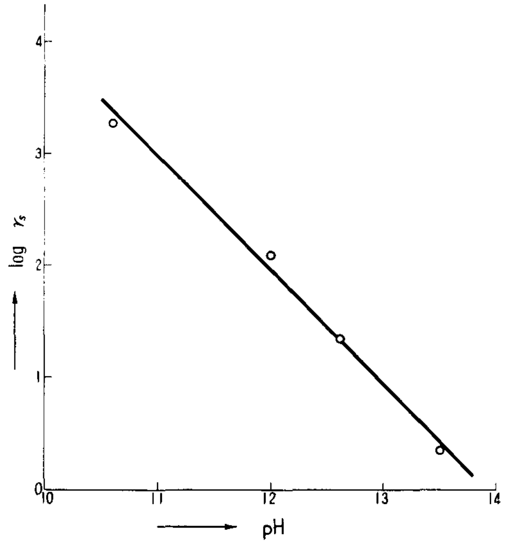

Fig. 7. The logarithm of the ohmic resistance r_s vs. pH.

of the appropriate proportionality constant $r_s = \eta_\Omega / i$, *i.e.* the resistance of the solution is now plotted against the relevant value of pH as shown in Fig. 7. The linear relation in the Figure is of inclination $d \log r_s / d$ pH$=-1$, which shows that the resistance is inversely proportional to the concentration of the sodium hydroxide, hence warrants the above procedure of assigning the initial vertical jump of the build up curve to the ohmic overvoltage.

2. 2) Steady state and anomaly

The potential difference E between the test and the reference electrodes attained a constant value after switch on of the polarizing current, in the case of the solutions 13.68 pH and 12.68 pH within a fraction of a second at current densities higher than *ca.* 1 mA/cm² and at a lower current densities within a few seconds and the constant value was kept for more than 15 min., whether the solution was bubbled with hydrogen or not. In case of solutions of 11.92 pH and 10.72 pH on the other hand, the potential difference E after the switch

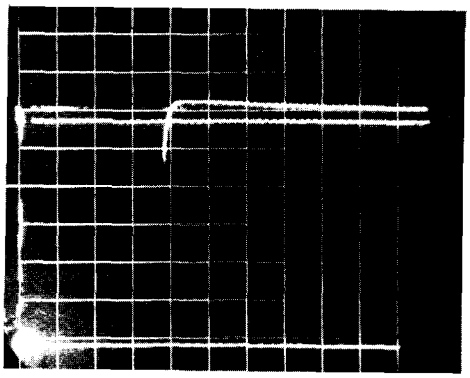

Fig. 8. Build up curve in dilute solution not bubbled, 200 mv/div, 100 msec/div, $i=7.5\cdot10^{-3}$ A/cm², 12.00 pH.

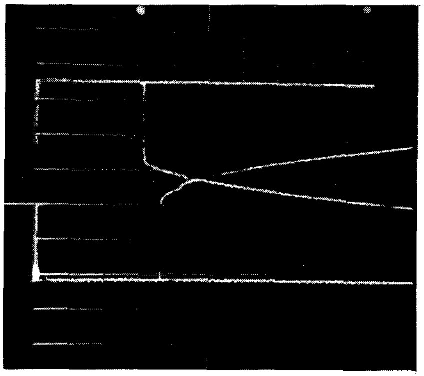

Fig. 9. Decay curve, 20 mv/div, 100 msec/div, $i=2.4\cdot10^{-5}$ A/cm², 10.72 pH.

on attained a constant value which was kept constant at long as observed, if bubbled with hydrogen, but if not, E passed a maximum and from there decreased monotonously as shown in Fig. 8, rate of the descrease being the greater, the higher the current density and the lower the concentration. The E was found to be brought back approximately to the maximum value but sensibly to fluctuate therabout, if the solution was sufficiently bubbled.

This decrease of E was subjected to further investigation with the solution of the lowest pH as below. After the polarizing current of 3 mA/cm² was switched on and the maximum of the potential difference E was passed over, the polarizing current was switched off; E was

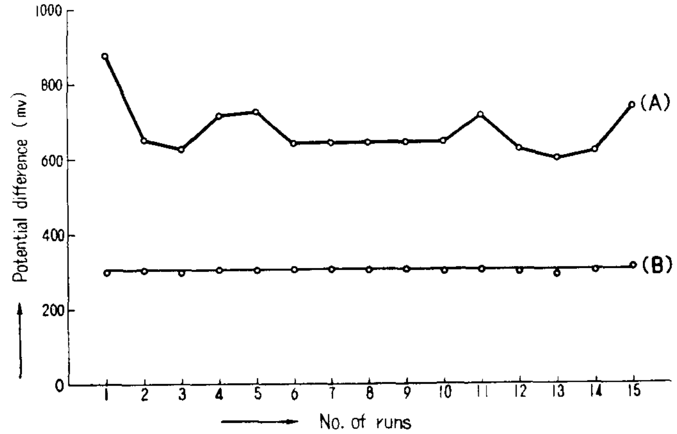

Fig. 10. Potential eifference between (R) and (C) at successive switches off, $i=3\cdot10^{-3}$ A/cm², 10.72 pH.

Curve—(A): the potential difference immediately before switch off.
Curve—(B): the potential difference immedialely after switch off.

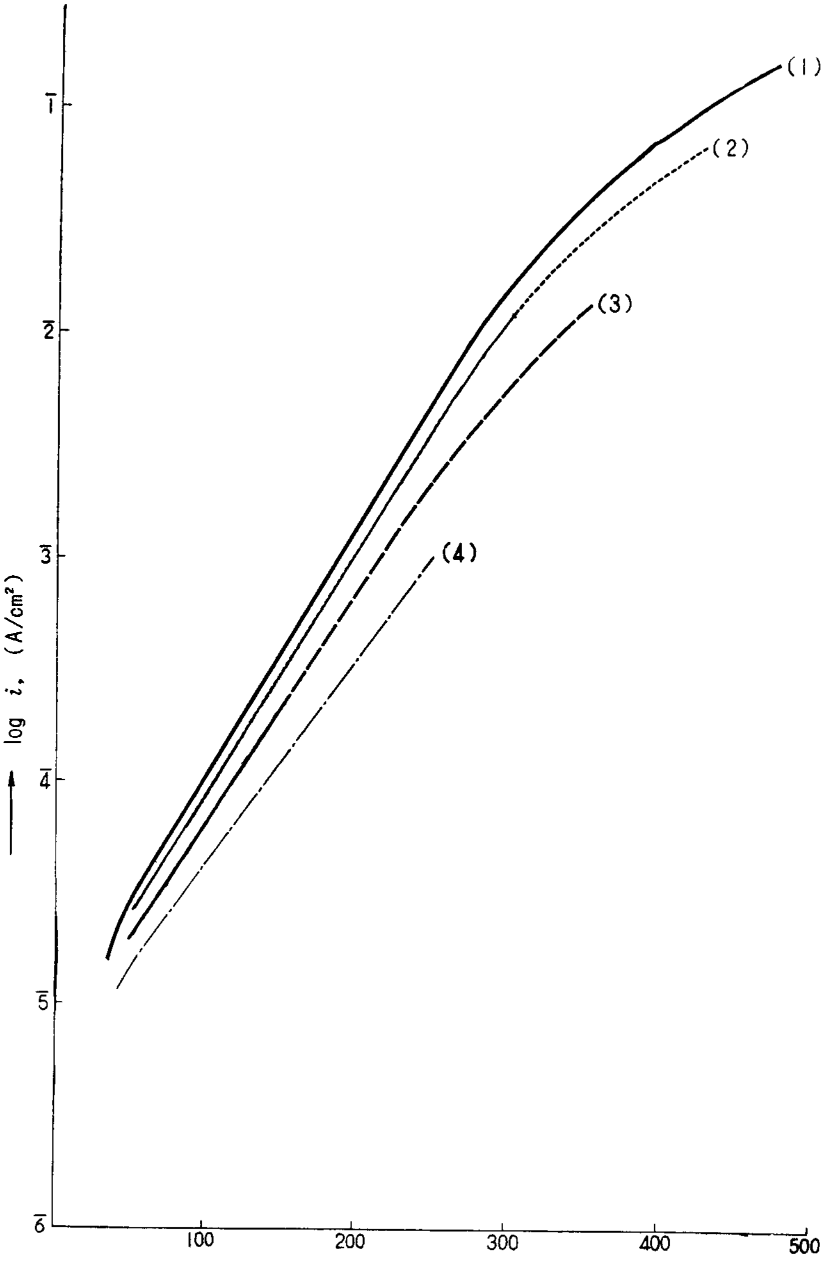

Fig. 11. Log i vs. $\eta_A = E - \eta_\Omega$

(1): 13.68 pH, (2): 12.68 pH, (3): 11.92 pH, (4): 10.72 pH

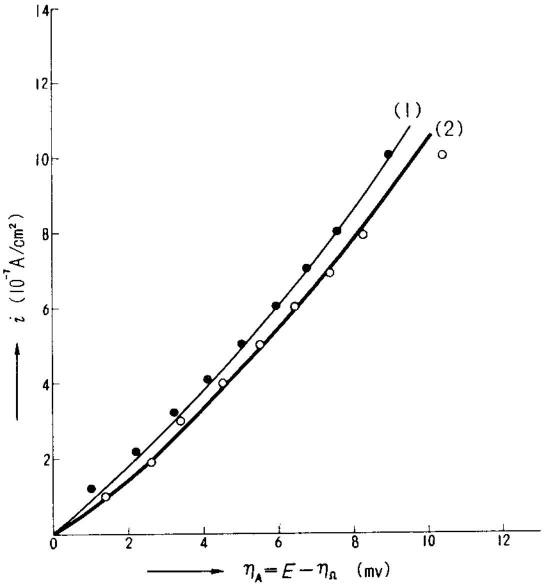

Fig. 12. The current density i *vs.* $\eta_A = E - \eta_\Omega$. (1): 13.10 pH, (2): 11.10 pH.

then found to drop instantaneously as indicated by the vertical jump downwards in Fig. 9. The electrolytic cell was now left without any polarizing current for a few tens seconds, then the same polarizing current as before was switched on again and kept constant for about the same while; such switch on followed by switch off was repeated a number of times and the associated change of E was followed by means of the arrangement shown in Fig. 4. Curve (A) in Fig. 10 is the plot of E-value immediately before switches off against the number of the successive runs. Curve (B) shows the E-value immediately after each switch off. The effect of bubbling on E was observed with runs Nos. 4, 5, 11 and 15 as follows. The bubbling was begun a few second after the switch on preceding the switch off of these numbers. The E was found then instantaneously raised and subsequently decreases slowly down to the E-value at the swich off on Curve (A).

The above experimental results with solution of the lowest pH was interpreted as follows. The gradual decay of E after switch on in the solution without bubbling may be caused by a gradual set in of concentration polarization of electrolyte or that of molecular hydrogen, *i.e.* its retarded diffusion. The latter possibility is excluded, since, if then, the same would be the case with E for the same current density at higher pH, which contradicts the observation. The concentration polarization in question must in consequence be that of electrolyte. Along with the progress of the concentration polarization, the concentration of electrolyte should increase in the neighbourhood of the electrode surface to lower the resistance of solution there. Since the current density in solution must be highest in the neighbourhood of the test electrode, the decrease of resistance there effectively diminishes the ohmic overvoltage, hence the decrease of potential difference E as observed.

According to the above interpretation of the phenomena the concentration polarization should reveal themselves in the case of lower concentration and of higher current densities. Figs. 11 and 12 show the current density of the polarizing current plotted against the apparent overvoltage $\eta_A = E - \eta_\Omega$ observed without bubbling the solution. Dotted or full line shows η_A associated with the anomaly of E described in 2.2) or not respectively. The above inference is verified by the fact that the dotted lines appear only in the region of more dilute solution and stronger current.

On the basis of the above interpretation experimentally verified, we might infer as follows. The true overvoltage is not now given by $\eta_A = E - \eta$ in case of concentration polarization existing, since the true overvoltage in the latter case must be referred to a reversible hydrogen electrode in the concentrated solution in the neighbourhood of the test electrode but not to the real reference electrode (R) in more dilute solution. The true overvoltage must be smaller than η_A, admitted that only small potential difference remains in the interior of the solution after switch off. The η_A should however approach the true one with increase of electrolyte concentration and with decrease of current strength. We see in Figs. 11 and 12 that full lines at different pH are almost congruent with each other at lower current densities or that the overvoltage at a given current density is independent of pH within experimental errors, which establishes the conclusion from the catalytic mechanism.

Acknowledgment

The authors would like to express their sincere thanks to Professor Juro HORIUTI for his kind advises and valuable discussions on the present work.

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