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Instructions for use

# HYDROGEN OVERVOLTAGE ON PLATINUM IN AQUEOUS SODIUM HYDROXIDE

## Part II. The pH-dependence of Overvoltage

By

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## Abstract

The pH-dependence of the hydrogen overvoltage on Pt in aqueous NaOH was studied in the range of pH 11∼14 to determine the rate-determining step of the hydrogen evolution reaction. No pH-dependence of the overvoltage in steady states was observed in this pH range. It is concluded that the reaction scheme of the hydrogen evolution reaction can be expressed as

$$Na^+ + e \rightarrow Na(I), \ Na(I) + H_2O \rightarrow H(a) + Na^- + OH^-, \ 2H(a) \rightarrow H_2,$$
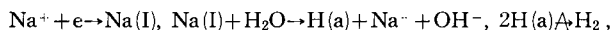
with the last step rate-determining.

## Introduction

In the previous paper[1] it has been verified that the discharge reaction of sodium ion is a constituent elementary step of the hydrogen electrode reaction on platinum in $NaOH_{aq}$ but not rate-determining. The present paper is concerned with the determination of the rate-determining step of the same reaction by observing pH-dependence of overvoltage in steady state.

## 1. Experimental

Experimental apparatus and procedures are the same as described in the previous paper. After switching on or off a current, the build up or decay of the overvoltage was followed with time on a memoscope screen until it attains a steady value or zero respectively. The overvoltage fluctuates in steady states due to fluctuations of the ohmic part caused by hydrogen bubbles, as seen from Plate I. The ohmic overvoltage can be discriminated from the true one as the initial instantaneous drop in the decay curves, so that the value of the overvoltage immediately after switching off the current was taken as the

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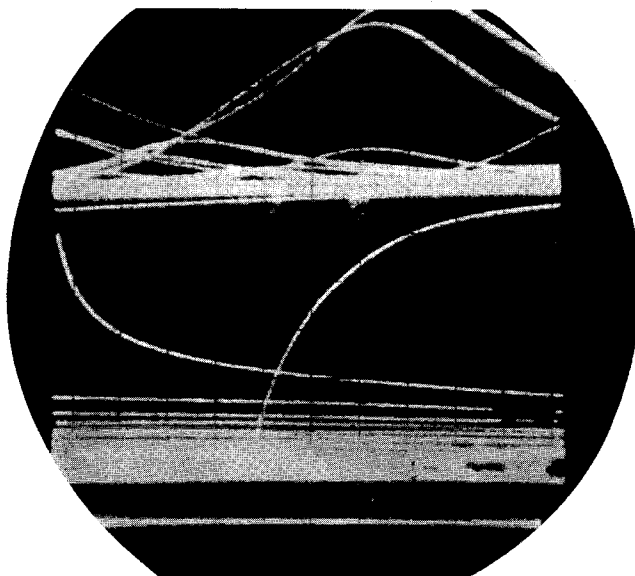*Hydrogen Overvoltage on Platinum in Aqueous Sodium Hydroxide Part II.*



**Plate 1.** The potential-time variations after switching on and off a polarizing current on an evaporated platinum film electrode in $NaOH_{aq}$, pH 13.10, $i = 2 \cdot 10^{-3}$ amp/cm$^2$; the ordinate 20 mv/Div, the abscissa 1 m sec/Div.
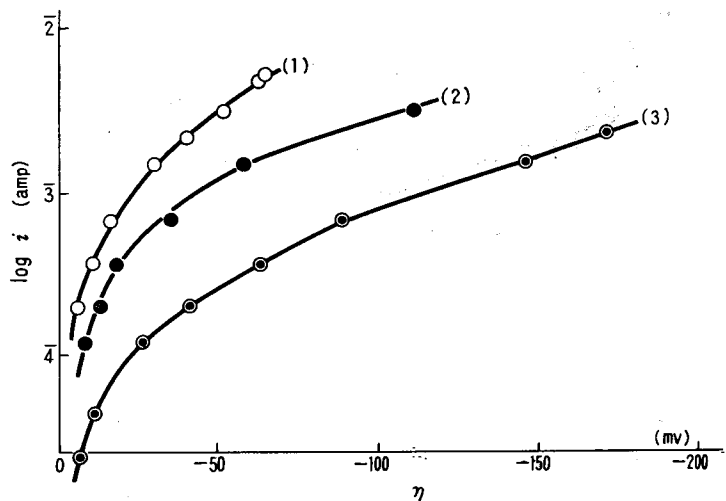


**Fig. 1.** The relation between logarithm of current strength and over-voltage in $NaOH_{aq}$, pH 12.3, on a platinum film, apparent area 0.3 cm$^2$, $C_D$ 45 $\mu$F.

(1): immediately after the solution is introduced into the cell, or after the anodic activations, (2): after the electrode is left in solution for 24 hours. (3): after the electrode is polarized cathodically for several hours.

true one in the steady state. The value of the overvoltage thus determined includes mean errors *ca.* ±5%.

The evaporated platinum film shows initially very high activity in the hydrogen evolution reaction as compared with plates and wires, but becoms less active by repeated cathodic polarization, as shown in Fig. 1. The initial activity of the electrode was recovered by anodically polarizing the electrode for a few seconds several times at oxygen evolution potentials. The potential-time curves in the anodic activations are quite similar to the charging curves observed in nitrogen atmosphere, as shown in Plate 2. It was found from
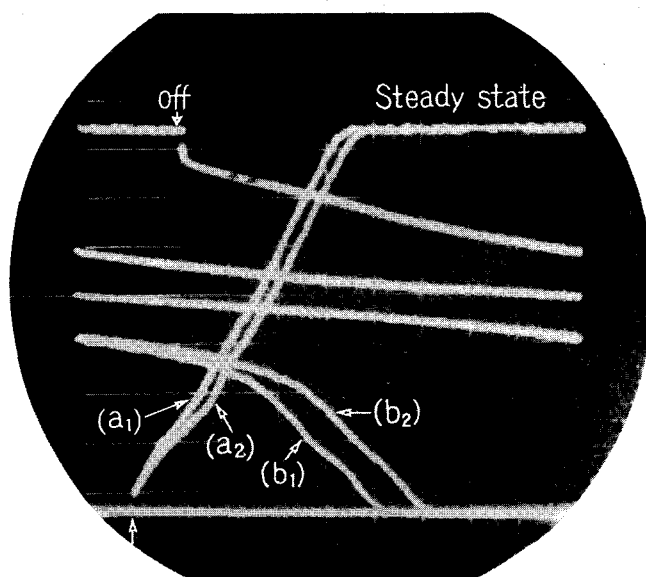


**Plate 2.** The potential-time curves in the anodic activation of an evaporated platinum film electrode in $NaOH_{aq}$, pH 12.30; $(a_1)$ and $(b_1)$ correspond respectively to the build up and the decay curves in a less active state; $(a_2)$ and $(b_2)$ to those in an active state; $i = 1.4 \cdot 10^{-3}$ amp/cm$^2$, the ordinate 200 mv/Div, the adscissa 1 sec/Div.

decay curves observed in course of the activation that the potential fall in the hydrogen region was rapid in case of less active electrode and became slower by repeated anodidic activation. The log $i \sim \eta$ relations have been determined in the most active states of the electrode thus anodically activated.

## 2. Experimental results and discussions

Fig. 2 shows the relation between the logarithm of the current strengh

and the overvoltage in various concentrations of $NaOH_{aq}$. The curves (1) and (2) in the Figure are those obtained with the evaporated platinum films of apparent area 0.3 and 0.1 cm² respectively. The differential capacities of these electrodes as determined from the initial part of the build up curve[1] are 45 and 14 $\mu$F respectively, which are proportional to the apparent areas. It is found from Fig. 2 that there exists no pH-dependence of the overvoltage within experimental errors in the range of pH 11.9~13.45. The true area
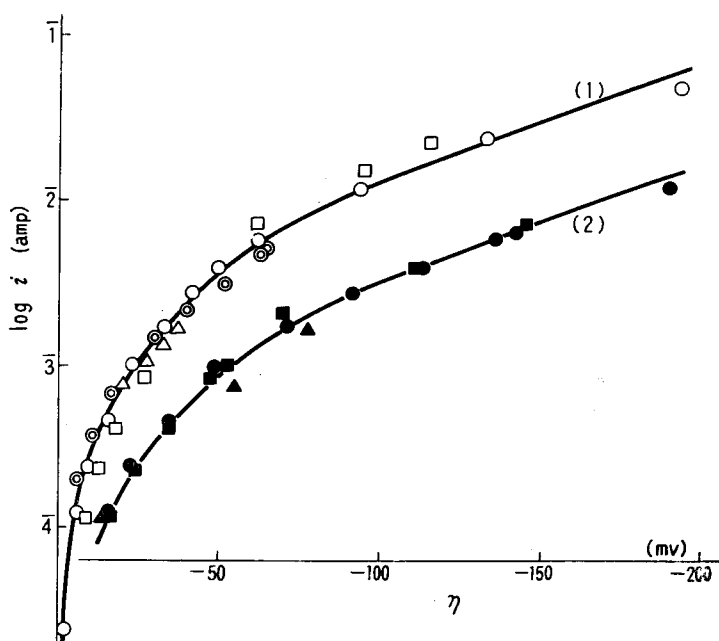


**Fig. 2.** The relation between logarithm of current strength and overvoltage in $NaOH_{aq}$ on platinum films, (1): apparent area 0.3 cm², $C_D$ 45 $\mu$F; (2): apparent area 0.1 cm², $C_D$ 14 $\mu$F; pH: (◎) 12.3, (○) and (●) 12.5, (□) and (■) 13.45, (△) and (▲) 11.9.

of these electrodes was determined to be 2.5 and 0.78 cm² respectively from the values of the differential capacity mentioned above on the basis of 18 $\mu$F/cm² on the mercury electrode obtained by FRUMKIN[2]. The current density assigned to the true unit area is plotted against the overvoltage in Fig. 3 in place of the current strength, which shows that the curves for electrodes of different area coincide with each other. Fig. 4 shows the latter curve in the neighbourhood of the equilibrium, where the current density is proportional to the overvoltage. From the gradient of the linear part of the $i\sim\eta$ curve
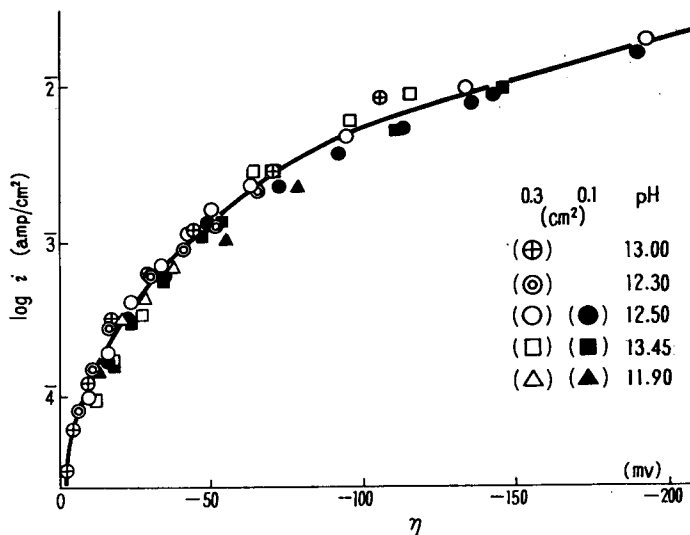
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**Fig. 3.** The relation between logarithm of current density and overvoltage in $NaOH_{aq}$, ($\oplus$): apparent area of electrode 0.13 cm², $C_D = 18\,\mu F$; pH 13; other signs correspond to those in Fig. 2.
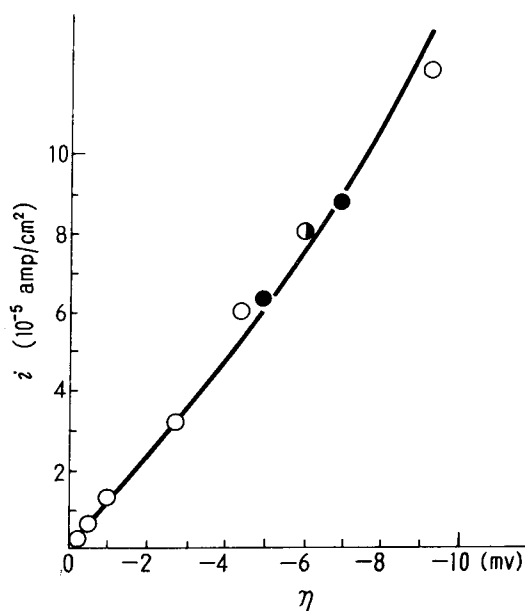


**Fig. 4.** The relation between current density and overvoltage in $NaOH_{aq}$ in the neighbourhood of the equilibrium, pH: (O) 13, (●) 12.3.

in Fig. 4 the exchange current of the hydrogen electrode reaction is found $3.1 \cdot 10^{-4}$ amp/cm$^2$ by the relation $i_0 = (RT/F)(di/d\eta)_{\eta=0}$. It is concluded from these experimental results that the catalytic mechanism fits in with the hydrogen evolution reaction on platinum in NaOH$_{aq}$[3].

The hydrogen evolution reaction is now formulated incorporating that the electron transfer step is the discharge of sodium ion, as

$$\text{Na}^+ + \text{e} \longrightarrow \text{Na (I)}, \tag{I}$$

$$\text{Na (I)} + \text{H}_2\text{O} \longrightarrow \text{H (a)} + \text{Na}^+ + \text{OH}^-, \tag{II}$$

$$2\text{H (a)} \longrightarrow \text{H}_2, \tag{III}$$

with the last step determining the rate. The above mechanism implies two kinds of intermediate, Na (I) and H (a). The change of the work function of the electrode referred to in Part I may be attributed to either or both of them, which is going to be discussed in the following paper.

## Acknowledgement

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