



HOKKAIDO UNIVERSITY

Title	GALVANOSTATIC TRANSIENT STUDIES OF PLATINUM HYDROGEN ELECTRODE : Application of Periodic Square Current Pulses
Author(s)	NOTOYA, R. ; MATSUDA, A.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 15(3), 247-255
Issue Date	1968-02
Doc URL	https://hdl.handle.net/2115/24842
Type	departmental bulletin paper
File Information	15(3)_P247-255.pdf



GALVANOSTATIC TRANSIENT STUDIES OF PLATINUM HYDROGEN ELECTRODE Application of Periodic Square Current Pulses

By

R. NOTOYA*¹⁾ and A. MATSUDA*¹⁾

(Received December 15, 1967)

Abstract

In the galvanostatic transient studies of the platinum hydrogen electrode reaction, double square pulses were used as a current signal and the responsive standing waves of overvoltage were observed. From the latter observation there were derived the exchange current of the electron transfer step of the electrode reaction and the differential capacity of the electric double layer at the metal-solution interface; this procedure essentially facilitated the galvanostatic transient studies previously effected by analysis of single sweep of overvoltage produced severally by switching on and off a constant current.

Introduction

In the galvanostatic transient studies of an electrode reaction, we usually observe the potential-time curve of a polarized electrode with constant current density. The initial stage of the potential-time curve is of special interest, since the change of the electrode potential in this region is reasonably attributed to charging up of the electric double layer at the metal-solution interface; the differential capacity of the electric double layer and the exchange current of the electron transfer step of the reaction are hence derived, as already described in the previous works.¹⁾

Individual sweeps of overvoltage are, however, mostly disturbed by hydrogen bubbles used for stirring the solution, undisturbed observation thus being rendered hazardous. This difficulty is overcome by frequently repeating the switching on and off of a constant current "automatically" by means of a train of square current pulses and recording the responsive standing wave of overvoltage instead of producing and analyzing single sweeps of overvoltage severally.

The present work is concerned with the application of a train of double

*¹⁾ Research Institute for Catalysis, Hokkaido University, Sapporo, Japan.

square pulses of current to the galvanostatic transient studies of platinum hydrogen electrode reaction in aqueous sodium hydroxide.

Experimentals and Discussion

A hydrogen electrode is polarized from its reversible state with a train of double square pulses of current each composed of two single square current strokes of opposite direction to observe the responsive standing wave of overvoltage about the reversible potential.

The test, reference and counter electrodes, T, R and A, are, as shown in Fig. 1, platinum films evaporated on ground surface inside an electrolytic cell of quartz glass. The shape and structure of the cell are quite similar to those described in the previous paper.¹⁾

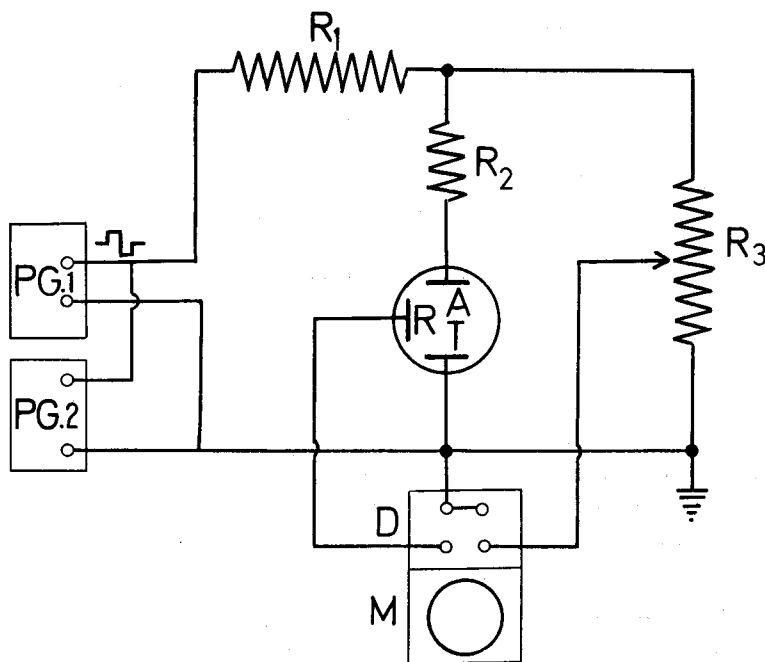


Fig. 1. Arrangement for observation of potential-time curves with double square pulse current.

The arrangement for the observation of overvoltage-time curves is shown in Fig. 1, where PG. 1 and PG. 2 are single square pulse generators (Hewlett Packard Co. model 214), R₁ a resistor for current control, R₂ that for determination of a current strength and R₃ that for compensation of the ohmic overvoltage, M an oscilloscope and D a differential preamplifier of high sensitivity

Galvanostatic Transient Studies of Pt Hydrogen Electrode

(Hughes Aircraft Co.). The rise or fall time of a pulse produced by PG. 1 or PG. 2 is *ca.* 15 nana sec. The double square pulses are generated by connecting PG. 1 with PG. 2 as follows. PG. 1 is set to generate periodic single square pulses with its trigger mode internal, and PG. 2 to generate the same pulses as PG. 1 but of opposite polarity with its trigger mode external. Applying periodic pulses of PG. 1 to the trigger input of PG. 2, the pulse of PG. 2 is shot by each pulse of PG. 1. A double square pulse of desired width is thus generated periodically by adjusting the delay time of the trigger of PG. 2 and applied to the reversible hydrogen electrodes T and A through a resistor R_1 , as shown in Fig. 1. The responsive standing wave of overvoltage is observed with an oscilloscope screen. Oscillograms of the current pulse and the standing wave of overvoltage η thus obtained are shown in Figs. 2(a) and 2(b) respectively. Fig. 2(a) shows that a double square pulse current

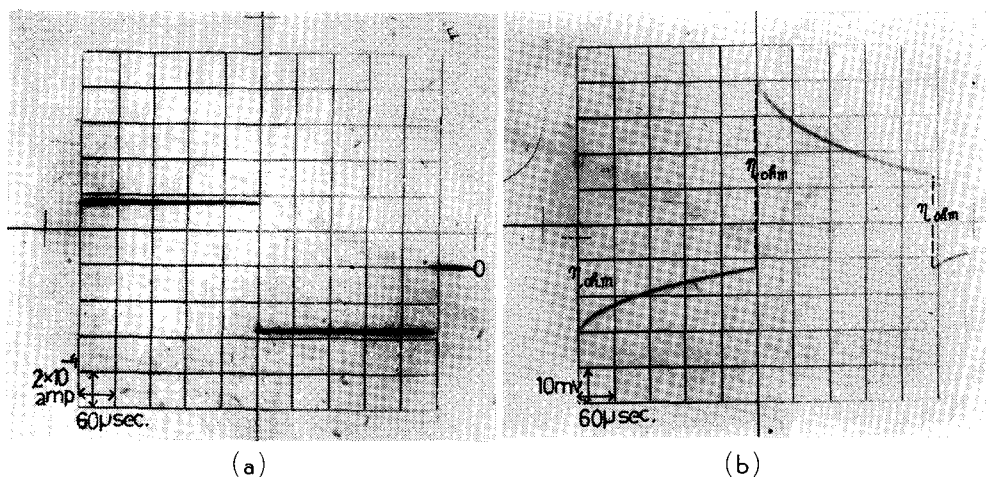


Fig. 2. (a): double square pulse current, $2 \cdot 10^{-4}$ A/Div., $60 \mu\text{sec/Div.}$
 (b): standing wave of overvoltage, 10 mV/Div. , $60 \mu\text{sec/Div.}$

consists of two single square current strokes of the same height and length but of opposite direction, and Fig. 2(b) a standing wave of overvoltage composed of two branches respectively responsive to the first and the second current strokes associated with ohmic overvoltage η_0 appearing at the moment of the current changes at the beginning and end of each branch. The time interval between two consecutive current strokes is arranged long enough for the electrode to recover the reversible state, so that the overvoltage starts from zero in every pulse. Figs. 3(a) and 4(a) show the standing waves of overvoltage observed with different double square pulses in $0.2\text{N NaOH}_{\text{aq}}$. It is seen from these Figures that the $\eta-t$ curves are symmetrically turned over around

R. NOTOYA and A. MATSUDA

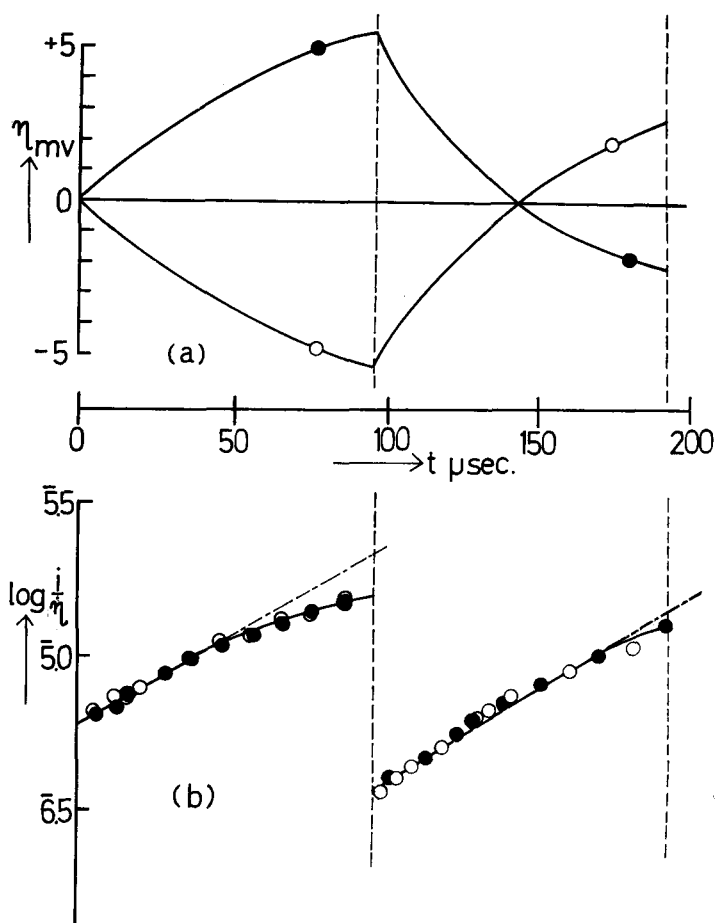


Fig. 3. (a): standing wave of overvoltage in 0.2N NaOH_{aq} observed with $5.7 \cdot 10^{-4}$ A pulse height and 100-100 μsec pulse width.
 (b): the $\log(i/\eta)-t$ relation derived from the $\eta-t$ curves in (a);
 (●) or (○) refers to the specification relevant to the same symbol in (a).

the $\eta=0$ axis by reversing the direction of the current stroke. From these $\eta-t$ curves are derived the differential capacity of the electric double layer, C_D , and the time constant of the electron transfer step, τ_1 , at the reversible hydrogen electrode potential, as follows.

The change of overvoltage was previously¹⁾ assumed to be due to charging up of the electric double layer at the metal-solution interface. Along this line we have an equation for the material balance of electrons, *i. e.*

Galvanostatic Transient Studies of Pt Hydrogen Electrode

$$C_D \delta \eta = (i - i_1) \delta t, \quad (1)$$

and another for the proportionality of η to i_1 in the region of overvoltage, where $|\eta| \ll RT/F$, *i. e.*

$$\eta = r_1 i_1; \quad (2)$$

i is the pulse height, i_1 the current density of the electron transfer step, r_1 a constant reciprocally proportional to the exchange current of the electron transfer step,¹⁾ R the gas constant and T or F the absolute temperature or the Faraday respectively. The i , i_1 and η are taken positive for the anodic region. Eliminating i_1 from Eqs. (1) and (2), and integrating over time, we have

$$\ln |\eta - r_1 i| = -\frac{t}{r_1 C_D} + k, \quad (3)$$

where k is an integration constant, and t the time measured from the beginning of the current pulse. The integration constant k is determined for the respective branches as,

$$k = \ln |r_1 i| \quad \text{for the first branch, where } \eta = 0 \text{ at } t=0, \text{ and}$$

$$k = \ln |r_1 (i - i_{11})| + \frac{t_1}{\tau_1}, \quad \text{for the second branch, where } \eta = r_1 i_{11} \text{ at } t=t_1;$$

t_1 is the width of the first pulse, and i_{11} is i_1 at $t=t_1$ or at the beginning of the second branch. Eliminating η and $i - i_1$ from Eqs. (1), (2) and (3), we have

$$\ln(\tau_1 \dot{\eta}) = -\frac{t}{\tau_1} + k, \quad (4a)$$

where

$$\tau_1 = r_1 C_D, \quad (4b)$$

is the time constant and substituting k -value for the first or second branch into Eq. (4a) with reference to Eq. (4b)

$$\ln |i/\dot{\eta}| = \frac{t}{\tau_1} + \ln C_D, \quad (5)$$

or

$$\ln |i/\dot{\eta}| = \frac{t-t_1}{\tau_1} - \ln \left| 1 - \frac{i_{11}}{i} \right| + \ln C_D, \quad (6)$$

respectively; τ_1 and C_D are determined in terms of Eqs. (5) or (6) from the observed $\eta-t$ curve in the first or second branch respectively.

Figs. 3(b) and 4(b) show the $\log(i/\dot{\eta})-t$ relation derived respectively from $\eta-t$ curves of Figs. 3(a) and 4(a). We see from these Figures that $\log(i/\dot{\eta})-t$

R. NOTOYA and A. MATSUDA

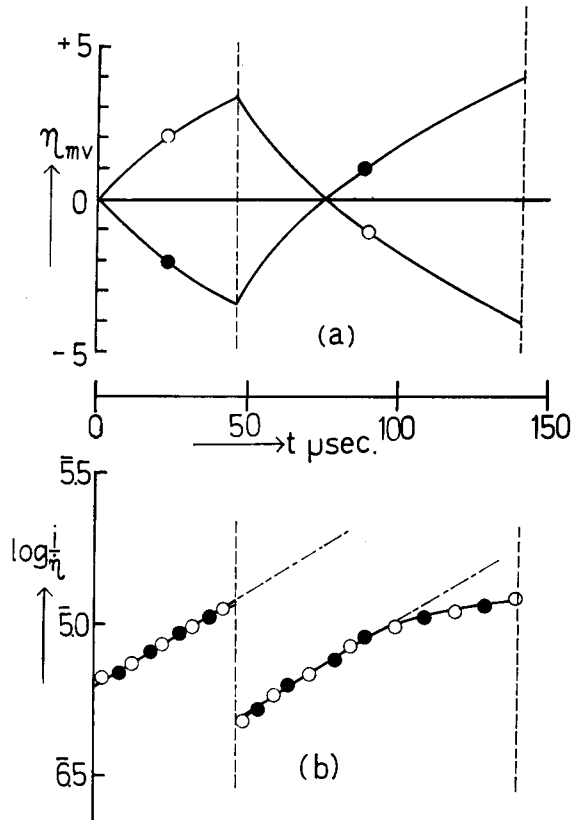


Fig. 4. (a): the standing wave of overvoltage in 0.2N NaOH_{aq}; $6.6 \cdot 10^{-4}$ A pulse height and 50-100 μsec pulse width.
 (b): the $\log(i/\eta)-t$ relation derived from the $\eta-t$ curves in (a).

relations of the first and the second branches are satisfactorily reproduced in the initial stage by Eq. (5) and Eq. (6) respectively with the common values of τ_1 and C_D both to the branches. The value of τ_1 in 0.2N NaOH_{aq} is found $70 \pm 5 \mu\text{sec}$ from these Figures. The value of C_D is determined to be $5.9 \pm 0.3 \mu F$ from the value of $\ln(i/\eta)$ at $t=0$ as derived from the first branch, which equals the value of $\ln(i/\eta)$ at $\eta=0$ from the second branch*).

*) It follows from Eq. (6) as regards the second branch

$$\ln |i/\eta_{\tau=0}| = \frac{t_{\tau=0} - t_1}{\tau_1} - \ln \left| 1 - \frac{i_{11}}{i} \right| + \ln C_D \quad (i)$$

and from Eq. (3) with reference to Eq. (4b)

Continued on next page

Galvanostatic Transient Studies of Pt Hydrogen Electrode

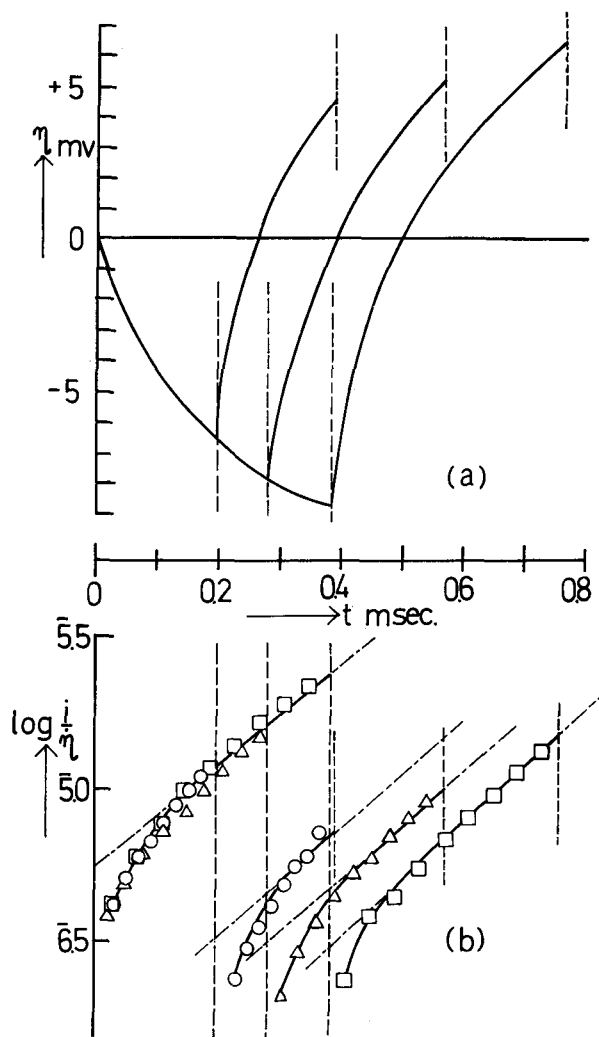


Fig. 5. (a): the standing wave of overvoltage in 0.01 N NaOH_{aq}; $1.93 \cdot 10^{-4}$ A pulse height and 200-200, 300-300 and 400-400 μ sec pulse width.

(b): the $\log(i/\dot{\eta})-t$ relation derived from results of (a).

$$\ln |r_1 i| = -\frac{t_{\eta=0}}{\tau_1} + \ln |r_1(i-i_{11})| + \frac{t_1}{\tau_1},$$

$$\text{or } 0 = \frac{t_1 - t_{\eta=0}}{\tau_1} + \ln \left| 1 - \frac{i_{11}}{i} \right|, \quad (\text{ii})$$

where suffix $\eta=0$ signifies the particular values at $\eta=0$. We have from Eqs. (i) and (ii)

$$\ln |i/\dot{\eta}_{\eta=0}| = \ln C_D.$$

Figs. 5(a) and 5(b) show the standing waves of overvoltage observed with double square pulses of the same height but of different width in 0.01N NaOH_{aq} and $\log(i/\dot{\eta})-t$ curves hence derived respectively. As seen from these Figures the $\log(i/\dot{\eta})-t$ relations are reasonably reproduced by Eqs. (5) and (6) except in their initial stage. The values of τ_1 is found to be $245 \pm 20 \mu\text{sec}$ and that of C_D $5.3 \pm 0.3 \mu F$ from Fig. 5(b). The deviation from linearity in the initial stage in Fig. 5(b) may be due to the ohmic tail of the potential jump owing to small conductivity of this solution.

As seen from Figs. 3(b), 4(b) and 5(b), the linear part of the $\log(i/\dot{\eta})-t$ relation of the second branch is somewhat longer than that of the first branch, which may be concerned with the fact that the overvoltage is extended over both sides of zero overvoltage in the second branch, while only to one side in the first branch.

The values of τ_1 obtained from Figs. 4(b) and 5(b) are plotted against the concentration of sodium ion in Fig. 6 together with those previously obtained

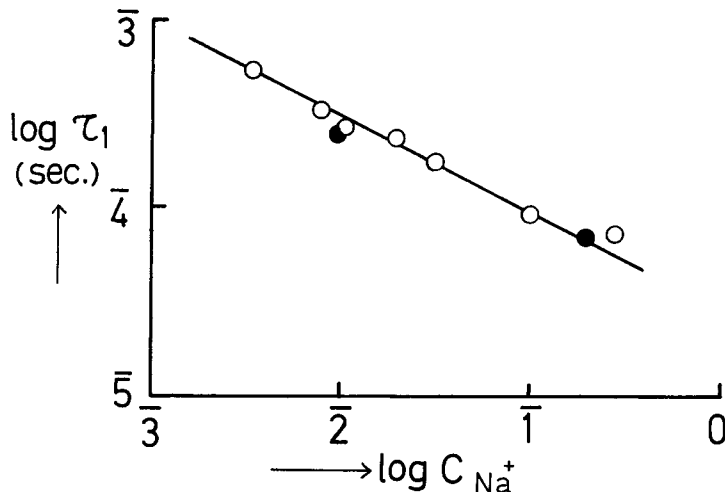


Fig. 6. The relation between $\log \tau_1$ and $\log C_{\text{Na}^+}$; (●): obtained from the standing wave and (○): from the single sweep of overvoltage.

from the single sweep of overvoltage,¹⁾ which shows practically perfect an agreement of τ_1 -values obtained by the two procedures, verifying their reliability.

The C_D values derived from Figs. 4(b) and 5(b) for 0.2 and 0.01N NaOH_{aq} respectively show, on the other hand, by their coincidence within experimental errors, such independence of C_D from concentration.

Galvanostatic Transient Studies of Pt Hydrogen Electrode

Acknowledgement

The authors wish to express their sincere thanks to Prof. Emeritus J. HORIUTI for his valuable discussions in the present work.

References

- 1) A. MATSUDA and R. NOTOYA, This Journal, **14**, 165 (1966).