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DETERMINATION OF DIFFERENTIAL CAPACITY OF MERCURY HYDROGEN ELECTRODE FROM CHARGING AND DECAY CURVES OF OVERVOLTAGE

By

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Abstract

The differential capacity of a mercury hydrogen electrode in hydrochloric acid solution was determined in the range of overvoltage from -0.134 V to -0.350 V by analysing the charging curve and the decay curve of overvoltage η on the basis of the electrochemical mechanism. It was found that the capacity C_k of the Helmholtz layer remained at a nearly constant value independent of the change of η from -0.067 V to -0.467 V while the differential capacity had a minimum and a maximum value at about -0.15 V and -0.18 V respectively, and tended to a fixed value equal to C_k in the range more negative than -0.25 V of η. The present results are in good accord with the experimental and theoretical results of MITUYA,[1] MATSUDA,[2] MATSUDA and HORIUTI,[3] PAST and JOFA[4] and others.[5,6] The present authors conclude that the electrochemical mechanism may be operative on a mercury hydrogen electrode, with reference to another experimental result on Tafel's slope which has a break at the point of zero charge with the same inclination, as has previously been reported by one of the present authors.

Theoretical

MITUYA[1] has previously shown that the hydrogen electrode reaction on a mercury electrode could occur through the electrochemical mechanism on the basis of his experimental results obtained between the steady current i_s and the overvoltage η and also between the number of charge E to be supplied along with the creation of new unit surface of the electrode and η, when the electrode is working as the hydrogen electrode at a given η. By differentiation of the E *vs.* η curve on the figure, the differential capacity curve *versus* η on a mercury hydrogen electrode which has one minimum at the point of zero charge could be obtained, and passing through a maximum, it decreases monotonously at the larger η region. MATSUDA[2)] has theoretically deduced that when the electrochemical mechanism is operative, the differential capacity should have a minimum at the point of zero charge and should tend to the constant value of C_k of the Helmholtz layer passing through a maximum higher than $2C_k$.

We determined the differential capacity C of the mercury hydrogen electrode from the charging and decay curves of overvoltage by analysing them on the basis of electrochemical mechanism as follows.

The quantity of electricity δQ, with which the electrode of unit area is charged with increase of $\delta\eta$ of the overvoltage, consists of two parts, one for charging up the electrode surface and the other for the formation of hydrogen molecule ion H_2^+ (a) on the surface according to the increase of $\delta\theta$ of the coverage θ, as

$$\delta Q = C_k \delta\eta - \left(\frac{G\boldsymbol{F}}{N_A}\right)\delta\theta\,, \qquad (1)$$

where C_k is the capacity of the Helmholtz layer, G is the number of adsorption sites, $\boldsymbol{F}$ is the Faraday constant and N_A is Avogadro's number. Since the differential capacity C is defined as $C = dQ/d\eta$, it follows from Eq. (1) that

$$C = \frac{dQ}{d\eta} = C_k - \frac{G\boldsymbol{F}}{N_A}\frac{d\theta}{d\eta}\,. \qquad (2)$$

The electrochemical mechanism consists of two elementary reactions, *i.e.*,

$$2H^+ + e \rightleftarrows H_2^+(a)\,, \qquad (3)$$

$$H_2^+(a) + e \xrightarrow{\Lambda} H_2\,, \qquad (4)$$

where $\xrightarrow{\Lambda}$ denotes the rate determining step.

The reaction velocities of Eq. (3) and Eq. (4) can be expressed in terms of current densities i_1 and i_2, respectively. The current density i, supplied to the electrode in a time δt, is the sum of these currents; one is that for charging up the Helmholtz layer and the others are i_1 and i_2. It follows that

$$\delta Q = -i\delta t\,, \qquad (5\text{–}1)$$

$$\delta Q' = C_k \delta\eta\,, \qquad (5\text{–}2)$$

$$\delta Q'' = -i_1\delta t\,, \qquad (5\text{–}3)$$

$$\delta Q''' = -i_2\delta t\,, \qquad (5\text{–}4)$$

$$\delta Q = \delta Q' + \delta Q'' + \delta Q'''\,. \qquad (5\text{–}5)$$

Introducing Eqs. (5–1, 2, 3, 4) into (5–5), we have

$$C_k = -\frac{i-(i_1+i_2)}{\left(\frac{d\eta}{dt}\right)} . \tag{6}$$

At $t=0$ no reaction in either Eq. (3) or (4) occurs so that we have

$$C_k = -\frac{i_{t=0}}{\left(\frac{d\eta}{dt}\right)_{t=0}} . \tag{7}$$

Eq. (7) holds for the cases of varying the overpotential from a steady value to any other value, *i.e.*,

$$C_k = -\frac{\Delta i_{t=0}}{\left(\frac{d\eta}{dt}\right)_{t=0}} , \tag{8}$$

where $\Delta i_{t=0}$ denotes the increase of current density at $t=0$. In the steady state of the hydrogen electrode process, the steady current density i_s is the sum of i_1 and i_2 of Eq. (3) and (4) only, and as the latter is the rate determining step, we have

$$i_s = i_1 + i_2 = 2i_2 . \tag{9}$$

Now the supply of current is interrupted at this steady state, and i in Eq. (6) becomes zero; and so together with Eq. (9), we have

$$C_k = \frac{i_s}{\left(\frac{d\eta}{dt}\right)_{t=0}} . \tag{10}$$

Since the increase of $\delta\theta$ in Eq. (1) is the difference of the amount of hydrogen molecule ions produced by reaction (3) and consumed by reaction (4) in a time δt, it follows that

$$\left(\frac{\boldsymbol{GF}}{N_A}\right)\delta\theta = (i_1 - i_2)\,\delta t . \tag{11}$$

The coverage θ at a given stationary state can be obtained by integrating Eq. (11) from time $t=0$ to $t=t_s$, *i.e.*, from the time of the commencement of charging to the time to reach the stationary state,

$$\left(\frac{\boldsymbol{GF}}{N_A}\right)\theta = \int_0^{t_s} (i_1 - i_2)\,dt . \tag{12}$$

The coverage θ should be a one-valued function of η, we have

$$\frac{GF}{N_A}\cdot\frac{d\theta}{d\eta}=\frac{d}{d\eta}\left[\int_0^{t_s}(i_1-i_2)\,dt\right]. \tag{13}$$

From Eqs. (2) and (13), we have

$$C=C_k-\frac{d}{d\eta}\left[\int_0^{t_s}(i_1-i_2)\,dt\right]. \tag{14}$$

Rearranging Eq. (6) gives

$$i_1+i_2=i+C_k\frac{d\eta}{dt}. \tag{15}$$

Now we assume that for a slow build-up process of η as in the case of the mercury hydrogen reaction, $2i_2$ equals i_s not only for the steady steate but also for the transient state, *i.e.*, the overvoltage changes quasi-statically. Then we have

$$i_1-i_2=(i_1+i_2)-2i_2=(i_1+i_2)-i_s. \tag{16}$$

Inserting Eq. (16) into Eq. (14), we have

$$C=C_k-\frac{d}{d\eta}\left[\int_0^{t_s}\left\{(i_1+i_2)-i_s\right\}dt\right]. \tag{17}$$

Observing C_k by Eq. (7), (i_1+i_2) by Eq. (15), and i and i_s directly, we can obtain the value of C according to Eq. (17) with graphical integration. For the decay process of η, we have from Eq. (6),

$$i_1+i_2=C_k\frac{d\eta}{dt} \tag{18}.$$

In this case, the decrease of $H_2^+(a)$ in a time δt is given as $-(i_1-i_2)\,\delta t$, and so together with Eq. (16), we have

$$C=C_k+\frac{d}{d\eta}\left[\int_0^{t_s}\left\{(i_1+i_2)-i_s\right\}dt\right]. \tag{19}$$

Experimental

The electrolytic cell used is shown in Fig. 1. It was made of Pyrex glass and

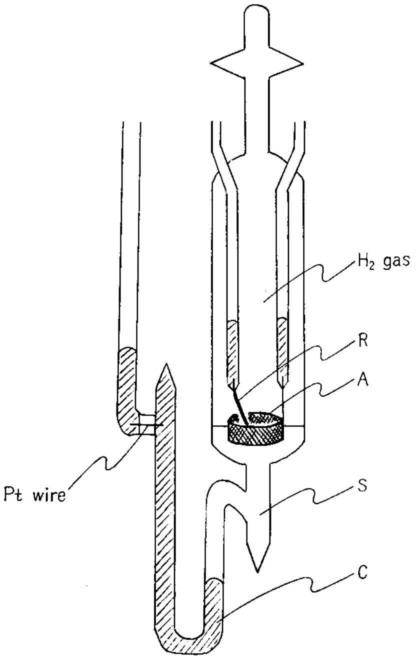

Fig. 1. Electrolytic cell.
C: mercury cathode; A: anode; R: reference electrode; S: 0.075 N HCl solution; Pressure of H_2 gas = 720 mmHg; Radius of capillary tube of cathode = 0.265 cm,

was cleaned and charged with 0.075 N–HCl solution and pure H_2 gas at 720 mmHg pressure both of which had been purified and charged under high vacuum into the cell following MITUYA's method.[1] Both the ring platinum anode and the reference electrode were platinized and they worked as the reversible hydrogen electrode in the preliminary tests. So that the potential of the mercury cathode referred to the reference hydrogen electrode in the cell was −67 mV more negative *versus* N.H.E. In the following the overvoltage value is referred to the N.H.E. throughout.

1. Determination of the double layer capacity C_k

Fig. 2 shows the circuit for the determination of C_k from build-up and decay curves of overvoltage. This method has been reported in detail elsewhere.[7]

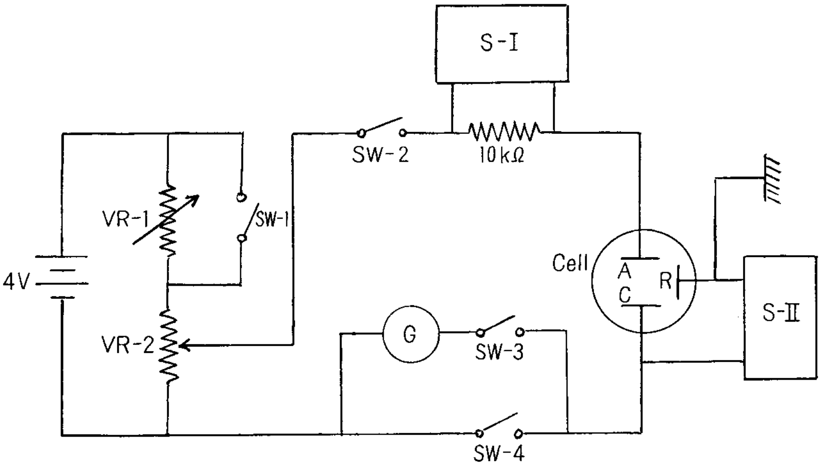

Fig. 2. The electric circuit for the measurement of C_k.
SW-1, SW-2: mercury switches; VR-1, VR-2: variable resistances (500 Ω): S-I, S-II: synchroscopes; G: galvanometer.

2. Determination of the differential capacity C.

In the determination of C_k, it was necessary to obtain the value of $(d\eta/dt)_{t=0}$. As the charging-up process of the double layer is very rapid the sweep time must be short. But in the determination of C of the mercury hydrogen electrode, both the build-up and decay processes of the overvoltage are, except for a short time at the outset of the processes, very slow, and the changes in the overvoltage and in the current can be followed by a vibrating reed electrometer and a current recorder. Fig. 3 shows the circuit for the determination of C.

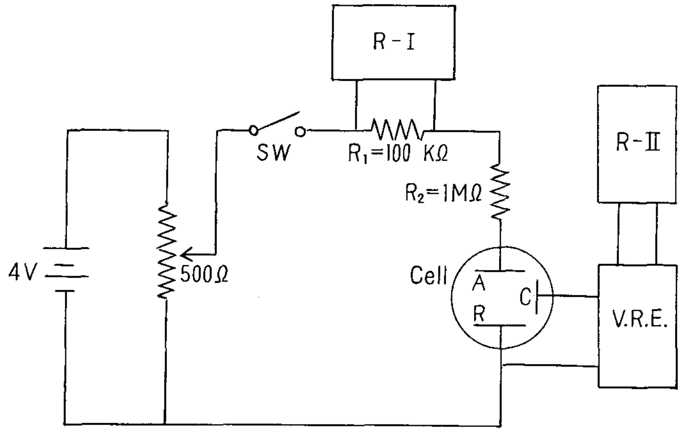

Fig. 3. The electric circuit for the measurement of C.
SW: mercury switch; R-I, R-II: recorders;
V.R.E.: vibrating reed electrometer.

The changes of i and η were recorded simultaneously together with the steady current i_s at the steady overvoltage.

Result

1. The values of C_k at several overvoltages obtained by build-up and decay curves of η.

Fig. 4 shows the relation between C_k and sweep time of the synchroscope. As the sweep time becomes short, the value of $(d\eta/dt)_{t=0}$ approaches a constant value to give a definite C_k. In Table 1 these C_k values at several overvoltages obtained from build-up and decay curves are listed. The values are almost constant in the range from -67 mV to -470 mV of η. The mean value is $10.5 \pm 0.9\,\mu F$. Using the reported value,[4~6] $18\,\mu F/\mathrm{cm}^2$, of the double layer capacity, the real electrode area can be calculated $0.58\,\mathrm{cm}^2$, which is in good accord with the calculated geometrical area of $0.44\,\mathrm{cm}^2$, assuming a hemispherical mercury surface in the capillary tube; the effective value of the latter must be somewhat larger than the calculated value because the wetted side surface of the mercury should also be added to the hemispherical surface to give the real electrode area. Thus we adopted the value of $0.58\,\mathrm{cm}^2$ for the electrode area as obtained experimentally by C_k-determination.

2. The relation between η and C.

The values of (i_1+i_2) in Eqs. (15) and (18), for the build-up process and the decay process respectively, were calculated from the recorded values of i

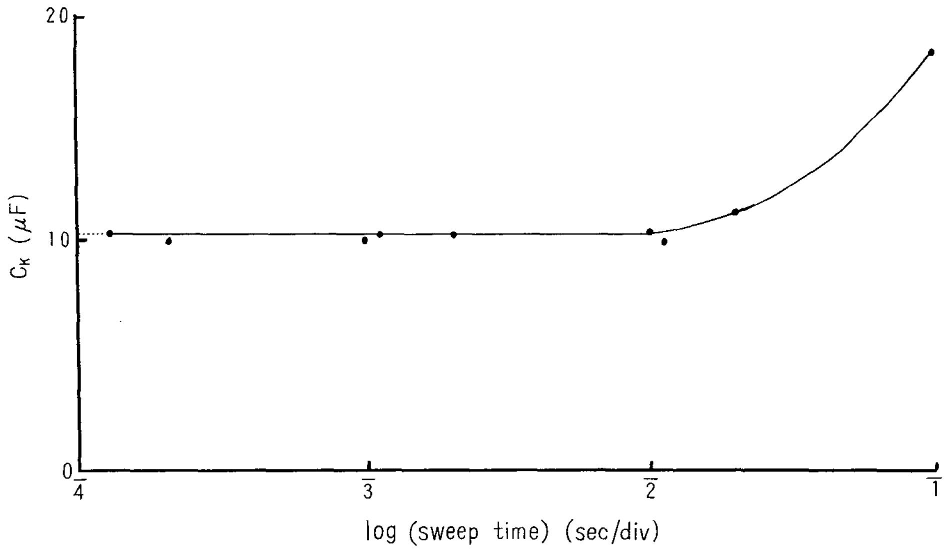

Fig. 4. C_k *vs.* log (sweep time) relation.
$\eta=-267$ mV, calculated from build-up curve of η.

TABLE 1 Values of C_k at different overvoltages.

η (mV)	C_k (μF)	
	calculated from build-up curve of η	calculated from decay curve of η
− 67	11.5	—
−137	12.5	—
−167	11.0	—
−217	11.8	—
−267	10.0	9.0
−317	9.3	11.6
−367	10.0	10.6
−417	10.0	9.7
−467	—	9.9

and η on the figure utilizing the circuit shown in Fig. 3. Fig. 5 shows the relations of log i_s *vs.* η (Tafel's relation), log (i_1+i_2) *vs.* η for the build-up and the decay process. Tafel's relation has a characteristic break on the curve at about -0.15 V of η showing the change in the value of the inclination, $\tau=(RT/F)\cdot(\partial \log i_s/\partial\eta)$, from $2-\alpha$ to $1-\alpha$, as has been reported by MITUYA and also theoretically had been deduced by MATSUDA and HORIUTI.3)

Curve a in Fig. 6 shows the build-up curve of η *versus* t. The η value on the figure specifies t, (i_1+i_2), and $2i_2$ values simultaneously, and so it gives (i_1+i_2) *vs.* t and $2i_2$ *vs.* t relations according to the $\log(i_1+i_2)$ *vs.* η and log i_s *vs.* η relations in Fig. 5 and with Eq. (16); curves b and c in Fig. 6 show the

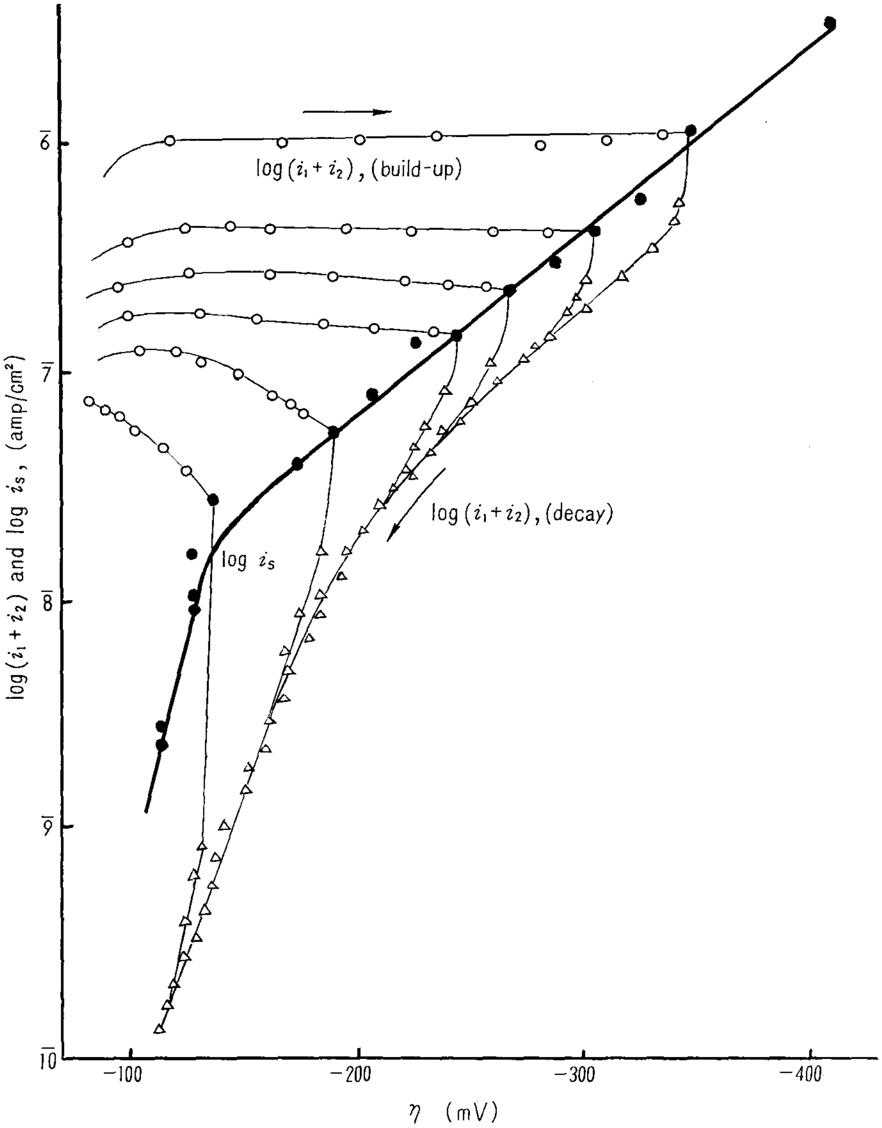

Fig. 5. log i_s *vs.* η relation and $\log(i_1+i_3)$ *vs.* η relationn.

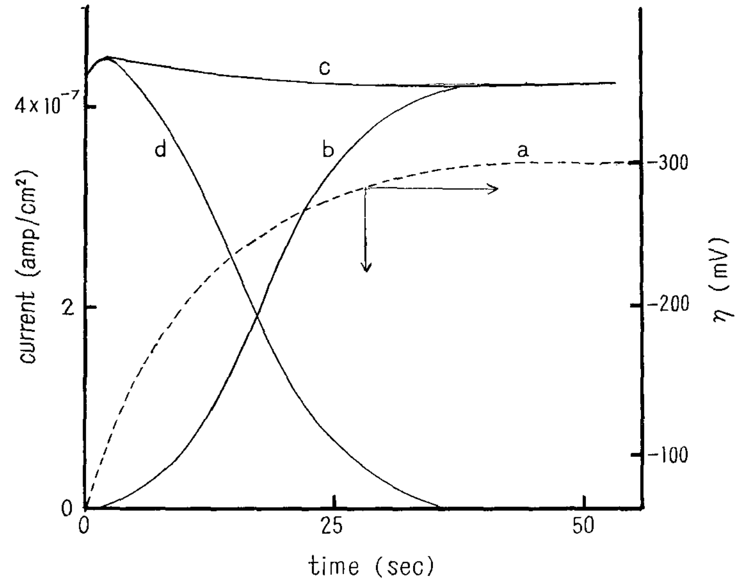

Fig. 6. The calculation of $(GF/N_A)\cdot\theta$ by graphic integration.
a : η vs. t; b : $2i_2$ vs. t; c : (i_1+i_2) vs. t; d : $\{(i_1+i_2)-i_s\}$ vs. t;
$\eta=-301$ mV; $GF/N_A\cdot\theta=7.24$ (μcoulomb/cm²).

$2i_2$ *vs.* t and (i_1+i_2) *vs.* t relations respectively. Cuvre d in Fig. 6 shows the $\{(i_1+i_2)-i_s\}$ *vs.* t relation. The area surrounded by curve b and c and the ordinate and also the area surrounded by curve d and by both axes gives the value of $\int_0^{t_s}\{(i_1+i_2)-i_s\}dt$ in Eq. (17) at a given η. Fig. 7 shows the $\{(i_1+i_2)$

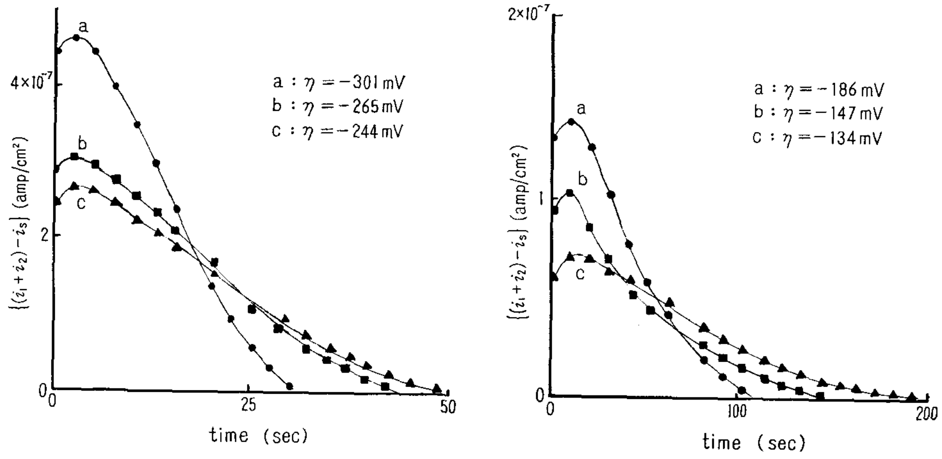

Fig. 7. $\{(i_1+i_2)-i_s\}$ *vs.* time relation for the build-up process of η.

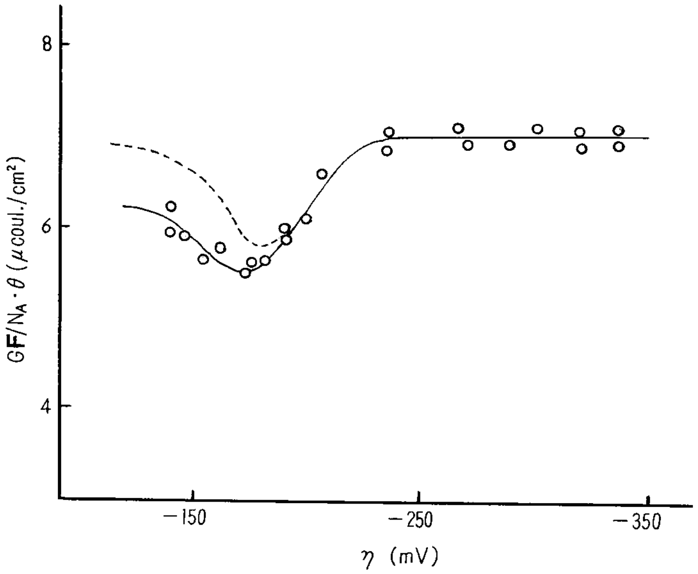

Fig. 8. $(GF/N_A)\cdot\theta$ *vs.* η relation.

—○— : observed value ; ---- : theoretical value.2)

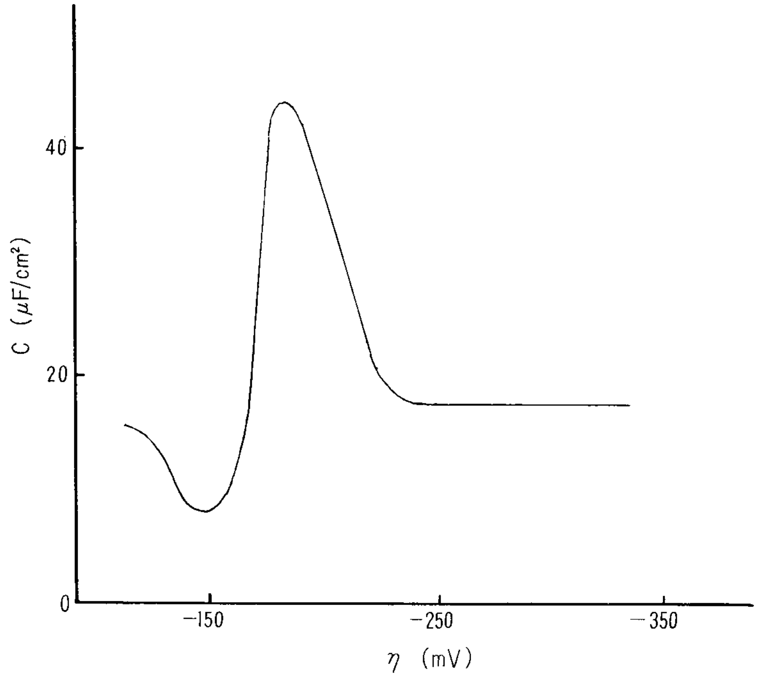

Fig. 9. C *vs.* η relation.

$-i_s\}$ *vs.* t relations at different η values. When overvoltage becomes more positive, the t value, where $\{(i_1+i_2)-i_s\}$ is zero, becomes large causing difficulty in the calculation of the area, as is seen in the figures. In Fig. 8 the relation between $(G\boldsymbol{F}/N_A)\cdot\theta$ and η is shown. The value of $(G\boldsymbol{F}/N_A)\cdot\theta$ varies with η and has a minimum at about -170 mV, and approches a constant value in the region more negative than -250 mV. The minimum value of $(G\boldsymbol{F}/N_A)\cdot\theta$ is 5.5 μcoulomb/cm^2, and the constant value is 6.9 μcoulomb/cm.^{2} These $(G\boldsymbol{F}/N_A)\cdot\theta$ values in the more positive region can not be calculated with accuracy because of the reason mentioned above for the description of $\{(i_1+i_2)-i_s\}$ *vs.* t relation at these overvoltages. The broken line in Fig. 8 shows the supposed theoretical value derived by MATSUDA,[2)] and it coincides with the experimental line in the large overvoltage region.

Fig. 9 shows the differential capacity C *vs.* η curve; the values of C at various η can be obtained by differentiation on the figure in Fig. 8, and by inserting the values into Eq. (17).

The curve has a minimum value smaller than C_k and a maximum value larger than $2C_k$ at about -0.15 V and -0.18 V of η respectively. The curve has also a fixed C_k value of 18 μF/cm^2 in the range of η more negative than 0.25 V.

Discussion

MATSUDA and HORIUTI[3)] have fully discussed the dependence of Tafel's constant $\tau=(RT/\boldsymbol{F})(\partial \log i_s/\partial\eta)$ on η, for the cases of the slow discharge and electrochemical mechanism. They have concluded that τ of the slow discharge mechanism can never exceed 1 throughout the whole region of overvoltage, whereas τ of the electrochemical mechanism, particularly when there is little adsorption of H_2^+(a) on the electrode, takes the value $\tau=2-\alpha$ where $0<\alpha<1$; and when the surface coverage θ of H_2^+(a) is large, τ takes the value $1-\alpha$.

MATSUDA has derived the differential capacity C of the mercury hydrogen electrode on the basis of the electrochemical mechanism. He deduced that (I) C is minimum at the point of zero charge and (II) C approaches C_k with increase of overvoltage. He inferred further that (III, a) in the presence of H_2^+(a), C passes through at least one maximum higher than $2C_k$ before tending to C_k, whereas (III, b) in the absence of H_2^+(a), C increases from a value smaller than C_k monotonously to approach C_k.

Fig. 10 shows the comparison of the experimental results of C *vs.* η relations with the theoretical conclusions of MATSUDA. Curve a of the present work is in good agreement with the suppositional curve e of the theory.

Curve b has the same feature as a and e but the value is nearly twice. The discrepancy can be explained as follows: curve b was obtained in a large cell in which the mercury electrode level was changed for the purpose of creating new electrode surface. This new electrode surface area was determined only by the geometry of the cell. In view of the determination of the surface area in the present work, the real electrode area of MITUYA's former work[1]

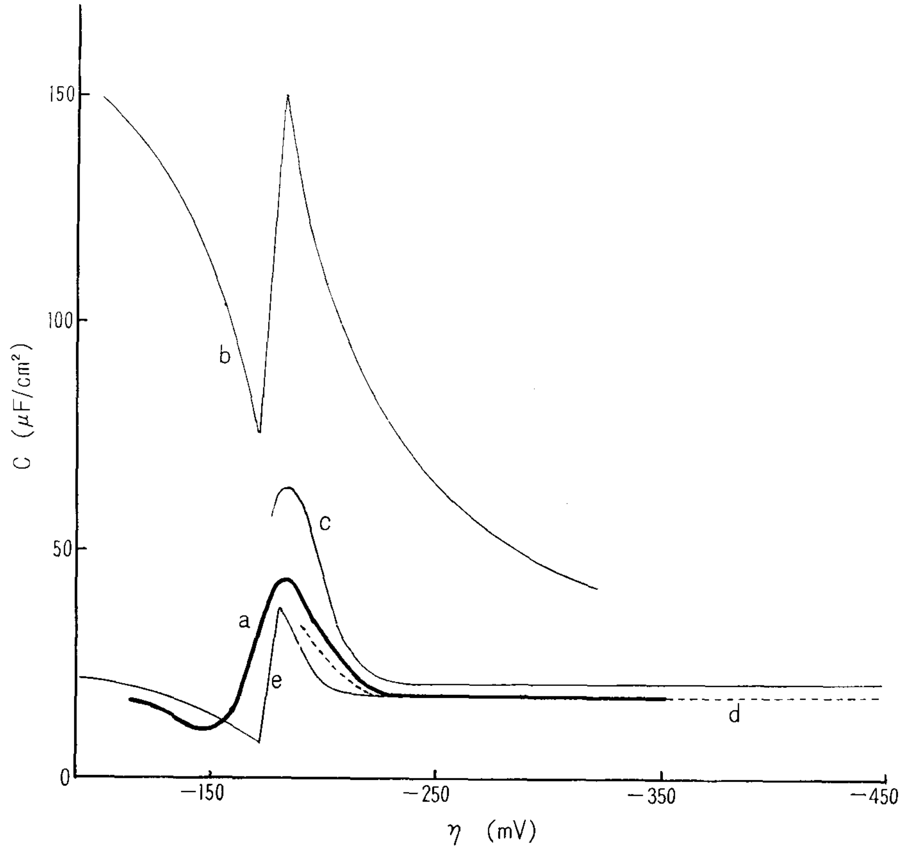

Fig. 10. Comparison of experimental results of C vs. η relation with theoretical curve.

a: present work; b: MITSUYA,[1] 0.1 N HCl; c: PHILPOT,[5] 0.16 N HCl; d: ENYO,[6] 0.1N HCl; e: theoretical curve[2] (being drawn supposedly).

should have been much larger than the calculated value from geometry.*) It is shown in the present work that even in a rest capillary tube, the real area is 1.3 times larger than the calculated value. It may be concluded that curve b should be reduced to nearly half the value of C at the same η value.

The agreement between the theory and our experiments clearly suggests that the electrochemical mechanism is operative on the mercury hydrogen electrode and the slow discharge mechanism is not, as has long been maintained by HORIUTI and collaborators.

Acknowledgement

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*) The electrode area of the cell, used by MITSUYA, was changed by a glass prism which had been inserted into the mecury electrode: when the cell was inclined, the prism was immersed into the mercury and gave a change in the mercury surface area at the part in contact with the prism. The rate of variation of the electrode area was calculated from the geometry of the prism. In view of the present results, we suppose that the rate of the variation of the electrode area in MITUYA's cell was larger than the reported value because of its complicatedness.