HOKKAIDO UNIVERSITY

Title	ON THE DIFFERENTIAL CAPACITIES OF IRON AND NICKEL HYDROGEN ELECTRODES OBSERVED BY PAST AND JOFA
Author(s)	MATSUDA, Akiya
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 8(2), 151-156
Issue Date	1960-10
Doc URL	https://hdl.handle.net/2115/24724
Type	departmental bulletin paper
File Information	8(2)_P151-156.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

ON THE DIFFERENTIAL CAPACITIES OF IRON AND NICKEL HYDROGEN ELECTRODES OBSERVED BY PAST AND JOFA

By

Akiya MATSUDA*)

(Received July 1, 1960)

PAST and JOFA[1),2)] have recently studied the decay curve, *i.e.* the abrupt change of overvoltage with time when the polarization current in a steady state is switched off, and deduced the differential capacity from the initial part of the decay curve**). They have thus obtained the relations between the differential capacity C and the overvoltage η in the cathodic polarization region on mercury, iron and nickel. According to their results, the differential capacity of a mercury hydrogen electrode in sulphuric acid solution remains at a constant equal to that of the HELMHOLTZ layer independent of change of η from -0.975 v to -1.298 v, while that of iron decreases monotonously from 400 $\mu\phi/cm^2$ to 100$\mu\phi/cm^2$ with decrease of η from -0.4 v to -0.6 v in 1N KOH solution, or from 60 $\mu\phi/cm^2$ to 20 $\mu\phi/cm^2$ with decrease of η from -0.375 v to -0.5 v in 1N H_2SO_4 solution, and that of nickel does similarly from 80 $\mu\phi/cm^2$ to 20 $\mu\phi/cm$ with decrease of η from -0.2 v to -0.6 v in alkaline solutions.

PAST and JOFA have concluded from the results of a mercury hydrogen electrode on the basis of the slow discharge mechanism of FRUMKIN[3)] that there exists no adsorbed hydrogen atom on a mercury electrode even in such low η as -1.3 v, and from the dependence of C upon η of iron and nickel hydrogen electrodes that neither the slow discharge mechanism nor the catalytic mechanism could account for the results on the basis of the classical kinetics and the semilog isotherm of an adsorbed hydrogen atom derived experimentally by FRUMKIN and SLYGIN[4)] and theoretically by TEMKIN and PYZHEV[5)].

The present author[6)] has previously shown on the basis of the electrochemical mechanism that the differential capacity of a mercury hydrogen electrode tends to that of the HELMHOLTZ layer with decrease of the electrode potential and remains constant there in accordance with PAST and JOFA's experimental results, where the electrode surface is, however, nearly fully occupied by

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

**) See Appendix.

hydrogen molecule ions.

The other results of PAST and JOFA are of extreme interest with regard to the concentration of hydrogen intermediates. The present paper is devoted to the explanation of these experimental results on the basis of the catalytic mechanism which was developed by HORIUTI[7] based on the homogeneous plane theory allowing for the repulsive interaction potential among adsorbed hydrogen atoms.

Differential Capacity of Hydrogen Electrode in Catalytic Mechanism

The hydrogen evolution reaction consists of the following two elementary steps in the catalytic mechanism

$$H^+ + e \longrightarrow H(a), \qquad (I)$$

$$2H(a) \longrightarrow H_2, \qquad (II)$$

where H(a) is the adsorbed hydrogen atom. The first step is assumed to be at equilibrium and the second determining the rate.

The model of the hydrogen electrode is the same as described in the previous work[6], where the specific adsorption occurs on a plane P parallel to the electrode surface C and ions in solution are distributed from just outside P towards the bulk of solution in thermal equilibrium under the electrostatic potential of the diffuse layer. In the present work it is postulated that H(a) is the only species specifically adsorbed.

The differential capacity C is expressed on the basis of the catalytic mechanism in accordance with the model described above, as

$$C = C_1 - \frac{GF}{N_A}\frac{d\theta}{d\eta}, \qquad (1)$$

where C_1 is the differential capacity of the double layer, θ the surface coverage of H(a), G the number of adsorption sites of the electrode surface per unit area, F the FARADAY and N_A the AVOGADRO number respectively. The C_1 is expressed in accordance with Eq. (9.b) in the previous work[6] as

$$\frac{1}{C_1} = \frac{1}{k} + \frac{1}{C_2}\left(1 + \frac{ds}{dq}\right), \qquad (2.a)$$

where k is the capacity of the HELMHOLTZ layer, C_2 that of the diffuse layer and s or q the charge density on P or C respectively. In the catalytic mechanism s equals zero because of absent charge of H(a), so that

$$\frac{1}{C_1}=\frac{1}{k}+\frac{1}{C_2}\,. \tag{2. b}$$

The second term in (1) is the differential capacity due to the change of θ with η, which is given on the ground of the equilibrium of (1) from the adsorption isotherm of H(a)[8], *i. e.*

$$-RT\ln\frac{\theta}{1-\theta}=\varepsilon^{\mathrm{H(a)}}-\mu^{\mathrm{H(a)}}\,, \tag{3. a}$$

where $\varepsilon^{\mathrm{H(a)}}$ is the reversible work required to bring up H(a) to a definite preliminary evacuated adsorption site from the standard state[9),10)]. The $\varepsilon^{\mathrm{H(a)}}$ thus defined is expressed in terms of the potential $uRT\theta$ due to the repulsive interaction among H(a)'s, assumed to be proportional to θ with the proportionality constant uRT, as

$$\varepsilon^{\mathrm{H(a)}}=\varepsilon_0^{\mathrm{H(a)}}+uRT\theta\,. \tag{3. b}$$

The chemical potential $\mu^{\mathrm{H(a)}}$ of H(a) is expressed on account of the equilibrium of (I) as

$$\mu^{\mathrm{H(a)}}=\mu^{\mathrm{H^+}}+\mu^e\,, \tag{3. c}$$

where $\mu^{\mathrm{H^+}}$ and μ^e are the chemical potentials of H^+ ion in solution and metal electron respectively. The overvoltage η is expressed by definition as

$$\eta=\frac{1}{F}(\mu_0^e-\mu^e)\,, \tag{3. d}$$

where μ_0^e is μ^e at equilibrium, *i. e.* that of the reversible hydrogen electrode in the same environments. Substituting (3. b), (3. c) and (3. d) into (3. a) we have

$$-RT\left(\ln\frac{\theta}{1-\theta}+u\theta\right)=\varepsilon_0^{\mathrm{H(a)}}-\mu^{\mathrm{H^+}}-\mu_0^e+F\eta\,. \tag{4. a}$$

The adsorption isotherm of H(a) is given from (4. a) for constant $\mu^{\mathrm{H^+}}$ in the differential form as, *i. e.*

$$-\delta\theta=\frac{F}{RT}\,\frac{\theta(1-\theta)}{1+u\theta(1-\theta)}\,\delta\eta\,. \tag{4. b}$$

Putting $\frac{d\theta}{d\eta}$ from (4. b) into (1) we have

$$C=C_1+fg\,, \tag{5}$$

where

$$f\equiv\frac{\theta(1-\theta)}{1+u\theta(1-\theta)}\,,\qquad g\equiv\frac{GF^2}{N_ART}\,. \tag{6. a), (6. b)}$$

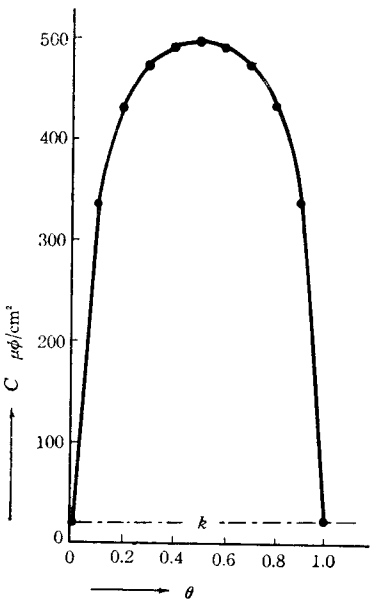

Fig. 1. The relation between the differential capacity C and the surface coverage θ.

The C_2 in (2.b) is far larger than k[6] in concentrated acidic or alkaline solutions as in the case of PAST and JOFA's experiment, so that

$$C_1 = k\,, \tag{7}$$

hence from (5) and (7)

$$C = k + fg\,. \tag{8}$$

Assuming here $G = 10^{15}$, $u = 10$ and $k = 20\,\mu\phi/\mathrm{cm}^2$, the change of C with θ is expressed as shown in Fig. 1.

It is readily seen from (8) and (6) that:

i) at $\theta = 0$ or 1,

$$f = 0\,,\quad C = k\,, \tag{9.a), (9.b)}$$

ii) when $\theta \ll 1$,

$$f = \theta\,,\quad C = k + g\theta\,, \tag{10.a), (10.b)}$$

iii) at $\theta = 1/2$, f is maximum and

$$f_{\max} = \frac{1}{u+4}\,,\quad C_{\max} = k + \frac{g}{u+4}\,, \tag{11.a), (11.b)}$$

iv) when $u\theta(1-\theta) \gg 1$,

$$f = \frac{1}{u}\,,\quad C = k + \frac{g}{u}\,. \tag{12.a), (12.b)}$$

Eqs. (10.b) and (12.b) are equivalent to the corresponding equations respectively derived on the basis of the calssical kinetics and the semilog isotherm of H(a).

It can be seen from (4) that θ tends monotonously to zero with increase of η and to unity with decrease of η. It follows that the differential capacity approaches that k of the HELMHOLTZ layer with increase or decrease of η, passing through a maximum given by (11.b) at an intermediate value of η where θ equals 1/2.

Thus it can be concluded that the change of the differential capacities of nickle and iron with η obtained by PAST and JOFA in the cathodic polarization region is duly attributed to the catalytic mechanism when θ is larger than 1/2*).

*) The TAFEL constant of nickel hydrogen electrode was calculated by HORIUTI on the basis of the catalytic mechanism at ca. 0.5 in the region of θ from 0.4 to 0.9[7].

It can also be expected that the differential capacity of iron or nickel decreases with increase of η tending to k in a more anodic polarization region than that applied by PAST and JOFA, although two parameters G and u involved in (8) cannot be determined definitely at present from their experimental results, where the absolute values of C vary with preliminary treatments of electrode metals and with solutions used.

Appendix

Determination of Differential Capacity from Charging Curve and Decay Curve

The differential capacity of a hydrogen electrode is determined as follows. The increment $\delta\eta$ of η within the time δt after switching the steady current of density i_0 to another constant current density i is expressed as

$$C\delta\eta = (i-i_r)\,\delta t\,, \qquad \text{(i)}$$

where i_r is the Faradic current density. Dividing (i) by δt, we have at $t=0$,

$$C\left(\frac{d\eta}{dt}\right)_{t=0} = i-i_0\,, \qquad \text{(ii)}$$

inasmuch as i_r equals i_0 at $t=0$.

If $i=0$, we have from (ii)

$$C\left(\frac{d\eta}{dt}\right)_{t=0} = -i_0\,. \qquad \text{(iii)}$$

The differential capacity of hydrogen electrode in a steady state can be determined from (iii), where $\left(\frac{d\eta}{dt}\right)_{t=0}$ is measured from the initial part of η, t curves after switching off the steady current, as studied by PAST and JOFA[1),2)].

If $i_r=0$ instead, we have from (i)

$$C\delta\eta = i\delta t\,. \qquad \text{(iv)}$$

Since $i\delta t$ equals the quantity of electricity δQ passed through the electrode within the time δt, we have

$$C = \frac{dQ}{d\eta}\,. \qquad \text{(v)}$$

The relation between Q and η in this case is given from the charging curve which has been extensively studied by FRUMKIN and SLYGIN[4)]. The differential capacity of hydrogen electrode is thus given experimentally from the charging curve and the decay curve.

Acknowledgement

The author is much indebted to Professor Juro HORIUTI for his helpful discussions and encouragement in the course of this work.

References

1) V. E. PAST and Z. A. JOFA, J. Phys. Chem. USSR, **33**, 913 (1959).
2) V. E. PAST and Z. A. JOFA, *ibid.* **33**, 1230 (1959).
3) A. FRUMKIN, Z. physik. Chem. **A 164**, 121 (1933).
4) A. SLYGIN and A. FRUMKIN, Acta Physicochim. USSR, **3**, 791 (1935).
5) M. TEMKIN and V. PYZHEV, *ibid.* **12**, 327 (1940).
6) A. MATSUDA, this Journal, 8, 29 (1960).
7) J. HORIUTI, this Journal, **4**, 55 (1956).
8) A. MATSUDA and J. HORIUTI, this Journal, **6**, 231 (1958).
9) J. HORIUTI, this Journal, **1**, 8 (1958).
10) J. HORIUTI, this Journal, **3**, 52 (1954).