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

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(Received July 1, 1960)

PAST and JOFA 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 \( \eta \) 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 \( \eta \) from \(-0.975\) to \(-1.298\) V, while that of iron decreases monotonously from \(400 \mu F/cm^2\) to \(100 \mu F/cm^2\) with decrease of \( \eta \) from \(-0.4\) to \(-0.6\) V in 1N KOH solution, or from \(60 \mu F/cm^2\) to \(20 \mu F/cm^2\) with decrease of \( \eta \) from \(-0.375\) to \(-0.5\) V in \(1N\) \(H_2SO_4\) solution, and that of nickel does similarly from \(80 \mu F/cm^2\) to \(20 \mu F/cm^2\) with decrease of \( \eta \) from \(-0.2\) 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 that there exists no adsorbed hydrogen atom on a mercury electrode even in such low \( \eta \) as \(-1.3\) V, and from the dependence of \( C \) upon \( \eta \) 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 and theoretically by TEMKIN and PYZHEV.

The present author 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...
Differential Capacity of Hydrogen Electrode in Catalytic Mechanism

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

\[
\begin{align*}
H^+ + e^- \rightarrow H(a), & \quad (I) \\
2H(a) \rightarrow H_2, & \quad (II)
\end{align*}
\]

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

\[
C = C_i - \frac{GF}{N_A} \frac{d\theta}{dq},
\]

where \(C_i\) is the differential capacity of the double layer, \(\theta\) 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 \(C_i\) is expressed in accordance with Eq. (9. b) in the previous work\(^6\) as

\[
\frac{1}{C_i} = \frac{1}{k} + \frac{1}{C_2} \left(1 + \frac{ds}{dq}\right),
\]

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
\[
\frac{1}{C_1} = \frac{1}{k} + \frac{1}{C_2} .
\]  

(2. b)

The second term in (1) is the differential capacity due to the change of \( \theta \) with \( \gamma \), which is given on the ground of the equilibrium of (1) from the adsorption isotherm of \( \text{H}(a) \), \( i.e. \)

\[-RT \ln \frac{\theta}{1-\theta} = \epsilon_{\text{H}(a)^{\pm}} - \mu_{\text{H}(a)} ,
\]

(3. a)

where \( \epsilon_{\text{H}(a)^{\pm}} \) is the reversible work required to bring up \( \text{H}(a) \) to a definite preliminary evacuated adsorption site from the standard state \( \text{H}(a)^{\pm} \). The \( \epsilon_{\text{H}(a)^{\pm}} \) thus defined is expressed in terms of the potential \( uRT \theta \) due to the repulsive interaction among \( \text{H}(a)^{\pm} \)’s, assumed to be proportional to \( \theta \) with the proportionality constant \( uRT \), as

\[\epsilon_{\text{H}(a)^{\pm}} = \epsilon_{\text{H}(a)^{\pm}} + uRT \theta .\]

(3. b)

The chemical potential \( \mu_{\text{H}(a)} \) of \( \text{H}(a) \) is expressed on account of the equilibrium of (1) as

\[\mu_{\text{H}(a)} = \mu_{\text{H}^{\pm}} + \mu^{\varepsilon} ,\]

(3. c)

where \( \mu_{\text{H}^{\pm}} \) and \( \mu^{\varepsilon} \) are the chemical potentials of \( \text{H}^{\pm} \) ion in solution and metal electron respectively. The overvoltage \( \gamma \) is expressed by definition as

\[\gamma := \frac{1}{F} \left( \mu^{\varepsilon} - \mu^{\varepsilon} \right) ,\]

(3. d)

where \( \mu^{\varepsilon} \) is \( \mu^{\varepsilon} \) 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

\[-RT \left( \ln \frac{\theta}{1-\theta} + u\theta \right) = \epsilon_{\text{H}(a)^{\pm}} - \mu_{\text{H}^{\pm}} - \mu^{\varepsilon} + F\gamma .\]

(4. a)

The adsorption isotherm of \( \text{H}(a) \) is given from (4. a) for constant \( \mu_{\text{H}^{\pm}} \) in the differential form as, \( i.e. \)

\[-\delta \theta = \frac{F}{RT} \frac{\theta (1-\theta)}{1 + u\theta (1-\theta)} \delta \gamma .\]

(4. b)

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

\[C = C_1 + f g ,\]

(5)

where

\[f = \frac{\theta (1-\theta)}{1 + u\theta (1-\theta)} , \quad g = \frac{GF^2}{N_p RT} .\]

(6. a), (6. b)
The $C_s$ in (2.2) is far larger than $k^o$ in concentrated acidic or alkaline solutions as in the case of PAST and JOFA's experiment, so that

$$C_s = k,$$  \hfill (7)

hence from (5) and (7)

$$C = k + f g.$$  \hfill (8)

Assuming here $G = 10^{18}$, $u = 10$ and $k = 20 \mu F/cm^2$, the change of $C$ with $\theta$ is expressed as shown in Fig. 1.

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

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

$$f = 0, \quad C = k,$$  \hfill (9. a), (9. b)

ii) when $\theta \ll 1$,

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

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

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

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

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

Eqs. (10. b) and (12. b) are equivalent to the corresponding equations respectively derived on the basis of the classical kinetics and the semi-log isotherm of H(a).

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

Thus it can be concluded that the change of the differential capacities of nickel and iron with $\eta$ obtained by PAST and JOFA in the cathodic polarization region is duly attributed to the catalytic mechanism when $\theta$ 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 $\theta$ from 0.4 to 0.9.)
Differential Capacities of Iron and Nickel Hydrogen Electrodes Observed by Past and Jofa

It can also be expected that the differential capacity of iron or nickel decreases with increase of $\gamma$ 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 $\eta$ within the time $\Delta t$ after switching the steady current of density $i_o$ to another constant current density $i$ is expressed as

$$C \Delta \eta = (i - i_o) \Delta t,$$

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

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

inasmuch as $i_e$ equals $i_o$ at $t=0$.

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

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

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 $\eta, t$ curves after switching off the steady current, as studied by PAST and JOFA$^{(n,p)}$.

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

$$C \Delta \eta = i \Delta t. \quad (\text{iv})$$

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

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

The relation between $Q$ and $\eta$ in this case is given from the charging curve which has been extensively studied by FRUMKIN and SLYGIN$^{(n)}$. 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.

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