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TRACER STUDIES ON THE ELEMENTARY REACTION RATES OF THE HYDROGEN ELECTRODE ON NICKEL IN THE CATHODIC REGION^{*})

By

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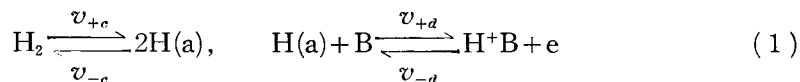
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Introduction

Mechanistic studies of the hydrogen electrode reaction (*her*), $H_2 + 2B = 2H^+B + 2e$ ($B = H_2O$ or OH^-), were frequently based on the kinetics of the overall reaction rate¹⁾, *e.g.*, the Tafel slope. Such techniques are, however, insufficient to understand detailed mechanism of the reaction; tracer and transient techniques are powerful tools to have a closer look of the mechanism. Recent investigations²⁾ with deuterium tracer on various metals have shown that (i) the *her* at the reversible potential consists of two steps, dissociation of H_2 to hydrogen adatom, $H(a)$, and (ionized) dissolution of the latter into solution, and (ii) exchange rates of the steps are of comparable magnitudes with each other. For complete description of the kinetics, it is thus necessary to resolve the overall reaction rate into the rates of the individual steps and then to study their kinetics. The present work concerns the analysis in the cathodic region on nickel.

Determination of the step rates

We will discuss the isotopic composition of the hydrogen gas during the exchange reaction which takes place through the *her* in the system consisting of deuterium gas, an abundant amount of electrolytic solution in light water, and a test electrode. The *her* on Ni takes place through the following two steps²⁾,



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where v_{+c} etc. denote uni-directional rates of the steps specified. Based on the steady state condition, the following relations can be derived (suffix 0 signifies the initial value),

$$V_- = -V \ln(X_0/X) / \ln(N_{g,0} - Vt) / N_{g,0} \quad (2)$$

$$\left[\frac{X^{\text{HD}}}{X} - 2 + \frac{2f_c^2 X}{f_c^2 - 1} \right] X^{-f_c} = \left[\frac{X_0^{\text{HD}}}{X_0} - 2 + \frac{2f_c^2 X_0}{f_c^2 - 1} \right] X_0^{-f_c} \quad (3)$$

where N_g is the total number of hydrogen molecules, X the deuterium atomic fraction in the hydrogen gas, X^{HD} the mole fraction of HD, V the net rate (negative in the cathodic region), t time, $V_- \equiv v_{-c}v_{-d}/(2v_{-c} + v_{+d})$ the backward overall uni-directional rate, and $f_c \equiv 2v_{+c}/v_{-d}$. Thus, both V_- and f_c are calculated from X and X^{HD} .

Individual step rates are then obtained utilizing the following relations: $v_{-c} = V_-(f_c + 1)$, $v_{+c} = V + v_{-c}$, $v_{-d} = 2v_{+c}/f_c$, and $v_{+d} = 2V + v_{-d}$.

Experimental

The exchange reaction was conducted in a closed gas-circulation system. Nickel wire in the form of a net (1300 cm² apparent area) served as the test electrode. A Pd-Ag alloy thimble was placed in a separated compartment and its outer face used as the counter electrode; its inside was connected with a hydrogen reservoir. Deuterium gas was circulated by means of an all-glass pump, while the test electrode was polarized with a constant current. Sample gases were analyzed by means of a gas-chromatograph.

Results

The hydrogen pressure rose gradually with time in the constant volume system. In order to maintain the pressure increase under a tolerable level, the reaction time was always chosen so that $1 - Vt/N_{g,0}$ did not exceed 1.2 except a few cases at high overpotentials.

(I) Reaction Route

We first examined if the rate expressions derived above can interpret the experimental data. If the reaction obeys the route given in eq. (1), f_c in eq. (3) should be constant independent of X (the isotope effect in the direction of hydrogen ionization is small^{2,3)}). Indeed, f_c was found constant at $-\eta = 0 \sim 100$ mV. Accordingly, this route is confirmed to be operative in the cathodic region.

(II) *Dependence of Rates upon η*

We start the exchange reaction with pure deuterium and end with X only slightly reduced from X_0 . The ratio X^{H_2}/X^{HD} was larger for larger $-\eta$.

(A) The overall reaction rates

The uni-directional rate V_- evaluated is plotted in Fig. 1 in current density unit, $i_- \equiv 2FV_-/AN_A$ where A is the surface area and N_A the Avogadro's number; i denotes the applied c.d. The relation between $\log i_-$ and $-\eta$ did not give a good linearity at low overpotentials. The slope was roughly 100 mV, but it became 120 mV at higher overpotentials. At $-\eta > 50$ mV, i_- practically agreed with $-i$.

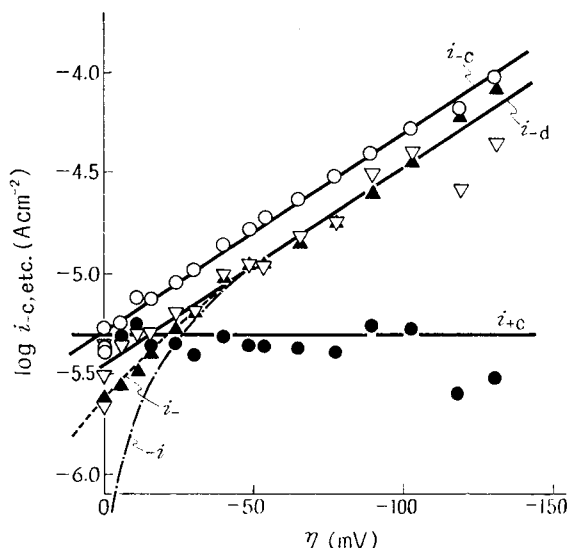


Fig. 1. Overpotential dependence of the overall reaction rate and step rates on Ni cathode, 20°C. $P = 18.5 \pm 0.2$ cmHg

(B) Dependence of f_c upon η and hydrogen pressure P

f_c was found close to unity at the reversible potential and $\log f_c$ decreased linearly with $-\eta$ with about 100 mV slope. At a fixed η , f_c depended upon P with the power of 0.7, irrespective of the η value.

(C) Dependence of the step rates upon η

The step rates obtained are shown in Fig. 1, in c.d. units. $\log i_{+c}$ was constant independent of η , whereas $\log i_{-c}$ linearly depended upon $-\eta$ with about 100 mV slope. On the other hand, $\log i_{-d}$ depended linearly upon η with the same slope as i_{-c} . No reliable value of i_{+d} was obtained.

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(D) Pressure dependence of the step rates

The step rates under various pressures are shown in Fig. 2. The dependence of i_{-c} upon P was with the power of 0.6 at $-\eta=35$ mV, but the value diminished with $-\eta$. Those for i_{+c} and i_{-a} were unity and 0.3, respectively, irrespective of η .

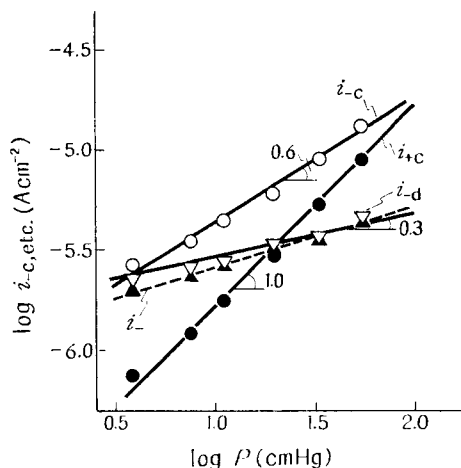


Fig. 2. Pressure dependences of the step rates on Ni, 20°C. $-\eta=34.5 \pm 0.8$ mV.

(E) Affinities associated with the steps

These can be calculated by the following relations⁴⁾,

$$\eta_c = (RT/2F) \ln (v_{+c}/v_{-c}), \quad \eta_a = (RT/F) \ln (v_{+a}/v_{-a}) \quad (4 \text{ c, d})$$

and are related to various chemical potentials as

$$\mu^{\text{H}_2} - 2\mu^{\text{H}} = 2F\eta_c, \quad \mu^{\text{H}} + \mu^{\text{B}} - \mu^{\text{H}^+\text{B}} - \mu^e = F\eta_a \quad (5 \text{ c, d})$$

The step rates directly yield η_c , but not η_a because of lack of reliable data of i_{+a} . The η_c shared about 30% of η at 20 cmHg P , and the fraction increased with decrease of P .

Discussion

(I) *Kinetics of Step c*

Under a fixed P , η_c is related to a_{H} , the activity of H(a),

$$Fd\eta_c = -d\mu^{\text{H}} = -RTd \ln a_{\text{H}} \quad (6)$$

Assuming that electrode potential does not directly influence upon the rates

of step c , the reaction orders $\zeta_{+c}(\text{H})$ and $\zeta_{-c}(\text{H})$ with respect to $\text{H}(\text{a})$ are given by,

$$\begin{aligned} -(RT/F)(d \ln i_{+c}/d\eta_c) &= \zeta_{+c}(\text{H}), \\ -(RT/F)(d \ln i_{-c}/d\eta_c) &= \zeta_{-c}(\text{H}) \end{aligned} \quad (7)$$

The slopes of η_c vs. $\log i_{+c}$ and $\log i_{-c}$ were ∞ and 30 mV, respectively, or we find $\zeta_{+c}(\text{H}) = 0$ and $\zeta_{-c}(\text{H}) = 2$. These are well acceptable for step c , provided that the surface coverage of $\text{H}(\text{a})$ is much smaller than unity⁵⁾. The dependencies of i_{+c} and i_{-c} upon P can also be explained on this model.

(II) Kinetics of Step d

Taking a_{H} and electrode potential, ϕ , as variables, we write, under constant P and in a fixed solution composition,

$$-\frac{RT}{F} \frac{d \ln i_{-d}}{d\phi} = \alpha_{-d} - \zeta_{-d}(\text{H}) - \frac{RT}{F} \frac{d \ln a_{\text{H}}}{d\phi} \quad (8)$$

where $\alpha_{-d} \equiv -(RT/F)(\partial \ln i_{-d}/\partial \phi)$ represents direct influence of ϕ upon i_{-d} and $\zeta_{-d}(\text{H})$ is the reaction order with respect to $\text{H}(\text{a})$. The lhs of eq. (8) was found 0.58 (Fig. 1) independent of P , whereas $-(RT/F)(d \ln a_{\text{H}}/d\phi) = d\eta_c/d\eta$ was strongly dependent upon P , being 0.3 at 20 cmHg. The results indicate that $\zeta_{-d}(\text{H})$ is small and hence $\alpha_{-d} \simeq 0.6$. These are consistent with the charge transfer model for step d . Further, the observation $(d \ln v_{-d}/d \ln P)_\eta = 0.3$ is also explicable on this model. However, the fact that i_{-d} at $\eta=0$ is independent of solution pH in the range of pH 13.5~7²⁾ would not be explained on the basis of the charge transfer model. It is probably necessary to investigate the rate of step d by means of other methods as well, *e.g.*, a transient method. It is to be noted that the rate of step d determined by means of deuterium tracer represents the rate of the process between $\text{H}(\text{a})$ and H^+B , and it does not necessarily imply a pure charge transfer step.

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