



HOKKAIDO UNIVERSITY

Title	EXCHANGE RATE OF ELECTRON TRANSFER STEP OF HYDROGEN EVOLUTION REACTION ON GOLD
Author(s)	SASAKI, Takeshi; MATSUDA, Akiya
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 21(2), 157-161
Issue Date	1974-09
Doc URL	https://hdl.handle.net/2115/24956
Type	departmental bulletin paper
File Information	21(2)_P157-161.pdf



Short Note

EXCHANGE RATE OF ELECTRON TRANSFER STEP OF HYDROGEN EVOLUTION REACTION ON GOLD

By

Takeshi SASAKI* and Akiya MATSUDA**)

(Received Dec. 3, 1973)

The mechanism of the hydrogen evolution reaction (h.e.r.) on gold has been discussed by several authors mainly based on the Tafel slope of the polarization curve in steady states¹⁻⁷⁾. Experimental results on the Tafel slope, however, are noted for their wide variations among different authors. On the other hand, according to the theoretical calculation of HORIUTI *et al.*^{8,9)} the expected value of the Tafel slope of the h.e.r. may vary from $2 \times 2.3 RT/F$ to $2.3 RT/2F$ depending upon the mutual interaction of the intermediate species including the activated complex of the reaction, even if the reaction proceed through the single catalytic or electrochemical mechanism. Therefore the Tafel slope cannot necessarily be regarded as a criterion for the mechanism of the h.e.r.

It is desirable for the elucidation of the mechanism of the h.e.r. to divide the overall reaction into its constituent elementary steps by some experimental method and to compare directly their rates. The present report is concerned with the exchange rate of the electron transfer step of the h.e.r. on gold in aqueous sulfuric acid and sodium hydroxide solutions which can be determined separately from other steps by means of a galvanostatic transient method.

The differential capacity C_D at the metal-solution interface and the time constant τ_{10} and the exchange current density i_{10} of the electron transfer step of the h.e.r. were determined separately by a galvanostatic transient method, as reported previously from the initial stage of the overvoltage-time curves based on the following equations^{10,11)},

$$\ln(-i/i_0) = (t/\tau_{10}) + \ln C_D, \quad (1)$$

$$\tau_{10} = C_D r_{10}, \quad (2)$$

$$r_{10} = (RT/F)(1/i_{10}), \quad (3)$$

* Department of Metallurgical Engineering, Faculty of Engineering, Hokkaido University, Sapporo.

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

T. SASAKI and A. MATSUDA

where i is the polarizing current density, $\dot{\eta}$ the time derivative of overvoltage, r_{10} the reaction resistance of the electron transfer step at the reversible potential, and R , T and F are in their usual meaning.

Sulfuric acid was prepared from SO_3 gas distilled under vacuum and sodium

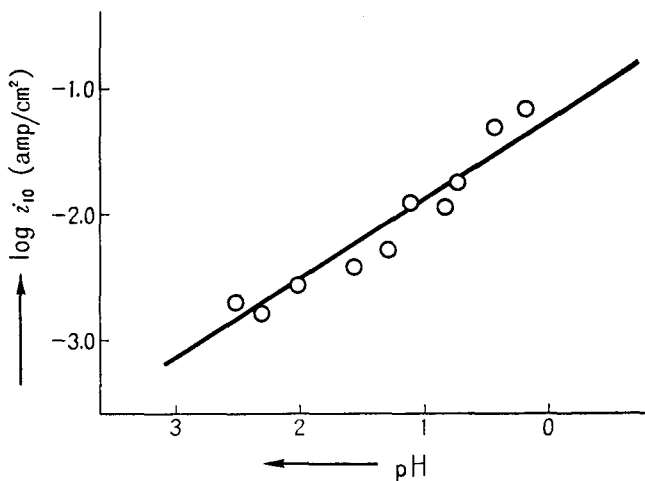


Fig. 1. The relation between the exchange rate of the electron transfer step of the h.e.r. on gold and pH in sulfuric acid.

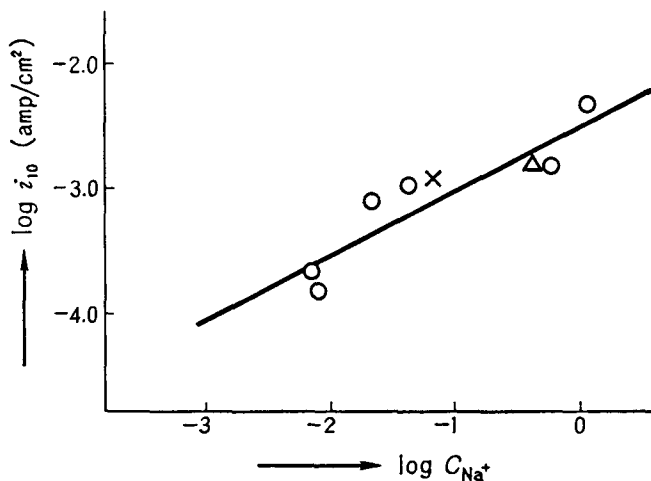


Fig. 2. The relation between the exchange rate of the electron transfer step of the h.e.r. on gold and the concentration of Na^+ ion in alkaline solutions, (○) pure NaOH, (×) and (△) mixed solutions of NaOH+ Na_2SO_4 of pH 10.8 and 12.1 respectively.

Exchange Rate of Electron Transfer Step of Hydrogen Evolution Reaction on Gold

hydroxide was purified from analytically pure grade by recrystallization in water distilled in quartz glass vessel. Gold foils degassed or gold films prepared by evaporation under vacuum were put in the cell of quartz glass as the test, reference and counter electrodes respectively. The change of overvoltage which was caused by a constant current pulse was observed at 25°C under strong stirring of solution by forced hydrogen bubbles.

Figs. 1 and 2 show respectively the exchange current of the electron transfer step obtained on the basis of Eqs. 1.2 and 3 from the $\eta-t$ curves around the reversible potential in acid and alkaline solutions. The current density in these Figures is assigned to the true unit area of the electrode surface, as determined on the basis of the double layer capacitance.

As seen from Fig. 1, $\log i_{10}$ in sulfuric acid changes almost linearly with pH of the solution with a gradient 0.6 ± 0.15 . This suggests that the electron transfer step in sulfuric acid consists of the discharge of hydronium ion. The exchange rate of the overall reaction i_0 in sulfuric acid determined from the steady state $i_s-\eta_s$ relation around the reversible potential was found to be nearly constant at $(4.3 \pm 0.8) \times 10^{-4}$ A/cm² in the range of the concentration of the solution from 1.3 to 3.2×10^{-3} N, as exemplified in Fig. 3. This value of i_0 is quite close to that reported by SCHULDINER and HOARE²⁾. It can be seen from the comparison of this value of i_0 with those of i_{10} in Fig. 1 that the exchange rate of the electron transfer step is larger than that of the overall reaction by about an order of magnitude even in the most dilute solution studied.

In alkaline solutions i_{10} was determined in pure aqueous NaOH and in mixed solutions of NaOH+Na₂SO₄ in order to find whether i_{10} changed depending upon pH or Na⁺ ion concentration. Fig. 2 shows $\log i_{10}$ plotted against $\log C_{\text{Na}^+}$ in pure NaOH and mixed solutions. As seen from Fig. 2, $\log i_{10}$ linearly changes with $\log C_{\text{Na}^+}$ with a gradient of 0.5 ± 0.1 independent of pH of the solution. It may be concluded from this fact that the electron transfer step in alkaline solutions proceeds through the discharge of sodium ion as in the case of platinum¹⁰⁾ and nickel¹²⁾.

The exchange rate of the overall reaction in alkaline solutions is scattered in the range 10^{-6} – 10^{-8} A/cm² because of the change of the surface condition of the electrode with time during the measurements of the polarization curve. However it should be stressed that the exchange rate of the electron transfer step is not affected by the change of the surface condition of the electrode in alkaline solutions.

It can be seen from the comparison of Figs. 1 and 2 that the exchange rate of the discharge of hydronium ion is faster than that of sodium ion by about an order of magnitude. In any case the electron transfer step of the h.e.r. on

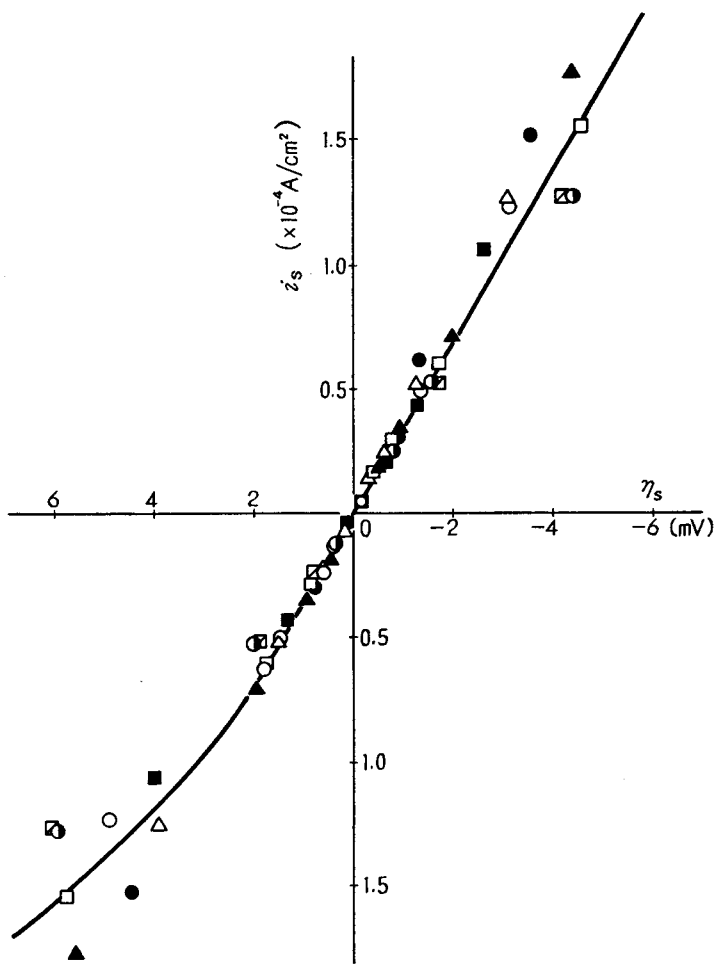


Fig. 3. The steady state i_s - η_s relation of the h.e.r. on gold in sulfuric acid, the concentration, (○)—1.3 N, (\triangle)— 6.7×10^{-1} N, (●)— 1.2×10^{-1} N, (\blacktriangle)— 7.7×10^{-2} N, (\square)— 3.7×10^{-2} N, (\blacksquare)— 1.2×10^{-2} N, (\circ)— 5.3×10^{-3} N, (\diamond)— 3.2×10^{-3} N.

gold cannot be rate-determining at the reversible potential in sulfuric acid or in aqueous sodium hydroxide. A comprehensive study of the gold hydrogen electrode will be reported in a later work.

References

- 1) A. T. KUHN and M. BYRNE, *Electrochim. Acta*, **16**, 391 (1971).
- 2) S. SCHULDINER and J. P. HOARE, *J. phys. Chem.*, 705 (1957).

Exchange Rate of Electron Transfer Step of Hydrogen Evolution Reaction on Gold

- 3) M. BREITER and R. CLAMROTH, *Z. Elektrochem.*, **58**, 493 (1954).
- 4) M. BREITER, H. KAMMERMAIER and C. A. Knorr, *ibid.*, **60**, 454 (1956).
- 5) K. GOSSNER and C. LOEFFLER, *Z. physik. Chem., Frankfurt* **37**, 115 (1963).
- 6) G. M. SCHMID, *Electrochim. Acta*, **12**, 449 (1967).
- 7) E. D. LEVIN and A. L. ROTINYAN, *Elektrokhimiya*, **8**, 240 (1972).
- 8) J. HORIUTI, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **4**, 55 (1956).
- 9) A. MATSUDA and J. HORIUTI, *ibid.*, **6**, 231 (1958).
- 10) A. MATSUDA and R. NOTOYA, *ibid.*, **14**, 165 (1966).
- 11) A. MATSUDA and R. NOTOYA, *ibid.*, **18**, 59 (1970).
- 12) T. OHMORI and A. MATSUDA, *ibid.*, **15**, 201 (1967).