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HYDROGEN ELECTRODE REACTION ON A THIN LAYER OF COPPER AND SILVER DEPOSITED ON PALLADIUM

By

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Abstract

Galvanostatic overpotential rise and decay transients observations were carried out on the electrode of a thin layer of Cu and Ag deposited on a Pd foil substrate. The overpotential components similar to those on Pd electrodes were observed, and their behaviours led to the conclusion that mechanism of the hydrogen electrode reaction on Cu and Ag was the Tafel-Volmer type. Kinetic parameters of the elementary steps were evaluated.

Introduction

It has been demonstrated in earlier reports¹⁻⁴⁾ that galvanostatic overpotential rise and open-circuit decay transients on Pd foil electrode in aqueous solution, both in cathodic and anodic regions, yield important information on the mechanism of the hydrogen electrode reaction (HER). This was essentially based on the peculiar nature of Pd which absorbs a large amount of hydrogen, and thus provides a simple way of separation of the overpotential components responsible to the constituent elementary steps. The Tafel-Volmer reaction route with the exchange c. d. ratio, $m_o = i_{ov}/i_{oT}$, of *ca.* 10 was derived. This value of m_o means that both the steps are out of equilibrium under polarization conditions so that the reaction intermediate, hydrogen adatom, H(a), acquires an activity not equal to the value at the equilibrium potential of the HER nor to the value calculated by the Nernst equation applied to the overpotential. Extension of the analysis to the distribution of the reaction affinity to the constituent steps, synthesis of the overall reaction kinetics from those of the elementary steps, etc. were also carried out.⁴⁻⁶⁾

The technique was thus very powerful to investigate mechanism of the HER, but was unfortunately limited only to Pd. There might be a further possibility of applying the technique to several other hydrogen absorbing metals such as Ti, Zr, etc., as the analysis is entirely based on permeation

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of hydrogen in the bulk metal, but so far the trials were not successful because of low catalytic activity of those metals for the HER and/or insufficient rate of the hydrogen permeation.

Another possibility may be the deposition on a substrate Pd electrode of a very thin layer of the metal which is by itself not a good absorber of hydrogen. If the permeation of hydrogen through the thin layer, and hence through the Pd substrate, is sufficiently rapid, the electrode may have characteristics such that the component overpotentials are separated on the overpotential transient curves just as in the case of Pd, and yet the surface represents the property of the deposited metal as long as its catalytic activity is concerned. The work applied to Cu and Ag is reported in this paper.

Experimental

Pd foil electrodes of 5×10 mm and $12.5 \mu\text{m}$ in thickness (Ventron, 99.9%) were used as the substrate. These were cleaned in chromic acid mixture, followed by rinses with the Millipore water. Experiments were conducted in 0.5 M H_2SO_4 , 30°C , under hydrogen atmosphere with the use of an ordinary three compartment cell. Transient polarization measurements were conducted by the method reported elsewhere.^{3,4)} After the measurements were conducted on Pd, a trace amount ($\sim 10^{-6}$ mole) of CuSO_4 or AgNO_3 was introduced into the solution (160~200 m ℓ), which immediately led to deposition of the metal on the Pd electrode. The polarization measurements were conducted after an overnight standing. No particular measurement of the amount of the deposited metal was conducted but the amount was roughly estimated from the total amount of the salt added to the solution.

Potentiodynamic observations of the underpotential deposition (upd) of Cu or Ag were carried out (Nikko Keisoku, DPGS-1 potentiostat) in a separate experiment with much a higher metal ion concentration (Cu^{2+} ; 1.5×10^{-3} M/ ℓ , Ag^+ ; 3×10^{-3} M/ ℓ).

Results

(1) Copper

A typical decay transient in 0.5 M H_2SO_4 after the deposition of *ca.* 5×10^{-7} mole Cu/ cm^2 on the Pd substrate is shown in Fig. 1. The overpotential could be separated into the component overpotentials without much difficulty. In this example, η'_2 was evaluated to be -50 mV from the decay curve observed with the time window of 0.2 sec. The curve gave a linear but not horizontal portion, in contrast with a horizontal line observed on Pd electrode in earlier reports^{3,4)} with the time window of about 10^{-3} sec.

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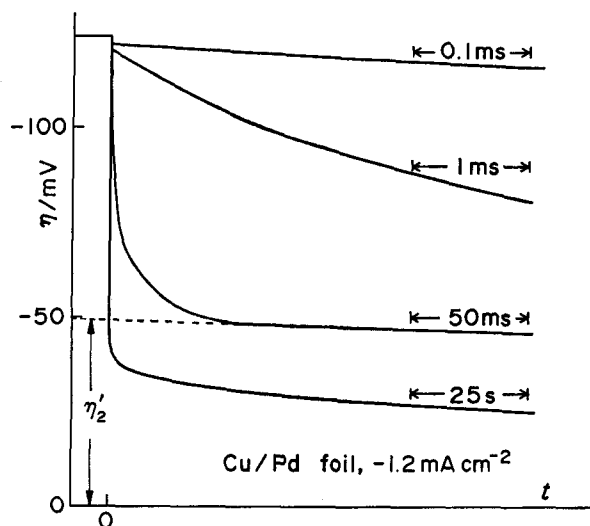


Fig. 1. Overpotential decay transients with various time windows Cu/Pd electrode (5×10^{-7} mole Cu was deposited on both faces of a $5 \times 10 \text{ mm} \times 12.5 \mu\text{m}$ Pd foil.)

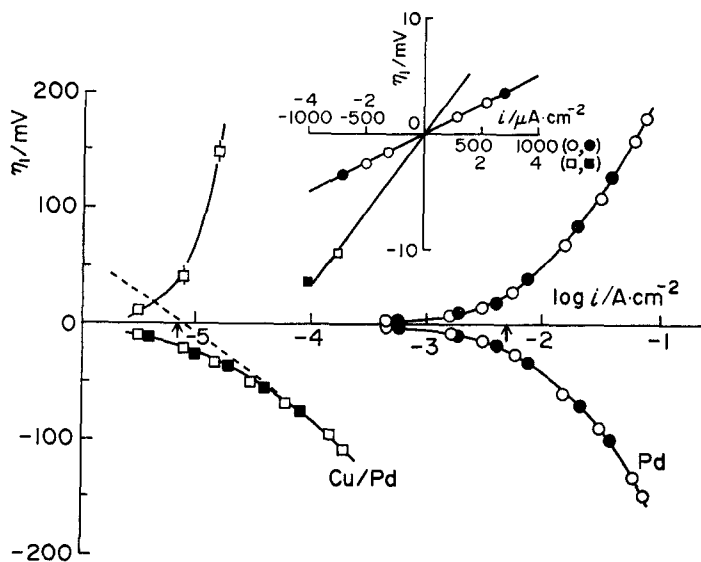


Fig. 2. Dependence upon polarization c.d. of the rapidly growing overpotential component, η_1 , on Pd and on the Cu/Pd electrode

Pd: Pd foil, $5 \times 10 \text{ mm} \times 12.5 \mu\text{m}$ (both faces), Cu/Pd: 5×10^{-7} mole Cu deposited on the Pd foil electrode. $0.5 \text{ M H}_2\text{SO}_4$, 30°C . The arrows on the abscissa indicate the exchange c.d. (i_{0v}) as evaluated from the linear plot at low η_1 (the inset Figure).

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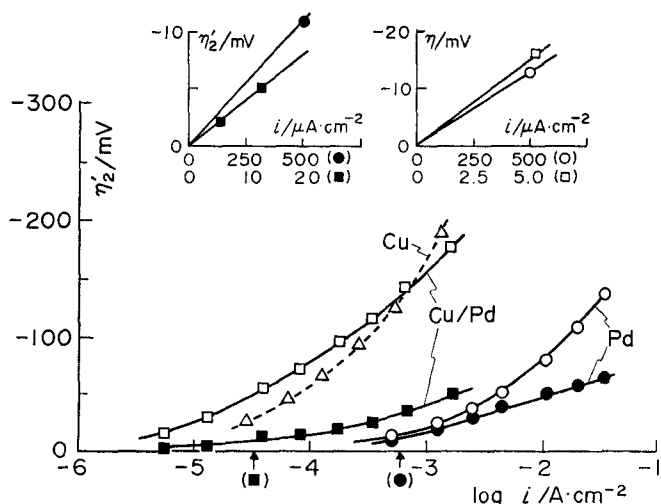


Fig. 3. Dependence upon polarization c.d. of the total overpotential η and the slowly decaying overpotential component η_2 on Pd and the Cu/Pd electrode

η : open symbols, η_2 : filled symbols. See Fig. 2 for details. The arrows on the abscissa indicate the exchange c.d. (i_{0T}) as evaluated from the linear plot of η_2 at low values (the inset Figure).

The initial decay on the Cu/Pd electrode was slower than the case on Pd, indicating much a lowered rate of the charge transfer (Volmer) process on the former electrode.

Results of the polarization measurements on the Cu/Pd electrode are shown in Figs. 2 and 3. Results on Pd foil and on Cu plate (no datum is available on η_1) are shown for comparison. The Pd foil electrode reproduced general behaviours reported in earlier publications.^{3,4} Figure 2 shows the behaviour of the rapidly growing overpotential component named η_1 in both anodic and cathodic regions. As discussed already,⁴ η_1 represents the overpotential component associated with the discharge process. After the Cu deposition of $ca. 5 \times 10^{-7}$ mole/cm², the discharge reaction rate was decreased by a factor of about $10^{2.5}$ (Fig. 2) and general polarization behaviours became somewhat different from those on Pd in that a limiting current behaviour was suggested on the Cu/Pd electrode in the anodic region.

The total overpotential η on the Cu/Pd electrode (Fig. 3, open squares) was in fair agreement with that observed on the Cu plate (broken line). Some difference in shape particularly at high c.d.'s. on the Cu/Pd electrode was not well understood, but much steeper curves and hence better agreement

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with the Cu electrode were often observed in other series of experiments. The slowly decaying overpotential component η'_2 (Fig. 3, filled squares) was more widely separated from η as compared with the case of the Pd foil. This would mean, on the Cu electrode as well, that the Volmer step is much slower than the Tafel step and hence the polarization characteristics in the cathodic region is practically determined by the Volmer process. This supports the often proposed slow discharge followed by rapid Tafel mechanism on Cu in hydrogen evolution reaction, but with a reservation that it doesn't mean that the Tafel step is in quasi-equilibrium under that polarization condition.

The exchange c. d. ratio $m_0 = (\Delta g_T / \Delta g_V)_{\eta=0} = i_{0V} / i_{0T}^{4,5}$ is around 0.3 in contrast with the value of about 10 on Pd. This value is not sufficiently small and hence the affinity value for the Tafel process is not always negligible, as also seen from the finite values of η'_2 in Fig. 3. As discussed already,^{5,6} under such a magnitude of m_0 , the Tafel step should soon overwhelm the Volmer step in the *anodic* region in determining the polarization characteristics.

The affinity distribution on those two elementary steps, $m = \Delta g_T / \Delta g_V$, is presented in Fig. 4, together with the corresponding data on Pd. It is seen

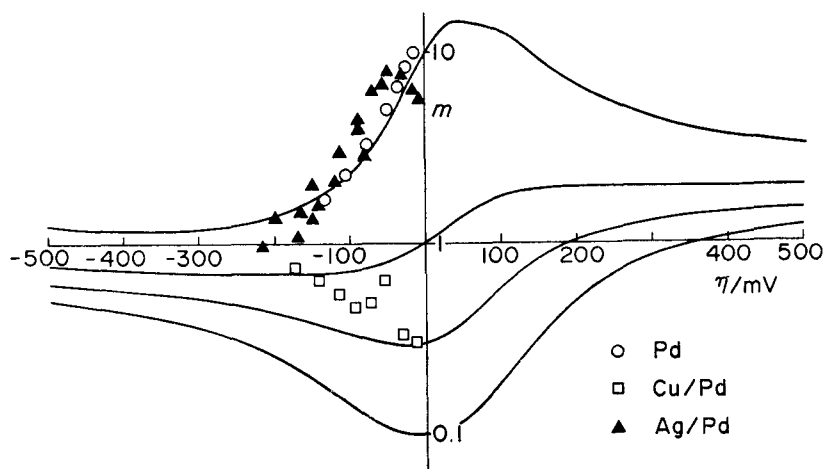


Fig. 4. Distribution to the constituent steps of the reaction affinity for the Tafel-Volmer mechanism, $m \equiv \Delta g_T / \Delta g_V$, as a function of η

○: Pd foil electrode, □: Cu/Pd electrode (5×10^{-7} mole Cu/cm² Pd) and ▲: Ag/Pd electrode (2×10^{-7} mole Ag/cm² Pd). 0.5 M H₂SO₄, 30°C.

Curves are theoretical lines^{5,6} calculated with $m_0 = i_{0V} / i_{0T}$ of 10, 1, 0.3, and 0.1 on Temkin isotherm with $\theta_0 = 0.01$.

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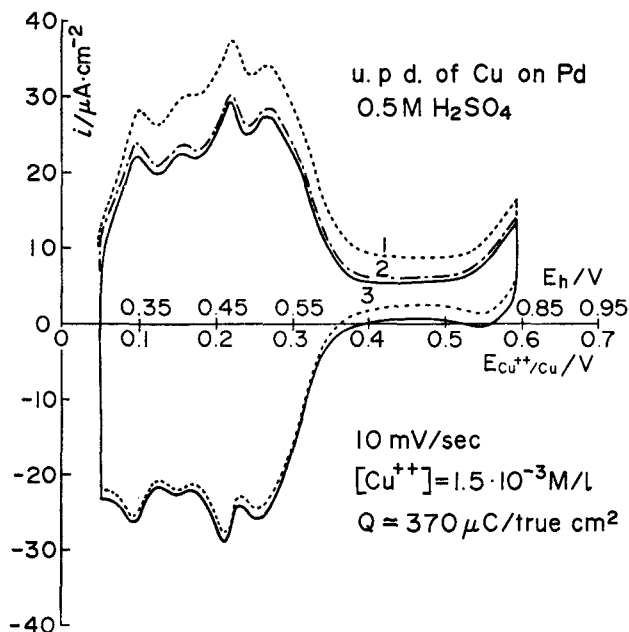


Fig. 5. Potentiodynamic sweep experiments on Pd in Cu^{2+} -containing solution. (underpotential deposition of Cu on Pd)

E_h : Electrode potential on the reversible hydrogen electrode potential scale, $E_{\text{Cu}^{2+}/\text{Cu}}$: Electrode potential on the reversible Cu^{2+}/Cu potential scale.

that m on the Cu/Pd electrode distributes around the theoretical line calculated⁶⁾ for $m_0=0.3$ (or somewhat larger) with $\theta_0 \ll 1$ where θ_0 is the H(a) coverage at the reversible hydrogen electrode potential.

It is essential in the present work that the deposited Cu completely covers the Pd substrate as the latter is electrocatalytically far more active than the former. We may probably expect such a coverage if Cu exhibits the upd on Pd. Potentiodynamic observations on Pd in Cu^{2+} -containing solution were therefore conducted, as shown in Fig. 5. The upd in $1.5 \times 10^{-3} \text{ M}$ Cu^{2+} in $0.5 \text{ M H}_2\text{SO}_4$ took place in the potential region of $0.30\text{--}0.60 \text{ V RHE}$ or $0.05\text{--}0.35 \text{ V}$ on the reversible Cu^{2+}/Cu potential scale. The amount of electricity was approximately $660 \mu\text{C/app. cm}^2$ or $370 \mu\text{C/true cm}^2$ as evaluated on the basis of the double layer capacitance of $C_{dl}=32 \mu\text{F/app. cm}^2$ and $C_{dl}=18 \mu\text{F/true cm}^2$. Assuming the amount of electricity of $210 \mu\text{C/true cm}^2$ for a monolayer coverage with a univalent species,⁷⁾ the charge required for completion of a monolayer coverage with Cu assuming two-electron transfer process must be $750 \mu\text{C/app. cm}^2$. The observed value is rather close to

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the latter value, particularly when we take into account the fact that still a certain amount of electricity should be needed in the potential region below 0.3 V RHE.

(2) *Silver*

Similar observations were conducted on a thin Ag electrode deposited on a Pd foil. After routine observations on the Pd foil electrode, 0.65×10^{-6} mole AgNO_3 was added to the solution of 160 ml 0.5 M H_2SO_4 and observations were carried out on the Ag/Pd electrode thus obtained. The behaviour was very similar to the case of the Cu/Pd electrode, but the extent of reduction of i_{ov} from the value on Pd was less, being by a factor of about 30 on the electrode of approximately 2×10^{-7} mole Ag deposited per unit area of Pd (Fig. 6).

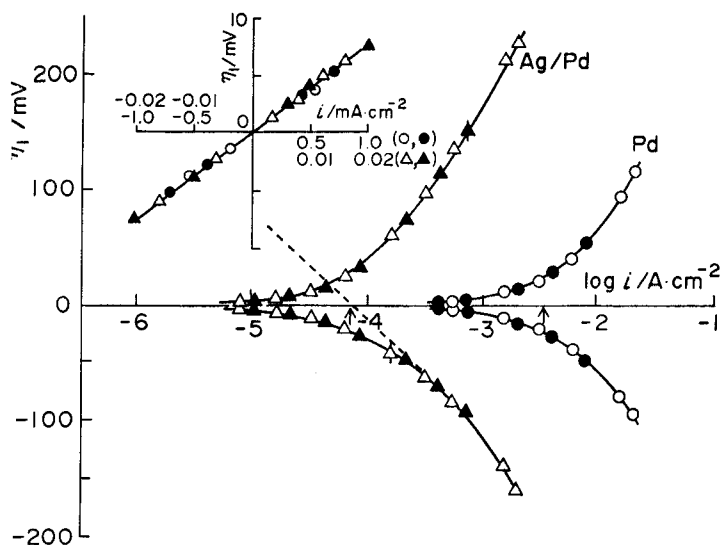


Fig. 6. Dependence upon polarization c.d. of the rapidly growing overpotential component, η_1 , on Pd and the Ag/Pd electrode

Pd: Pd foil, $5 \times 10 \text{ mm} \times 12.5 \text{ } \mu\text{m}$ (both faces), Ag/Pd: 2×10^{-7} mole Ag deposited on the Pd foil electrode. For other details, see Fig. 2.

General shapes of the Tafel plot of η and η'_2 on the Ag/Pd electrode were not much different from those on the Pd electrode but the current value at a given η was reduced by a factor of roughly 30 (Fig. 7). The total overpotential on the Ag/Pd electrode was in good agreement with the one observed on a Ag plate (the broken line, Fig. 7).

The values of m or m_0 were already shown in Fig. 4. The value $m_0 \approx$

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10 as suggested in this figure from the m vs. η relation or $m_0 \simeq 4.2$ as obtained near the equilibrium potential (Table 1) are well comparable with that (3~5) obtained in earlier work⁹⁾ by mean of a tracer technique employing deuterium, but roughly 10 times lower than that reported by Kunimatsu and Matsuda.^{9)*} The values of m as well as their dependence upon η were analogous to the case of Pd. In this way, Ag electrode appeared to behave very similarly to Pd, except that the electrocatalytic activity was roughly 30 times smaller.

The upd of Ag on Pd in 3×10^{-3} M Ag^+ solution was not observed (Fig. 8). The lack of the upd peak in this system is probably due to the

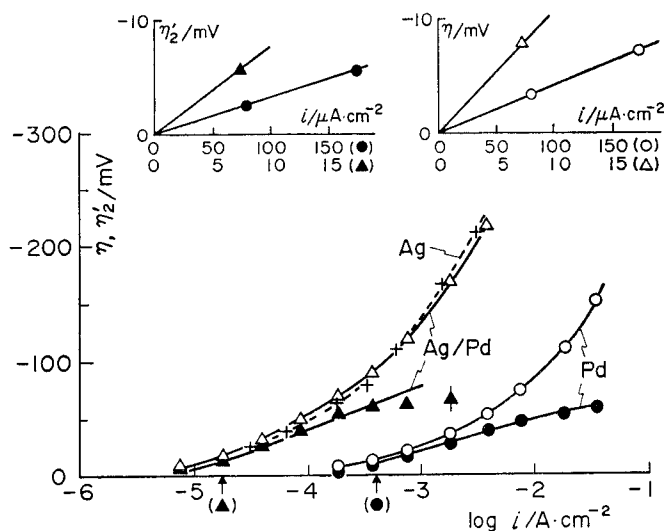


Fig. 7. Dependence upon polarization c.d. of the total overpotential η and the slowly decaying overpotential component, η_2' , on Pd and the Ag/Pd electrode

η : open symbols, η_2' : filled symbols

The arrows on the abscissa indicate the exchange c. d. (i_{0T}) as evaluated from the linear plot of η_2' at low values (the inset Figure).

^{*}) Electrochemical activities for the overall HER of the electrodes used in those experiments were comparable with each other but the exchange c. d. of the discharge step was about 10 times greater in the work of Kunimatsu and Matsuda⁹⁾ than in the present work. Further, there existed a significant difference in the shape of the Tafel line in that the Tafel line on the Ag/Pd electrode as well as Ag electrode in this work had a lower slope at low overpotentials and then assumed an ordinary slope of ca. 0.12 V at high overpotentials (Fig. 7), whereas only the steeper slope was seen in their work. Whether this was due to any differences in the electrocatalytic activities of the electrodes or to different techniques used was not clear yet.

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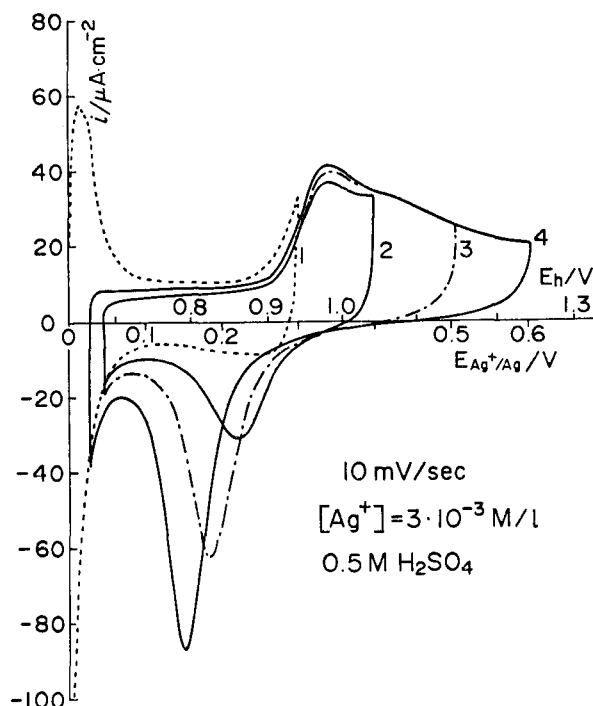


Fig. 8. Potentiodynamic sweep experiments on Pd in Ag^+ -containing solution (absence of underpotential deposition of Ag on Pd)
 $0.5 \text{ M H}_2\text{SO}_4 + 3 \times 10^{-3} \text{ M AgNO}_3$.

fact that the equilibrium potential of the Ag^+/Ag reaction is located at such a positive potential that either the upd current overlaps with the current due to oxygen adsorption/desorption or the upd was inhibited by the surface oxygen layer. The reversible hydrogen electrode potential is located at a potential far more cathodic to the reversible Ag^+/Ag potential so that Ag^+ is readily deposited on the Pd electrode in the HER system as was indeed visible when the amount of deposition was much larger.

Discussion

(1) *The Reaction Mechanism*

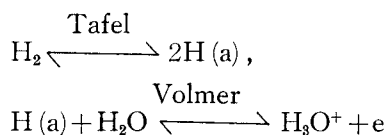
Figure 9 shows the relation between η'_2 and the rate of decay of the cathodic overpotential at the moment η'_2 was reached. The slope of this plot gives the order with respect to hydrogen adatom activity a_{H} of the reaction of removal of hydrogen from the electrode. The latter during the steady-state polarization is related to η'_2 by a simple relation,⁴⁾

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$$-\eta'_2 = (RT/F) \ln (a_H/a_{H,0})$$

The order was found to be approximately 2.1, 2.0, and 2.1 on the Pd foil, the Cu/Pd electrode, and the Ag/Pd electrode, respectively. The value indicates the second order dependence of the hydrogen removal reaction and hence supports the Tafel reaction to be responsible to the HER on those electrodes.

Taking into account the well explicable behaviour of η_1 on both the Cu/Pd (Fig. 2) and the Ag/Pd electrode (Fig. 6), we may reach a conclusion that the HER on Cu and Ag, as well as on Pd, proceeds through the Tafel-Volmer mechanism



(2) Rate of the Elementary Steps

Exchange c.d.'s of the Volmer step are listed in Table 1 in the first column. These were obtained from the linear plot of η_1 vs. polarization c.d. (inset of Figs. 2 and 6) using the relation $i_{oV} = (RT/F) (di/d\eta_1)_{\eta_1=0}$. The values indicated by the arrow on the abscissa in Fig. 2 or 6 are in good agreement with the intercept with zero η_1 axis of the cathodic unidirectional current of the Volmer step (i_{-V} ; dotted lined) calculated by the relation

$$i_{-V} = i_{oV} e^{-(1-\beta) F \eta_1 / RT} = i / [e^{F \eta_1 / RT} - 1].$$

TABLE 1. Exchange c.d.'s of the Elementary Steps
0.5 M H₂SO₄, 30°C

Electrode	$\log i_{oV}/\text{A cm}^{-2}$	$\log i_{oT}/\text{A cm}^{-2}$	m_o
Cu/Pd	-5.15	-4.5	0.23
Ag/Pd	-4.15	-4.8	4.2
Pd	-2.3 ~ -2.5	-3.2 ~ -3.4	8

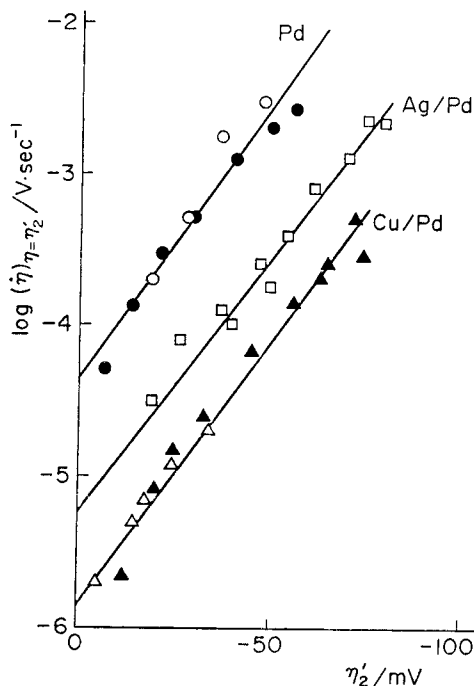


Fig. 9. The relation between η'_2 and its initial decay rate on Pd, Cu/Pd, and Ag/Pd electrode

0.5 M H₂SO₄, 30°C.

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The shape of the η_1 vs. $\log i$ relation under cathodic polarization was roughly the one expected for a simple charge transfer reaction, but it tended to deviate from the ordinary shape as the potential was moved to the anodic region. In connection with this, the slope at $\eta_1=0$, $(1-\beta)\simeq 0.82$, was significantly greater than the value 0.5 reported for many simple charge transfer reactions. It appears likely that this is due to a very low coverage of the Cu surface with H(a) and insufficient rate of the Tafel step so that the coverage inevitably decreases during the anodic current pulse for the η_1 measurements.

On the other hand, η'_2 gives an approximate value of i_{oT} . The values given from a linear plot of η'_2 vs. i (inset of Figs. 3 and 7) using the relation²⁾ $i_{oT}=(RT/2F)(di/d\eta'_2)_{\eta'_2=0}$ were listed in the second column of Table 2 and indicated by the arrows in Figs. 3 and 7. In this relation, the stoichiometric number of the responsible step was taken to be unity in accordance with the Tafel-Volmer mechanism deduced above.

Comparison of those step rates readily explain the total polarization characteristics. On the Cu/Pd electrode, the smaller value of i_{oV} than i_{oT} gives rise to the cathodic polarization characteristics to be of the "slow-discharge type", or the Volmer step plays a greater role in determining the polarization characteristics. In accordance with this, i_{oV} appears to be close to the "Tafel-extrapolated exchange c.d." given from the total overpotential η vs. $\log i$ relation (Fig. 3).

No steady-state polarization measurement was carried out on the Cu/Pd electrode in the anodic region because of very sharp rise of η with increase of the c.d. This was partly suggested already in Fig. 2 with steeper rise of η_1 in the anodic region. As discussed above, such a sharp increase of η_1 is not expected in the Volmer step, and this is likely to be due to an interference of the Tafel step which is not sufficiently rapid as compared with the Volmer step. Indeed, the polarization c.d. was already close to i_{oT} in this region.

Analogous results were obtained on the Ag/Pd electrode (Figs. 6 and 7). The Volmer step rate was *ca.* 30 times lower than that of the Pd electrode (Fig. 6) but 10 times greater than the Cu/Pd electrode. The polarization characteristics of η_1 are in good accordance with the Volmer equation, and the Tafel constant in the cathodic direction was $(1-\beta)\simeq 0.65$ at the equilibrium potential and gradually decreased with cathodic polarization.

The steady-state cathodic polarization characteristics were in an excellent agreement with those on the Ag plate (Fig. 7). It is seen that in low cathodic overpotential region, η'_2 was not much separated from η ; namely, the polari-

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zation characteristics in that region was practically determined by the Tafel step. At high *cathodic* overpotentials, the total kinetics tended to be controlled by the Volmer step. This was what anticipated from a general analysis of the mixed-controlled electrode reactions.^{5,6)}

(3) *Comparison of Electrocatalytic Activity among Various Metals*

It is anticipated on the basis of a general analysis of polarization characteristics⁴⁾ that kinetics of the HER on many electrode metals under deep *cathodic* polarization were determined by those of the Volmer process on the respective metals, unless the rate of the Tafel process was extremely slow. Such a control of the overall reaction rate by the Volmer step could possibly be an interpretation of a common trend of linear and mostly parallel Tafel lines of the HER observed on practically all the metals.¹⁰⁾ The relative magnitudes of i_{oV} observed in this work on Cu, Ag, and Pd were indeed comparable with the Tafel-extrapolated exchange c.d.'s reported in the literature.^{10,11)} Conversely, this was not the case for i_{oT} ; for example, i_{oT} value on Cu was greater than, or at least comparable with, that on Ag, in spite of a notion that Ag is more active than Cu for the HER by roughly one order of magnitude.

Along this line, it appears likely that comparison of electrocatalytic activity of many metals, taking the Tafel-extrapolated exchange c.d.'s or else c.d. values at a given overpotential value as a measure of the activity, would in fact be comparing the Volmer reaction rates on those metals. It then follows that search for a high performance cathode material for water electrolysis, but not necessarily for the anodic oxidation of hydrogen in the fuel cell because then the Tafel process would become more important, is to be directed to the one with a high i_{oV} value. Although Pt is practically only the choice of such materials if pure elements alone are concerned, it seems interesting to inspect other materials including composite materials from that point of view.

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