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Electrocatalysis in Metal Hydride Electrode. I. Hydrogen Electrode Reaction on Group-IB and VIII Metals Deposited on Palladium Substrates

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Hydrogen electrode reactions (HER) on thin-layer electrodes of group-IB and VIII metals (Cu, Ag, Au, Ni, and Pt) prepared by electro-deposition on Pd foil substrates were studied (together with the Pd foil itself) in 0.5 M H_2SO_4 and 1.0 M NaOH (M=mol dm^{-3}) at 303 K by a transient technique. The reactions on these metals were concluded to proceed via a Volmer-Tafel reaction route and the exchange current densities of the elementary steps, i_{0V} and i_{0T}, were then evaluated. The electrocatalytic activities towards the Volmer step were observed to be in the order Pt>Pd>Au>Ag>Cu in an acidic solution and Pt>Pd>Ni≧Ag≧Au≧Cu in an alkaline solution. The activities towards the Tafel step were Pt≧Pd>Au>Cu>Ag in an acidic solution and Pd>Pt>Au>Cu=Ag>Ni in an alkaline solution. The results were summarized in terms of the parameter m_0 $(=i_{0V}/i_{0T})$. This parameter was used to describe the electrochemistry of the energy efficiency of a hydride-type hydrogen-storage electrode, when the metals were employed for the purpose of modifying the electrode surface. Pt and Ag (among the group-IB metals) in both acidic and alkaline solutions were revealed to be suitable electrocatalysts.

The entry of hydrogen into metal or alloy electrodes during the electrochemical evolution of hydrogen has been studied for a long time, mainly in connection with the problem of the hydrogen embrittlement of substrate metals.[1,2] On the other hand, the potential of hydrogen-absorbing metals or alloys as a means of energy storage has been noted during the last ten years.[3] Secondary batteries using hydrogen-storage matrices, such as alloys based on alkaline earth metals or lanthanoid metals, possess (in principle) larger capacitance per unit weight than lead-acid batteries. According to Videm,[4b] their theoretical energy densities are as follows: MgH_2/air; 1900, CaH_2/air; 680, and $LaNi_5H_6$/air; 458 Wh kg^{-1}, whereas the conventional lead-acid battery is 161 Wh kg^{-1}.

The construction of hydride cells using aqueous[4–7] electrolytes may be divided into two types: The direct type in which hydrogen-storage materials (metal hydrides) are directly immersed in the electrolyte,[4a,b,d] and the indirect type in which a hydrogen-permeable membrane (such as Pd foils) is employed as a hydrogen electrode at the same time as a container of metal hydrides.[4b,4c,5–7] The latter may also include a type in which hydrogen is stored outside the cell by means of, e.g. metal hydrides. While alkaline media might only be practical for the former type, both acid and alkaline solutions might be used in the latter.

The present discussion is not concerned with the latter indirect type since it is essentially a H_2/air fuel cell (with a combined operation as a water electrolyzer) equipped with a suitable device of H_2 storage. This type is probably suitable for a large-scale energy storage device. On the other hand, a more detailed analysis would be required regarding the former type. This is the topic of the present work.

Basic Concepts. In the direct-type electrochemical hydrogen energy storage system, hydrogen produced on the cathode is dissolved into the electrode material and then ionized during its use as a current generator. The efficiency of the energy conversion through charging and discharging processes may be lowered by various factors, such as hydrogen diffusion in the metal hydride. However, the most important factor concerning its electrochemistry is the overpotentials involved in those processes. In this respect, for a given metal-hydride system chosen for hydrogen storage, a surface modification with other (metallic) materials might be required in order to improve the efficiency.

Further, it is well known that many of the metal hydrides tend to pulverize during hydrogen charging/discharging cycles and, thus, introduce difficulties concerning practical devices. To prevent this, a microcapsulation technique involving the coating of a metal hydride powder with a ductile metal has been proposed.[8] This may completely change the electrocatalytic property of the hydride electrode; hence, one should know the surface modification effects of each candidate metal.

The majority of hydrogen-absorbing metals or alloys have a plateau region in the absorption isotherm, e.g. the α-β phase transition region in the Pd–H system. This provides the basic character of that hydrogen-storage system. Naturally, one should cover this region during operation in order to maximize the storage capacity.

The extent of hydrogen absorption into metals or alloys which are polarized in aqueous or other protonic environments is intimately related to the HER mechanism. If HER proceeds through the Volmer-Tafel reaction route:

Volmer step,

$$H^+B + e \rightleftharpoons H(a) + B \quad (B=H_2O,\ OH^-)$$

Tafel step,

$$2\,H(a) \rightleftharpoons H_2,$$

the overpotential components for these elementary steps (η_V and η_T) under steady-state polarization are given, respectively, by,[9]

$$\eta_V = \eta + \frac{RT}{F} \ln \gamma_H, \tag{1}$$

$$\eta_T = - \frac{RT}{F} \ln \gamma_H, \tag{2}$$

where $\gamma_H = a_H/a_{H,o}$, a_H is activity of the hydrogen adatom, H(a), established during the steady-state polarization. The subscript o indicates the equilibrium of the overall reaction. The overall overpotential, η, is related to the component overpotentials by $\eta = \eta_V + \eta_T$.[9]

If an electrode material with an extensive and rapid hydrogen absorption is used, a plateau region (in the time window of 10^{-3}—10^{0} seconds in the case of thin Pd foil) usually appears on the galvanostatic overpotential rise transient curves or on the overpotential decay transients after current interruption. The plateau overpotential value on the rise transient curve may be explained[9] as the overpotential component required for the Volmer step to proceed with the rate predetermined by the applied current. No overpotential component for the Tafel step should be required at the very beginning of the transient, provided that a_H is effectively equal to $a_{H,o}$, owing to high rate of dissolution of H(a) into the electrode and, hence, the insignificant growth of a_H during this very short period of time. Only after a prolonged polarization time does a growth of a_H take place and, hence, of η beyond this level. Accordingly, an extrapolation of the plateau to time zero yields the overpotential component, η_1. An analysis of η_1 readily provides the kinetic parameters of the Volmer step, e.g. i_{oV} and the symmetry factor, β, being separated from those of the Tafel step (see below, Fig. 3, etc.).

Likewise, an extrapolation of the plateau on the overpotential decay transient to time zero after a current interruption should divide η into two overpotential components: η'_1 for the short time process and η'_2 for the long time process, where $\eta = \eta'_1 + \eta'_2$. As discussed elsewhere,[9] η'_2 is related to γ_H, the activity level reached during a steady-state polarization as,

$$\frac{RT}{F} \ln \gamma_H = -\eta'_2. \tag{3}$$

Hence, we find, referring to Eq. 2,

$$\eta'_2 = \eta_T. \tag{4}$$

Similarly,

$$\eta'_1 = \eta - \eta'_2 = \eta - \eta_T = \eta_V. \tag{5}$$

Equation 3 may be related to the equivalent hydrogen pressure/fugacity $\overline{P}_{H_2}$ of the plateau region of the metal hydride electrode, given as the ratio over the reference pressure $\overline{P}_{H_2,o}$ (usually the atmospheric pressure), by combining it with the Nernst equation for a concentration cell,

$$E = - \frac{RT}{2F} \ln (\overline{P}_{H_2}/\overline{P}_{H_2,o}) \tag{6}$$

and to the relation (in terms of chemical potentials concerning the hypothetical hydrogen adsorption equilibrium) $\mu_{H_2} = 2\,\mu_{H(a)}$. Thus, we find,[10]

$$\eta'_2 = - \frac{RT}{2F} \ln (\overline{P}_{H_2}/\overline{P}_{H_2,o}). \tag{7}$$

This indicates that the value of η required to charge up an electrode with hydrogen should be such that it contains a magnitude of η'_2 that at least satisfies Eq. 7. Since $\overline{P}_{H_2}$ should, in principle, be larger than the reference hydrogen pressure in the same system, η'_2 must always be finite. Its magnitude is determined by the type of the hydride used and the operating conditions chosen.

On the other hand, η'_1 is the overpotential component, or additional amount of energy which is required to produce hydrogen from water. Accordingly, the smaller the magnitude, the smaller will be the energy consumption during the charging (also discharging). Hence, the higher will be the efficiency of the energy storage. It may be said, therefore, that the surface modification electrocatalysts that have small η'_1 values compared with η'_2 should be employed in order to minimize the energy loss.

The ratio η'_1/η'_2 (or η_V/η_T) is determined by the specific rates of the elementary reaction steps. A series of studies[11] on HER (by means of a deuterium tracer technique) have already revealed the rates of the Volmer and Tafel steps on several electrocatalysts (Rh, Ir, Ni, Pt, Ag, and Au). Also, in our recent studies,[12,13] details regarding HER characteristics on Pd, Cu, Ag, and Ni have been investigated by means of a galvanostatic overpotential transient analysis.

In the present work, the HER characteristics of group-IB and VIII metal catalysts, particularly the ratio of the rates of the Volmer and Tafel elementary steps, are reported and the use of these metals as surface modification electrocatalysts in metal-hydride type secondary batteries is discussed.

Experimental

Preparation of Electrodes. Pd foils (a rectangular form of 5×5 mm, 12.5 μm in thickness) were used as substrates of the electrodes, which provided the hydrogen storage characteristics needed to carry out the transient polarization analysis mentioned above. Pd foil electrodes coated with one of the group-IB metals or with Pt were prepared by electro-deposition from 0.5 M H_2SO_4 solutions containing $CuSO_4\cdot5H_2O$, $AgNO_3$, $HAuCl_4\cdot4H_2O$, or $H_2PtCl_6\cdot6H_2O$, respectively. This was done up to a thickness corresponding to 2—5X10^{-7} mol cm^{-2} (apparent) or of the order of 10^{-6} cm in thickness (as judged from the amount of electricity applied, assuming 100% current efficiency). A series of preliminary experiments indicated that these coatings were sufficient to give rise to their own electrodic characteristics and yet retain an acceptable level of hydrogen permeability into the Pd foil substrates. This is required for the present type of transient analysis.

Electrochemical Measurements. The galvanostatic and potentiostatic polarization experiments were carried out in 0.5 M H_2SO_4 and 1.0 M NaOH at 303 K by using a previously described technique.[14] The electrolytic solution was prepared from a special grade H_2SO_4 (Wako, Tokyo) and pro analysi grade NaOH (Merck Japan, Ltd.) with water obtained from a Millipore pure water system. The real surface areas of the test electrodes were evaluated from double-layer capacitance data obtained by a pulse technique, assuming a value of 18 μF cm^{-2} (true).

The amount of hydrogen stored in the electrode was determined by measuring the quantities of electricity needed for its potentiostatic anodic ionization at 400 mV (RHE). The measurements were carried out after a steady-state polarization for several hours which was set at a desired overpotential between η=−20 and 200 mV. The overpotential component η_2' was evaluated from short time decay transients taken during the steady-state polarization.

Results and Discussion

Overpotential Transients. For all the electrodes prepared in this work, the overpotential plateau in a short-time transient curve (several seconds) has been easily recognized. Thus, the electrodes are considered to have good hydrogen permeabilities. Typical long-time rise and decay transient curves observed on a Pd foil and Au- or Pt-coated Pd foils in acidic and alkaline solutions are shown in Figs. 1 and 2, respectively. Similar behaviors were also observed on the other electrodes. The ratio η_1'/η_2' was generally observed to be larger in an acidic than in an alkaline solution.

Palladium. This element has a high hydrogen permeability, allowing a detailed study of the HER characteristics by a previously reported transient technique.[9,10,12,14]

Typical "Tafel" plots of η_1 on a bare Pd foil electrode in both acidic and alkaline solutions are shown in Fig. 3. The polarization characteristics in these solutions were very similar to each other. The slope of the linear portions in their Tafel plots was usually close to 120 mV decade^{-1} (both in the anodic and cathodic sides). Thus, they are practically symmetric on the abscissa. This form well substantiates the view that η_1 originates from the Volmer step. The i_{0V} values were estimated from linear plots of η_1 vs. i near the reversible potential (the inset figures) by the relation[9] $i_{0V}=(RT/F)/(di/d\eta_1)_0$. These were in good agreement with those

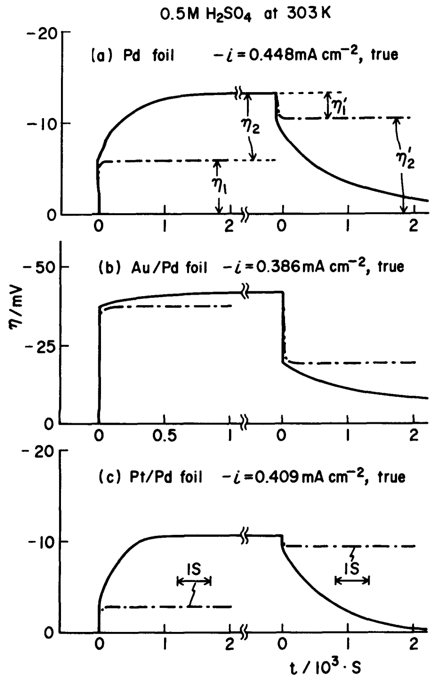

Fig. 1. Typical rise and decay transients of galvanostatic overpotentials on (a) Pd foil, (b) Au-deposited Pd foil, and (c) Pt-deposited Pd foil electrodes. 0.5 M H_2SO_4, 303 K.

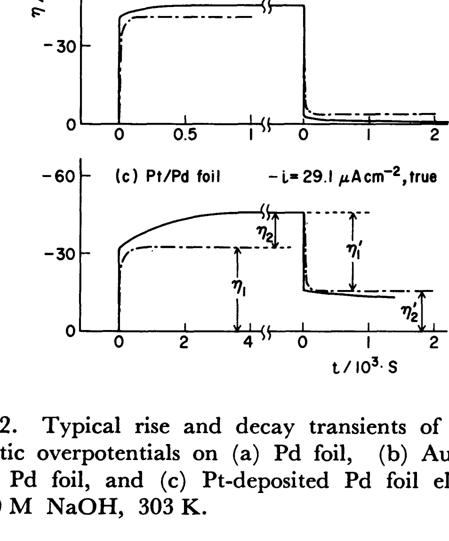

Fig. 2. Typical rise and decay transients of galvanostatic overpotentials on (a) Pd foil, (b) Au-deposited Pd foil, and (c) Pt-deposited Pd foil electrodes. 1.0 M NaOH, 303 K.

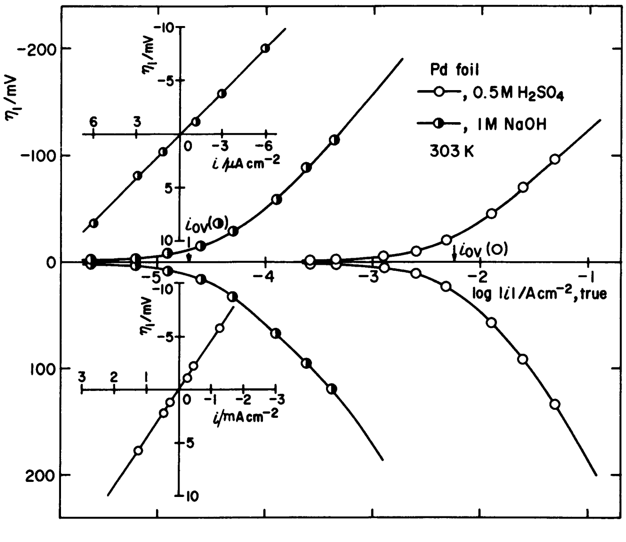

Fig. 3. Cathodic and anodic polarization behaviors of the rapidly rising overpotential component η_1 on a Pd foil. The arrows on the abscissa indicate i_{0V} evaluated from the linear plots (the inset figure) of η_1 vs. i near the reversible potentials.
0.5 M H_2SO_4 and 1.0 M NaOH, 303 K.

anticipated from the Tafel plots, being about 5×10^{-3} and 2×10^{-5} A cm^{-2} (true) in the acidic and alkaline solutions, respectively.

The total overpotential, η, and the slowly decaying overpotential component, η_2', are shown in Fig. 4. Tafel plots of η and η_2' are seen to possess a linear portion with a slope of about 120—140 or 30—40 mV decade^{-1}, respectively. The latter value indicates that η_2' can be attributed to the Tafel step.[9] This again confirms the former conclusion that the HER on Pd proceeds via the Volmer-Tafel reaction route. The exchange current density of the Tafel step was evaluated by the relation[9] $i_{0T}=(RT/2F)/(di/d\eta_2')_0$ to be about 5×10^{-4} and 1×10^{-4} A cm^{-2} (true) in the acidic and alkaline electrolyte, respectively.

In an alkaline solution, the rate of the overall HER was slower than in the acidic solution. In this case, the decrease in the rate was particularly significant for the Volmer step as compared with the Tafel step. As a consequence, the value of i_0 in the alkaline solution evaluated from the linear η vs. i plot (the reaction resistance) at low η by the relation[9] $i_0=(RT/F)/(di/d\eta)_0$ (approximately valid when $i_{0V} \ll i_{0T}$) became fairly close to i_{0V} and smaller than i_{0T}. Thus, the HER kinetics were mostly dominated by the Volmer step. Correspondingly, the m_0 value became as small as 0.2. This is very small compared with that in an acidic solution (m_0=10). Accordingly, Pd in acidic solutions should yield a high energy storage efficiency if used by itself or to modify the surfaces of other hydrogen-storage electrode materials. However, that would not be the case in an alkaline solution.

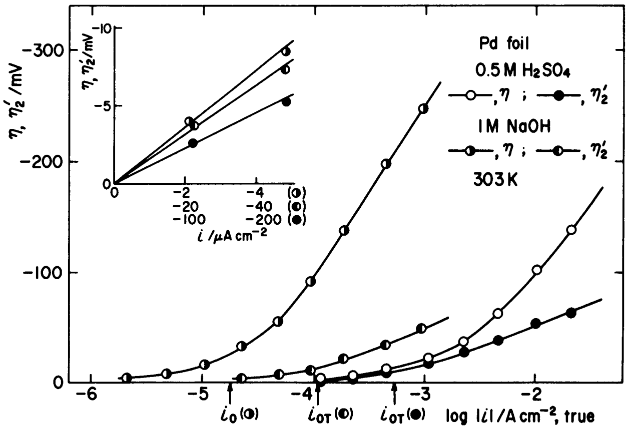

Fig. 4. Cathodic polarization behaviours of the total overpotential η and the slowly decaying overpotential component η_2' on a Pd foil electrode. The arrows on the abscissa indicate i_{0T} and i_0 obtained at low overpotentials (the inset figure).
0.5 M H_2SO_4 and 1.0 M NaOH, 303 K.

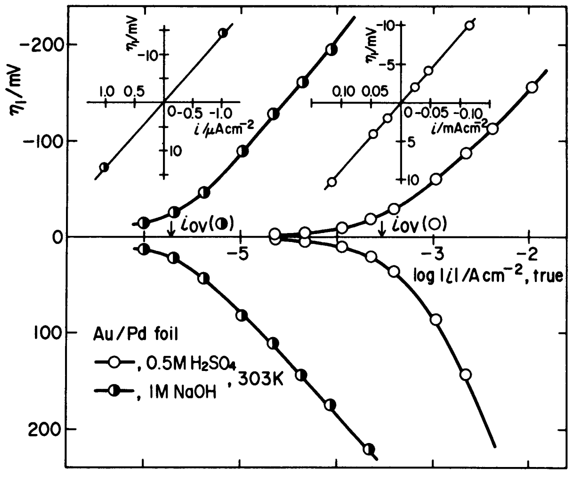

Fig. 5. Cathodic and anodic polarization behaviors of the rapidly rising overpotential component η_1 on Au-deposited Pd foils. The arrows indicate i_{0V} obtained at low overpotentials (the inset figure).
0.5 M H_2SO_4 and 1.0 M NaOH, 303 K.

Group-IB Metals. As is well known, the HER on these elements does not proceed as rapidly as on group-VIII metals. The i_0 values have been reported to be 10^{-5}—10^{-7} A cm^{-2} (true) both in acidic and alkaline solutions,[15,16] except that Au after anodic activation occasionally shows a very high activity.

The cathodic and anodic polarization behaviors of η_1 on an Au/Pd foil electrode are shown in Fig. 5. Like Pd, the polarization characteristics are quite acceptable as that of the Volmer step. The i_{0V} values were, however, scattered between 3×10^{-3} and 3×10^{-6} A cm^{-2} (true). Among them, the Volmer step on Au

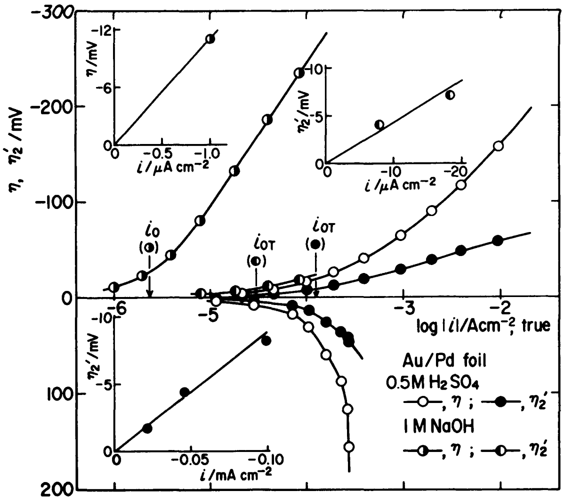

Fig. 6. Cathodic and anodic polarization behaviors of the total overpotential η and the slowly decaying overpotential component η_2' on Au-deposited Pd foils. The arrows indicate i_{0T} and i_0 obtained at low overpotentials (the inset figure).
0.5 M H_2SO_4 and 1.0 M NaOH, 303 K.

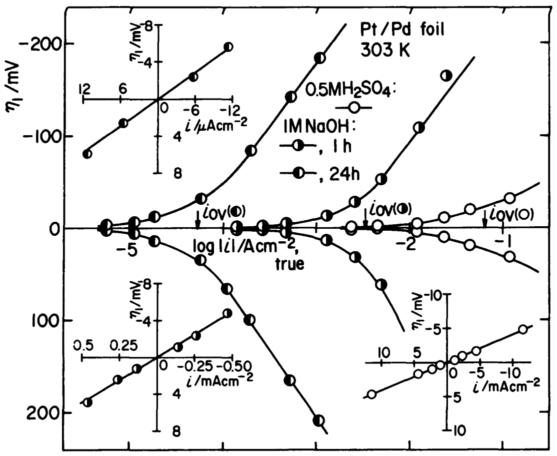

Fig. 7. Cathodic and anodic polarization behaviors of the rapidly rising overpotential component η_l on Pt-deposited Pd foils. The arrows indicate i_{0V} obtained at low overpotentials (the inset figure).
0.5 M H_2SO_4 and 1.0 M NaOH, 303 K.

in an acidic solution only was very fast. On the other hand, the Tafel plots on η and η_2' (Fig. 6) had a slope of about 120 and 30 mV decade^{-1}, respectively. This was the same as for the previously observed values on Pd. The overpotential component η_2' was, hence, attributed to the Tafel step, yielding the i_{0T} values in the range 10^{-4} to 10^{-6} A cm^{-2} (true). These results on Cu and Ag in 0.5 M H_2SO_4 were in good agreement with those reported earlier.[12] The value of m_0 was in the order Ag>Au>Cu in an acidic solution or Ag>Cu>Au in an alkaline solution (see Table 1 below). Among the group-IB metals, Ag was, thus, found to be an acceptable electrocatalyst in metal hydride secondary batteries in acidic (or alkaline) solutions.

Nickel. Details of HER on $LaNi_5$ film, Ni-Ti alloy films, amorphous Ni-Ti alloy ribbons, and Ni-V alloy ingots (all having a high hydrogen permeability) in 1.0 M NaOH were reported in previous papers.[13] The electrocatalytic characteristics on those alloys could essentially be attributed to the nickel on their surfaces. This idea was supported by SEM observations and XPS surface analyses.[13] The HER on these metals was also concluded to proceed via the Volmer-Tafel reaction mechanism with mixed rate-determining characteristics. Both the i_{0V} and i_{0T} values were estimated to be around 10^{-6} A cm^{-2} (true). Among these alloys in an alkaline solution, the m_0 value on a $LaNi_5$ film was considerably larger ($m_0=4$) than the others ($m_0=1$—2.5). The scatter of the data among the alloys is not well understood. It may be due to an effect related to the different ways of preparation or to a synergistic effect due to the alloying component. The reasonably high values of m_0 on Ni indicate that Ni may be an acceptable electrocatalyst in metal-hydride secondary batteries, or that a surface modification may not be required if Ni-based hydrogen storage materials are used without microcapsulation, etc.

Platinum. The exchange current density of HER on Pt is around 10^{-3} and 10^{-4} A cm^{-2} (true) in acidic and alkaline solutions, respectively.[15,16] However, in the latter media, the electrocatalytic activity of Pt is occasionally unstable and becomes considerably lower with time.

Figure 7 shows Tafel plots of η_l in 0.5 M H_2SO_4 and 1.0 M NaOH. The polarization characteristics clearly show that η_l originates from the Volmer step. As seen from the figure, the discharge process on Pt in an acidic solution was very rapid and i_{0V} was 6×10^{-2} A cm^{-2} (true). On the other hand, the activity in an alkaline solution was rather unstable and, after one day of standing, it became lower by nearly two orders of magnitude compared with the level immediately after the cell was set up. The i_{0V} values were 3.3×10^{-3} and 5.4×10^{-5} A cm^{-2} (true) for the former and the latter cases, respectively.

The cathodic and anodic polarization behaviors of η and η_2' are presented in Fig. 8. The slope of the Tafel plots of η_2' was about 30 mV decade^{-1}, indicating that this overpotential component was caused by the Tafel step (plus possibly a minor degree of contribution from the H_2 diffusion in the case of the acidic solution). The i_{0T} values on Pt (after one day of standing) were 5×10^{-4} and 1.3×10^{-5} A cm^{-2} (true) in acidic and alkaline solutions, respectively. Consequently, the m_0 values were

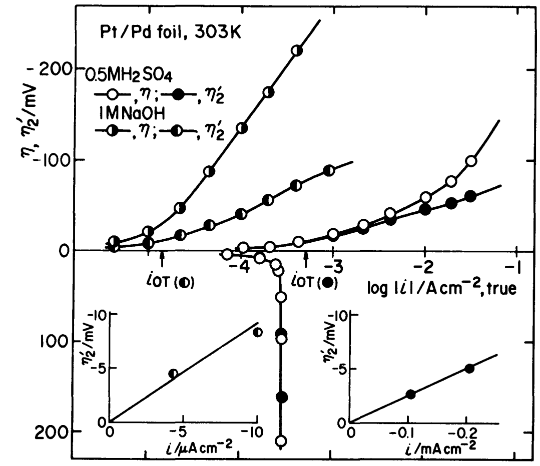

Fig. 8. Cathodic and anodic polarization behaviors of the total overpotential η and the slowly decaying overpotential component η_2' on Pt-deposited Pd foils. The arrows indicate i_{0T} and i_0 obtained at low overpotentials (the inset figure.)
0.5 M H_2SO_4 and 1.0 M NaOH, 303 K.

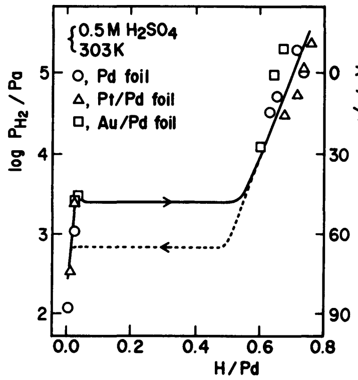

Fig. 9. Typical desorption isotherm (η_2' or $\log P_{H_2}$ vs. H/Pd) obtained on Pd and Au- or Pt-deposited Pd foil electrodes after polarizations between $\eta = -20$ and 200 mV at 303 K for several hours. The absorption/desorption isotherm[17)] at ca. 300 K is shown for comparison.

evaluated to be 120 and 4 in the acidic and alkaline solutions, respectively. The value for an acidic solution is particulary large and, thus, Pt is an excellent electrocatalyst for a surface modification regarding this type of battery.

Amount of the Electrochemical Hydrogen Storage. The hydrogen absorbed into electrodes covered with Cu, Ag, Au, and Pt during hydrogen evolution is expected to obey Eq. 7, as the HER is concluded to proceed via the Volmer-Tafel reaction route, just as for the Pd or Ni electrodes.[12,13)] In Fig. 9, the relationship between the hydrogen content and the overpotential component η_2' (and not η) observed on a bare Pd foil and a Pt- or Au-coated Pd foil electrodes are shown together with a typical absorption/desorption isotherm for Pd.[17)] It can be seen that the experimental data are reasonably close to the isotherm curve in spite of the fact that the data were obtained on different metals with only the substrate being common (Pd). None of the data were found on the plateau region, presumably due to the sharp variation of the isotherm in this region. These observations substantiate the above analysis that the effective pressure of the electrochemically evolved hydrogen is determined by η_2' (Eq. 7) regardless of the type of electrode material as long as the HER obeys the Volmer-Tafel mechanism.

Comparison of Metals as Electrocatalysts. The obtained kinetic parameters are summarized in Table 1. In 0.5 M H_2SO_4, the Volmer step was generally more rapid than the Tafel step, or m_0 was for the most part larger than unity. The order of the elementary step rates was Pt>Pd>Au>Ag>Cu for the Volmer step and Pt≧Pd>Au>Cu>Ag for the Tafel step, respectively. Consequently, that for m_0 was Pt>Pd>Ag>Au>Cu. Hence, Pt was concluded to be the most suitable material for an electrode surface modification in the present context.

In 1.0 M NaOH, the rates of the Volmer step were considerably decreased (as a whole) compared with the Tafel step. Hence, the efficiency in question should be lowered. Their electrocatalytic activity was in the order Pt>Pd>Ni≧Ag≧Au≧Cu for the Volmer step and Pd>Pt>Au>Cu=Ag>Ni for the Tafel step. A relatively high m_0 value was observed on Pt or Ni ($LaNi_5$ film), although the value for Ni was somewhat dispersed if Ti, Zr, or V was used instead of La as the alloying element. These are considered suitable for alkaline systems.

Conclusion

The HER on the electrodes of Cu, Ag, Pd, and Pt, was concluded to proceed via the Volmer-Tafel reaction route in both acidic and alkaline solutions, as well as on Ni in alkaline media. The relationship between the amount of hydrogen absorbed in the electrodes during a hydrogen evolution reaction and the overpotential component η_2' for the Tafel step, shows that this overpotential component is the quantity which determines the absorption conditions. On the other hand, η_1' represents the reaction affinity necessary for producing hydrogen from water. Thus, it entirely gives rise to a corresponding amount of energy consumption. The energy efficiency in the charge/discharge cycles of metal-hydride secondary batteries, therefore, dependes on the fraction of η_2' which shares in the overall

Table 1. Kinetic Parameters[a] of the Hydrogen Electrode Reaction on Group-IB and VIII Metals

Electrode		0.5 M H_2SO_4			1.0 M NaOH		
		$\log i_{oV}$	$\log i_{oT}$	m_o	$\log i_{oV}$	$\log i_{oT}$	m_o
Cu	(Cu/Pd foil)	−5.15[b]	−4.5[b]	0.23[b]	−5.8	−5.2	0.25
Ag	(Ag/Pd foil)	−4.15[b]	−4.8[b]	4.2[b]	−5.5	−5.2	0.50
Au	(Au/Pd foil)	−3.53	−3.9	2.4	−5.6	−4.5	0.06
Ni	(amorphous Ni-Ti alloys)[c]				−5.1	−5.5	2.5
	(Ni-Ti alloy films)[d]				−5.6	−6.0	2.5
	($LaNi_5$ film)[d]				−5.5	−6.1	4.0
	(Ni-V alloys)[e]				−5.3	−5.3	1.0
Pd	(Pd foil)	−2.3	−3.3	10	−4.7	−4.0	0.20
Pt	(Pt/Pd foil)[f]	−1.2	−3.3	120	−4.3	−4.9	4.0

a) The i_o values are given per true unit surface area. b) Ref. 12. c) Ref. 13a. d) Ref. 13b. e) Ref. 13c. f) The i_{oT} value observed on this electrode (RF=ca. 5) was probably underestimated because of involvement in part of limiting rate of diffusion of H_2: The true value of m_o might hence be smaller than this value.

overpotential, η. This has been discussed here in terms of m_o. Among the metals studied, Pt in acidic solutions and Pt or Ni (or Ag among the group-IB metals) in alkaline solutions are considered to be suitable regarding the present purpose.

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