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Structure of Mercury Layer Deposited on Platinum and Hydrogen-evolution Reaction at the Mercury-coated Platinum Electrode

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The thermal evaporation of mercury is investigated in order to ascertain the structure of mercury electrodeposited on platinum. At first, Pt_2Hg is formed on platinum, and a hydrogen(H)-overpotential at the surface is identical with that at the mercury-free platinum. With the increase in the amount of mercury to more than the amount corresponding to PtHg, the H-overpotential increases. When a large amount of mercury is deposited, the layer is composed of three mercury compounds (Pt_2Hg, Pt_2Hg_2, and $PtHg_4$), metallic mercury, and adatom mercury. Even when a sufficiently large amount of mercury is deposited, *e.g.*, several thousand atomic layers, the H-overpotential is much less than that at a hanging mercury drop electrode (HMDE). From the general relationship between the hydrogen evolution at a metal electrode and the work function of the metal, the change in the H-overpotential with the increase in the amount of mercury is attributable to the work-function change.

In spite of the importance of hydrogen-evolution reaction at the surface of thin metal film deposited on a foreign metal from the viewpoints of corrosion and electrocatalytic reactions[1,2) at the surface and the utility of thin film electrodes, there have been only a few quantitative investigations of hydrogen evolution at thin metal film. Furuya *et al.* investigated hydrogen-evolution reaction at platinum[3) or palladium[4) deposited on gold and copper,[5) gold,[3) or arsenic[6) deposited on platinum. Through these studies they concluded that, when a monolayer metal was deposited, the hydrogen evolution at the surface was identical with that at the bulk metal to be deposited. On the other hand, at the surface of thin mercury film deposited on platinum[7) or silver,[8) the hydrogen evolution was far from that at pure mercury itself, even when the amount of mercury was sufficiently large. This phenomenon has been well known, because platinum- or silver-based thin mercury film electrodes (TMFE) have been widely used[7–14) as indicator electrodes in electroanalytical chemistry. Like mercury, silver on platinum[15) also behaved similarly. Many authors have empirically discussed the preparation and stability of the TMFE with regard to hydrogen evolution. Bruckenstein *et al.*[16) investigated the adsorption behavior of the hydrogen atom at less than a monolayer amount of mercury-coated platinum surface with regard to the structure of deposited mercury. In general, hydrogen-evolution reaction at a metal surface can be correlated to the work function of the electrode as well as the potential of zero charge and the strength of hydrogen adsorption.[17–22)

In this report, hydrogen-evolution reactions at the mercury layer, from less than a monolayer to several thousand atomic layers, deposited on platinum are described with regard to the structure of mercury. The structure of the deposited mercury was investigated by means of the thermal evaporation of the mercury, followed by the determination of the mercury atoms using flameless atomic absorption spectrophotometry (AAS).[23,24) Using this procedure, the quantitative determination of a trace amount of mercury as well as the characterization of the deposited mercury layer from the evaporation temperature are possible.

Experimental

The electrolysis and the determination of the mercury were carried out with the same electrolytic cell, potentiostat, and flameless AAS mercury analyzer as those reported previously.[23,24) A Hokuto Denko Co., Model HB-107A, wave-function generator was used for the linear-potential sweep.

The mercuric perchlorate solution was prepared by dissolving mercuric oxide in 2.5×10^{-1} M (1 M=1 mol dm^{-3}) perchloric acid, and the concentration of mercury (II) was determined by EDTA titration. Triple-recrystallized potassium perchlorate was used as the electrolyte, and the other chemicals used were of a reagent grade. The water used was distilled over 3% potassium permanganate in the presence of 0.1 M sulfuric acid, and then distilled twice. Argon (99.99% or more) was purified by passing it through a titanium sponge (700 °C). All the electrolytic measurements were carried out at 25 ± 0.2 °C, and the potentials were referred to a saturated calomel electrode (SCE). The electrode surface area was 1.13 cm^2.

Pretreatment of Platinum.[25) The platinum plate ($15\times 20\times0.3$t in mm) used as an electrode had a purity above 99.99%. It was electropolished anodically at 4—4.5 V *vs.* the platinum cathode for 10 s in a mixture of potassium chloride and sodium chloride (1+1) fused at 650 °C. Then it was kept in (1+1) perchloric acid for a few min and washed with water.

Deposition of Mercury. Mercury was deposited on the platinum by means of controlled-potential electrolysis at +0.55 V (underpotential region) or +0.20 V (more negative than the reversible potential for mercury (II)/(0)), unless otherwise mentioned. Electrolysis was carried out for 15 min in a deaerated electrolyte solution (1×10^{-1} M in potassium perchlorate and 1×10^{-3} M in perchloric acid) containing 10^{-6}—10^{-4} M of mercury (II).

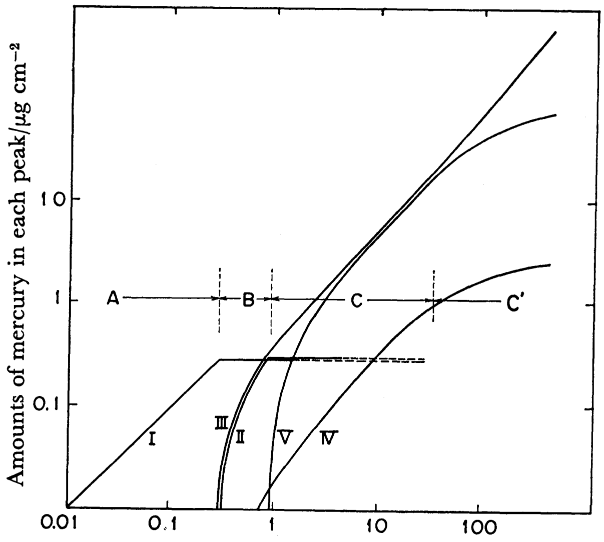
Investigation of Hydrogen-evolution Reaction. *Cylic Voltammetry*: After the deposition of mercury, the solution containing mercury (II) was drained off and the cell was washed with an electrolyte solution (1×10^{-1} M potassium perchlorate and 1×10^{-3} M perchloric acid) five times. A voltammogram was run cathodically and then anodically at a rate of 2 mV s^{-1} in 10 ml of an electrolyte deaerated for 15 min by passing argon through.

Tafel Plot: The relation between the electrode potential and the current density (10^{-7}—10^{-3} A cm^{-2}) was galvanostatically investigated in 1×10^{-1} M of potassium perchlorate and 1×10^{-1} M of perchloric acid.

Thermal Evaporation. Immediately after the completion of the electrolysis, the mercury-coated platinum was washed with water and then ethanol; it was thereafter heated in a quartz tube while the temperature was raised at a rate of 20 °C min^{-1}. The evaporated mercury was introduced into the mercury analyzer by means of an argon stream (2 l min^{-1}). The absorption intensity of mercury was recorded against the temperature (T-Hg curve).[23)]

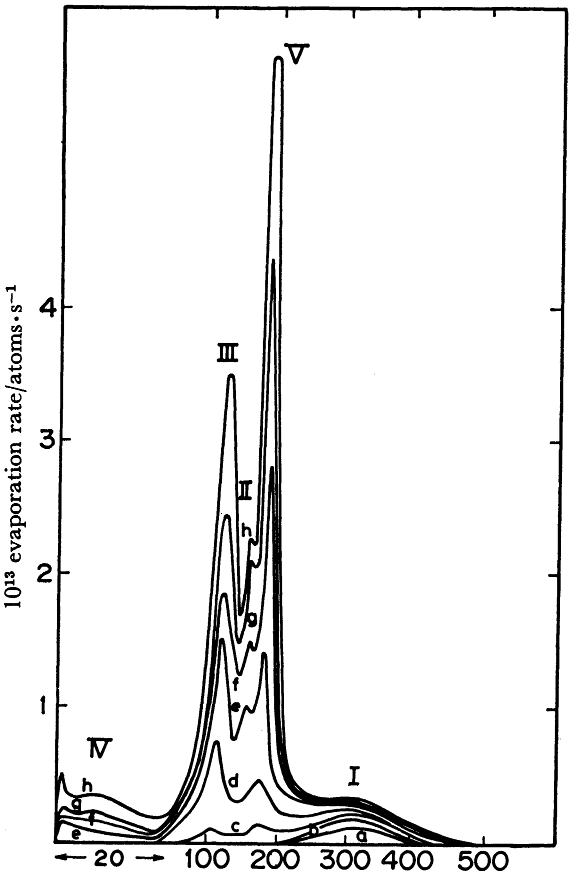
Results

Structure of Mercury Layer Deposited on Platinum. The T-Hg curves of mercury (0.12—4.1 μg cm^{-2}) deposited on platinum are illustrated in Fig. 1. With the increase in the amount of mercury deposited, one to five peaks are observed. The development of each peak with the increase in the total mercury deposited is shown in Fig. 2. With a small amount of mercury (less than 0.29 μg cm^{-2}), only Peak I at 300 °C is observed (Region A in Fig. 2). After the saturation of Peak I at 0.29 μg cm^{-2}, Peak II at 160 °C and Peak III at 110 °C start to be observed (Region B). Peak II is also saturated; the saturated amount under Peak II is 0.29 μg cm^{-2}. With more mercury, Peak III develops, and Peak IV at around 20 °C and Peak V at 190 °C appear (Regions C and C′). While the ratio of the amount of mercury under Peak III to that under Peak V nearly equals unity in Region C, the ratio increases with the increase of mercury in Region C′.



Total amount of mercury deposited/μg cm^{-2}

Fig. 2. Developments of various peaks in T-Hg curve with the increase of the amount of mercury deposited.



Temperature/°C

Fig. 1. T-Hg curves of mercury deposited on platinum. Amounts of mercury deposited (μg cm^{-2}): (a) 0.12, (b) 0.20, (c) 0.35, (d) 0.87, (e) 1.7, (f) 2.4, (g) 3.2, (h) 4.1.

The character of each peak is as follows;

Peak I. When mercury is deposited at +0.55 V (underpotential region), even in a rather concentrated mercury (II) solution (10^{-4} M), the amount of mercury under this peak, I, is also saturated at 0.29 μg cm^{-2}. Similarly to the determination of the underpotential shift, ΔU, for mercury deposition on gold,[23)] the ΔU value for mercury deposition on platinum was determined to be 0.45 V from the relation between the electrode potential of controlled-potential electrolysis and the amount of mercury deposited (E-Hg plot). Moreover, the first wave in the E-Hg plot is saturated at 0.29 μg cm^{-2} of mercury, which agrees well with the saturation of Peak I in the T-Hg curve. In this connection, the relation between the amount of mercury deposited and the amount of hydrogen adsorbed at the platinum surface, Q_H-Hg, was investigated according to the procedure proposed by Bruckenstein *et al.*[16)] The quantity of adsorbed hydrogen, Q_H, decreases linearly with the increase of mercury, and with 0.29 μg cm^{-2} of mercury Q_H comes to be zero. This indicates that the deposition of the first mercury layer proceeds *via* a site mechanism[16)] showing a combination of two platinum surface atoms with one mercury atom deposited. According to the results obtained by the E-Hg and Q_H-Hg measurements, it is evident that Peak I in the T-Hg curve corresponds to the evaporation of mercury from the stable mercury layer, Pt_2Hg, which is deposited at the underpotential. Actually, the saturated value, 0.29 μg cm^{-2}, is about one-half of the amount of mercury calculated by assuming that each platinum surface atom is associated with one mercury atom and that a roughness factor of the electrode is unity.

Peak II. Because Peak II is saturated with the same amount of mercury as Peak I (0.29 μg cm^{-2}), this peak corresponds to the evaporation of one mercury

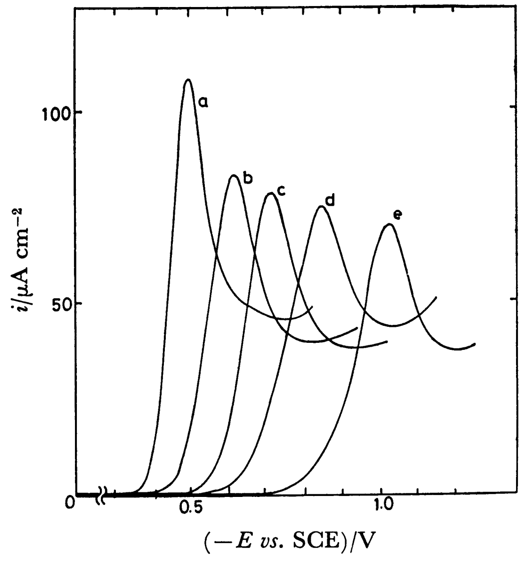


Fig. 3. Voltammograms for hydrogen evolution at platinum electrode with and without mercury. Electrolyte: 1×10^{-1} M potassium perchlorate and 1×10^{-3} M perchloric acid. Rate of potential scanning: 2 mV s^{-1}. Amounts of mercury deposited (μg cm^{-2}): (a) 0—0.29, (b) 8, (c) 22, (d) 60, (e) more than 200.

atom from Pt_2Hg_2 (or 2PtHg), thus forming Pt_2Hg.

Peaks III and IV. Peaks III and IV were previously reported to be due to the evaporation of metallic mercury and adatom mercury,respectively.[23,24]

Peak V. Peak V is identical with that of the evaporation of mercury from the $PtHg_4$ alloy produced by the procedure reported by Barlow *et al.*[26] and identified by X-ray diffraction.

Hydrogen-evolution Reaction at the Mercury-coated Platinum Electrode. Voltammograms for hydrogen-evolution reaction at the platinum electrode with and without mercury are illustrated in Fig. 3. Although the reduction potential of the hydrogen ion should be determined using a constant and small current density, the hydrogen-reduction peak potential, $E_{\rm p}$, in the voltammogram is employed for convenience for the study of the H-overpotential in the present study. The peak potential, $E_{\rm p}$, in the second cathodic potential scan is adopted because $E_{\rm p}$ in the second scan is more negative than that in the first scan as a result of the structural change of mercury film during the first cathodic polarization.[7] $E_{\rm p}$ at the mercury-free platinum electrode is -0.50 V. The relation between $E_{\rm p}$ at the mercury-coated platinum electrode and the amount of mercury deposited is shown by Curve (a) in Fig. 4. With less than 0.29 μg cm^{-2} of mercury, $E_{\rm p}$ is identical with that at platinum. With more than 0.29 μg cm^{-2}, $E_{\rm p}$ shifts to a negative value with the increase in the amount of mercury. With more than 200 μg cm^{-2}, $E_{\rm p}$ is constant at -1.05 V, $E_{\rm p}^{1}$. Even when 20 mg cm^{-2} of mercury is deposited, $E_{\rm p}$ halts at $E_{\rm p}^{1}$.

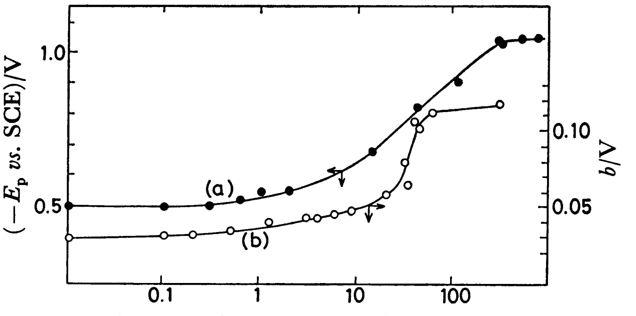


Fig. 4. Hydrogen evolution reaction at mercury-coated platinum electrode with various amount of mercury.
(a): Peak potential in cyclic voltammogram, $E_{\rm p}$, (b): Tafel slope b.

As may be seen in Fig. 3, the slope of the voltammogram in the range of low current density decreases when an electrode with a larger amount of mercury is used. To study the polarization characteristics more quantitatively, a galvanostatical investigation of the Tafel plot was carried out. The b slope in the Tafel equation, $\eta=a+b\log i$, where a and b are constants and η is the overpotential, for a hydrogen-evolution reaction is changed with the amount of mercury deposited, as is illustrated by Curve (b) in Fig. 4. With less than 1 μg cm^{-2} of mercury, b is about 0.030 V, which is identical with the value observed at mercury-free platinum. With the mercury is between 1 and 40 μg cm^{-2}, the slope changes from 0.030 to 0.085 V, and with more than 40 μg cm^{-2} of mercury, the slope is from 0.085 to 0.120. The b slope, 0.120 V, is identical with that at a hanging mercury drop electrode (HMDE). The amount of mercury, 40 μg cm^{-2}, corresponds to the boundary amount of mercury between C and C′ in Fig. 2.

Stability of Mercury Layer Deposited on Platinum. The stability of the mercury layer was investigated by measuring the T-Hg and the hydrogen-evolution reaction after lefting it stand at 25 °C in a deaerated supporting electrolyte for a definite period of time. The relation between the amount of mercury and $E_{\rm p}$, or the b value obtained at the electrode on which mercury had been deposited for 15 min in 10^{-4}—10^{-6} M mercury (II) and which was left standing for 30 min (Fig. 4), was identical with that obtained at the electrode on which mercury had been deposited for 30 s in 10^{-3}—10^{-5} M mercury (II) and which left standing for 2—5 min. Therefore, it is concluded that a standing time within 30 min exerts no significant effect on hydrogen evolution at the surface, regardless of the amount of mercury deposited. When the amount of mercury deposited was less than 10 μg cm^{-2}, no discrepancy was found in T-Hg and hydrogen evolution between those obtained after standing for 30 h and those obtained after only 30 min. When platinum coated with more than 10 μg cm^{-2} of mercury was allowed to stand for more than 3 h, the T-Hg curve changed from that obtained after 30 min standing; *i.e.*, Peak III decreased and Peak V increased. Also, after more than 20 h's standing, T-Hg showed only Peak V. Hydrogen evolution also changed with the standing time, much as with the T-Hg curve. After 2 h's standing, $E_{\rm p}$ began to shift to a more positive value; after 3, 5, and 12 h's standings, $E_{\rm p}$ were -0.95, -0.82, and -0.65 V, respectively.

Table 1. Structure of mercury deposited on platinum and hydrogen-evolution reaction at the surface

Region	Amount of mercury deposited / μg cm^{-2}	Structure of mercury layer	E_p *vs.* SCE / V	b / V
A	0—0.29	Pt_2Hg	−0.50	0.030
B	0.29—1	Pt_2Hg_2+Hg	−0.50→−0.53	0.030→0.035
C	1—40	Pt_2Hg_2+Hg+ $PtHg_4$+Hg_{adatom}	−0.53→−0.80	0.035→0.085
C′	More than 40	As region C but Hg>$PtHg_4$	−0.80→−1.05	0.085→0.118

With more than 20 h's standing, E_p reached −0.60 V, which was only 100 mV more negative than that at platinum.

The platinum contents in a mercury layer at various standing times were determined colorimetrically by means of a modified tin(II) chloride method[27] after dissolving the deposited mercury layer in nitric acid (60 °C) and treating it with aqua regia. The platinum content increased with the standing time; after standing for 3, 5, 12, and more than 20 h, the platinum contents were 10.5, 12.8, 16.0, and 19.2 at. %. The final platinum content, 19.2%, agrees well with the finding that Peak V in the *T*-Hg curve is $PtHg_4$.

Discussion

The structure of the mercury layer deposited on platinum and the hydrogen-evolution reaction at the surface are summarized in Table I as a function of the amount of mercury deposited. Although many platinum–mercury alloys, such as $PtHg_4$, $PtHg_2$, PtHg, Pt_2Hg, and Pt_3Hg, have been identified,[28] $PtHg_4$, PtHg, and Pt_2Hg are the main components in the mercury layer deposited on platinum. Particularly in the underpotential region, Pt_2Hg is preferentially formed (Region A in Fig. 2).

Bruckenstein *et al.*,[16] on the basis of the results of Q_H-Hg measurement, suggested the formation of Pt_2Hg in the initial step of the deposition. They deposited mercury at a more negative potential than the reversible potential for mercury (II)/(0) and reported that Q_H was not equal to be zero even when the platinum surface was covered with mercury in an amount large enough to saturate the Pt_2Hg layer. In the present study, if mercury is deposited on platinum in the underpotential region, Q_H comes to be zero at the electrode with mercury corresponding to the completion of the Pt_2Hg layer; this indicates that Pt_2Hg is preferentially formed at the underpotential. The reoxidation current peak, from which Pt_2Hg can be identified, was not observed in the anodic stripping voltammograms reported by Bruckenstein *et al.* Two evaporation peaks, Peak I and Peak II in the *T*-Hg curve in Region B, of mercury from Pt_2Hg_2 (or 2PtHg) indicates that the evaporation of one mercury atom from Pt_2Hg_2 requires less energy than that required for the evaporation of mercury from Pt_2Hg. This evaporation behavior obviously supports the preferential formation of Pt_2Hg at the initial step of the deposition. Bruckenstein *et al.* also described the development of $PtHg_4$. The anodic stripping peak of mercury from $PtHg_4$, however, was too broad to be distinguished from such other layers as Pt_2Hg. A well-defined peak, V, which corresponds to the evaporation of mercury from $PtHg_4$, is observed in the *T*-Hg curve in the present work. Although Bruckenstein *et al.* reported that $PtHg_2$ was formed on PtHg, $PtHg_2$ was not observed in the *T*-Hg curve.

The rate-determining step of the hydrogen-evolution reaction has been widely recognized[1] to be one of the following three reaction steps: (*i*) the discharge of the hydrogen ion, (*ii*) the chemical desorption of the hydrogen molecule, or (*iii*) electrochemical desorption. Because the Tafel slopes, *b*, for hydrogen evolution at Pt_2Hg and mercury-free platinum are 0.030 V, it is considered that the rate-determining step at their surfaces is (*ii*).[29] In the C′ region, the *b* value is 0.110—0.120 V, which is identical with that at the HMDE. The rate-determining step at their surfaces is (*i*),[30] which agrees with the dominant formation of metallic mercury in the C′ region, Peak III in the *T*-Hg curve. Although Peak III is observed in the *T*-Hg curves whenever more than 0.29 μg cm^{-2} of mercury is deposited (Regions B, C, and C′), the electrode property of the surface is far from that of mercury in Regions B and C. In the C and C′ regions, E_p is shifted in the negative direction with the increase in mercury. The relation between E_p and the amount of mercury, given as Curve (a) in Fig. 4, can be expressed empirically by the following equation:

$$E_p = E_p^{Pt} + \alpha W(E_p^{l} - E_p^{Pt})/(1 + \alpha W), \qquad (1)$$

where E_p^{Pt} and W are E_p at mercury-free platinum and the amount of mercury in μg cm^{-2}, respectively. Comparing the experimental results illustrated as Curve (a) in Fig. 4 with Eq. 1, the constant, α, is determined to be 0.026.

Even at a freshly prepared electrode with a large amount of mercury, the hydrogen-evolution peak was at −1.05 V, far positive than that at the HMDE. The platinum content in the mercury layer on such an electrode was confirmed by chemical analysis to be less than 0.01 wt%. Butler *et al.*[31] discovered, by using a dropping mercury electrode, that the presence of 0.027 wt% platinum did not affect the hydrogen-evolution reaction. The present study also confirmed the absence of any effect when a hanging mercury drop containing 0—0.35 wt% platinum was used. Therefore, the lower H-overpotential at the mercury-coated platinum with a **large** amount of mercury is not attributed to the trace amount of platinum dissolved in the mercury layer.

Furuya *et al.*[15] reported that the exchange-current density for hydrogen evolution at twenty atomic layers of silver deposited on platinum was far from that at pure silver metal. On the other hand, in such systems as copper on platinum,[5] gold on platinum,[3] platinum on gold,[3] and palladium on gold,[4] with the deposition of a monolayer metal, hydrogen evolution changed from that at the base metal to that at the deposited metal. Considering the hydrogen-evolution reaction at the deposited thin metal film, the combinations of deposited metal and base metal can be classified into two groups as follows: (*i*) Deposited metal forms stable intermetallic compounds with the base metal. The chemical interaction is too strong, and the property of the surface of the deposited metal is affected by an underlying layer, such as the base metal itself and/or a stable-compound layer formed. This group includes Pt/Hg and Pt/Ag, which show intermetallic compounds, PtHg, $PtHg_2$, and $PtHg_4$, and Pt_3Ag, PtAg, and $PtAg_3$, in the phase diagrams.[28] (*ii*) Deposited metal forms a solid solution with the base metal at any ratio instead of the formation of the stable intermetallic compounds. The property of the deposited metal atom is rather independent of the property of the base metal, and the electrochemical property of the deposited metal surface is hardly affected by the base metal when the base metal surface is completely covered with the deposited metal film. This group includes Pt/Cu, Pt/Au, and Pd/Au.

The remarkable standing-time effect on mercury-coated platinum is explained by the growth of stable intermetallic compounds because of the large interaction between mercury and platinum. In addition, it is also considered that the diffusion coefficient of base-metal atoms in metallic (liquid) mercury is much larger than that in other solid metals. In connection with the work function of the thin metal film surface, it has been reported that metal monolayers deposited on foreign substrates, such as alkali metals deposited on nickel or tungsten,[32-34] show the same work-function value as that of bulk alkali metal. In these systems, no intermetallic compounds have been reported, and the diffusion coefficient of nickel or tungsten in an alkali solid metal is smaller than that in liquid metal.

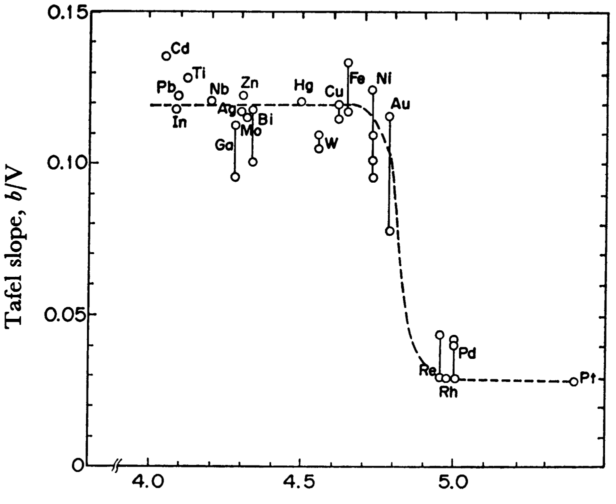


Fig. 5. Relation between Tafel slope *b* and work function of metal.
Tafel slopes *b* are cited from Ref. 35. Work function of metals are cited from Refs. 17 and 18.

Generally, hydrogen evolution at the metal surface is related to the work function of the metal.[19,20] Trasatti suggested a linear relationship between the H-overpotential at a metal surface and the work function of the metal (see Fig. 1 in Ref. 19). The relation between the Tafel slope, *b*, previously reported and the work function of the metal is shown in Fig. 5. It is evident that the *b* slopes are constant at 0.030 and 0.120 V, when the work-function values are more than 4.9 eV and less than 4.7 eV, respectively. When the work function of the metal is between 4.7 and 4.9 eV, the *b* slope shows an intermediate value of 0.030—0.120 V.

Because E_{p} and the *b* slope at the surface of monolayer mercury deposited on platinum is identical with those at the platinum surface, the work function of monolayer mercury film can be said to be close to that of platinum, but not to that of mercury. It is also estimated, from the difference between $E_{\mathrm{p}}^{\frac{1}{2}}$ and E_{p} at the HMDE, that the work function at the electrode surface with a large amount of mercury deposited is still different from that of pure mercury. The experimental relation (Curve(b) in Fig. 4) shows a remarkable change in the *b* slope when 40 μg cm^{-2} of mercury is deposited. Therefore, it is considered that the work function of the surface is around 4.8 eV. This is supported by the facts that the E_{p} values observed at gold, nickel, and copper, the work-function values of which are 4.78, 4.73, and 4.70 eV, are −0.74, −0.68, and −0.84 V, respectively, and that the E_{p} value at the mercury-coated platinum with 40 μg cm^{-2} of mercury is −0.8 V.

Through the present study it is clear that the hydrogen-evolution reaction at the mercury-coated platinum is characterized by the structure of the mercury layer, which affects the work function of the electrode surface.

Because the platinum-based TMFE is found to be troublesome with respect to the stability, the property of thin mercury film deposited on various metals will be discussed in a subsequent paper in preparation for developing an ideal TMFE.

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References

1) J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry," Plenum Press, New York (1970), Vol. 2.

2) D. M. Kolb, "Advances in Electrochemistry and Electrochemical Engineering," Wiley-Interscience, New York (1978), Vol. 11, p. 125.

3) N. Furuya and S. Motoo, *J. Electroanal. Chem.*, **88**, 151 (1978).

4) N. Furuya and S. Motoo, *Denki, Kagaku*, **41**, 364 (1973).

5) N. Furuya and S. Motoo, *J. Electroanal. Chem.*, **72**, 165 (1976).

6) N. Furuya and S. Motoo, *J. Electroanal. Chem.*, **78**, 243 (1977).

7) A. M. Hartly, A. G. Hiebert, and J. A. Cox, *J. Electroanal. Chem.*, **17**, 81 (1968).

8) Z. Stojek and Z. Kublik, *J. Electroanal. Chem.*, **60**, 349 (1975).

9) Z. Stojek and Z. Kublik, *J. Electroanal. Chem.*, **77**, 205 (1977).

10) W. R. Matson, D. K. Roe, and D. E. Carrit, *Anal. Chem.*, **37**, 1594 (1965).

11) T. M. Florence, *J. Electroanal. Chem.*, **27**, 273 (1970).

12) G. E. Bartley and T. M. Florence, *J. Electroanal. Chem.*, **55**, 23 (1974).

13) R. Neeb, *Z. Anal. Chem.*, **180**, 161 (1961).

14) G. D. Robbins and C. G. Enke, *J. Electroanal. Chem.*, **23**, 343 (1969).

15) N. Furuya and S. Motoo, *Denki Kagaku*, **41**, 307 (1973).

16) M. Z. Hassan, D. F. Untereker, and S. Bruckenstein, *J. Electroanal. Chem.*, **42**, 161 (1973).

17) S. Trasatti, *J. Electroanal. Chem.*, **33**, 351 (1971).

18) S. Trasatti, *J. Chem. Soc. Faraday Trans. 1*, **68**, 229 (1972).

19) S. Trasatti, *J. Electroanal. Chem.*, **39**, 163 (1972).

20) A. T. Kuhn, C. J. Mortimer, G. C. Bond, and J. Lindley, *J. Electroanal. Chem.*, **34**, 1 (1972).

21) L. Y. Firsiva and V. N. Gramm-Osipova, *Z. Fiz. Khim.*, **52**, 3166 (1978).

22) E. W. Brooman and A. T. Kuhn, *J. Electroanal. Chem.*, **49**, 325 (1974).

23) Z. Yoshida and S. Kihara, *J. Electroanal. Chem.*, **86**, 167 (1978).

24) Z. Yoshida and S. Kihara, *J. Electroanal. Chem.*, **95**, 159 (1979).

25) P. B. Hirsch, A. Howie, P. B. Nicholson, D. M. Pashley, and M. J. Whelan, "Electron Microscopy of Thin Crystals," Butterworths, London (1965), p. 455.

26) M. Barlow and P. J. Planting, *Z. Metallkde*, **60**, 292 (1969).

27) F. E. Beamish and J. C. Van Loon, "Recent Advances in the Analytical Chemistry of the Noble Metals," Pergamon Press, Oxford (1972), p. 306.

28) M. Hansen and K. Anderko, "Constitution of Binary Alloys," McGraw-Hill, New York (1958).

29) A. N. Frumkin, "Advances in Electrochemistry and Electrochemical Engineering," Interscience Pub., New York (1963), Vol. 3, p. 307.

30) A. N. Frumkin, "Advances in Electrochemistry and Electrochemical Engineering," Interscience Pub., New York (1961), Vol. 1, p. 65.

31) J. N. Butler and A. C. Makrides, *Trans. Farad. Soc.*, **60**, 938 (1964).

32) L. D. Schmidt and R. Gomer, *J. Chem. Phys.*, **42**, 3573 (1965).

33) L. D. Schmidt and R. Gomer, *J. Chem. Phys.*, **45**, 1605 (1966).

34) R. L. Gerlach and T. N. Rhodin, *Surface Sci.*, **19**, 403 (1970).

35) H. Kita, *J. Electrochem. Soc.*, **133**, 1095 (1966).