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HYDROGEN ELECTRODE REACTION IN ALKALINE SOLUTION

III Hydrogen overvoltage at Ga, In, Tl and Pb electrodes and its periodic variation with atomic number of electrode metals

By

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Abstract

Periodic change of the hydrogen overvoltage with atomic number of electrode metals was studied in alkaline solution.

Tafel lines on Ga, In, Tl and Pb were observed by galvanostatic pulse method using $(CH_3)_4NOH$ solution in order to prevent the deposition of alkali metal on these high overvoltage metals as concluded on Hg in NaOH solution (Part I and II). The hydrogen overvoltages at $i = 1$ mA/cm^2, $\eta_{1\,mA}$, on these metals were supplemented in the review of $\eta_{1\,mA}$ on various metals.

The review shows that (a) the hydrogen overvoltage in alkaline solution is essentially the periodic function of the atomic number as in acidic solution and (b) its value is higher in alkaline solution than in acidic solution for transition metals including IB (d-metals), whereas the reverse phenomenon was found for the metals after IIB (sp-metals). The fact (b) was discussed on the basis that the catalytic and the electrochemical mechanisms are operating on d- and sp-metals respectively.

Liquid Ga shows higher overvoltage than the solid one and the heat of activation, $-RT^2(\partial \ln i/\partial T)_{\eta=0\ 7v}$, was found at 2.8 and 15~22 kcal/mole on liquid and solid Ga.

Introduction

One of the present authors has reported[1] the periodic change of the electrocatalytic activity for the hydrogen electrode reaction (h.e.r.) with atomic number of electrode metals by using literature values obtained in acidic and alkaline solutions, where the electrocatalytic activity is defined as the exchange current density at a given condition.

The hydrogen overvoltage at a given current density will be also used as a measure of the activity, *i.e.*, the more active the electrode is the lower

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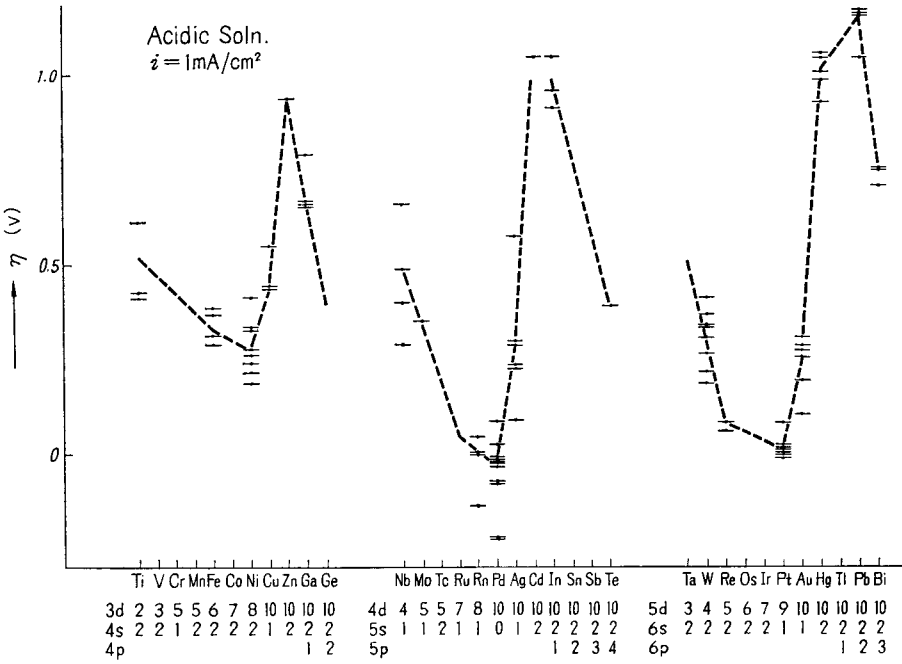

Fig. 1. Periodic variation of the hydrogen overvoltage in acidic solution with atomic number of electrode metals.
Each value was estimated at $i = 1\ mA/cm^2$ from Table 1 of Ref. 1.

the overvoltage*) is. Direct comparison of the hydrogen overvoltages at a constant current density, will avoid the uncertainty which might be included in the evaluation of the exchange current density by the long "extrapolation" of the Tafel line. Figure 1 shows hydrogen overvoltages at $1\ mA/cm^2$ on various electrodes in acidic solutions, estimated from the Table 1 of Ref. 1. One can see from Fig. 1 the periodic variation of the hydrogen overvoltage within three long periods of the Periodic Table. Results in alkaline solutions, however, are not so many in the kind of electrode metals studied as in acidic solution.

Part III in the present series of papers aims to establish the relation between the hydrogen overvoltage and the atomic number in alkaline solution and to obtain information for the elucidation of reaction mechanism by comparing the relation with that in acidic solution.

Experiments were carried out on Ga, In and Tl of which the experi-

*) Overvoltage is defined as the minus of the electrode potential referred to the reversible hydrogen electrode (r.h.e.) in the same solution.

mental results are absent in Table 1 of Ref. 1. Lead electrode was also subjected to the measurements, whose reported result is in far deviation from those in acidic solution. Alkaline solution was used of a strong organic base, tetramethylammonium hydroxide (TMA–OH), according to the conclusion of Part I[2] and II[3] that the TMA–OH solution allows us to observe the h.e.r. in wider potential range than in NaOH solution owing to the more negative potential of tetramethylammonium ion (TMA^+) discharge than Na^+'s.

§ 1 Experimental

All electrode materials are supplied from Johnson Matthey & Co., Ltd, of which specification on purity is shown in the second column of Table 1. Electrodes of each metal were prepared as follows.

Ga: Sample of Ga rod, degreased by benzene, was melted under the stream of the purified hydrogen and introduced onto the spoon in the main compartment of the cell.[3] The spoon was located at the lower end of J shape glass tube, set by means of the sleeve joint to the cell. Surface film of the melt was removed by its sticking action on the wall of glass container. Ga on the spoon which reflected metallic colour served as electrode where the electrical contact was obtained by W wire sealed into a depression in the center of spoon. Apparent surface area was 0.385 cm^2. The electrode was kept above the solution by pulling up the holder (J shape glass tube with spoon) during pre-electrolysis to prevent dissolving in contact with the alkaline solution.

In: Indium wire (dia., 1.6 mm) was first degreased by benzene and cut by sharp glass knife. The sample thus obtained was mounted on the spoon of the holder and then heated to above the melting point, *i.e.*, to 200°C under the purified H_2 of *ca.* 1 cm Hg. Heating and cooling rates were 100°C/hr. Indium on the spoon was then electropolished with a current density of 0.3 A/cm^2 for 10~30 minutes in mixture of conc. HNO_3 and CH_3OH (ratio of 1 to 2).[4] After rinsing thoroughly with conductivity water, the holder with In on the spoon was set to the main compartment. Cathodic pre-polarization was applied in variety of conditions to In. It was found that the reproducible results were obtained with the cathodic pre-polarization at $-1.2\sim-1.5$ v (r.h.e. scale) with 5~60 mA/cm^2 for 15 hrs, resulting in no hysteresis in the Tafel relations taken with increasing and decreasing current density. Apparent surface area was 0.385 cm^2.

Tl: Tl wire (dia 1.6 mm) degreased by benzene was cut by sharp glass knife. The sample was then immersed in ethyl alkohol for 10 minutes. The surface film of darkish colour dissolves and the sample became soft with metallic brightness and whitened gray colour. After rinsing with conductivity water,*) the sample was mounted on the spoon and subjected to the heat treatment as In, where the temperature was raised to 340°C (melting point, 302.5°C) and lowered to 20°C with the rate of 100°C/1 hr. Thus, the holder with Tl on the spoon was set to the main compartment. Apparent surface area was 0.403 cm^2.

*) When the sample is exposed to air after the treatment in dilute sulfuric acid, it became hard and its colour rapidly changed from metallic to gray one.

Pb: Pb rod (dia., 6 mm) was cut by steel knife after degreased by benzene. The sample was mounted on the spoon where the W contact at the depression of the spoon was previously plated with Pb. Heat treatment was carried out under the purified N_2 atmosphere in a similar way with that of In. The temperature was raised to 400°C (melting point, 327.4°C). The holder was then set to the main compartment after eliminating the surface film of darkish violet colour by the glass knife. The sample was subjected to the anodic dissolution with current density of 0.4 A/cm² for 30 seconds in the electrolyte solution for study. The solution was then replaced completely with new one in advance of measurements. Apparent surface area was 0.644 cm².

Form of the electrodes and their pre-treatments described above are summarized in Table 1.

TABLE 1. Purity, form and pre-treatment of electrodes

Metal	Spectroscopic analysis (ppm)	Form	Pre-treatment
Ga	Cu, Mg, Ag; each less than 1	Disk	Degreased by benzene. Surface film was removed by its sticking action on glass wall upon melting at 35°C under H_2. Disk electrode was prepared in H_2.
In	Pb, 2; Fe, Tl, 1; Mg, less than 1	Disk	Degreased by benzene. Thermally treated at 200°C under H_2 for disk electrode preparation. Electropolished with 0.3 A/cm² for 10 ~ 30 mins. in conc. $HNO_3 + CH_3OH$ (1 : 2). Prepolarized cathodically at $-1.2 \sim -1.5$ v (r.h.e.) for 15 hrs.
Tl	Fe, 1; Cd, Ca, Li, Mg, Na, each less than 1	Disk	Degreased by benzene, Dissolved in C_2H_5OH for 10 mins. Thermally treated at 340°C in H_2 for disk electrode preparation.
Pb	Cd, Fe, 1; Al, Bi, Cr, Mg, Ti, each less than 1	Disk	Degreased by benzene. Thermally treated at 400°C in N_2 for disk electrode preparation. Surface film was removed by glass knife. Dissolved by anodic polarization with 0.4 A/cm² for 30 seconds in 1N $(CH_3)_4NOH$.
Hg	99.999%	Hanging drop	Distilled thrice in vacuum

Solution was prepared from 10.4% TMA-OH of special grade (Kishida Chemicals Ltd., Osaka, Japan; residue on ignition. <0.02%; chloride, <0.001%; iron <0.003%) and the conductivity water. Solutions used, 1N TMA-OH in most cases, were purified by pre-electrolysis with current of 5 mA for more than 48 hrs.

Measurements were carried out by the galvanostatic pulse method at 25 ± 0.05°C. In the case of Ga, temperature was changed over the range between 10 and 50°C.

Cell, purification of gas, order of measurements, control of pH, *etc.* are the same as described elsewhere.[2)]

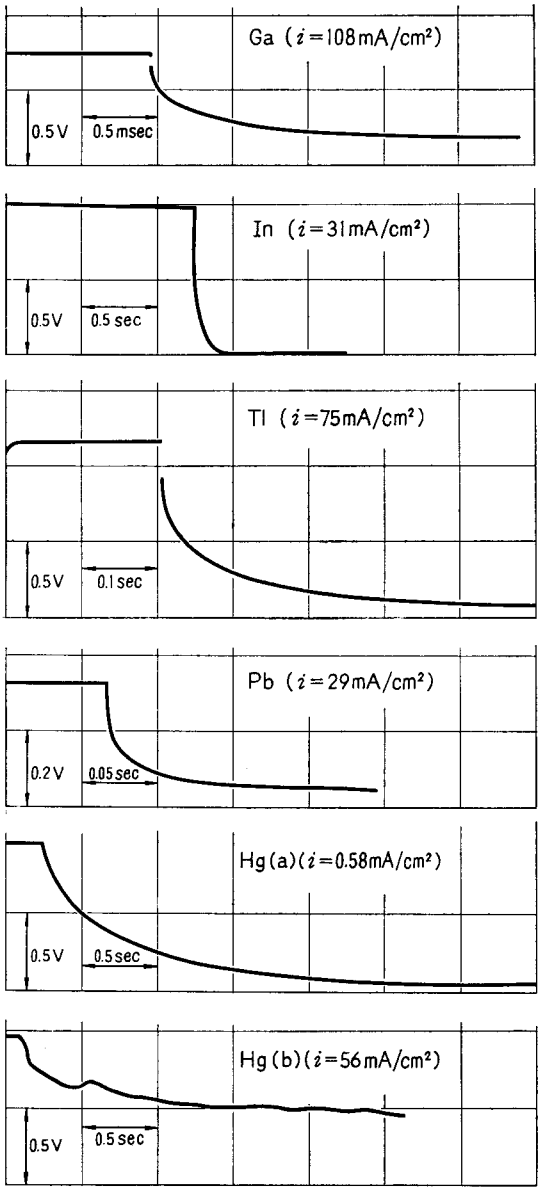

Fig. 2. Decay curves of the galvanostatic transient on Ga, In, Tl, Pb and Hg in 1N TMA-OH solution.
Ga, at 11°C; Others, at 25°C

§ 2 Results

2-1 Decay curve

Galvanostatic transients are illustrated in Fig. 2 for each metal studied and for mercury.[3] Previously,[3] we concluded on Hg that TMA^+ ion discharges and the discharged substance starts to accumulate to a detectable extent at the potential, −1.8 v (NHE). Decay curve on Hg which starts from the potential more negative than −1.8 v shows irregular variation of potential as exemplified in Fig. 2, Hg (b). At more positive starting potentials, on the other hand, the potential decays monotonously without any irregular variation of potential (Hg (a) in Fig. 2). Decay curves on other metals are quite similar to that of Hg (a) at all current densities studied ranging from 3×10^{-5} to 0.3 A/cm.^{2} Thus, we conclude that the accumulation of the discharged substance does not occur to a detectable extent on Ga, In, Tl and Pb in the potential range concerned; namely, that the steady potential observed at a given current density is attributed to the h.e.r. and is not disturbed by the deposition of TMA^+ ion on the electrode surface.

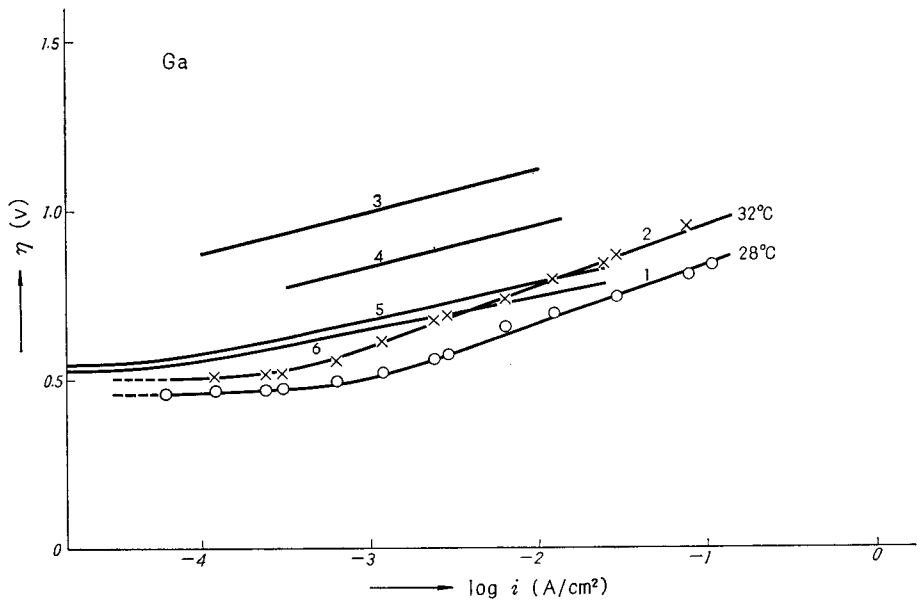

Fig. 3. Tafel relations on solid and liquid Ga.
1, 2, present data in 1N TMA-OH (Dotted horizontal lines represent the rest potential);
3, liquid Ga in 1N NaOH[5]; 4, liquid Ga in 0.5N NaOH[6];
5, liquid Ga in 1N H_2SO_4[7]; 6, solid Ga in 1N H_2SO_4[1].

2-2 Tafel line

Ga: Rest potential was found at $-0.45\sim-0.50$ v (r.h.e.) in 1.25N TMA-OH (pH=13.7). Such a high deviation from the potential of the r.h.e. might be due to the dissolution of Ga.

Tafel lines at liquid and solid electrodes are presented in Fig. 3, in comparison with the reported ones in literature[5~7] (curves 3~6). Present results show lower overvoltage and higher slope than the others in alkaline solution. Tafel equations are,

$$\eta\,(\mathrm{v}) = 1.13 + 0.175 \cdot \log i \qquad \text{on liq. Ga at } 32^\circ\mathrm{C}$$

$$\eta\,(\mathrm{v}) = 1.01 + 0.17 \cdot \log i \qquad \text{on sol. Ga at } 28^\circ\mathrm{C}$$

at $i>1$ mA/cm.^{2} At $i<1$ mA/cm^2, the value of η approaches each rest potential, -0.46 and -0.50 v (dotted lines) with decrease of current density.

BAGOTSKAYA *et al.* conducted extensive studies on Ga electrode but as seen from Fig. 3, their results in 1N[5] and 0.5N[6] NaOH (curves 3 and 4)

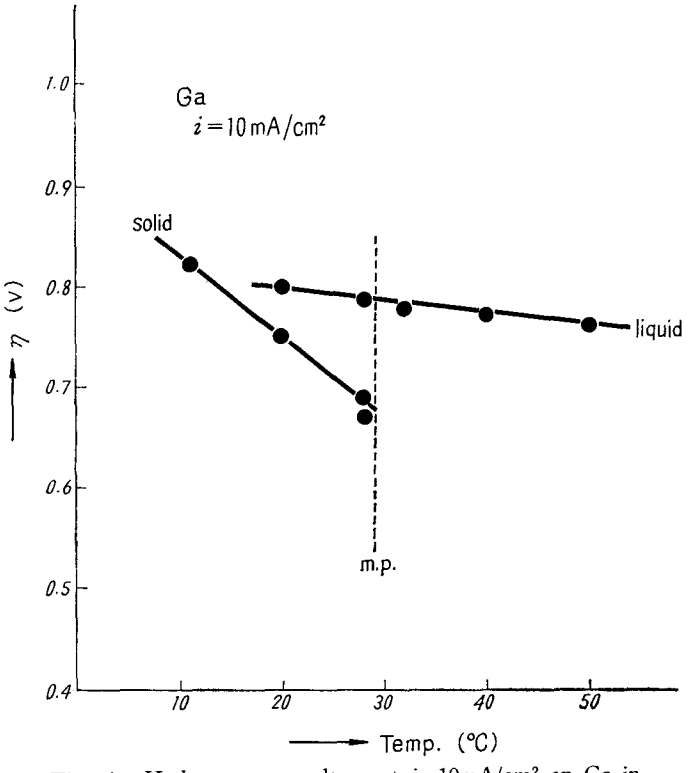

Fig. 4. Hydrogen overvoltage at $i=10$mA/cm^2 on Ga in 1N TMA-OH as a function of temperature.

show large difference between them with higher overvoltage than those in 1N H_2SO_4 solution[7] (curves 5 and 6). Present overvoltage in 1.25N TMA-OH, however, is lower than the latter's for the respective liquid and solid Ga except for the part at high current densities. MOROZOV *et al.*[8] studied the effect of tetrabutylammonium ion on the overvoltage in acidic solution at liquid Ga (32°C) and found the increase of overvoltage by *ca.* 200 mV. If such an effect holds with respect to TMA^+ ion in alkaline solution, the present data may indicate the upper value of overvoltage.

Figure 4 shows the variation of overvoltage at $i=10$ mA/cm^2 with temperature. In the case of liquid Ga, the supercooling was observed down to 20°C. It is seen from Fig. 4 that the overvoltage on liquid Ga is higher than that on solid one, by 0.11 v at melting point. Higher value of overvoltage on liquid Ga has been reported in acidic solution by many workers[9~13] in contrast to the results by CHRISTOV *et al.*[14,15] The latter authors discussed the earlier

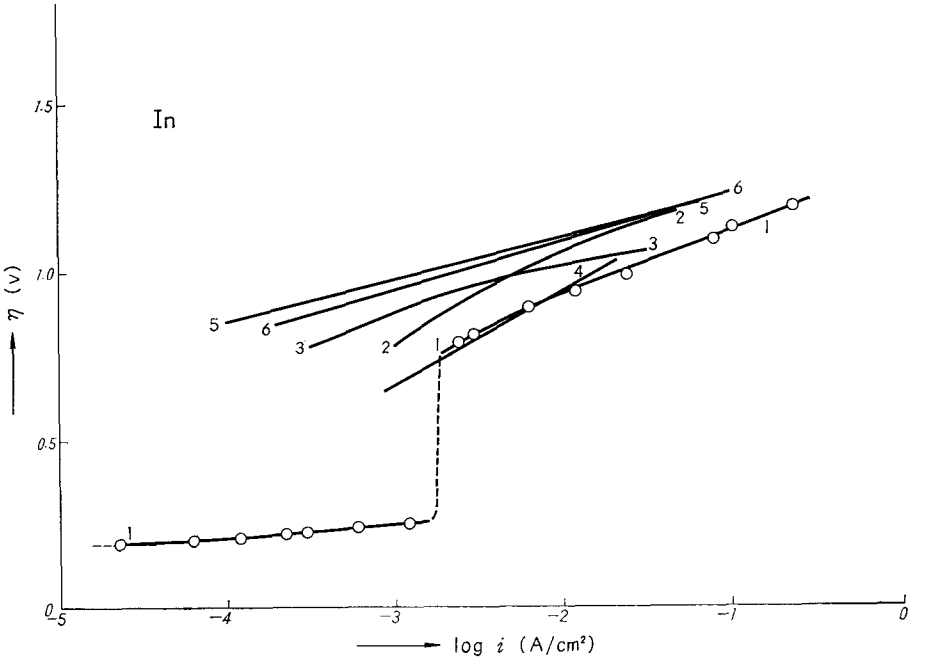

Fig. 5. Tafel relations on In.
1, present data in 1N TMA-OH at 25°C (Dotted horizontal line represents the rest potential.); 2, 1N HCl[17];
3, 1% $In_2(SO_4)_3+H_2SO_4$, pH=0.86[18];
4, 0.1 M $In_2(SO_4)_3+H_2SO_4$, pH=2.5[19];
5, 1 M $HClO_4$[4] 6, 2N H_2SO_4[20].

results of higher overvoltage on liquid Ga in terms of impurities in the system. Present results, conducted in the purified system, however, reproduce the higher overvoltage at liquid Ga even in alkaline solution.

SABO and BAGOTSKAYA[12] concluded that the contradictory results of CHRISTOV *et al.* are due to the effect of oxygen in the system. BELOBA *et al.*[16] also assume the effect of oxygen as a possible explanation.

The heat of activation, defined by $\Delta H^{\ddagger} = -RT^2(\partial \ln i/\partial T)_{\eta=0.7v}$, was found at 2.8 and 15~22 kcal/mole on liquid and solid Ga respectively.

In: Rest potential was $-0.17 \sim -0.19$ v (r.h.e.) at 25°C.

A typical Tafel relation is shown in Fig. 5 where the resluts in acidic solution reported in literature are quoted for comparison.[4,17~20] Present result at high current densities (curve 1) is expressed by the equation,

$$\eta\,(\mathrm{v}) = 1.30 + 0.19 \log i \qquad \text{at } 25°\mathrm{C}.$$

Comparison with others shows that the present overvoltage in alkaline solution is lower than those in acidic solution (curves 2, 3, and 5), though the result of KOCHEGAROV *et al.*[19] (curve 4) is close to the present one. With decrease of current density, abrupt change of overvoltage occurs at around 2 mA/cm²

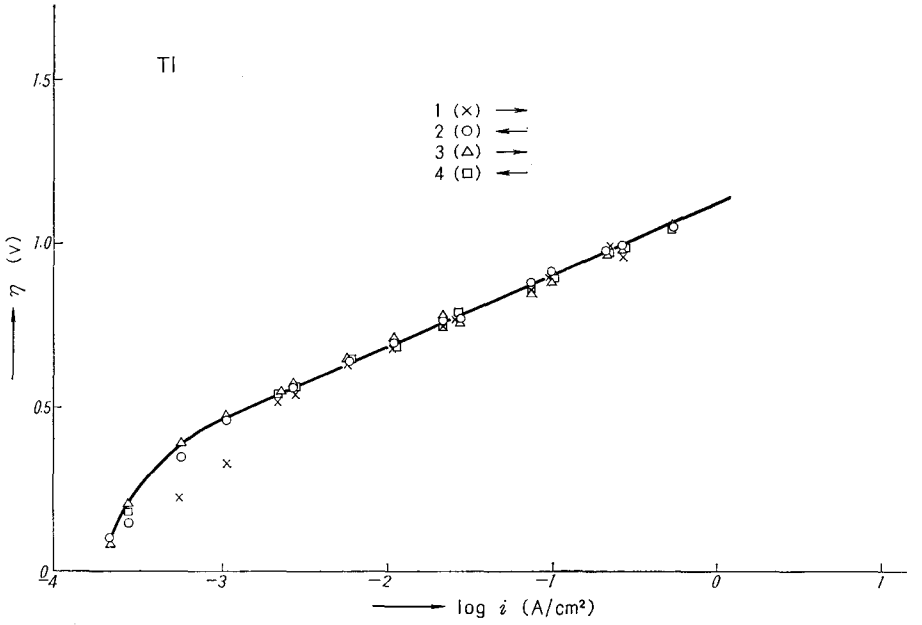

Fig. 6. Tafel relations on Tl in 1N TMA-OH solution at 25°C. The number and arrows in the figure show the sequence of measurements.

and overvoltages at $i<2\text{mA/cm}^2$ are close to the rest potential (dotted line). Further detailed study will be required for understanding of the behaviour of the Tafel relation at these low current densities.

Tl: Rest potential was found at the reversible potential of the h.e.r. immediately after immersion of the electrode, shifted gradually in the positive direction and became finally steady at 0.21～0.22 v (r.h.e.). The Tafel relation was then measured several times with increasing or decreasing direction of current density. Results in Fig. 6 are reproducible except for the part at $i<1\text{ mA/cm}^2$, where the depolarization is noticed. The Tafel equation at $i>1\text{ mA/cm}^2$ is

$$\eta\,(\text{v}) = 1.12 + 0.21 \cdot \log i \qquad \text{at } 25°\text{C}.$$

At $i>100\text{ mA/cm}^2$, superpolarization appears in the galvanostatic transients. Here, the steady values are taken for plotting the Tafel relation.

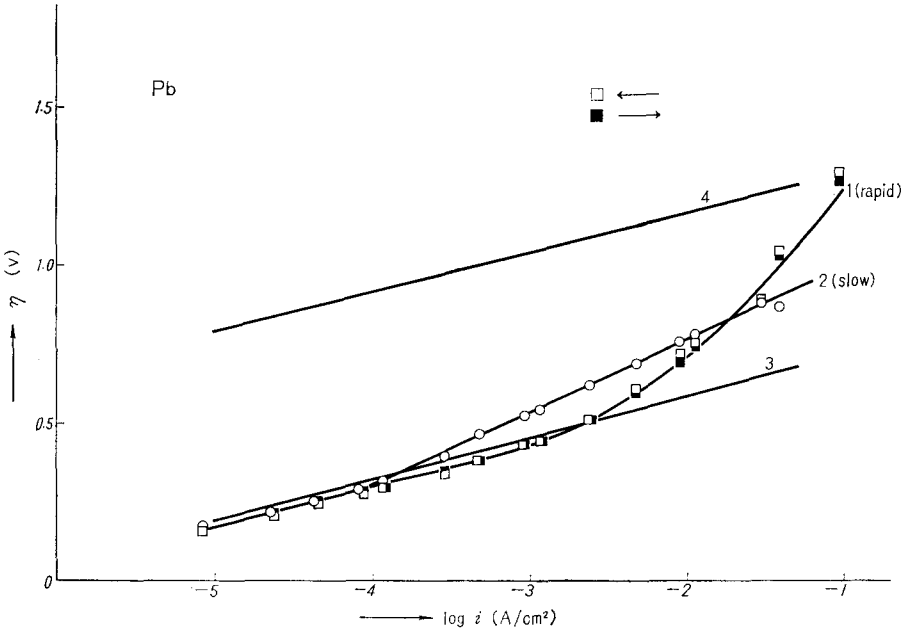

Fig. 7. Tafel relations on Pb.
1 and 2, present data in 1N TMA-OH at 25°C;
3, 0.5N NaOH[20]; 4, 0.5N H_2SO_4[20].

Pb: Rest potential was close to the reversible potential, being slightly positive, *i.e.*, 10～15 mv (r.h.e). Tafel relations are illustrated in Fig. 7. Slow increase of potential with time was noticed at the current densities between 0.1 and

20 mA/cm² and superpolarization at the higher current densities. Thus, the rapid measurement gives curve 1 in Fig. 7, whereas the slow one gives curve 2. Each point in the latter case was obtained after the steady state which takes usually a few minutes. Results obtained by BOCKRIS and SRINIVASAN[21] were inserted in the figure (curves 3 and 4). Comparison shows the significant decrease of overvoltage by changing the solution from acidic to alkaline

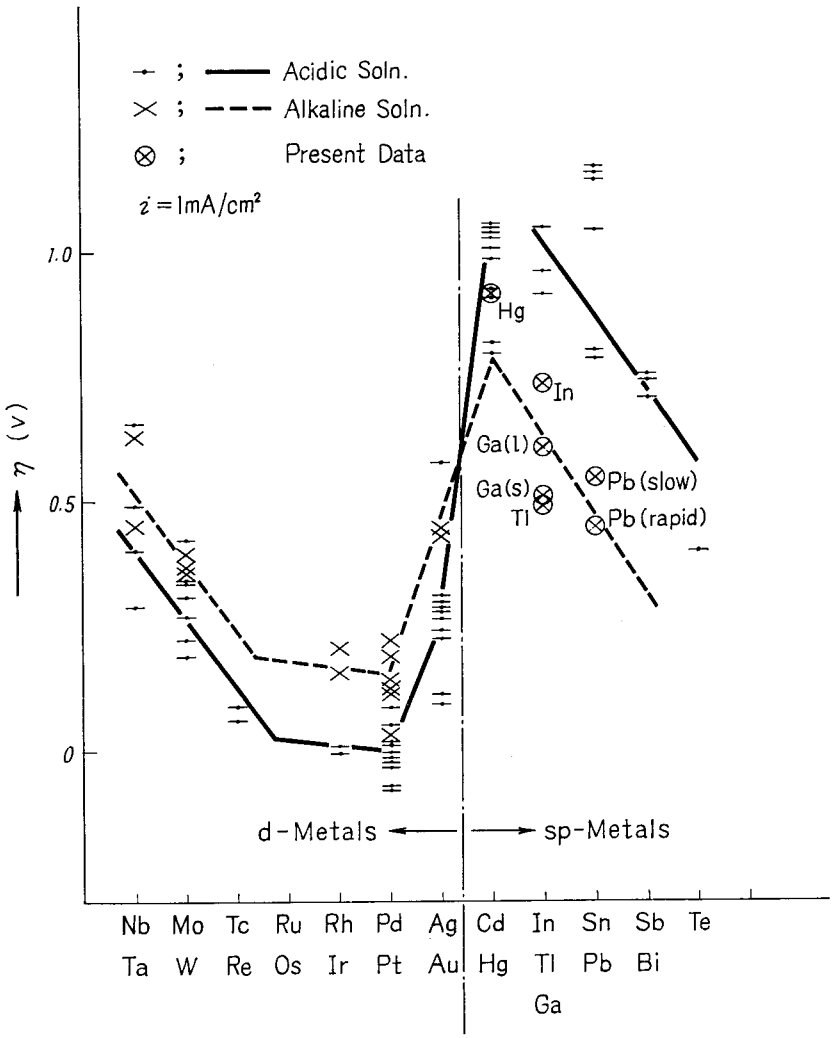

Fig. 8. Periodic variation of overvoltage at $i=1$ mA/cm² with atomic number of electrode metals.
-•-, —, in acidic solution; ×, - - -, in alkaline solution; ⊗, present data in 1N TMA-OH at 25°C.

one and the good agreement of the present result in 1N TMA–OH with that in 0.5N NaOH (curve 3) at low current densities. Such a coincidence indicates no effect of cation on the hydrogen overvoltage in alkaline solution. The Tafel equation at low current densities is expressed as

$$\eta\,(\mathrm{v}) = 0.83 + 0.13 \cdot \log i\,,$$

while at high current densities (slow measurement) as

$$\eta\,(\mathrm{v}) = 1.23 + 0.23 \cdot \log i\,,$$

respectively.

2-3 Periodic variation of the hydrogen overvoltage

The hydrogen overvoltage at 1 mA/cm^2 was estimated on Ga, In, Tl and Pb from the present data in § 2–2 and inserted in Fig. 8 (⊗), which includes that of Hg[3] and others (×) from the Table 1 of Ref. 1. The symbol, –•–, represents the data in acidic solution.

Figure 8 indicates that the hydrogen overvoltage in alkaline solution is also essentially the periodic function of the atomic number, being the smallest at the metals of VIII group in the Periodic Table and the highest at IIB or IIIB metals. Thus, it is concluded that the most important factor in determining the activity is the intrinsic property of metal. It is further noticed that for d-metals (transition metals including IB), the overvoltage in alkaline solution is higher than that in acidic solution whereas, for sp-metals (metals after IIB), the reverse relation is observed, *i.e.*, the overvoltage in alkaline solution is lower than that in acidic solution. Such a contrast seems to reflect the difference in the mechanism operating at d- and sp-metals respectively.

§ 3 Discussion

Experimental results described above are summarized as follows: (1) Decay curves of galvanostatic transient indicates no accumulation of the discharged substance from TMA^+ ion on Ga, In, Tl and Pb electrodes. Thus, the hydrogen evolution reaction proceeds on these electrodes without disturbance owing to the accumulation in contrast to the case of Hg in NaOH solution,[2] where sodium accumulates at high current densities. (2) Overvoltage at $i = 1$ mA/cm^2 in alkaline solution, is essentially the periodic function of the atomic number as in the case of acidic solution, showing the lowest value (highest activity) at the metals of VIII group and the highest value (lowest activity) at IIB or IIIB metals in the Periodic Table. (3) The overvoltage at Hg, Ga, In, Tl and Pb electrodes is lower in alkaline solution than in acidic solution in contrast to the behaviour at d-metals, their overvoltage

being higher instead in alkaline solution.

One of the present authors[1] applied the catalytic or the electrochemical mechanism to d- or sp-metals in extension of the conclusion drawn by HORIUTI and OKAMOTO.[22] The effect on the overvoltage of changing solution from the acidic to the alkaline one will be discussed on the basis of the respective mechanisms as follows.

d-metals (catalytic mechanism)

The chemical potential of metal electron, $\mu(e^-)$, is defined as

$$\mu(e^-) \equiv -F(V+\phi_e), \qquad (1)$$

where V is the electrostatic potential of the electrode and ϕ_e is the work function respectively. Defining the overvoltage as $F\eta = \mu(e^-) - \mu(e^-)_{rev}$, we have the following relation for the h.e.r.,

$$2\mu(H^+) + 2\mu(e^-) - 2F\eta = \mu(H_2), \qquad (2)$$

where $\mu(e^-)_{rev}$ is the value of $\mu(e^-)$ at the r.h.e. and the other μ's represent the chemical potential of the species indicated in parenthesis. From Eqs. (1) and (2), we obtain

$$FV = \mu(H^+) - \frac{1}{2}\mu(H_2) - F\eta - F\phi_e .$$

Thus, the variation of V with $\mu(H^+)$ is given as

$$F\Delta V = \Delta\mu(H^+) \qquad \text{at const. } \mu(H_2),\ \eta \text{ and } \phi_e\text{*)} \qquad (3)$$

or from Eq. (2)

$$\Delta\mu(e^-) = -\Delta\mu(H^+) \qquad \text{at const. } \mu(H_2) \text{ and } \eta. \qquad (4)$$

When the acidic solution is replaced with the alkaline one, $\mu(H^+)$ decreases and hence from Eq. (3), the potential of electrode becomes more negative. It is thus expected that the water molecule in contact with the electrode surface is suffered from more enhanced polarization in alkaline solution by increase of potential gradient at boundary and will be more tightly bound to the surface than in acidic solution.

Rate-determining step of the catalytic mechanism, *i.e.*, the recombination of the adsorbed hydrogen atoms, includes none of the charged species and as a first approximation, no effect of solution composition will be expected.

*) MATSUDA *et al.*[23] have discussed the change of ϕ_e during the occurrence of the h.e.r. in alkali metal hydroxide solution, on the basis of the formation of intermetallic compound.

Present result of higher overvoltage in alkaline solution for d-metals is not in harmony with this expectation. One of the possible explanations will be the hindrance effect of the more tightly bound water molecule in alkaline solution on the occurrence of the recombination step.

sp-metals (electrochemical mechanism)

Rate expression for the electrochemical mechanism, where the rate-determining step is $H_2^+(a)+e^- \rightarrow H_2$, has been given[1] on the basis of the generalized theory of reaction rate developed by HORIUTI[24] as,*)

$$i_+ = 2e(kT/hA)N^* \theta_{\sigma^*(0)} q^* / p^{H_2^+} p^{e^-} \qquad (5)$$

or

$$i_+ = 2e(kT/hA)N^* \theta_{\sigma^*(H_2^+)} q^* / q^{H_2^+} p^{e^-}, \qquad (6)$$

where i_+ is the forward rate of the h.e.r., A the surface area, $\ddagger$ the critical complex of the rate-determining step, σ^* the site for $\ddagger$, N^* the number of site, $\theta_{\sigma^*(0)}$ or $\theta_{\sigma^*(H_2^+)}$ the probability of σ^* being vacant or occupied with the adsorbed hydrogen molecule ion, $H_2^+(a)$, and q's or p's are the function defined as

$$q^\delta = \exp\{-\varepsilon(\delta)/RT\}, \qquad \delta = \ddagger,\ H_2^+(a) \qquad (7.a)$$

or

$$p^\delta = \exp\{-\mu(\delta)/RT\}, \qquad \delta = H_2^+(a),\ e^-, \qquad (7.b)$$

respectively. The $\varepsilon(\delta)$ in Eq. (7. a) is the reversible work required to bring δ from its standard state to a vacant σ^*. The reversible work for $\delta = \ddagger$, $\varepsilon(\ddagger)$, is related to the potential energy of the initial system of the rate-determining step, *i.e.*, $\varepsilon(H_2^+)+\mu(e^-)$, by the treatment of HORIUTI and POLANYI[25] as

$$\varepsilon(\ddagger) = \text{const.} + \beta\{\varepsilon(H_2^+) + \mu(e^-)\}, \qquad (8)$$

where β is the positive proper fraction. The reversible work for $\delta = H_2^+(a)$, $\varepsilon(H_2^+)$, on the other hand, is expressed as

$$\varepsilon(H_2^+) = \varepsilon_0(H_2^+) + F\phi_H, \qquad (9)$$

where ϕ_H is the electrostatic potential at the place where $H_2^+(a)$ is situated and $\varepsilon_0(H_2^+)$ is the constant independent of ϕ_H. The change of ϕ_H with $\mu(H^+)$

*) Equating I of Eqs. (15) and (16) of Ref. 1 to $H_2^+(a)+e^-$ and $iA(a)$ to $H_2^+(a)$, we have Eqs. (5) and (6). The symbol (a) of $H_2^+(a)$ is conventionally omitted in the present equations.

at constant $\mu(H_2)$, η and ϕ_e, has been treated by HORIUTI[26] and is given as

$$F\Delta\phi_H = \alpha_h \Delta\mu(H^+), \tag{10}$$

where α_h is the positive proper fraction.

The chemical potential of H_2^+(a), $\mu(H_2^+)$, in Eq. (7.b) is given from the partial equilibrium condition of the step, $2H^+ + e^- = H_2^+$(a), as

$$\mu(H_2^+) = 2\mu(H^+) + \mu(e^-). \tag{11}$$

Equation (5) or (6) is now applied to the following two extreme cases.

(i) $\theta_{\sigma^*(0)} = 1$. Equation (5) is rewritten by using Eqs. (7), (8), (9) and (11) as

$$RT \cdot \ln i_+ = \text{const.} - \left[\beta\left\{\varepsilon_0(H_2^+) + F\phi_H + \mu(e^-)\right\} - 2\left\{\mu(H^+) + \mu(e^-)\right\}\right].$$

Partial differentiation of the above equation with respect to $\mu(H^+)$, and Eqs. (4) and (10) yield

$$RT\frac{\partial \ln i_+}{\partial \mu(H^+)} = \beta(1-\alpha_h). \tag{12}$$

Since the factors, β and α_h, are the positive proper fraction, the right hand side of Eq. (12) is the positive quantity. Thus, the current density at a given overvoltage increases with $\mu(H^+)$ or decreases with increase of pH, which results in the increase of overvoltage with pH at a constant current density. Hence, Eq. (12) cannot explain the present solution effect for sp-metals.

(ii) $\theta_{\sigma^*(H_2^+)} = 1$. Equation (6) is rewritten by using Eqs. (7), (8) and (9) as

$$RT \cdot \ln i_+ = \text{const.} - (\beta-1)\left\{\varepsilon_0(H_2^+) + F\phi_H + \mu(e^-)\right\}.$$

Partial differentiation of the above equation, and Eqs. (4) and (10) yield

$$RT\frac{\partial \ln i_+}{\partial \mu(H^+)} = -(\alpha_h - 1)(\beta - 1) \tag{13}$$

Since α_h and $\beta > 0$, the right hand side of Eq. (13) is the negative quantity. Hence, on the contrary to the case (i), the overvoltage at a constant current density is expected to decrease with increase of pH.

Thus, Eq. (13) is qualitatively in agreement with the present solution effect for sp-metals. Since Eq. (13) is obtained at the limiting case of $\theta_{\sigma^*(H_2^+)} = 1$, the question arises at which value of $\theta_{\sigma^*(H_2^+)}$, the overvoltage starts to decrease with increase of pH in accordance with the experimental results. However, no useful information is now available on the isotherm of H_2^+(a) for sp-

metals. Further experimental studies will be required to solve the above question.

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