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Author(s)	KITA, Hideaki; KURISU, Takao
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Review

ELECTROCATALYSIS BY d- AND sp-METALS

By

Hideaki KITA*) and Takao KURISU**)

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Summary

A detailed analysis of the large number of available experimental data for the hydrogen electrode reaction furnishes the information that the catalytic activity of metal electrode is a periodic function of the atomic number within three long periods. The activity increases with successive addition of an electron to the d-orbital and sharply decreases after the completion of the d-orbital with one or two electrons in the s-orbital. The activity is found to have a secondary dependence on the solution composition and the surface state of metals. Of the various properties of metals the work function provides a key for understanding the reaction mechanism. When the activity is plotted against the work function, the family of metals is divided into two groups (d- and sp-metals). Each group of metals exhibits an entirely different behaviour in phenomena related to the hydrogen electrode reaction.

To summarize observations on the electrolytic reduction of organic compounds it is stated that the d- and sp-metal electrodes, respectively, reduce the non-polar unsaturated bond and polar groups of organic compounds. This is supported by several examples of the selective reduction between different functional groups in a molecule. Formation of cis- and trans-isomers is also found to be characteristic for the d- and sp-metals, respectively. These results are viewed against the background of the hydrogen electrode reaction. Electronic distribution to be expected at the d- and sp-metal surfaces is discussed.

I. Introduction

The hydrogen electrode reaction, $2H^+ + 2e^- = H_2$, is an heterogeneous catalysis where an electrode material acts as catalyst. The electrochemical approach to heterogeneous catalyses provides many advantages in comparison with the usual chemical one. Much emphasis should be given especially to the fact that we can easily apply a wide range of potential to an electrode, so that one can study kinetics even on the very inactive catalyst such as mercury. The hydrogen electrode reaction is the only case in which the

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*) Dept. of Chemistry, Faculty of Science, Hokkaido Univ., Sapporo, Japan

**) Kawasaki Steel Co., Chiba, Japan

kinetics have been observed on most of metals except for alkali and alkali earth metals. Hence, it is a good example in which to see the catalytic action of metals.

The purpose of the present article is to survey the catalytic action of electrode metals for the hydrogen electrode reaction as well as for the electrolytic reduction of organic compounds, and to deduce a common nature in the catalytic action. There will also be discussion of which property of metal is the most important in connection with the hydrogen electrode reaction, of what kind of regularities are found in the electrolytic reduction of organic compounds, and of what kind of electronic distribution is expected at metal surface.

II. Hydrogen electrode reaction

II-1 Catalytic activity of electrode metals

It is well known that there is a linear relation between hydrogen overvoltage, η, and logarithm of current density, i(A/cm^2), called the Tafel line;

$$\eta = a + b \log i\,, \qquad (1)$$

where a and b are constants and η is defined as

$$F\eta \equiv \mu(\mathrm{e}^-) - \mu(\mathrm{e}^-)_{\mathrm{rev}}\,, \qquad (2)$$

$\mu(\mathrm{e}^-)$ and $\mu(\mathrm{e}^-)_{\mathrm{rev}}$ being the electrochemical potential of electron at working and reversible hydrogen electrodes, respectively. Since the value of b is found around 0.12 V on most of metals[1], the constant a may reflect how active the electrode metal is. The larger a is, the less active the electrode is. In the present article, we will take the exchange current density, i_0, as a measure of the activity. Extrapolation of Eq. (1) to $\eta=0$ gives,

$$\log i_0 = -a/b\,. \qquad (3)$$

Exchange current density represents the unidirectional rate of the reaction at equilibrium. An active catalyst accompanies a large i_0.

One of the present authors summarized literature values of the activity on various electrode metals reported up to 1966[2]. He confirmed a periodic variation of the activity with the atomic number of metals and examined relation between the activity and many physical properties. Recently, HEIFETS *et al.*[3], KUHN *et al.*[4] and TRASATTI[5] reviewed the hydrogen electrode reaction on various metals. They also discussed the relation between the value of a or log i_0 and properties such as the potential of zero charge, the work function, the heat of adsorption of hydrogen, etc. In the present article, the previous periodic change of log i_0 was reexamined by using the reported data mainly from 1950 up to 1972. Values of log i_0 chosen were those in acidic solution which does not contain organic additives or the anions such as Br^- and I^-. Only one value is taken from each publication for respective metals as KUHN *et al.* did[4)] except single crystal. In the latter case, values of each lattice plane were chosen. When the kind of acids, their concentration, and temperature were varied, the values chosen were those of H_2SO_4 or HCl and closest to 1 N and 25°C. With respect to the Tafel line with a break, the lower current density region was used for the estimation of log i_0. However, in the case where the potential is so close to the reversible or mixed potential that the observed current is taken to be affected by the reverse reaction of the hydrogen electrode reaction or other anodic reaction, the higher current density region was used. On the metals after IIB in the periodic table, the Tafel line often appears after a potential jump at a certain current density. In such cases, the Tafel line at higher current densities after the potential jump was used. At lower current densities, the Tafel line does not hold in many cases. In general, one can say that the value of log i_0 was estimated from the Tafel line around 1 mA/cm^2, except for Pt, Pd (larger than 1 mA/cm^2) and W (smaller). Though pre-electrolysis has been conducted in most cases, it was not taken as a strict criteria for the selection of data; it is of primary importance to find a general trend in the behaviour of log i_0 by using all data available.

Figure 1 shows the plot of log i_0 values on various metals[*)] against the atomic number of the electrode metals. In Fig. 1, the symbol × represents the mean value of log i_0 on each metal (Table 1) and is connected by lines each other. Dotted lines indicate uncertain trend because of a single or no value of log i_0 or the possibility of the molecular hydride formation instead of the hydrogen evolution reaction.

Figure 1 shows a periodic change of log i_0 with the atomic number of the electrode metal as discussed earlier[2)]. However, an abnormal behaviour becomes clear in the first long period. The log i_0 value on Mn is expected to be exceptionally small[**)]. It is of interest to remind that a similar "cut-in"

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[*] See appendix.

[**] HURLEN and VALAND[6)] studied the cathodic and anodic polarizations on Mn in 0.02 M HCl+0.98 KCl solution. Mn is very much corrosive and the diffusion of H^+ controls the corrosion potential (−1.232 volt). The observed cathodic Tafel line gives −12.8 for log i_0 which is extremely small. This value, however, was not included in Fig. 1, since they concluded the discharge of water molecule. KUHN *et al.*[4)] quoted a value of −7.8 for log i_0 on Mn.

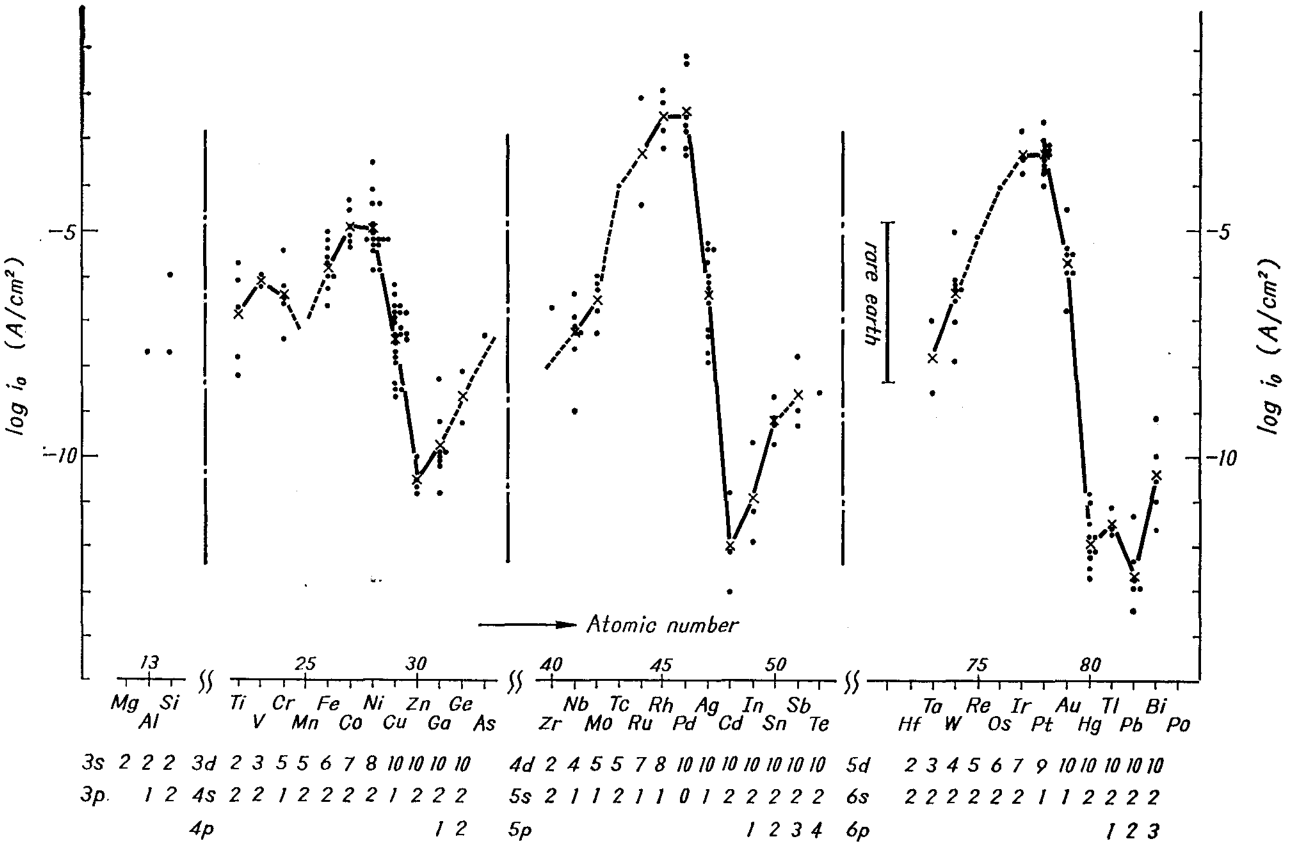


Fig. 1. Observed log i_0 on various metals in acidic solutions (see Appendix). The full and dotted lines indicate the periodic variation of log i_0 with the atomic number.

TABLE 1. Mean values of log i_0(A/cm^2) on various metals in acidic solution.

Ti	− 6.9	Zr	− 6.7	Hf	—
V	− 6.1	Nb	− 7.3	Ta	− 7.8
Cr	− 6.4	Mo	− 6.5	W	− 6.4
Mn	—	Tc	(− 4.0)	Re	− 5.1
Fe	− 5.8	Ru	− 3.3	Os	− 4.0
Co	− 4.9	Rh	− 2.5	Ir	− 3.3
Ni	− 5.2	Pd	− 2.4	Pt	− 3.3
Cu	− 7.4	Ag	− 6.4	Au	− 5.7
Zn	−10.5	Cd	−12.0	Hg	−11.9
Ga	− 9.8	In	−10.9	Tl	−11.5
Ge	(− 8.7)	Sn	− 9.2	Pb	−12.6
As	(− 7.3)	Sb	(− 8.7)	Bi	−10.4
		Te	(− 7.5)	Po	—

( ) indicates an uncertain value.

at Mn is observed for the melting point of metals. The melting point of T_c in the second long period shows also a cut-in but log i_0 value is relatively large though only one value is available.

II-2 Factors which determine the activity

The above periodic behaviour of the activity indicates that the factor of primary importance in determination of the activity is closely related to the electronic configuration of the element. Solution composition and surface state of the metal have only a secondary effect on the activity[2]. Many physical properties are known to show periodic gradation within the long periods. Comparison of the activity with these properties leads to the following conclusions;

"*A plot of log i_0 with metallic radius, density, compressibility or hardness gives a monotonously decreasing or increasing relation.*" (*i*)

"*A plot of log i_0 with melting point, boiling point, heat of fusion, heat of sublimation or heat of vaporization gives a volcano-type relation.*" (*ii*)

Other properties which should be taken into consideration are the work function of metal and the heat of adsorption of hydrogen. Since a metal electron takes part in the reaction, giving an hydrogen intermediate, the ease of releasing an electron from metal and the affinity of the metal surface towards hydrogen may affect the activity. Thus, the mean value of log i_0 is plotted against the work function and heat of adsorption of hydrogen. Examples are shown in Figs. 2 and 3. Figure 2 was obtained by using the values of work function of TRASATTI5), where two dotted lines represent the relations proposed by TRASATTI5). The similar plot is shown in Fig. 3 where the values of work function were those of EASTMAN8) observed by the plotoelectric method on the polycrystalline films of the transition metals and those used in HEINE and HODGES' paper9) for the non-transition metals. Two linear lines in Fig. 3 were obtained by the least square method.

In both figures, the family of metals is divided into two groups as discussed previously2,10). However, the quantitative relation between log i_0 and the work function largely depends on values of the work function. In fact, when log i_0 on the non-transition metals is plotted against the work function of MICHAELSON11) or BOND12), log i_0 appears independent of the work function as one of the present authors concluded2).

The same grouping of metals is obtained2) when log i_0 is plotted against the heat of adsorption of hydrogen calculated by ELEY-STEVENSON's equation13).

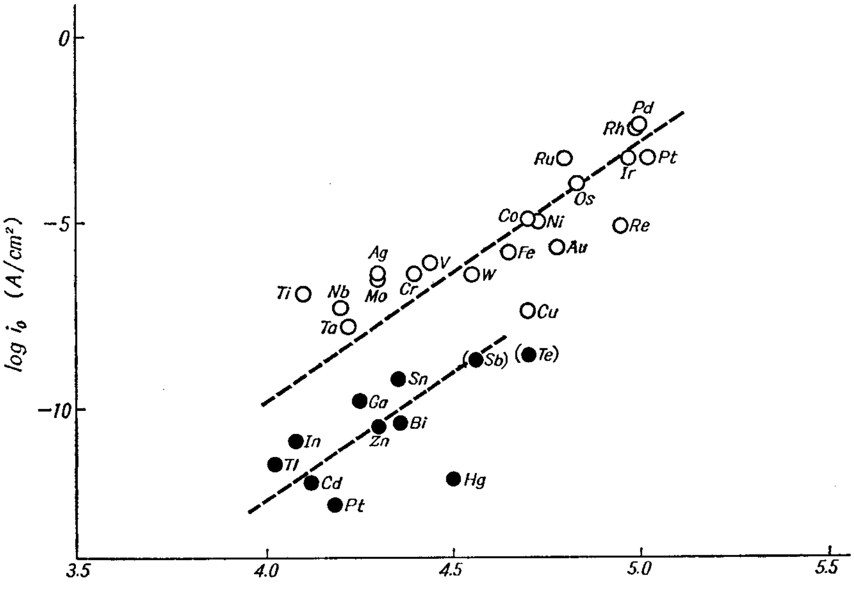


Fig. 2. log i_0 vs. work function (Φ_e) of electrode metals. Values of Φ_e are quoted from ref. 5. Dotted lines represent TRASATTI's relation5).

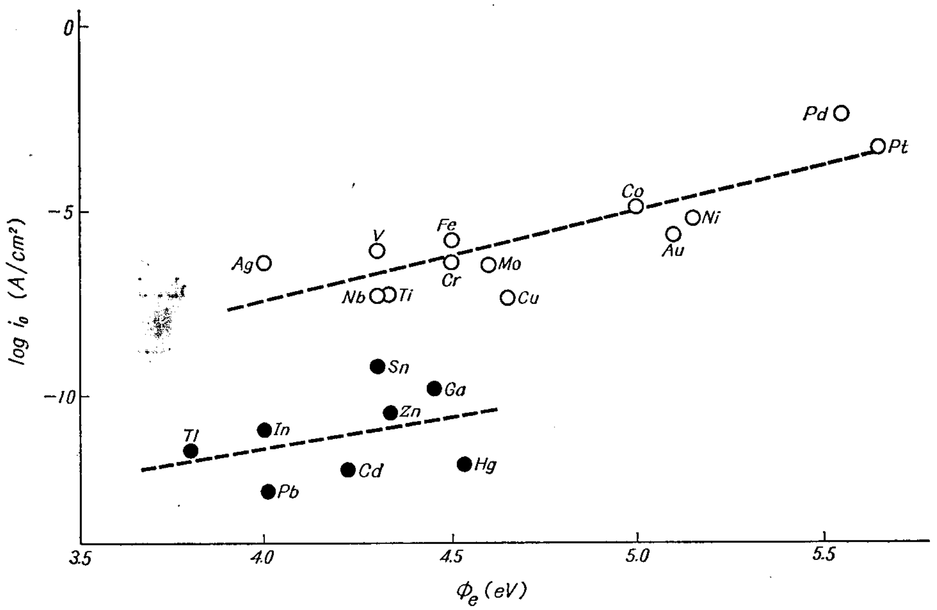


Fig. 3. log i_0 vs. work function (Φ_e) of electrode metals. Values of Φ_e are quoted from ref. 8 and 9.

From these results, the following conclusion is drawn;

> "*A plot of log* i_0 *with work function or heat of adsorption of hydrogen divides the family of metals into two groups.*" (*iii*)

Three relations described above, (i) to (iii), should be finally understood in connection with the electronic configuration of elements, but a question arises as to which property among the three relations is most important.

II-3 Experimental results bearing on the relations, (i) to (iii)

Let us examine other experimental results on the hydrogen electrode reaction. Figure 4[2] shows experimental data on the separation factor of various electrode metals. It will be seen that the separation factor on the transition and IB metals are relatively large and those on metals after IIB are relatively small. Metals are divided into two groups.

Figure 5 illustrates the effect of solution pH on the hydrogen overvoltage at 1 mA/cm² on various metals[14]. We will see from this figure that the hydrogen overvoltage on the transition and IB metals is higher in alkaline than in acidic solution, while that on metals after IIB is lower in alkaline

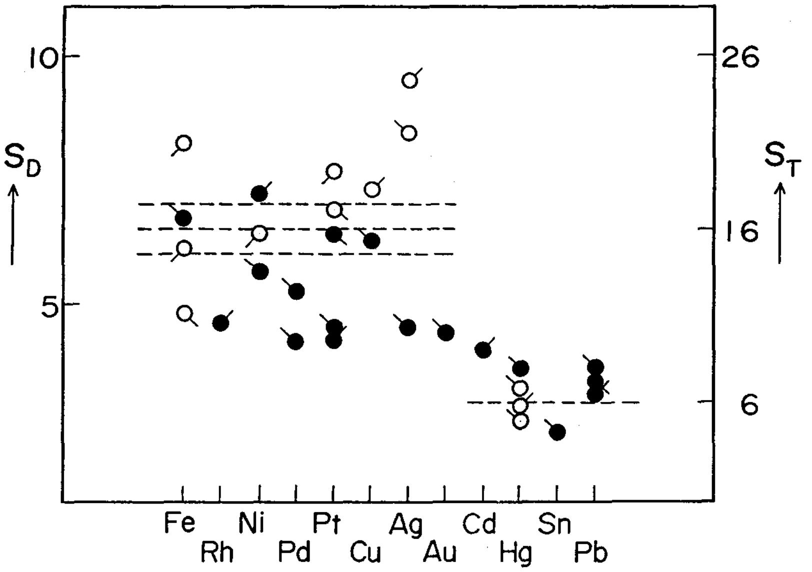


Fig. 4. Electrolytic separation factor observed on various metals[2].

Symbols are

Soln.	A/cm^2	S_D	S_T
acidic	0.01	●	●
	0.1	○	○
alkaline	0.01	●	●
	0.1	○	○

than in acidic solution. Effect of solution pH is thus different between these two groups of metals.

Effect of surface-active substances on the hydrogen overvoltage at a constant current density is also different between these two groups of metals. Table 2 shows the effect of I^- and $(C_4H_9)_4N^+$ surface-active ions for several metals[15~24]. I^- ion increases the hydrogen overvoltage on Fe, Co, Ni, Cu, Zr, and Ag, while decreases on Zn, Ga (liq.), Hg, and Pb, though a few exceptional cases are reported on Cr[25] and Ga (sol.)[26]. On Cr, the hydrogen overvoltage is reported to decrease by the presence of I^-, though Cr is the transition metal. On solid Ga, BAGOTSKAYA *et al.*[26] reporeted the increase of the hydrogen overvoltage in contrast to the other data. The cation, $(C_4H_9)_4N^+$, on the other hand, seems to increase the hydrogen overvoltage on all electrodes studied. ANTROPOV[27] concluded that any type of surface-active substances increases the hydrogen overvoltage of metals

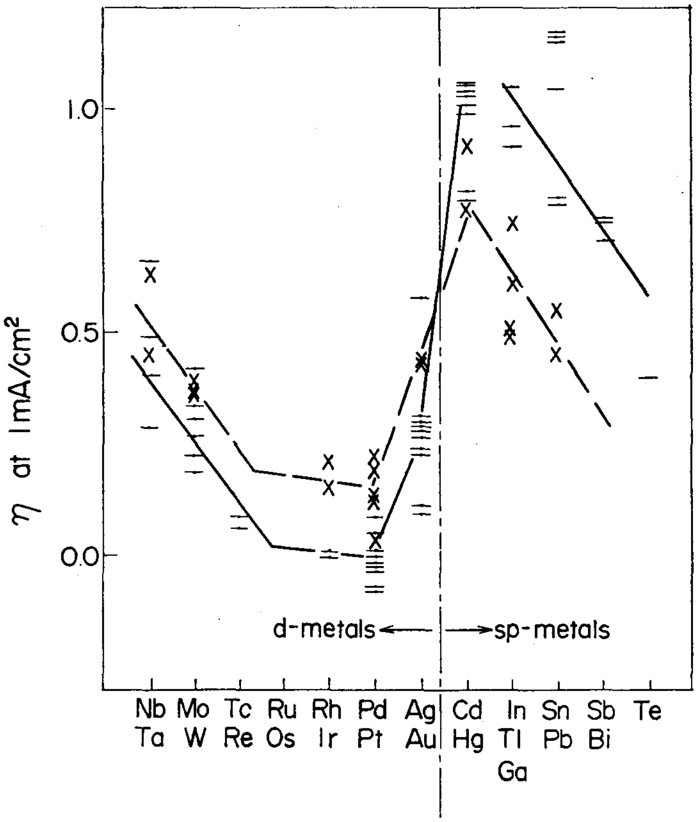


Fig. 5. Hydrogen overvoltage at $i=1$ mA/cm^2 on various metals in acidic, -•-, and in alkaline, ×, solutions[14].

TABLE 2. Effect of surface-active substances on the hydrogen overvoltage[15~24]. Symbols, + and −, respectively indicate increase and decrease of the hydrogen overvoltage upon the presence of adsorbates.

Adsorbate	Fe	Co	Ni	Cu	Zr	Ag	Zn	Ga	Hg	Pb
I^-	+	+	+	+	+	+	−	−	−	−
$(C_4H_9)_4N^+$	+						+	+	+	

which adsorb hydrogen well, while on the metals which do not adsorb hydrogen well, cationic and neutral types of surface-active substances increase and the anionic one decreases the hydrogen overvoltage, respectively.

His conclusion may be extended by taking into account the facts of Table 2 as follows. The hydrogen overvoltage of the transition and IB metals generally increases by the presence of any types of surface-active substances, while that of metals after IIB decreases or increases depending on the charge of surface-active substances. The effect of surface-active substances is thus different between the two groups of metals.

Comparison of the above experimental results with the relation, (i) to (iii), leads to the following conclusion;

> *"One of the factors of primary importance in determination of the catalytic activity is the work function or the heat of adsorption of hydrogen."* (*iv*)

The work function and heat of adsorption are semi-empirically interrelated by Eley-Stevenson's relation and hence are not independent each other.

It may be noted qualitatively from the electron configuration of outer shells of the elements included in Fig. 1 that the activity in each long period increases first with the increase of the d-electron, reaches a maximum at nearly filled d-orbital, decreases quite sharply after its completion, with one or two electrons in the s-orbital, and then increases again with further addition of electrons to the p-orbital. In the following discussion, we denote the transition metals including IB metals by *"d-metals"* and the metals following them in the periodic table by *"sp-metals"*. The words of d- and sp-types of metals have been proposed by DOWDEN[28] in connection with chemisorption phenomena of gases.

II-4 Reaction mechanism

Grouping of metals into two groups indicates that the reaction mechanisms of the hydrogen electrode reaction is different between these groups of metals. HORIUTI and OKAMOTO[29] first found two groups of electrode metals which give the value of ca. 7 or 3 for the deuterium separation factor and proposed the catalytic mechanism,

$$H^+ + e^- \rightleftarrows H(a)\,;\quad 2H(a) \mathrel{A\!\!\!\rightarrow} H_2 \qquad (4)$$

for the metals of high separation factor and the electrochemical mechanism,

$$2H^+ + e^- \rightleftarrows H_2^+(a)\,;\quad H_2^+(a) + e^- \mathrel{A\!\!\!\rightarrow} H_2 \qquad (5)$$

for the metals of low value, where H(a) and $H_2^+(a)$ denote the adsorbed hydrogen atom and hydrogen molecule ion, and $\mathrel{A\!\!\!\rightarrow}$ the rate-determining step, respectively. One of the present authors explained qualitatively his results for log i_0 vs. the work function plots[2], assuming the catalytic and electrochemical mechanisms for the d- and sp-metals.

The point which should be stressed here is that the reaction intermediate on the d-metals is the neutral adsorbed hydrogen atom, H(a), and that on the sp-metals is the charged hydrogen molecule ion, H_2^+(a). Presence of H_2^+(a) has not being confirmed experimentally yet. Even if we would stand on so-called "*slow discharge mechanism*", the activated complex of the rate-determining step will be charged. Hence, so far as a charge is concerned, one could characterize the rate-determining step of the d- and sp-metals as being non-charged and charged, respectively.

III. Electrolytic reduction of organic compounds

Electrolytic reduction of organic compounds in aqueous solution is the electrolytic hydrogenation reaction, where the source of hydrogen is a proton in the solution and an electron in the metal. Hence, a close relation might be expected between the electrolytic reduction of organic compounds and hydrogen electrode reaction.

Previous works reported on the electrolytic reduction have been mainly concerned with synthesis of organic compounds and less attention has been paid to its kinetics. Thus, it makes the comparison difficult of the catalytic action of each metal in terms of the activity as in the case of the hydrogen electrode reaction. Since many organic compounds have a variety of functional groups to be reduced and generally have many steps of partial reduction, it will be of interest to see what group of and to what degree each metal electrode reduces organic compounds. ANTROPOV has already pointed out[27] that the metals which adsorb or do not adsorb hydrogen, behave in a different way in the electrolytic reduction of organic compounds. We will summarize the reported results below.

III-1 Electrolytic reduction of carbonyl group

Table 3[27,30~35] lists which metals are good or poor catalyst for the electrolytic reduction of ketone and aldehyde. It is seen from the table that each organic compound of the type RR'CO is well reduced on metals of the sp-metals and hardly reduced on those of the d-metals. The carbonyl group of carboxylic acid and esters is also reduced on metals such as Hg and Pb (*e.g.* $(COOH)_2$[27], X–C_6H_4–COOH[36]).

Electrolytic reduction of acetone might be a typical example to see the current efficiency and the product distribution. Reported results[37~39] are summarized in Table 4. Current efficiency is very high (73~90%) on the sp-metals such as Hg, Pb, Cd, Zn and very low (1~3%) on the d-metals

TABLE 3. Electrolytic reduction of RR'CO on various metals[27,30~35] ($\Phi = C_6H_5$).

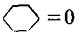
Ref.	R	R'	good	poor
27, 30	CH_3-	-H, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_3H_6OH$	Hg, Pb, Cd, Zn, Sn, Al	Fe, Ni, Cu, Ag
27, 21	Φ-	$-\Phi$, $-CH_3$, $-C_2H_5$	Hg, Pb, Cd, Zn, Sn, Bi	Cu, Ni, Pt
32	$(CH_3)_2CH$-	$-CH(C_3H)_2$	Hg, Pb, Cd, Zn	
30	$(CH_3)_2CHCH_2$-	$-CH_2CH(CH_3)_2$	Hg, Pb, Cd	
33	H-	$-CH(OH)CH_2OH$	Pb, Cd, Zn, Sn	Fe, Ni, Cu, Ag, Pt
34			Hg, Pb, Cd, Zn, Sn	Cu, Ag, Ti
35	Streptomycin	-CHO	Zn, Cd, Sn, Pb	Ni, Cu Stainless

TABLE 4. Electrolytic reduction of acetone[37~39].
Number before or in parentheses indicates the current efficiency or the distribution of products in (%), [gr] and {yield}.

		Hg	Pb	Cd	Zn	Cu	Ni
Acidic[37]	P	73 (2)	86 (25)	90 (100)	86 (97)	3 (100)	1 (100)
	A	73 (95)	86 (68)		86 (3)		
	D	73 (3)	86 (7)				
Neutral[38]	P	95 [0]	76 [0]	70 [0]			
	A	95 [7.00]	76 [0.82]	70 [0.66]			
	D	95 [3.37]	76 [3.08]	70 [3.46]			
Alkaline[39]	P						
	A						
	D	{25}	{17}	{23}	{30}	{3}	{7}

P; $CH_3CH_2CH_3$, A; $(CH_3)_2CHOH$, D; $(CH_3)_2(OH)C-C(OH)(CH_3)_2$

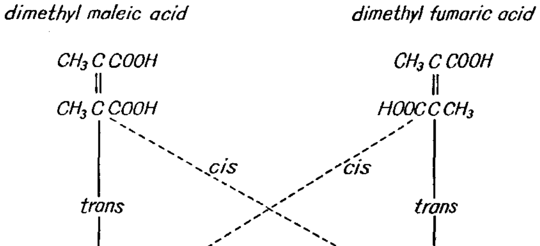
such as Cu and Ni. In the latter case, most of electricity is exhausted in the production of hydrogen molecule.

An interesting example from the point of view of stereochemistry is the electrolytic reduction of 2, 4-dimethylcyclohexanone to alcohol[40]. Copper electrode of the d-metals produces cis-2, 4-dimethylcyclohexanol, while Hg and Pb electrodes of the sp-metals produce trans-isomer. Such a difference clearly suggests that the reaction mechanism is different between these two groups of metals.

III-2 Electrolytic reduction of unsaturated bond

According to ANTROPOV[27)], the triple or double bond in organic compounds such as $HC\equiv CR$ (R ; H-, $CH_2=CH$-), R-COOH(R ; $CH_3CH=CH$-, $CH_3CH=CHCH=CH$-, $CH_3(CH_2)_7CH=CH(CH_2)_7$-), and phenol, is reduced on metals which adsorb hydrogen well and is hardly reduced on metals which do not adsorb hydrogen well. Partial reduction of alkynes to olefins takes place on Ni, Cu and Ag. Cathodic reduction of dialkyl acetylenes (*e.g.* $CH_3CH_2CH_2\cdot C\equiv C\cdot CH_2CH_2CH_3$) and diphenylacetylene ($\Phi\cdot C\equiv C\cdot\Phi$) on a spongy Ni cathode in alcoholic H_2SO_4 solution gives exclusively cis-olefin but no reduction was observed at Cd, Pb or amalgamated Pb electrodes[41)]. From these facts, a general conclusion will be made that the d-metals are good catalyst and the sp-metals are poor catalyst in the electrolytic reduction of unsaturated bond. This tendency is the reverse to the case of the electrolytic reduction of the carbonyl group.

Reduction of the triple to double bond provides the possibility of cis- or trans-addition of hydrogen. The above examples of dialkyl- and diphenylacetylenes show the formation of cis-isomer on Ni. In solutions which contain alkali metal ion, dialkylacetylenes are reported to be reduced to olefin on Hg[42)]. The products in this case, however, are the trans-olefin ($>92\%$ in all cases studied). Similar selectivity is found in the electrolytic reduction of 2-butyne-1, 4-diol in KOH solution[43)]. Cis-addition selectively takes place on the d-metals studied, *i.e.*, Ag, Cu, Ni, Co, Pt, Fe, and Pd, and trans-addition, though its rate is low, takes place on the sp-metals of Pb, Sn, Cd, Hg (Cu amalgam) and Zn. An interesting example is the electrolytic reduction of dimethyl maleic and fumaric acids on Hg in HCl-KCl buffer solution (pH=1.9)[44)]. The product from maleic acid is the racemic form of α,α'-dimethylsuccinic acid and that from fumaric acid is the meso



form. These results directly prove the trans-addition of hydrogen on Hg.

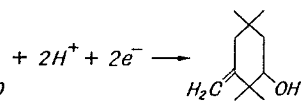
Thus, the formation of cis- and trans-isomer seems to be characteristic for the d- and sp-metals, respectively. Trans-isomer formation on the sp-metals may include a possibility that the electrolytic reduction does not take place via direct reduction at the electrode but instead by alkali metal formed *in situ.*

III-3 Selectivity in the electrolytic reduction of organic compounds

From the results of III-1 and III-2, we extend the conclusion of Antropov[27] and Petrenko[45] as follows ;

> "*Electrodes of the sp-metals reduce selectively polar bonds and electrodes of the d-metals reduce selectively non-polar bonds.*" (*v*)

The above conclusion will be confirmed by data from the electrolytic reduction of a molecule which contains both polar and non-polar groups to be reduced. An example is the electrolytic reduction of $CH_2{=}CHC{\equiv}N$. Iron of the d-metals (0.7 N NaOH) yields $CH_3CH_2C{\equiv}N$ with a current efficiency of 61.8%[46], whereas Pb of the sp-metals (H_2SO_4 acidic methanolic solution) yields $CH_2{=}CHCH_2NH_2$ with a current efficiency of 55% and by-product of $CH_3CH_2CH_2NH_2$ with a current efficiency of 13%[47]. Recently, it is shown that electrolytic reduction of β, γ-unsaturated ketone, 2, 2, 5, 5-tetra methyl-3-methylene cyclohexanone, gives the corresponding unsaturated alcohol on Hg[48].



Electrolytic reduction of 2-cyclohexene-1-one in 1 N H_2SO_4 aqueous solution gives cyclohexane-1-one on Pt but not on Hg[49].

IV. Discussion

We see that the behaviour of each group of metals is distinctly different both in the hydrogen electrode reaction and in the electrolytic reduction of organic compounds as stated in II and III. The intermediate in the hydrogen electrode reaction is suggested to be the neutral H(a) on the d-metal and the charged H_2^+(a) on the sp-metals. In the electrolytic reduction of organic compounds, electrodes of the d-metals reduce selectively non-polar unsaturated bonds and those of the sp-metals reduce selectively polar groups such as $\rangle C=O$ or $-C\equiv N$. Hence, so far as an electricity is concerned, there is a similarity between these two reactions.

From the analogy that a polar solvent dissolves a polar solute and a non-polar solvent dissolves a non-polar solute, the above facts lead to the following suggestion on the nature of the electrode surface; "Electronic distribution at the metal surface may be rather homogeneous for the d-metal and may be rather heterogeneous or localized for the sp-metal, since the non-polar processes take place on the d-metal and the polar processes take place on the sp-metal". This suggestion has been discussed in detail by O. JOHNSON[50] from the view of his theory of "an interstitial electron model for metals"[51].

Table 5 indicates the deviation in th lattice from the ideal ones; each figure gives the deviation of the ratio of c_0/a_0 from unity in the cases of f.c.c., b.c.c., rhombic, and b.c. tet., the deviation of $(c_0/a_0)/1.63$ from unity in the case of h.c.p., and the deviation of angle/90 from unity in the case of rhombohedral, respectively. c_0 and a_0 are lattice constants. The sp-metals show a large deviation in contrast to the d-metals except for Al and Pb. Thus, it may be expected that the ion core of these sp-metals deforms from the spherical one and hence that the electronic distribution will not be isotropic. According to JOHNSON's theory, the sp-metals are characterized

TABLE 5. Deviation in the lattice from the ideal ones.

* rhombo-hed.

$\mathrm{V_b}$	$\mathrm{VI_b}$	$\mathrm{VII_b}$	VIII			$\mathrm{I_b}$	$\mathrm{II_b}$	$\mathrm{III_a}$	$\mathrm{IV_a}$	$\mathrm{V_a}$
								Al f.c.c. 0	Si	
V b.c.c. 0	Cr b.c.c. 0	Mn	Fe b.c.c. 0	Co h.c.p. 0	Ni f.c.c. 0	Cu f.c.c. 0	Zn h.c.p. 0.14	Ga rhombic 0.04	Ge	As
Nb b.c.c. 0	Mo b.c.c. 0	Tc	Ru h.c.p. −0.03	Rh f.c.c. 0	Pd f.c.c. 0	Ag f.c.c. 0	Cd h.c.p. 0.16	In b.c.tet. 0.08	Sn b.c.tet. −0.46	Sb * −0.37
Ta b.c.c. 0	W b.c.c. 0	Re h.c.p. −0.01	Os h.c.p. −0.03	Ir f.c.c. 0	Pt f.c.c. 0	Au f.c.c. 0	Hg * −0.17	Tl h.c.p. −0.02	Pb f.c.c. 0	Bi * −0.37

………………………… d-metals …………………………|…………… sp-metals ……………

with weak positive field perpendicular to the surface but strong positive field in the lateral direction[50]. On the other hand, most of the d-metals may have spherical ion cores which extend symmetrical positive field. Electronic distribution on the surface is much smoothened and rather homogeneous[50] at the d-metals.

In section III, the present authors stated a general tendency in electrolytic reduction of organic compounds. To know details of the electrolytic reduction, one will be required to examine many other factors such as effects of solution composition, electrolysis condition, a neighbouring group next to the one to be reduced, *etc.* An attempt has been reported to find the relation between the rate constant and the polarization or hindrance factor of neighbouring alkyl group in the electrolytic reduction of RR'CO[30]. Electrolytic reduction of nitrobenzene has been studied from the beginning of this century. Products vary widely depending on the electrode metal, solution composition, and electrolysis conditions. Establishement of the effect of secondary factors on the catalysis will further make it possible to predict the selectivity in more detailed level. Finally, it will be worth while to mention possible routes in electrolytic reduction of organic compounds. They can be via ;

(a) formation of organic radical after electron transfer,
(b) intermediates of the hydrogen electrode reaction, H(a) or H_2^+(a),
(c) formation[52] of metal hydride on the sp-metals,
(d) formation[53] of alkali metal on the electrode surface in alkaline solution, and
(e) formation of organo-metallic compounds.

As stated above, kinetics have not been given much attention in the electrolytic reduction of organic compounds. Any mechanistic knowledge may feed back useful information to the elucidation of the mechanism of the hydrogen electrode reaction.

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APPENDIX

The following table shows the summary of the kinetic parameters of the hydrogen electrode reaction on various metals in acidic solutions which do not contain organic or surface active substances. The data chosen are those reported mainly from 1950. Meanings of the superffixes in the Table, a, b, * and † are as follows.

a, values referred to the reversible hydrogen electrode.
b, region of log i where the Table line holds.
*, values estimated from figures or from a and b.
†, values quoted in Fig. 1 of the text.

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)^{a}	Range of log i	log i_0	b (mV)	a (V)
Ag	J. O'M. BOCKRIS and B. E. CONWAY, Trans. Faraday Soc., **48**, 724 (1952).									
			1N HCl	1A/cm^2,3.1× 10^4 Coulomb	Room temp.		$-6\sim-1$	$-5.4\pm0.4^{\dagger}$ -3.7 ± 0.4	60 ± 5 130 ± 5	0.32 ± 0.02 0.48 ± 0.02
	J. O'M. BOCKRIS and A. M. AZZAM, Trans. Faraday Soc., **48**, 145 (1952).									
	Wire	Chem. polished, heated in H_2 at 600°C for 2∼3 hr	5N HCl	1 A/cm^2 ∼10^5 Coulomb	25		$-3\sim+2^{b}$	$-5.3^{*\dagger}$	120	0.64
	H. GERISCHER and W. MEHL, Z. Elektrochem., **59**, 1049 (1955).									
	Wire	Chem. polished	1N H_2SO_4	Conducted			$-4\sim-2$	$-5.7^{*\dagger}$	110	
	J. O'M. BOCKRIS, I. A. AMMAR and A. K. M. S. HUQ, J. Phys. Chem., **61**, 879 (1957).									
	Wire	Heated in H_2 at 700°C for 1 hr, sealed into glass bulb	0.4N HCl	10 mA/cm^2, 60 hr	23 ± 2		$-7\sim-3$	$-6.6^{\dagger}$ -5.35	57 ± 2 101 ± 9	

YA. M. KOLOTYRKIN, Trans. Faraday Soc., **55**, 455 (1959).								
		1.0N H_2SO_4		20		−7~−3.5	−6.42*†	119*
A. A. ANTONIOU and F. E. W. WETMORE, Can. J. Chem., **37**, 222 (1959).								
Single or poly-crystal	Electropolished, held in hot H_2 for a few days, gently anodized	2N H_2SO_4	Conducted	Room temp.	+0.35~+0.45 V, occasionally 0~+18mv	−7.5~−2.7	~−6*†	59 116
B. E. CONWAY, Proc. Roy. Soc., **A 256**, 128 (1960).								
Wire	Sealed into glass bulb	0.1N HCl	0.1 A/cm^2, 24~36 hr	26±1		−5.5~−2	−6.10±0.2† −4.80±0.15	72±7 12(5)±5
		0.1N DCl					−7.05±0.2 −5.40±0.15	72±7 122±5
K. GOSSNER, CHR. LÖFFLER and G. M. SCHWAB, Z. Phys. Chem., **28**, 229 (1961).								
Foil	Heated in H_2 at 450°C for 24 hr, sealed with paraffin	2N H_2SO_4	0.1 A, 60 hr	Room temp.		−2.3~−1.3	−5.4†	120
V. I. BYSTROV and L. I. KRISHTALIK, Elektrokhimiya, **3**, 1345 (1967).								
Wire	Alkali, HNO_3, polished with fine glass powder	0.1N H_2SO_4	Conducted			−8~−4.5 −6~−4.5[b]	−7.2*†	115* at higher c.d.
V. I. BYSTROV and L. I. KRISHTALIK, Elektrokhimiya, **3**, 1499 (1967).								
Wire	Alkali, HNO_3, polished with fine glass powder	0.1M K_3PO_4 +H_2SO_4 pH=1.6	Conducted	25		−6.3~−4.6[b]	−7.3*†	~120* at higher c.d.
V. I. BYSTROV and L. I. KRISHTALIK, Elektrokhimiya, **4**, 233 (1968).								
Wire	Alkali, HNO_3, polished with fine glass powder	0.1N H_2SO_4	Conducted	25		−7~−4.5	−6.3*†	135 at higher c.d.

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)[a]	Range of log i	log i_0	b (mV)	a (V)
Ag	K. GOSSNER and F. MANSFELD, Z. phys. Chem. N.F., **58**, 24 (1968).									
			2N H_2SO_4					$-7.92^{*\dagger}$	120	0.95
	A. B. KILIMNIK and A. L. ROTINIAN, Elektrokhimiya, **6**, 330 (1970).									
	Section of rod, 2.5 mm, dia	99.99%, mechanically polished, kept with 0.1 mA/cm^2 for 1 hr	2N H_2SO_4		25		$-5 \sim 0$	$-7.75^{*\dagger}$	120	0.93 ± 0.02
								after potential jump		1.32 ± 0.02
Al	A. K. VIJH, J. Phys. Chem., **72**, 1148 (1968).									
	Wire (99.98%)	Chemipolished (2 min, 90°C, 85% H_3PO_4+15% HNO_3), washed, dipped in 1 N NaOH, 10 min, washed	0.2~1.7N H_2SO_4	3~5 hr with the highest c.d. studied	25 ± 1.5°C	Mixed potential	$-5 \sim -1$	-7.7	110	0.847
As	E. A. EFIMOV and I. G. ERUSALIMCHIK, Elektrokhimiya, **1**, 1133 (1965).									
		99.9990%	1N H_2SO_4				$-3 \sim -4$	$-7.0 \sim -7.6^{*\dagger}$	110~120	0.84
Au	N. PENTLAND, J. O'M. BOCKRIS and E. SHELDON, J. Electrochem. Soc., **104**, 182 (1957).									
	Wire	Sealed into glass bulb	0.1N HCl	27 mA/cm^2, 42 hr		Value of r.h.e.	$-5.63 \sim -4.02^{b}$ $-3.67 \sim -2.41^{b}$	$-6.83^{\dagger}$ -5.64	71 97	
	D. J. G. IVES, Can. J. Chem., **37**, 213 (1959).									
	Wire	Cleaned chemically	0.1N HCl	Conducted		Value of r.h.e.	$-6 \sim -3$	$-5.5^{*\dagger}$	123	
	B. E. CONWAY, Proc. Roy. Soc., **A 256**, 128 (1960).									
	Wire	Sealed into glass bulb	0.1N DCl 0.1N HCl	0.1 A/cm^2, 24~36 hr	26 ± 1		$-5 \sim -1.5$	-6.23 ± 0.22 $-5.60 \pm 0.18^{\dagger}$	120 ± 5 110 ± 5	

	K. GOSSNER and C. LÖFFLER, Z. phys. Chem. N. F., **37**, 123 (1963).									
	Wire	Sealed with paraffin or araldite, scraped with sharp glass bar	2N H_2SO_4		20		$-3\sim-1$	$-5.36^{\dagger}$	116 ± 4	
	G. M. SCHMID, Electrochim. Acta, **12**, 449 (1967).									
	Bead	Melt in H_2, washed in hot cleaning soln. degreased, washed in dist. water	1M $HClO_4$ (pH = 0.1)	14 hr, 50 mA	20 ± 2		$-4\sim0$	$-4.52^{\dagger}$	110 ± 10 on fresh elect.	
	K. GOSSNER and F. MANSFELD, Z. phys. Chem. N.F., **58**, 19 (1968).									
	Wire	99.99%	1N H_2SO_4		21 ± 0.1		$-3\sim0.7$	$-5.86^{\dagger}$	103	0.603
	K. GOSSNER and F. MANSFELD, Z. phys. Chem., N. F., **63**, 143 (1969).									
	Cross section		1N H_2SO_4		22.5		$-3\sim0$	$-5.86^{\dagger}$	103	0.603
	A. T. KUHN and M. BYRNE, Electrochimica Acta, **16**, 391 (1971).									
	Foil	+1.3V for 10min −0.1V for 5min	1.0M H_2SO_4		20			$-5.52^{\dagger}$		
Bi	A. HICKLING and F. W. SALT, Trans. Faraday Soc., **44**, 860 (1948).									
		Melted, poured into glass tube, scraped with a hard steel knife	1N HCl		$17\sim20$		$-3\sim-1$	$-9.09^{*\dagger}$	110	1.0
	U. W. PAL'M and V. E. PAST, Zh. Fɪz. Khim., **38**, 773 (1964).									
	Plate	Previously polarized	0.9N HCl 0.9N H_2SO_4 0.9N $HClO_4$	Conducted, $20\sim25$ hr			$-7\sim-1$	-9.32, $-10.45^{\dagger}$ -10.4	118 ± 5 101 ± 5 100 ± 5	

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)[a]	Range of log i	log i_0	b (mV)	a (V)
Bi	A. B. KILIMNIK and A. L. ROTINIAN, Elektrokhimiya, **5**, 1234 (1969).									
		99.99%	2N H_2SO_4		25			-7.75^{*}	120 ± 5	0.93 ± 0.01
								after potential jump		
								$-10.00^{*\dagger}$	115 ± 5	1.15 ± 0.01
	T. T. TENNO and U. V. PAL'M, Elektrokhimiya, **8**, 1381 (1972).									
	Rod	Conducted	1N $HClO_4$	80~100 hr, 10 mA/cm^2	20		−8~−2	$-11.0^{*\dagger}$	97 at 1 mA/cm^2	
	U. PAL'M and T. TENNO, J. Electroanal. Chem., **42**, 457 (1973).									
		Prepared from melt, impurities less than 10^{-5}%	1M $HClO_4$	10 mA/cm^2, 80~100 hr				$-11.6^{*\dagger}$	90 at 10^{-4}A/cm^2	
Cd	YA. M. KOLOTYRKIN and L. A. MEDVEDEVA, Zh. Fiz. Khim., **25**, 1365 (1951).									
			1.3N H_2SO_4					$-12.08^{*\dagger}$	120	1.45
	YA. M. KOLOTYRKIN and L. A. MEDVEDEVA, Zh. Fiz. Khim., **27**, 1344 (1953).									
	Rod		1N H_2SO_4	Conducted with Cd electrode		Mixed potential	−8~−3	$-13^{*\dagger}$ at higher c.d.	105^{*} at higher c.d.	
	J. O'M. BOCKRIS and S. SRINIVASAN, Electrochim. Acta, **9**, 31 (1964).									
	Wire	Heated in H_2 at 200°C	0.5N H_2SO_4	1 mA/cm^2, 15~20 hr	Room temp.		−5~−2	$-10.77 \pm 0.75^{\dagger}$	135 ± 12	
Co	A. G. PECHERSKAYA and V. V. STENDER, Zh. Prikl. Khim., **19**, 1303 (1946).									
			2N H_2SO_4					$-5.2^{*\dagger}$	100	0.52
	A. M. MURGAZAEV, Zh. Fiz. Khim., **23**, 1247 (1949).									
			1N HCl					$-4.47^{*\dagger}$	150	0.67

α-Co	Z. A. IOFA and VEI BAO-MIN, Zh. Fiz. Khim., **37**, 2301 (1963).								
	Electrodeposited	1N H_2SO_4		20		−7∼−2.2	−5.24*†	145*	
β-Co	S. RASHKOV, K. L. HAMPARTZUMIAN and N. A. PANGAROV, Electrochim. Acta, **9**, 841 (1964).								
	Electrodeposited from 250g/ℓ $CoSO_4 \cdot 7H_2O$ + 25 g/ℓ H_3BO_3 + 34 g/ℓ NaCl+HCl, 30 mA/cm², 16°C	1N H_2SO_4		25		−4.5∼−3.0	−4.86*†	109*	
α-Co	Z. A. IOFA and VEI BAO-MIN, Elektrokhimiya, **2**, 755 (1966).								
	Electrodeposited from 500g/ℓ $CoSO_4 \cdot 7H_2O$ +45 g/ℓ H_3BO_3, pH, 5 (with NH_4OH), 15 mA/cm², 60°C	1N H_2SO_4					−4.33*†	120	
β-Co	Z. A. IOFA and VEI BAO-MIN, Elektrokhimiya, **2**, 755 (1966).								
	Electrodeposited from 250g/ℓ $CoSO_4 \cdot 7H_2O$ 22.5g/ℓ H_3BO_3, pH, 1.3∼1.9 (with H_2SO_4), 0.1 A/cm², 20°C	1N H_2SO_4					−5.08*†	150	
Cr	L. KISHSH, Dis. LGU, L., 1957.								
		1.3N HCl					−6.15*†	130	0.80
Cubic Cr	ST. G. CHRISTOV and N. A. PANGAROV, Z. Elektrochem., **61**, 113 (1957).								
	Electrodeposited from 350g/ℓ CrO_3 +3.5g/ℓ H_2SO_4 with 0.35 A/cm² for 2 hr at 45°C	HCl+0.1N KCl pH=2.70	Conducted	20 ± 0.5	Mixed. pot.	−7∼−3.5	−6.60*†	108*	

Metal	Erom	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)[a]	Range of log i	log i_0	b (mV)	a (V)
Hexagonal Cr	ST. G. CHRISTOV and N. A. PANGAROV, Z. Elektrochem., **61**, 113 (1957).									
		Electrodeposited from 600g/ℓ CrO_3 +32.4 g/ℓ sugar, 0.075N H_2SO_4 with 0.16 A/cm^2 for 4hr at 18.5°C	HCl+0.1N KCl pH=2.85	Conducted	20±0.5	Mixed. pot.	−7~−3.5	−5.37*†	112	
Cr	KHO NGOK BA and NGUEN DYK VI, Elektrokhim., **4**, 990 (1968).									
	on Cu plate	Polished by fine powder, washed, cathodized with 0.2 A/cm^2 for 15~20 min in 1N H_2SO_4	1N H_2SO_4					−7.43†	107	0.795
Active Cr	B. E. WILDE and F. G. HODGE, Electrochim. Acta, **14**, 619 (1969).									
	99.999%	Polished mechanically with mirror finish, degreased in *i*-propyl alc. and washed in ethanol, cathodic prepolarization at −1.0 V (SCE) for active Cr.	1N H_2SO_4	70 mA, 24 hr	25	−0.708 V (S.C.E.)		−6.46†	126	0.81*
Cu	V. N. KABANOV and A. N. FRUMKIN, Zh. Fiz. Khim., **5**, 418 (1934).									
			1N H_2SO_4					−7.70*†	100	0.77
	G. M. MAITAK, Zap. In-at Khim., AH USSR, **6**, 61 (1939).									
			1N H_2SO_4					−6.96*†	115	0.80

A. G. PECHERSKAYA and V. V. STENDER, Zh. prikl. Khim., **19**. 1303 (1946).									
		2N H_2SO_4					$-6.69^{*\dagger}$	130	0.87
W. HIMMLER, Z. phys. Chem., **196**, 205 (1951).									
		2N H_2SO_4				$-5\sim-2$	$-6.4^{*\dagger}$	91*	
W. P. SENETT and C. F. HISKEY, J. Am. Chem. Soc., **74**, 3754 (1952).									
Electrodeposited from acidified copper sulfate soln. 9 mA/cm^2, 2 hr, 26 ± 1°C		1N HCl	Conducted				$-8.35\pm0.04^{\dagger}$		
J. O'M. BOCKRIS and N. PENTLAND, Trans. Faraday Soc., **48**, 833 (1952).									
Wire		0.1N HCl		20		$-5.0\sim-2.5$	$-6.76^{\dagger}$	117	0.79
S. E. EL WAKKAD, I. A. AMMAR and H. SABRY, J. Chem. Soc., 3020 (1956).									
Electrodeposited from cyanide bath, 60 mA/cm^2, 20 min, 70°C		1N HCl	40 mA/cm^2, 20 hr	30		$-6\sim-1.5$	$\begin{cases}-7.4^{\dagger}\\-4.49\end{cases}$	60 130	
Electrodeposited from sulfate bath, 70 mA/cm^2		1N HCl	"	30		$-6.5\sim-3.0$	-6.0^{*}	105	
N. PENTLAND, J. O'M. BOCKRIS and E. SHELDON, J. Electrochem. Soc., **104**, 182 (1957).									
Wire	Sealed into glass bulb	0.1N HCl	75 mA/cm^2, 37 hr			$-4.51\sim-3.47^{b}$	$-6.84^{\dagger}$	114 ± 8	
B. E. CONWAY, Proc. Roy. Soc., **A 256**, 128 (1960).									
	Sealed into glass bulb	$\begin{rcases}\text{0.1N DCl}\\\text{0.1N HCl}\end{rcases}$	0.1 A/cm^2, 24∼36 hr	26 ± 1		$\begin{cases}-5.5\sim-2\\-5.5\sim-2\end{cases}$	$-6.7\pm0.15^{\dagger}$ -7.6 ± 0.15	120 ± 5 120 ± 5	
B. E. CONWAY, E. M. BEATTY and P. A. DEMAINE, Electrochimica Acta, **7**, 39 (1962).									
Wire	Heated to red hot in H_2, sealed into glass bulb	0.1N HCl	0.25 A/cm^2, 24 hr	38 ± 1		$-5\sim-1$	$-6.21^{*\dagger}$		

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)[a]	Range of log i	log i_0	b (mV)	a (V)
Cu	K. GOSSNER, Z. phys. Chem. N. F., **36**, 392 (1963).									
			2N H_2SO_4					$-6.8^{\dagger}$	120 ± 10	
	S. NOMOTO, K. FUJIMOTO and T. YOSHIDA, Denki Kagaku, **34**, 629 (1966).									
	Rod	Polished by Emery, degreased by EtOH, treated with 1M HCl	1M HCl	Conducted, 24∼48 hr	30 ± 0.1		$-4\sim-1$	$-6.90^{\dagger}$	110	
	M. MYAKI and U. PAL'M, V. PAST, Uch, zap. Tartussk, un-ta, **193**, 96 (1966).									
			1N H_2SO_4					$-7.80^{*\dagger}$	100	0.73
	K. GOSSNER and F. MANSFELD, Z. phys. Chem. N.F., **58**, 24 (1968).									
	Wire	99.99%	2N H_2SO_4		21 ± 0.1		$-3\sim0.7$	$-7.25^{*\dagger}$	105	0.765
	K GOSSNER and U. FREYER, Z. phys. Chem. N.F., **63**, 132, 143 (1969).									
	Wire	99.99%	1M H_2SO_4		23 ± 0.1		$-3\sim1$	$-7.25^{\dagger}$	105	0.761
	I. V. KUDRYASHOV and L. A. FALIN, Elektrokhimiya, **7**, 1770 (1971).									
	(100)	Mech. polished, cathodized	0.1N H_2SO_4	Conducted, 7∼8 hr				$-7.26^{*\dagger}$	128	0.93
	(110)							$-7.43^{*\dagger}$	125	0.93
	(111)							$-7.20^{*\dagger}$	131	0.945
	V. V. BATRAKOV, YU. DITTRIKH and A. N. POPOV, Elektrokhimiya, **8**, 640 (1972).									
	Wire, annealed	99.999%, after stretching or rolling, heated at 500°C for 6 hr under vac. and H_2	1N H_2SO_4					-7.90^{*}	100 ± 1	$0.790 \pm .005$
	Wire, 20% stretched		"					-7.90^{*}	100 ± 1	$0.790 \pm .005$
	Plate, annealed		"					-8.10^{*}	100 ± 2	$0.810 \pm .015$

	Cont'd									
	Bead	Then melted (dia, 1.4~1.6mm)	1N H_2SO_4					−7.90*†	100 ± 1	0.790 ± .005
	(100)	Polished mechanically and then electrochemically. Density of dislocation, $10^7/cm^2$	”					−8.55*†	96 ± 3	0.825 ± .020
	(110)		”					−8.65*†	96 ± 3	0.830 ± .020
	(111)		”					−8.45*†	96 ± 3	0.810 ± .020
		All electrodes were polarized at 0.625 V (nhe) for 3 min in 72% H_3PO_4, then cathodized in the cell for 1/2 hr with $10 mA/cm^2$.								
Fe	A. G. PECHERSKAYA and V. V. STENDER, Zh. prikl. Khim., **19**, 1303 (1946).									
			2N H_2SO_4					−6.03*†	116	0.70
	V. A. KUZNETSOV and Z. A. IOFA, Zh. Fiz. Khim., **21**, 201 (1947).									
			1N HCl					−5.60*†	125	0.70
	H. F. FISCHER and H. HEILING, Z. Elektrochem., **54**, 187 (1956).									
			2N H_2SO_4					−6.00*†	120	0.72
	N. PENTLAND, J. O'M. BOCKRIS and E. SHELDON, J. Electrochem. Soc., **104**, 182 (1957).									
	Wire	Sealed into glass bulb	0.01N HCl	$18 mA/cm^2$, 36 hr			−4.06~−3.19^b	−6.29†	118 ± 15	
	TOR HURLEN, Acta Chemica Scandinavica, **14**, 1533 (1960).									
	Sheet	Annealed, 1 hr 700°C, vac., polished with emery paper, etched in dil. HNO_3, washed	HCl (pH = 0)		20 ± 0.5		−5~−2	−5.36†	116	
	J. O'M. BOCKRIS and D. F A. KOCH, J. Phys. Chem., **65**, 1941 (1961).									
	Wire	Sealed into glass bulb	0.5N HCl 0·5N DCl	$15 mA/cm^2$, 20 hr				−5.18 ± 0.1† −5.77 ± 0.14	133 ± 4 134 ± 4	

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)^a	Range of log i	log i_0	b (mV)	a (V)
Fe	Kho Ngok Ba, Dis. MGU, M., 1964.									
			1N H_2SO_4					$-5.00^{*\dagger}$	120	0.60
	Kho Ngok Ba, Dis. MGU, M., 1964.									
			1N H_2SO_4					$-6.67^{*\dagger}$	120	0.80
	E. J. Kelly, J. Electrochem. Soc., **112**, 124 (1965).									
	Cylindrical	Mounted on Teflon holder, etched in 0.5M H_2SO_4	0.5M H_2SO_4	Conducted	25.00 ± 0.03		~3.9~−1.6	$-5.65^{*\dagger}$	118	
α-Fe (Armco)	J. O'M. Bockris, J. McBreen and L. Nanis, J. Electrochem. Soc., **112**, 1025 (1965).									
			0.1N H_2SO_4	Conducted	26 ± 0.5		−4~−1.5		115	
Ga	St. G. Christov and L. Rajceva, Z. Elektrochem., **66**, 486 (1962).									
			0.1N HCl	Conducted	20.5 35		−6~−3	$-10.0^{\dagger}$ $-10.1^{\dagger}$	112 93	
	K. Sabo and I. A. Bagotskaya, Dok. Akad. Nauk SSSR, **149**, 139 (1963).									
		99.99%	1N H_2SO_4		28 32		−5~−3	$-9.9^{*\dagger}$ $-10.2^{*\dagger}$	95 95	
	E. Preis, K. Sabo, S. Raicheva and I. A. Bagotskaya, Elektrokhimiya, **2**, 1209 (1966).									
		99.9998%	1N H_2SO_4		28 32			$-9.33\sim-9.05^{*\dagger}$	110~115	
	J. N. Butler and M. L. Meehan, Trans. Faraday Soc., **62**, 3524 (1966).									
		99.999%	0.1M $HClO_4$	Conducted, 4~16 hr	32.0 ± 0.1		−4~−2	$-9.90 \pm 0.10^{\dagger}$	$\alpha = 0.582 \pm 0.008$	

	A. B. KILIMNIK and A. L. ROTINYAN, Elektrokhimiya, **5**, 1234 (1969).									
		99.999%	2N H_2SO_4		25			−8.36*	110±5	0.92±0.01
								after potential jump		
								−10.75*†	120±5	1.29±0.02
	A. M. MOROZOV, I. A. BAGOTSKAYA and E. A. PREIS, Elektrokhimiya, **5**, 40 (1969).									
		99.998~99.9999%	1N H_2SO_4 or 1N $HClO_4$		32			−10.15~−10.8*†	95~100	1.015~1.025
	I. A. BAGOTSKAYA and T. I. KHALTURINA, Elektrokhimiya, **6**, 1013 (1970).									
		99.9998%	1N $HClO_4$		28		−4~−2		120	
Ge (n-, p-)	E. A. EFIMOV and I. G. ERUSALIMCHIK, Zh. Fiz. Khim., **32**, 1967 (1958).									
		Single crystal, n-, and p-type, prepolarized cathodically with 10mA/cm², 1 hr	0.1N HCl		20		−5~−3[b]	−8.08*†	120	0.97
								after potential jump		
							−2~−1[b]	−11.08*	120	1.33
Ge (n-)	V. A. LAVRENKO, L. N. YAGUPOL'SKAYA and E. V. KOZACHENKO, Elektrokhimiya, **8**, 921 (1972).									
	Single crystal (no specification for lattice)	Chem. polished, 25 cc conc. HNO_3, 15 cc HF, 15 cc CH_3COOH at 40°C for 20 sec.	1N H_2SO_4		25		−7.4~−4.7	−9.23†	170	1.58
Hg	V. N. KABANOV and A. N. FRUMKIN, Zh. Fiz. Khim., **5**, 418 (1934).									
			1N H_2SO_4					−12.52*†	113	1.415
	Z. A. IOFA, Zh. Fiz. Khim., **19**, 118 (1945).									
			1N HCl					−12.12*†	116	1.406
	A. J. DE BETHUNE, J. Am. Chem. Soc., **71**, 1556 (1949).									
	Pool	Redistillation	1.005N HCl		25±0.02		−4.6~−1	−11.53±0.05†	118±2	

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)[a]	Range of log i	log i_0	b (mV)	a (V)
Hg	B. Post and C. F. Hiskey, J. Am. Chem. Soc., **72**, 4203 (1950).									
	Pool	Triply distilled, then distilled in vacuum	0.1N HCl	Conducted	21 ± 0.1		−6∼−1	−12.11*†	116	
	B. Post and C. F. Hiskey, J. Am. Chem. Soc., **73**, 161 (1951).									
			0.1M HCl 0.1M DCl		20		−6∼−2.2	−12.21*† −12.48*	116 119	1.416 1.485
	J. O'M. Bockris and A. M. Azzam, Trans. Faraday Soc., **48**, 145 (1952).									
			5N HCl	1A/cm², ∼10^5 coulombs	25		−2∼2[b]	−10.97*†	113	1.24
	S. Minc and J. Sobkowski, Bull. Akad. Polon. Sci., **8**, 29 (1959).									
	Pool		0.1M HCl solution of H_2O, CH_3OH, C_2H_5OH, n-C_3H_7OH		20 ± 0.5			−11.8† −11.5 −10.8 −10.8	117 107 104 102	
	J. N. Butler and A. C. Makrides, Trans. Faraday Soc., **60**, 938 (1964).									
	Drop	Triply distilled	0.1N $HClO_4$	1 mA/cm², overnight	25		−4∼−1.7	−11.82†	118	
	B. E. Conway and M. Salomon, J. Chem. Phys., **41**, 3169 (1964).									
	Pool	Redistilled, anodic polarization in HNO_3-$Hg_2(NO_3)_2$, distillation in vacuum	1N HCl solution of CH_3OH 1N DCl solution of CH_3OD	Conducted	27		−4∼−2 −4∼−3	−10.8*† −11.3*	119* 119*	
	J. N. Butler and A. C. Makrides, Trans. Faraday Soc., **60**, 1664 (1964).									
	Dropping		0.1M $HClO_4$	1 mA/cm², overnight	25			−12.65†		

Hg	O. NAGASHIMA and H. KITA, J, Res. Inst. Catalysis, Hokkaido Univ., **15**, 49 (1967).									
		Distilled in vac.	1N H_2SO_4	6 mA, 170 hr	25	70	$-2\sim0$	$-11.8^\dagger$	124 ± 15	1.462 ± 0.017
In	J. N. BUTLER and A. C. MAKRIDES, Trans. Faraday Soc., **60**, 1664 (1964).									
			0.1M $HClO_4$	1 mA/cm^2, overnight	25		$-3.5\sim-1.15$	$-11.85^\dagger$	118	
	A. T. PETRENKO, Elektrokhimiya, **1**, 839 (1965).									
			2N H_2SO_4					$-9.71^{*\dagger}$	140	1.36
	J. N. BUTLER and M. DIENST, J. Electrochem. Soc., **112**, 226 (1965).									
	Cylindrical	99.999%, electropolished, polarized overnight at −1.0 V.	0.1M $HClO_4$	Conducted with pt-Pt, 10 mA, 16 hr	25 ± 0.2		$-6.3\sim-2.8$	$-11.15\pm0.03^\dagger$	$\alpha=$ 0.498 ± 0.002	
Ir	J. R. HOARE and S. SCHULDINER, J. Chem. Phys., **25**, 786 (1956).									
			2N H_2SO_4					$-2.79^{*\dagger}$	122	0.34
	D. B. MATTHEWS, Ph. D. Thesis, Univ. of Pennsylvania, 1965 (from Trasatti's paper, J. Electroanal. Chem., **39**, 163 (1972)).									
			0.5M H_2SO_4					$-3.7^\dagger$		
	R. J. MANNAN, Ph. D. Thesis, Univ. of Pennsylvania, 1967 (from Trasatti's paper, J. Electroanal. Chem., **39**, 163 (1972)).									
			0.5M H_2SO_4					$-3.4^\dagger$		
Mn	T. HURLEN and T. VALAND, Electrochimica Acta, **9**, 1077 (1964).									
	Sheet	Electrolytic Mn, chem. polished, etched in 1M HCl or H_2SO_4	HCl+KCl+ small amount of ammonium sulfite		$22\sim23$				117	

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)^a	Range of log i	log i_0	b (mV)	a (V)
Mo	A. G. PECHERSKAYA and V. V. STENDER, Zh. prikl. Khim., **19**, 1303 (1946).									
			2N H_2SO_4					$-6.29^{*\dagger}$	105	0.66
	N. PENTLAND, J. O'M. BOCKRIS and E. SHELDON. J. Electrochem. Soc., **104**, 182 (1957).									
	Wire	Flushed in vacuum, sealed into glass bulb	0.1N HCl	75 mA/cm^2, 37 hr			$-5.52\sim-3.48^b$ $-3.34\sim-1.80^b$	$-7.30^\dagger$ -6.40	80±4 104±4	
	I. V. KUDRIASHOV and S. D. KAMYSHCHENKO, Elektrokhimiya, **7**, 1284 (1971).									
	(100)	Electropolished	1N HCl		20		$-4.0\sim-1.5$	$-6.00^\dagger$	105	0.63
	(110)	"	"		20		$-4.0\sim-1.5$	$-6.16^\dagger$	95	0.585
	(111)	"	"		20		$-4.0\sim-1.5$	$-6.8^\dagger$	75	0.510
	(111)	"	1N H_2SO_4		22		$-4.0\sim-2.0$	-6.58	79	0.520
	(100)	"	"		22		$-4.0\sim-2.0$	-5.96	108	0.645
Nb	J. O'M. BOCKRIS, Trans. Faraday Soc., **43**, 417 (1947).									
			1N HCl				$-3\sim-1$	$-9^{*\dagger}$	110	
	T. I. KONONCHUK and I. V. VARMASHENKO, Ukr. Khim. Zh., **26**, 25 (1960).									
			1N H_2SO_4					$-7.75^{*\dagger}$	120	0.93

	A. L. ROTINYAN and N. M. KOZHEVNIKOVA, Zh. Fiz. Khim., **37**, 1818 (1963).									
	Plate	Polished with emery paper, cathodic polarization (5mA/cm^2, 96 hr)	1N H_2SO_4	10 mA/cm^2, 6 hr			−5∼−2.3	$-6.33^{\dagger}$	120	
	A. L. ROTINYAN and N. M. KOZHEVNIKOVA, Elektrokhimiya, **1**, 664 (1965).									
			1N H_2SO_4					$-7.26^{*\dagger}$	106	0.77
	V. M. ARTEMOVA, Elektrokhimiya, **3**, 1219 (1967).									
		Mechanically polished	2N H_2SO_4		25			$-6.91^{*\dagger}$	110	0.76
Ni	A. G. PECHERSKAYA and V. V. STENDER, Zh. prikl. Khim., **19**, 1303 (1946).									
			2N H_2SO_4					$-5.20^{*\dagger}$	95	0.49
	J. O'M. BOCKRIS and N. PENTLAND, Trans. Faraday Soc., **43**, 417 (1947).									
			1N HCl					$-5.91^{*\dagger}$	110	0.65
	J. O'M. BOCKRIS and E. C. POTTER, J. Chem. Phys., **20**, 614 (1952).									
	Wire	Sealed into glass bulb	1.0N HCl	0.1 A/cm^2, 18 hr	20 ± 0.5		−6∼−2.3	$-5.4 \pm 0.1^{\dagger}$	109 ± 9	
	J. O'M. BOCKRIS and A. M. AZZAM, Trans. Faraday Soc., **48**, 145 (1952).									
	Wire	Heated in H_2 at 600°C for 2∼3hr	5N HCl	1A/cm^2, ∼10^5 coulombs	25		−3∼1	saturation current		
	J. P. HOARE and S. SCHULDINER, J. Phys. Chem., **62**, 229 (1958).									
			2N H_2SO_4	Conducted.	30 ± 1	−4		$-3.48^{*\dagger}$	123	
			1N HCl	Conducted.	30 ± 1			$-4{\cdot}6^{*}$	120	

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)[a]	Range of log i	log i_0	b (mV)	a (V)
Ni	R. PIONTELLI, L. P. BICELLI and A. LA VECCHIA, Accad. Nazionale Dei Lincei VIII, **27**, 312 (1959).									
	Single crystal (100) (110) (111)	Anodic treatment in 70% H_2SO_4	0.1N $HClO_4$ 0.15N $HClO_4$ 0.15N $HClO_4$		25		$-6\sim-3$	$-4.85^†$ $-5.2^†$ $-5.2^†$	100 155 150	
	B. E. CONWAY, Proc. Roy. Soc., **A 256**, 128 (1960).									
	Wire	Sealed into glass bulb	0.1N HCl 0.1N DCl	0.1 A/cm², 24~36 hr	26 ± 1		$-5\sim-1.35$	$-5.87 \pm 0.15^†$ -6.35 ± 0.15	118 ± 3 124 ± 3	
	B. E. CONWAY, E. M. BEATTY and P. A. DEMAINE, Electrochimica Acta, **7**, 39 (1962).									
		Heated to red hot in H_2, sealed into glass bulb	0.1N HCl	0.25 A/cm², 24 hr	38 ± 0.1		$-5\sim-1$	$-5.24^†$	95*	
	J. O'M. BOCKRIS and S. SRINIVASAN, Electrochim. Acta, **9**, 31 (1964).									
	Wire	Heated in H_2 at 700°C	0.5N H_2SO_4	1 mA/cm², 15~20 hr	Room temp.			$-5.22 \pm 0.53^†$	124 ± 10	
	A. K. M. S. HUQ and A. J. ROSENBERG, J. Electrochem. Soc., **111**, 270 (1964).									
	Cross section of rod	Mounted in pyrex holder by Kel-F wax, polishings, treated by chromic acid/sulfuric acid	1M $HClO_4$ pH = 0.04	30 mA, 6 hr	25 ± 0.1		$-6\sim-1.2$	$-5.3^†$	125	
	E. I. MIKHAILOVA and Z. A. IOFA, Elektrokhimiya, **1**, 107 (1965).									
	Plate	Polished with fine glass powder, cathodic polarization with 20 mA/cm², 10 min	1N H_2SO_4	Conducted with Pt, 24 hr	20 ± 1		$-7\sim-1$	$-5.25^{*†}$	100	0.525

	I. MIELUCH, Bull. Acad. Poln Sci. Ser. Sci. Chim., **17**, 43 (1969). Values of *a* and *b* were those obtained by a sweep rate of −250 mV/min.									
	Plate (110)	Electropolished	1N H_2SO_4	5mA/cm², 24hr	24±1		−5~−2	$-4.37^{*\dagger}$	120	0.525
	(100)	”	”					$-4.37^{*\dagger}$	120	0.525
	(111)	”	”					$-4.08^{*\dagger}$	120	0.490
	L. V. TAMM, YU. K. TAMM and V. E. PAST, Elektrokhimiya, **9**, 1382 (1973).									
		Polished by fine silica powder, treated in boil. 10% KOH, cathodized	0.1N H_2SO_4	Purified electrochemically			−5.5~−2.5	$-5.2^{*\dagger}$	120~125	
Os	A. T. KUHN and P. M. WRIGHT, J. Electroanal. Chem., **27**, 319 (1970).									
		99.9% 1.0 V 10 s, −1.0 V 10 min, repeat more than six times, with final cathodic pulse 10 min.	HCl, pH=0.0	10 mA, 24 hr	25±1	4		$-3.98^{\dagger}$	120	
Pb	Z. A. IOFA, Zh. Fiz. Khim., **19**, 117 (1945).									
		Cathodic polarization (0.1~1mA/cm²)	0.1, 0.01N H_2SO_4		20		−6.6~−2.8	$-12.9^{*\dagger}$	118	
	A. G. PECHERSKAYA and V. V. STENDER, Zh. prikl Khim., **19**, 1303 (1946).									
			2N H_2SO_4					$-13.40^{*\dagger}$	100	1.34
	P. RÜETSCHI and B. D. CAHAN, J. Electrochem. Soc., **104**, 406 (1957).									
			1N H_2SO_4					$-12.25^{*\dagger}$	120	1.47
	YA. M. KOLOTYRKIN, Trans. Faraday Soc., **55**, 455 (1959).									
			1.0N H_2SO_4		20			$-12.92^{*\dagger}$ at higher c.d.	116 at higher c.d.	

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr $(\mathrm{mV})^{a}$	Range of log i	log i_0	b (mV)	a (V)
Pb	P. RÜETSCHI, J. B. OCKERMAN and R. AMLIE, J. Electrochem. Soc., **107**, 325 (1960).									
	Sponge	Battery plate, 15.9 m^2	5M H_2SO_4		30 ± 0.05				120	
	U. PAL'M and V. PAST, Dokl. Akad. Nauk SSSR, **146**, 1374 (1962).									
			1N H_2SO_4 } 1N HCl }				−4.2∼−0.5	{ $-12.7^{\dagger}$ { −12.9	120 117	1.53 1.51
	J. O'M. BOCKRIS and S. SRINIVASAN, Electrochim. Acta, **9**, 31 (1964).									
	Wire	Chem. polished	0.5N H_2SO_4	1 $\mathrm{mA/cm^2}$, 40 hr	Room temp.		−5∼−1.3	$-11.33 \pm 1.40^{\dagger}$	125 ± 14	
Pd	J. O'M. BOCKRIS and A. M. AZZAM, Trans. Faraday Soc., **48**, 145 (1952).									
	Wire	Heated in H_2 at 600°C for 2∼3hr	5N HCl	1A/cm^2, ∼10^5 coulombs	25		−2∼2	saturation current		
	R. CLAMROTH and C. A. KNORR, Z. Elektrochem., **57**, 399 (1953).									
	Wire	Anodic polarization	2N H_2SO_4		Room temp.		−4.4∼0	{ $-2.7^{\dagger}$ {	29 0	
	J. P. HOARE and S. SCHULDINER, J. Electrochem. Soc., **102**, 485 (1955).									
	Bead α-phase	Anodic (5 mA, 15 min), cathodic (50 mA, 30min) polarizations.	1.05N H_2SO_4 pH = 0.40	Conducted.	39 ± 1		−2.0∼−0.5	{ {	40 0	
		Anodic (10 mA, 30 min), cathodic (50 mA, 30min) polarizations.	0.514N H_2SO_4 + 0.5N Na_2SO_4 pH = 0.84	Conducted.	39 ± 1		−2.0∼−0.6	{ { $-1.25^{*\dagger}$	42 126	
	N. PENTLAND, J. O'M. BOCKRIS and E. SHELDON, J. Electrochem. Soc., **104**, 182 (1957).									
	Wire	Sealed into glass bulb	0.1N HCl	0.24 A/cm^2, 13 hr		Value of r.h.e.	$-2.89 \sim -1.41^{b}$	$-3.25^{\dagger}$	99	

	J. P. Hoare and S. Schuldiner, J. Electrochem. Soc., **104**, 564 (1957).									
	Membrane α-phase	Anodic polarization (10mA, 45 min)	2N H_2SO_4 pH=0	Conducted.	32±2	+49.5	−4.5~−0.5	−1.2*†	(42) 124	
			0.3N H_2SO_4+ 0.7N Na_2SO_4 pH=0.9				−4.5~−1.4	−1.85*	(30) 125	
	B. E. Conway, Proc. Roy. Soc., **A 256**, 128 (1960).									
	Wire α-phase	Sealed into glass bulb	0.1N HCl	0.1 A/cm², 24~36 hr	26±1		−5~−1.5	−2.8*†	(25±3) 110±10	
			0.1N DCl				−5~−2.2	−3.7*	(25±3) 120±10	
	H. Shiratori, Denki Kagaku (Electrochemistry), **29**, 765 (1961).									
	Membrane		2N H_2SO_4		20		−4~−2	−3.2*†	120	
	M. C. Barton and F. A. Lewis, Z. phys. Chem. N.F., **33**, 99 (1962).									
	Wire	Palladized	1.0N HCl		25±0.2		−3.4~0	−2.5*†	29.5	
Pt	J. O'M. Bockris and A. M. Azzam, Trans. Faraday Soc., **48**, 145 (1952).									
	Wire	Heated in H_2 at 600°C for 2~3hr	5N HCl	1A/cm², ~10^5 coulombs	25		−2~2	hysteresis at high c.d.		
	S. Schuldiner, J. Electrochem. Soc., **101**, 426 (1954).									
	Bead		0.205M H_2SO_4 pH=0.5	5~10 mA overnight	25±1			−3.2*†	26	0.25
	K. J. Vetter and D. Otto, Z. Elektrochem., **60**, 1072 (1956).									
	Wire		1N H_2SO_4		20	<+2 mV	−7~−2	−3.65*†	129	

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)^a	Range of log i	log i_0	b (mV)	a (V)
Pt	J. O'M. Bockris, I. A. Ammar and A. K. M. S. Huq, J. Phys. Chem., **61**, 879 (1957).									
	Wire	Heated in H_2 at 600°C for 10 min, anodic polarization (0.1 A/cm^2, 10 sec)	1N HCl	0.1 A/cm^2, 10 hr	23 ± 2		$-3\sim-1$	$-3.0^{\dagger}$	29 ± 1	
	R. Parsons, Trans. Faraday Soc., **56**, 1340 (1960).									
	Small sphere	Soaked in chromic+sulfuric acid mixture for 24hr, anodic and cathodic polarization (0.1 A/cm^2, 5 sec)	0.5M HCl	10 mA/cm^2, 18 hr	25 ± 0.5	Value of r.h.e.	$-3.4\sim-1$	$-2.59 \pm 0.09^{\dagger}$	27.8 ± 1.4	
	B. E. Conway, Proc. Roy. Soc., **A 256**, 128 (1960).									
	Wire	Platinized	0.1N HCl 0.1N DCl	0.1 A/cm^2, 24∼36 hr	26 ± 1			$-3.16 \pm 0.1^{\dagger}$ -3.33 ± 0.1	30 ± 2 31 ± 2	
	S. Schuldiner, J. Electrochem. Soc., **106**, 891 (1959); *ibid.*, **108**, 384 (1961).									
	Bead	Anodic polarization	1N H_2SO_4	5∼10 mA, overnight	25 ± 1	±0.5 mV	$-4\sim-0.6$	$-3.1^{*\dagger}$	25	
	E. Yeager, "Transactions of the Symposium on Electrode Processes", John Wiley and Sons, Inc,. New York (1961).									
			1N H_2SO_4	Conducted, 15 hr	25.0		$-4\sim+0.4$	$-3.6^{*\dagger}$	26*	
	J. O'M. Bockris and S. Srinivasan, Electrochim. Acta, **9**, 31 (1964).									
	Wire	Anodic polarization	0.5N H_2SO_4	1 mA/cm^2, 15∼20 hr	Room temp.			$-3.35 \pm 0.05^{\dagger}$	30 ± 1	

	E. J. KELLY, J. Electrochem. Soc., **112**, 124 (1965).									
	Wire	Heated in H_2, sealed into glass bulb, anodic polarization (10mA/cm^2, 10 sec)	0.5N HCl 0.5N DCl	15 mA/cm^2. 20 hr				$-3.33 \pm 0.14^{\dagger}$ -3.62 ± 0.45	29 ± 3 26 ± 6	
	M. HAMMERLI, J. P. MISLAN and W. J. OLMSTEAD, J. Electrochem. Soc., **116**, 779 (1969).									
	Bead	Reduced in H_2, at 800°C or 1050°C for a few hours, extracted with warm electrolyte overnight	1.2N HCl 10% D_2O	10~15 mA, overnight	25 ± 0.1		$-2.7 \sim 0.4$	$-3.33^{*\dagger}$	30 ± 1.5	0.1*
	I. I. PHYSHNOGRAEVA, A. M. SKUNDIN, YU. B. VASILIEV and V. S. BAGOTSKY, Elektrokhimiya, **6**, 142 (1970).									
	Poly- (111) (100)	Polarized at $\Phi_r = 1.2$ V for 20sec.	1N H_2SO_4		20			$-3.4^{\dagger}$ $-3.1^{\dagger}$ $-4.0^{\dagger}$	35 36 32	
Re	M. J. JONCICH, L. S. STEWART and F. A. POSEY, J. Electrochem. Soc., **112**, 717 (1965).									
	Wire	Mounted in Teflon holder, cleaned in HCl	0.037N HCl 0.145N HCl	4~5mA, 50hr	25 ± 0.1		$-6 \sim -2$	-4.95 $-5.14^{\dagger}$	43 29.2	
Rh	J. P. HOARE and S. SCHULDINER, J. Chem. Phys., **25**, 786 (1956).									
			2N H_2SO_4		29			$-2.80^{*\dagger}$	118	0.33
	N. PENTLAND, J. O'M. BOCKRIS and E. SHELDON, J. Electrochem. Soc., **104**, 182 (1957).									
	Wire	Sealed into glass bulb	0.01N HCl	Conducted,		Value of r.h.e.	$-3.38 \sim -3.08^{b}$	$-3.80^{\dagger}$	55 ± 3	
	S. SHULDINER, J. Electrochem. Soc., **107**, 452 (1960).									
	Bead	Anodic, cathodic polarizations	1M H_2SO_4	Conducted,	27 ± 1		$-5 \sim -0.5$ $-2.5 \sim -1.5^{b}$ > -1.5	$-3.0^{*\dagger}$ -2.2^{*}	27.5 60	

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)^a	Range of log i	log i_0	b (mV)	a (V)
Rh	J. HOARE, J. Electrochem. Soc., **107**, 820 (1960).									
	Bead	Anodic, cathodic polarization (0.3 A/cm^2, 90 min)	2N H_2SO_4		25±1		−3.5~0	$-1.85^{*\dagger}$	120	
	J. O'M. BOCKRIS and S. SRINIVASAN, Electrochim. Acta, **9**, 31 (1964).									
	Wire	Anodic polarization (10 mA/cm^2)	0.5N H_2SO_4	1 mA/cm^2, 15~20 hr	Room temp.			$-3.22\pm0.06^{\dagger}$	28±2	
Ru	A. T. KUHN and P. M. WRIGHT, J. Electroanal. Chem., **27**, 319 (1970).									
		1.0V 10s, −1.0V 10 min, repeat more than six times, with final cathodic pulse 10 min.	HCl, pH=0.0	10 mA, 24 hr	25±1	−1	$-4\sim-2^b$	$-4.35^{\dagger}$	117	
	N. M. SHMELEVA, E. D. LEVIN and A. L. ROTINIAN, Elektrokhimiya, **7**, 1539 (1971).									
		Electrodeposition	2N H_2SO_4		25		$-1.5\sim-1.0^b$	$-2.08^{*\dagger}$	120	0.25±.03
Sb	A. G. PECHERSKAYA and V. V. STENDER, Zh. prikl. Khim., **19**, 1303 (1946).									
			2N H_2SO_4					$-9.30^{*\dagger}$	100	0.93
	P. RÜETSCHI and B. D. CAHAN, J. Electrochem. Soc., **104**, 406 (1957).									
			2N H_2SO_4					$-9.00^{*\dagger}$	100	0.90
	A. B. KILIMNIK and A. L. ROTINIAN, Elektrokhimiya, **5**, 1234 (1969).									
		99.99%	2N H_2SO_4		25			-5.08^{*}	120±5	0.61±0.01
								after potential jump		
								$-7.78^{*\dagger}$	117±5	0.91±0.01

Si	E. A. EFIMOV and I. G. ERUSALIMCHIK, Dokl. Akad. Nauk SSSR, **124**, 609 (1959).									
	Single crystal (111) n and p types	Treated with solutions; HF : HNO_3=1 : 2 and 42% HF	2N H_2SO_4		20		−6∼−1	$-6.0^{\dagger}$	180	
	E. A. EFIMOV, I. G. ERUSALIMCHIK and G. P. SOKOLOVA, Zh. Fiz. Khim., **36**, 1005 (1962).									
	Single crystal (111) n and p types	Treated with solutions; HF : HNO_3=1 : 2 and 42% HF	2.5N HF		20		−6∼−1	$-7.7^{*\dagger}$	170	
	A. K. M. S. HUQ and A. J. ROSENBERG, J. Electrochem. Soc., **111**, 270 (1964).									
	Flat surface of cylindrical specimen	After polishing treated with chromic acid-sulfuric acid cleaning soln.	1M $HClO_4$ pH = 0.04		25 ± 0.1			No Tafel region		
Sn	A. G. PECHERSKAYA and V. V. STENDER, Zh. prikl. Khim., **19**, 1303 (1964).									
			2N H_2SO_4					$-9.30^{*\dagger}$	100	0.93
	K. GOSSNER, Z phys. Chem. N.F., **36**, 392 (1963).									
			2N H_2SO_4					$-8.66^{\dagger}$	120 ± 10	
	L. I. ANTROPOV (1960); Ref. 26 of the paper by V. L. HEIFETS, B. S. KRASIKOV and A. L. ROTINYAN, Elektrokhimiya, **6**, 916 (1970).									
			2N H_2SO_4					$-9.23^{*\dagger}$	130	1.20
	A. B. KILIMNIK and A. L. ROTINIAN, Elektrokhimiya, **5**, 1234 (1969).									
		99.99%	2N H_2SO_4		25			-7.7^{*}	115 ± 5	0.89 ± 0.01
								after potential jump		
								$-9.74^{*\dagger}$	115 ± 5	1.12 ± 0.01

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)[a]	Range of log *i*	log i_0	*b* (mV)	*a* (V)
Sn	T. I. KONONCHUK and I. V. VARMASHENKO. Ukr. Khim. Zh., **26**, 25 (1960).									
			1N H_2SO_4					−7.00*†	120	0.84
Ta	N. M. KOZHEVNIKOVA and A. L. ROTINIAN, Elektrokhimiya, **1**, 664 (1965).									
			1N H_2SO_4					−8.58*†	120	1.03
Tc	G. H. CARTLEDGE, J. Electrochem. Soc., **118**, 1752 (1971).									
		Reduced in H_2 at 425°C or cathodized in 1N NaOH for 10min at 0.5A/cm², then dipped in 12N HCl for a few sec, rinsed	1N H_2SO_4		24		−5.5∼−2	−4.05	41.2±1.8	
Te	I. A. AMMAR and S. A. AWAD, J. Electrochem. Soc., **103**, 182 (1956).									
	Rod		1N HCl	30∼40 mA/cm², 20 hr	30		−6∼−2	−10.1* − 6.4*†	53 115	
	V. A. FISHMAN, V. I. LAINER and I. G. ERUSALIMCHIK, Elektrokhimiya, **5**, 530 (1969).									
			1N HCl				−5∼−4.3	−8.64*†	120	1.04*
Ti	M. E. STRAUMANIS, S. T. SHIH and A. W. SCHLECHTEN, J. Phys. Chem., **59**, 317 (1955).									
	Bar	99.99%, polished through emery paper, immersed in 1N HF for 1 min, rinsed.	1N H_2SO_4				−3∼−0.7	−5.7*†	160*	

	YA. M. KOLOTYRKIN and P. S. PETROV, Zh. Fiz. Khim., **31**, 659 (1957).									
	Wire	10 min in hot 1N NaOH, 1~2 min in hot 2N H_2SO_4, cathodic polarization in 2N H_2SO_4 (5mA/cm^2, 1 hr)	1N H_2SO_4				−5~−2.5	$-6.07^{\dagger}$	135	
			1N HCl					−6.30	130	
	A. T. PETRENKO, Zh. Fiz. Khim., **36**, 1527 (1962).									
	Plate	10 min in hot 1N NaOH, 1~2 min in hot 2N H_2SO_4, cathodic polarization in 2N H_2SO_4 (5mA/cm^2, 1 hr)	2N H_2SO_4				−5~−1.5	$-8.15^{*\dagger}$	119	0.97
	V. M. ARTEMOVA, Elektrokhimiya, **3**, 1219 (1967).									
		Hot 1N NaOH for 10 min, hot 2N H_2SO_4 for 1~2 min. Cathodized in 2N H_2SO_4 (5 mA/cm^2, 1 hr)	2N H_2SO_4		25			$-6.74^{*\dagger}$	135	0.91
	N. T. THOMAS and KEN NOBE, J. Electrochem. Soc., **117**, 622 (1970).									
	Rod	Annealed under vac. at 700°C for 1 hr, 1N HF for 1 min.	H_2SO_4 pH=0.25		24±1	corrosion pot.	$-4.8\sim-3^{b}$	$-7.81^{\dagger}$	150	
Tl	YA. M. KOLOTYRKIN and L. A. MEDVEDEVA, Zh. Fiz. Khim., **25**, 1365 (1951).									
			1.6N H_2SO_4					$-11.07^{*\dagger}$	140	1.55

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)^a	Range of log i	log i_0	b (mV)	a (V)
Tl	O. L. KABANOVA and A. N. DORONIN, Elektrokhimiya, **6**, 222 (1970).									
	Rod	Impurity, less than 10^{-4}%. Surface was cut by glass, cathodized for 1 hr with 0.83 mA/cm^2	0.1N $HClO_4$	1mA/cm^2, 20hr	25 ± 0.1		−5∼−2	−8.8* after potential jump $-11.68^\dagger$	138* 125	 1.46 ± 0.03
	O. L. KABANOVA, A. N. DORONIN and L. A. SEMENIUTENKO, Elektrokhimiya, **7**, 1390 (1971).									
	Rod	Impurity, less than 10^{-4}%, treated with HNO_3 (1 : 1)	0.1N HCl or 0.1N $HClO_4$	Conducted.				after potential jump $-11.6^{*\dagger}$	 120	
V	I. V. KUDRYASHOV and L. A. FALIN, Elektrokhimiya, **8**, 1029 (1972).									
	(100) (110)	Electropolished in 25% alcoholic H_2SO_4	0.2N H_2SO_4		20			$-6.00^\dagger$ $-6.22^\dagger$	196 204	1.18 1.27
W	J. O'M. BOCKRIS and A. M. AZZAM, Trans. Faraday Soc., **48**, 145 (1952).									
	Wire	Heated in H_2 at 600°C for 2∼3 hr	5N HCl	1 A/cm^2, 10^5 coulombs	25		−3∼+2	$-5.0^\dagger$	110	0.55
	J. O'M. BOCKRIS, I. A. AMMAR and A. K. M. S. HUQ, J. Phys. Chem., **61**, 879 (1957).									
	Wire	Heated in vacuum at 300°C for 1 min, in H_2 at 1000°C for 2∼3 min.	0.1N HCl	10 mA/cm^2, 60 hr	23 ± 2			$-6.11^\dagger$ −5.55	60 ± 3 105 ± 13	
	J. O'M. BOCKRIS and D. F. A. KOCH, J. Phys. Chem., **65**, 1941 (1961).									
		Cleaning with molten $NaNO_3$	0.5N HCl	15 mA/cm^2, 20 hr				$-7.87 \pm 0.31^\dagger$ −6.30 ± 0.23	70 ± 5 112 ± 9	
			0.5N DCl					−8.34 ± 0.27 −7.10 ± 0.42	69 ± 6 101 ± 4	

	J. O'M. BOCKRIS and S. SRINIVASAN, Electrochim. Acta, **9**, 31 (1964).									
	Wire	Cleaning with molten $NaNO_3$, heating in H_2 at 200°C	0.5N H_2SO_4	1 mA/cm^2, 15∼20 hr	Room temp.			−6.63±0.22† −5.90±0.09	84±6 116±3	
	I. V. KUDRYASHOV, S. D. KAMYSHCHENKO and E. M. MAKARYAN, Elektrokhimiya, **9**, 478 (1973).									
	(100)	Mechanically polished	1N H_2SO_4	Conducted	20			−6.32*†	68±1	0.43±.01
	(110)							"	"	"
	(111)							−7.00*†	60±1	0.42±.01
	Poly.							−6.14*†	70±1	0.43±.01
	(100)	Mech. polished, then cathodized with 30 mA/cm^2 for 10 min	"	"	20			−6.46*	65±1	0.42±.01
	(110)							"	"	"
	(111)							−6.89*	61±1	"
	Poly.							−6.46*	65±1	"
	(100)	Electrochemically polished in 2% NaOH	"	"	20			−8.27*	75±1	0.62±.01
	(110)							−6.95*	95±1	0.66±.01
	(111)							−8.29*	70±1	0.58±.01
	Poly.							−6.89*	90±1	0.62±.01
	(100)	Electrochem. polished, then cathodized with 30 mA/cm^2 for 10 min	"	"	20			−7.38*	80±1	0.59±.01
	(110)							−6.20*	100±1	0.62±.01
	(111)							−7.22*	79±1	0.57±.01
	Poly.							−6.04*	96±1	0.58±.01
Zn	A. N. FRUMKIN, V. S. BAGOTSKII, Z. A. IOFA and B. N. KABANOV, "Kinetics of electrode processes", 1952.									
			2N H_2SO_4					−10.51*†	118	1.24
	A. L. ROTINIAN, N. P. FEDOTIEFF and LI UN SOK, Zh. Fiz. Khim., **31**, 1295 (1957).									
			1N H_2SO_4		20		−4.6∼−1.8	−10.8*†	120	
	LI UN SOK, A. L. ROTINIAN and N. P. FEDOT'EV, Zh., Fiz. Khim., **32**, 2514 (1958).									
		Anodic polishing Electrodeposition	0.05N H_2SO_4		20			−11.90* calc. at $\eta=1.0$ V −10.66* calc. at $\eta=0.9$ V		

Metal	Form	Pre-treatment	Solution	Pre-electrolysis	Temp. (°C)	Vr (mV)[a]	Range of log i	log i_0	b (mV)	a (V)
Zn	K. GOSSNER, Z. phys. Chem. N.F., **36**, 392 (1963).									
			2N H_2SO_4					$-10.0^{\dagger}$	120 ± 10	
Zr	V. M. ARTEMOVA, Elektrokhimiya, **3**, 1219 (1967).									
		Mecanically polished, treated with 0.05% HF for 1 min.	2N H_2SO_4		25			$-6.65^{*\dagger}$	185	1.23
Rare earth metals, S. L. MORSE, N. D. GREENE, Electrochimica Acta, **12**, 179 (1967).										