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<th>Title</th>
<th>ELECTROCATALYSIS BY d- AND sp-METALS</th>
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<tr>
<td>Author(s)</td>
<td>KITA, Hideaki; KURISU, Takao</td>
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<td>Citation</td>
<td>JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 21(3): 200-246</td>
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ELECTROCatalysis by d- and sp-Metals

By

Hideaki Kita and Takao Kurisu

(Received February 4, 1974)

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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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, $\eta$, and logarithm of current density, $i$ ($A/cm^2$), called the Tafel line;

$$\eta = a + b \log i,$$

where $a$ and $b$ are constants and $\eta$ is defined as

$$\eta = \mu(e^-) - \mu(e^-)_{rev},$$

$\mu(e^-)$ and $\mu(e^-)_{rev}$ 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, $i_o$, as a measure of the activity. Extrapolation of Eq. (1) to $\eta=0$ gives,

$$\log i_o = -a/b.$$  

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

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, HEIFFETS 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 $\log i_o$ 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) 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$_2$SO$_4$ or HCl and closest to 1N 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 $\times$ 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). 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) studied the cathodic and anodic polarizations on Mn in 0.02M 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. 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.

<table>
<thead>
<tr>
<th>Metal</th>
<th>log $i_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>-6.9</td>
</tr>
<tr>
<td>Zr</td>
<td>-6.7</td>
</tr>
<tr>
<td>Hf</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>-6.1</td>
</tr>
<tr>
<td>Nb</td>
<td>-7.3</td>
</tr>
<tr>
<td>Ta</td>
<td>-7.8</td>
</tr>
<tr>
<td>Cr</td>
<td>-6.4</td>
</tr>
<tr>
<td>Mo</td>
<td>-6.5</td>
</tr>
<tr>
<td>W</td>
<td>-6.4</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td>Tc</td>
<td>(-4.0)</td>
</tr>
<tr>
<td>Re</td>
<td>-5.1</td>
</tr>
<tr>
<td>Fe</td>
<td>-5.8</td>
</tr>
<tr>
<td>Ru</td>
<td>-3.3</td>
</tr>
<tr>
<td>Os</td>
<td>-4.0</td>
</tr>
<tr>
<td>Co</td>
<td>-4.9</td>
</tr>
<tr>
<td>Rh</td>
<td>-2.5</td>
</tr>
<tr>
<td>Ir</td>
<td>-3.3</td>
</tr>
<tr>
<td>Ni</td>
<td>-5.2</td>
</tr>
<tr>
<td>Pd</td>
<td>-2.4</td>
</tr>
<tr>
<td>Pt</td>
<td>-3.3</td>
</tr>
<tr>
<td>Cu</td>
<td>-7.4</td>
</tr>
<tr>
<td>Ag</td>
<td>-6.4</td>
</tr>
<tr>
<td>Au</td>
<td>-5.7</td>
</tr>
<tr>
<td>Zn</td>
<td>-10.5</td>
</tr>
<tr>
<td>Cd</td>
<td>-12.0</td>
</tr>
<tr>
<td>Hg</td>
<td>-11.9</td>
</tr>
<tr>
<td>Ga</td>
<td>-9.8</td>
</tr>
<tr>
<td>In</td>
<td>-10.9</td>
</tr>
<tr>
<td>Tl</td>
<td>-11.5</td>
</tr>
<tr>
<td>Ge</td>
<td>(-8.7)</td>
</tr>
<tr>
<td>Sn</td>
<td>-9.2</td>
</tr>
<tr>
<td>Pb</td>
<td>-12.6</td>
</tr>
<tr>
<td>As</td>
<td>(-7.3)</td>
</tr>
<tr>
<td>Sb</td>
<td>(-8.7)</td>
</tr>
<tr>
<td>Bi</td>
<td>-10.4</td>
</tr>
<tr>
<td>Te</td>
<td>(-7.5)</td>
</tr>
<tr>
<td>Po</td>
<td>-</td>
</tr>
</tbody>
</table>

( ) indicates an uncertain value.

at Mn is observed for the melting point of metals. The melting point of Tc 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. 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 sur-
face 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 TRASATTI\(^5\), where two dotted lines represent the relations proposed by TRASATTI\(^6\). The similar plot is shown in Fig. 3 where the values of work function were those of EASTMAN\(^5\) observed by the plotoelectric method on the polycrystalline films of the transition metals and those used in HEINE and HODGES' paper\(^3\) 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 previously\(^2,10\). 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 MICHAELSON\(^11\) or BOND\(^12\), log \( i_0 \) appears independent of the work function as one of the present authors concluded\(^2\).

The same grouping of metals is obtained\(^2\) when log \( i_0 \) is plotted against the heat of adsorption of hydrogen calculated by ELEY-STEVenson's equation\(^13\).

\[ \log i_0 \text{ vs. work function (} \Phi_0 \text{) of electrode metals.} \]

Values of \( \Phi_0 \) are quoted from ref. 5. Dotted lines represent TRASATTI's relation\(^5\).
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/cm\(^2\) on various metals\(^{10}\). 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
Electrocatalysis by $\delta$- and sp-Metals

Fig. 4. Electrolytic separation factor observed on various metals\textsuperscript{2)}.

Symbols are

<table>
<thead>
<tr>
<th>Soln.</th>
<th>A/cm\textsuperscript{2}</th>
<th>$S_D$</th>
<th>$S_T$</th>
</tr>
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<tr>
<td>acidic</td>
<td>0.01</td>
<td>(\bullet)</td>
<td>(\sigma)</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>(\bigcirc)</td>
<td>(\sigma)</td>
</tr>
<tr>
<td>alkaline</td>
<td>0.01</td>
<td>(\bullet)</td>
<td>(\bigcirc)</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>(\bigcirc)</td>
<td>(\sigma)</td>
</tr>
</tbody>
</table>

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 $\Gamma^-$ and (C\textsubscript{6}H\textsubscript{5})\textsubscript{4}N$^+$ surface-active ions for several metals\textsuperscript{15-24).} $\Gamma^-$ 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\textsuperscript{25} and Ga(sol.)\textsuperscript{26}. On Cr, the hydrogen overvoltage is reported to decrease by the presence of $\Gamma^-$, though Cr is the transition metal. On solid Ga, BAGOTSKAYA et al.\textsuperscript{25} reported the increase of the hydrogen overvoltage in contrast to the other data. The cation, (C\textsubscript{6}H\textsubscript{5})\textsubscript{4}N$^+$, on the other hand, seems to increase the hydrogen overvoltage on all electrodes studied. ANTROPOV\textsuperscript{27} concluded that any type of surface-active substances increases the hydrogen overvoltage of metals.
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Fig. 5. Hydrogen overvoltage at \( i=1 \text{ mA/cm}^2 \) on various metals in acidic, \( \times \), and in alkaline, \( \times \), 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.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zr</th>
<th>Ag</th>
<th>Zn</th>
<th>Ga</th>
<th>Hg</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(^-)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(C(_4)H(_4))N(^+)</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.
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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 Dowden28) 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 Okamoto29) 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,

\[ H^+ + e^- \rightleftharpoons H(a); \quad 2H(a) \rightleftharpoons H_2 \] (4)

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

\[ 2H^+ + e^- \rightleftharpoons H_2^+(a); \quad H_2^+(a) + e^- \rightleftharpoons H_2 \] (5)

for the metals of low value, where \( H(a) \) and \( H_2^+(a) \) denote the adsorbed hydrogen atom and hydrogen molecule ion, and \( \rightleftharpoons \) the rate-determining step, respectively. One of the present authors explained qualitatively his results for \( \log i_0 \) vs. the work function plots29), 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. ANTOPPOV has already pointed out 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 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 \( R'R'CO \) 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. \( (COOH)_2 \), \( X-C_6H_4-COOH \)).

Electrolytic reduction of acetone might be a typical example to see the current efficiency and the product distribution. Reported results 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.
Electrocatalysis by d- and sp-Metals

TABLE 3. Electrolytic reduction of RR'CO on various metals\textsuperscript{27,30-35} ($=C_6H_5$).

<table>
<thead>
<tr>
<th>Ref.</th>
<th>R</th>
<th>R'</th>
<th>good</th>
<th>poor</th>
</tr>
</thead>
<tbody>
<tr>
<td>27, 30</td>
<td>CH$_3^-$</td>
<td>-H, -CH$_3$, -C$_2$H$_5$, -C$_3$H$_7$, -C$_6$H$_5$OH</td>
<td>Hg, Pb, Cd, Zn, Sn, Al</td>
<td>Fe, Ni, Cu, Ag</td>
</tr>
<tr>
<td>27, 21</td>
<td>$\Phi^-$</td>
<td>-$\Phi$, -CH$_2$, -C$_2$H$_5$</td>
<td>Hg, Pb, Cd, Zn, Sn, Bi</td>
<td>Cu, Ni, Pt</td>
</tr>
<tr>
<td>32</td>
<td>(CH$_3)$_2CH$^-$</td>
<td>-CH(NO)$_2$C$_6$H$_5$</td>
<td>Hg, Pb, Cd</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>H$^-$</td>
<td>-CH(OH)$_2$C$_6$H$_5$</td>
<td>Pb, Cd, Zn, Sn</td>
<td>Fe, Ni, Cu, Ag, Pt</td>
</tr>
<tr>
<td>34</td>
<td>$\bigcirc$ = 0</td>
<td></td>
<td>Hg, Pb, Cd, Zn, Sn</td>
<td>Cu, Ag, Ti</td>
</tr>
<tr>
<td>35</td>
<td>Streptomycin</td>
<td>-CHO</td>
<td>Zn, Cd, Sn, Pb</td>
<td>Ni, Cu Stainless</td>
</tr>
</tbody>
</table>

Table 3. Electrolytic reduction of RR'CO on various metals\textsuperscript{27,30-35} ($=C_6H_5$).

TABLE 4. Electrolytic reduction of acetone\textsuperscript{37-39}.

<table>
<thead>
<tr>
<th></th>
<th>Hg</th>
<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
<th>Cu</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic\textsuperscript{37}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>73 [95]</td>
<td>86 [68]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutral\textsuperscript{38}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>95 [0]</td>
<td>76 [0]</td>
<td>70 [0]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>95 [0.00]</td>
<td>76 [0.82]</td>
<td>70 [0.66]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>95 [3.37]</td>
<td>76 [3.08]</td>
<td>70 [3.46]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkaline\textsuperscript{39}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>25</td>
<td>17</td>
<td>23</td>
<td>23</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>

P: CH$_3$CH$_2$CH$_3$, A: (CH$_3$)$_2$CHOH, D: (CH$_3$)$_2$(OH)$_2$-C-(OH)CH$_2$

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\textsuperscript{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\(^2\), the triple or double bond in organic compounds such as \( \text{HC} \equiv \text{CR} (R; \text{H}, \text{CH}_2=\text{CH}-), \text{R}-\text{COOH} (\text{R}; \text{CH}_2\text{CH}=\text{CH}-, \text{CH}_2=\text{CH}=\text{CH}-, \text{CH}_2(\text{CH}_2)\text{CH}=\text{CH}(\text{CH}_2)-), \) 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. \( \text{CH}_3\text{CH}_2\text{CH}_2\cdot\text{C}=\text{C} \cdot \text{CH}_2\text{CH}_3\)) and diphenylacetylene (\( \phi \cdot \text{C} \equiv \text{C} \cdot \phi \)) on a spongy Ni cathode in alcoholic \( \text{H}_2\text{SO}_4 \) solution gives exclusively cis-olefin but no reduction was observed at Cd, Pb or amalgamated Pb electrodes\(^4\). 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 diphenyl-acetylenes 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\(^5\). 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\(^5\). 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)\(^4\). The product from maleic acid is the racemic form of \( \alpha, \alpha' \)-dimethylsuccinic acid and that from fumaric acid is the meso
Electrocatalysis by d- and sp-Metals

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 ANTOPOV\(^{27}\) and PETRENKO\(^{65}\) as follows;

"Electrodes of the sp-metals reduce selectively polar bonds and electrodes of the d-metals reduce selectively non-polar bonds."

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≡N. Iron of the d-metals (0.7N NaOH) yields CH\(_3\)CH\(_2\)C≡N with a current efficiency of 61.8%\(^{46}\), whereas Pb of the sp-metals (H\(_2\)SO\(_4\) acidic methanolic solution) yields CH\(_2\)=CHCH\(_2\)NH\(_2\) with a current efficiency of 55% and by-product of CH\(_3\)CH\(_2\)CH\(_2\)NH\(_2\) with a current efficiency of 13%\(^{47}\). Recently, it is shown that electrolytic reduction of \(\beta,\gamma\)-unsaturated ketone, 2, 2, 5, 5-tetra methyl-3-methylene cyclohexanone, gives the corresponding unsaturated alcohol on Hg\(^{48}\).

\[
\begin{align*}
\text{H}_2\text{C} & \quad + 2\text{H}^+ + 2e^- \\
\text{H}_2\text{C} & \quad \text{OH}
\end{align*}
\]

Electrolytic reduction of 2-cyclohexene-1-one in 1N H\(_2\)SO\(_4\) 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\(^+_t\)(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 $\equiv C=O$ or $\equiv C=N$. 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\textsuperscript{50} from the view of his theory of “an interstitial electron model for metals”\textsuperscript{51}).

Table 5 indicates the deviation in the 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>
<thead>
<tr>
<th>Table 5. Deviation in the lattice from the ideal ones.</th>
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<tbody>
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<td>$V_b$</td>
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<tr>
<td>V</td>
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<tr>
<td>b.c.c.</td>
</tr>
<tr>
<td>Nb</td>
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<tr>
<td>b.c.c.</td>
</tr>
<tr>
<td>Ta</td>
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<tr>
<td>b.c.c.</td>
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</table>

* rhombo-hed.
with weak positive field perpendicular to the surface but strong positive field in the lateral direction\(^5\). 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\(^5\) 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, \textit{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\(^3\). 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. Establishment 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\(^2\) of metal hydride on the sp-metals,
- (d) formation\(^3\) 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.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Form</th>
<th>Pre-treatment</th>
<th>Solution</th>
<th>Pre-electrolysis</th>
<th>Temp. (°C)</th>
<th>(V_r) (mV)(^a)</th>
<th>Range of log (i)</th>
<th>(\log i_0)</th>
<th>(b) (mV)</th>
<th>(a) (V)</th>
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<tbody>
<tr>
<td></td>
<td>Chern. polished, 1 A/cm(^2)</td>
<td></td>
<td>1N HCl</td>
<td>1A/cm(^2), 3.1 \times 10(^6) Coulomb</td>
<td>Room temp.</td>
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<td></td>
<td>(-6.5) ± 0.05</td>
<td>(-5.4) ± 0.05</td>
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<td></td>
<td>(-6.7) ± 0.05</td>
<td>(-5.7) ± 0.05</td>
<td>130 ± 5</td>
<td>0.48 ± 0.02</td>
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<td></td>
<td>(-6.9) ± 0.05</td>
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<tr>
<td>Wire</td>
<td>Chem. polished, heated in H(_2) at 600°C for 2~3 hr</td>
<td></td>
<td>5N HCl</td>
<td>1 A/cm(^2) ~ 10(^6) Coulomb</td>
<td>25</td>
<td>-3~+2(^b)</td>
<td>-5.3(^*)</td>
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<td>120</td>
<td>0.64</td>
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<tr>
<td>Wire</td>
<td>Chem. polished</td>
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<td>1N H(_2)SO(_4)</td>
<td>Conducted</td>
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<td>110</td>
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<tr>
<td>Wire</td>
<td>Heated in H(_2) at 700°C for 1 hr, sealed into glass bulb</td>
<td></td>
<td>0.4N HCl</td>
<td>10 mA/cm(^2), 60 hr</td>
<td>23±2</td>
<td>-7~3</td>
<td>(-6.6)^1</td>
<td>(-5.35)</td>
<td>57±2</td>
<td>101±9</td>
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<td>Authors</td>
<td>Journal</td>
<td>Volume</td>
<td>Page</td>
<td>Temperature</td>
<td>Voltage</td>
<td>Current Density</td>
<td>Conducted</td>
<td>Notes</td>
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<tr>
<td>1.0N H₂SO₄</td>
<td>20</td>
<td>-7~3.5</td>
<td>-6.42±1</td>
<td>119*</td>
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<tr>
<td>A. A. ANTONIOU and F. E. W. WETMORE, Can. J. Chern., 37, 222 (1959).</td>
<td>Single or poly-crystal</td>
<td>Electropolished, held in hot H₂ for a few days, gently anodized</td>
<td>2N H₂SO₄</td>
<td>Conducted</td>
<td>Room temp.</td>
<td>+0.35~+0.45 V, occasionally 0~+18mv</td>
<td>-7.5~2.7</td>
<td>{~-6±1}</td>
<td>59</td>
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<td>B. E. CONWAY, Proc. Roy. Soc., A256, 128 (1960).</td>
<td>Wire</td>
<td>Sealed into glass bulb</td>
<td>0.1N HCl</td>
<td>0.1A/cm², 24~36 hr</td>
<td>26±1</td>
<td>-5.5~2</td>
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<td>-6.10±0.2±1</td>
<td>72±7</td>
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<td>0.1N DCI</td>
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<td>K. GOSSNER, CHR. LÖFFLER and G. M. SCHWAB, Z. Phys. Chern., 28, 229 (1961).</td>
<td>Foil</td>
<td>Heated in H₂ at 450°C for 24 hr, sealed with paraffin</td>
<td>2N H₂SO₄</td>
<td>0.1A, 60 hr</td>
<td>Room temp.</td>
<td>-2.3~1.3</td>
<td>-5.4±</td>
<td>120</td>
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<td>V. I. BYSTROV and L. I. KRISHTALIK, Elektrokhimiya, 3, 1345 (1967).</td>
<td>Wire</td>
<td>Alkali, HNO₃, polished with fine glass powder</td>
<td>0.1N H₂SO₄</td>
<td>Conducted</td>
<td></td>
<td></td>
<td></td>
<td>-8~4.5</td>
<td>-6~4.5</td>
<td>-7.2±</td>
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<td>at higher c.d.</td>
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<tr>
<td>V. I. BYSTROV and L. I. KRISHTALIK, Elektrokhimiya, 3, 1499 (1967).</td>
<td>Wire</td>
<td>Alkali, HNO₃, polished with fine glass powder</td>
<td>0.1M K₃PO₄, +H₂SO₄ pH=1.6</td>
<td>Conducted</td>
<td>25</td>
<td>-6.3~4.6</td>
<td>-7.3±</td>
<td>~120±</td>
<td>at higher c.d.</td>
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<tr>
<td>V. I. BYSTROV and L. I. KRISHTALIK, Elektrokhimiya, 4, 233 (1968).</td>
<td>Wire</td>
<td>Alkali, HNO₃, polished with fine glass powder</td>
<td>0.1N H₂SO₄</td>
<td>Conducted</td>
<td>25</td>
<td>-7~4.5</td>
<td>-6.3±</td>
<td>135</td>
<td>at higher c.d.</td>
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<tr>
<td>Metal</td>
<td>Form</td>
<td>Pre-treatment</td>
<td>Solution</td>
<td>Pre-electrolysis</td>
<td>Temp. (°C)</td>
<td>Vr (mV)</td>
<td>Range of log i</td>
<td>log ( i_0 )</td>
<td>( b ) (mV)</td>
<td>( a ) (V)</td>
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<tr>
<td></td>
<td>Section of rod, 2.5 mm, dia</td>
<td>99.99%, mechanically polished, kept with 0.1 mA/cm(^2) for 1 hr</td>
<td>2N H(_2)SO(_4)</td>
<td>25</td>
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<tr>
<td>Al</td>
<td>Wire (99.98%)</td>
<td>Chemipolished (2 min, 90°C, 85% H(_3)PO(_4)+15% HNO(_3)), washed, dipped in 1 N NaOH, 10 min, washed</td>
<td>0.2~1.7N H(_2)SO(_4)</td>
<td>3~5 hr with the highest c.d. studied</td>
<td>25 ± 15°C</td>
<td>Mixed potential</td>
<td></td>
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<td>0.847</td>
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<td>As</td>
<td>E. A. Efimov and I. G. Erusalimchik, Elektrokhimiya, 1, 1133 (1965).</td>
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<td>99.999%</td>
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<td>1N H(_2)SO(_4)</td>
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<tr>
<td>Au</td>
<td>Wire</td>
<td>Sealed into glass bulb</td>
<td>0.1N HCl</td>
<td>27 mA/cm(^2), 42 hr</td>
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<td>Value of r.h.e.</td>
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<td>{−5.63~−4.02}</td>
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<td>B E. Conway, Proc. Roy. Soc., A 256, 128 (1960).</td>
<td>Wire</td>
<td>Sealed into glass bulb</td>
<td>0.1N HCl(0.1N HCl)</td>
<td>0.1 A/cm(^2), 24~36 hr</td>
<td>26 ± 1</td>
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<tr>
<td>Wire</td>
<td>Sealed with paraffin or araldite, scraped with sharp glass bar</td>
<td>2N H₂SO₄</td>
<td>20</td>
<td>-3 ~ -1</td>
<td>-5.36 †</td>
<td>116 ± 4</td>
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<tr>
<td>Bead</td>
<td>Melt in H₂, washed in hot cleaning soln. degreased, washed in dist. water</td>
<td>1M HClO₄ (pH = 0.1)</td>
<td>14 hr, 50 mA</td>
<td>20 ± 2</td>
<td>-4 ~ 0</td>
<td>-4.52 †</td>
<td>110 ± 10 on fresh elect.</td>
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<tr>
<td>Cross section</td>
<td>1N H₂SO₄</td>
<td>22.5</td>
<td>-3 ~ 0</td>
<td>-5.86 †</td>
<td>103</td>
<td>0.603</td>
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<tr>
<td>Foil</td>
<td>+1.3V for 10min -0.1V for 5min</td>
<td>1.0M H₂SO₄</td>
<td>20</td>
<td>-5.52 †</td>
<td></td>
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</tr>
<tr>
<td>Wire</td>
<td>99.99%</td>
<td>1N H₂SO₄</td>
<td>21 ± 0.1</td>
<td>-3 ~ 0.7</td>
<td>-5.86 †</td>
<td>103</td>
<td>0.603</td>
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<tr>
<td>Cross section</td>
<td>1N H₂SO₄</td>
<td>22.5</td>
<td>-3 ~ 0</td>
<td>-5.86 †</td>
<td>103</td>
<td>0.603</td>
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<tr>
<td>Foil</td>
<td>+1.3V for 10min -0.1V for 5min</td>
<td>1.0M H₂SO₄</td>
<td>20</td>
<td>-5.52 †</td>
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<tr>
<td>Bi</td>
<td>Melted, poured into glass tube, scraped with a hard steel knife</td>
<td>1N HCl</td>
<td>17 ~ 20</td>
<td>-3 ~ -1</td>
<td>-9.09 †</td>
<td>110</td>
<td>1.0</td>
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<tr>
<td>Plate</td>
<td>Previously polarized</td>
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<td>Plate</td>
<td>Conducted, 20 ~ 25 hr</td>
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<td>Metal</td>
<td>Form</td>
<td>Pre-treatment</td>
<td>Solution</td>
<td>Pre-electrolysis</td>
<td>Temp. (°C)</td>
<td>Vr (mV)</td>
<td>Range of log i</td>
<td>log i_r</td>
<td>b (mV)</td>
<td>a (V)</td>
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<tr>
<td>Bi</td>
<td>A. B. KILIMNIK and A. L. ROTINIAN, Elektrokhimiya, 5, 1234 (1969).</td>
<td>99.99%</td>
<td>2N H₂SO₄</td>
<td>25</td>
<td></td>
<td></td>
<td>[-7.75^*]</td>
<td>[120 \pm 5]</td>
<td>[0.93 \pm 0.01]</td>
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<tr>
<td>T. T. TENNO and U. V. PÁLM, Elektrokhimiya, 8, 1381 (1972).</td>
<td>99.9%</td>
<td>1N HClO₄</td>
<td>1000 hr</td>
<td>80</td>
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<tr>
<td>Material</td>
<td>Source</td>
<td>Conditions</td>
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<tr>
<td>$\alpha$-Co</td>
<td>Z. A. IOFA and VEI BAO-MIN, Zh. Fiz. Khim., 37, 2301 (1963).</td>
<td>Electrodeposited from $300g/ℓ$ CoSO$_4$.7H$_2$O + $22.5g/ℓ$ H$_3$BO$_3$, pH 1.3~1.9 (with H$_2$SO$_4$), 0.1 A/cm$^2$, 20°C</td>
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<tr>
<td>$\beta$-Co</td>
<td>S. RASHKOV, K. L. HAMPARTZUMIAN and N. A. PANGAROV, Electrochim. Acta, 9, 841 (1964).</td>
<td>Electrodeposited from $250g/ℓ$ CoSO$_4$.7H$_2$O + $25g/ℓ$ H$_3$BO$_3$ + $34g/ℓ$ NaCl+HCl, 30 mA/cm$^2$, 16°C</td>
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<td>$\alpha$-Co</td>
<td>Z. A. IOFA and VEI BAO-MIN, Elektrokhimiya, 2, 755 (1966).</td>
<td>Electrodeposited from $600g/ℓ$ CoSO$_4$.7H$_2$O + $45g/ℓ$ H$_3$BO$_3$, pH 5 (with NH$_4$OH), 15 mA/cm$^2$, 60°C</td>
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<tr>
<td>$\beta$-Co</td>
<td>Z. A. IOFA and VEI BAO-MIN, Elektrokhimiya, 2, 755 (1966).</td>
<td>Electrodeposited from $250g/ℓ$ CoSO$_4$.7H$_2$O + $22.5g/ℓ$ H$_3$BO$_3$, pH 1.3~1.9 (with H$_2$SO$_4$), 0.1 A/cm$^2$, 20°C</td>
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<tr>
<td>Cr</td>
<td>L. KISHSH, Dis. LGU, L., 1957.</td>
<td>Electrodeposited from $350g/ℓ$ CrO$_3$ + $3.5g/ℓ$ H$_2$SO$_4$, with 0.35 A/cm$^2$ for 2 hr at 45°C</td>
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<tr>
<td>Cubic Cr</td>
<td>ST. G. CHRISTOV and N. A. PANGAROV, Z. Elektrochem., 61, 113 (1957).</td>
<td>Electrodeposited from $350g/ℓ$ CrO$_3$ + $3.5g/ℓ$ H$_2$SO$_4$, pH 2.70</td>
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</table>

Electrodeposited from $350g/ℓ$ CrO$_3$ + $3.5g/ℓ$ H$_2$SO$_4$, pH 2.70 Conducted 20 ± 0.5 Mixed. pot. -7~3.5 -6.60+t 0.80
<table>
<thead>
<tr>
<th>Metal</th>
<th>Erom</th>
<th>Pre-treatment</th>
<th>Solution</th>
<th>Temp. (°C)</th>
<th>Vr (mV)</th>
<th>Range of log i</th>
<th>log i₀ (mV)</th>
<th>b (mV)</th>
<th>a (V)</th>
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</thead>
<tbody>
<tr>
<td>Hexagonal Cr</td>
<td>ST. G. CHRISTOV and N. A. PANGAROV, Z. Elektrochem., 61, 113 (1957).</td>
<td>Electrodeposited from 600g/ℓ CrO₂ + 32.4 g/ℓ sugar, 0.075N H₂SO₄ with 0.16 A/cm² for 4 hr at 18.5°C</td>
<td>HCl+0.1N KCl pH=2.85</td>
<td>Conducted</td>
<td>20 ± 0.5</td>
<td>Mixed. pot.</td>
<td>−7～−3.5</td>
<td>−5.37*†</td>
<td>112</td>
</tr>
<tr>
<td>Cr</td>
<td>KHO NGOK BA and NGUEN DYK VI, Elektrokhim., 4, 990 (1968).</td>
<td>Polished by fine powder, washed, cathodized with 0.2 A/cm² for 15～20 min in 1N H₂SO₄</td>
<td>1N H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td>−7.43†</td>
<td>107</td>
<td>0.795</td>
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<tr>
<td>Active Cr</td>
<td>B. E. WILDE and F. G. HODGE, Electrochim. Acta, 14, 619 (1969).</td>
<td>Polished mechanically with mirror finish, degreased in i-propyl alc. and washed in ethanol, cathodic polarization at −1.0 V (SCE) for active Cr.</td>
<td>1N H₂SO₄</td>
<td>70 mA, 24 hr</td>
<td>25</td>
<td>−0.708 V (S.C.E.)</td>
<td>−6.46†</td>
<td>126</td>
<td>0.81*</td>
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<tr>
<td>Cu</td>
<td>V. N. KABANOV and A. N. FRUMKIN, Zh. Fiz. Khim., 5, 418 (1934).</td>
<td></td>
<td>1N H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td>−7.70†</td>
<td>100</td>
<td>0.77</td>
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<td></td>
<td>G. M. MAITAK, Zap. In-at Khim., AH USSR, 6, 61 (1939).</td>
<td></td>
<td>1N H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td>−6.96†</td>
<td>115</td>
<td>0.80</td>
</tr>
<tr>
<td>Author(s)</td>
<td>Concentration and Conditions</td>
<td>Potential (V)</td>
<td>Current Density (mA/cm²)</td>
<td>Temperature (°C)</td>
<td>Time (h)</td>
<td>Reaction</td>
<td>Reference</td>
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<tr>
<td>A. G. Pecherskaya and V. V. Stender, Zh. prikl. Khim., 19, 1303 (1946).</td>
<td>2N H₂SO₄</td>
<td>-6.69±1</td>
<td>130</td>
<td>0.87</td>
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<tr>
<td>W. Himmler, Z. phys. Chem., 196, 205 (1951).</td>
<td>2N H₂SO₄</td>
<td>-5～-2</td>
<td>64±1°</td>
<td>91*</td>
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<tr>
<td>W. P. Senett and C. F. Hiskey, J. Am. Chem. Soc., 74, 3754 (1952).</td>
<td>Electrodeposited from acidified copper sulfate soln. 9 mA/cm², 2 hr, 26±1°C</td>
<td>-8.35±0.04</td>
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<tr>
<td>J. O'M. Bockris and N. Pentland, Trans. Faraday Soc., 48, 833 (1952).</td>
<td>Wire 0.1N HCl, 20 hr, 26±1°C</td>
<td>-5.0～-2.5</td>
<td>117</td>
<td>0.79</td>
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<tr>
<td>S. E. El Wakkad, I. A. Ammar and H. Sabry, J. Chem. Soc., 3020 (1956).</td>
<td>Electrodeposited from cyanide bath, 60 mA/cm², 20 min, 70°C</td>
<td>-6～-1.5</td>
<td>60</td>
<td></td>
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<tr>
<td>B. E. Conway, Proc. Roy. Soc., A 256, 128 (1960).</td>
<td>Sealed into glass bulb 0.1N DCl, 0.1 A/cm², 24～36 hr, 26±1°C</td>
<td>-5.5～-2</td>
<td>120±5</td>
<td>120±5</td>
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<tr>
<td>B. E. Conway, E. M. Beatty and P. A. DeMaine, Electrochimica Acta, 7, 39 (1962).</td>
<td>Heated to red hot in H₂, sealed into glass bulb 0.1N HCl, 0.25 A/cm², 38±1°C</td>
<td>-5～-1</td>
<td>6.21±1</td>
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<tr>
<td>Metal</td>
<td>Form</td>
<td>Pre-treatment</td>
<td>Solution</td>
<td>Pre-electrolysis</td>
<td>Temp. (°C)</td>
<td>Vr (mV)</td>
<td>Range of log i</td>
<td>log i₀</td>
<td>b (mV)</td>
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<td></td>
<td></td>
<td>Polished by Emery, degreased by EtOH, treated with 1M HCl</td>
<td>1M HCl</td>
<td>Conducted, 24~48 hr</td>
<td>30 ± 0.1</td>
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<td>-4~1</td>
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<tr>
<td>Wire</td>
<td>99.99%</td>
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<td>Wire</td>
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<tr>
<td>(100)</td>
<td>Mech. polished, cathodized</td>
<td>0.1N H₂SO₄</td>
<td>Conducted, 7~8 hr</td>
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<td>(110)</td>
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<td>(111)</td>
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<tr>
<td>V. V. BATRAKOV, Yu. DITTRIKH and A. N. POPOV, Elektrokhimija, 8, 640 (1972).</td>
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<tr>
<td>Wire, annealed</td>
<td>99.999%, after stretching or rolling, heated at 500°C for 6 hr under vac. and H₂</td>
<td>1N H₂SO₄</td>
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<tr>
<td>Wire, 20% stretched</td>
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<tr>
<td>Plate, annealed</td>
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Note: Range of log i = −6.8' to −6.90, log i₀ = 100 ± 1, b = 120 ± 10, a = 0.73.
<table>
<thead>
<tr>
<th>Bead</th>
<th>Then melted (dia, 1.4-1.6mm)</th>
<th>1N H₂SO₄</th>
<th></th>
<th></th>
<th>(-7.90^{\pm})</th>
<th>100 ± 1</th>
<th>0.790 ± 0.005</th>
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<tbody>
<tr>
<td>(100)</td>
<td>Polished mechanically and then electrochemically.</td>
<td>&quot;</td>
<td></td>
<td></td>
<td>(-8.55^{\pm})</td>
<td>96 ± 3</td>
<td>0.825 ± 0.020</td>
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<tr>
<td>(110)</td>
<td>Density of dislocation, 10⁷/cm²</td>
<td>&quot;</td>
<td></td>
<td></td>
<td>(-8.65^{\pm})</td>
<td>96 ± 3</td>
<td>0.830 ± 0.020</td>
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<tr>
<td>(111)</td>
<td></td>
<td>&quot;</td>
<td></td>
<td></td>
<td>(-8.45^{\pm})</td>
<td>96 ± 3</td>
<td>0.810 ± 0.020</td>
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All electrodes were polarized at 0.625 V (nhe) for 3 min in 72% H₃PO₄, then cathodized in the cell for 1/2 hr with 10 mA/cm².

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Fe

<p>| A. G. Pecherskaya and V. V. Stender, Zh. prikl. Khim., 19, 1303 (1946). | | | | | 2N H₂SO₄ | (-6.03^{\pm}) | 116 | 0.70 |
| V. A. Kuznetsov and Z. A. Iofa, Zh. Fiz. Khim., 21, 201 (1947). | | | | | 1N HCl | (-5.60^{\pm}) | 125 | 0.70 |
| H. F. Fischer and H. Heiling, Z. Elektrochem., 54, 187 (1956). | | | | | 2N H₂SO₄ | (-6.00^{\pm}) | 120 | 0.72 |
| N. Pentland, J. O'M. Bockris and E. Sheldon, J. Electrochem. Soc., 104, 182 (1957). | | | | | 0.01N HCl | (-4.06 \sim -3.19^{b}) | (-6.29^{f}) | 118 ± 15 |
| Tor Hurlen, Acta Chemica Scandinavica, 14, 1533 (1960). | | | | | Annealed, 1 hr 700°C, vac., polished with emery paper, etched in dil. HNO₃, washed HCl (pH=0) | 20 ± 0.5 | (-5 \sim -2) | (-5.36^{f}) | 116 |
| Sheet | | | | | | 0.5N HCl | 15 mA/cm², 20 hr | {(-5.18 \pm 0.1^{f}) | 133 ± 4 |</p>
<table>
<thead>
<tr>
<th>Metal</th>
<th>Form</th>
<th>Pre-treatment</th>
<th>Solution</th>
<th>Pre-electrolysis</th>
<th>Temp. (°C)</th>
<th>$V_r$ (mV)\textsuperscript{a}</th>
<th>Range of log $i$</th>
<th>log $i_0$</th>
<th>$b$ (mV)</th>
<th>$a$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>KHO NGOK BA, Dis. MGU, M., 1964.</td>
<td></td>
<td>1N H$_2$SO$_4$</td>
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<td></td>
<td>KHO NGOK BA, Dis. MGU, M., 1964.</td>
<td></td>
<td>1N H$_2$SO$_4$</td>
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<td></td>
<td>Cylindrical, Mounted on Teflon holder, etched in 0.5M H$_2$SO$_4$</td>
<td></td>
<td>0.5M H$_2$SO$_4$</td>
<td>Conducted</td>
<td>25.00 ± 0.03</td>
<td><del>3.9</del>−~1.6</td>
<td><del>5.65</del>\textsuperscript{tt}</td>
<td>118</td>
<td></td>
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<tr>
<td>$\alpha$-Fe (Armco)</td>
<td>J. O'M. BOCKRIS, J. McBREEN and L. NANIS, J. Electrochem. Soc., 112, 1025 (1965).</td>
<td></td>
<td>0.1N H$_2$SO$_4$</td>
<td>Conducted</td>
<td>26 ± 0.5</td>
<td><del>4</del>−~1.5</td>
<td>115</td>
<td></td>
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<tr>
<td>Ga</td>
<td>ST. G. CHRISTOV and L. RAJCEVA, Z. Elektrochem., 66, 486 (1962).</td>
<td></td>
<td>0.1N HCl</td>
<td>Conducted</td>
<td>20.5 (25)</td>
<td><del>6</del>−~3</td>
<td>{<del>−10.0\textsuperscript{f}</del>}</td>
<td>112</td>
<td>93</td>
<td></td>
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<tr>
<td></td>
<td>K. SABO and I. A. BAGOTSKAYA, Dok. Akad. Nauk SSSR, 149, 139 (1963).</td>
<td></td>
<td>99.99%</td>
<td>1N H$_2$SO$_4$</td>
<td>28 (32)</td>
<td><del>5</del>−~3</td>
<td>{<del>−9.9\textsuperscript{tt}</del>}</td>
<td>95</td>
<td>95</td>
<td></td>
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<tr>
<td></td>
<td>E. PREIS, K. SABO, S. RAICHEVA and I. A. BAGOTSKAYA, Elektrokhimiya, 2, 1209 (1966).</td>
<td></td>
<td>99.9998%</td>
<td>1N H$_2$SO$_4$</td>
<td>28 (32)</td>
<td><del>9.33</del>−~9.05\textsuperscript{tt}</td>
<td>110~−~115</td>
<td></td>
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<tr>
<td></td>
<td>J. N. BUTLER and M. L. MEEHAN, Trans. Faraday Soc., 62, 3524 (1966).</td>
<td></td>
<td>99.999%</td>
<td>0.1M HClO$_4$</td>
<td>Conducted, 4~−~16 hr</td>
<td>32.0 ± 0.1</td>
<td><del>4</del>−~2</td>
<td>~9.90 ± 0.10\textsuperscript{f}</td>
<td>$a$ = 0.582 ± 0.008</td>
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<tr>
<td>Single crystal, n-, and p-type, prepolarized cathodically with 1mA/cm², 1 hr</td>
<td>0.1N HCl</td>
<td>20</td>
<td>( -5 \sim -3^b )</td>
<td>120</td>
<td>0.97</td>
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<td></td>
<td></td>
<td>( -2 \sim -1^b )</td>
<td>120</td>
<td>1.33</td>
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<tr>
<td>Single crystal (no specification for lattice)</td>
<td>Chem. polished, 25cc conc. HNO₃, 15cc HF, 15cc CH₃COOH at 40°C for 20 sec.</td>
<td>1N H₂SO₄</td>
<td>25</td>
<td>(-7.4 \sim -4.7)</td>
<td>170</td>
<td>1.58</td>
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<td></td>
<td>1N H₂SO₄</td>
<td></td>
<td></td>
<td>(-12.52^e)</td>
<td>113</td>
<td>1.415</td>
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<tr>
<td></td>
<td>1N HCl</td>
<td></td>
<td></td>
<td>(-12.12^e)</td>
<td>116</td>
<td>1.406</td>
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<tr>
<td>Pool</td>
<td>Redistillation</td>
<td>1.005N HCl</td>
<td>25 ± 0.02</td>
<td>(-4.6 \sim -1)</td>
<td>118 ± 2</td>
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<tr>
<td>Metal</td>
<td>Form</td>
<td>Pre-treatment</td>
<td>Solution</td>
<td>Pre-electrolysis</td>
<td>Temp. (°C)</td>
<td>Vr (mV)</td>
<td>Range of log i</td>
<td>log $i_0$</td>
<td>$b$ (mV)</td>
<td>$a$ (V)</td>
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<td>Hg</td>
<td>B. POST and C. F. HISKEY, J. Am. Chem. Soc., 72, 4203 (1950).</td>
<td>Triply distilled, then distilled in vacuum</td>
<td>0.1N HCl</td>
<td>Conducted 21 ± 0.1</td>
<td>−6~−1</td>
<td>−12.11*</td>
<td>116</td>
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<td>B. POST and C. F. HISKEY, J. Am. Chem. Soc., 73, 161 (1951).</td>
<td></td>
<td>0.1M HCl {0.1M DCl}</td>
<td>20</td>
<td>−6~−2.2</td>
<td>−12.21*</td>
<td>116</td>
<td>1.416</td>
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<td>S. MINC and J. SOBKOWSKI, Bull. Akad. Polon. Sci., 8, 29 (1959).</td>
<td></td>
<td>0.1M HCl solution of H₂O₂, CH₃OH, C₂H₅OH, n-C₃H₇OH</td>
<td>20 ± 0.5</td>
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<td>J. N. BUTLER and A. C. MAKRIDES, Trans. Faraday Soc., 60, 938 (1964).</td>
<td></td>
<td>0.1N HClO₄</td>
<td>1 mA/cm², overnight</td>
<td>25</td>
<td>−4~−1.7</td>
<td>−11.82*</td>
<td>118</td>
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<td>B. E. CONWAY and M. SALOMON, J. Chem. Phys., 41, 3169 (1964).</td>
<td></td>
<td>Redistilled, anodic polarization in HNO₃−H₂(NO₃)₂, distillation in vac-</td>
<td>1N HCl solution of CH₃OH</td>
<td>Conducted 27</td>
<td>−4~−2</td>
<td>−10.8*</td>
<td>119*</td>
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<td>J. N. BUTLER and A. C. MAKRIDES, Trans. Faraday Soc., 60, 1664 (1964).</td>
<td></td>
<td>0.1M HClO₄</td>
<td>1 mA/cm², overnight</td>
<td>25</td>
<td>−12.65*</td>
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<td>Element</td>
<td>Reference</td>
<td>Conditions</td>
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<td>Hg</td>
<td>O. Nagashima and H. Kita, J. Res. Inst. Catalysis, Hokkaido Univ., 15, 49 (1967).</td>
<td>Distilled in vac. 1N H₂SO₄ 6 mA, 170 hr 25 70</td>
<td>-2 0 -11.8 124 15 1.462 ± 0.017</td>
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<td>In</td>
<td>J. N. Butler and A. C. Makrides, Trans. Faraday Soc., 60, 1664 (1964).</td>
<td>0.1M HClO₄ 1 mA/cm², overnight 25</td>
<td>-3.5 1.5 0.017</td>
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<td></td>
<td>J. N. Butler and M. Dienst, J. Electrochem. Soc., 112, 226 (1965).</td>
<td>Cylindrical 99.999%, electro-polished, polarized overnight at -1.0 V. 0.1M HClO₄ Conducted with pt-Pt, 10 mA, 16 hr 25 ± 0.2</td>
<td>-6.3 2.8 0.03 0.498 0.002</td>
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<td>Mn</td>
<td>T. Hurlen and T. Valand, Electrochimica Acta, 9, 1077 (1964).</td>
<td>Sheet Electrolytic Mn, chem. polished, etched in 1M HCl or H₂SO₄ HCl+KCl+ small amount of ammonium sulfite</td>
<td>22 23 117</td>
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<td>Pre-electrolysis</td>
<td>Temp. (°C)</td>
<td>Vr (mV)</td>
<td>Range of log i</td>
<td>log ( i_0 ) (mV)</td>
<td>b (mV)</td>
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<td>Mo</td>
<td></td>
<td>A. G. Pecherskaya and V. V. Stender, Zh. prikl. Khim., 19, 1303 (1946).</td>
<td>2N ( \text{H}_2\text{SO}_4 )</td>
<td></td>
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<td></td>
<td></td>
<td>-6.29( ^* )</td>
<td>105</td>
<td>0.66</td>
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<td></td>
<td>Wire</td>
<td>N. Pentland, J. O'M. Bockris and E. Sheldon. J. Electrochem. Soc., 104, 182 (1957).</td>
<td>0.1N HCl</td>
<td>75 mA/cm(^2), 37 hr</td>
<td></td>
<td></td>
<td>-5.52~ -3.48( ^b )</td>
<td>-7.30( ^r )</td>
<td>80 ± 4</td>
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<td></td>
<td>Wire</td>
<td>I. V. Kudriashov and S. D. Kamyschenko, Elektrokhimiya, 7, 1284 (1971).</td>
<td>1N HCl</td>
<td>20</td>
<td>-4.0~ -1.5</td>
<td>-6.00( ^r )</td>
<td>105</td>
<td>0.63</td>
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<td></td>
<td>Wire</td>
<td>J. O'M. Bockris, Trans. Faraday Soc., 43, 417 (1947).</td>
<td>1N HCl</td>
<td>20</td>
<td>-4.0~ -1.5</td>
<td>-6.16( ^r )</td>
<td>95</td>
<td>0.585</td>
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<td>Wire</td>
<td></td>
<td>22</td>
<td>-4.0~ -2.0</td>
<td>-5.96</td>
<td>108</td>
<td>0.645</td>
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<td>T. I. Kononchuk and I. V. Varmashenko, Ukr. Khim. Zh., 25, 25 (1960).</td>
<td>1N ( \text{H}_2\text{SO}_4 )</td>
<td></td>
<td>-7.75( ^*r )</td>
<td>120</td>
<td>0.93</td>
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<td>Plate</td>
<td>Polished with emery paper, cathodic polarization (5 mA/cm², 96 hr)</td>
<td>1N H₂SO₄</td>
<td>10 mA/cm², 6 hr</td>
<td>-5 ~ -2.3</td>
<td>-6.33†</td>
<td>120</td>
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<td>1N H₂SO₄</td>
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<tr>
<td>Ni</td>
<td>Mechanically polished</td>
<td>2N H₂SO₄</td>
<td>25</td>
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<td>2N H₂SO₄</td>
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<tr>
<td></td>
<td>1N HCl</td>
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<tr>
<td>Wire</td>
<td>Sealed into glass bulb</td>
<td>1.0N HCl</td>
<td>0.1 A/cm², 18 hr</td>
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<tr>
<td>Wire</td>
<td>Heated in H₂ at 600°C for 2~3 hr</td>
<td>5N HCl</td>
<td>1A/cm², ~10⁶ coulombs</td>
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<td></td>
<td>2N H₂SO₄</td>
<td>Conducted</td>
<td>30 ± 1</td>
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<td>1N HCl</td>
<td>Conducted</td>
<td>30 ± 1</td>
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<tr>
<td>Metal</td>
<td>Form</td>
<td>Pre-treatment</td>
<td>Solution</td>
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<td>Ni</td>
<td>R. PIONTELLI, L. P. BICELLI and A. LA VECCHIA, Accad. Nazionale Dei Lincei VIII, 27, 312 (1959).</td>
<td>Single crystal (100)</td>
<td>Anodic treatment in 70% $\text{H}_2\text{SO}_4$</td>
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<td></td>
<td></td>
<td>(110) (111)</td>
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<td>B. E. CONWAY, Proc. Roy. Soc., A 256, 128 (1960).</td>
<td>Wire</td>
<td>Sealed into glass bulb</td>
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<td></td>
<td>B. E. CONWAY, E. M. BEATTY and P. A. DEMAINe, Electrochimica Acta, 7, 39 (1962).</td>
<td>Wire</td>
<td>Heated to red hot in $\text{H}_2$, sealed into glass bulb</td>
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<td>J. O'M. BOCKRIS and S. SRINIVASAN, Electrochim. Acta, 9, 31 (1964).</td>
<td>Wire</td>
<td>Heated in $\text{H}_2$ at 700°C</td>
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<td></td>
<td>A. K. M. S. HUQ and A. J. ROSENBERG, J. Electrochem. Soc., 111, 270 (1964).</td>
<td>Cross section of rod</td>
<td>Mounted in pyrex holder by Kel-F wax, polishings, treated by chromic acid/sulfuric acid</td>
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<td>E. I. MIKHAILOVA and Z. A. IOFA, Elektrokhimiya, 1, 107 (1965).</td>
<td>Plate</td>
<td>Polished with fine glass powder, cathodic polarization with 20 mA/cm$^2$, 10 min</td>
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<tr>
<td>Plate</td>
<td>Electropolished</td>
<td>1N H₂SO₄</td>
<td>5mA/cm², 24hr</td>
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<tr>
<td>(110)</td>
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<td>(111)</td>
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<tr>
<td>Polished by fine silica powder, treated in boil. 10% KOH, cathodized</td>
<td>0.1N H₂SO₄</td>
<td>Purified electrochemically</td>
<td>-5.5~2.5</td>
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<td>99.9% 1.0 V 10 s, -1.0 V 10 min, repeat more than six times, with final cathodic pulse 10 min.</td>
<td>HCl, pH=0.0</td>
<td>10 mA, 24 hr</td>
<td>25 ± 1</td>
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<td>Cathodic polarization (0.1~1mA/cm²)</td>
<td>0.1, 0.01N H₂SO₄</td>
<td>20</td>
<td>-6.6~2.8</td>
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<tr>
<td>A. G. PECHERSKAYA and V. V. STENDER, Zh. prikl Khim., 19, 1303 (1946).</td>
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<td>2N H₂SO₄</td>
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<td>1N H₂SO₄</td>
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<tr>
<td>1.0N H₂SO₄</td>
<td></td>
<td>20</td>
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at higher c.d. at higher c.d.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Form</th>
<th>Pre-treatment</th>
<th>Solution</th>
<th>Pre-electrolysis</th>
<th>Temp. (°C)</th>
<th>Vr (mV)</th>
<th>Range of log i</th>
<th>log io (mV)</th>
<th>b (V)</th>
<th>a (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Sponge Battery plate, 15.9 m²</td>
<td>5M H₂SO₄</td>
<td>30 ± 0.05</td>
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<td></td>
<td>120</td>
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</tr>
<tr>
<td>Pd</td>
<td>Wire Chem. polished</td>
<td>0.5N H₂SO₄</td>
<td>1 mA/cm², 40 hr</td>
<td>Room temp.</td>
<td></td>
<td></td>
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<td></td>
<td>125 ± 14</td>
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<tr>
<td></td>
<td>J. P. HOARE and S. SCHULDNER, J. Electrochem. Soc., 102, 485 (1955).</td>
<td>Anodic (5 mA, 15 min), cathodic (50 mA, 30 min) polarizations.</td>
<td>1.05N H₂SO₄ pH=0.40</td>
<td>Conducted.</td>
<td>39 ± 1</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Anodic (10 mA, 30 min), cathodic (50 mA, 30 min) polarizations.</td>
<td>0.514N H₂SO₄ +0.5N Na₂SO₄ pH=0.84</td>
<td>Conducted.</td>
<td>39 ± 1</td>
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<tr>
<td></td>
<td>N. PENTLAND, J. O'M. BOCKRIS and E. SHELDON, J. Electrochem. Soc., 104, 182 (1957).</td>
<td>Sealed into glass bulb</td>
<td>0.1N HCl</td>
<td>0.24 A/cm², 13 hr</td>
<td>Value of r.h.e.</td>
<td></td>
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</tbody>
</table>

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<table>
<thead>
<tr>
<th>Membrane</th>
<th>Anodic polarization (10mA, 45 min)</th>
<th>Conducted.</th>
<th>(+49.5)</th>
<th>(-4.5 \sim -0.5)</th>
<th>(-1.2^*)</th>
<th>(42)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2N \text{ H}_2\text{SO}_4)</td>
<td>(\text{pH}=0)</td>
<td>(0.2N \text{ H}_2\text{SO}_4+0.7N \text{ Na}_2\text{SO}_4)</td>
<td>(\text{pH}=0.9)</td>
<td>(32 \pm 2)</td>
<td>(124)</td>
<td></td>
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</tbody>
</table>

| Wire | Sealed into glass bulb | 0.1N HCl | 0.1 A/cm\(^2\), 24~36 hr | 26 \pm 1 | \(-5 \sim -1.5\) | \(-2.8^*\) | (25 \pm 3) | \(110 \pm 10\) |
| Wire | Palladized | 1N HCl | 25 \pm 0.2 | \(-3.4 \sim 0\) | \(-2.5^*\) | 29.5 |
| Pt | Heated in H\(_2\) at 600°C for 2~3hr | 5N HCl | 1A/cm\(^2\), \(~10^6\) coulombs | 25 | \(-2\sim 2\) | hysteresis at high c.d. |

| Bead | 0.205M H\(_2\)SO\(_4\) | 5\~10 mA overnight | 25 \pm 1 | \(-3.2^*\) | 26 | 0.25 |

<p>| Wire | 1N H(_2)SO(_4) | 20 | (&lt;+2 \text{ mV}) | (-7 \sim -2) | (-3.65^*) | 129 |</p>
<table>
<thead>
<tr>
<th>Metal</th>
<th>Form</th>
<th>Pre-treatment</th>
<th>Solution</th>
<th>Pre-electrolysis</th>
<th>Temp. (°C)</th>
<th>$V_r$ (mV)</th>
<th>Range of log $i$</th>
<th>log $i_0$ (mV)</th>
<th>$b$ (mV)</th>
<th>$a$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Wire</td>
<td>Heated in H$_2$ at 600°C for 10 min, anodic polarization (0.1 A/cm$^2$, 10 sec)</td>
<td>1N HCl</td>
<td>0.1 A/cm$^2$, 10 hr</td>
<td>23 ± 2</td>
<td>$-3 \sim -1$</td>
<td>$-3.0^b$</td>
<td>29 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R. PARSONS, Trans. Faraday Soc., 56, 1340 (1960).</td>
<td>Soaked in chromic + sulfuric acid mixture for 24 hr, anodic and cathodic polarization (0.1 A/cm$^2$, 5 sec)</td>
<td>0.5M HCl</td>
<td>10 mA/cm$^2$, 18 hr</td>
<td>25 ± 0.5</td>
<td>Value of r.h.e.</td>
<td>$-3.4 \sim -1$</td>
<td>$-2.59 \pm 0.09^f$</td>
<td>27.8 ± 1.4</td>
<td></td>
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<tr>
<td></td>
<td>B. E. CONWAY, Proc. Roy. Soc., A 256, 128 (1960).</td>
<td>Wire</td>
<td>Platinized</td>
<td>0.1N HCl, 0.1N DCl</td>
<td>0.1 A/cm$^2$, 24 ± 36 hr</td>
<td>26 ± 1</td>
<td></td>
<td>${ -3.16 \pm 0.1^f$</td>
<td>${ -3.33 \pm 0.1$</td>
<td>30 ± 2</td>
</tr>
<tr>
<td></td>
<td>S. SCHULDINER, J. Electrochem. Soc., 106, 891 (1959); ibid., 108, 384 (1961).</td>
<td>Bead</td>
<td>Anodic polarization</td>
<td>1N H$_2$SO$_4$</td>
<td>5 ± 10 mA, overnight</td>
<td>25 ± 1</td>
<td>± 0.5 mV</td>
<td>$-4 \sim -0.6$</td>
<td>$-3.1^{*t}$</td>
<td>25</td>
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<tr>
<td></td>
<td>E. YEAGER, &quot;Transactions of the Symposium on Electrode Processes&quot;, John Wiley and Sons, Inc., New York (1961).</td>
<td></td>
<td></td>
<td>1N H$_2$SO$_4$ Conducted, 15 hr</td>
<td>25.0</td>
<td>$-4 \sim +0.4$</td>
<td>$-3.6^{*t}$</td>
<td>26$^*$</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>J. O'M. BOCKRIS and S. SRINIVASAN, Electrochim. Acta, 9, 31 (1964).</td>
<td>Wire</td>
<td>Anodic polarization</td>
<td>0.5N H$_2$SO$_4$</td>
<td>1 mA/cm$^2$, 15 ± 20 hr</td>
<td>Room temp.</td>
<td></td>
<td>$-3.35 \pm 0.05^f$</td>
<td>30 ± 1</td>
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</tbody>
</table>

a: Value of $i_0$.
b: Range of $i$.c: Value of $i_0$.d: Range of $i$.e: Value of $i_0$.f: Range of $i$.
| Wire | Heated in H₂, sealed into glass bulb, anodic polarization (10mA/cm², 10 sec) | 0.5N HCl | 15 mA/cm², 20 hr | \(-3.33 \pm 0.14\) | 29 ± 3 |
|      | 0.5N DCI |                |               | \(-3.62 \pm 0.45\) | 26 ± 6 |

| Bead | Reduced in H₂ at 800°C or 1050°C for a few hours, extracted with warm electrolyte overnight | 1.2N HCl 10% D₂O | 10~15 mA, overnight | \(-2.7 \pm 0.4\) | \(-3.33^*\) | 30 ± 1.5 | 0.1* |

| Polymorph (111) | Polarized at \(\phi_r\) = 1.2 V for 20 sec. | 1N H₂SO₄ | 20 | \(-3.4^*\) | 35 |
| Polymorph (100) | | | | \(-3.1^*\) | 36 |
| | | | | \(-4.0^*\) | 32 |

| Wire | Mounted in Teflon holder, cleaned in HCl | 0.037N HCl 0.145N HCl | 4~5mA, 50hr | 25 ± 0.1 | \(-6 \sim -2\) | \(-4.95\) | 43 |
|      | | 0.01N HCl | Conducted | Value of r.h.e. | \(-3.38 \sim -3.08^b\) | \(-3.80^t\) | 55 ± 3 |

| Wire | 2N H₂SO₄ | 29 | \(-2.80^t\) | 118 | 0.33 |

| Wire | Sealed into glass bulb | 0.01N HCl | Conducted | Value of r.h.e. | \(-3.38 \sim -3.08^b\) | \(-3.80^t\) | 55 ± 3 |

| Bead | Anodic, cathodic polarizations | 1M H₂SO₄ | Conducted | 27 ± 1 | \(-5 \sim -0.5\) | \(-2.5 \sim -1.5^b\) | \(-3.0^t\) | 27.5 |

<p>|  |  |  |  | (-1.5) | (-2.2^*) | 60 |</p>
<table>
<thead>
<tr>
<th>Metal</th>
<th>Form</th>
<th>Pre-treatment</th>
<th>Solution</th>
<th>Temp. (°C)</th>
<th>$V_r$ (mV)</th>
<th>Range of log $i$</th>
<th>log $i_0$ (mV)</th>
<th>$b$ (mV)</th>
<th>$a$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>J. HOARE, J. Electrochem. Soc., 107, 820 (1960).</td>
<td>Bead</td>
<td>Anodic, cathodic polarization (0.3 A/cm², 90 min)</td>
<td>2N H₂SO₄</td>
<td>25 ± 1</td>
<td>-3.5~0</td>
<td>-1.85*†</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>J. O'M. BOCKRIS and S. SRINIVASAN, Electrochim. Acta, 9, 31 (1964).</td>
<td>Wire</td>
<td>Anodic polarization (10 mA/cm²)</td>
<td>0.5N H₂SO₄</td>
<td>1 mA/cm², 9~10 hr</td>
<td>Room temp.</td>
<td>-3.22 ± 0.06†</td>
<td>28 ± 2</td>
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<tr>
<td>Ru</td>
<td>A. T. KUHN and P. M. WRIGHT, J. Electroanal. Chem., 27, 319 (1970).</td>
<td></td>
<td>1.0 V 10 s, −1.0V 10 min, repeat more than six times, with final cathodic pulse 10 min.</td>
<td>HCl, pH=0.0</td>
<td>10 mA, 24 hr</td>
<td>25 ± 1</td>
<td>-1</td>
<td>-4~2b</td>
<td>-4.35†</td>
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<td></td>
<td>N. M. SHMELEVA, E. D. LEVIN and A. L. ROTINIAN, Elektrokhimiya, 7, 1539 (1971).</td>
<td>Electrodeposition</td>
<td>2N H₂SO₄</td>
<td>25</td>
<td>-1.5~1.0b</td>
<td>-2.08*†</td>
<td>120</td>
<td>0.25 ± .03</td>
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<tr>
<td>Sb</td>
<td>A. G. PECHERSKAYA and V. V. STENDER, Zh. prikl. Khim., 19, 1303 (1946).</td>
<td></td>
<td>2N H₂SO₄</td>
<td></td>
<td></td>
<td>-9.30*†</td>
<td>100</td>
<td>0.93</td>
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<td>A. B. KILIMNIK and A. L. ROTINIAN, Elektrokhimiya, 5, 1234 (1969).</td>
<td>99.99%</td>
<td>2N H₂SO₄</td>
<td>25</td>
<td></td>
<td></td>
<td>(−5.08* after potential jump)</td>
<td>120 ± 5</td>
<td>0.61 ± 0.01</td>
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<td></td>
<td></td>
<td>(−7.78*†)</td>
<td>117 ± 5</td>
<td>0.91 ± 0.01</td>
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<tr>
<td>Single crystal (111) n and p types</td>
<td>Treated with solutions: HF : HNO₃ = 1: 2 and 42% HF</td>
<td>2N H₂SO₄</td>
<td>20</td>
<td>-6 ~ -1</td>
<td>-6.0</td>
<td>180</td>
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<td>Single crystal (111) n and p types</td>
<td>Treated with solutions: HF : HNO₃ = 1: 2 and 42% HF</td>
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<tbody>
<tr>
<td>Flat surface of cylindrical specimen</td>
<td>After polishing treated with chromic acid-sulfuric acid cleaning soln.</td>
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</tbody>
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<tr>
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<td>2N H₂SO₄</td>
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<td>2N H₂SO₄</td>
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<td>2N H₂SO₄</td>
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<td></td>
<td>99.99%</td>
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<tr>
<td>Metal</td>
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<td></td>
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<tr>
<td>Ta</td>
<td>N. M. KOZHEVKOVKA and A. L. ROTINIAN, Elektrokhimija, 1, 664 (1965).</td>
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<td></td>
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<td>Te</td>
<td>G. H. CARTLEDGE, J. Electrochem. Soc., 118, 1752 (1971).</td>
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<tr>
<td>Wire</td>
<td>10 min in hot 1 N NaOH, 1~2 min in hot 2 N H₂SO₄, cathodic polarization in 2 N H₂SO₄ (5 mA/cm², 1 hr)</td>
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<tr>
<td>Plate</td>
<td>10 min in hot 1 N NaOH, 1~2 min in hot 2 N H₂SO₄, cathodic polarization in 2 N H₂SO₄ (5 mA/cm², 1 hr)</td>
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<td></td>
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<tr>
<td>V. M. ARTEMONOVA, Elektrokhimiya, 3, 1219 (1967).</td>
<td>Hot 1 N NaOH for 10 min, hot 2 N H₂SO₄ for 1<del>2 min. Catho- [</del> \text{dized in 2 N H₂SO₄} ] (5 mA/cm², 1 hr)</td>
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<tr>
<td>N. T. THOMAS and KEN NOBE, J. Electrochem. Soc., 117, 622 (1970).</td>
<td>Annealed under vac. at 700°C for 1 hr, 1 N HF for 1 min.</td>
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</table>

Electroanalysis by δ- and α-Metals
<table>
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<tr>
<th>Metal</th>
<th>Form</th>
<th>Pre-treatment</th>
<th>Solution</th>
<th>Pre-electrolysis</th>
<th>Temp. (°C)</th>
<th>( V_r ) (mV)</th>
<th>Range of ( \log i )</th>
<th>( \log i_0 ) (mV)</th>
<th>( b ) (V)</th>
<th>( a ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>O. L. KABANOVA and A. N. DORONIN, Elektrokhimiya, 6, 222 (1970).</td>
<td>Rod</td>
<td>Impurity, less than ( 10^{-4}% ). Surface was cut by glass, cathodized for 1 hr with 0.83 mA/cm²</td>
<td>0.1N HClO₄</td>
<td>1mA/cm², 20hr</td>
<td>25 ± 0.1</td>
<td>(-5 \sim -2)</td>
<td>{-8.8*}</td>
<td>138*</td>
<td>{-11.68*}</td>
</tr>
<tr>
<td></td>
<td>O. L. KABANOVA, A. N. DORONIN and L. A. SEMENIUTENKO, Elektrokhimiya, 7, 1390 (1971).</td>
<td>Rod</td>
<td>Impurity, less than ( 10^{-4}% ), treated with 0.1N HClO₄ or 0.1N HClO₄</td>
<td>Conducted</td>
<td></td>
<td></td>
<td>{ after potential jump }</td>
<td>{-11.6*}</td>
<td>120</td>
<td></td>
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<tr>
<td>V</td>
<td>I. V. KUDRYASHOV and L. A. FALIN, Elektrokhimiya, 8, 1029 (1972).</td>
<td>(100) (110)</td>
<td>Electropolished in 25% alcoholic H₂SO₄</td>
<td>0.2N H₂SO₄</td>
<td></td>
<td></td>
<td>{-6.00*}</td>
<td>196</td>
<td>1.18</td>
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<td></td>
<td></td>
<td>{-6.22*}</td>
<td>204</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>J. O'M. BOCKRIS and A. M. AZZAM, Trans. Faraday Soc., 48, 145 (1952).</td>
<td>Wire</td>
<td>Heated in ( H_2 ) at 600°C for 2~3 hr</td>
<td>5N HCl</td>
<td>1 A/cm², ( 10^6 ) coulombs</td>
<td>25</td>
<td>(-3 \sim +2)</td>
<td>{-5.0*}</td>
<td>110</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>J. O'M. BOCKRIS, I. A. AMMAR and A. K. M. S. HUQ, J. Phys. Chem., 61, 879 (1957).</td>
<td>Wire</td>
<td>Heated in vacuum at 200°C for 1 min, in ( H_2 ) at 1000°C for 2~3 min.</td>
<td>0.1N HCl</td>
<td>10 mA/cm², 60 hr</td>
<td>23 ± 2</td>
<td>{-6.11*}</td>
<td>60 ± 3</td>
<td>105 ± 13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>J. O'M. BOCKRIS and D. F. A. KOCH, J. Phys. Chem., 65, 1941 (1961).</td>
<td>Cleaning with molten NaNO₃</td>
<td>0.5N HCl</td>
<td>15 mA/cm², 20 hr</td>
<td></td>
<td></td>
<td>{-7.87 \pm 0.31*}</td>
<td>70 ± 5</td>
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<td></td>
<td>{-6.30 \pm 0.23}</td>
<td>112 ± 9</td>
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<td></td>
<td></td>
<td>{-8.34 \pm 0.27}</td>
<td>69 ± 6</td>
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<td></td>
<td></td>
<td>{-7.10 \pm 0.42}</td>
<td>101 ± 4</td>
<td></td>
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<tr>
<td>Wire</td>
<td>Cleaning with molten NaN(_2)SO(_4), heating in H(_2) at 200°C</td>
<td>1 mA/cm(^2), 15~20 hr</td>
<td>Room temp.</td>
<td>{(-6.63 \pm 0.22)} (\pm 84 \pm 6)</td>
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<td></td>
<td></td>
<td>{(-5.90 \pm 0.09)} (\pm 116 \pm 3)</td>
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<tr>
<td></td>
<td>Mech. polished, then cathodized with 30 mA/cm(^2) for 10 min</td>
<td>&quot;</td>
<td>&quot;</td>
<td>{(-6.46^*)} (\pm 65 \pm 1) (\pm 0.43 \pm 0.01)&amp;</td>
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<tr>
<td>Poly.</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>{(-6.89^*)} (\pm 61 \pm 1) (\pm 0.42 \pm 0.01)&amp;</td>
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<td>&quot;</td>
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<td>&quot;</td>
<td>{(-6.46^*)} (\pm 65 \pm 1) (\pm 0.43 \pm 0.01)&amp;</td>
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| (100) | Electrochemically polished in 2% NaOH | "                         | "               | {\(-8.27^*\)} \(\pm 75 \pm 1\) \(\pm 0.62 \pm 0.01\)& |
|       | "                                                                | "                         | "               | {\(-8.56^*\)} \(\pm 95 \pm 1\) \(\pm 0.66 \pm 0.01\)& |
| (110) | "                                                                | "                         | "               | {\(-8.29^*\)} \(\pm 70 \pm 1\) \(\pm 0.58 \pm 0.01\)& |
|       | "                                                                | "                         | "               | {\(-6.89^*\)} \(\pm 90 \pm 1\) \(\pm 0.62 \pm 0.01\)& |

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<tr>
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<td>2N H(_2)SO(_4)</td>
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<tr>
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<td>1N H(_2)SO(_4)</td>
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<tr>
<td></td>
<td>Anodic polishing</td>
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<tr>
<td>Metal</td>
<td>Form</td>
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<td>-------</td>
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<tr>
<td>Zn</td>
<td>K. Gossner, Z. phys. Chem. N.F., 36, 392 (1963).</td>
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<tr>
<td>Zr</td>
<td>V. M. Artemova, Elektrokhimiya, 3, 1219 (1967).</td>
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Rare earth metals, S. L. Morse, N. D. Greene, Electrochimica Acta, 12, 179 (1967).