Electrolytic Reduction by Electron or by Hydrogen Adatom on Pd

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Hydrogen overpotential decay transients on Pd were observed during electrolytic reduction or hydrogenation reactions in 0.5 M H_2SO_4. The overpotential component which manifests itself on the overpotential decay curve with its very slow decay rate represents activity of hydrogen adatom on the Pd surface. Its behaviour can be employed to determine whether or not the reduction of a reducible substance introduced into the system consumes the hydrogen adatom. Indications were obtained that I_2 and possibly benzoquinone were reduced by electron, whereas reduction of butynediol, butenediol, allyl alcohol, vinylacetic acid, and nitrosobenzene involved consumption of the hydrogen adatom.

1 Introduction

Several investigations have been reported in the literature concerning the question of whether electrolytic hydrogenation takes place through addition of hydrogen adatom H_ia to the substance to be reduced (electrohydrogenation^1^) or the radical mechanism^2^) or through reduction by electron followed or preceded by the addition of H^+ from the solution phase (electroreduction^3^ or the ionic mechanism^4^). This is one of the basic information in selecting electrode materials and fixing experimental conditions suitable to a desired electrolytic reduction reaction.

Stackelberg and Weber^5^ conducted the electrolytic reduction of benzoquinone etc. on a Pd foil bi-electrode in 0.1 M phosphate buffer solution of pH 6.2–6.8. They observed that e.g. 13.7% quinone was reduced on the front face of the membrane electrode at which electrolysis was conducted, while only 0.7% was reduced on the back side to which the electrolytic hydrogen was diffused. Further, no appreciable change in the reduction rate was observed when the reduction was conducted on one face of the Pd membrane electrode while hydrogen was in addition supplied from the back side by permeation. On the basis of these observations, they concluded that benzoquinone was reduced by electron.

An elaborate technique was proposed by Wagner^6^ and Takehara^7^ which employed relationships among electrode potentials of the working electrode in cells of various construction and polarization characteristics during the reduction reaction. Benzoquinone, for example, was thus concluded to be reduced by electron, while allyl alcohol by H(a).

The present work is concerned with a test of another way of distinguishing those two reaction pathways on Pd electrode through observations of overpotential decay transients in the presence and the absence of the reducible substance.

2 Principle of the Method

The Pd hydrogen electrode has been the subject of a number of investigations owing to its peculiar nature, namely a large amount of absorption of hydrogen into the bulk metal^8^ and a high catalytic activity to this reaction, probably next to Pt. Through mechanistic studies, it has been demonstrated that the hydrogen electrode reaction (HER) takes place via the Tafel-Volmer route involving hydrogen adatom H(a) as the reaction intermediate

\[
\text{H}_2 \xrightarrow{\text{Tafel}} 2 \text{H}(a), \quad \text{H}(a) + \text{H}_2\text{O} \xrightarrow{\text{Volmer}} \text{H}_3\text{O}^+ + e
\]

with roughly ten times more rapid Volmer step compared with the Tafel step^9^.

Overpotential transients as shown in Fig. 1 were observed when a Pd hydrogen electrode was polarized with a constant current, or the polarization current was terminated after the electrode has attained a steady-state polarization. We call each overpotential components as indicated in the Figure. The rapidly growing and decaying components, \( \eta_1 \) and \( \eta_1' \), have a short time constant, typically 10^-s in acidic solutions. The other components, \( \eta_2 \) and \( \eta_2' \), have a very long time constant which depends on the electrode dimension, typically 10^6 s for a Pd foil electrode of 10^-1 cm in thickness.

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It has been demonstrated in a previous work\(^\text{13}\) that the overpotential transients readily yield various kinetic information; e.g. \(\eta_1\) yields the exchange c.d. of the Volmer step, and \(\eta_1'\) and \(\eta_2'\) yield \(-\Delta g_V\) and \(-\Delta g_T\), the affinity values of the respective steps during the steady-state polarization. Further, it can be shown that the overpotential component \(\eta_1'\) is related to the activity \(a_H\) of the hydrogen adatom under the steady-state polarization prior to the termination of the current in the form\(^\text{13}\)

\[
\eta_1' = (1/F) \ln \frac{a_H}{a_H^o},
\]

where \(F = F/RT\) and subscript \(o\) indicates the quantity at equilibrium of the HER.

If electron is directly responsible to the electrolytic hydrogenation reaction, a portion of the applied current is consumed by the reduction reaction and the rest of the current is used by the HER. The overpotential \(\eta\) as well as \(\eta_1'\) will decrease correspondingly, but relative magnitude of the component overpotentials \(m = 2\eta_1/\eta_1' = \Delta g_T/\Delta g_V\)\(^\text{13}\) will not change appreciably unless existence of the reducible substance and the reduced products affects the relative rates of the constituent elementary steps.

Conversely, if \(H(a)\) is reponsible to the hydrogenation reaction, the consumption of \(H(a)\) by the reaction will lead to a decrease of \(\eta_1'\) in accordance with lowered \(a_H\) in eqn. (1), but \(\eta_1'\) will not change much as it is practically independent of \(a_H\)\(^\text{13}\). Hence, introduction of such a Pd of reducible substance should lead to a significant decrease of \(m\). Comparison of values of \(m\) observed in the presence and the absence of the reducible substance in the system therefore yields an indication to discriminate those two pathways.

### 3 Experimental

A Pd foil electrode \((10^{-3} \times 0.2 \times 5 \text{ cm}^3)\) was used in \(0.5 \text{ M} \text{ H}_2\text{SO}_4\), which was always employed as a supporting electrolyte. All the experiments were conducted under \(\text{H}_2\) atmosphere. Reagent grade chemicals were used without further purification. No chemical analysis of the reduction product was conducted except for the case of allyl alcohol reduction\(^\text{13}\). A probable reduction product in each system was usually added to the solution in the control experiment in order to avoid complexities due to changes in electrocatalytic activity of the electrode caused by the reduction product, which may give rise to variations of \(\eta_1\) and \(\eta_2\) simultaneously with the variations due to the reduction reaction.

A constant current was applied to the electrode for a sufficient time ranging from \(10^1\) to \(10^4\) s until a steady overpotential was reached. The overpotential decay transient observations were conducted during a short time current interruption by means of a switch circuit controlled by a pulse generator (YHP 8003 A) and a transient recorder (Biomation 8100 with a preamplifier) with the time window ranging from \(2 \times 10^{-1}\) to \(10^2\) s.

The control experiment was carried out first, which was followed by the electrolytic reduction experiment with a reducible substance added into the system. Observation were repeated in some occasions after raising the concentration of the reducible substance.

That the electrolytic reduction reaction was indeed taking place in each system was readily judged by observation of a shift of the open-circuit electrode potential, \(E_{oc}\), to significantly a

\(^{13}\) It has been reported\(^\text{13}\) that electrolytic reduction of allyl alcohol on Pt yields propene and propane. As the electrolytic reduction of propanol was not likely to take place, this was considered as an indication of the scission of the C-OH bond at the first stage while the allyl group was present, followed by hydrogenation of the product propene. In contrast with this, during the electrolytic reduction of allyl alcohol in this experiment on Pd, propanol was only the product detected other than \(\text{H}_2\), and no hydrocarbons beyond trace amounts were detected.
Table 1  The open-circuit potential, $E_{oc}$, of a Pd foil electrode under hydrogen atmosphere in solutions containing a reducible substance at 30°C (The background solution is 0.5 M H$_2$SO$_4$)

<table>
<thead>
<tr>
<th>Solution composition</th>
<th>$E_{oc}$/mV (RHE)</th>
<th>Solution composition</th>
<th>$E_{oc}$/mV (RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06 M KI + ca. 0.01 M I$_2$</td>
<td>530-590</td>
<td>0.1 M vinylacetic acid</td>
<td>~49</td>
</tr>
<tr>
<td>0.1 M 2-butyne-1,4-diol</td>
<td>42~47</td>
<td>0.05 M aniline</td>
<td>530-55*1</td>
</tr>
<tr>
<td>+0.1 M I$_2$ 1,4-butanediol</td>
<td></td>
<td>+0.05 M nitrosobenzene</td>
<td></td>
</tr>
<tr>
<td>0.05 M cis-2-buten-1,4-diol</td>
<td>~23</td>
<td>0.05 M succinic acid</td>
<td>~4</td>
</tr>
<tr>
<td>+0.05 M 1,4-butanediol</td>
<td></td>
<td>+0.05 M maleic acid</td>
<td></td>
</tr>
<tr>
<td>0.06 M allyl alcohol</td>
<td>~19</td>
<td>0.05 M succinic acid</td>
<td>2.3</td>
</tr>
</tbody>
</table>

*1 The larger value was observed soon after the introduction of the nitrosobenzene to the solution. The value was decayed to the smaller value after an overnight standing.

positive value on RHE scale after the addition of the substance under investigation. The $E_{oc}$ values observed are listed in Table 1. No further measurements were conducted on maleic and fumaric acid as $E_{oc}$ values were so small that the reduction rates were judged very low.

4 Results and Discussion

(1) Reduction by electron

In order to verify the concept underlying the present technique, the reduction of I$_2$ to I$^-$ was conducted first, as there would be no doubt that this is reduced by electron$^{15}$. The polarization curves obtained are shown in Fig. 2. Both $\eta$ and $\eta'_1$ were lowered by the addition of I$_2$ to the solution (which already contained I$^-$), but their variations were almost in a parallel manner. The behaviours may be explained in terms of consumption of a greater portion of the applied current by the reduction of I$_2$ and the rest of the current was used by the HER which would be taking place independently of the reduction reaction. The plot of $m$ against $\eta$ is shown in Fig. 3 (A). It is clear that $m$ is practically

![Dependence of m upon overpotential during electrolytic reduction reaction on Pd: The case of reduction by electron Pd foil (10$^{-3}$×0.2×5 cm), 30°C. Open symbols are for the control experiment and closed symbols for the electrolytic reduction reaction. (A) I$_2$ (10$^{-2}$ M/l), (B) benzoquinone (1.5 × 10$^{-2}$ M/l).](image)
unaffected by the presence of $I_1$. It may hence be concluded that the reduction proceeds by means of electron, as in fact is expected for this reaction.\(^{11}\)

Figure 3 (B) show the result in the case of reduction of benzoquinone which is reduced by electron according to previous researchers.\(^{12,13}\) In this case too, variation of $m$ by the presence of the reduction reaction was not noticeable and hence reduction by electron was indicated.\(^{12}\)

(2) Reduction by hydrogen adatom

Figure 4 shows overpotential decay transients with various values of the full-scale time, $t_{FS}$, during the butynediol reduction at low overpotential, −3.6 mV in this example. As seen, $\eta_1'$ was positive (+7.6 mV) which indicated that $a_H$ was lower than $a_{H,O}$ in spite of the net cathodic HER as indicated by the negative value of $\eta$. This fact indicated that $H(a)$ was consumed by reduction reaction.

It can be shown\(^{14}\) that the initial slope of the decay transient at the moment of interruption of the polarization current, $(d\eta/dt)_{\delta}$, is related to the effective exchange c.d., $i_{OV}$, of the charge transfer Volmer step under the steady-state polarization condition

$$i_{OV} = C \left( \frac{d\eta}{dt} \right)_{\delta} \left[ e^{-(\gamma - \eta_1')/RT} - e^{\delta \gamma - \delta \eta_1'} \right]$$

(2)

where $C$ is the double layer capacitance obtainable from the initial slope of the build-up transients. Accordingly, under the condition $- (\gamma - \eta_1') = -\eta_1' \gg RT/F$, we have

$$\log C (d\eta/dt)_{\delta} = \log i_{OV} (1 - \beta) f_{\eta_1'}/2.303$$

(3)

This plot for the butynediol reduction is shown in Fig. 5 (A). Curve I was obtained in the solution of 0.5 M H$_2$SO$_4$ + 0.1 M 1,4-butanediol, whereas curve 2 and 3 were obtained respectively, in the solution after a further addition of 0.11 and 0.4 M 2-butyne-1,4-diol. The shifts of the curves from the control experiment were

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Partially visible text continues:

Fig. 4 Overpotential decay transients on Pd during electrolytic reduction of 2-butynediol at low overpotentials Pd foil (10××0.2××5 cm), 30°C, 0.5 M H$_2$SO$_4$ + 0.1 M 1,4-butanediol + 0.4 M butylnediol, $i = -0.305$ mA cm$^{-2}$, $\eta = -3.6$ mV, $\eta_1' = +7.6$ mV

Decay curves were obtained with various time windows indicated by full-scale time, $t_{FS}$, ranging from $2 \times 10^{-4}$ to 50 s.

Fig. 5 Overpotential decay rates during electrolytic reduction of 2-butynediol on Pd Pd foil (10××0.2××5 cm), 30°C curve 1, 0.5 M H$_2$SO$_4$ + 0.1 M 1,4-butanediol: curve 2, after addition of 0.11 M or curve 3, 0.4 M butylnediol (A) Dependence of the initial overpotential decay rate upon the overpotential component $\eta_1'$. Plot of eqn. (3) (B) Dependence of the overpotential decay rate at the moment $\eta_1'$ is reached upon the overpotential component $\eta_1'$

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\(^{11}\) A possibility of reduction by $H(a)$ was not entirely excluded in this case because of observation of a positive value of $\eta_1'$ under negative $\eta$ in a low overpotential region, similar to Fig. 4 below.
not significant within the experimental error indicating that the presence of the butynediol did not contribute to the charge transfer reaction rate.

In contrast with this, the "initial" overpotential decay slope just after the moment the overpotential reached \( \eta_i' \), \( (d\eta/dt)_{\eta_i'} \), which indicates the initial rate of the H(a) removal reaction, was systematically dependent on the butynediol concentration, as seen in Fig. 5 (B). If HER is only the responsible process, the slope is determined by the rate of removal of hydrogen from the Pd electrode by the Tafel step. Based on the kinetics of the Tafel process and the absorption isotherm of hydrogen in Pd, we can derive the relation (4)

\[
\ln \frac{1-\exp(2f\eta_i')}{1-\exp(2f\eta)} = kt \quad (-\eta < -\eta_i') \quad (4)
\]

where \( k \) is a constant involving the exchange c.d. of the Tafel step, dimension of the Pd foil, parameters of the absorption isotherm, etc. At the initial stage where \(-\Delta \eta = (\eta_i' - \eta) \ll 1/f\), we find from eqn. (4)

\[
\Delta \eta = -\frac{kt}{2f} \exp(-2f\eta_i') \quad (-\Delta \eta \ll 1/f)
\]

The initial decay rate at \( \eta \approx \eta_i' \) is therefore given as,

\[
-(\frac{d\Delta \eta}{dt})_{\eta_2} = -(\frac{d\eta}{dt})_{\eta_2} = (\frac{d\eta}{dt})_{\eta_1} = (\frac{k}{2f}) \exp(-2f\eta_i')
\]

Fig. 6  Dependence of \( m \) upon overpotential during electrolytic reduction reaction on Pd : The case of reduction by hydrogen adatom, Pd foil (10^{-2}x0.2x5 cm), 30°C
(A) Butynediol : curve 1, 0.5 M H₂SO₄ + 0.1 M 1,4-butanediol; curve 2, after addition of 0.11 M or curve 3, 0.4 M 2-butyne-1,4-diol
(B) Butynediol : curve 1, 0.5 M H₂SO₄ + 0.05 M 1,4-butanediol; curve 2, after addition of 0.05 M or curve 3, 0.25 M cis-2-butene-1,4-diol
(C) Allyl alcohol : curve 1, 0.5 M H₂SO₄; curve 2, after addition of 0.08 M or curve 3, 0.5 M allyl alcohol
(D) Vinylacetic acid : curve 1, 0.5 M H₂SO₄; 2, after addition of 0.1 M vinylacetic acid
(E) Nitrosobenzene : curve 1, 0.5 M H₂SO₄ + 0.05 M aniline; curve 2, after addition of 0.05 M nitrosobenzene, curve 3, after an overnight standing
This gives the dependence of the initial decay rate upon the value of $\gamma \gamma$ at which the rate was observed. Accordingly, we obtain
\[
\frac{d \log (\gamma)}{dt} = \frac{2f}{2.303}
\]
which gives the slope of (30 mV)$^{-1}$ in the plot of Fig. 5(B). This was what actually observed in this work, as seen in the Figure, dotted line.

During the electrolytic reduction, the removal rate would be increased and also the effective reaction order with respect to hydrogen adatom activity which was 2 for the HER as indicated in eqn.(4) would be reduced. As seen in Fig. 5(B), the slope corresponding to eqn. (6) was indeed lowered during the electrolytic reduction of butynediol down to approximately (45 mV)$^{-1}$ or the reaction order of 1.3. This clearly indicates that the butynediol reduction reaction consumes H(a).

In the same context, the reduction was accompanied with a significant variation of $m$, as shown in Fig. 6 (A), and the variation was magnified with the increased concentration of the butynediol.

Analogous results were obtained in the reduction reactions of butynediol$^{19}$, allyl alcohol$^{19}$, vinylic acid$^{19}$, and nitrosobenzene$^{19}$, as shown in Fig. 6 (B)-(E). In the case of nitrosobenzene, the $m$ vs. $\gamma$ relation obtained after an overnight standing of the system after the addition of the substance, curve 3 in Fig. 6 (E), was less separated from the control curve as compared with the case observed at soon after the addition (curve 2). This was probably due to a decreased rate of the reduction reaction caused by masking of the electrode surface with black deposits which became visible after hours of standing.

Based on a significant variation of $m$ commonly observed in these cases, one may conclude that reduction of these substances is effected by H(a). This conclusion was in agreement with those reported in the literature cited above, except for nitrosobenzene.

The cause of the disagreement for nitrosobenzene is not well understood. This might be due to different experimental condition such as (1) difference in the solution composition, 0.5 M H$_2$SO$_4$ in this work vs. 0.1 M phosphate buffer solution of pH 6.8 in the work of Stackelberg and Weber$^{19}$ and (2) presence of 20% alcohol and a saturated amount of As$_2$O$_3$ in their work. It may also be possible that the reduction involves H(a) but that reduction route shares only a minor portion of the total reduction reaction as indicated by their work.

5 Conclusion

Simple observations of overpotential decay transients on Pd readily yield information on whether the electron or the hydrogen adatom is responsible to the electrolytic reduction reaction. It was seen that both the reaction pathways were possible on Pd, depending on the nature of the substance to be reduced. Thus, choice of the pathway is not solely determined by the electrode material. Conclusions here obtained with several reducible substances are in satisfactory agreement with those in the literature. In general, it appeared likely that substances which involve ionized form at the functional group in question before or after the reduction reaction are reduced by electron, and those which are not, such as C-C double bond, are reduced chemically by H(a).

The agreement supports further the general analysis of the overpotential transients on Pd hydrogen electrode and the reaction mechanism derived. It was reported earlier$^{19}$ that the step rates of the Tafel–Volmer reaction route may be individually controlled to some extent by addition of a properly chosen catalytic “poison” to the system. This suggests that by selecting a suitable additive, one might be able to control the reaction in a way to meet the particular aim of the reaction. It is hoped that in the case of reduction of a substance which involves more than one kind of the reducible functional groups, the above concept may open a way to control the selectivity of the reduction reaction.

Acknowledgement:

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References:

生物・医用電気化学関連文献紹介（18）
補酵素ニコチンアミドアデニンジヌクレオチド（NAD⁺）の電解還元生成物をクロマトグラフィーで分離同定。Hg 電極で -1.1 V vs. SCE の定電位還元を行なうと、1 電子還元が進み、さらに 2 電子が生成する（90%）。この 2 電子量は、90%が 4、16' 結合、10%が 1.6' 結合である。-1.8 V vs. SCE の定電位還元では、2 電子還元が進み、50%が 1.4 - NADH、30%が 1.6 - NADH、20%が 2 電子である。酵素的に活性な 1,4 - NADH の収率は pH の減少にもとない増大している。

スルホン化ステレン、テトラクリルオキシプロピルトリメトキシシラン共重合体の架橋化ポリアニオン膜を白金電極表面に形成し、Ru(NH₃)₅²⁺, Cr(bpy)₃²⁺、メチルビロログリーンを静電的に包埋化している。この膜は非常に安定に電極表面に着着している。膜と液相とのチオ酸の分配係数（Kₐ）は、Ru(NH₃)₅²⁺ で 2400, MV²⁺ で 100 であった。この高分子膜中におけるチオ酸を表層、さらにポリビリフェロセン膜を重層した 2 層膜をつくり、その特性を明らかにしている。

（筑波大学物質工学系 相澤益男）

半導体・積層回路技術シンポジウム 演講論文集 <第 3 集>
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☆本シンポジウムは、毎年春秋を 2 回、関連学会協の協賛を得て、材料・プロセス・デバイス・評価と広範囲に亘り、貴重な発表と活発な討論を重ねて、研究者・技術者諸氏のテクノロジーの相互理解を図ってきた。

将来の技術革新は、今日までの長い間の技術の蓄積によるところ大であり、本シンポジウムのこれまでの講演論文をまとめ第 1 回から 10 回までのものを「第 1 集」、さらに第 11 回から 15 回までのものを「第 3 集」にまとめたものである。これらの「第 3 集」は、1979 年 5 月から第 20 回（1981 年 5 月）までの内容をまとめたものであり、その内容については、技術的に考察しやすいように分類・再編集して刊行することになった。本講演論文集、今後この分野の研究、開発・生産を志す人々にとっても、またそれぞれの専門分野に携わっている人々にとっても参考になれば幸いである。なお、各集とも部数が限定されておりますので早急にお申し込み下さい。

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☆第 1 集（2 冊付） 第 1 回（1971 年 10 月）～第 10 回（1976 年 5 月）の分

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