Transient Behavior in Electroreductions of Ethylene and Acetylene on Pt in H₂SO₄ Solution

Takeshi MASUI* and Hideaki KITA**

Transients under potentiostatic electroreductions of ethylene and acetylene show significantly different behavior. Reduction current of ethylene increases gradually with time to a steady value, whereas that of acetylene decreases via a maximum. Analysis of their pressure and potential dependences leads to the conclusion that the reductions of ethylene and acetylene are controlled respectively by the surface combination of adsorbed species from ethylene and adsorbed hydrogen atom, and by the surface diffusion of adsorbed hydrogen atom to adsorbed species of acetylene. Open circuit potential measurements under the contact of the electrode prepolarized at 0 V with ethylene and acetylene show that among three kinds of the adsorbed hydrogen atoms on Pt the secondly stable one takes part in the reactions while the most stable one is inactive.

1 Introduction

During the last decade, many articles have been reported on the electrocatalytic reductions of ethylene and acetylene on a platinum electrode. They treat mainly the kinetics at a steady state.

In the case of ethylene, Byrne and Kuhn¹⁾ concluded that overall rate of the electroreduction was controlled by the first addition of adsorbed hydrogen atom; $C_2H_4(ads) + H(ads) \rightarrow C_2H_5(ads)$. On the other hand, one of the present authors (H.K.) and his coworkers²⁻⁶⁾ have concluded that the second addition of adsorbed hydrogen atom is rate determining; $C_2H_5(ads) + H(ads) \rightarrow C_2H_6(sol)$. Isotopic study shows furthermore that the rapid first addition step proceeds via two pathways with significantly different rates⁶⁾. Langer *et al.*⁷⁾ carried out the isotopic study in the electrogenerative hydrogenation of ethylene in $DClO_4 + D_2O$ solution using a Pt fuel-cell electrode but no detailed mechanistic analysis on the D-atom distribution was attempted. Recently, Hubbard *et al.*⁸⁾ also suggested two parallel pathways from the studies on single crystal and polycrystalline Pt electrodes; One is $C_2H_4(ads) + 2H^+ + 2e^- \rightarrow C_2H_6(sol)$ and the other is $C_2H_4(sol) + 2H(ads) \rightarrow C_2H_6(sol)$. Their parallel pathway model, however, seems to require more detailed kinetic observations to be confirmed, though the surface state

is examined intensively by a modern technique.

The reduction of acetylene has been studied by Burke *et al.*⁹⁾ on palladized palladium and platinized platinum electrodes in aqueous HCl and NaOH solutions. They have reported non-stationary behavior that the reduction is initially rapid but becomes slow with time and concluded the greater tendency of acetylene to form strongly adsorbed species than that of ethylene. Byrne *et al.*¹⁰⁾ have indicated from kinetic parameters obtained in H₂SO₄ solution that the rate-determining step is in combinations of strongly adsorbed species of acetylene with adsorbed hydrogen.

The aim of the present work is to obtain a deeper insight into reaction mechanisms by observing the transient phenomena and to compare the reduction mechanism of ethylene with that of acetylene.

2 Experimental

An apparatus used was a closed circulation system which included a three compartment Pyrex cell. Test electrode was a platinized platinum foil (apparent surface area, 4.0 cm²). The electrode was first subjected to several triangular potential pulses to monitor an initial surface state, polarized at 1.6 V for 2 min to oxidize the surface and then at 1.2 V for 3 min to remove an evolved oxygen by He bubbling. Solution was 0.5 M H₂SO₄ saturated with He. This pretreatment was followed by a constant polarization at a desired potential ϕ , where reaction gas (ethylene or acetylene + He, 1 atm)

* AISIN SEIKI Co., LTD (Kariya 448)

** Department of Chemistry, Faculty of Science, Hokkaido University (Sapporo 060)

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Fig. 1 Potential program for the pretreatment and the following polarization

was introduced 2 min later (Fig. 1). Current-time curves ($i-t$ curves) during the reactions were observed as a function of ϕ at various ethylene and acetylene pressures.

Other details have been described elsewhere²⁾. All experiments were carried out at room temperature. Potentials were referred to the reversible hydrogen electrode (rhe).

3 Results and Discussion

3.1 Open circuit potential

We first examined open circuit potential of the electrode which was brought into contact with ethylene or acetylene. Open circuit potential (ϕ_{OC}) provides a useful information on the surface state during reaction, especially on the reactivity of various types of adsorbed hydrogen atoms present on the electrode surface.

Figure 2 shows a time dependence of ϕ_{OC} of the electrode aged in advance in the He-saturated solution at 0 V after the pretreatment.

Fig. 2 Time variation of the open circuit potential, ϕ_{OC} , at $P_E(\bigcirc)=P_A(\bullet)=112$ mmHg after the aging at 0 V

In the case of ethylene (pressure of ethylene, $P_E=112$ mmHg), ϕ_{OC} of the 0 V-aged electrode rises gradually up to 220 mV and stays constant. This means that ethylene consumes upon its contact with the electrode a part of the adsorbed hydrogen atoms which exist initially at a full coverage. The presence of different adsorption states of hydrogen atoms is well known on a platinum electrode in acidic solution as shown by a cyclic voltammogram ($i-\phi$ curve). Main two peaks in the $i-\phi$ curve (0.5 M H_2SO_4) appear at 144 ± 5 and 288 ± 5 mV¹¹⁾. The present result shows that the adsorbed hydrogen atoms which ionize at $\phi < 220$ mV react rapidly with ethylene but not the adsorbed hydrogen atoms which ionize at $\phi_{OC} > 220$ mV. This statement is based on our previous conclusion that ϕ_{OC} under the reduction of ethylene is determined by $H^+ + e^- \rightleftharpoons H(ads)^{2)}$.

In the case of acetylene (pressure of acetylene, $P_A=112$ mmHg), ϕ_{OC} of the 0 V-aged electrode rapidly rises up to 210 mV and then gradually fall down to 160 mV.

From these results, the most stable hydrogen atom which has an ionization peak at ca. 0.29 V in $i-\phi$ curve is concluded to be inactive in the hydrogenations of ethylene and acetylene. This is also the case in the hydrogenation of 1,3-butadiene¹²⁾.

3.2 Time variation of the reduction current

Next, we observed the current change during potentiostatic polarization ($\phi=0.05 \sim 0.3$ V).

Figure 3 shows typical transient phenomena

Fig. 3 Transient phenomena of the reduction currents of ethylene ($\bigcirc$) and acetylene ($\bullet$) at $P_E=P_A=112$ mmHg under various potentiostatic conditions

of the reduction currents of ethylene and acetylene ($P_E = P_A = 112 \text{ mmHg}$) at the pretreated platinum electrode. As shown in Fig. 1, the reaction gas was introduced two minutes after the potential was set at a final, desired value. Transients of ethylene ($-\circ-$) are significantly different from those of acetylene ($-\bullet-$). Namely, in the former case the reduction current except during the very initial part increases gradually and then attains a steady value, whereas in the latter case it decreases via a maximum.

(1) *Anodic current in the very initial region*

Anodic current peak is observed at potentials more positive than 0.15 and 0.1 V in the ethylene and acetylene reductions, respectively. At these positive potentials, there exist only few of the secondly stable adsorbed hydrogen. The anodic current will be due to a dissociative adsorption of the reactants on vacant sites, releasing their hydrogen atoms which ionize at a given potential or/and an anodic displacement⁽¹³⁾ at occupied sites by the most stable adsorbed hydrogen. Dissociative adsorption of ethylene has been concluded by Gilman⁽¹⁴⁾.

Anodic current for acetylene larger than that for ethylene, as exemplified by the curves at 0.20 V in Fig. 3, will be attributed to a faster diffusion rate of acetylene in solution as expected from ten times larger solubility⁽¹⁵⁾ and two times larger diffusion constant⁽¹⁶⁾ of acetylene than those of ethylene.

(2) *Rising part of the reduction currents*

At potentials more positive than 0.15 or 0.1 V, a reduction current follows the anodic peak whereas at potentials more negative than 0.15 or 0.10 V, a reduction current rises from the beginning without the anodic peak. Current rise is much faster in acetylene in accordance with the faster diffusion rate. The reduction current of ethylene reaches a steady value in a monotonous manner but that of acetylene decreases via a maximum. In the following paragraph, this decreasing current is examined in detail.

(3) *Decrease in the acetylene reduction current*

The decrease via maximum clearly shows an occurrence of a retarding process. To clarify the process, the decreasing current is plotted against $t^{-1/2}$ in Fig. 4. Linear relations hold

Fig. 4 Plots of the reduction currents of acetylene ($P_A = 112 \text{ mmHg}$) against $t^{-1/2}$ at different potentials

between these two quantities. Thus, some diffusion process is suggested to be concerned with the decrease of the reduction current. The linear relations at $\phi \geq 0.1 \text{ V}$ apparently tend to meet at the origin but that of $\phi = 0.05 \text{ V}$ deviates considerably from the origin. This deviation represents the current at $t = \infty$; i. e., a current at steady state. Now, the slope of the linear relations is plotted against the potential in Fig. 5. It decreases with the increase

Fig. 5 Slope of the linear relation between i and $t^{-1/2}$ as a function of potential. Dotted curve was obtained from eq. (1)

$$P_A = 112 \text{ mmHg}$$

of ϕ in a S-shape. The present result, the linear relation between i and $t^{-1/2}$, is similar to the transient observed for methanol oxidation on Pt electrode by Hampson *et al.*⁽¹⁷⁾. However, there is no linear relation between the potential and $\log(di/dt^{-1/2})$ as in the methanol oxidation.

The dotted curve in the figure is the calculated one so as to reproduce the data by the following equation

$$\text{slope} = \frac{A}{B + e^{F\phi/RT}}, \quad (1)$$

where A and B are selected as $2.58 \times 10^3 \text{ mA cm}^{-2} \text{ s}^{1/2}$ and 180, respectively. Equation (1) is a typical equation for isotherm of the species which is formed by an electron transfer such as

$$X^- + e^- \rightleftharpoons X(\text{ads}). \quad (2)$$

Hence, one can assume that some species formed by rapid step (2) takes part in the retarding process. The transients of the acetylene reduction current are formulated as follows,

$$i = t^{-1/2} \cdot \frac{A}{B + e^{F\phi/RT}}. \quad (3)$$

When the potential is less than 0.05 V, a second term for the steady current is added. To clarify the retarding process in more detail, effect of pressure was examined.

3.3 Time variation of the reduction current as a function of pressure

The time variation was observed as a function of P_E and P_A ($\phi = \text{const}$). The pressure effect on i - t curves is also found to be entirely different in both the cases; *i. e.*, a positive effect in ethylene whereas a negative effect in acetylene.

(1) Ethylene reduction current

The transients themselves are essentially the same as those of Fig. 3. The current increases with the ethylene pressure. We analyse here the steady current. The plot of the reciprocal of the steady currents against the reciprocal of P_E gives a straight line (Fig. 6), *i. e.*,

Fig. 6 The Langmuir plot of the steady reduction current of ethylene ($\phi = 0.1 \text{ V}$)

$$\frac{1}{i} = \frac{a}{P_E} + b, \quad (4)$$

where a and b are constants and given from the figure as $a = 52.4 \text{ cm}^2 \text{ mmHg/mA}$ and $b = 0.13 \text{ cm}^2/\text{mA}$. When the reduction current is assumed to be proportional to the surface coverage of ethylene (θ_E), $i = c \cdot \theta_E$, eq. (4) gives the following relation;

$$\theta_E = \frac{P_E}{(a + b \cdot P_E)c}, \quad (5)$$

where c is a constant. Equation (5) shows that ethylene adsorbs on a platinum electrode according to the Langmuir isotherm with an adsorption coefficient of $b/a = 2.4 \times 10^{-3} \text{ mmHg}^{-1}$.

(2) Acetylene reduction current

Figure 7 shows the transients of the acetylene

Fig. 7 Transient phenomena of the reduction currents of acetylene at various pressures ($\phi = 0.1 \text{ V}$)

Fig. 8 Plots of the reduction currents of acetylene against $t^{-1/2}$ at different pressures ($\phi = 0.1 \text{ V}$)

reduction current at various pressures ($\phi=0.1V$). The current decrease is enhanced with the increase of acetylene pressure. However, the linear relation between i and $t^{-1/2}$ holds as shown in Fig. 8. The slope depends on P_A and is expressed as follows,

$$\text{slope (mA } t^{1/2}\text{cm}^{-2}) = 6.4 P_A^{-0.34}. \quad (6)$$

Hence, eq. (3) becomes

$$i = \text{const} \cdot t^{-1/2} \cdot \frac{A}{B + e^{F\phi/RT}} \cdot P_A^{-0.34}. \quad (7)$$

3.4 A model for the surface process

(1) Diffusion in solution

We first examine a diffusion rate of the reactants to the electrode surface. The diffusion rate of ethylene through solution at 112 mmHg is estimated as 1.8 mA for unit apparent surface area from $i_D(\text{mAcm}^{-2}) = 0.16 \cdot P_E(\text{cmHg})$ observed on a smooth platinum electrode in 1M HClO_4 ⁵⁾. Though this value depends sensitively on the stirring rate of solution, we assume 1.8 mAcm^{-2} for the limiting diffusion current of ethylene and calculated the time required for the diffusion of a monolayer amount of ethylene. This time is estimated as $2F \cdot (1000 \cdot 10^{15} / 2.5 \cdot N_A) / 1.8 \cdot 10^{-3} = 1$ min, provided that a roughness factor of the electrode is 1000 and that each ethylene molecule occupies 2.5 platinum atoms on the surface³⁾. In Fig. 3, the transients of ethylene cease within 5 to 10 minutes. Hence, it is possible that the diffusion of ethylene in solution affects partly the transients.

In the case of acetylene, the time required for the diffusion of a monolayer amount is expected much less (few seconds) because of its larger solubility and diffusion constant. Therefore, the transients after the maximum should be understood from an entirely different view.

(2) Surface process of ethylene reduction

Plot of the current against $\sqrt{t}$ does not give a simple linear relation, showing that the transients are also affected by the surface process. Any further analysis was not attempted because of a complex nature of the transients.

At a steady state, the adsorption of ethylene is taken to be in equilibrium as shown by eq. (5). This fact is in agreement with the fol-

lowing mechanism, since step IV is concluded to be rate determining⁵⁾. In the mechanism, $\text{C}_2\text{H}_4(\text{s})$ denotes the ethylene molecule near the surface. Rapid occurrence of steps I and II leads to the adsorption equilibrium.

(3) Surface process of acetylene reduction

Equation (7) is commented as follows. The first factor of $t^{-1/2}$ clearly suggests that a diffusion process is concerned. As discussed earlier, the process is not the diffusion through solution.

Most likely is a surface diffusion of a certain species. This species decreases with time from an initial value.

As seen from the second factor of eq. (7), this diffusing species must be in equilibrium with respect to a charge transfer step of eq. (2). The second factor will give the initial value of the diffusing species. On the other hand, the third factor, *i. e.*, the negative effect of acetylene pressure excludes the possibility that the diffusing species arises from acetylene. Thus, the diffusion of the adsorbed hydrogen to a reacting site will be taken as the most plausible process. We have previously concluded that $\text{H}^+ + \text{e}^- \rightarrow \text{H}(\text{ads})$ is always in equilibrium during the reduction of olefins on a platinum electrode^{5,12)}. The negative effect of acetylene pressure will be understood by a blocking effect of acetylene caused by its strong adsorption on the hydrogen sites.

In connection with the present work, a further quantitative analysis for the adsorption of the respective reactants and the kinetics at a steady state of the acetylene electroreduction are now under investigation.

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References:

- 1) M. Byrne and A.T. Kuhn, *J. Chem. Soc., Faraday I*, **68**, 355 (1972); **68**, 1898 (1972).
- 2) K. Fujikawa, H. Kita and K. Miyahara, *J. Chem. Soc., Faraday I*, **69**, 481 (1973).
- 3) K. Fujikawa, A. Katayama and H. Kita, *J. Chem. Soc., Faraday I*, **70**, 1 (1974).
- 4) K. Fujikawa, H. Kita, K. Miyahara and S. Sato, *J. Chem. Soc., Faraday I*, **71**, 1573 (1975).
- 5) K. Fujikawa and H. Kita, *J. Chem. Soc., Faraday I*, **75**, 2638 (1979).
- 6) K. Fujikawa, H. Kita and S. Sato, *J. Chem. Soc., Faraday Trans., I*, **77**, 3055 (1981).
- 7) S.H. Langer, I. Feiz and C.P. Quinn, *J. Am.*

- Chem. Soc.*, **93**, 1092 (1971).
- 8) A.T. Hubbard, M.A. Young and J.A. Schoeffel, *J. Electroanal. Chem.*, **114**, 273 (1980).
 - 9) L.D. Burke, F.A. Lewis and C. Kemball, *Trans. Faraday Soc.*, **60**, 919 (1964).
 - 10) M. Byrne, A.T. Kuhn and V.J. Whittle, *J. Chem. Soc., Faraday I*, **69**, 787 (1973).
 - 11) M. Nakamura and H. Kita, *J. Electroanal. Chem.*, **68**, 49 (1976).
 - 12) K. Shimazu and H. Kita, *Electrochim. Acta*, **24**, 1085 (1979).

- 13) W.E. Triaca, T. Rabockai and A.T. Arvia, *J. Electrochem. Soc.*, **126**, 218 (1979); **127**, 827 (1980).
- 14) S. Gilman, *Trans. Faraday Soc.*, **62**, 466, 481 (1966).
- 15) Handbook of Chemistry, ed. E. Large, McGraw-Hill, N.Y., (1967).
- 16) A.A. Unver and D.M. Himmelbrau, *J. Chem. Eng. Data*, **9**, 428 (1964).
- 17) N.A. Hampson and M.J. Willars, *J. Chem. Soc., Faraday I*, **75**, 2535 (1979).

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会員のページ

導電性高分子膜ポリピロールを被膜した電極

最近話題となっている導電性高分子の中の一つポリピロールは、ほうふつ化テトラ-*n*-アルキルアンモニウムとピロールを含むアセトニトリル溶液中での電解酸化重合から容易に白金などの金属表面へ被膜としてつけることができる。この膜は空气中 250°C でも安定で、導電率は $10 \sim 100 (\Omega \text{ cm})^{-1}$ 、構造式は と報告されている。被膜の生成には純粋なアセトニトリル溶液中よりも 1% の水を含むアセトニトリル溶液中の方が密着力、均一電着性が優れているとの報告があるが、水の影響の理由は不明である。

ポリピロール膜のおもな研究目的は何んと言っても半導体の光電極の溶解を抑えることである。バンドギャップが小さい *n* 型半導体, Si, GaAs, CdSe, CdS にポリピロール被覆が試みられている。たとえば、裸の *n*-Si は 1~2 回の scan で光電流はゼロになるのにくらべ、表面に 1200 Å のポリピロール膜を被覆した *n*-Si は 0.15 M FeSO₄, 0.15 M FeNH₄(SO₄)₂·12H₂O, 0.1 M Na₂SO₄ 水溶液 (pH 1) 中、50 mV·s⁻¹ で 50 回 scan をしても光電流に僅かの変化があるだけで報告されている。一方ポリピロール被覆 *n*-GaAs/Fe(CN)₆^{3-/4-}/Pt の光電池での短絡光電流は約 39% 減少するが、100 mV·s⁻¹ で 50 cycle をしても被膜に大きな影響はなく 10.5% のエネルギー変換効率が達成されている。しかしこれら *n* 型半導体に被覆したポリピロールは水溶液中で容易にはげるのが欠点でこの現象を抑えるためのくふうもおこなわれている。すなわち *n*-Si 上に 5 Å の白金被膜を真空蒸着し、その上にポリピロールを 100~250 単分子層被覆させた *n*-Si/Pt/ポリピロール電極は I₃⁻/I⁻ 中、約 9 mA·cm⁻² で 6 日間連続作動してもはがれないが、白金被膜なしの *n*-Si/ポリピロール電極では数分以内にはがれてしまうと報告されている。白金以外にも金を *n*-Si 上に

10~20 Å 電気メッキしたあとポリピロールを被覆した例もある。最近 *n*-Si 上に (RO)₃Si グループ、たとえば

N-(3-trimethoxysilyl-propyl)pyrrole ( )

を用いて、これを半導体表面の -OH を錨として共有させ、Si 表面をポリピロール被覆した電極 (式 1 参照) が報告されている。この *n*-Si / / ポリピロール電極を用いると Fe³⁺/Fe²⁺ 中、-0.41 V (SCE) で 7.6 mA·cm⁻² の光電流が 25 時間も続いたが、共有させないポリピロール *n*-Si 電極では 8 時間以内に光電流が 6.5 mA·cm⁻² から 1.8 mA·cm⁻² に減少するとの報告もあり、ポリピロール被覆への化学修飾が効果的に作用していることを示している。ポリピロールに関する 1982 年に報告されたおもな文献を以下に示す。

- 1) R.A. Bull, F-R.F. Fan, A.J. Bard, *J. Electrochem. Soc.*, **129**, 1009 (1982).
- 2) J. Prejza, I. Lundström, T. Skotheim, *ibid.*, **129**, 1685 (1982).
- 3) T. Skotheim, L-G. Petersson, O. Inganäs, I. Lundström, *ibid.*, **129**, 1737 (1982).
- 4) A.J. Frank, Kenji Honda, *J. Phys. Chem.*, **86**, 1933 (1982).
- 5) G. Cooper, R. Noufi, A.J. Frank, A.J. Nozik, *Nature*, **295**, 578 (1982).
- 6) R.A. Simon, A.J. Ricco, M.S. Wrighton, *J. Am. Chem. Soc.*, **104**, 2031 (1982).
- 7) W.K. Ford, C.B. Duke, W.R. Salaneck, *J. Chem. Phys.*, **77**, 5030 (1982).

(東京大学工学部 李 柱性)