Dynamical Desorption Process of Oxygen on Platinum by Using a Gas Controllable H_2 | H^+ Electrolyte | Pt Cell

Kunio Matsuda^{1,*} and Shuji Harada²

¹Graduate School of Science & Technology, Niigata University, Niigata 950-2181, Japan

²Faculty of Engineering, Niigata University, Niigata 950-2181, Japan

The dynamical desorption process of oxygen on platinum was investigated by an electrochemical method. By using a gas controllable H_2 | H^+ electrolyte | Pt cell, the value of electromotive force (EMF) has been measured as a function of lapse of time after an oxygen adsorbing treatment on the Pt electrode. The time dependence of EMF value has been classified into three stages. In the base stage, the value of EMF was discussed on the oxygen concentration on the Pt electrode. The 1st stage was interpreted by using the electrochemical theory on a diffusion model. The 2nd stage has been analyzed by using a random desorption model. The behavior of EMF was in good agreement with these models. From above analyses, the activation energy of oxygen diffusion process and the adsorption energy of oxygen on the Pt electrode were evaluated. The inflection point as a boundary point of the 1st to 2nd stage was related to the dynamical desorption process of oxygen.

(Received January 21, 2005; Accepted March 30, 2005; Published May 15, 2005)

Keywords: oxygen, platinum, desorption, adsorption, electromotive force, electrochemical method, fuel cell, gas controllable cell, diffusion, electrode

1. Introduction

Dynamical surface phenomena such as adsorption, surface diffusion, surface reaction and desorption have been investigated. The surface potential, interaction energy and adsorption sites play important role to clarify the mechanisms.¹⁻³⁾ The oxygen and/or hydrogen with platinum system are suitable and desirable for the investigation of above fundamental subjects. The adsorption state is classified into two types that are a molecular adsorption state and an atomic one.⁴⁾ Recently, the energy state as a function of the bonding distance for the adsorption site of the atomic oxygen and the molecular one on a Pt surface have been calculated by using cluster model.⁵⁾ In this study, Kokaji *et al.* have discussed on the interaction of oxygen with the Pt surface as a function of distance. Experimentally, Davis and Mullins have measured the translational energy of the oxygen molecule on the Pt surface by using a molecular beam spectroscopy.⁶⁾ Capitano *et al.* showed that atomic hydrogen is more reactive than coadsorbed hydrogen during reaction with both adsorbed atomic and molecular oxygen on the Pt surface.⁷⁾ Verheij and Hugenschmidt have observed a phase separation between hydrogen and oxygen, indicating a decreased binding energy of H atoms inside O islands on the Pt surface,⁸⁾ and the hydrogen and oxygen reaction on Pt with molecular beam relaxation spectroscopy.⁹⁾

There are many kinds of electrochemical methods to obtain the dynamical properties on an electrode surface, for instance, cyclic voltammetry, chrono-potentiometry, chrono-amperometry and so on. Gyenge has studied the electrochemical oxidation of BH_4^- in NaOH on Pt and Au by above methods, and has proposed that thiourea could improve the BH_4^- utilization efficiency and the coulombic efficiency of direct borohydride fuel cells using catalytic anodes.¹⁰⁾ These typical methods are, however, due to control the surface state on a specimen electrode by applying voltage and/or current

with an outer source, continuously.¹¹⁾ We have offered another electromotive force (EMF) method without an outer source to investigate a metal-hydrogen system.¹²⁾ Our method is suitable for evaluation the dynamical properties of hydrogen on a metal surface because of the isolated system without an outer source.

By means of our EMF method, we have investigated the adsorption and desorption process of hydrogen by using a H_2 | H^+ electrolyte | Pt cell and have had a discussion on adsorption and desorption energy.¹³⁾ These measurements were, however, performed by using this cell with atmospheric oxygen. In these measurements, we have recognized that the fluctuation of the EMF of the cell was about 4 mV. Our preliminary experiments showed that the EMF fluctuation is very sensitive to dissolved oxygen. Therefore, we have designed a gas controllable H_2 | H^+ electrolyte | Pt cell.

In this paper, the dynamical desorption process of oxygen on a Pt surface will be investigated by using the gas controllable cell. The value of EMF will be measured as a function of lapse of time after an adsorbing oxygen treatment on the Pt electrode. The time dependence of EMF behavior will be analyzed by using the electrochemical theory on a diffusion model and a random desorption model. From above analyses, the activation energy of the oxygen diffusion process and the adsorption energy of oxygen on the Pt electrode were evaluated.

2. Experimental Procedure

A Pt wire with a diameter of 0.5 mm was heated in a gas burner with reducing flame and quenched into pure water. This Pt wire was used for the sample Pt electrode and counter electrode. A normal hydrogen electrode (NHE) was made of platinum black with a diameter of 0.5 mm, which was prepared by the electrochemical treatment with $\text{H}_2\text{PtCl}_6 + \text{Pb}$ at about 350 K. The purity of Pt in this cell was 99.95%.

The schematic view of present cell is shown in Fig. 1. The gas control technology and the clean technology were

*Graduate Student, Niigata University

Fig. 1 Gas controllable H₂ | H⁺electrolyte | Pt cell. The dissolved oxygen in the electrolyte was removed by Ar gas bubbling. The leakage of air into the cell was prevented by Ar continuous purging.

referred to the gas bubbling method.¹⁴⁾ This cell was made of a PYREX[®] glass with leak tightness. The dissolved oxygen in the electrolyte was removed by 10⁻³ m³/min Ar gas bubbling for 8 h. The leakage of air into the cell was prevented by Ar continuous purging. In order to block the hydrogen gas dissolving into the electrolyte, the NHE was covered with the enclosure and was contact with the electrolyte through the 1 mmφ hole. The backpressure of exhaust gas from the cell was kept constant at atmospheric pressure. The amount of electrolyte was 10⁻³ m³ with 500 mol/m³ H₂SO₄ acid solution. This electrolyte was stirred up quickly to make equalization of dissolved gas concentration. The EMF measurement was performed by using a digital electrometer (Advantest R8240) with 10¹³ Ω input impedance. The NHE and the sample electrode in the circuit were opened normally and just connected with this electrometer at the measurement. The sampling interval was 5 seconds.

An oxygen adsorbing treatment to the sample Pt electrode was done by electrolysis method; *i.e.*, (-) counter electrode | H⁺electrolyte | sample Pt electrode (+) cell by supplying 3.1 V for 4.5 s. This supplying condition for the oxygen adsorbing treatment was decided by the reproducibility of the base stage before/after the treatment and the maximization of

Fig. 2 The EMF of the gas controllable H₂ | H⁺electrolyte | Pt cell with Ar gas continuous bubbling in order to confirm the influence of dissolved air in electrolyte.

the time of inflection point on a EMF reduction profile, where the EMF profile will be mentioned in a following section. By using this method, we could get the reproducible conditions that the sample Pt electrode is saturated with oxygen without excessive oxygen dissolving into the electrolyte. After the oxygen adsorbing treatment, the EMF measurement was immediately started, and the EMF value of H₂ | H⁺electrolyte | Pt* cell was measured as a function of lapse of time, where Pt* means the oxygen adsorbing treated sample Pt electrode.

3. Experimental Results

3.1 Preliminary experiment

Figure 2 shows the EMF as a function of lapse of time of the gas controllable H₂ | H⁺electrolyte | Pt cell with Ar gas continuous bubbling in order to confirm the influence of dissolved air in electrolyte. The value of EMF before bubbling was 0.8 V in the atmosphere, which is the value as was shown in a previous paper.¹³⁾ The value, however, decreased to 0.05 V with lapse of time by Ar bubbling as was recognized in the figure. This value was kept constant by preventing the leakage of air into the cell. We will call the 0.05 V as the base value. When the air supplied to the electrolyte of the cell under the base value, the EMF returned back to the initial value (0.8 V). This means that the EMF value of the cell before Ar bubbling depends on the dissolving the air into the electrolyte. In order to investigate which component of the air has influenced, O₂, CO₂ and N₂ gas was supplied to the electrolyte, respectively. Only the O₂ gas can increase the EMF of the cell dramatically. Therefore, the reaction of this cell is given by

This means that the initial value (0.8 V) of the EMF is

Fig. 3 The temperature dependency of EMF of $\text{H}_2 \mid \text{H}^+$ electrolyte $\mid \text{Pt}^*$ cell as a function of lapse of time, where Pt^* means the oxygen adsorbing treated sample Pt electrode.

brought to the O_2 gas in the electrolyte under the atmosphere, and the base value (0.05 V) of the EMF would be lead to remove the dissolved O_2 by Ar bubbling with this new technique, which will be discussed in a following section. The EMF measurement in the low dissolved O_2 region will play important role as a base.

3.2 Time and temperature dependence of EMF measurements

In order to investigate the dynamical desorption process of oxygen on the sample Pt electrode, the value of EMF was measured by using the $\text{H}_2 \mid \text{H}^+$ electrolyte $\mid \text{Pt}^*$ cell after Ar bubbling. Figure 3 shows the EMF of the cell as a function of lapse of time. The behavior of time dependence is explained by using a typical result of 285.5 K (triangle) in the figure. The time dependence of the EMF will be classified into the three stages of $t < 0$ s, $0 < t < 741$ and $741 \leq t < 1026$ as will be discussed in a following section. In the range of $t < 0$, i.e., before the oxygen adsorbing treatment, the cell was kept at Ar atmosphere by the Ar continuous purging method. The EMF value at $t < 0$ was the base value 0.05 V. Under the condition with the base value, the oxygen adsorbing treatment was done and just stopped at $t = 0$ in the figure. This treatment was effective in generating oxygen on the sample Pt electrode without excessive oxygen dissolving into the electrolyte. In the next stage of $0 < t < 741$, the EMF value was 1.64 V momentarily, and it decreased abruptly ($0 < t < 100$) and gradually ($100 \leq t < 741$) with lapse of time. The origin of 1.64 V will be discussed in a following section. The EMF in the last stage of $741 \leq t < 1026$ fell rapidly, and it returned back to the base value at $t \geq 1026$, where $t = 741$ means the point of inflection. The temperature dependency of the EMF was also shown in Fig. 3. The each behavior as a function of lapse of time was similarly as the above typical result of 285.5 K. The inflection point is $t = 741$ at 285.5 K, $t = 490$ at 295.2 K, $t = 282$ at 305.1 K, $t = 66$ at 315.3 K and $t = 56$ at 325.2 K, which was shortened with increasing the temperature.

4. Experimental Analysis and Discussion

As was mentioned before, the EMF behavior of $\text{H}_2 \mid \text{H}^+$ electrolyte $\mid \text{Pt}^*$ cell was classified into three stages as a function of lapse of time. These stages were called to the base stage that is the stable state with Ar bubbling before the oxygen adsorbing treatment, the 1st stage that is from after the oxygen adsorbing treatment to the inflection point, and the 2nd stage that is from the inflection point to the end of the stage. The EMF value of the cell is equal to the difference of the chemical potential.¹⁵⁾ In this chapter, we will analyze and discuss on the three stages: In the base stage, the value of EMF will be discussed on the O_2 molecule concentration on the sample Pt electrode. In the next 1st stage, the lapse of time of the EMF will be analyzed by using the electrochemical theory on a diffusion model. The last 2nd stage, however, will not be interpreted by the model. This stage can be analyzed by using a random desorption model as was shown in a previous paper.¹³⁾

After the oxygen adsorbing treatment on the sample Pt electrode, the EMF, E , of the (I) $\text{H}_2 \mid \text{H}^+$ electrolyte $\mid \text{Pt}^*$ (II) cell under the reaction of eq. (3) is given by

$$-FE = \frac{1}{2} \left[\mu_{\text{H}_2\text{O}}^{\text{Pt}^*} - \left(\mu_{\text{H}_2}^{\text{H}_2} + \frac{1}{2} \mu_{\text{O}_2}^{\text{Pt}^*} \right) \right] \equiv \Delta\mu, \quad (4)$$

where $\mu_{\text{H}_2\text{O}}^{\text{Pt}^*}$, $\mu_{\text{H}_2}^{\text{H}_2}$ and $\mu_{\text{O}_2}^{\text{Pt}^*}$ are the chemical potential of H_2O on the sample Pt^* electrode, H_2 on the NHE and O_2 on the sample Pt^* electrode, respectively, and F means the Faraday's constant, and (I) and (II) mean the terminals of the cell made by Pt. The derivation of the equation is summarized as follow: In the case of a charged particle system, the electrochemical potential $\tilde{\mu}_\alpha^i$ of α species in an i phase can be described as

$$\tilde{\mu}_\alpha^i = \mu_\alpha^i + z_\alpha F \phi_\alpha^i, \quad (5)$$

where z and ϕ mean the valance and the electrostatic potential, respectively. When there is a reaction $\alpha \rightleftharpoons \alpha_1 + \alpha_2$, the chemical potential μ_α^i is written by

$$\mu_\alpha^i = \mu_{\alpha_1}^i + \mu_{\alpha_2}^i \quad (6)$$

on equilibrium conditions in a same i phase. By using eqs. (5) and (6), we can get the following relations

$$\mu_{\text{H}_2}^{\text{H}_2} = 2\mu_{\text{H}}^{\text{H}_2} = 2\tilde{\mu}_{\text{H}^+}^{\text{H}_2} + 2\tilde{\mu}_{\text{e}^-}^{\text{H}_2}, \quad (7)$$

$$\frac{1}{2} \mu_{\text{O}_2}^{\text{Pt}^*} + 2\tilde{\mu}_{\text{H}^+}^{\text{Pt}^*} + 2\tilde{\mu}_{\text{e}^-}^{\text{Pt}^*} = \mu_{\text{H}_2\text{O}}^{\text{Pt}^*}. \quad (8)$$

Equation (4) can be derived as follow:

$$\begin{aligned} & \frac{1}{2} \left[\mu_{\text{H}_2\text{O}}^{\text{Pt}^*} - \left(\mu_{\text{H}_2}^{\text{H}_2} + \frac{1}{2} \mu_{\text{O}_2}^{\text{Pt}^*} \right) \right] \\ &= \frac{1}{2} \left[2\tilde{\mu}_{\text{H}^+}^{\text{Pt}^*} + 2\tilde{\mu}_{\text{e}^-}^{\text{Pt}^*} - (2\tilde{\mu}_{\text{H}^+}^{\text{H}_2} + 2\tilde{\mu}_{\text{e}^-}^{\text{H}_2}) \right] \\ &= \tilde{\mu}_{\text{H}^+}^{\text{Pt}^*} + \tilde{\mu}_{\text{e}^-}^{\text{Pt}^*} - (\tilde{\mu}_{\text{H}^+}^{\text{H}_2} + \tilde{\mu}_{\text{e}^-}^{\text{H}_2}). \end{aligned} \quad (9)$$

Since the electrochemical potential of H^+ is equal to the interface between both electrodes and electrolyte, we can obtain the following contact equilibrium conditions,

$$\tilde{\mu}_{\text{H}^+}^{\text{Pt}^*} = \tilde{\mu}_{\text{H}^+}^{\text{electrolyte}} = \tilde{\mu}_{\text{H}^+}^{\text{H}_2}. \quad (10)$$

While, the equilibrium conditions of electron between terminal and electrode lead to the following relations

$$\tilde{\mu}_{e^-}^I = \tilde{\mu}_{e^-}^{H_2}, \quad \tilde{\mu}_{e^-}^{II} = \tilde{\mu}_{e^-}^{Pt*}. \quad (11)$$

Equations (10) and (11) are substituted for eq. (9), the equation can be rewritten in the intended eq. (4)

$$\begin{aligned} \Delta\mu &\equiv \frac{1}{2} \left[\mu_{H_2O}^{Pt*} - \left(\mu_{H_2}^{H_2} + \frac{1}{2} \mu_{O_2}^{Pt*} \right) \right] \\ &= \tilde{\mu}_{H^+}^{Pt*} + \tilde{\mu}_{e^-}^{Pt*} - (\tilde{\mu}_{H^+}^{H_2} + \tilde{\mu}_{e^-}^{H_2}) = \tilde{\mu}_{e^-}^{II} - \tilde{\mu}_{e^-}^I \\ &= (\mu_{e^-}^{II} - \mu_{e^-}^I) - F(\phi_{e^-}^{II} - \phi_{e^-}^I) = -FE, \end{aligned}$$

where the electrochemical potential $\mu_{e^-}^{II}$ is equal to the $\mu_{e^-}^I$, because the terminals of the cell are made of same material.

4.1 Base stage on the EMF behavior of the cell with Ar bubbling

In this section, we will analyze the base stage on the EMF behavior of the cell with Ar bubbling by using the electrochemical theory. The chemical potential μ_α^i is expressed by using the activity a_α^i

$$\mu_\alpha^i = \mu_\alpha^{\circ i} + RT \ln a_\alpha^i, \quad (12)$$

where $\mu_\alpha^{\circ i}$ is the standard chemical potential and R is the gas constant. By using the relation, we can obtain

$$E = E^\circ + \frac{RT}{2F} \ln \left[\frac{(a_{H_2}^{H_2})(a_{O_2}^{Pt})^{1/2}}{(a_{H_2O}^{Pt})} \right], \quad (13)$$

where $\mu_{H_2O}^{Pt} = \mu_{H_2O}^{\circ Pt} + RT \ln a_{H_2O}^{Pt}$, $\mu_{H_2}^{H_2} = \mu_{H_2}^{\circ H_2} + RT \ln a_{H_2}^{H_2}$ and $\mu_{O_2}^{Pt} = \mu_{O_2}^{\circ Pt} + RT \ln a_{O_2}^{Pt}$ are used. The standard potential $E^\circ = 1/2F[(\mu_{H_2}^{\circ H_2} + 1/2\mu_{O_2}^{\circ Pt}) - \mu_{H_2O}^{\circ Pt}]$ is equal to 1.229 V which is the value at 298.15 K, 1.013 MPa.¹¹⁾ By using the definition of $a_{H_2}^{H_2} = 1$ on the NHE, eq. (13) can be rewritten as

$$E = E^\circ + \frac{RT}{2F} \ln \left[\frac{(a_{O_2}^{Pt})^{1/2}}{(a_{H_2O}^{Pt})} \right]. \quad (14)$$

In the case of our experimental result by sufficient bubbling, we got the following relation $[(a_{O_2}^{Pt})^{1/2}/(a_{H_2O}^{Pt})] = 2.3 \times 10^{-42}$ by using the base value 0.05 V of EMF. This means that the O₂ concentration C on the sample Pt electrode became extremely low by using the relation of $a_{O_2}^{Pt} = \gamma_{O_2} C$, where γ is the fugacity coefficient.

4.2 1st stage on the EMF behavior of the cell after the oxygen adsorbing treatment

After the oxygen adsorbing treatment, the EMF value indicated 1.64 V momentarily and it decreased abruptly and gradually with lapse of time as was shown in Fig. 3. The value of 1.64 V should be explained that the O₂ concentration on the sample Pt* electrode is very high compared with the standard equilibrium condition. The dynamical behavior of the EMF can be caused by the time dependence of the 2nd term in eq. (14). The rate determining process in high O₂ region, however, will be due to the diffusion process of the recombined O₂ molecule on/nearby the sample Pt* electrode, because the recombined O₂ does not dissolve in the electrolyte easily under the saturation state of O₂ nearby the sample Pt* electrode. In this situation, the time dependence of O₂

Fig. 4 1st stage on the EMF behavior of the cell after the oxygen adsorbing treatment. The solid line is theoretical curve by the diffusion model of O₂.

concentration $C(t)$ will be assigned by the diffusion equation, $C(t) = C_0(\pi D_{O_2} t)^{-1/2}$, $t > 0$, where C_0 is the initial concentration of O₂ on the sample Pt* electrode after the oxygen adsorbing treatment, D_{O_2} is the diffusion coefficient of recombined O₂ into the electrolyte. By using this rate determining model, eq. (14) is rewritten as

$$E = E^\circ + \frac{RT\zeta}{2F} \ln \left[\frac{\eta^{1/2}}{t^{1/4}} \right], \quad (15)$$

$$\eta^{1/2} = \frac{(\gamma_{O_2} C_0)^{1/2}}{(a_{H_2O}^{Pt*})(\pi D_{O_2})^{1/4}}, \quad (16)$$

where $a_{O_2}^{Pt*} = \gamma_{O_2} C(t)$ is substituted in eq. (14). The $a_{H_2O}^{Pt*}$ should be constant ($a_{H_2O}^{Pt*} \ll 1$) without the current flow condition, i.e., the H₂O is not produced by the reaction of $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$. In eq. (15), ζ means the enhancement coefficient. As was recognized in Fig. 4, the experimental reduction curve of the 1st stage on the EMF behavior was in good agreement with this theoretical result by the diffusion model of O₂. From the temperature dependence of the EMF, we can obtain that the ζ is 49 as an independent value on the temperature in this stage. The η , as a function of the temperature, is 7.95 at 285.5 K, 6.74 at 295.2 K, 5.60 at 305.1 K, 3.82 at 315.3 K and 3.06 at 325.2 K. The enhancement coefficient ζ ($= 49$) became very high compared with the equilibrium condition ($\zeta = 1$) in eq. (13). This is explained by the high O₂ concentration on/nearby the Pt* electrode, i.e., $n_{O_2}^{Pt*} \sim \zeta$, $\Delta G = n_{H_2O}^{Pt*} \mu_{H_2O}^{Pt*} - (n_{H_2}^{H_2} \mu_{H_2}^{H_2} + n_{O_2}^{Pt*} \mu_{O_2}^{Pt*})$ and $-FE = 1/2[\mu_{H_2O}^{Pt*} - (\mu_{H_2}^{H_2} + \zeta/2 \mu_{O_2}^{Pt*})]$. By using the relation $\eta \sim (D_{O_2})^{-1/2}$ from eq. (16), the activation energy $\varepsilon_{D_{O_2}}$ of $D_{O_2} = D_0 \exp(-\varepsilon_{D_{O_2}}/k_B T)$ is evaluated as 0.4 eV and D_0 is 1.4×10^5 from the Arrhenius plot, where k_B is the Boltzmann constant.

4.3 2nd stage on the EMF behavior of the cell after the inflection point

In this section, we will analyze the 2nd stage on the EMF behavior of the cell after the inflection point. In this stage, the rate determining process will be due to the desorption process

of the O_2 from the sample Pt^* electrode, because the recombined O_2 concentration become low sufficiently to dissolve the O_2 into the electrolyte in contrast to the 1st stage. In this situation, the time dependence of O_2 concentration on the sample Pt^* electrode will be applied by using a random desorption model of O_2 molecule on it. In this model, we will note that t_0 is the time at the inflection point, t_f is the time at the end of 2nd stage (for instance, $t_f = 410$ s at 305.1 K), n_0 and n_f is the number of O_2 on the sample Pt^* electrode at the time t_0 and t_f , respectively. By using the relation of $\Delta G = \Delta H - T\Delta S$, the free energy will be written as

$$\Delta G \approx n\varepsilon - k_B T \ln[n_0!/(n_0 - n)!n!], \quad (17)$$

in the random desorption model on the sample Pt^* electrode. In the equation, ε is the binding energy of O_2 on the electrode. By using the Stirling's equation, eq. (17) is rewritten to

$$\Delta G \approx n\varepsilon - k_B T \ln[n_0 \ln n_0 - (n_0 - n) \ln(n_0 - n) - n \ln n].$$

Then, we can obtain the relation,

$$-FE = \Delta\mu = \partial(\Delta G)/\partial n \approx \varepsilon - k_B T \ln[(n_0/n) - 1].$$

In the eV unit,¹⁶⁾

$$E = -\varepsilon + k_B T \ln[(n_0/n) - 1], \quad (18)$$

where $F = 1e$ and the unit of E is given by volt. To evaluate the time dependent of the EMF, we will write the number of O_2 in an exponential form,

$$n = Ne^{-t/\tau}, \quad (19)$$

where N is the initial number of O_2 on the sample Pt^* electrode, and τ is the mean stay time of O_2 on the electrode.¹²⁾ By using eq. (19), the n_0 over n ratio is

$$n_0/n = e^{-t_0/\tau}/e^{-t/\tau} = e^{(t-t_0)/\tau}.$$

This ratio is substituted in eq. (18),

$$E = -\varepsilon + \zeta k_B T \ln[\exp((t - t_0)/\tau) - 1], \quad (20)$$

where ζ is the enhancement coefficient as was mentioned in a previous section. The typical fitting curve at 305.1 K is shown in Fig. 5. The theoretical fitting curve given by eq. (20) was in good agreement with the experimental result as a function of time dependency of the EMF. From the temperature dependence of the EMF, we can obtain the $\varepsilon = -0.83$ eV as an independent value on the temperature in this stage, $\tau = 280$ s at 285.5 K, 205 s at 295.2 K, 128 s at 305.1 K, 32 s at 315.3 K and 26 s at 325.2 K, where $\zeta = 3$ is used as a best fit value. From the Arrhenius plot, the adsorption energy $\Delta\varepsilon_{ad}$ of $\tau = \tau_0 \exp(-\Delta\varepsilon_{ad}/k_B T)$ is evaluated as -0.53 eV and τ_0 is 1.6×10^{-7} s. The enhancement coefficient $\zeta (= 3)$ becomes low compared with the last stage ($\zeta = 49$), but this is not equal to the equilibrium condition ($\zeta = 1$) in eq. (13). This means that the influence of recombined O_2 concentration on/nearby the sample Pt^* electrode may remain a little. The adsorption energy $\Delta\varepsilon_{ad} (= -0.53$ eV) is close to the calculated interaction energy⁵⁾ for the bridge site bonded O_2 molecule and/or 2O atoms on a linear Pt_3 cluster at the O_2 -surface distance of 0.2 nm. The inflection point in the EMF behavior could have the following meaning: $\tau = t_f - t_0$, $\Delta\varepsilon_{ad} \approx E_{t_f} - E_{t_0}$, $\varepsilon \approx -E_{t_0}$. For instance, in a typical case at 305.1 K, $\tau (= 128$ s) is equal to the difference

Fig. 5 The typical experimental value of EMF behavior in the 2nd stage at 305.1 K. The open circles show the experimental values. The solid line is theoretical curve by the random desorption model.

of $t_f (= 410$ s) and $t_0 (= 282$ s), $\Delta\varepsilon_{ad} (= -0.53$ eV) $\approx E_{t_f} - E_{t_0} (= 0.19 - 0.86$ eV) and $\varepsilon (= -0.83$ eV) $\approx -E_{t_0} (= -0.86$ eV).

5. Conclusions

By using a gas controllable $H_2 | H^+$ electrolyte | Pt cell, the value of electromotive force (EMF) was measured as a function of lapse of time after an oxygen adsorbing treatment on the sample Pt electrode. The time dependence of EMF value decreased with a lapse of time, and classified into the three stages: The base stage is in the stable state with Ar bubbling, the 1st stage is from after the oxygen adsorbing treatment to the inflection point, and the 2nd stage is from the inflection point to the end of the stage. In the base stage, the value of EMF was discussed on the electrochemical theory by the O_2 concentration on the sample Pt electrode. In the 1st stage on the EMF behavior of the cell after the oxygen adsorbing treatment, the time dependence of the EMF behavior was explained by using the electrochemical theory on a diffusion model of the recombined O_2 on the sample Pt^* electrode, because the recombined O_2 does not dissolve in the electrolyte easily under the saturation state of O_2 nearby the sample Pt^* electrode, where Pt^* means the oxygen adsorbing treated sample Pt electrode. The detailed analysis of this process showed that the activation energy $\varepsilon_{D_{O_2}}$ of $D_{O_2} = D_0 \exp(-\varepsilon_{D_{O_2}}/k_B T)$ is evaluated as 0.4 eV from the Arrhenius plot, D_0 is 1.4×10^5 . In the 2nd stage on the EMF behavior of the cell after the inflection point, the lapse of time of the EMF was interpreted by using a random desorption model of the O_2 on the sample Pt^* electrode, because the recombined O_2 concentration becomes low sufficiently to dissolve the O_2 into the electrolyte in contrast to the 1st stage. We can obtain the adsorption energy $\Delta\varepsilon_{ad} (= -0.53$ eV) of $\tau = \tau_0 \exp(-\Delta\varepsilon_{ad}/k_B T)$. We will propose the physical meaning of inflection point in the EMF behavior as the mean stay time $\tau = t_f - t_0$, $\Delta\varepsilon_{ad} \approx E_{t_f} - E_{t_0}$, the binding energy $\varepsilon \approx -E_{t_0}$.

By using the gas controllable $H_2 | H^+$ electrolyte | Pt cell,

the adsorption energy of O₂ molecule on the Pt electrode has been evaluated. This method will be powerful to investigate the electrodes on a fuel cell and a gas sensor.

Acknowledgment

The authors would like to thank Mr. M. Yashiro for supporting the experiments.

REFERENCES

- 1) H. Butt, K. Graf and M. Kappl: *Physics and Chemistry of Interfaces* (Wiley-Vch, Weinheim, 2003) pp. 177–205.
- 2) R. Tilley: *Understanding Solids* (John Wiley & Sons, West Sussex, 2004) pp. 201–291.
- 3) J. Yoshinobu, T. Moriwaki and M. Kawai: *Butsuri* (Physics) **53** (1998) 350–354 [in Japanese].
- 4) K. Sawabe, Y. Matsumoto, J. Yoshinobu and M. Kawai: *J. Chem. Phys.* **103** (1995) 4757–4764.
- 5) A. Kokaji, A. Lesar and M. Hodoscek: *Chem. Phys. Lett.* **263** (1997) 43–49.
- 6) J. E. Davis and C. B. Mullins: *Surf. Sci.* **380** (1997) L513–L520.
- 7) A. T. Capitano, A. M. Gabelnick and J. L. Gland: *Surf. Sci.* **419** (1999) 104–113.
- 8) L. K. Verheij and M. B. Hugenschmidt: *Surf. Sci.* **324** (1995) 185–201.
- 9) L. K. Verheij and M. B. Hugenschmidt: *Surf. Sci.* **416** (1998) 37–58.
- 10) E. Gyenge: *Electrochimica Acta* **49** (2004) 965–978.
- 11) A. Fujishima, M. Aizawa and T. Inoue: *Denki Kagaku Sokuteihou* (Electrochemical Measurement Method) (Gihoudou, Tokyo, 1984) pp. 49–195 [in Japanese].
- 12) S. Harada: *J. Phys. Soc. Jpn.* **54** (1985) 430–437.
- 13) S. Harada: *J. Phys. Soc. Jpn.* **68** (1999) 1746–1750.
- 14) Y. Ishihara, S. Yamane, H. Yamazaki and H. Tsuge: *J. Electrochem. Soc.* **142** (1995) 2352–2357.
- 15) S. Harada: *J. Phys. Soc. Jpn.* **58** (1989) 2200–2206.
- 16) $1\text{ eV} = 1.602 \times 10^{-19}\text{ J}$, $k_B = 8.617 \times 10^{-5}\text{ eV/K}$.