

Design of Gas Controllable H_2 | H^+ electrolyte | Pt Cell and the Evaluation Method of a Dilute Hydrogen and Oxygen Gas in the Electrolyte

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A gas handling technique of the gas controllable H_2 | H^+ electrolyte | Pt cell has been reported in order to obtain the reproducible gas environmental condition. The small amount of dissolved hydrogen and oxygen gas in the electrolyte has been evaluated by measurements of the temperature dependence of electromotive force (EMF) of the cell. The gas controllable technique and the evaluation method of a dilute H and O gas dissolved in an electrolyte should contribute to clarify the interfacial phenomena on electrode materials.

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1. Introduction

Recently, we have reported that the electrochemical measurement of a H_2 | H^+ electrolyte | Metal cell is an attractive technique to investigate the fundamental subject of interfacial properties of hydrogen and/or oxygen on a metal.¹⁻³⁾ The value of electromotive force (hereafter referred to as EMF) of the cell is due to the difference of the chemical potential of hydrogen atom between the H_2 electrode and metal one. The EMF value mainly depends on the concentration of the dissociated H and O atom on a metal electrode, which forms so-called a concentration cell and a fuel cell, respectively. As was reported in a previous paper,¹⁾ the EMF of the cell is dramatically change by the H_2 and O_2 gas, and is unaffected by the N_2 , CO_2 , and Ar gas.

The nature of the adsorption on metals is classified into two different types of nondissociative adsorption and dissociative one. In the former, the adsorbing molecules stay intact during adsorption, and in the latter process, molecular bonds break on adsorb. The elementary process of dissociative adsorption has been interpreted by using Lennard-Jones's model.⁴⁾ Their model to try to put the distinction between molecular adsorption and dissociative one is shown by the interaction of B_2 molecule, for instance, with a surface via Lennard-Jones potential and the potential for the interaction of two separate B atoms with the same surface via dissociative adsorption potential. These potential curves of the molecular state and the dissociated state will interact to avoid the curve crossing. The energy profile gives the three cases of pure molecular adsorption, activated dissociative adsorption, and unactivated dissociative adsorption.⁴⁾ Typical specimen of unactivated dissociative adsorption for H_2 molecule on a metal is a platinum as spontaneous dissociate materials.⁵⁾

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. These methods are, however, due to control surface state on a specimen electrode by applying

voltage and/or current with an outer source.⁶⁾ We have offered another EMF method without an outer source in order to investigate a metal-hydrogen system.^{7,8)} 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.⁷⁾ These measurements were, however, performed by using a simple cell under atmospheric conditions. Our preliminary experiments showed that the EMF fluctuation is sensitive to dissolved oxygen. Therefore, we have designed a gas controllable H_2 | H^+ electrolyte | Pt cell.

In this paper, a gas handling technique of a gas controllable H_2 | H^+ electrolyte | Pt cell has been proposed in order to obtain the reproducible gas environmental condition. The evaluation method of the small amount of the hydrogen and oxygen gas in the electrolyte of the cell has been presented as a function of the temperature dependence of the EMF of the cell. The gas controllable technique and the evaluation method of a dilute H and O gas dissolved in an electrolyte will contribute to understand interfacial phenomena on electrode materials.

2. Experiment 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, where the purity of Pt was 99.95%. This Pt wire was used for the sample Pt electrode and reference electrode. A normal hydrogen electrode (hereafter referred to as NHE) was made of platinum black with a diameter of 0.5 mm, which was prepared by the electrochemical treatment in a 1 g of $H_2PtCl_6 \cdot 6H_2O$ per 30 ml of H_2O solution with a current density of 30 mA/cm² at 303 K.

The schematic view of the present chamber is shown in Fig. 1. A gas clean technology was referred to the gas bubbling method.⁹⁾ The chamber was made of PYREX[®]

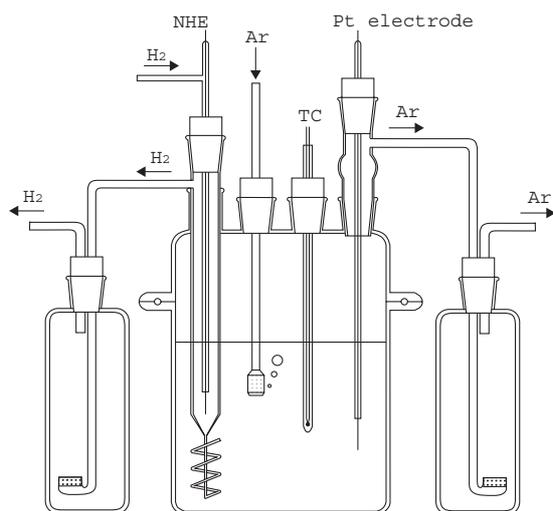


Fig. 1 The gas controllable H_2 | H^+ electrolyte | Pt cell. The dissolved H_2 and O_2 gas in the electrolyte was removed by Ar gas bubbling. The leakage of the air into the cell was prevented by Ar continuous gas purging.

glass with leak tightness. 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 a capillary tube with the inside diameter of $\phi 1 \text{ mm} \times$ the length of 500 mm. The rate of H_2 gas in to the NHE chamber was $0.025 \times 10^{-3} \text{ m}^3/\text{min}$ H_2 gas via an oxygen elimination column. The gas outlines from the chamber was connected with a gas washing-bottle attached a porous bubbling ceramics. The certified value of the oxygen elimination column is 0.002 ppm or under. The dissolved H_2 and O_2 gases in the electrolyte of the sample chamber was removed by $0.3 \times 10^{-3} \text{ m}^3/\text{min}$ Ar gas bubbling via an oxygen elimination column. The gas outlines from the chamber was also connected with another gas washing-bottle. The bubbling time was determined with regard to stabilization of the EMF value of the cell. The air leakage into the chamber was prevented by Ar continuous gas purging by using the pulled Ar gas pipe out the electrolyte.

In order to obtain the stabilized and reproducible gas handling condition, we made attempt to remove the anti-backward-flow water in the gas washing-bottle to keep out the pulsating level fluctuation of the electrolyte. The influence of the backward flow of the air was measured by doping hydrogen gas into the gas washing-bottle, because hydrogen gas is very sensitive for the EMF value of the cell. This pre-experimental result showed that the no-response of the EMF value of the cell was observed by doping hydrogen gas. Consequently, we can obtained the important gas handling technique to keep constant of the differential pressure between the NHE cell and sample cell by withdrawing the anti-backward-flow water from the gas washing-bottle.

The amount of electrolyte was 10^{-3} m^3 with $500 \text{ mol}/\text{m}^3$ H_2SO_4 acid solution. This electrolyte was stirred up quickly to make equalization of dissolved gas concentration in the electrolyte. The EMF measurement was performed using a digital electrometer (Advantest R8240) with $10^8 \text{ M}\Omega$

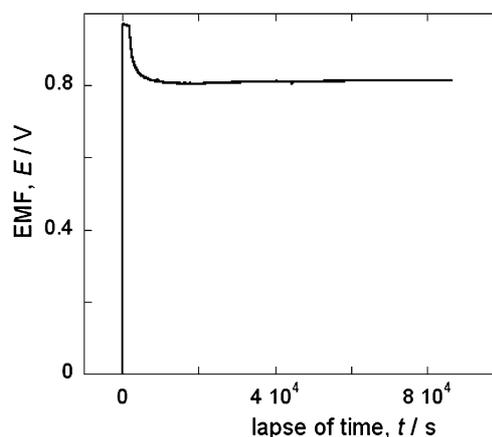


Fig. 2 The EMF of the gas controllable H_2 | H^+ electrolyte | Pt cell with Ar gas continuous bubbling in order to confirm the influence of the dissolved air in electrolyte.

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 s.

3. Experimental Results

3.1 Reproducibility of the EMF measurements

Figure 2 shows the EMF as a function of lapse of time of the H_2 | H^+ electrolyte | Pt cell with Ar gas continuous bubbling. The EMF value before $t = 0$ indicated around 0 V. This value is that of the Pt | H^+ electrolyte* | Pt cell, where the notation “*” means under gas un-control conditions of the electrolyte.

At time $t = 0$, H_2 gas was introduced into the NHE cell, and at the same time Ar gas bubbling in the sample cell was started. The EMF value at $t \sim 0$ was around 1 V as the H_2 | H^+ electrolyte* | Pt cell, which value depends on the concentration of dissolved O_2 gas in the electrolyte.¹⁾ The EMF value decreased and achieved at 0.82 V with the lapse of Ar bubbling time as was recognized in the figure. The reproducibility of this gas handling was checked by several repetitions of the measurements. All that measured led the EMF values of 0.82 V. This value was kept constant by preventing the leakage of the air into the cell. Therefore, we will call the 0.82 V as the EMF base value for the present cell.

3.2 Temperature dependence of the EMF measurement

We have measured the temperature dependence of the EMF, in order to evaluate the gas environmental condition of the gas controllable H_2 | H^+ electrolyte | Pt cell. The theoretical details of the evaluation will be explained in a following section.

Figure 3 shows the EMF base value of the H_2 | H^+ electrolyte | Pt cell and the temperature of the cell as a function of lapse of time. The temperature of the cell was cooled from 303 K to 283 K and warmed in order to hold the dissolution amount of the gases in the electrolyte. The temperature dependence of the EMF base value is summarized in Fig. 4.

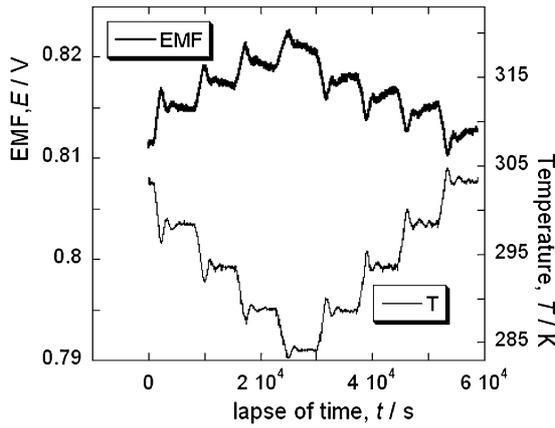


Fig. 3 The temperature dependency of EMF base value of $\text{H}_2 | \text{H}^+ \text{electrolyte} | \text{Pt}$ cell as a function of lapse of time.

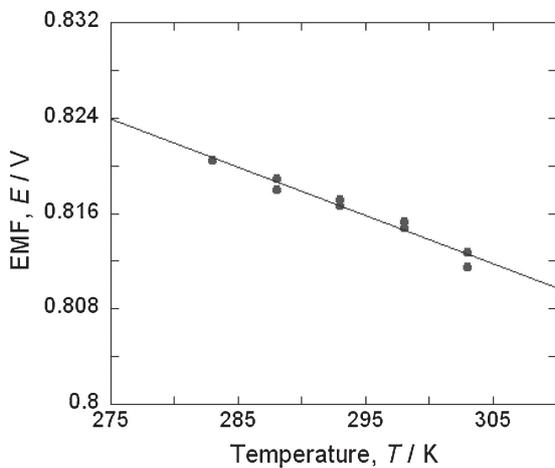
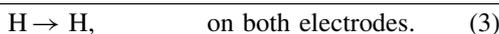
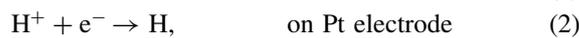


Fig. 4 The temperature dependence of EMF base value of $\text{H}_2 | \text{H}^+ \text{electrolyte} | \text{Pt}$ cell.

4. Experimental Analysis and Discussion

In this section, we will evaluate the gas environmental condition of the gas controllable (I) $\text{H}_2 | \text{H}^+ \text{electrolyte} | \text{Pt}$ (II) cell. As was shown in the previous paper,¹⁾ the EMF value mainly depends on the H and O concentration on a metal electrode, which is generated by the hydrogen concentration cell and the fuel cell, respectively.

In the hydrogen concentration cell, the reaction equation of the cell is given by



The observed value of EMF, E_{H} , under the reaction of eq. (3) is given by

$$-FE_{\text{H}} = \mu_{\text{H}}^{\text{Pt}} - \mu_{\text{H}}^{\text{H}_2}, \quad (4)$$

where $\mu_{\text{H}}^{\text{Pt}}$ and $\mu_{\text{H}}^{\text{H}_2}$ are the chemical potential of H on the sample Pt electrode and H on the NHE, respectively, and F means the Faraday's constant,¹⁰⁾ and (I) and (II) mean the terminals of the cell. The derivation of the equation is summarized as follow:¹¹⁾ In the case of a charged particle

system, the electrochemical potential $\tilde{\mu}_{\alpha}^i$ of the α particle in the i phase can be described as

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

where z means the valance of the α charged particle and ϕ is the electrostatic potential. When there is a reaction $\alpha \rightleftharpoons \alpha_1 + \alpha_2$, the electrochemical potential $\tilde{\mu}_{\alpha}^i$ is written by

$$\tilde{\mu}_{\alpha}^i = \tilde{\mu}_{\alpha_1}^i + \tilde{\mu}_{\alpha_2}^i, \quad (6)$$

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

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

where the $\tilde{\mu}_{\text{H}^+}^{\text{H}_2}$ is equal to the $\mu_{\text{H}^+}^{\text{H}_2}$ because of the neutral particle. The eq. (4) can be derived as follow:

$$\begin{aligned} \mu_{\text{H}}^{\text{Pt}} - \mu_{\text{H}}^{\text{H}_2} &= (\tilde{\mu}_{\text{H}^+}^{\text{Pt}} + \tilde{\mu}_{\text{e}^-}^{\text{Pt}}) - (\tilde{\mu}_{\text{H}^+}^{\text{H}_2} + \tilde{\mu}_{\text{e}^-}^{\text{H}_2}). \end{aligned} \quad (8)$$

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

$$\tilde{\mu}_{\text{H}^+}^{\text{Pt}} = \tilde{\mu}_{\text{H}^+}^{\text{electrolyte}} = \tilde{\mu}_{\text{H}^+}^{\text{H}_2}. \quad (9)$$

While, the equilibrium condition of electron between terminal and electrode leads to the following relations

$$\tilde{\mu}_{\text{e}^-}^{\text{I}} = \tilde{\mu}_{\text{e}^-}^{\text{H}_2}, \tilde{\mu}_{\text{e}^-}^{\text{II}} = \tilde{\mu}_{\text{e}^-}^{\text{Pt}}. \quad (10)$$

The eqs. (9) and (10) are substituted for the eq. (8), the equation can be rewritten in the intended eq. (4)

$$\begin{aligned} \Delta\mu &\equiv \mu_{\text{H}}^{\text{Pt}} - \mu_{\text{H}}^{\text{H}_2} \\ &= (\tilde{\mu}_{\text{H}^+}^{\text{Pt}} + \tilde{\mu}_{\text{e}^-}^{\text{Pt}}) - (\tilde{\mu}_{\text{H}^+}^{\text{H}_2} + \tilde{\mu}_{\text{e}^-}^{\text{H}_2}) = \tilde{\mu}_{\text{e}^-}^{\text{II}} - \tilde{\mu}_{\text{e}^-}^{\text{I}} \\ &= (\mu_{\text{e}^-}^{\text{II}} - \mu_{\text{e}^-}^{\text{I}}) - F(\phi_{\text{e}^-}^{\text{II}} - \phi_{\text{e}^-}^{\text{I}}) = -FE, \end{aligned}$$

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

The chemical potential μ_{α}^i is expressed by using the activity a_{α}^i , which is a virtual concentration in a nonideal system

$$\mu_{\alpha}^i = \mu_{\alpha}^{\circ i} + RT \ln a_{\alpha}^i, \quad (11)$$

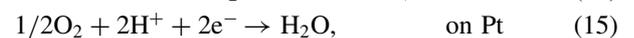
where $\mu_{\alpha}^{\circ i}$ is the standard chemical potential and R is $R \equiv N_{\text{A}} k$ given by the Avogadro constant N_{A} and the Boltzmann one k . The relation (4) can be rewritten as

$$E_{\text{H}} = E_{\text{H}}^{\circ} + \frac{RT}{F} \ln \left[\frac{a_{\text{H}_2}^{\text{H}_2}}{a_{\text{H}}^{\text{Pt}}} \right], \quad (12)$$

where $\mu_{\text{H}}^{\text{Pt}} = \mu_{\text{H}}^{\circ \text{Pt}} + RT \ln a_{\text{H}}^{\text{Pt}}$ and $\mu_{\text{H}_2}^{\text{H}_2} = \mu_{\text{H}_2}^{\circ \text{H}_2} + RT \ln a_{\text{H}_2}^{\text{H}_2}$ are used. By using the definition of $a_{\text{H}_2}^{\text{H}_2} = 1$ on the NHE and that of $E_{\text{H}}^{\circ} = 0$, the eq. (12) is

$$E_{\text{H}} = \frac{RT}{F} \ln \left[\frac{1}{a_{\text{H}}^{\text{Pt}}} \right]. \quad (13)$$

In the fuel cell reaction, the reaction equation is given by



The observed value of EMF, E_O , under the reaction of eq. (16) is given by

$$-FE_O = \frac{1}{2} \left[\mu_{\text{H}_2\text{O}}^{\text{Pt}} - \left(\mu_{\text{H}_2}^{\text{H}_2} + \frac{1}{2} \mu_{\text{O}_2}^{\text{Pt}} \right) \right], \quad (17)$$

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 H₂O on the sample Pt electrode, H₂ on the NHE and O₂ on the sample Pt electrode, respectively.¹⁾ By using the activity, the relation (17) can be rewritten as

$$E_O = E_O^\circ + \frac{RT}{2F} \ln \left[\frac{(a_{\text{H}_2}^{\text{H}_2})^2 (a_{\text{O}_2}^{\text{Pt}})}{(a_{\text{H}_2\text{O}}^{\text{Pt}})} \right], \quad (18)$$

where $a_{\alpha_2}^i = (a_{\alpha_2}^i)^2$ is used. By using the relation of $a_{\text{H}_2\text{O}}^{\text{Pt}} \simeq 1$ in an liquid electrolyte, the eq. (18) is

$$E_O \simeq E_O^\circ + \frac{RT}{2F} \ln [a_{\text{O}_2}^{\text{Pt}}]. \quad (19)$$

The standard potential $E_O^\circ = 1/2F[(\mu_{\text{H}_2}^{\circ\text{H}_2} + 1/2\mu_{\text{O}_2}^{\circ\text{Pt}}) - \mu_{\text{H}_2\text{O}}^{\circ\text{Pt}}]$ is equal to 1.229 V which is the value at 298.15 K, 1.013 MPa.⁶⁾

4.1 The evaluation of the amount of the residual H₂ and O₂ gas in the electrolyte

When the both reduction reaction and oxidation one are concurrent in the cell, the EMF observational value is given by the mixed potential of

$$E^{\text{observe}} = \frac{r_O E_H + r_H E_O}{r_H + r_O}, \quad (20)$$

where r_H and r_O are equivalent resistance for the reduction reaction cell and the oxidation one, respectively. By using eqs. (13) and (19), eq. (20) is rewritten as

$$E^{\text{observe}} = \frac{E_H^\circ + \eta E_O^\circ}{1 + \eta} + \frac{RT}{F(1 + \eta)} \ln \left[\frac{(a_{\text{O}_2}^{\text{Pt}})^{\eta/2}}{a_{\text{H}_2}^{\text{Pt}}} \right], \quad (21)$$

where $\eta = r_H/r_O$ is used.

We have obtained that $E^{\text{observe}} = 0.9356 - 0.406 \times 10^{-3}T$ from the temperature dependence of the EMF base value of the H₂ | H⁺electrolyte | Pt cell as was shown in Fig. 4. These experimental values give that $\eta = 3.19$, i.e., $0.936 = 1.229\eta/(1 + \eta)$ and

$$-0.406 \times 10^{-3} = \frac{1}{(1 + \eta)} \frac{R}{F} \ln [(a_{\text{O}_2}^{\text{Pt}})^{\eta/2} (a_{\text{H}_2}^{\text{Pt}})^{-1}], \quad (22)$$

i.e.,

$$(a_{\text{O}_2}^{\text{Pt}})^{\eta/2} (a_{\text{H}_2}^{\text{Pt}})^{-1} = \exp[-0.406 \times 10^{-3}(1 + \eta)F/R]. \quad (23)$$

We will attempt to evaluate the $a_{\text{H}_2}^{\text{Pt}}$ and $a_{\text{O}_2}^{\text{Pt}}$ by using three approaches: (1) Under a simple approximation of $a_{\text{H}_2}^{\text{Pt}} \sim a_{\text{O}_2}^{\text{Pt}}$, we can evaluate as $a_{\text{H}_2}^{\text{Pt}} \sim a_{\text{O}_2}^{\text{Pt}} = 3.8 \times 10^{-15} = \gamma x \simeq x$, where γ and x mean the activity coefficient and the molar fraction, respectively. The γ is 1 in the ideal solution. (2) The above estimation is, however, impractical because the Henry's constant of the H₂ in H₂O and that of O₂ have different value. By using the Henry's constant of the H₂ gas in H₂O is 1.75×10^2 Pa/molar fraction at 298 K, and the O₂ gas in H₂O is 2.83×10^2 Pa/molar fraction at 298 K,¹²⁾ we can obtain the relation, $a_{\text{H}_2}^{\text{Pt}} \sim 0.618 \times a_{\text{O}_2}^{\text{Pt}}$, i.e., $0.618 = 175/283$. In this assumption, we may evaluate the values of $a_{\text{O}_2}^{\text{Pt}} \sim 1.7 \times 10^{-15}$ and $a_{\text{H}_2}^{\text{Pt}} \sim 1.1 \times 10^{-15}$. (3) We will have, however, another

estimation because the O₂ gas was removed by the elimination column. Therefore, by using the certified value of the O₂ elimination column is 0.002 ppm, and that value of the H₂ is 1 ppm in a carrier gas of Ar, we can have the relation of $a_{\text{H}_2}^{\text{Pt}} \sim 309 \times a_{\text{O}_2}^{\text{Pt}}$, i.e., $309 = (1 \times 175)/(0.002 \times 283)$ with the Henry's low. In the assumption, we may also evaluate the values of $a_{\text{O}_2}^{\text{Pt}} \sim 5.9 \times 10^{-11}$ and $a_{\text{H}_2}^{\text{Pt}} \sim 1.8 \times 10^{-8}$. This last evaluation might be reasonable as will be discussed in the next subsection.

4.2 On the evaluation of the η

The loss of the fuel cell reaction is mainly caused by four major terms: Ohmic loss, concentration loss on reactants, activation loss related to electrode catalysis, and fuel cross-over and internal current.¹³⁾ The origin of the resistance of r_H and r_O in eq. (20), i.e., $\eta = r_H/r_O$ should be given by the loss of the reaction. In the present measurement as was shown in Fig. 2, the E^{observe} value was given by $E^{\text{observe}} = 0.9356 - 0.406 \times 10^{-3}T$ from the temperature dependence of the EMF base value of the H₂ | H⁺electrolyte | Pt cell. The E^{observe} value is very sensitive to dissolved hydrogen and/or oxygen gas as was mentioned before. We have actually observed a variety of the temperature dependence of the EMF base value in preliminary experiments; for instance, $E^{\text{observe}; A} = 1.069 - 1.08 \times 10^{-3}T$ or $E^{\text{observe}; B} = 1.14 - 0.900 \times 10^{-3}T$, where the both electrolyte was the same 500 mol/m³ H₂SO₄ acid solution. The case of the $E^{\text{observe}; A}$ gives as $\eta = 6.68$, and that of the $E^{\text{observe}; B}$ is $\eta = 12.8$. These results show that the η depends on the concentration of H₂ and O₂, and suggest that $a_{\text{H}_2}^{\text{Pt}} < a_{\text{O}_2}^{\text{Pt}}$ in the just previous subsection. This suggests that the amount of residual gases in the cell are around $a_{\text{O}_2}^{\text{Pt}} \sim 1.7 \times 10^{-15}$ and $a_{\text{H}_2}^{\text{Pt}} \sim 1.1 \times 10^{-15}$.

5. Conclusions

In this paper, we have proposed the evaluation method of the amount of H₂ and O₂ gas in the electrolyte of the gas controllable H₂ | H⁺electrolyte | Pt cell by measuring the temperature dependence of the electromotive force (EMF) of the cell as was shown in Fig. 2 and Fig. 4, respectively. The EMF value of the cell is given by the mixed potential of $E^{\text{observe}} = (E_H + \eta E_O)/(1 + \eta)$ as was given by eq. (20), where η means the equivalent resistance ratio of $\eta = r_H/r_O$. The EMF value is rewritten as $E^{\text{total}} = \eta E_O^\circ (1 + \eta)^{-1} + RTF^{-1}(1 + \eta)^{-1} \ln \{(a_{\text{O}_2}^{\text{Pt}})^{\eta/2} (a_{\text{H}_2}^{\text{Pt}})^{-1}\}$ as was given by eq. (21), where a_α^i is the activity which means a virtual concentration in a nonideal system. By measuring the EMF value as a function of temperature, we can obtain the activity ratio of $(a_{\text{O}_2}^{\text{Pt}})^{\eta/2} (a_{\text{H}_2}^{\text{Pt}})^{-1}$.

The present gas controllable technique and the evaluation method of a dilute H and O gas dissolved in an electrolyte should contribute to clarify the interfacial phenomena on electrode materials.

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REFERENCES

- 1) K. Matsuda and S. Harada: *Mater. Trans.* **46** (2005) 1058–1063.
- 2) S. Harada: *J. Phys. Soc. Jpn.* **68** (1999) 1746–1750.
- 3) S. Harada: *J. Phys. Soc. Jpn.* **66** (1997) 2921–2926.
- 4) R. I. Masel: *Principles of Adsorption and Reaction on Solid Surfaces*, (Wiley-Vch, Weinheim, 1996) pp. 116–120.
- 5) K. Christmann: *Surf. Sci. Rep.* **9** (1988) 1–163.
- 6) A. Fujishima, M. Aizawa and T. Inoue: *Denki Kagaku Sokuteihou*, (Electrochemical Measurement Method) (Gihoudou, Tokyo, 1984) [in Japanese]. Chap. 2–4 and 6.
- 7) S. Harada: *J. Phys. Soc. Jpn.* **54** (1985) 430–437.
- 8) S. Harada and S. Tamaki: *J. Phys. Soc. Jpn.* **54** (1985) 1642–1647.
- 9) Y. Ishihara, S. Yamane, H. Yamazaki and H. Tsuge: *J. Electrochem. Soc.* **142** (1995) 2352–2357.
- 10) In the eV unit, $F = 1 e$ and the unit of E is given by volt, where $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$, $k = 8.617 \times 10^{-5} \text{ eV/K}$.
- 11) S. Harada: *J. Phys. Soc. Jpn.* **58** (1989) 2200–2206.
- 12) Chemical Society of Japan (ed.): *Kagaku Binran Kisoheh II (Chemical Data Book II)*, (Maruzen, Tokyo, 1984) II-158 [in Japanese].
- 13) Ed. by A. Zuttel, A. Borgschulte and L. Schlapbach: *Hydrogen as a Future Energy Carrier*, (Wiley-Vch, Weinheim, 2008) 364–371.