Dissolution Rate of Noble Metals for Electrochemical Recycle in Polymer Electrolyte Fuel Cells

Hidenobu SHIROISHI, Shinjiro HAYASHI, Minoru YONEKAWA, Ryo SHOJI, Itaru KATO, and Masayuki KUNIMATSU

Tokyo National College of Technology, Kunugida 1220-2, Hachioji, Tokyo, Japan
Kanagawa Industrial Technology Center, Shimoimaizumi 705-1, Ebina, Kanagawa, Japan
* Corresponding author: h-shiroishi@tokyo-ct.ac.jp

ABSTRACT
An electrochemical recycling process of the noble metal such as Pt and Ru from the membrane electrode assemblies (MEAs) in fuel cells was investigated for the environment-friendly process without aqua regia. The dissolution rate of Pt in HCl solution was about 50 times as fast as those in H₂SO₄ and HClO₄ solutions. The Pt dissolution rate increased linearly with HCl concentration. Pt dissolution under fluctuating potential using saw-tooth wave is 15 times faster than that under constant potentials. The electrochemical dissolution method can also be applied to the dissolution of Pt and Ru in the PtRu catalysts. The chemical methods using aqua regia, HCl-H₂O₂ mixed solution, and HCl only were also investigated for the comparison as the electrochemical methods. The vaporization rate of oxidants (NOCl and Cl₂) from aqua regia at 333 K was 40 times as fast as that at 298 K by a dissolution of Pt and Ru in the PtRu catalysts. The chemical methods using aqua regia, HCl-H₂O₂ mixed solution, and HCl only were also investigated for the comparison as the electrochemical methods. The vaporization rate of the oxidants from aqua regia was investigated by a spectrochemical method.

Keywords : Recycle, Fuel Cell, Dissolution of Noble Metal

1. Introduction

The mainstream of the studies for polymer electrolyte fuel cells (PEFCs) has been for the early commercialization such as the downsizing of the system, enhancing durability and power densities, and reducing manufacturing costs. These subjects have been solved gradually, and fuel cells are about to become popular. In such situation, it becomes important to study the environment adaptability and recycling capability for fuel cells.

Recycling noble metals in PEFCs has been reported by Zhao and co-workers using aqua regia, and by Feng et al. with sulfuric acid. The other techniques used in the automotive catalysts recycling with HCl-H₂O₂ mixed solution would be applicable to the PEFC systems. The combustion of membrane electrode assemblies (MEAs) would be the candidate for the recycling method. However, incinerators would be damaged by the fluorine gas derived from the combustion of fluorinated membranes such as Nafion, Flemion, and Aciplex. Additionally, SOₓ gas produced by the combustion of the sulfonate group in the membranes should be removed from the exhaust gas. In the case of the chemical methods using chloride ion, the permeation of chloride ion through Nafion, which is the cation exchange membranes, is not expected so high to the purpose of the dissolution of the noble metals in the MEAs. Chemical methods with aqua regia are undesirable, since amount of the noble metals calculated stoichiometrically cannot be processed by the volatile oxidants such as nitrosyl chloride and chlorine gas, which are harmful materials with high environmental burden.

In this study, the electrochemical recycling process of the noble metals such as Pt and Ru from the MEAs in fuel cells was investigated for the environment-friendly process without aqua regia. The chemical methods using aqua regia, HCl-H₂O₂ mixed solution, and HCl were also investigated for the comparison as the electrochemical methods. The vaporization rate of the oxidants from aqua regia was investigated by a spectrochemical method.

2. Experimental

2.1 Fabrication of modified electrode
A Pt/C- or PtRu/C- loaded on the carbon paper (TGP-H-060, Toray) (abbreviated as Pt/CP or PtRu/CP) was prepared with a spray coating machine (SI-I, Acing Technologies). The amount of the catalyst was adjusted to 0.3 mg cm⁻². The carbon paper cut in a circle (5 mm diameter, 0.196 cm²) was attached to a glassy carbon disk electrode (Nikkou Keisoku) with a carbon ink which was a suspension of carbon (XC72R, Cabot) in 5 wt% Nafion (Sigma Aldrich Chemical).

2.2 Electrochemical dissolution of noble metals in carbon paper
Electrochemical measurements were carried out with a conventional three electrode system in nitrogen atmosphere with the modified disk electrode fabricated in section 2.1, a Ag/AgCl electrode, and a Au wire counter electrode separated from the working and reference electrodes to avoid the deposition of the Pt dissolved at the working electrode (Fig. 1). Sulfuric acid (Kishida Chemical), perchloric acid (Wako Pure Chemical), and hydrochloric acid (Wako Pure Chemical) were used as electrolytes. Electrochemical dissolution tests were performed using various potential waves shown in Fig. 2. The change of electrochemical surface area (ECSA) was evaluated by the hydrogen adsorption/desorption region in cyclic voltammograms (CVs). After the dissolution test, the concentration of Pt and/or Ru was determined by ICP-AES (SPS-7800, SII).

The electrochemical study was carried out by using a multi-potentiostat (Hokuto Denko, HA-1510) with a function generator (Toho Giken, FG-05) and an electrochemical measurement and analysis program.
The aqua regia was prepared in a vial, and nitrogen gas flowed through the vial at 20 mL/min. The vaporized oxidants were trapped in the potassium iodine solution. The amount of trapped oxidants was measured by iodine produced by the oxidant using UV/Vis spectroscopy (Ocean Optics USB2000 with tungsten-halogen lamp). The iodine concentration was estimated with the absorbance of 450 nm ($\leq 9 \times 10^{-3}$ M), the average of 500 and 550 nm ($\leq 3 \times 10^{-3}$ M), 600 nm ($\leq 9 \times 10^{-3}$ M) and 650 nm (more than $9 \times 10^{-3}$ M), respectively.

3. Result and discussion

3.1 Dissolution for Pt and PtRu by electrochemical methods

Figure 3 shows cyclic voltammograms of a Pt/CP-modified electrode immersed in 1 M H2SO4 and HCl in alternate shifts. It is well known that the ECSA of a Pt bare electrode cannot be estimated in solutions containing chloride ion because of the adsorption of chloride ions onto Pt atoms, whereas the ECSA of Pt/CP in H2SO4 (19.6 cm$^2$) was only 4% larger than that in HCl (18.6 cm$^2$) indicating that Nafion ionomer, which has a large pK$_a$ (70), prevents the adsorption of chloride ions onto Pt atoms within a short time period. Thus, the measurements of ECSA during Pt dissolution tests in HCl solution were performed in the same solution. In a HCl solution, Pt atoms were electrochemically oxidized to be dissolved as tetrachloroplatinate or hexachloroplatinate ions as shown below:

$$\text{Pt} + 4\text{Cl}^- \rightarrow [\text{PtCl}_4]^{2-} + 2e^- \quad E^c = +0.758 \text{ V vs. SHE} \quad (1)$$
$$\text{Pt} + 6\text{Cl}^- \rightarrow [\text{PtCl}_6]^{2-} + 4e^- \quad E^c = +0.744 \text{ V vs. SHE} \quad (2)$$

These reactions can be confirmed in the cyclic voltammogram based on the increase in the anodic current above 0.55 V vs. Ag/AgCl, and the cathode peak around 0.2 V vs. Ag/AgCl in 1 M HCl might be attributable to the reduction of platinum chloride complexes ([PtCl$_4$]$^{2-}$ and [PtCl$_6$]$^{3-}$).

Figure 4 shows the cyclic voltammograms of Pt/CP electrodes in various electrolytes before and after 1 min of an electrochemical Pt dissolution test. The RSD of ECSA for Pt/CPs based on hydrogen adsorption/desorption region in CVs was 6.0%. The deviation is probably due to the difference in degree of electrolyte penetration into CPs.

In HCl solution, ECSA decreased after 1 min of the Pt dissolution test. On the other hand, in H2SO4 or HClO$_4$ solution, ECSA increased after 1 min of the Pt dissolution test probably due to the atomization of Pt and the oxidative elimination of adsorbates on Pt. ECSA started decreasing after 2 to 3 min of the Pt dissolution test in the solutions.

2.3 Chemical dissolution of noble metals in carbon paper

A 2 x 2 cm of Pt/CP or PtRu/CP was floated on aqua regia or HCl-H2O$_2$ (Kishida Chemical) mixed solution with continuous stirring at 300 rpm in a 50 mL Erlenmeyer flask. Since the volume of the samples was not constant due to the bubble evolution both in aqua regia and in HCl-H2O$_2$ mixed solution, each volume of the sample was measured after the sampling. The amount of dissolved metals was analyzed by ICP-AES (SPS-7800, SII).

Time dependence of the redox potential of solutions was measured using a tantalum wire electrode which had aqua regia-resistant feature and an Ag/AgCl reference electrode at 298 and 333 K.

The volatilization rate of oxidant in aqua regia was measured as follows: The aqua regia was prepared in a vial, and nitrogen gas flowed through the vial at 20 mL/min. The vaporized oxidants were trapped in the potassium iodine solution. The amount of trapped oxidants was measured by iodine produced by the oxidant using UV/Vis spectroscopy (Ocean Optics USB2000 with tungsten-halogen lamp). The iodine concentration was estimated with the absorbance of 450 nm ($\leq 9 \times 10^{-3}$ M), the average of 500 and 550 nm ($\leq 3 \times 10^{-3}$ M), 600 nm ($\leq 9 \times 10^{-3}$ M) and 650 nm (more than $9 \times 10^{-3}$ M), respectively.

3. Result and discussion

3.1 Dissolution for Pt and PtRu by electrochemical methods

Figure 3 shows cyclic voltammograms of a Pt/CP-modified electrode immersed in 1 M H2SO4 and HCl in alternate shifts. It is well known that the ECSA of a Pt bare electrode cannot be estimated in solutions containing chloride ion because of the adsorption of chloride ions onto Pt atoms, whereas the ECSA of Pt/CP in H2SO4 (19.6 cm$^2$) was only 4% larger than that in HCl (18.6 cm$^2$) indicating that Nafion ionomer, which has a large pK$_a$ (70), prevents the adsorption of chloride ions onto Pt atoms within a short time period. Thus, the measurements of ECSA during Pt dissolution tests in HCl solution were performed in the same solution. In a HCl solution, Pt atoms were electrochemically oxidized to be dissolved as tetrachloroplatinate or hexachloroplatinate ions as shown below:

$$\text{Pt} + 4\text{Cl}^- \rightarrow [\text{PtCl}_4]^{2-} + 2e^- \quad E^c = +0.758 \text{ V vs. SHE} \quad (1)$$
$$\text{Pt} + 6\text{Cl}^- \rightarrow [\text{PtCl}_6]^{2-} + 4e^- \quad E^c = +0.744 \text{ V vs. SHE} \quad (2)$$

These reactions can be confirmed in the cyclic voltammogram based on the increase in the anodic current above 0.55 V vs. Ag/AgCl, and the cathode peak around 0.2 V vs. Ag/AgCl in 1 M HCl might be attributable to the reduction of platinum chloride complexes ([PtCl$_4$]$^{2-}$ and [PtCl$_6$]$^{3-}$).

Figure 4 shows the cyclic voltammograms of Pt/CP electrodes in various electrolytes before and after 1 min of an electrochemical Pt dissolution test. The RSD of ECSA for Pt/CPs based on hydrogen adsorption/desorption region in CVs was 6.0%. The deviation is probably due to the difference in degree of electrolyte penetration into CPs.

In HCl solution, ECSA decreased after 1 min of the Pt dissolution test. On the other hand, in H2SO4 or HClO$_4$ solution, ECSA increased after 1 min of the Pt dissolution test probably due to the atomization of Pt and the oxidative elimination of adsorbates on Pt. ECSA started decreasing after 2 to 3 min of the Pt dissolution test in the solutions.
Figure 5 depicts the time dependence of relative ECSA in various electrolytes during an electrochemical Pt dissolution test. In H₂SO₄ and HClO₄ solutions, it is expressed that the time at maximum ECSA value was zero for a lifetime analysis. Assuming that decreasing rate of ECSA of Pt is proportional to ECSA to estimate apparent reaction rates, the time dependence of relative ECSA (A/A₀) is expressed as:

\[ A/A₀ = \exp(-t/\tau) \]  

where \( A \) (cm²) is the ECSA at \( t \) (s), \( A₀ \) (cm²) is initial ECSA, \( \tau \) (s⁻¹) is a dissolution time constant. The time constants, \( \tau \) in Eq. (3) in the solutions were estimated by using non-linear least square method. The summary was shown in Table 1. It is demonstrated that the dissolution rate of Pt in a HCl solution was about 50 times as fast as those in H₂SO₄ and HClO₄ solutions. Table 1 also shows the amount of Pt dissolution determined by ICP-AES after 20 min of the Pt dissolution test. Almost all Pt in Pt/C was dissolved in the solution using a 1 M HCl solution. Pt dissolution in H₂SO₄ solution was well studied by Kamiya et al.,16,17 and the mechanism of Pt dissolution in HClO₄ seems to be similar to that in H₂SO₄ solution.

Figure 6 shows the time dependence of relative ECSA estimated by hydrogen adsorption/desorption region in CVs during the Pt dissolution test. The kinetic analysis is summarized in Table 2. The Pt dissolution rate increased linearly with HCl concentration. On the basis of ICP-AES analysis, Pt in Pt/C was dissolved up to 95% (0.5 M HCl), 94% (1 M), and 96% (2 M) HCl, respectively. The rest would be trapped in Naﬁon ionomer or insulated platinum produced by oxidation of carbon support.

Figure 7 shows the dependence of relative ECSA on time with electrochemical fluctuations shown in Fig. 2 in 1 M HCl. Since the dissolution of Pt and the formation of Pt oxide species occur competitively, the rate of Pt dissolution decreases with time at higher potentials, thus the reduction of Pt surface species is needed in the electrochemical dissolution method. The influence of Pt oxide formation rate can be investigated with waveforms of (f) and (g). The kinetic analysis is also summarized in Table 2. Using constant potentials, the Pt dissolution rate increased with potential, and the maximum rate was exhibited at 0.9 V though

Table 1. Result of Pt dissolution tests in various electrolytes.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>( \tau )/s</th>
<th>Std. error</th>
<th>( R^2 )</th>
<th>Dissolution /%</th>
<th>Analysis range /s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M H₂SO₄</td>
<td>3712</td>
<td>1.6 \times 10²</td>
<td>0.967</td>
<td>17</td>
<td>0–840</td>
</tr>
<tr>
<td>1 M HClO₄</td>
<td>2758</td>
<td>1.3 \times 10²</td>
<td>0.961</td>
<td>20</td>
<td>0–660</td>
</tr>
<tr>
<td>1 M HCl</td>
<td>78</td>
<td>5</td>
<td>0.991</td>
<td>94</td>
<td>0–360</td>
</tr>
</tbody>
</table>
Table 2. Result of Pt dissolution tests in HCl.

<table>
<thead>
<tr>
<th>Potential waveform</th>
<th>[HCl] /M</th>
<th>( \tau /s )</th>
<th>Std. error</th>
<th>( R^2 )</th>
<th>Analysis range /s</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 0.7 V</td>
<td>1.0</td>
<td>665</td>
<td>26</td>
<td>0.969</td>
<td>0–480</td>
</tr>
<tr>
<td>(b) 0.9 V</td>
<td>1.0</td>
<td>302</td>
<td>6.3</td>
<td>0.995</td>
<td>0–480</td>
</tr>
<tr>
<td>(c) 1.2 V</td>
<td>1.0</td>
<td>426</td>
<td>12</td>
<td>0.990</td>
<td>0–480</td>
</tr>
<tr>
<td>(d) SW-1</td>
<td>0.5</td>
<td>155</td>
<td>16</td>
<td>0.953</td>
<td>0–480</td>
</tr>
<tr>
<td>(d) SW-1</td>
<td>1.0</td>
<td>78</td>
<td>5.0</td>
<td>0.991</td>
<td>0–360</td>
</tr>
<tr>
<td>(d) SW-1</td>
<td>2.0</td>
<td>33</td>
<td>2.1</td>
<td>0.997</td>
<td>0–300</td>
</tr>
<tr>
<td>(e) RW-1</td>
<td>1.0</td>
<td>27</td>
<td>0.41</td>
<td>0.999</td>
<td>0–360</td>
</tr>
<tr>
<td>(f) SW-2</td>
<td>1.0</td>
<td>49</td>
<td>2.1</td>
<td>0.999</td>
<td>0–480</td>
</tr>
<tr>
<td>(g) SW-3</td>
<td>1.0</td>
<td>204</td>
<td>8.8</td>
<td>0.983</td>
<td>0–480</td>
</tr>
<tr>
<td>(h) SW-4</td>
<td>1.0</td>
<td>16</td>
<td>0.41</td>
<td>0.998</td>
<td>0–180</td>
</tr>
</tbody>
</table>

Figure 7. Time dependence of Pt dissolution with various waveforms shown in Fig. 2 in 1 M HCl at R.T. The curves are the best fitted ones according to Eq. (3).

Figure 8. Time dependence of Pt dissolution with (d) SW-1 at R.T.

Figure 9. Time dependence of Pt dissolution with aqua regia (×), 1 M HCl-0.36 M H₂O₂ (○), 1 M HCl-10.3 M H₂O₂ (□), and 11.3 M HCl-0.36 M H₂O₂ mixture (●) at R.T.

the rate decreased with the potential over 0.9 V. This is because the formation of Pt oxide species, which are produced by competitive reactions with the Pt dissolution, quickened at higher potential above 0.9 V. It is elucidated that the Pt dissolution under potential fluctuations as shown in Fig. 2 is faster than that under constant potentials. This is because the Pt oxide species are repetitively removed under lower potentials applied by the potential fluctuations. When high potential was applied shortly, the total efficiency of Pt dissolution would decrease. Since the Pt dissolution rates with (d) SW-1 and (g) SW-3 was slower than those with other waveforms, it is suggested that the reduction of Pt oxide species does not need so long time. The Pt dissolution rate using SW-4 was faster than any other potential waveform in Fig. 2 since SW-4 consists of high potentials enough to dissolve Pt during long time compared to RW-1. The Pt dissolution rate reached 15 times as fast as that with constant potentials. Ninety-seven percent of ECSA of a Pt/CP decreased within 1 min with SW-4. It was confirmed that the 97% of Pt in the Pt/CP was dissolved using the analysis of the solution after 20 min by ICP-AES.

The results of electrochemical dissolution test of PtRu/CP were shown in Fig. 8. The dissolution rate of PtRu/CP was similar to that of Pt/CP, indicating that the electrochemical dissolution method can also be applied to the dissolution of PtRu catalysts. The amount of Pt and Ru in solution increased with time, and reached a plateau at 10 min. The final percentages of Pt and Ru are 83 and 79%, respectively. These values were lower than that with Pt/CP. The large catalyst loading of PtRu/CP (2.9 mg cm⁻²) compared to that of Pt/CP (0.3 mg cm⁻²) formed the thicker layer of the catalysts to prevent metal particles from dissolving.

3.2 Dissolution of Pt by chemical methods

Time dependence of relative amount of Pt during chemical dissolution tests are shown in Fig. 9. The Pt dissolution rate decreased according to the order of aqua regia, 11.3 M HCl-0.36 M H₂O₂, 1 M HCl-10.3 M H₂O₂, and 1 M HCl. The increase of hydrogen peroxide concentration hardly raised the Pt dissolution rate in 1 M HCl. Although Pt was usually dissolved under heated condition with aqua regia, Pt nanoparticles in Pt/CP were dissolved under room temperature (R.T.) because of the high surface area. However, 20% of Pt in Pt/CP still remained in Pt/CP with aqua regia even after 2 h. Moreover, Pt dissolution rates with other chemical methods were so slow that it does not reach steady state. That is why the percentages of residue could not be determined.

The reactions of Pt dissolution in aqua regia are:

\[
\text{HNO}_3 + 3\text{HCl} \rightarrow \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O} \tag{4}
\]

\[
\text{Pt} + 2\text{NOCl} + \text{Cl}_2 + 2\text{Cl}^- \rightarrow [\text{PtCl}_6]^{2-} + 2\text{NO} \tag{5}
\]

A Pt atom is dissolved as a hexachloroplatinate(IV) ion. Since Pt atoms in Pt/CP are incorporated into Nafton® ionomer, the Pt dissolution rate is controlled by low permeation coefficients of anion such as chloride, which is derived from a strong pKₐ of Nafton® as mentioned above.
The regions where Pt particles existing can be assumed to be distinguished as follows: the one is the region 1 where Nafion® ionomer covering Pt particles are so thick that the Pt dissolution is slow, the other is the region 2 where Nafion® ionomer are so thin that the Pt dissolution rate is fast. On the basis of the assumption described above, the Pt dissolution rates can be analyzed by the two terms expressed as the addition of each region.

\[ S_T = S_1\exp(-t/\tau_1) + S_2\exp(-t/\tau_2) \]  
\[ \text{where } S_T(\%)\text{ is the total percentage of Pt, } S_1(\%) \text{ and } S_2(\%) \text{ are the percentage of Pt in region 1 and 2, respectively. } \tau_1(s) \text{ and } \tau_2(s) \text{ are time constants corresponding to the region 1 and 2, respectively. The relationship between } S_1 \text{ and } S_2 \text{ must be as follows:} \]
\[ S_1 + S_2 = 100 \]  
(6)  
(7)

Equation (6) was applied to the relationship between time and the percentage of dissolved Pt in Fig. 9 using a nonlinear least-square method. The result are summarized in Table 3. Twenty-six percent of Pt particles still existed in region 1, and its time constant was 4.2 × 10^4 s. The time constant in region 2 was larger than that by the electrochemical method.

Since volatile NOCl and Cl₂, whose bubbles are visually confirmed even in R.T., are strong oxidants in aqua regia as shown above, the shorter dissolution time is more favorable for more quantitative use with less loss. The oxidation potential of aqua regia should be decreased with the vaporization of such oxidant gasses. Thus, it may not be suitable to use aqua regia for the dissolution of Pt existing in a Nafion ionomer.

The reactions of the Pt dissolution with HCl-H₂O₂ mixed solution are represented as follows:\textsuperscript{10,11}

\[ \text{Pt} + H_2O_2 + 4HCl \rightarrow [PtCl_4]^{2-} + 2H^+ + 2H_2O \]  
\[ \text{Pt} + 2H_2O_2 + 6HCl \rightarrow [PtCl_6]^{2-} + 2H^+ + 4H_2O \]  
\[ H_2O_2 + 2HCl \rightarrow Cl_2 + 2H_2O \]

Cl₂ evolution expressed by Eq. (10) proceeds as well as the Pt dissolution by Eqs. (8) and (9) using HCl-H₂O₂ mixed solution. The solution of 11.3 M HCl-0.36 M H₂O₂ turned yellow, which color is originated from Cl₂, and a large quantity of Cl₂ evolved immediately after the preparation. It is therefore difficult to use the solution without any loss. Therefore, chemical methods have common problems as follows: difficulty of a quantitative use and the low recovery rate of Pt.

Figure 10 shows time dependence of Pt dissolution in 1.0 M HCl at 298 K (○), 313 K (◇), 328 K (+), and 343 K (×).

Figure 11 shows time dependence of equilibrium potential in aqua regia at 298 K (○), at 333 K (●), and 1 M HCl at R.T. (−−). The time dependences of the total amount of volatile oxidant are shown in Fig. 12. The initial volatilization rates were analyzed as follows: The deviation of the oxidant concentration in the solution (C₁ mol cm⁻³) is expressed as:

\[ \frac{dc_1}{dt} = -\frac{k_1S_1C_1}{V_s} \]  
(11)

where \( k_1 \) (mol⁻¹ cm² s⁻¹) is the volatilization rate constant, \( S_1 \) (cm²) is the gas-liquid interface, \( t \) (s) is the time, and \( V_s \) (cm³) is the volume of the solution. The deviation of the oxidant concentration in the gas phase (C₂ mol cm⁻³) is represented as:

\[ \frac{dc_2}{dt} = -\frac{k_1S_1C_1 - C_2Q}{V_g} \]  
(12)

where \( Q \) (cm³ s⁻¹) is the volumetric flow rate for N₂ gas. Equations (11) to (12) were solved as:

\[ C_1(t) = C_T \exp\left(-\frac{k_1S_1}{V_s}\right) \]  
(13)
Electrochemistry, 80(11), 898–903 (2012)

Figure 12. (Color online) Time dependence of the total amount of oxidants from aqua regia. O, condition 1 (V_S = 4 mL, V_G = 9.2 mL, S = 3.6 cm², $Q = 0.33 \text{ cm}^3 \text{s}^{-1}$, $T = 298 \text{ K}$); ▼, condition 2 (V_S = 4 mL, V_G = 32.8 mL, S = 5.2 cm², $Q = 0.33 \text{ cm}^3 \text{s}^{-1}$, $T = 298 \text{ K}$); O, condition 3 (V_S = 4 mL, V_G = 32.8 mL, S = 5.2 cm², $Q = 0.33 \text{ cm}^3 \text{s}^{-1}$, $T = 333 \text{ K}$).

$C_1(t) = \frac{k_1 C_1 S V_S}{Q V_S - k_1 S V_G} \left[ \exp \left( -\frac{k_1 S V_G}{V_S} \right) - \exp \left( -\frac{Q t}{V_G} \right) \right]$ (14)

where $C_1$ (mol cm⁻³) is the total concentration of oxidants. The total amount of volatile oxidant $n_{\text{vol}}$ (mol) is represented as follows:

$n_{\text{vol}} = \int_0^t C_2(t) dt$

$= \frac{Q}{Q V_S - k_1 S V_G} \left[ k_1 S V_G \left\{ \exp \left( -\frac{Q t}{V_G} \right) - 1 \right\} - Q V_S \left\{ \exp \left( -\frac{k_1 S V_G}{V_S} \right) - 1 \right\} \right]$ (15)

The volatilization rate constant, $k_1$, was estimated with Eq. (15) by non-linear least square method. The best fitting curves are also shown in Fig. 12. The summary of the analysis is shown in the Table 4. It is elucidated that the volatilization rate at 333 K was 40 times as fast as that at 298 K.

4. Conclusions

An electrochemical Pt dissolution method was developed with potential fluctuation waves. The Pt dissolution rate with a saw-tooth wave was 15 times as fast as that with constant potentials and those with chemical methods. Although the dissolution method using fluctuated potentials can be applied to the dissolution of metals in PtRu/CP, the further investigation is needed for the improvement of recovery rate when the amount of catalyst loadings is high such as direct methanol fuel cells. It is elucidated that chemical methods have common problems such as difficulty of a quantitative use and the low recovery rate of Pt.

Acknowledgment

This study was partly supported by a Grant-in-Aid for Scientific Research on Waste from the Ministry of the Environment of Japan.

Table 4. Volatilization rate constants based on Eq. (15) using a non-linear least square method.

<table>
<thead>
<tr>
<th>T/K</th>
<th>$k_1$ /mol⁻¹ cm³ s⁻²</th>
<th>Error of $k_1$ /mol⁻¹ cm³ s⁻²</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$1.28 \times 10^{-6}$</td>
<td>$6.6 \times 10^{-8}$</td>
<td>0.91</td>
</tr>
<tr>
<td>333</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>0.90</td>
</tr>
</tbody>
</table>

References