Meniscus Formation and Hydrogen Oxidation on Partially Immersed Pt-Carbon Electrode

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Meniscus formation and hydrogen oxidation on partially immersed Nafion® coated and uncoated electrodes were investigated as a model of the reaction sites in polymer electrolyte fuel cells. Hydrogen oxidation current was measured at 0.4 V with raising the electrode, and simultaneously the optical microscope observation was carried out. The intrinsic meniscus developed from the boundary between Nafion®-coated (Pt-loaded) and the uncoated parts. A liquid thin film, which would have sub-micron order thickness, was observed above the intrinsic meniscus on the uncoated electrode under hydrogen atmosphere after development of the intrinsic meniscus was terminated. At the same time, hydrogen oxidation current was further increased. Therefore, the liquid thin film behaved as an effective supermeniscus on the uncoated electrode. On Nafion®-coated electrode, hydrogen oxidation current was small in the intrinsic meniscus region; however, it became larger with an increase in the exposed area of Nafion®-coated part to the gas phase. This fact showed that hydrogen oxidation reaction occurred mainly in the exposed Nafion®-coated part. The current distribution in the supermeniscus region was discussed, and it was found that the effective area is controlled by the ohmic drop in the Nafion® coating.

Key Words: PEFCs, Triple-phase Boundary, Supermeniscus, Hydrogen Oxidation Reaction

1 Introduction

Polymer electrolyte fuel cells (PEFCs) have been developed intensively for the power sources of electric vehicles and for stationary co-generation systems.1-2 A dramatic reduction of Pt amounts in the catalyst layers and a remarkable improvement of durability of the cell components are major concerns for the commercialization of PEFCs.3-10 As for the former issue, an improvement in the activity of platinum catalyst and an increase of Pt utility in the catalyst layer are necessary to reduce the catalyst cost. In PEFCs, the electrochemical reactions, hydrogen oxidation (HOR) and oxygen reduction (ORR), only occur at the interface among the electrode, the electrolyte, and the reactant gas, so-called triple-phase boundary (TPB), in the porous catalyst layer. Because water is fixed in the polymer electrolyte as swelling water, no free liquid electrolyte solution penetrates into pores in the catalyst layer. This restricts effective reaction area. In order to expand TPB, localizing platinum particles and impregnation of Nafion® solution in the catalyst layer have been attempted.11-14 In fact, the discharge current of PEFCs is significantly increased by the impregnated Nafion®.14

In spite of the importance of gas-diffusion electrodes in PEFCs, fundamental aspects such as mass transport of gases and proton in the gas-diffusion electrodes have not been sufficiently understood so far. This is partly because the microstructure of the catalyst layer in practical gas-diffusion electrodes is very complicated. Several reports have been published on the modeling of the gas-diffusion electrodes in PEFCs.15-18 In these papers, Nafion®-coated electrodes were fully immersed in the electrolyte solution, and therefore their configurations are fairly different from the microstructure of the catalyst layer in PEFCs and thereby give less useful information.

We have applied partially immersed electrode systems for the investigation of the gas-diffusion electrode in PEFCs.19 20 Mass transport of the gases and proton in these systems will be very similar to that in the catalyst layer of PEFCs. In particular, on the partially immersed Nafion®-coated electrode system as represented in Fig. 1, hydrogen diffuses across the Nafion® film and reacts on the electrode catalysts and the current is carried by pro-
ton through the Nafion® film, and finally diffuses into the bulk electrolyte solution. Our previous study suggested that the exposed Nafion® film in the gas phase was effective for HOR, and hence formation of the meniscus, including not only intrinsic meniscus (IM) but also supermeniscus (SM), is a key factor for clarifying the mass transport in this system.

In the present study, we attempted the visualization of the meniscus formation under HOR with raising the Nafion®-coated electrode to estimate the meniscus length and discussed the correlation between meniscus formation and HOR current.

2 Experimental

2.1 Reagents

Highly pure water was obtained by circulating distilled water through a Nanopure water purification system (Barnstead, D4746). Hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, 99.9%, Aldrich) and sulfuric acid (98%, Nakarai, analytical grade) were diluted with the highly pure water. Argon gas was of ultra-high purity (Teisan Inc.) and hydrogen gas was obtained from hydrogen generator (Parker Barston Model H2-500). Nafion® solution (Aldrich, equivalent weight: 1100 g mol⁻¹, 5 wt% dissolved in a mixture of lower aliphatic alcohols and 10% water) was diluted with ethanol (Nakarai Tesque) and used for Nafion® coating.

2.2 Preparation of Nafion®/Pt/GC electrode

A mirror polished glassy carbon plate (GC, 1.2 × 0.5 × 0.02 cm, Tokai Carbon Co. Ltd., GC-SS20) was employed as a substrate. Pt particles were deposited on the GC plate by electrodeposition. The upper part (0.6 cm from the top) of the GC was covered with polytetrafluoroethylene (PTFE) tape, and platinum particles were electrodeposited on the exposed part of both surfaces (0.6 × 0.5 cm, total area: 0.6 cm²). The electrolyte solution for electrodeposition of Pt particles was 5 mmol dm⁻³ H₂PtCl₆ dissolved in 0.5 mol dm⁻³ (M) H₂SO₄. The counter electrode was a Pt wire with a surface area larger than that of GC. Electrodeposition was carried out under argon atmosphere with a current pulse from a voltammetry system (Hokuto Denko, HSV-100). The pulse current was 1.0 mA and the pulse width was 50 s. Hereafter this electrode is denoted as Pt/GC. After deposition, the Pt/GC electrode was thoroughly rinsed with highly pure water and then dried in air.

Nafion® solution was diluted with ethanol, and was dropped carefully on the Pt-loaded part of Pt/GC using a micro-syringe to obtain a film of 250-nm thickness. The upper Pt-unloaded part of the electrode was covered with PTFE tape again to restrict Nafion® film only on the Pt-loaded part. The thickness of Nafion® film was calculated using the density of Nafion® solution (0.874 g cm⁻³) and the polymer density of Nafion® (1.98 g cm⁻³). The electrode was placed immediately in a glass chamber to shield the electrode from irregular air stream. After a stable film was formed on the electrode, the PTFE tape was removed and the electrode was further dried overnight at room temperature. This electrode is hereafter called Nafion®/Pt/GC. The well-dried electrode surface was observed by scanning electron microscopy (SEM, Hitachi, S-3000H).

Contact angles for water on these materials were evaluated to determine their wettability using a contact angle meter (Kyowa Interface Science, Model CA-A).

2.3 Electrochemical measurements and microscope observation

A three-electrode electrochemical cell made of a flat, optically polished glass was used for the electrochemical measurements and in-situ microscope observation. The cell was placed on an anti-vibration table to avoid vibrations. The Pt/GC or Nafion®/Pt/GC electrode was set at the lower end of a PTFE-coated stainless steel rod, and placed in the center of the cell. The upper end of the rod was attached to a micrometer head and the height of the electrode, h, was adjusted using the micrometer within an accuracy of ± 0.01 mm. A reversible hydrogen electrode (RHE) connected through a Luggin capillary was used as a reference electrode. All potentials in this paper are given against RHE. Platinum mesh were placed on the bottom of the cell and used as a counter electrode. The electrolyte solution was aqueous 0.5 mol dm⁻³ H₂SO₄ solution. All electrochemical measurements were carried out at room temperature using a potentiostat (ALS, Model 900).

Pt-loaded part of the electrode was fully immersed in the electrolyte solution and the cyclic voltammograms (CVs) were obtained in the potential range of 0.05 to 1.5 V under an argon atmosphere to activate the Pt catalysts and to confirm the purity of the electrochemical system. After the CV measurements, the electrolyte solution was saturated with hydrogen and then steady state polarization curves were obtained at the fully immersed position in the potential range of OCP to 0.6 V. A constant potential of 0.4 V was then applied to the working electrode, and the electrode was raised stepwise from the fully immersed position (h = 0 mm) to h = 6 mm in the same manner as reported elsewhere. Steady-state HOR current was measured as a function of electrode position (h).

The electrode surface was observed at different h’s with an optical microscope (Keyence Corp., VH-Z75), which was placed at a few centimeters apart from the
electrochemical cell. The upper edge of the intrinsic meniscus formed on the electrode [Fig. 1 a)] was focused to observe the morphology changes of the boundary between the gas and liquid phase on the electrode; i.e. TPB. Because TPB might be affected by the electrochemical reaction, the microscope observation was also carried out under argon atmosphere as well as under hydrogen atmosphere.

3 Results and Discussion

3.1 Characterization of the electrode materials

Figure 2 shows a typical SEM image of the surface of Nafion/Pt/GC. Pt particles of ca. 200 nm in size were thickly deposited on the GC surface. The thickness of Nafion® film was determined as 250 nm to cover all Pt particles, though the thickness of the electrolyte thin film in the electrode catalyst layer of PEFCs might be thinner. Because Pt particles in nanometer size are used as catalysts in PEFCs, optimization of the deposition parameters to obtain uniform Pt nanoparticles is still necessary to construct the idealized model of TPB in PEFCs.

The shape and the maximum height of the meniscus formed on a partially immersed electrode are greatly affected by physical properties of the surface of the electrodes, in particular wettability. The contact angles for a water drop of the electrode materials are summarized in Table 1. The contact angle for wet Nafion/Pt/GC was quickly measured after immersing the dry one in water for two days and wiped off water drops on the surface by filter paper. As shown in Table 1, the contact angle of Pt/GC was lower than that of bare GC. There are two reasons for the decrease in wettability by Pt deposition. One is an increase in surface roughness by Pt deposition and the other is the hydrophilic nature of deposited Pt particles. Furthermore, Nafion® coating resulted in a significant decrease in contact angle when it was wetted. Based on these results, it can be predicted that intrinsic meniscus develops from the boundary between Pt loaded and unloaded parts for Pt/GC, while it develops from the boundary between Nafion®-coated and uncoated parts for Nafion/Pt/GC when the electrodes are raised from h = 0 mm.

3.2 Cyclic voltammograms in argon atmosphere

Figure 3 shows the cyclic voltammogram in the 100th cycle obtained for Pt/GC and Nafion/Pt/GC. The Pt-loaded part was fully immersed in the electrolyte solution (h = 0 mm) in each case. Both electrodes showed well-defined voltammograms typical of platinum in aqueous H₂SO₄. These facts insure high activity of the platinum layer as well as cleanliness of the system. The estimated roughness factors of Pt/GC and Nafion/Pt/GC were ca. 3.9 and 3.5, respectively.

3.3 Steady-state polarization curves at the fully immersed position in hydrogen atmosphere

Steady-state polarization curves for HOR current on Pt/GC and Nafion/Pt/GC at h = 0 mm are shown in Fig. 4. On each electrode, the current increased with increasing potential up to 0.1 V, and it remained constant at potentials more positive than 0.1 V. The constant current was hardly affected by the presence of Nafion® film at the fully immersed position, and therefore HOR current was limited by the diffusion of hydrogen in the bulk solution at potentials more positive than 0.1 V. Because the primary object in the present study is to understand the mass-transport aspects of the gas-diffusion electrodes in PEFCs, a relatively large overvoltage of 0.4 V was employed in the following experiments, though the anode overvoltage in practical PEFCs is much lower.

3.4 Hydrogen oxidation on Pt/GC and Nafion/Pt/GC when raised from the fully immersed position

Figure 5 shows the HOR current observed at 0.4 V of Pt/GC and Nafion/Pt/GC electrodes. HOR current was nearly constant (ca. 40 μA) up to h = 20 mm on the both electrodes, where the intrinsic meniscus was partially

Table 1 Contact angles of water drop of electrode materials used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Contact angle/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare GC</td>
<td>63</td>
</tr>
<tr>
<td>Pt/GC</td>
<td>37</td>
</tr>
<tr>
<td>Nafion/Pt/GC</td>
<td>5</td>
</tr>
</tbody>
</table>

Fig. 2 SEM image of Nafion/Pt/GC electrode surface.

Fig. 3 Cyclic voltammograms of Pt/GC (solid line) and Nafion/Pt/GC (dashed line) in argon-saturated 0.5 M H₂SO₄.
developed on the electrode surface as shown later. This result shows that the current was limited by hydrogen diffusion in the bulk solution up to \( h = 2.0 \) mm even though the intrinsic meniscus was partially developed. On Pt/GC electrode, the current steeply increased with raising the electrode in the range of \( h = 2.0 \) to 42 mm, and finally it became constant again until \( h = 6.0 \) mm. In contrast, on the Nafton/Pt/GC electrode, the oxidation current was reached to the maximum at \( h = 3.4 \) mm, and the maximum current was smaller than that for the uncoated one. This is due to a difference in intrinsic and supermeniscus formation between the two electrodes as will be described in the following sections.

3. 5 Meniscus formation on Pt/GC under inert conditions

A constant potential of 0.4 V was applied under argon atmosphere to observe meniscus formation on Pt/GC. In this condition, we did not observe any significant current due to the electrochemical reactions. The boundary between the gas and the liquid phase on the electrode was flat; that is, no meniscus was formed at \( h = 0 \) mm. The electrode was raised from the fully immersed position, and at every 200 \( \mu \)m the current and the electrode surface were monitored. Microscope images obtained at various positions are summarized in Fig. 6. Figure 6 a) shows the image at \( h = 3.0 \) mm, at which the intrinsic meniscus was almost fully developed. The upper half of the image shows the bare GC surface (i.e., Pt unloaded part); on the other hand, adhered liquid is seen in the lower half, which shows that the intrinsic meniscus developed on the electrode as a consequence of raising the electrode. The electrode surface image obtained at \( h = 3.2 \) mm is shown in Fig. 6 b). When compared with Fig. 6 a), the upper edge of the meniscus was moved upward with a 200-\( \mu \)m raise of the electrode. This fact proved that the intrinsic meniscus is developed from the interface between the Pt loaded and unloaded parts. This is due to the difference in wettability to water between the two parts as shown in Table 1. In addition, the upper part of the intrinsic meniscus was pale brown while the lower part was black, which indicated that the thickness of the meniscus becomes thinner with an increase in the distance from the bulk electrolyte solution.

The electrode was then carefully raised upward to \( h = 3.4 \) mm [Fig. 6 c)]. Optical interference was observed just above the intrinsic meniscus edge, which shows the formation of supermeniscus. The optical interference indicates the formation of a liquid thin film with a thickness of the order of sub-micrometers as is observed on soap bubbles.\(^{22}\) Observation was continued with further rising of the electrode, and the length of the supermeniscus was extended to ca. 0.4 mm at \( h = 3.6 \) mm in Fig. 6 d). At the fully raised position (\( h = 6.0 \) mm), the supermeniscus length was extended to ca. 2.8 mm while the intrinsic meniscus height was remained at ca. 3.2 mm from the bottom of the electrode.

3. 6 Meniscus formation on Pt/GC under hydrogen atmosphere

Figure 7 shows optical microscope images of Pt/GC electrode surface at 0.4 V under hydrogen atmosphere. All of the images were recorded when the steady-state HOR current was obtained. The images obtained up to \( h = 3.2 \) mm [Figs. 7 a) and b)] were almost the same as those under inert atmosphere [Figs. 6 a) and b)], showing the growth of the intrinsic meniscus. The intrinsic meniscus developed and became sharper with raising the electrode in this region. The image obtained at \( h = 3.4 \) mm is shown in Fig. 7 c). Optical interference similar to Fig. 6 c) was observed above the intrinsic meniscus while the development of the intrinsic meniscus was terminated. Hence, the maximum height of the intrinsic meniscus was 3.2 mm under hydrogen atmosphere, which was equal to that under inert atmosphere as shown in Fig. 6.

Figure 7 d) shows the image obtained at \( h = 3.6 \) mm. The supermeniscus region showed optical interference with several fringes, which were not observed under inert conditions [Fig. 6 d)]. The presence of the fringes

![Fig. 4](image-url) Steady-state polarization curves for hydrogen oxidation on Pt/GC and Nafton/Pt/GC at the fully immersed position in hydrogen-saturated 0.5 M H\(_2\)SO\(_4\).

![Fig. 5](image-url) Variations of hydrogen oxidation current at 0.4V with electrode position on partially immersed Pt/GC and Nafton/Pt/GC in hydrogen-saturated 0.5 M H\(_2\)SO\(_4\).
suggested that the thickness of the supermeniscus was irregular and larger than that observed under the inert conditions. Moreover, the fringes developed upward from the upper edge of the intrinsic meniscus when the electrode was raised, which suggested that the electrolyte solution crept up by HOR, and made the supermeniscus thicker. The creep of the electrolyte can be explained by electromigration of sulfate ion in the upward direction from the solution. The microscope image obtained at $h = 6$ mm is shown in Fig. 7 e), at which the length of the intrinsic meniscus remained unchanged (ca. 3.2 mm). The fringes were observed at the top and the bottom edges of the supermeniscus, and in between the interference disappeared. This would be due to a further growth of the supermeniscus to form a thicker liquid thin film by HOR, and hence the maximum length of the effective supermeniscus can be estimated to be ca. 1.0 mm including the fringe region while the thickness of the supermeniscus is not determined.

Bockris and Cahan\textsuperscript{21} reported similar observation results that fringes and liquid film appeared above the upper edge of the intrinsic meniscus on a partially wetted Pt film electrode surface under hydrogen and oxygen atmosphere. Furthermore, they observed that the intrinsic meniscus was destructed by applying potentials and a finite-contact angle meniscus (termed FCAM) formed above the intrinsic meniscus. The liquid thin film was formed by the destruction of the intrinsic meniscus and was isolated from the intrinsic meniscus in their observation, and hence they concluded that the liquid thin film (supermeniscus) is not effective for electrochemical reactions.\textsuperscript{22,23} In this regard, our results are different from theirs. As shown in Figs. 7 d) and e), an increase of the thickness of the supermeniscus was observed, but the supermeniscus was still connected through the fringe region to the intrinsic meniscus at 0.4 V in hydrogen atmosphere. Therefore, not only the intrinsic meniscus, but also the supermeniscus effectively worked for HOR in the present study.

The change in the morphology of the supermeniscus and its effectiveness were also confirmed by the results shown in Fig. 8, which shows the variation of HOR current [Fig. 8 a]) and the morphology changes of the supermeniscus with time obtained at $h = 6.0$ mm. Before polarization [Fig. 8 b)], the supermeniscus similar to Fig. 6 e)
in the inert atmosphere was observed. As shown in Fig. 8 a), when a constant potential of 0.4 V was applied, the current once slightly increased up to 30 s, and then monotonously decreased with time. The thickness of the supermeniscus gradually increased from the upper edge of the intrinsic meniscus with rising the electrolyte solution as shown in Fig. 8 b) and c). Then, at 1 min, several fringes were observed at the edge of intrinsic meniscus as shown in Fig. 8 d). Finally its length had reached ca. 1.0 mm at 3 min [Fig. 8 e)]. Thus, thickening of the supermeniscus progressed as a consequence of HOR, but still large currents were obtained. This proves effectiveness of the supermeniscus for HOR.

3.7 Meniscus formation on Nafion/Pt/GC under hydrogen atmosphere

The meniscus formation on Nafion/Pt/GC was observed at 0.4 V under hydrogen atmosphere in the same manner. The results for Nafion/Pt/GC electrode under inert conditions are not described because they were quite similar to those observed under hydrogen atmosphere.

The variation of the TPB region on Nafion/Pt/GC is summarized in Fig. 9. Figure 9 a) shows the image obtained at \( h = 2.4 \) mm. Bare GC surface and the fully

![ Optical microscopic images of Pt/GC electrode surface at \( h = a) 3.0, b) 3.2, c) 3.4, d) 3.6, and e) 6.0 \) mm under polarized at 0.4 V in hydrogen-saturated 0.5 M H\(_2\)SO\(_4\). Vertical bars indicate 0.2 mm. Un: unloaded part; IM: intrinsic meniscus; SM: supermeniscus. ](image-url)
developed intrinsic meniscus are seen at the upper and lower half, respectively. When the electrode was raised further to \( h = 2.6 \) mm, Nafion\(^\circledR\) film coated on the electrode was exposed by 0.1 mm to the gas phase as shown in Fig. 9 b). Thus, the maximum height of the intrinsic meniscus formed on Nafion/Pt/GC can be estimated to be ca. 2.4 mm, which was shorter than that formed on the uncoated one. Additionally, the upper edge of the intrinsic meniscus was shinning and seemed roughly, which suggests that the contact angle between the electrode surface and the intrinsic meniscus would be larger than that on the uncoated electrode. Hence, the thickness of the upper part of intrinsic meniscus on the coated electrode would be larger than that formed on the uncoated electrode. The differences in the maximum height and the contact angle might be attributed to a change in surface tension by Nafion\(^\circledR\) coating and/or a change in surface roughness.

Figure 9 c) shows the image at \( h = 3.4 \) mm, at which HOR current reached the maximum as shown in Fig. 4. The height of the intrinsic meniscus was ca. 2.4 mm. The liquid thin film was not observed on Nafion/Pt/GC electrode, though it was formed on the uncoated electrode. The image obtained at the fully raised position (\( h = 6.0 \) mm) is shown in Fig. 9 d). This image was very similar to Fig. 9 c) and the maximum height of the intrinsic meniscus remained to be 2.4 mm. Therefore, a raise of the electrode led to an expansion of the exposed area of Nafion\(^\circledR\) film in the region of \( h > 2.4 \) mm, which worked as a kind of supermeniscus to increase HOR current. Because the maximum HOR current was obtained at \( h = 3.4 \) mm, the length of the effective supermeniscus, which is Nafion\(^\circledR\) film in this case, can be estimated to be 1.0 mm, though the precise length could not be obtained from optical image observation in the present study.

3. 8 Correlation between meniscus formation and hydrogen oxidation on Pt/GC and Nafion/Pt/GC

Because liquid thin film was observed on Pt/GC, the thin film model is used to explain the correlation between meniscus formation and HOR in the following discussion.\(^{26,27}\) The FCAM model proposed by Bockris and Cahn would be applied for the formation of the intrinsic meniscus.\(^{23,25}\)

Figure 10 shows the estimated length of intrinsic meniscus and supermeniscus on partially immersed elec-

![Fig. 8 Chronoamperogram of Pt/GC for hydrogen oxidation at \( h = 6.0 \) mm at 0.4 V. Optical microscopic images of the supermeniscus formed on Pt/GC electrode surface at \( h = 6.0 \) mm b) before polarized and at c) 10 sec, d) 1 min, and e) 3 min after polarized at 0.4 V in hydrogen-saturated 0.5 M H\(_2\)SO\(_4\).]
trodes. At $h = 0$ mm, no meniscus was formed on both electrodes; therefore, HOR current was limited by the diffusion of hydrogen in the bulk of the solution. On raising the electrode, the intrinsic meniscus was formed and gradually developed up to $h = \text{ca. } 3.2$ mm for Pt/GC, and the oxidation current increased simultaneously as shown in Fig. 5. Hence, the increase in HOR current in this region is attributed to the development of the intrinsic meniscus. Here, the intrinsic meniscus developed from the interface between Pt loaded and unloaded parts, and became sharper with raising the electrode from the solution (see Fig. 7 a) and b). This made hydrogen diffusion easier, and thereby hydrogen oxidation current increased. The maximum height of the intrinsic meniscus was estimated as $\text{ca. } 3.2$ mm for Pt/GC as shown in Fig. 10 a), at which the contribution of the intrinsic meniscus to the maximum current reached to about 50%.

Similar development of the intrinsic meniscus was also observed in the case of Nafion/Pt/GC electrode. The maximum height of the intrinsic meniscus on the Nafion coated electrode was 2.4 mm as summarized in Fig. 10 b), and hence the development of the intrinsic meniscus was responsible for the increase in HOR current up to $h = 2.4$ mm. However, its contribution to the maximum oxidation current was only 7%, which is significantly lower than that for the uncoated one. This would be due to a difference in the sharpness of the meniscus edge, i.e. the thickness of the intrinsic meniscus, between the Nafion-coated and uncoated electrodes.

Regardless of Nafion coating, HOR current increased with raising the electrode after the intrinsic meniscus reached the maximum length. As shown in Fig. 7, on Pt/GC electrode, a liquid thin film was observed above the upper edge of the intrinsic meniscus at $h > 3.2$ mm and its maximum length was estimated to be 1.0 mm (including the fringe region). Furthermore, the oxidation current reached to the maximum at $\text{ca. } h = 4.2$ mm. Based on these results, it was considered that the liquid thin film behaves as an effective supermeniscus for HOR. Although the thickness of the liquid thin film was not determined, it was estimated to be sub-micrometers to several micrometers, which must be thinner than the intrinsic meniscus. Hence, the diffusion of hydrogen was much easier than that through the intrinsic meniscus, which resulted in a further increase in the oxidation current. The current remained almost constant at $h > 4.2$ mm as shown in Fig. 5 (C), which would be mainly due to the ohmic drop along the thin liquid film.

In contrast, on the Nafion-coated electrode, the oxidation current increased linearly with raising the electrode up to $h = 3.4$ mm, though any liquid thin film was not observed on the exposed Nafion film as shown in Figs. 9 b) - d). This fact clearly shows that the Nafion film itself worked as an effective supermeniscus for HOR when it was exposed in the gas phase. This would be ascribed to the higher solubility of hydrogen in Nafion film than the bulk sulfuric acid solution.\textsuperscript{30}
The current distributions in the supermeniscus region were calculated using the results from the microscope observation and the oxidation current measurements. The variations of the current distribution with the length of the supermeniscus for Pt/GC and Nafion/Pt/GC are shown in Fig. 11. At null supermeniscus length, the contributions of the intrinsic meniscus region were 50 and 7% for Pt/GC and Nafion/Pt/GC, respectively, as described above. The current distribution in the supermeniscus region on the Pt/GC electrode becomes higher as the electrode was raised from the bulk electrolyte solution, but it was not linearly. In our previous study, it was shown that the current and the effective length of the supermeniscus have a linear relationship when the ohmic drop in the supermeniscus region restricts the current. As shown in Fig. 4, the current is also observed in the lower overpotential range; therefore, on the Pt/GC electrode, the current and potential distribution in the supermeniscus region was considered by not only an ohmic drop but also the some other factors such as some geometric factors. In fact, we also confirmed that the oxidation current was influenced by the size and agglomeration of Pt particles. Furthermore, the irregular thickness of the liquid thin film as shown in Fig. 7 e) might be a possible reason. In contrast to Pt/GC, the current distribution in the exposed Nafion® film as the supermeniscus increased linearly as shown in Fig. 11 (c). This result suggests that the ohmic drop in the Nafion® film restricts the effective length as the supermeniscus.

Thus, optical microscope observation is an effective method for investigating the current distribution on a partially immersed electrode system as a model of the gas-diffusion electrode in PEFCs. Unfortunately, further study with employing the smaller Pt particles as well as establishment the further suitable system without electrolyte solution are necessary to understand the potential and current distributions in practical TPB in PEFCs.

4 Conclusion

The meniscus formation on partially immersed Pt/GC and Nafion/Pt/GC electrodes and hydrogen oxidation reaction on the electrode systems were investigated as models of gas-diffusion electrodes of PEFCs. Regardless of Nafion® coating, the intrinsic meniscus was formed and developed on the electrode surface with raising the electrode under both hydrogen and inert atmospheres. On Pt/GC electrode, the liquid thin film was formed in the TPB region after the development of the intrinsic meniscus was terminated. The current greatly depended on the electrode height; in particular, it increased with the development of intrinsic meniscus and liquid thin film. The liquid thin film worked as a supermeniscus for hydrogen oxidation reaction. As a consequence of hydrogen oxidation reaction, the thickness of the supermenisc-
cus increased, which restricted the effective length to ca. 1.0 mm in hydrogen atmosphere.

In contrast, no liquid thin film was observed on the Nafion®-coated electrode after the intrinsic meniscus had fully developed. In this case, Nafion® film was exposed and its area expanded with raising the electrode. Hydrogen oxidation current increased with an increase in exposed Nafion® area; therefore, the Nafion® film behaves as an effective supermeniscus for hydrogen oxidation reaction.

Based on these results, we considered the current distribution in the supermeniscus region. In the Nafion/Pt/GC electrode case, a linear plot was obtained between the current distribution and supermeniscus length while the relationship was not linear on the uncoated electrode. The former result indicated that an ohmic drop formed by proton migration restricts the effective area in the supermeniscus region, i.e. in the exposed Nafion® film.

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