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Method of measuring oxygen diffusivity in microporous media

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ABSTRACT

It is known that the mass transfer characteristics of gas diffusion layers (GDLs) are closely related to cell performance in PEFCs. In this study, a method for measuring oxygen diffusivity in microporous media by means of an oxygen sensor based on a galvanic cell has been developed. This method is expected to be useful for measuring oxygen diffusivity in microporous media in a wet condition. Oxygen diffusivity in two kinds of microporous GDL media was evaluated. Experimental results indicate that diffusivity in microporous media cannot be determined on the basis of porosity alone, but that it may be influenced by some other factor, such as tortuosity. Additionally, there are some GDL materials that exhibit anisotropic diffusivity.

1. Introduction

The aim of this research was to develop a method for measuring oxygen diffusivity in microporous materials such as the gas diffusion layers (GDLs) of polymer electrolyte fuel cells (PEFCs). At the cathode of a PEFC, oxygen is transported as the reactant gas from the gas channel through the GDL to the catalyst layer. The moisture that forms on the catalyst layer as a result is evacuated into the gas channel in the opposite direction of oxygen transport. Such mass transport in the GDL mainly takes the form of gas diffusion, the characteristics of which substantially affect the power generation performance of a PEFC. For example, under operating conditions of low humidification and high temperature, a dryout phenomenon can occur in which a decline in proton conductivity in the electrolyte causes the cell voltage to drop. Another problem that occurs under conditions of high humidification and high current density is flooding, whereby moisture reaches a saturation state and condenses in the microporous medium. The liquid water that forms as a result blocks the transport of oxygen, leading to a decline in cell voltage.

These phenomena must be thoroughly understood in order to improve the power generation performance of PEFCs. In this regard, what is needed first of all is a simple and highly accurate method of measuring gas diffusivity, representing one of the basic properties of microporous media such as GDLs. Measurements must be obtainable under a dry condition and also under a wet condition with liquid water present in some of the micropores.

Various studies have been done to date concerning gas diffusivity in porous media. Numerical analysis has been applied to study gas diffusivity by modeling micropores with parallel pore models [1–3], random pore models [4–7], pore network models [8] and with models analogous to electrical conductivity [9]. A parallel pore model is based on the concept of parallel and independent cylindrical pores. A random pore model assumes that there are macropores and micropores which are randomly combined with one another. A pore network model consists of nodes and arms that form a network of pores. As the name suggests, models analogous to electrical conductivity are premised on the idea that gas diffusivity in solid porous media can be likened to electrical conductivity. These models attempt to express effective diffusivity in a porous medium in terms of its porosity or a combination of porosity and tortuosity.

For example, Wakao and Smith [4] proposed a random pore model, Mezedur et al. [8] a pore network model and Meredith and Tobias [9] a model analogous to electrical conductivity using a Bruggeman-type related equation for electrical conductivity in porous media. All of these models provide equations for predicting molecular diffusion and Knudsen diffusion in porous media based on porosity alone. Scott and Dullien [1] proposed a parallel pore model that provides equations for predicting molecular diffusion and Knudsen diffusion in porous media using porosity and tortuosity.

However, the actual structures of porous media generally consist of intricate, geometrical forms that differ considerably in

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Nomenclature

A	permeation area of porous specimen ($d^2\pi/4$), m^2
d	diameter of porous specimen, m
D_{O_2}	effective oxygen diffusivity in porous specimen, m^2/s
F	Faraday constant, C/mol
I_{out}	output current of oxygen sensor, A
k	characteristic constant of oxygen sensor, 1/A
L	thickness of porous specimen (holder length), m
t	temperature of measurement environment, °C
$\dot{V}_{O_2}$	oxygen permeability of sensor per unit time, m^3/s

Greek symbols

ω_0	oxygen mass fraction at porous specimen surface on the air side
ω_1	oxygen mass fraction of porous specimen surface on the cathode side

shape. It is hard to conceive that gas diffusivity in porous media can be expressed in terms of porosity alone. Parallel pore models for finding effective diffusivity in terms of a combination of porosity and tortuosity also have certain modeling limitations because of the difficulty in identifying tortuosity accurately, among other reasons. Accordingly, in actuality, it is necessary to rely on experimental measurements in order to find effective diffusivity with high accuracy.

Various methods of experimental analysis have also been applied to find effective diffusivity. These include indirect methods based on the measured rate of adsorption [12,13] or rate of reaction [14] of a gas on the surface of a porous medium or the use of zirconia as an oxygen sensor [8]. A technique similar to the porous diaphragm method [10] has been used to find effective diffusivity by directly measuring gas permeability through a porous medium. With this technique, diluted gases of different concentrations are passed through channels sandwiching a porous medium and the difference in concentration between the upper and lower flows is measured. Instead of using a gas, porous medium samples have been filled with an electrolyte, and the rate of ion transfer in the electrolyte was measured to estimate the effective gas diffusivity [15,16].

For example, Kawazoe [12] and Hamai and Mitani [13] proposed an adsorption method, while Wakao and Funagi [14] proposed a reaction method. With both approaches, mass transport in the porous material of interest is modeled on the basis of certain assumptions. The model is then used in conducting a simulation to find the relationship between the mass transfer rate in the porous material and effective diffusivity. After that step, effective diffusivity is found from the change in the measured carrier gas concentration with elapsed time. Accordingly, the accuracy of the diffusion coefficient thus determined greatly depends not only on measurement accuracy but also on how the simulation model is defined. This dependence is especially pronounced when the simulation model deviates from the intricate pore structure or pore distribution of the porous material being investigated.

The scope of application of the adsorption method is porous media consisting of micropores (fine pore diameter of 2 nm or smaller) and mesopores (fine pore diameter of 50 nm or smaller). It is difficult to apply this method to the substrate of GDLs used in fuel cells as the materials mainly consist of micropores ranging in size from several μm to several tens of μm.

Mezedur et al. [8] used an oxygen sensor with a yttrium-stabilized zirconia electrolyte to measure gas diffusivity in porous electrode catalysts. This type of sensor is based on the principle that oxygen ion transfer in zirconia produces an electric current. Effective oxygen diffusivity is found by simultaneously measuring the permeated oxygen flux in the porous medium and the oxygen concentration on the porous medium surface (i.e., the sensor surface and opposite side). However, this sensor is generally used at temperatures above 300 °C, and it is difficult to obtain measurements under a wet condition where liquid water is present in some of the micropores.

Kawazoe et al. [10] used the diaphragm method to measure the effective diffusivity of $^{85}Kr–N_2$ in porous solids having a mixture of macro- and micro-pores. Henry et al. [11] used a similar method to measure the effective diffusivity of $N_2–CO_2$, N_2–He and CO_2–He in porous media having a mean pore size of several nm. The former method requires a special gas supply system and measurement system, while the latter method requires a gas chromatograph for measuring the gas concentration. Both measurement systems are rather complex and require a lot of time for calibration and operation in order to obtain highly accurate measurements. Additionally, it is also difficult to measure the degree of liquid water saturation of porous media under a wet condition with the diaphragm method.

Freunberger et al. [15] and Fluckiger et al. [16] assumed that gas diffusivity in porous media was analogous to ion conductivity in an electrolyte filled in the pores. Based on that assumption, they found the effective diffusivity in GDLs for PEFC use by measuring the conductivity of the electrolyte permeated into the porous media. However, because it is necessary to fill the pores with the electrolyte, it is difficult to obtain accurate measurements under a wet condition where liquid water is present in some of the micropores.

As explained here, no conventional measurement method was found that would facilitate simple and highly accurate measurement of gas diffusivity under the targeted conditions of this study, which included a wet condition with liquid water present in some of the micropores, in addition to a dry condition. Therefore, an investigation was made of a method for measuring oxygen diffusivity in porous media using a galvanic cell oxygen sensor as the basic structural element of the measurement system. The aim was to obtain a method for measuring oxygen diffusivity in microporous media such as GDL materials under both wet and dry conditions.

This paper describes the newly developed measurement method and presents examples of the measured results that validate its effectiveness.

2. Measurement apparatus and method

Fig. 1 shows the configuration of the experimental apparatus used in this study to measure oxygen diffusivity. A special holder for holding the porous medium specimen to be measured is fitted to a galvanic cell oxygen sensor, consisting of a noble metal (gold) cathode, an base metal (lead) anode, an electrolyte and a gas permeating membrane. The inner diameter (d) of the holder was 5 mm and its length (L) was varied over a range from 5 to 100 mm. One side of the porous specimen in the holder is exposed to the air and the other side faces the cathode. The oxygen mass fraction of the porous specimen surface on the cathode side and oxygen permeability of porous specimen are calculated from the output current of the galvanic cell oxygen sensor.

Oxygen that passes through the gas permeating membrane of the sensor is dissolved in the electrolyte and is reduced at the cathode surface by the chemical reaction shown in Eq. (1).

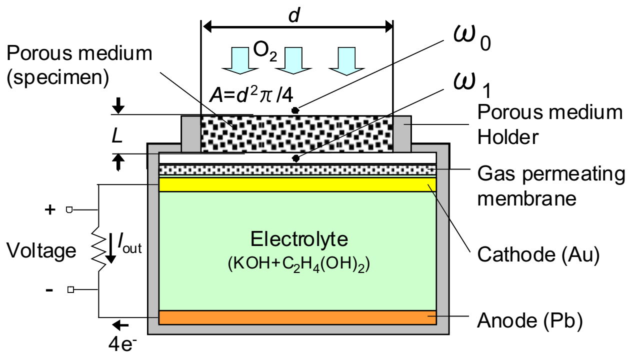

Fig. 1. Configuration of experimental apparatus for oxygen diffusivity measurement.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

Corresponding to this process, the lead anode electrode is oxidized according to the chemical reaction shown in Eq. (2).

$$2Pb \rightarrow 2Pb^{2+} + 4e^- \tag{2}$$

As indicated by the chemical reaction in Eq. (3), lead dissolves in the electrolyte and water is produced in the same quantity as the amount consumed at the cathode.

$$Pb^{2+} + 3OH^- \rightarrow HPbO_2^- + H_2O \tag{3}$$

The output current I_{out} resulting from the oxygen reduction reaction at the cathode surface is found by measuring the voltage drop of a in-circuit resistor, using the electromotive force of the galvanic cell. The output current is nearly proportional to the oxygen mass fraction ω_1 at the surface of the gas permeating membrane within the range shown in Fig. 2.

The oxygen mass fraction ω_1 at the porous specimen surface facing the cathode and the oxygen permeability $\dot{V}_{O_2}$ at that moment are calculated from the output current of the oxygen sensor using Eqs. (4) and (5), respectively. Eq. (4) is specific characteristics of sensor. Eq. (5) is derived from Faraday's second law of electrolysis and Boyle–Charle's law. Using the values thus found, the effective oxygen diffusivity D_{O_2} in the porous specimen being measured is found with Eq. (6). Eq. (6) is derived from law of mass conservation comprised of diffusion term and convective term for oxygen and nitrogen.

$$\omega_1 = 1 - Exp(I_{out}/k) \tag{4}$$

$$\dot{V}_{O_2} = 22.41 \times 10^{-3} \times \frac{273.15 + t}{273.15} \times \frac{I_{out}}{4F} \tag{5}$$

$$D_{O_2} = \frac{\dot{V}_{O_2} L}{A} \cdot \frac{1}{\ln\left(\frac{1-\omega_1}{1-\omega_0}\right)} \tag{6}$$

where A is permeation area of porous specimen, D_{O_2} is effective oxygen diffusivity in porous specimen, F is Faraday constant, I_{out} is output current of oxygen sensor, k is characteristic constant of oxygen sensor, L is thickness of porous specimen (holder length), t is temperature of measurement environment, $\dot{V}_{O_2}$ is oxygen permeability of sensor per unit time, ω_0 and ω_1 are oxygen mass fraction at porous specimen surface on the air side and the cathode side, respectively. As stated above, difference between ω_0 and ω_1 caused by oxygen passing through the gas permeating membrane of the sensor enables us to derive D_{O_2} from Eq. (6).

Fig. 3 shows the configuration of the experimental apparatus used to validate the four-electron oxygen reduction reaction given in Eq. (5). An oxygen concentration of 1000 ppm diluted with nitrogen was supplied to three galvanic cell oxygen sensors arranged in a row. The flow was varied in a range from 0.05 to 0.167 mL/s using a mass flow controller. Fig. 4 shows the total output current of the sensors as a function of the feed gas flow rate.

The open circles (○) indicate the output current of the first upstream oxygen sensor, the open triangles (△) show the total output current of the first and second oxygen sensors, and the open squares (□) indicate the total output current of all three oxygen sensors. The solid line shows the theoretical output current when all the supplied oxygen is consumed in the four-electron reaction. It is seen that the total output current approaches the solid line when the output currents I_2 and I_3 of the second and third downstream oxygen sensors are added to the output current I_1 of first oxygen sensor positioned the closest to the gas supply inlet. It is inferred that the total output current of the oxygen sensors gradually approaches the solid line as the number of sensors arranged in series is increased. Due to the incompleteness of oxygen passing through the gas permeating membrane of the sensors, higher flow rate makes a difference between the total output current of the oxygen sensors and theoretical output current when all the supplied oxygen is consumed in the four-electron sensor. These results thus verify that the galvanic cell oxygen sensors follow the four-electron reaction shown in Eqs. (1) and (2).

The characteristics of the gas permeating membrane were carefully selected so as to obtain a sufficient difference in the mass fraction values ω_1 and ω_0 of the porous specimen being measured. Care was taken concerning the selection of the characteristic constant k of the oxygen sensor so as to be able to determine the oxygen diffusivity D_{O_2} in porous media with sufficient accuracy. A temperature of 22 ± 2 °C and relative humidity of 50% were set as the baseline conditions of the ambient air in the measurement environment in order to ignore the effect of the moisture mass fraction of the air on oxygen diffusivity.

3. Results and discussion

Measurements were made of oxygen diffusivity in the air in the empty holder after removing the porous specimen from it (Fig. 1). The measured results are compared in Fig. 5 with values calculated with an equation given in the literature [17]. In calculating oxygen diffusivity in the air from the measured output current I_{out} of the oxygen sensor, the oxygen mass fraction (ω_0) of the porous specimen on the holder side exposed to the air was used as the oxygen

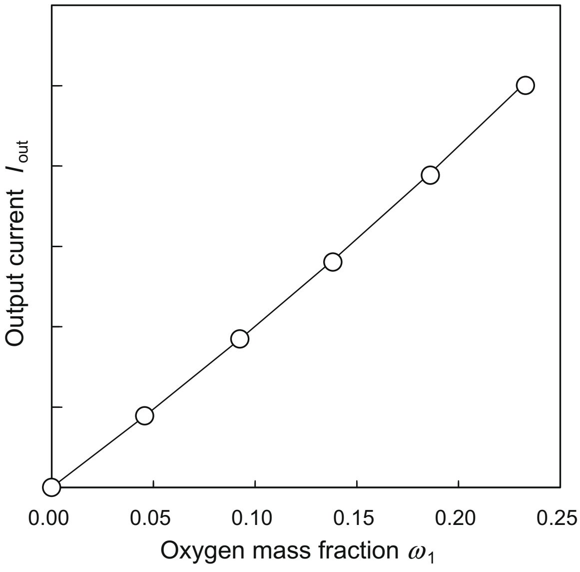

Fig. 2. Relationship between output current and oxygen mass fraction.

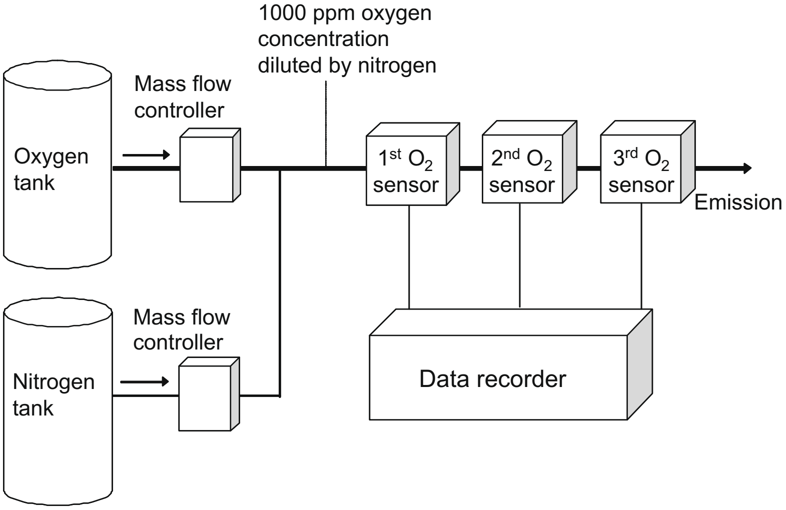

Fig. 3. Configuration of experimental apparatus for validation of reaction electron number.

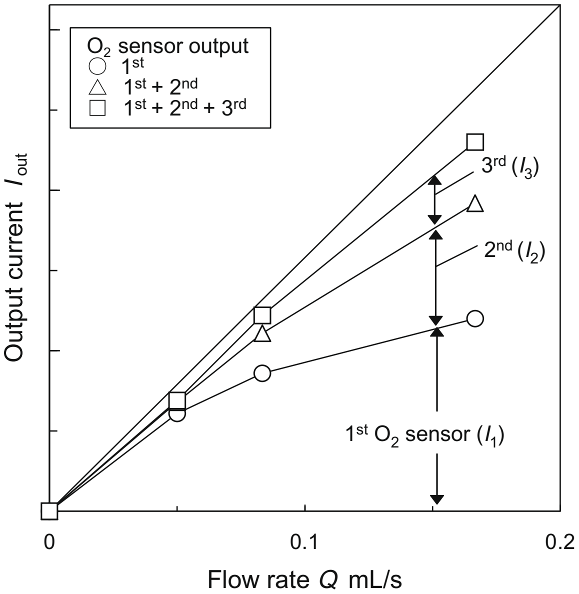

Fig. 4. Relationship between output current and flow rate.

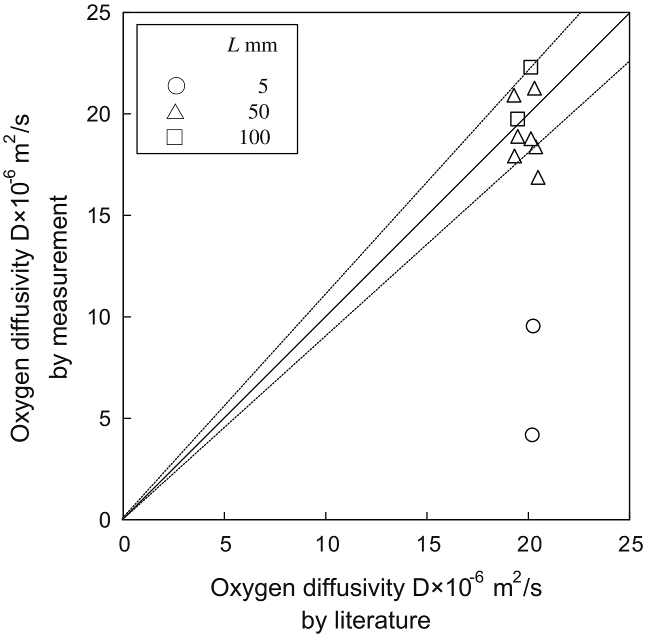

Fig. 5. Comparison of measured oxygen diffusivity in the air and calculated values.

mass fraction of the air. The circles, triangles and squares show the oxygen diffusivity values for holder lengths (L) of 5, 50 and 100 mm, respectively. The solid line indicates complete agreement between the experimental and calculated values, and the dashed lines represent a difference of plus or minus 10% from the calculated values. For a holder length of 5 mm, the experimental and calculated values diverge greatly, but for a holder length of 50 mm or larger, good agreement is seen between the two sets of data, as the difference between them is within ±10%. One presumable reason for the large divergence seen between the measured and calculated values for a holder length of 5 mm is that the oxygen mass fraction (ω_0) at the porous specimen surface on the side exposed to the air was lower than that of the oxygen mass fraction of the air owing to relatively large oxygen permeability. Another factor may have been increased error due to a smaller difference in the oxygen mass fractions on the two sides of the porous specimen owing to the relatively short holder length. The foregoing results thus indicate that this measurement apparatus can measure oxygen diffusivity with sufficient accuracy by selecting suitable measurement conditions, including a holder length matching the porous specimen to be evaluated.

Fig. 6 shows time histories of the measured output current I_{out} when the specifications examined in this study were varied. (A) A condition where the gas permeating membrane of the galvanic cell oxygen sensor was directly exposed to the ambient air. (B) A condition where the oxygen sensor was virtually sealed off from the air. (C) A condition where the holder attached to the oxygen sensor contained a solid core having an outer diameter smaller than that of the holder. (D) A condition where the holder attached to the oxygen sensor contained a porous medium. (E) A condition where droplets were added to the one side of the porous medium in the holder. (F) A condition where the porous medium was removed and the holder was empty. (G) The same condition as (A) at the start of the measurement.

The results for (A) and (G), representing the start and end of the measurement, indicate that the baseline output current was main-

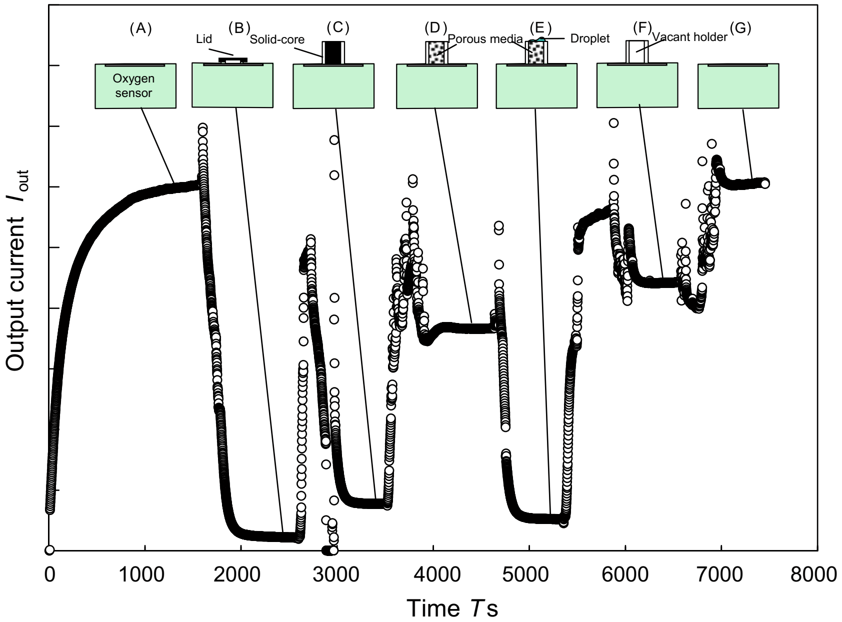

Fig. 6. Typical experimental results.

tained relative to the oxygen mass fraction in the air. The results for (B) indicate that the output current became nearly zero when the oxygen mass fraction was zero. The results for (C) through (F) are for a holder length of 5 mm with different materials in the holder. It is seen that the oxygen mass fraction of the porous specimen surface on the cathode side (ω_1) varied according to the change in the specification of the material in the holder. As stated above, it is confirmed that there was no change in the output current of the galvanic cell oxygen sensor at the start and end of the measurement, and that the output current of the oxygen sensor became virtually zero when a cover was put over the sensor to seal it tightly and prevent exposure to the air. Accordingly, it is inferred from the results that the effective oxygen diffusivity was accurately measured for each target specification.

This measurement method was then used to evaluate the effective oxygen diffusivity in a cloth-type GDL and a paper-type GDL, representing two porous media used in PEFCs. The temperature of the measurement environment was set at 24 °C. Fig. 7 shows enlarged photographs of the porous surface of the two types of GDL materials. Their specifications are given in Table 1. The pore size distribution found by the mercury intrusion method for the two porous medium samples A and B is shown in Figs. 8 and 9, respectively. The open circles indicate the cumulative intrusion volume of the micropores, and the black circles indicate the log differential intrusion volume. Both samples had nearly the same porosity of 0.78 and 0.81, respectively, but the representative pore diameter of sample B and its gas permeability were approximately three times and eleven times greater, respectively, than the corresponding values of sample A. The representative pore diameter given in Table 1 is the diameter of the pores in which the cumulative intrusion volume reaches 50% among all the pores.

Table 1
Specifications of gas diffusion layers.

Sample	Porosity	Diameter[a] (μm)	Permeability (μm^2)
A	0.78	32	3.2
B	0.81	97	36.8

[a] The diameter in which cumulative intrusion volume reaches 50% among all pores.

The measured oxygen diffusivity in each sample is shown in Fig. 10. The effective oxygen diffusivity in sample A was found to be 6.5×10^{-6} m^2/s and that in sample B was

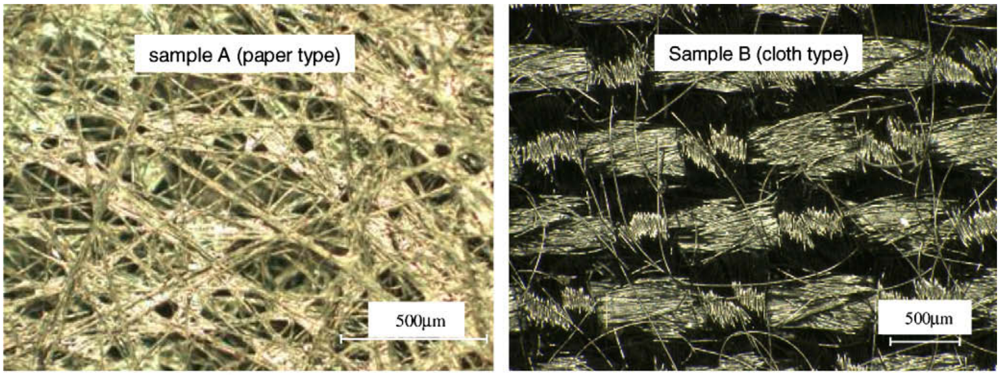

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Fig. 7. Structure of gas diffusion layers.

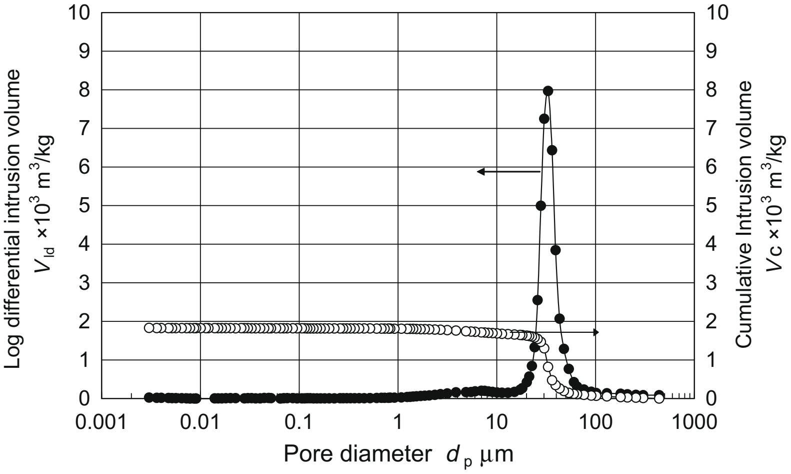

Fig. 8. Pore size distribution of sample A.

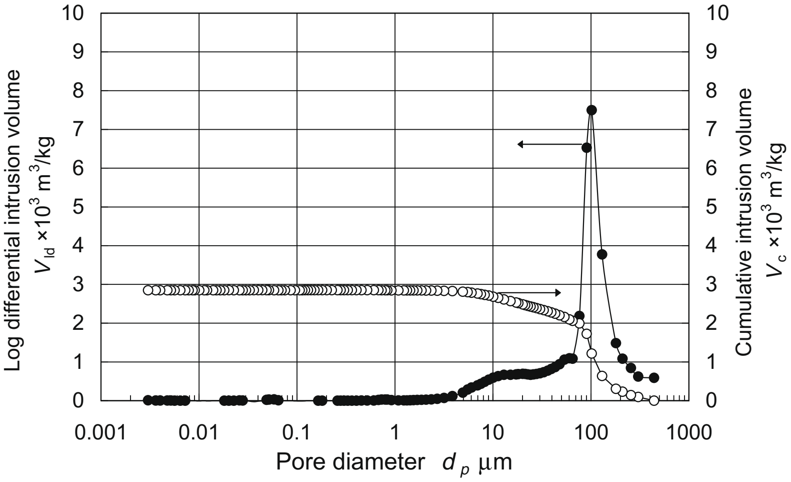

Fig. 9. Pore size distribution of sample B.

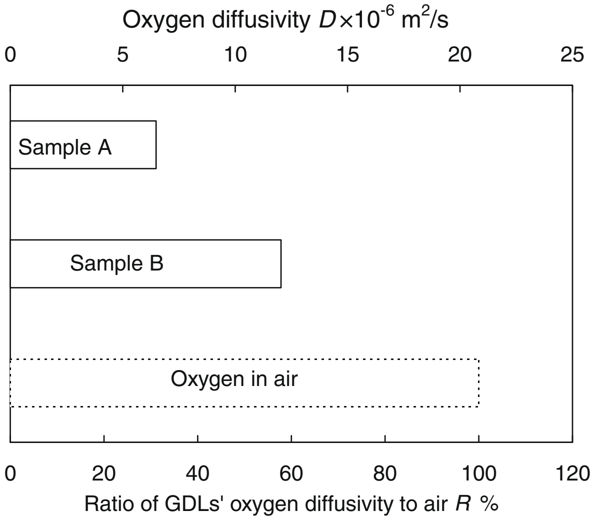

Fig. 10. Oxygen diffusivity

12.0×10^{-6} m²/s. The ratio of the foregoing values to the diffusivity of oxygen in the air was approximately 31% and 58%, respectively. A comparison of the measured results shows that oxygen diffusivity in sample B was quite twofold greater than that in sample A. As indicated in Table 1, both samples had virtually the same porosity, so it is assumed that the pore structure of sample B had smaller tortuosity than that of sample A. The results suggest that effective diffusivity in porous media cannot be determined on the basis of porosity alone and that it is also influenced by some other porous structure characteristic such as tortuosity.

The relationship between the through-plane and in-plane oxygen diffusivity in samples A and B is shown in Figs. 11 and 12, respectively. The vertical axis of each figure shows the nondimensionalized oxygen diffusivity relative to the through-plane oxygen diffusivity. The results in Fig. 11 show that the in-plane oxygen diffusivity in sample A was approximately 1.4 times greater than its through-plane oxygen diffusivity. This indicates that gas diffusivity in sample A had an anisotropic characteristic. It is inferred that this anisotropy originated in a structural characteristic of sample A in that its tortuosity differed depending on the direction. In contrast, the results in Fig. 12 show that the in-plane oxygen diffusivity in sample B was virtually the same as its through-plane oxygen diffusivity. This implies that the tortuosity of sample B was nearly same in both the through-plane and in-plane directions.

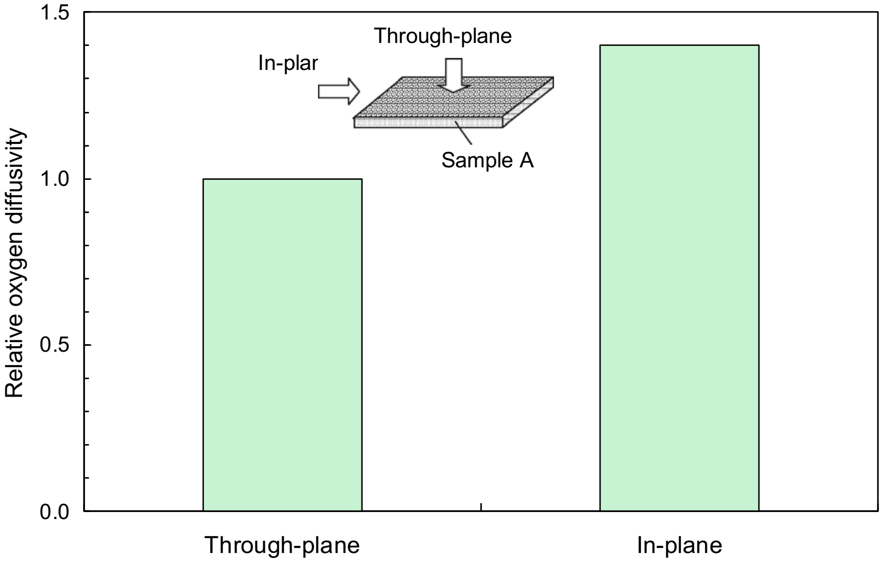

Fig. 11. Comparison between through-plane and in-plane oxygen diffusivity for sample A.

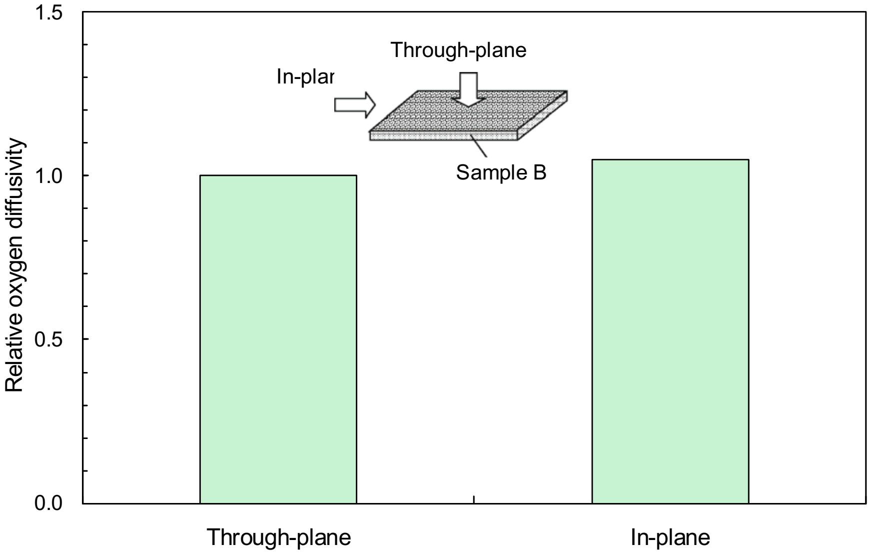

Fig. 12. Comparison between through-plane and in-plane oxygen diffusivity for sample B.

4. Conclusion

A method for measuring oxygen diffusivity was conceived and an experimental system was built that has a galvanic cell oxygen sensor as its basic structural element. After confirming the fundamental performance of the system, it was used to evaluate the effective oxygen diffusivity in two types of porous GDL materials for use in PEFCs. The following results were obtained.

(1) It was confirmed that the proposed method is an effective technique for measuring the effective oxygen diffusivity in microporous media.
(2) Measurements of the effective oxygen diffusivity in actual porous media used for the GDL of PEFCs revealed that oxygen diffusivity is not determined by the porosity of the material alone.
(3) The measured results showed that some porous media used for the GDL of PEFCs exhibit anisotropic oxygen diffusivity.

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