

Development of measurement technique of mass diffusion coefficient of aqueous methanol solutions in polymer electrolyte membranes based on infrared Soret forced Rayleigh scattering method using single crystal diamond window in a sample cell

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Received: 19 March 2018; Revised: 19 April 2018; Accepted: 24 April 2018

Abstract

We have developed an experimental apparatus for the measurement of diffusion coefficient of aqueous methanol solutions in a polymer electrolyte membrane (PEM) for direct methanol fuel cells (DMFCs), based on the infrared Soret forced Rayleigh scattering (IR-SFRS) method. Because mass transport phenomena in PEMs play significant roles, evaluation and understanding of the mass diffusion in PEMs is important. In the present study, we developed a new sample cell using a single crystal diamond window, which transmits both the heating laser with the wavelength of 9.714 μm and the probing laser with the wavelength of 639 nm. The heating wavelength was selected from the emission range of a valuable-wavelength carbon dioxide laser to utilize the absorption of methanol due to CO stretching. By using a single crystal diamond window, the scattered light of the probing laser generated at the window material which causes unpreferable effects on detection signals was reduced to about 1/150, compared to a polycrystalline diamond window. To evaluate the validity of the measurement system, we carried out experiments on the aqueous methanol solutions at a temperature of $T = 298.2$ K. The mass diffusion coefficient of the aqueous methanol solution with the mole fraction of 0.7 measured in the present study agreed with the measured values by the diaphragm cell technique within the relative standard uncertainty of 8.9%. After the validation, we performed experiments on three concentrations of aqueous methanol solutions in a PEM of Nafion 117 at $T = 298.2$ K. The mass diffusion in Nafion was observed in several hundreds of milliseconds. We obtained the mass diffusion coefficient with the relative standard uncertainties of 2.5–5.3%, depending on the methanol concentration. The mass diffusion coefficient in Nafion 117 was smaller than that of bulk aqueous methanol solutions, and increased with the increase in the methanol mole fraction.

Keywords : Diffusion coefficient, Mass transport in membranes, Aqueous methanol solutions, Polymer electrolyte membrane (PEM), Nafion, Direct methanol fuel cell (DMFC), Optical measurement

Nomenclature

c : mass fraction [-]

D_{12} : mass diffusion coefficient [$\text{m}^2 \cdot \text{s}^{-1}$]

$I_1(t)$: intensity of first order diffracted beam [$\text{W} \cdot \text{m}^{-2}$]

l :	distance between 1st order and –1st order diffracted beam [m]
L :	distance between acrylic plate and probing needle in measurement of fringe spacing [m]
t :	time [s]
T :	temperature [K]
θ_h :	incident angle of heating laser [rad]
θ_1 :	diffraction angle of first order diffracted beam of probing laser [rad]
λ_h :	wavelength of heating laser [m]
λ_p :	wavelength of probing laser [m]
τ_D :	relaxation time constant of concentration distribution [s]

Subscript

h:	heating laser
p:	probing laser
1:	first order diffracted beam

1. Introduction

Mass transport phenomena in polymer electrolyte membranes (PEMs) significantly affect the performance of direct methanol fuel cells (DMFCs) which are expected to be new power sources (Li and Faghri, 2013; Bahrami and Faghri, 2013). The transport of methanol in a PEM from the fuel electrode side to the air electrode side is known as the methanol crossover. This phenomenon is one of the factors that limit the efficiency of DMFCs, because the methanol crossover causes the waste of the fuel and the drop of the electromotive force (Li and Faghri, 2013; Bahrami and Faghri, 2013). Therefore, it is required to develop new PEMs which show low methanol permeability as well as high proton conductivity (Gloukhovski et al., 2017). Based on the importance of the evaluation and understanding of the mass transport phenomena in PEMs, mutual diffusion coefficient of aqueous methanol solutions in Nafion 117, which is a perfluorosulfonate ionomer and commonly used as a PEM (Mauritz and Moore, 2004), have been measured by several techniques; the permeation method using a diffusion cell (Verburgge, 1989), the voltammetric method based on a electrochemical technique (Ren et al., 2000), and the time-resolved Fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATR) (Hallinan and Elabd, 2007). In addition, measurement of the self-diffusion coefficient in Nafion have been carried out by the nuclear magnetic resonance (NMR) spectroscopy (Hietala et al., 2000; Every et al., 2005). However, the different trend of the diffusion coefficient in Nafion on the methanol concentration was reported and we consider that there is no an established experimental technique.

To contribute to the understanding of the mass transport in PEMs, in our laboratory we have tried to measure the diffusion coefficient in PEMs by the infrared Soret forced Rayleigh scattering (IR-SFRS) method (Sakai et al., 2012), which has been developed to apply the optical holographic grating technique of the Soret forced Rayleigh scattering (SFRS) or the thermal diffusion forced Rayleigh scattering (TDFRS) employing visible light lasers (Hayashida and Nagasaka, 1997; Yamamoto and Nagasaka, 2006a, 2006b; Niwa et al., 2009; Matsuura et al., 2015; Matsuura and Nagasaka, 2017; Matsuura and Nagasaka, 2018) to the measurement of solutions in PEMs. The feature of the IR-SFRS technique includes the following:

- 1) Mass transport in PEMs is induced by a carbon dioxide (CO₂) laser without dye for laser absorption, and contactless detection of the mutual diffusion is performed by another laser (probing laser).
- 2) In-plane direction mass diffusion in a very small diffusion length ($\sim 10^1 \mu\text{m}$) can be observed, which realizes a very short characteristic time of the mass diffusion ($\sim 10^2 \text{ ms}$).
- 3) Thickness of a PEM containing solutions is not required to obtain the mass diffusion coefficient. This leads to a measurement without annoying the uncertainty of the thickness as in the voltammetric method and the FTIR-ATR technique.
- 4) It is applicable to high methanol concentration solutions in PEMs, which may be difficult to measure by the FTIR-ATR technique due to the excessive membrane swelling.
- 5) Because the mass transport in the laser spot is detected, it has a potential to detect in-plane distribution of the mass diffusion coefficient.

We employ a variable-wavelength carbon dioxide (CO₂) laser which is able to adjust the emitting wavelength to the

absorption range due to the CO stretching of methanol, while a near infrared laser is used in the IR-TDFRS apparatus developed by Wiegand et al. (2007) to investigate the Soret effect (also called thermodiffusion or thermal diffusion, (Köhler and Morozov, 2016)) of aqueous mixtures. Because in our previous study (Sakai et al., 2012; Miyahara et al., 2013; Hoshino and Nagasaka, 2015) we experienced experimental problems due to the light scattering of the probing laser at the window material of polycrystalline diamond used in the sample cell, in the present study we introduced a single crystal diamond window which generates lower scattered lights. We report the experimental result of the mass diffusion coefficient of aqueous methanol solutions in Nafion membranes using a single crystal diamond window in a newly designed sample cell.

2. Measurement technique: infrared Soret forced Rayleigh scattering (IR-SFRS)

2.1 Principle of IR-SFRS

The measurement principle of the IR-SFRS technique is basically identical to that of the SFRS technique described in our previous paper (Niwa et al., 2009). Figure 1 shows the concept of the IR-SFRS technique.

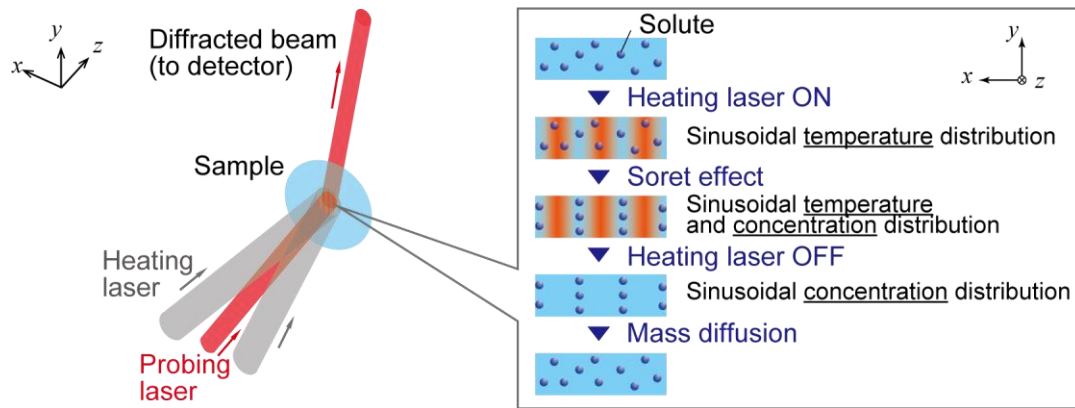


Fig. 1 The principle of the infrared Soret forced Rayleigh scattering (IR-SFRS) method. The mass transport is induced by the infrared heating laser, which interferes in the sample. The gratings of the temperature and concentration in the sample works as a diffraction gratings. The mass transport is observed by detecting the diffracted beam of the probing laser, because the diffraction efficiency includes the information of the concentration grating.

A sinusoidal temperature distribution is formed by the absorption of the infrared heating laser which interferes in the sample. This induces mass transport by the Soret effect, accordingly a sinusoidal concentration distribution is generated. When the heating laser is switched off, the relaxation of the temperature distribution begins. Following this, the relaxation of the concentration distribution by the mass diffusion begins. Because the temperature and concentration distribution forms a sinusoidal distribution of the refractive index in the sample, the sample works as a diffraction grating in this process. The diffraction efficiency includes the information of the mass transport. Thus, we detect the intensity of the first order diffracted beam of the probing laser, which enters the sample to satisfy the diffraction condition.

We assume that the mass transport in PEMs in an IR-SFRS experiment is described by the one-dimensional diffusion equation in x -axis.

$$\frac{\partial c}{\partial t} = D_{12} \frac{\partial^2 c}{\partial x^2} \quad (1)$$

in which c is the mass fraction, t is the time, and D_{12} is the mutual mass diffusion coefficient.

The intensity of the first order diffracted beam $I_1(t)$ in the relaxation process of the concentration distribution by the mass diffusion is described as Eq. (2) (Niwa et al., 2009).

$$I_1(t) \propto \exp\left(-\frac{2t}{\tau_D}\right) \quad (2)$$

in which τ_D is the relaxation time constant of the concentration distribution (Niwa et al., 2009).

$$\tau_D = \frac{1}{D_{12}} \left(\frac{\Lambda}{2\pi} \right)^2 \quad (3)$$

Λ is the fringe spacing of the heating laser.

With Eqs. (2) and (3), the mutual mass diffusion coefficient is obtained by the curve fitting analysis of the relaxation signals by the mass diffusion.

2.2 Wavelength of heating laser

In the IR-SFRS technique, by using an infrared laser as a heating laser, it is enable to form a temperature distribution in a sample to induce the Soret effect without doping a dye to support the laser absorption. Figure 2 shows the IR spectrum of methanol, aqueous methanol solutions, water, and Nafion 117 measured by the FTIR-ATR (Miyahara et al., 2013). Methanol shows absorption around the wavelength of 8.8 μm due to CH_3 rocking and 9.8 μm due to CO stretching (Plyler, 1952).

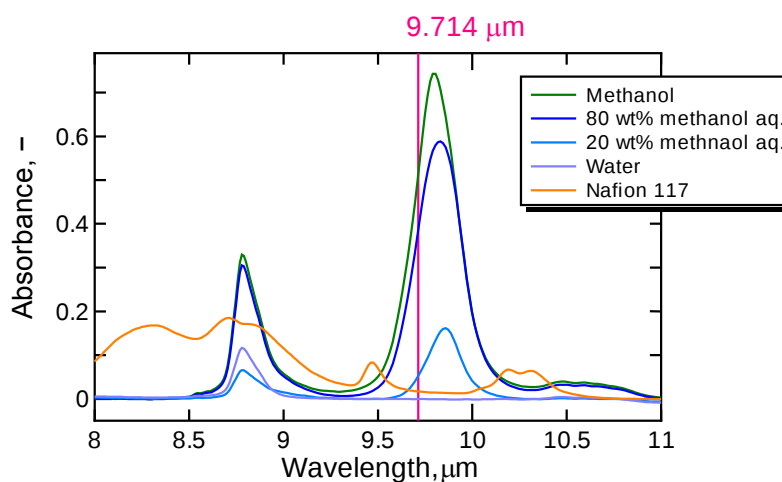


Fig. 2 The IR spectrum of methanol, aqueous methanol solutions, water and Nafion 117 measured by FTIR-ATR. Methanol shows absorption peaks around 9.8 μm (CO stretching) and 8.8 μm (CH_3 rocking). To form a temperature gratings in the sample effectively, the heating wavelength of 9.714 μm was selected from the emission range of the variable-wavelength CO_2 laser.

To form a temperature grating in aqueous methanol solutions in PEMs effectively, wavelength which shows stronger absorption by methanol and weaker absorption by PEM like Nafion is considered to be preferable for the heating laser. Therefore, we introduced a variable-wavelength CO_2 laser (L20G, Access Laser Company) which emits beam of the wavelength of 9.183–9.733 μm and 10.125–10.811 μm . The emitting wavelength of this laser is controlled by a micrometer on the laser head. The heating wavelength of $\lambda_h = 9.714 \mu\text{m}$ was selected after the consideration of the emitting power and the stability, which differ on the wavelength (Miyahara et al., 2013). Note that the variable-wavelength laser has a potential advantage that we are able to adjust the heating wavelength on samples. For example, it could be applicable to aqueous ethanol solutions, which show absorption around 9.4 μm due to CO stretching (Plyler, 1952).

2.3 Experimental apparatus

Figure 3 is a schematic of the experimental apparatus of the IR-SFRS technique designed and built for the homodyne (direct) detection scheme. A half-wavelength plate (#85-123; Edmund Optics) is employed to adjust the polarization to the acousto-optic modulator (1209-7-1064M, anti-reflective coating for 9.7 μm ; Isomet), which generates the diffracted beam while the modulation voltage is applied to the driver (RFA241; Isomet). The diffracted beam from the acousto-optic modulator is split into two beams by a non-polarizing beamsplitter (PIB-5005Z; Lambda Research Optics). The two beams cross in the sample.

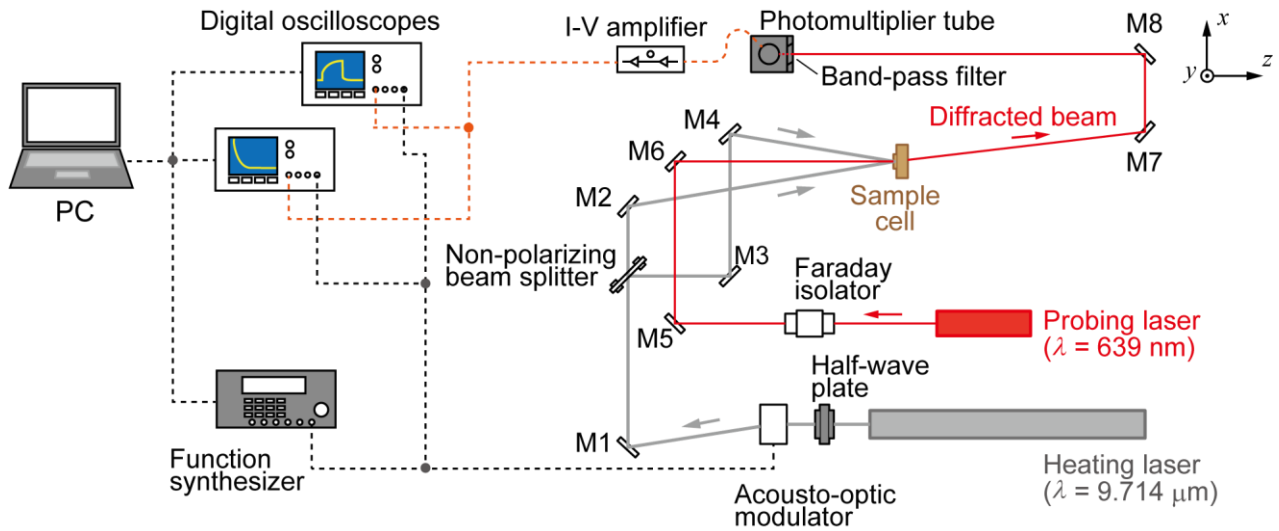


Fig. 3 The experimental apparatus of the infrared Soret forced Rayleigh scattering (IR-SFRS) method. The two beams of the heating laser ($\lambda_h = 9.714 \mu\text{m}$) cross in a sample cell. The first order diffracted beam of the probing laser ($\lambda_p = 639 \text{ nm}$) is detected by a photomultiplier tube.

The two heating laser beams symmetrically enter to the normal direction of the sample surface. The incident angle of the heating laser θ_h is adjusted to satisfy the designed interference fringe spacing (Matsuura and Nagasaka, 2018),

$$\theta_h = \sin\left(\frac{\lambda_h}{2\Lambda}\right) \quad (4)$$

in which λ_h is the wavelength of the heating laser.

A Faraday isolator (IO-3-633-LP/M; Thorlabs) is used to protect the probing laser (OBIS637-140LX-HTK) with the wavelength of $\lambda_p = 639 \text{ nm}$. The probing laser enters the sample vertically, because the Raman-Nath condition for the diffraction (Klein and Cook, 1967) is adopted in an IR-SFRS experiment due to the short absorption length (micrometer order) of the infrared heating laser, while the Bragg condition is adopted in the SFRS apparatus using visible light lasers (Matsuura and Nagasaka, 2018). The first order diffracted beam is aligned so as to enter the photomultiplier tube (R9110; Hamamatsu Photonics), which was installed in the housing with a bandpass filter (FF02-632/22-25; Semrock).

A variable gain current-voltage amplifier (DLPCA-200; Femto) amplifies the output current from the photomultiplier tube. The output signal is observed in real time by digital oscilloscopes (DPO3014 and TDS3032B; Tektronix). We observe the signals not only in relaxation processes but also in formation process independently via the two oscilloscopes (Matsuura and Nagasaka, 2018). Data analysis and control of the instruments including the digital oscilloscopes are carried out by the LabVIEW software on a PC.

2.4 Measurement method of fringe spacing

The fringe spacing Λ is required to determine the mass diffusion coefficient by the curve fitting analysis based on Eqs. (2) and (3). To determine the fringe spacing Λ , we evaluate the diffraction angle of $\pm 1\text{st}$ mode θ_1 . The relationship between Λ and θ_1 is described as:

$$\Lambda = \frac{\lambda_p}{\sin \theta_1} \quad (5)$$

in which λ_p is the wavelength of the probing laser ($\lambda_p = 639 \text{ nm}$).

After the alignment of the mirrors M1–M4 of the heating laser system and M5 and M6 of the probing laser system in Fig. 3, an acrylic plate with the thickness of 1 mm is mounted at the sample position. Then, interference grating is written in the acrylic plate by the heating laser so that stationary emitted diffracted beams are observed. We measure the

distance between the 1st order and -1 st order diffracted beams at each position from the acrylic plate. The diffraction angle of ± 1 st mode θ_1 is described as:

$$\theta_1 = \tan^{-1}\left(\frac{l/2}{L}\right) \quad (6)$$

in which l is the distance between the ± 1 st order diffracted beams and L is the distance from the acrylic plate (Fig. 4).

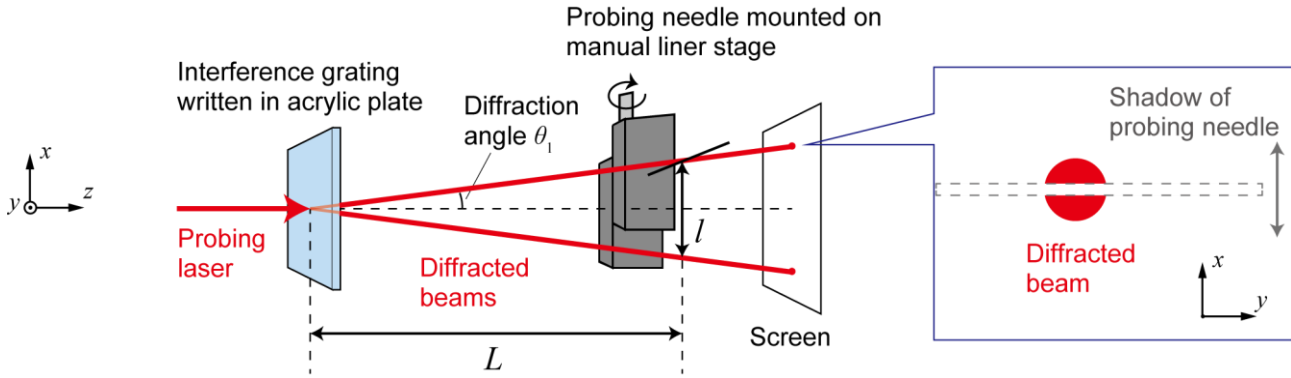


Fig. 4 The measurement method to determine the diffraction angle of ± 1 st mode θ_1 . After writing an interference grating in an acrylic plate by the heating laser, the distance between the ± 1 st order diffracted beams l is measured. The position of the probing needle is adjusted so that the shadow of the needle on the screen comes at the center of the diffracted beams. The diffraction angle θ_1 is determined by the relationship of $(l/2) = L \tan \theta_1$, in which L is the distance between the acrylic plate and the probing needle.

To determine the position of the diffracted beams, we use a probing needle (mechanical pencil lead of diameter $\phi 0.2$ mm) mounted on a manual linear translation stage. We adjust the position of the needle so that the shadow of the needle on the screen comes at the center of the diffracted beams. Figure 5 shows a typical result of a measurement of $l/2$ versus L . From Eq. (6), the diffraction angle θ_1 is determined by the slope of the fitting line in Fig. 5. In this case, the fringe spacing Λ was determined to be $29.5 \mu\text{m}$ from Eq. (5) and the standard uncertainty of Λ is evaluated within 1.0%.

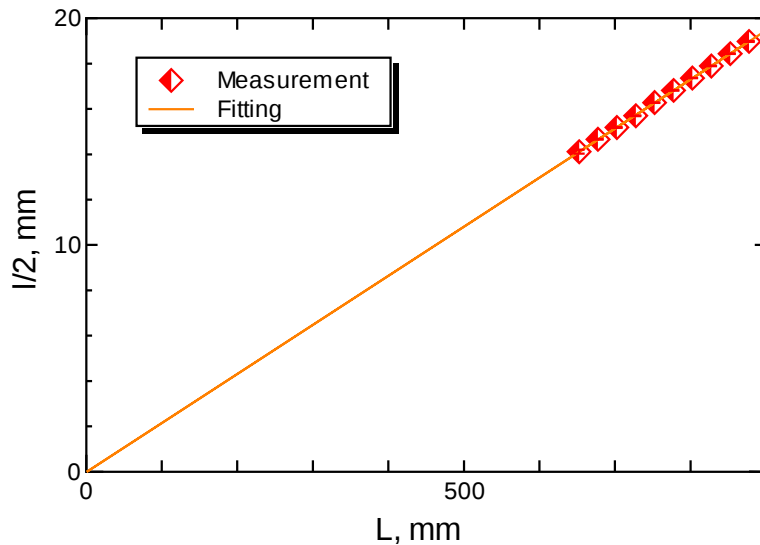


Fig. 5 A typical relationship of a half of the distance between the ± 1 st order diffracted beams $l/2$ and the distance between the acrylic plate and the probing needle L , which were measured to determine the fringe spacing Λ . The value of $\tan \theta_1$ is determined from the slope of the fitting line, in which θ_1 is the diffraction angle of ± 1 st mode.

3. Design of sample cell using a single crystal diamond window

3.1 Selection of window materials

In an IR-SFRS experiment, the sample of aqueous solutions in a PEM should be interposed between two windows in a sample cell. A window for the incidence side requires the following properties:

- 1) High transmittance at the wavelength of the heating laser ($\lambda_h = 9.714 \mu\text{m}$). Absorption of the heating laser by the window decreases the heating energy to induce the sinusoidal temperature distribution in the sample, which makes it difficult to obtain the signals. The heating energy required to obtain appropriate signals is dependent on the properties of samples such as the absorption coefficient at the heating wavelength and the Soret coefficient. Therefore, high transmittance is desirable for flexibility of experiment.
- 2) High transmittance at the wavelength of the probing laser ($\lambda_p = 639 \text{ nm}$). Low transmittance of the window causes the low signal intensity.
- 3) Stability under acidic environment due to PEMs which have sulfo groups.

Window materials satisfying these three requirements are very limited. For example, a ZnSe window transmits both the heating laser and the probing laser (transmittance at the heating wavelength $T_h = 71\%$ and at the probing wavelength $T_p = 67\%$, thickness of 5 mm, WG71050, Thorlabs), but reacts under acidic environment. A quartz glass window transmits the probing laser and stable under acidic environment, but does not transmit the heating laser ($T_h = 0\%$, $T_p = 94\%$, thickness of 1 mm, Fujiwara Scientific). Although a glass window is not suitable for the incidence side, it can be used as the exit side window.

We employed a polycrystalline diamond window ($T_h = 71\%$, $T_p = 67\%$, thickness of 0.5 mm, 155-104-0836, Element Six) for the incidence side in the previous study, but it was difficult to obtain reasonable signals due to the scattered light generated at the polycrystalline diamond window, because the scattered light coherent with the first order diffracted beam affected the signals (Sakai et al., 2012).

In the present study, we introduced a single crystal diamond window ($T_h = 71\%$, $T_p = 70\%$, thickness of 0.5 mm, 145-500-0390, Element Six) to reduce the effect of the scattered light. We evaluated the intensity of the scattered light by measuring the light intensity detected by the photomultiplier in Fig. 3, when the probing laser entered each window mounted at the sample position. Figure 6 shows the photo of window materials and the intensity of the scattered light normalized by that of a single crystal diamond window. The transparency of the two diamond windows in the visible wavelength range seems to be not so different in Fig. 6(a). As shown in Fig. 6(b), however, the intensity of the scattered light with a single crystal diamond window was about 1/150 of the polycrystalline diamond window. This was due to the difference of the scattering properties. The scattering intensity with the single crystal diamond window was as low as that of the quartz glass window. Therefore, the single crystal diamond window is considered to be suitable for the incidence side window.

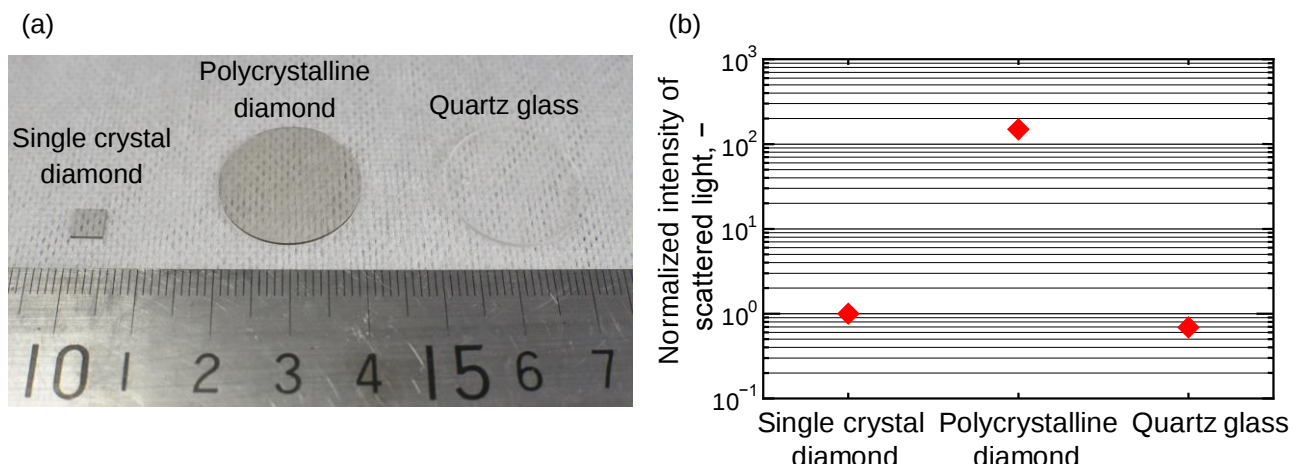


Fig. 6 The comparison of the single crystal diamond window, the polycrystalline diamond window, and the quartz glass window. (a) The photo of the windows. (b) The intensity of the scattered light normalized by that of the single crystal diamond window.

3.2 Configuration of new sample cell

We designed a new sample cell as shown in Fig. 7 to introduce a single crystal diamond window with the size of 4.5×4.5 mm and the thickness of 0.5 mm. The sample is interposed between a glass window and a single crystal diamond window, which is hold in a PTFE plate with a square hole. Silicone gaskets are employed for sealing. This sample cell is assembled easily by the screw cap structure. To deal with bulk solution samples as well as solutions in membranes, the exit side parts such as the Cu cover plate has two holes in addition to a center hole for the optical path, which enables the filling of sample liquid in the cell after assembling. When liquid samples are measured, a spacer made of silicone instead of a PEM sample in Fig. 7 is used. The sample cell is set on the mount made of copper, in which thermostatically controlled water is circulating.

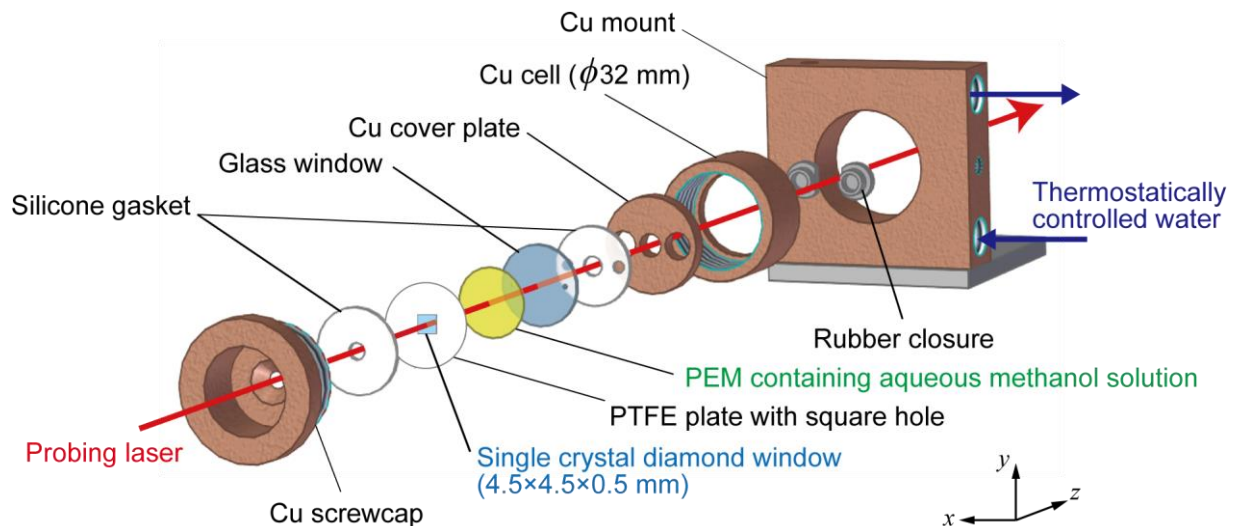


Fig. 7 The sample cell developed in the present study, in which a single crystal diamond window is employed as the incident side window.

4. Measurement of aqueous methanol solutions

Before the measurement of solutions in PEMs, we carried out the measurement on bulk aqueous methanol solutions to evaluate the validity of the measurement system. The aqueous methanol solutions were composed of methanol (> 99.8%, Wako) and pure water. Figure 8 shows the detected signals of the bulk aqueous methanol solutions with the methanol mole fraction of 0.059 (10 wt%) and 0.692 (80 wt%) at a temperature of $T = 298.2$ K.

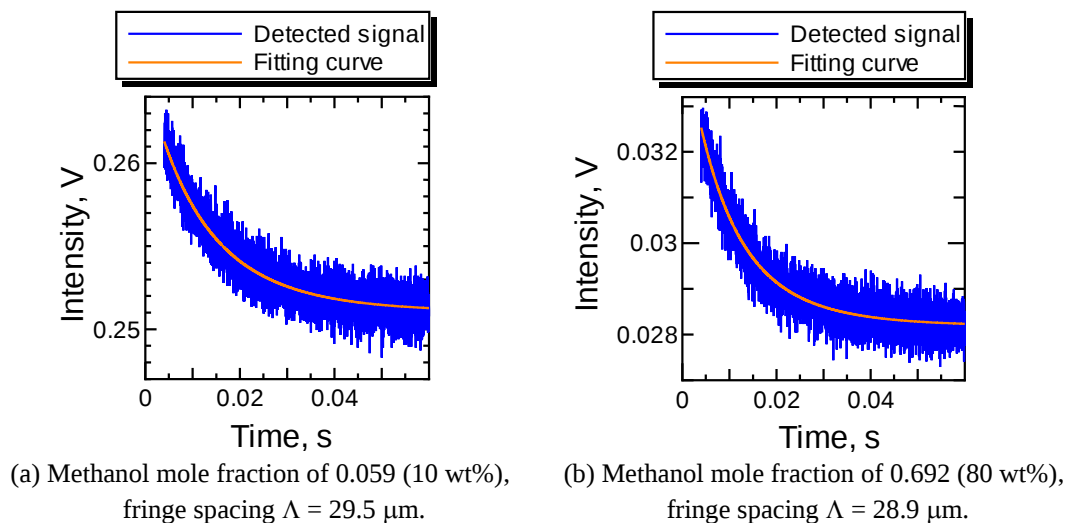


Fig. 8 The detected signals of aqueous methanol solutions at a temperature of $T = 298.2$ K. The relaxation of the concentration distribution by the mass diffusion were observed in several tens of milliseconds.

As shown in Fig. 8, signals decaying in several tens of milliseconds due to the mass diffusion were observed. Figure 9 compares the mass diffusion coefficient measured by the diaphragm cell technique (Derlacki et al., 1985) and measured values in the present study obtained by the analysis of detected signals based on Eqs. (2) and (3). The standard uncertainties of the mass diffusion coefficient in the present study were evaluated based on the Guide to the Expression of Uncertainty in Measurement (GUM) (ISO/IEC, 2008). The relative standard uncertainties of the mass diffusion coefficient were evaluated to be 4.0% and 8.9% for the methanol mass fraction of 0.059 (10 wt%) and 0.692 (80 wt%), respectively. The mass diffusion coefficient measured in the present study agreed with the reported values by Derlacki et al. (1985) within the range of the uncertainties. Therefore, we confirmed the validity of the IR-SFRS apparatus using a single crystal diamond window in a sample cell.

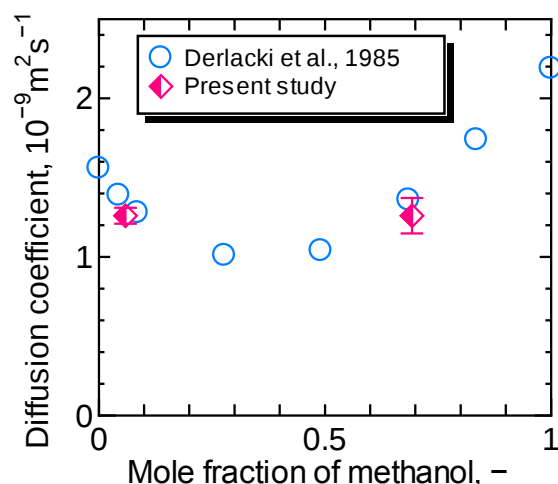


Fig. 9 The mass diffusion coefficient of aqueous methanol solutions measured at a temperature of $T = 298.2$ K. Error bars are the standard uncertainties.

5. Measurement of mass diffusion of aqueous methanol solutions in Nafion 117

We performed the measurement of the aqueous methanol solutions in Nafion 117. Before the measurement, membranes of Nafion 117 were immersed in the aqueous methanol solutions composed of methanol (> 99.8%, Wako) and pure water at least 24 h. Figure 10 shows the detected signals of the aqueous methanol solutions in Nafion 117 with the methanol mole fraction of 0.059 (10 wt%), 0.123 (20 wt%), and 0.692 (80 wt%) at a temperature of $T = 298.2$ K.

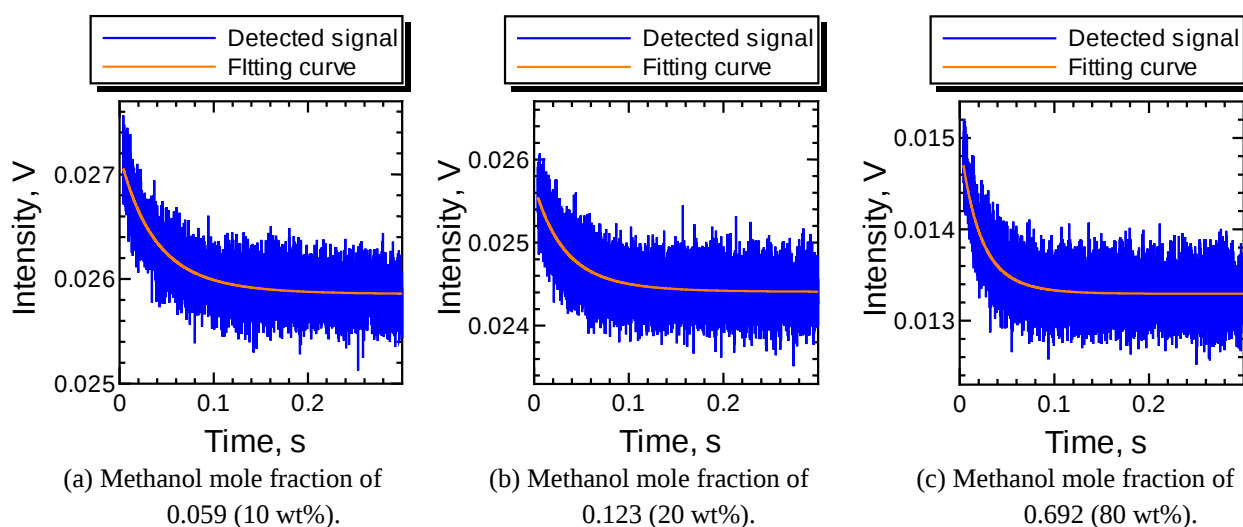


Fig. 10 The detected signals of aqueous methanol solutions in Nafion 117 at a temperature of $T = 298.2$ K. The fringe spacing of the heating laser was $\Lambda = 28.9$ μm .

Table 1 lists the experimental result of the present study. The relative standard uncertainties of the mass diffusion coefficient were 3.7%, 5.3% and 2.5% for the methanol mole fraction of 0.059 (10 wt%), 0.123 (20 wt%), and 0.692 (80 wt%), respectively. The mass diffusion coefficient were obtained in the order of 10^{-10} [m^2s^{-1}], while 10^{-9} [m^2s^{-1}] for the bulk methanol solutions (Fig. 9). This is probably because the mass transport of molecules are limited in PEMs, compared to bulk solutions. Figure 11 compares the mass diffusion coefficient in Nafion 117 in the present study and that measured by other techniques. Although there are differences in the time scale and the boundary conditions in the experiment by each technique, the comparable values of the mass diffusion coefficient were obtained in the present study. Note that only the IR-SFRS technique measured the in-plane mass diffusion. The mass diffusion coefficient by IR-SFRS technique increased with the increase in methanol mole fraction. The similar trends are seen in the results of Every et al. by NMR (2005) and Hallinan and Elabd by FTIR-ATR (2007). This may be due to an increase in the polymer free volume (Hallinan and Elabd, 2007), because the swelling rate of Nafion gets higher as the methanol concentration increases. Therefore, we consider that reasonable measurement of the mass diffusion coefficient of aqueous methanol solutions in Nafion 117 has been performed by the IR-SFRS technique.

Note that the IR-SFRS technique is applicable to Nafion containing higher methanol concentration solutions, while the FTIR-ATR technique has difficulty in the measurement of methanol rich solutions in Nafion 117 due to the excessive membrane swelling (Hallinan and Elabd, 2007). We would like to investigate higher methanol concentration samples to contribute the understanding of the mass transport in PEMs in the future work.

Table 1 The measurement result of the mass diffusion coefficient of aqueous methanol solutions in Nafion 117 at a temperature of $T = 298.2$ K.

Mole fraction of methanol [-]	Mass fraction of methanol [-]	Mass diffusion coefficient D_{12} [$10^{-10}\text{m}^2\text{s}^{-1}$]	Standard uncertainty $u(D_{12})$ [$10^{-10}\text{m}^2\text{s}^{-1}$]	Relative standard uncertainty $u(D_{12}) / D_{12}$ [-]
0.059	0.100	3.18	0.12	0.04
0.123	0.200	3.39	0.18	0.05
0.692	0.800	6.29	0.16	0.03

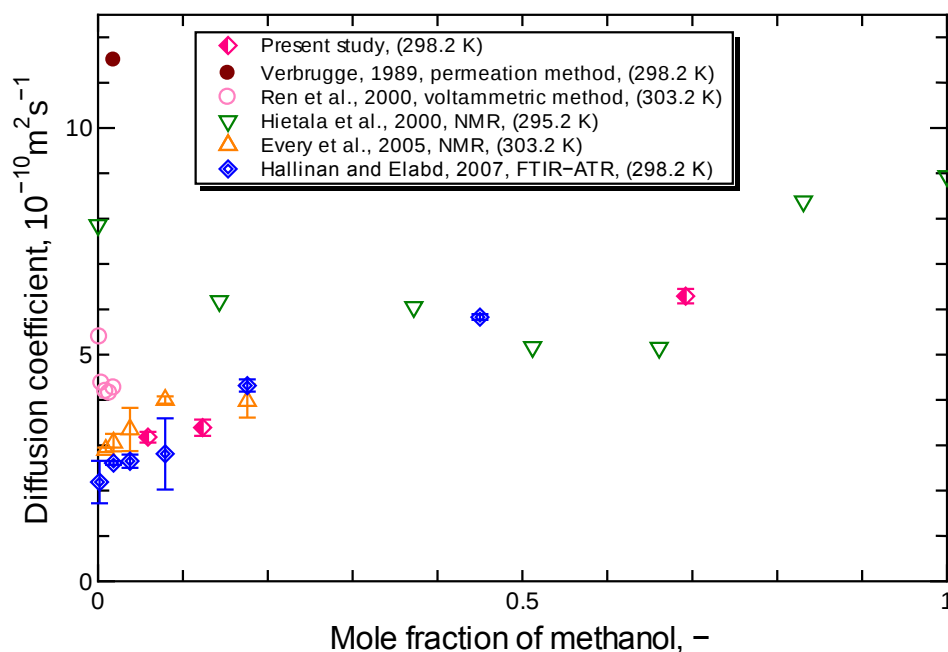


Fig. 11 The mass diffusion coefficient of aqueous methanol solutions in Nafion 117. Error bars of the present study are the standard uncertainties.

6. Conclusions

We presented the infrared Soret forced Rayleigh scattering (IR-SFRS) technique developed for the measurement of the mass diffusion coefficient of aqueous methanol solutions in a polymer electrolyte membrane (PEM) for direct methanol fuel cells (DMFCs). We designed a new sample cell using a single crystal diamond window, which generates significantly lower scattered light of the probing laser, compared to a polycrystalline diamond window. We first carried out on aqueous methanol solutions to evaluate the validity of the measurement system of the IR-SFRS. The mass diffusion coefficient were obtained with the standard uncertainties of 4.0% and 8.9% for aqueous methanol solutions with the methanol mass fraction of 0.059 (10 wt%) and 0.692 (80 wt%), respectively. There was good agreement between the measured values by the diaphragm cell technique and the IR-SFRS technique in the present study within the range of the standard uncertainties. After confirming the validity, experiments on aqueous methanol solutions in Nafion 117 were performed at $T = 298.2$ K. The mass diffusion coefficient were obtained with the relative standard uncertainties of 3.7%, 5.3%, and 2.5% for the methanol mole fraction of 0.059 (10 wt%), 0.123 (20 wt%), and 0.692 (80 wt%), respectively. The mass diffusion coefficient in Nafion 117 was in the order of 10^{-10} [m^2s^{-1}], while 10^{-9} [m^2s^{-1}] for the bulk methanol solutions, and increased with the increase in methanol concentration. This result corresponds with an assumption that the mass transport of molecules is limited in a PEM. Therefore, we consider that we showed the applicability of the IR-SFRS technique to investigate the mass diffusion in PEMs.

Acknowledgment

This work was supported by JSPS KAKNHI Grant Numbers JP24226006, JP17H01248, and JP16J02498.

References

- Bahrami, H. and Faghri, A., Review and advances of direct methanol fuel cells: Part II: Modeling and numerical simulation, *Journal of Power Sources*, Vol. 230, (2013), pp. 303–320.
- Derlacki, Z. J., Easteal, A. J., Edge, A. V. J., and Woolf, L. A., Diffusion coefficients of methanol and water and the mutual diffusion coefficient in methanol-water solutions at 278 and 298 K, *Journal of Physical Chemistry*, Vol. 89, No. 24, (1985), pp. 5318–5322.
- Every, H. A., Hickner, M. A., McGrath, J. E., and Zawodzinski, T. A., An NMR study of methanol diffusion in polymer electrolyte fuel cell membranes, *Journal of Membrane Science*, Vol. 250, No. 1-2 (2005), pp. 183–188.
- Gloukhovski, R., Tsur, Y., and Freger, V., A Nafion-filled polycarbonate track-etched composite membrane with enhanced selectivity for direct methanol fuel cells, *Fuel Cells*, Vol. 17, No. 1, (2017), pp. 56–66.
- Hallinan, D. T. and Elabd, Y. A., Diffusion and sorption of methanol and water in Nafion using time-resolved Fourier transform infrared-attenuated total reflectance spectroscopy, *Journal of Physical Chemistry B*, Vol. 111, No. 46 (2007), pp. 13221–13230.
- Hayashida, K. and Nagasaka, Y., Measurement of mutual diffusion coefficient by the Soret forced Rayleigh scattering method (1st Report, Examination of the method and measurement of polymer solutions), *Transactions of the Japan Society of Mechanical Engineers Series B*, Vol. 63, No. 610, (1997), pp. 2160–2165, (in Japanese).
- Hoshino, T. and Nagasaka, Y., Experimental study of measurement technique for mass diffusion coefficient of methanol aqueous solution in polymer electrolyte membrane by infrared Soret forced Rayleigh scattering method –Influence evaluation of the coherent scattered light–, *Proceedings of the 36th Japan Symposium on Thermophysical Properties*, (2015), D312, pp. 276–278, (in Japanese).
- Hietala, S., Maunu, S. L., and Sundholm, F., Sorption and diffusion of methanol and water in PVDF-*g*-PSSA and Nafion® 117 polymer electrolyte membranes, *Journal of Polymer Science Part B: Polymer Physics*, Vol. 38, No. 24 (2000), pp. 3277–3284.
- ISO/IEC Guide 98-3:2008, Uncertainty of Measurement—Part 3: Guide to the Expression of Uncertainty in Measurement (GUM:1995), (2008), International Organization for Standardization, Geneva.
- Köhler, W. and Morozov, K. I., The Soret effect in liquid mixtures – A review, *Journal of Non-Equilibrium Thermodynamics*, Vol. 41, No. 3, (2016), pp. 151–197.
- Klein, W. R. and Cook, B. D., Unified approach to ultrasonic light diffraction, *IEEE Transactions on Sonics and*

- Ultrasonics, Vol. 14, No. 3, (1967), pp. 123–134.
- Li, X. and Faghri, A., Review and advances of direct methanol fuel cells (DMFCs) part I: Design, fabrication, and testing with high concentration methanol solutions, *Journal of Power Sources*, Vol. 226, (2013), pp. 223–240.
- Matsuura, H., Iwaasa, S., and Nagasaka, Y., Mass diffusion coefficient and Soret coefficient of *o*-dichlorobenzene solutions of PCBM and [60]fullerene by the Soret forced Rayleigh scattering method, *Journal of Chemical & Engineering Data*, Vol. 60, No. 12, (2015), pp. 3621–3630.
- Matsuura, H. and Nagasaka, Y., Development of measurement technique for Soret coefficient and thermodiffusion coefficient of ternary systems by Soret forced Rayleigh scattering method with two probing lasers of different wavelengths, *Netsu Bussei*, Vol. 31, No. 2, (2017), pp. 89–96, (in Japanese).
- Matsuura, H. and Nagasaka, Y., Soret forced Rayleigh scattering instrument for simultaneous detection of two-wavelength signals to measure Soret coefficient and thermodiffusion coefficient in ternary mixtures, *Review of Scientific Instruments*, Vol. 89, No. 2, (2018), 024903.
- Mauritz, K. A. and Moore, R. B., State of understanding of Nafion, *Chemical Reviews*, Vol. 104, No. 10, (2004), pp. 4535–4586.
- Miyahara, S., Sakai, T., and Nagasaka, Y., Experimental study of measurement technique for mass diffusion coefficient of methanol aqueous solutions in polymer electrolyte membrane for fuel cell by infrared Soret forced Rayleigh scattering method –Development of apparatus using grating tunable infrared laser–, *Proceedings of the 34th Japan Symposium on Thermophysical Properties*, (2013), B222, pp. 220–222, (in Japanese).
- Niwa, M., Ohta, Y., and Nagasaka, Y., Mass diffusion coefficients of cellulose acetate butyrate in methyl ethyl ketone solutions at temperatures between (293 and 323) K and mass fractions from 0.05 to 0.60 using the Soret forced Rayleigh scattering method, *Journal of Chemical & Engineering Data*, Vol. 54, No. 9, (2009), pp. 2708–2714.
- Plyler, E. K., Infrared spectra of methanol, ethanol, and *n*-Propanol, *Journal of Research of the National Bureau of Standards*, Vol. 48, No. 4, (1952), pp. 281–286.
- Ren, X., Springer, T. E., Zawodzinski, T. A., and Gottesfeld, S., Methanol transport through Nafion membranes electro-osmotic drag effects on potential step measurements, *Journal of the Electrochemical Society*, Vol. 147, No. 2, (2000), pp. 466–474.
- Sakai, T., Hotta, J., and Nagasaka, Y., Development of measurement technique for mass diffusion coefficient of methanol aqueous solutions in polymer electrolyte membrane for fuel cell by Soret forced Rayleigh scattering, *Netsu Bussei*, Vol. 26, No. 4, (2012), pp. 196–202, (in Japanese).
- Verburgge, M. W., Methanol diffusion in perfluorinated ion-exchange membranes, *Journal of the Electrochemical Society*, Vol. 136, No. 2 (1989), pp. 417–423.
- Wiegand, S., Ning, H., and Kriegs, H., Thermal diffusion forced Rayleigh scattering setup optimized for aqueous mixtures, *Journal of Physical Chemistry B*, Vol. 111, No. 51, (2007), pp. 14169–14174.
- Yamamoto, Y. and Nagasaka, Y., Development of the Soret forced Rayleigh scattering method for measurement of mass diffusion coefficient (1st Report, Development of the measurement system and measurement of the fullerene in solution), *Transactions of the Japan Society of Mechanical Engineers Series B*, Vol. 72, No. 715, (2006a), pp. 709–714, (in Japanese).
- Yamamoto, Y. and Nagasaka, Y., Measurement of mass diffusion coefficient by the Soret forced Rayleigh scattering method (2nd Report, Theoretical analysis of systematic effect of experimental parameters), *Transactions of the Japan Society of Mechanical Engineers Series B*, Vol. 72, No. 715, (2006b), pp. 715–722, (in Japanese).