Measurement System for Solubility and Self-Diffusivity of Hydrogen Gas Dissolved in Polymer Electrolyte Membrane

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The characteristics of hydrogen gas permeation through a polymer electrolyte membrane (PEM) are important in determining the performance of electrochemical systems such as fuel cells and electrolyzers. However, the only available data related to these characteristics are those for the hydrogen permeability, which were obtained from measurements under a given pressure difference through the PEM. Although we can derive the solubility and self-diffusivity from the permeability, the derivation requires a mathematical procedure, such as providing a gas transport model and fitting experimental data with theoretical data from the model. In this study, we developed a measurement system that uses nuclear magnetic resonance and can quantify both the solubility and self-diffusivity in a rather straightforward manner. The system allows us to measure these two properties when hydrogen gas is dissolved in a dry Nafion membrane under a hydrogen gas pressure of up to 1 MPa at room temperature. The solubility increases linearly with increasing pressure, and the solubility coefficient is $(1.3 \pm 0.13) \times 10^{-5}$ mol/(cm$^3$ MPa). The self-diffusivity shows a constant value of $(2 \pm 0.4) \times 10^{-6}$ cm$^2$/s regardless of the pressure.

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The polymer electrolyte membrane (PEM) is an important functional material used in electrochemical systems. It acts as a gas barrier between the anode and cathode and is also an ionic conductor. Moreover, high mechanical strength and good durability, for example, robustness to changes in the humidity, are required in PEMs for practical use. These requirements have motivated many investigations of the transport and mechanical characteristics of PEMs.

Among the many functions of PEMs, the permeation of gases through them is significant. The permeation characteristics determine the oxygen dissolution into the PEM (more precisely, the ionomer) and the extent of the three-phase boundary, affecting the overvoltage and voltage efficiency of the electrochemical system. They also directly determine the system’s current efficiency.1,3 Especially for high-pressure water electrolyzers. Thus, the permeation characteristics should be clarified quantitatively. In addition, the solubility and self-diffusivity of gases in a PEM, which are components of the permeability, should be quantified individually. In addition to the permeability, the solubility and self-diffusivity, if available, can provide more concrete guidelines for developing PEMs.

To date, the permeability of hydrogen gas through PEMs has been measured by the volumetric, time-lag, gas chromatograph, and electrochemical methods. In the volumetric method,4 a pressure difference between two chambers divided by a PEM is imposed initially, and the time variation of the pressures in the chambers corresponds to the permeability of the PEM. Although the time-lag method is similar to the volumetric method, it can obtain the solubility and diffusivity using the time variation of the pressures and an assumed mathematical model.5,6 The gas chromatograph method can determine the permeability without an imposed pressure difference.5,6 Although the gas species is limited to hydrogen, the electrochemical method can derive the permeability by measuring the hydrogen pumping current that flows through the PEM under given DC voltages.6,9

Although the gas permeation characteristics have been evaluated experimentally and a certain amount of data is available, most reports give only the permeability. As mentioned above, the time-lag method can determine both the gas solubility and diffusivity in a PEM. However, it requires the assumption of mathematical models and is difficult to apply to humidified PEMs. Additionally, the permeability data specified to date in experimental studies were obtained under different conditions. Therefore, the permeation characteristics have not been assessed comprehensively. To support the development of PEMs to improve the performance of electrochemical systems, a novel measurement method is needed that can quantify both the gas solubility and self-diffusivity directly.

Against this background, we developed a method of direct measurement of both the solubility and self-diffusivity of hydrogen gas in PEMs by nuclear magnetic resonance (NMR). In this method, an electromagnetic wave excites the magnetization of hydrogen nuclei under a static magnetic field, and we measure the electromagnetic wave (NMR signal) from the excited hydrogen nuclei to obtain the density and mobility of hydrogen atoms (molecules). In particular, we specialize the NMR system as follows. We introduce a permanent magnet having a large opening that enables hydrogen gas to be supplied to the vessel, where a PEM sample is installed. We also introduce a water jacket on the magnet to stabilize its temperature, yielding long-duration NMR signal acquisition for a higher signal-to-noise ratio (S/N). Moreover, we place a small amount of water in a capillary tube located near the PEM in which hydrogen gas dissolves. This water acts as a reference to track the NMR frequency.

With the developed NMR system, we qualified the solubility and self-diffusivity of hydrogen gas in PEMs. In this system, a PEM sample installed in a vessel within the permanent magnet is exposed to hydrogen gas at room temperature under pressures up to 1 MPa. The sample is kept at a constant temperature to suppress undesirable temperature variation. The PEM sample and a solenoid coil are

Experimental

NMR system.—Figure 1 shows the NMR system for measuring the hydrogen gas solubility and self-diffusivity in PEMs. A permanent magnet produces a static magnetic field of 1 T, which is necessary for NMR. A large opening on the magnet enables us to easily install piping for in-situ characterization of gas permeation through the PEM. The amount of hydrogen gas dissolved in the PEM is small; therefore, repeated acquisition of NMR signals is required to improve the S/N. The NMR signal is highly sensitive to the temperature variation of the permanent magnet during the long-duration operation necessary for repeated acquisition. A water jacket is built on the magnet and supplied with water at a constant temperature to suppress undesirable temperature variation. The PEM sample and a solenoid coil are
mounted in the vessel, which is located in the permanent magnet. Gradient coils are also built next to the vessel. We carefully track the NMR frequency by referring to the NMR signal from bulk water enclosed in a capillary tube next to the vessel. As mentioned, the NMR signal acquisition in this study requires a long duration, but even a small change in the permanent magnet’s temperature changes the NMR frequency by causing the static magnetic field to vary. We may miss the NMR signal from the hydrogen gas dissolved in the PEM if we track only a constant NMR frequency. Thus, we refer to the NMR signal from the bulk water and occasionally calibrate the frequency of the NMR signal from the dissolved hydrogen gas in the PEM. This occasional calibration enables 6000 repeated NMR signal acquisitions, improving the S/N.

The solenoid and gradient magnetic field coil, which are mounted in the permanent magnet, are specified as follows. The solenoid coil emits electromagnetic waves to excite the magnetization of the hydrogen nuclei and receives the NMR signal from the nuclei. It is fabricated with seven turns of copper wire 0.5 mm in diameter so that it has a coiled shape with an inner diameter of 8.2 mm. The gradient magnetic field coil yields a gradient magnetic field with a specified current within a period. As explained below, it can separate the components of the NMR signal and extract the desired component. It also enables us to measure the hydrogen gas self-diffusivity in PEMs.

**PEM sample and its standardization.**—As the PEM samples into which hydrogen gas dissolves, two types of Nafion membranes (Nafion 112 and 117) are considered. Although Nafion 112 and 117 have different thicknesses, they possess almost the same physical properties, suggesting that they yield the same solubility and self-diffusivity of hydrogen gas. If the measurement results indicate the same properties in Nafion 112 and 117, this would indicate the reliability of the measurement method. The Nafion membrane samples were standardized and fabricated as follows. First, each membrane was cleaned by boiling in three types of solution (5% H2O2 solution, water, and 1 N HCl solution) in turn for 1 h each. The membrane was then rolled, using a 5% Nafion solution as a binder, so that it had a cylindrical shape. Next, the Nafion membrane was dried for several hours in an experimental room under an ambient temperature of 24°C and relative humidity of 50%. The cylindrical Nafion membrane was measured to be 6.5 mm in outer diameter, 1.8 mm in inner diameter, and 5 mm in height (150 mm3). Then, the membrane was dried under vacuum for one week. Next, it was placed in the vessel and again dried there under dried nitrogen gas ambient for two days. Thus, we completely dried the membrane so that water absorbed in it cannot appear as a noise component in the observed NMR signals.

Hydrogen gas is supplied to the vessel at room temperature at a flow rate of 30 NmL/min. The gas pressure in the vessel can be varied up to 1 MPa to investigate the pressure dependence of the permeation characteristics. After a specific gas condition is established and the solution equilibrium is confirmed by obtaining a stable NMR signal, signal acquisition for determining the solubility and self-diffusivity begins. Occasionally, nitrogen gas is supplied to dry the PEM sample, as mentioned above. The nitrogen gas also separates the background component of the obtained NMR signal, as described below.

**Measurement principle.**—The proton is the target nucleus in NMR measurement to quantify the hydrogen gas dissolved in the PEM. The permanent magnet’s intensity of 1 T produces a proton resonance frequency of approximately 45 MHz. Pulsed irradiation by an electromagnetic wave at the resonance frequency causes resonant excitation of the protons. After the pulse, the excited protons relax by emitting electromagnetic waves, which provide information on the quantity of protons and their state of motion. Thus, obtaining the wave (NMR signal) corresponds to measuring the quantity and motion of molecules containing hydrogen atoms, or measuring exactly the hydrogen gas solubility and self-diffusivity in the PEM.

The spin-echo (SE) sequence shown in Fig. 2a yields the solubility. In the SE sequence, two pulses are emitted in series: the so-called 90° pulse and a 180° degree pulse after a time (TE/2) has elapsed, yielding the SE signal ISE at the time TE. The obtained echo signal and the number density of hydrogen atoms pH are related as follows.

\[ I_{SE} = A \rho_H \left(1 - e^{-\frac{TE}{T_1}}\right) e^{-\frac{TE}{T_2}} \]

**Figure 2.** Pulse sequences. (a) Spin-echo (SE) sequence for measuring the solubility. (b) Pulsed-field gradient spin-echo (PGSE) sequence for measuring the diffusivity.
self-diffusivity $D$ is formulated as follows.

$$\ln\left(\frac{I_{SE}(G_i)}{I_{SE}(G_0)}\right) = -D \times d^2 \delta G^2,$$

where $G_i$ is the intensity of the gradient field, $d$ is the duration of the pulse gradient field, and $\delta$ is the pulse interval. Here, $d$ and $\delta$ are 2.5 and 6.0 ms, respectively. $G_i$ is calibrated by measurements of bulk water, whose self-diffusion is well known to be $2.3 \times 10^{-9} \text{ m}^2/\text{s}$.\(^{13}\)

The longitudinal relaxation time $T_1$ is measured by the inversion recovery (IR) method.\(^{11}\) Before the 90° pulse in the SE sequence, a 180° pulse is also applied, exciting the hydrogen nuclei and enabling us to measure the longitudinal relaxation of their magnetization vectors at the time between the additional 180° pulse and the 90° pulse. The duration $\tau$ between the two pulses can be adjusted arbitrarily. The longitudinal relaxation time $T_1$ and echo signal $I_{SE}$ are related to the duration $\tau$ as follows.

$$\frac{I_{SE}(\tau)}{I_{SE}(\tau = \infty)} = 1 - 2e^{-\frac{\gamma d \delta G^2}{T_1}}\text{[3]}$$

Similar to the self-diffusivity, $T_1$ can be obtained from $I_{SE} (\tau)$ by successively changing $\tau$.

$T_1$ is quantified using a method similar to the SE method. Equation 1 is simplified to the following expression in terms of $I_{SE}$, TE, and $T_2$, assuming the other variables are constant.

$$I_{SE} = C e^{-T_2/T_1}\text{[4]}$$

This equation suggests that $T_2$ can be obtained by measuring the SE signals for different TE values.

**Results and Discussion**

Extracting the component of the NMR signal originating in the hydrogen gas dissolved in the PEM is a significant issue in this study. This is because the RF coil mentioned above excites and detects all the NMR signals from all the hydrogen atoms within the measurement region, which depends on the coil size. In addition to the hydrogen gas in the PEM, the coil may detect the NMR signals from the following components: (1) hydrogen atoms in the PEM structure, (2) hydrogen gas in the gas phase (not dissolved in the PEM), and (3) other hydrogen atoms in the measurement system, such as those in the coating material on the coil.

Among these components, the NMR signal originating from hydrogen gas in the gas phase was eliminated by exploiting its high self-diffusivity, which is much larger than that of molecules in the PEM. As mentioned regarding the PGSE method, applying a gradient magnetic field during the SE sequence spreads the phase of the NMR signal and reduces its intensity. This reduction is enhanced if the hydrogen atom (molecule) actively moves. Therefore, we applied gradient magnetic field pulses and eliminated the NMR signal from the hydrogen gas around the PEM.

The NMR signals originating both from the PEM itself and from other materials in the measurement system are eliminated using a differential method. The NMR signals measured under a nitrogen gas ambient condition suggest that they come from these two sources. Thus, subtracting the signal under the nitrogen gas condition from that under the hydrogen gas condition extracts the signal from the hydrogen gas dissolved in the PEM.

Figure 3 shows the SE signals under ambient hydrogen and nitrogen gas for the Nafion 117 PEM sample in the RF coil. The maximum gas pressure is 1.0 MPa. The signals under the nitrogen gas condition are constant regardless of the pressure, whereas those under the hydrogen gas condition increase with increasing pressure. It is worth mentioning that the signal intensity extrapolated to 0 MPa in the hydrogen gas case agrees with that in the nitrogen gas case. As mentioned above, the signal difference between the two cases corresponds to the component of the signal from the hydrogen gas dissolved in the PEM. This signal difference is converted to the solubility as described below.

Figure 4a shows $T_1$ for the hydrogen gas dissolved in Nafion 117 obtained by the IR method. The signals on this diagram were measured by successively changing $\tau$, as described in the section on the experimental method. As explained in equation 1, $T_1$ is necessary for deriving the solubility from the echo signals shown in Fig. 3. Figure 4b shows $T_2$, which was obtained by measuring the SE signal for various values of TE. The signals in Fig. 4a and 4b change exponentially, in agreement with equations 3 and 4, respectively. Thus, the gradients of the signals on a single logarithmic chart yield $T_1$ and $T_2$.

The obtained $T_1$ and $T_2$ are summarized in Table 1, which shows the relaxation times for Nafion 112 and 117 under the hydrogen and nitrogen gas ambient conditions. The $T_1$ and $T_2$ values of the dissolved hydrogen gas in Nafion 112 are given as 172 and 26 ms, respectively, in the row labeled “Difference.” Those of the dissolved hydrogen gas...
Table I. NMR properties of Nafion 112 and 117 under dry conditions.

| Samples | Atmosphere | \(I_{\text{SE}}\) [\(\text{I}^{[-]}\)] | \(T_1\) [\(\text{ms}\)] | \(T_2\) [\(\text{ms}\)] |
|---------|------------|-----------------|-----------------|-----------------|
| Nafion 112 | H\(_2\) at 0.7 MPa | 4.02 ± 0.04 | 78.2 ± 2.1 | 19.4 ± 0.21 |
|          | N\(_2\) at 0.1 MPa | 1.10 ± 0.03 | 232 ± 17 | 17.4 ± 0.39 |
|          | Difference between H\(_2\) and N\(_2\) cases | 0.79 ± 0.06 | 167 ± 5.0 | 26.1 ± 1.76 |
| Nafion 117 | H\(_2\) at 1.0 MPa | 4.02 ± 0.04 | 192 ± 6.0 | 30.8 ± 0.39 |
|          | N\(_2\) at 0.1 MPa | 1.10 ± 0.03 | 210 ± 7.4 | 36.7 ± 1.2 |
|          | Difference between H\(_2\) and N\(_2\) cases | 2.92 ± 0.05 | 179 ± 7.9 | 28.5 ± 0.57 |

Figure 5. Hydrogen gas solubility derived from equation 1 using obtained signals in Fig. 3.

in Nafion 117 are 179 and 28 ms, respectively. The difference in \(T_1\) between the two membranes is within 7%, and that in \(T_2\) is within 9%. This consistency suggests that the measurement method developed here is reliable.

Like the signal intensity in Fig. 3, the relaxation time is also measured by subtracting the signal under nitrogen gas ambient from that under hydrogen gas ambient. The signal under hydrogen gas ambient shown in the relaxation time analysis of Fig. 4 involves the three components from the hydrogen atoms in the PEM structure, a trace of hydrogen molecules at room temperature. This ratio should be considered because the NMR measurement detects only the orthohydrogen molecules.

The solubility of hydrogen in Nafion 117 and 112 obtained by the above procedures is summarized in Fig. 5. For comparison, the solubility of hydrogen dissolved in Teflon is also shown. The solubility of hydrogen gas dissolved in the Nafion membranes increases in proportion to the ambient pressure of hydrogen gas within the given pressure range, and it follows Henry’s law. The solubility coefficient, which is the slope of the data in Fig. 5, is shown in Table II.

Table II. Comparison of hydrogen gas solubility and self-diffusivity in various materials obtained by different measurement methods.

| Researchers and Samples | Solubility \([\times 10^{-5} \text{mol/(cm}^3\text{MPa)}]\) | Diffusivity \([\times 10^{-10} \text{cm}^2/\text{s}]\) | Permeability \([\text{Barrer}]\) | Measurement Methods and Conditions |
|-------------------------|-----------------|-----------------|-----------------|-----------------|
| This work               | 1.8 ± 0.26      | 1.8 ± 0.6       | 9.8 ± 3.6       | NMR method      |
| Nafion 112              | 1.3 ± 0.13      | 2.0 ± 0.4       | 7.8 ± 1.6       | 297 ± 2 K, 0.1–1.0 MPa |
| This work               | 2.2 ± 0.21      | 1.8 ± 0.1       | 14 ± 1.6        | NMR method      |
| Teflon                  | 3.3             | 0.96            | 14              | Time-lag method |
| Chiu and Paul           | 1.4             | 1.4             | 5.79            | 308 K, 0–1.0 MPa |
| Nafion 117              | 2.3             | 2.0             | 9.30            | Time-lag method |
| Fontananova et al.      | 1.4             | 1.4             | 5.79            | 298 ± 1 K, 0-0.133 MPa |
| Nafion 117              | 2.3             | 2.0             | 9.30            | 303 K, 0–1.0 MPa |

Figure 6 shows the self-diffusivity of hydrogen gas in the Nafion 117 membrane obtained by the PGSE method under ambient hydrogen gas at 1.0 MPa. Equation 2 suggests that the slope of the single logarithmic plot of \(I_{\text{SE}}(\text{GHz})/I_{\text{SE}(0)}\) versus \(\gamma^2 d^2 G^2\) corresponds to the diffusivity. The self-diffusivities at each ambient pressure of hydrogen gas are summarized in Fig. 7. Because the hydrogen molecules dissolved in the Nafion membranes are confined in nanospaces, the self-diffusivity of hydrogen gas in the membranes is thought to be

water was used because the developed NMR system is customized for the rather weak NMR signal from the hydrogen gas dissolved in the PEM. The NMR signals become saturated when we simply use light water, which has a high hydrogen atom number density. Thus, we diluted the light water with heavy water and used this diluted light water to calibrate the constant \(A\). The calibration yields a value of \(2.27 \times 10^3 \text{cm}^2/\text{mol}\) for \(A\). We refer to this value when we quantify the solubility from the NMR signals.

Quantification of the hydrogen gas dissolved in the PEM requires an additional process. Substituting \(T_1\) and \(T_2\) in Table I and the echo signals in Fig. 3 into equation 1 yields the hydrogen atom number density \(\rho_{\text{H}2}\) dissolved.

\[
\rho_{\text{H}2,\text{dissolved}} = A \beta \rho_{\text{H}} = (1/2)(4/3) \rho_{\text{H}}. \tag{5}
\]

Here, \(\alpha\) is a conversion factor for converting hydrogen atoms to molecular hydrogen, and \(\beta\) is related to the ratio between ortho- and para-hydrogen molecules at room temperature. This ratio should be considered because the NMR measurement detects only the orthohydrogen molecules.
constant with changes in the ambient pressure. In agreement with this expectation, the self-diffusivity is independent of the pressure. The self-diffusivities in both Nafion 117 and Nafion 112 are approximately $2 \times 10^{-10}$ m$^2$/s, with good agreement between the two cases.

Table II also compares the solubility coefficients and self-diffusivities obtained in this study with those obtained with other methods.\textsuperscript{5–7} The properties obtained by the NMR method and time-lag methods appear to be consistent, indicating the reliability of the NMR method. The NMR method used in this study does not require any mass transport models for the derivation of the solubility and self-diffusivity. This is an advantage because we can directly measure the properties of the gas dissolved in the PEM. The NMR method can be applicable in more practical situations, such as when the PEM is wetted, although heavy water is required to wet it. Thus, the NMR method developed here is expected to contribute to the research and development of PEMs.

Conclusions

We developed an NMR method of measuring hydrogen gas permeation through PEMs. We applied it to measurements of the hydrogen gas solubility and diffusivity in dried Nafion membranes at 297 K and pressures up to 1.0 MPa. Our findings were as follows.

1. The NMR signal component from the hydrogen gas dissolved in Nafion can be separated from the components from the ambient hydrogen gas and hydrogen atoms involved in the Nafion. The different gas ambients, hydrogen and nitrogen, and the gradient magnetic field pulse imposed during the SE sequence are keys to the separation.

2. The hydrogen gas solubility increases in proportion to the ambient pressure. The solubility coefficient for Nafion 117 is $(1.3 \pm 0.13) \times 10^{-5}$ mol/(cm$^3$ MPa), and that for Nafion 112 is $(1.8 \pm 0.26) \times 10^{-5}$ mol/(cm$^3$ MPa). The results of the NMR method and other methods indicate good agreement in the solubility.

3. The self-diffusivities of hydrogen gas are almost the same in Nafion 117 and 112: $(2 \pm 0.4) \times 10^{-10}$ m$^2$/s and $(1.8 \pm 0.6) \times 10^{-10}$ m$^2$/s, respectively.

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