Proton Conductivity of the Reinforced Perfluorinated Membrane as a Function of Temperature and Humidity

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The proton conductivity of the reinforced perfluorinated membrane was measured under various conditions of humidity and temperature using a four-electrode impedance method. The conductivity of the membrane was over $8 \times 10^{-2} \text{ S cm}^{-1}$ with 70% relative humidity at 70 °C; it varied strongly with both humidity and temperature. A stable conductivity condition was observed when the relative humidity was over 20%. From the results, the activation energy was calculated to be less than 20 kJ mol⁻¹ at any humidity. These results suggested that the Grothuss-type proton conduction might be dominant for the proton migration inside the reinforced membrane at a wide range of humidity.

Key Words : Fuel Cell, Polymer Electrolyte, Conductivity, Humidity

1 Introduction

Polymer electrolyte fuel cells (PEFCs) operate at a lower temperature than other types of fuel cells, and have received considerable attention due to their applicability to electric vehicles and stationary generators. This attention has also recently stimulated the research and development of the materials which are essential to PEFC. An ion-exchange membrane is one of the key materials for PEFC, because the performance of PEFC strongly depends on the proton conductivity of the membrane. Analysis of the performance of a PEFC requires reliable conductivity data for the membrane at different humidities in combination with water uptake,¹⁻⁴⁾ water diffusion⁵⁾ and gas diffusion properties.⁹⁻¹⁴⁾

NAFION[®] is one of the most popular ion-exchange membranes applied to the fuel cell. It was developed in the 1960's, and was first applied to the fuel cell for the spacecraft 'BIO-SAT' which performed biological experiments in space¹⁵⁾. Recently, a lot of research has been performed to clarify the proton conducting performance of the membrane.

The ion conductivity of the membrane has been conventionally measured using an ac impedance method with two electrodes.^{3-5,12,13)} Application of a two-electrode method to a material with a low resistance requires a high frequency in order to separate membrane resistance from interfacial capacitance. It is very difficult to make a detailed discussion of the impedance dependence on temperature and humidity. Cahan and Wainright,¹⁴⁾ however, reported that they used a four-electrode system for impedance measurements and successfully mea-

sured membrane impedance, which is separated from interfacial capacitance over a wide range of frequency from dc to 10⁵ Hz. Deslouis and others used a four-electrode impedance method to study ionic conductivity of electronically conductive polymers,^{16,17)} and also mentioned the necessity of using a four-electrode arrangement to measure the very low impedance of the membranes.

Based on these concepts, we previously measured the impedance of NAFION 117[®] using the four-electrode impedance method.¹⁸⁾ We precisely reported the conductivity dependence on the relative humidity and the temperature. In addition, it was shown that the conductivity of the membrane increased with water uptake. When the content of water ($\lambda = \text{mol H}_2\text{O} / \text{mol SO}_3\text{H}$) was less than three, the conductivity of NAFION[®] increased exponentially with the increase in λ . On the contrary, the conductivity started to increase linearly with the water content when λ was over three. In our previous work, we measured the conductivity along the tangential direction of the membrane.¹⁸⁾ The relationship between conductivity and the geometry for the measurements has also been discussed.¹⁹⁾ This information is very important for the design of a fuel cell. Thus, the water transportation in the perfluorinated membranes is also discussed with the proton conductive mechanism of the membrane.^{20,21)}

Recently, a lot of effort has been made to improve the proton conducting membrane. Absorption of water by the membrane causes the thickness and the surface area of the membrane to increase. When the membrane is

applied to the fuel cell, it is very important to keep the contact between the electrode and the electrolyte. In most cases, catalyst is put on the surface of the membrane to make a membrane-electrode-assembly (MEA), which is sandwiched by the separators with gas flow channels. If the size of the membrane changes with water uptake during fuel cell operation, the membrane might be scratched or ripped by the stress from the separators.

In order to maintain the size of the membrane during the fuel cell operation, reinforced membranes have been developed. One example of such a membrane is commercially available GORE-SELECT®. In this membrane, perfluorinated ionomer is reinforced by the matrix of the polytetrafluoroethylene network. This reinforcement maintains the size of the membrane even during fuel cell operation.

For fuel cell applications, it is very important to understand the proton conductivity of the membrane precisely. In this research, the conductivity of the reinforced membrane was measured at various humidities and temperatures using the four-electrode impedance method. The performance of the membrane was compared with that of the conventional proton conducting membrane 'NAFION®'. The impedance of the membrane was successfully measured over a wide range of humidity. Using the results, the activation energy of the proton conduction was calculated, which suggested that the proton conduction inside the membrane might be dominated by the Grothuss-type mechanism.

2 Experimental

A commercial reinforced membrane, 'GORE-SELECT®' from GORETECHS Ltd., was used for measurements. The thickness of the dried membrane was 30 μm .

Figure 1 shows the configuration for the impedance measurement. The membrane was cut into the size of 1 cm $\times$ 3 cm, and put on the stage to fix the electrodes. Two platinum foil electrodes were placed 3 cm apart to feed current to the sample, and two platinum needles 1 cm apart to measure the potential drop along the film near the center. The sample with leads was placed in the vessel where the thermostatic heater controlled the temperature. The humidity in the vessel was controlled by humid nitrogen gas flow. Both relative humidity (RH) and temperature inside the glass vessel were detected simultaneously using a sensor unit (HYDROPALM 2 and HYDROCRIP HK40, rotronic ltd.), which was placed close to the sample. This cell configuration allowed the membrane to be exposed directly and to respond sensitively to changes in the relative humidity.

Using the cell, the impedance of the membrane was measured in the tangential direction, and the conductivity was calculated using the following equation,

$$\sigma = L/RS$$

where σ , L , R , and S denote the ionic conductivity, distance between the reference electrodes, the impedance

of the membrane, and the cross-sectional area of the membrane, respectively. The thickness of the membrane was 45 μm after the membrane was exposed to the humid conditions. The impedance measurements were carried out in the frequency region from 50 mHz to 100 kHz using a frequency-response analyzer (PAR-STAT 2263, Princeton Applied Research Ltd.). After the humidity was changed inside the vessel, the measurement of the impedance was repeated until a constant value for the impedance was obtained.

The results were compared with the performance of NAFION®. The conductivity of as-prepared NAFION 112® was measured using the same configuration for the GORE-SELECT®. The results were also compared with our previous measurements on NAFION 117®.¹⁸⁾

Fig. 1 Apparatus for measuring proton conductivity under exposure to a stream of humid gas.

Fig. 2 Typical Bode plot for the impedance measurement of the membrane using four-electrode method. The conductivity was measured at 30 °C. Dry nitrogen was initially supplied, and then the humid gas was mixed to increase 10% relative humidity.

3 Results and Discussion

Figure 2 shows a typical Bode plot obtained by the four-electrode ac impedance method. As shown in Fig. 2, a constant impedance, independent on the wide range of frequency, was observed. When the membrane was placed in the gas stream, the conductivity increased with time and reached a constant value after 1 hour.

Figure 3 shows the conductivity dependence of GORE-SELECT® on temperature and humidity. The temperature was varied from 26 to 70 °C. When the relative humidity was over 20%, the conductivity of the membrane was over 10^{-3} S cm⁻¹ and increased with humidity. When the membrane is applied to the fuel cell system, gases are often supplied to the fuel cell after humidification. When the gas for the measurement was well humidified, the conductivity of the membrane approached up to $\sim 10^{-1}$ S cm⁻¹.

The conductivity of NAFION 112® was also measured for comparison. It was measured at 60 °C with various humidities. As shown in Fig. 3, the conductivity of the GORE-SELECT® measured at 60 °C showed almost the same tendency for the humidity dependence as NAFION®. Furthermore, the proton conductivity obtained was also comparable with what was observed in previous work.¹⁸⁾

It is notable that even though the conductivity was measured at a lower temperature after the measurement at a higher temperature, the same conductivity was still observed. In the case of NAFION®, shrinking occurs after the heat-treatment. Thus, in previous work,¹⁸⁾ the membrane was first heat-treated, and then the measurement was started at a fixed temperature. In the case of a reinforced membrane, the structure of the ionomer is supported by the matrix of a polytetrafluoroethylene network, which should maintain the proton conduction through the membrane even after the measurement at

Fig. 3 Proton conductivity of GORE-SELECT® and NAFION 112® under various humid conditions. Conductivity of GORE-SELECT® was measured at 26 °C : (◇), 40 °C : (□), 60 °C : (○), and 70 °C : (△). As a reference, the conductivity of NAFION 112® was also measured at 60 °C : (●).

higher temperature.

Figure 4 shows the relationship between the conductivity and temperature. The relationship was calculated based on the experimental results shown in Fig. 3. As shown in Fig. 4, an Arrhenius-type plot was observed under all humidity conditions. Using these plots, the activation energy was calculated for the proton conduction inside the membrane, as shown in Fig. 5.

As shown in Fig. 3, the proton conductivity was dependent on the humidity. At 20% relative humidity, the proton conductivity of the reinforced membrane was approximately 3×10^{-3} S cm⁻¹ when the temperature was 70 °C. At this low humidity, it was hypothesized that the water for the proton migration should be lacking, and therefore the activation energy for proton migration should increase. However, the results obtained here depicted that the activation energy for the proton migration at low humidity was almost equal to that at higher humidity conditions. This indicated that the water network for the proton migration was established after the proton conductivity could be measured even at the dry conditions.

The activation energy obtained through these calculations was less than 20 kJ mol⁻¹. In this type of low-tem-

Fig. 4 Temperature dependence of proton conductivity under various humid conditions.

Fig. 5 Activation energy for proton conduction calculated under various humid conditions.

perature proton conductor, proton migration is primarily by Grothuss mechanism. In this mechanism, the proton which forms an H_3O^+ ion jumps to the neighbouring lone pair of electrons of a water molecule. For such a mechanism, the activation energy should be approximately 14 to 40 kJ mol^{-1} .²²⁾ The results obtained here suggest that the proton migration inside the reinforced membrane should be dominated mainly by the Grothuss mechanism at a wide region of humidity.

4 Conclusions

For fuel cell designs, it is very important to thoroughly understand the proton conductivity of the membrane under different conditions. In this research, the conductivity of the reinforced membrane was measured at various humidities and temperatures using the four-electrode impedance method. GORE-SELECT[®] was used as a reinforced membrane, and the results were compared with the conductivity of NAFION 112[®].

The conductivity of GORE-SELECT[®] was $8 \times 10^{-2} \text{ S cm}^{-1}$ with 70% relative humidity at 70 °C; it varied strongly with the humidity and temperature. A stable conductivity was observed when the relative humidity was over 20%. The humidity dependence of the GORE-SELECT[®] was almost the same as that of the NAFION 112[®].

From the results, the activation energy was calculated to be less than 20 kJ mol^{-1} at any humidity condition. These results revealed that the Grothuss-type proton conduction might be dominant for the proton migration inside the reinforced membrane at a wide range of humidity.

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