Short communication

Depression of proton conductivity in recast Nafion® film measured on flat substrate

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ABSTRACT

The proton conductivity of recast Nafion® thin films in the lateral direction (parallel to the interface) was measured in humidified atmospheres. The conductivity decreased with a decrease in the thickness of the film: e.g., the conductivity of a film with a thickness of about 100 nm was about an order of magnitude less than that of the bulk material. The dependence of the conductivity on temperature was also measured, and a thinner film showed a higher apparent activation energy for conduction. Since both the conductivity and the apparent activation energy for conduction were affected by the thickness, these phenomena may be due to an intrinsic change in the material. Based on the fact that the apparent activation energy for conduction in the bulk membrane under dry conditions is high, the high apparent activation energy for conduction in thin films may be due to the hindrance of water adsorption.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been the focus of much attention as power sources for electric vehicles and portable devices [1]. A high current density despite operation at a relatively low temperature is one of the strong advantages of PEM-FCs [2–4]. This is partly due to the absence of any specific anion adsorption on catalysts for the oxygen reduction reaction. Another important reason is the structural condition inside the gas diffusion electrode. A perfluorosulfonate ionomer (PFSI), like Nafion®, is an important material for PEMFCs as an electrolyte, and its ionic conductivity has been widely investigated [5–13]. The ionomer is used not only as a membrane between the anode and cathode to separate the reactant gases, but also as an important component of the gas diffusion electrodes to improve the reactivity. The procedures used to fabricate gas diffusion electrodes for PEMFCs include making thin ionomer films inside the catalyst layer. The method of casting the ionomer solution into a porous catalyst layer [14–16] was invented to improve the catalytic activity, and in recent years a catalyst layer was made from a slurry of catalyst powder containing an ionomer solution [17]. When these methods are used, a desirable microstructure of the electrolyte in the three-phase boundary regions is achieved and maintained. It is assumed that the existence of thin electrolyte films covering the catalyst particles is an important characteristic [18–20], since under such films the supplies of

the reactant gas and ions (protons) are compatible. A schematic of thin electrolyte films inside the gas diffusion electrode is shown in Fig. 1. According to our previous study [19], there should be an optimum thickness for such thin electrolyte films, since a thinner film can be penetrated by the reactant gas more easily while a thicker film has a lower ionic resistance. The influence of the thickness of the electrolyte film on the access of the reactant gas has been discussed using model electrodes [20]. On the other hand, only a few investigations have focused on ionic access inside a thin electrolyte film. An important feature of a thin electrolyte film near the three-phase boundary is that the direction of the ionic current is parallel to the film/carbon interface. Basically, the ionic resistance varies inversely with the thickness. However, the properties of a very thin film should be affected by the interface, and a change in the conductivity or its anisotropy may be induced. To optimize the microstructure of the gas diffusion electrode, the properties of the ionomer electrolyte film should be investigated. In the present study, the effect of thickness on conductivity in a recast thin film of Nafion® in the direction of the interface was investigated. To simplify the measurements and to avoid ambiguity in the results, each recast film for measurement was made on a flat substrate as a model instead of using real gas diffusion electrodes. Furthermore, to obtain the apparent activation energy for proton conduction, the dependence of conductivity on temperature was also measured.

2. Experimental

For the measurement of ionic conductivity in recast films by the four-electrode method, a quartz plate (10 mm × 20 mm) with
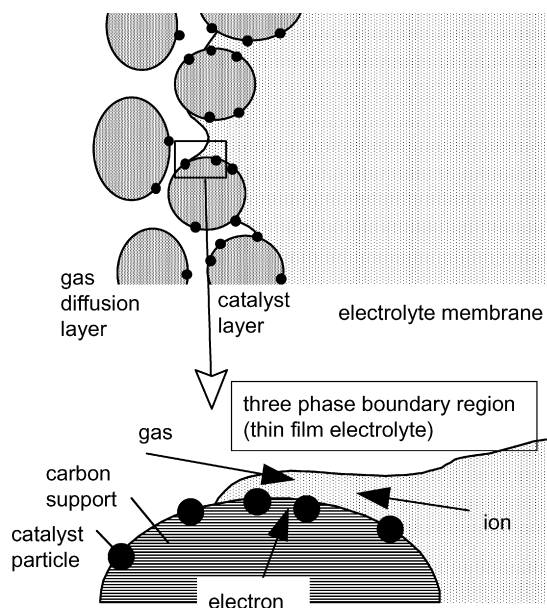
Fig. 1. Schematic of a thin-film electrolyte at the three-phase boundary region in a gas diffusion electrode.

several platinum microelectrodes deposited on the surface was prepared as a substrate for casting. The details have been described previously [21]. As shown in Fig. 2, five narrow (10 μm width) strips as potential-sensing electrodes are placed in parallel between the two current-carrying electrodes. By selecting two of these electrodes, we can change the distance between them, over which the potential difference is measured, from 10 to 210 μm. As a casting
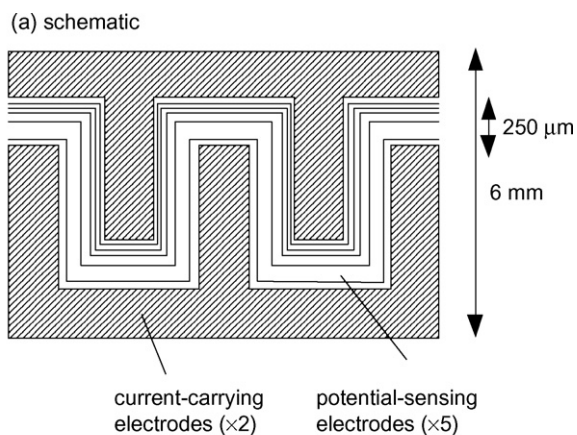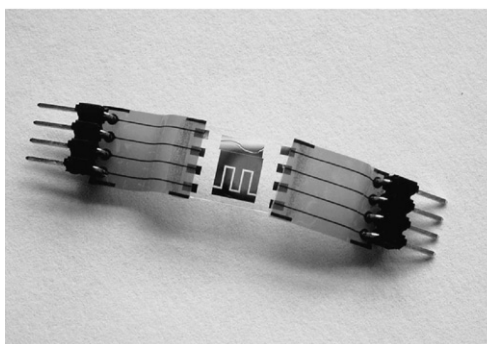

Fig. 2. Quartz plate with several platinum microelectrodes for four-electrode measurement.

solution, a solution of 5% Nafion® (equivalent weight (EW) = 1100, Aldrich Chemical) was diluted 2–20 times with ethanol. Casting was carried out by dropping 2–8 μL of the diluted solution over an area of about 0.5 cm^2 on the substrate followed by evaporation of the solvent at room temperature. For films thicker than 0.1 μm, Nafion® solution without dilution was used. Furthermore, for films thicker than 50 μm, self-standing films were made on a PTFE dish and measured in the manner described later for "bulk" membranes (Nafion® 112, 115, and 117). After a series of conductivity measurements of films on the quartz plate was complete, the recast film was partially removed from the substrate, and the difference in level at the step of the remaining film was measured using a profilometer (Dektak IIA, Sloan) to determine the film thickness. Observation by atomic force microscopy (SPA-300, Seiko Instruments) was also performed on the surface of the film to confirm the absence of cracks and holes. During the conductivity measurements, the film on the substrate was placed in an environmental control chamber (SH-220S3, Espec). The temperature and humidity were controlled from 10 to 85 °C and from 15 to 90% RH, respectively. The conductivity was measured by the four-electrode AC impedance method using an impedance analyzer (SI1287 electrochemical interface + SI1260 frequency response analyzer, Solartron). The impedance value obtained by the four-electrode method does not contain any information about the current-carrying electrodes. Therefore, an identical real value that is independent of frequency, without an imaginary part, is theoretically expected in our measurement. Amplitude of the AC voltage was varied in the range of 5–500 mV depending on the sample and spacing of the potential-sensing electrodes. Theoretically there is no need to apply DC voltage, however, sometimes there is an uncertain voltage between the potential-sensing electrodes before the measurement. In such a case, DC voltage of the same value of that under the open-circuit condition was applied during the impedance measurement.

Fig. 3 shows a typical result of the impedance measurement. Although some deviations are seen at higher and lower frequencies, almost all of the points converged, especially around 1 kHz. Therefore, the real part of the impedance value at 1 kHz was used for the resistance for each measurement.

As control data, the ionic conductivity in "bulk" membrane was also measured using Nafion® 112, 115 and 117 membranes (50, 125 and 175 μm, respectively, EW = 1100, E. I. du Pont de Nemours & Co.). These Nafion® membranes were pretreated using a common procedure [22]. For the conductivity measurement of these bulk membranes, two platinum black-plated platinum pieces were attached to both ends of a sample strip (5 mm width × 40 mm long) as current-carrying electrodes, and two platinum wires (Ø 0.2 mm) were stuck through the membrane at a distance of 3 mm from each other as potential-sensing electrodes.

3. Results and discussion

For each conductivity measurement for the recast film, several combinations of two potential-sensing electrodes with different spacings were used. There is a linear relation between the electrode spacing and resistance. The conductivity σ [S cm^{-1}] of the membrane can be calculated as

$$\sigma = \frac{1}{(R/d) \cdot t \cdot L} \qquad (1)$$

where (R/d) [Ω μm^{-1}] is the slope of the linear relationship between the spacing of the two electrodes and the resistance between them, t [μm] is the thickness of the film, and L (=1.8 cm) is the length of the microelectrodes. The equilibration of water between the film and the atmosphere seems to be quite fast, and no time-lag was observed between the conductivity change and humidity change. Each data point was collected 30 min after reach-
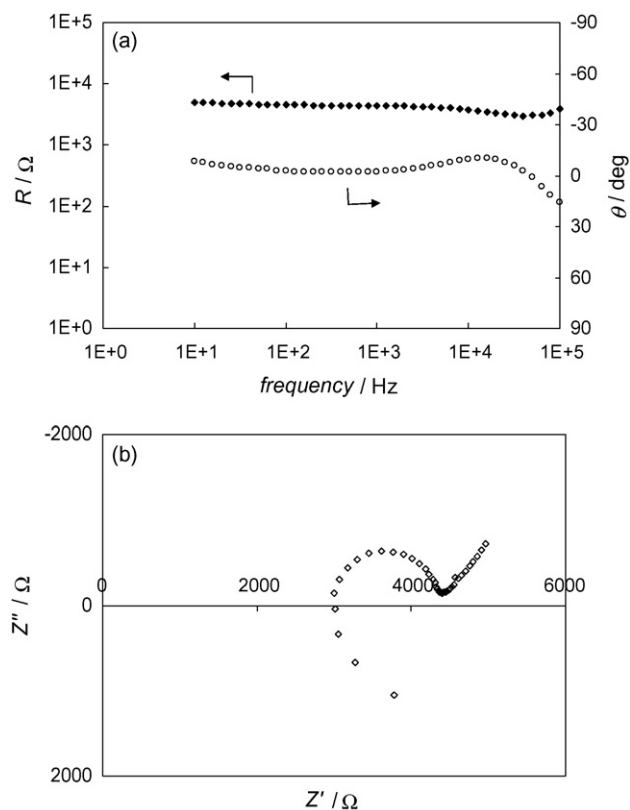
Fig. 3. An example of (a) Bode and (b) Nyquist diagrams of the impedance measurement. The sample is a cast film with a thickness of 146 nm. The spacing of two potential-sensing electrodes is 20 μm. Amplitude of the applied AC potential difference between them was set at 100 mV (p–p). The temperature and humidity are 85 °C and RH 85%, respectively.

ing the humidity and temperature at the set point. To confirm the time required for equilibration, the long-term stability of the conductivity was also measured using a Nafion® 117 sample at 50 °C, RH 100% for up to 140 h, as shown in Fig. 4(a). After the stability test, humidity was changed downward (region A), followed by upward to the original value again (region B). Relation between the humidity and conductivity during regions A and B is shown in Fig. 4(b). No hysteresial behavior was observed in Fig. 4(b), and 99% (0.134 S cm^{-1}) of the original value during the preceding equilibrium (0.135 S cm^{-1}) was obtained after reaching original condition

Fig. 5. Dependence of the conductivity of recast Nafion® thin film on the thickness. The temperature is 85 °C and the humidity is 85% (□) or 60% (○). Solid marks show bulk membranes (Nafion® 112, 115 and 117).

as shown in Fig. 4(a). This confirmed that our conductivity measurements were performed under almost equilibrated conditions even with a thick membrane.

The relation between the film thickness and ionic conductivity of the recast thin film at 85 °C, RH 85% and 85 °C, RH 60% is shown in Fig. 5. Although the data points are somewhat scattered, it is obvious that the conductivity decreases as the thickness of the film decreases. For comparison, the conductivities of the bulk membranes are also plotted in Fig. 5. The differences between recast films and bulk membranes are due not only to the difference in thickness but also to difference in the internal structure, which is suggested by the differences in some properties, such as the physical strength and solubility in alcohols [23–25]. However, based on Fig. 5, a recast film as thick as a bulk membrane has almost the same conductivity as bulk membranes, which indicates that the conductivity is dominated mainly by the thickness.

The main aim of the present study was to determine some effects of thickness on the conductivity. Although we expected to see some changes caused by thinning of the film, the "thickness effect" shown in Fig. 5 has two unexpected features: its wide range (including thickness greater than 10 μm), and its large magnitude (a decrease in a conductivity of almost one order of magnitude is seen when
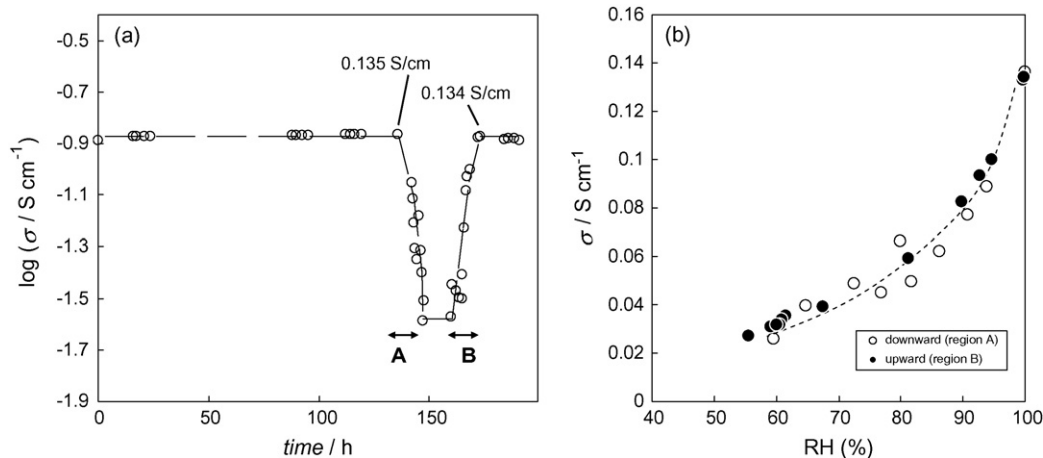

Fig. 4. (a) A long-term stability test under a constant humidity using Nafion® 117 sample at 50 °C and RH 100%, followed by changing of the humidity. (b) Relation between the humidity and conductivity in the regions A and B.
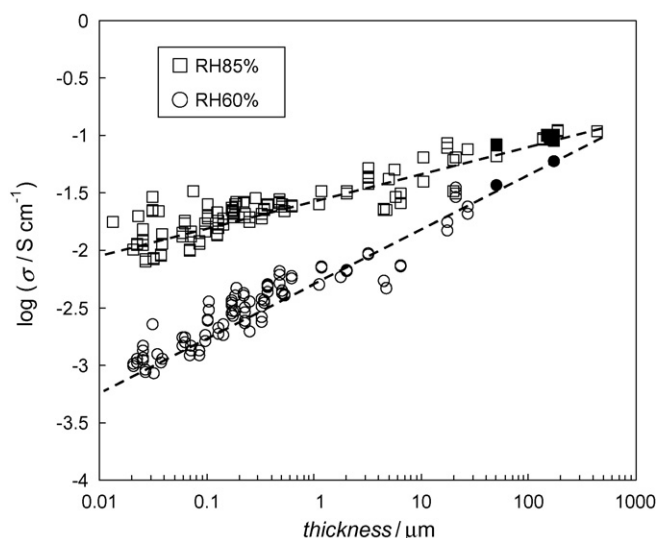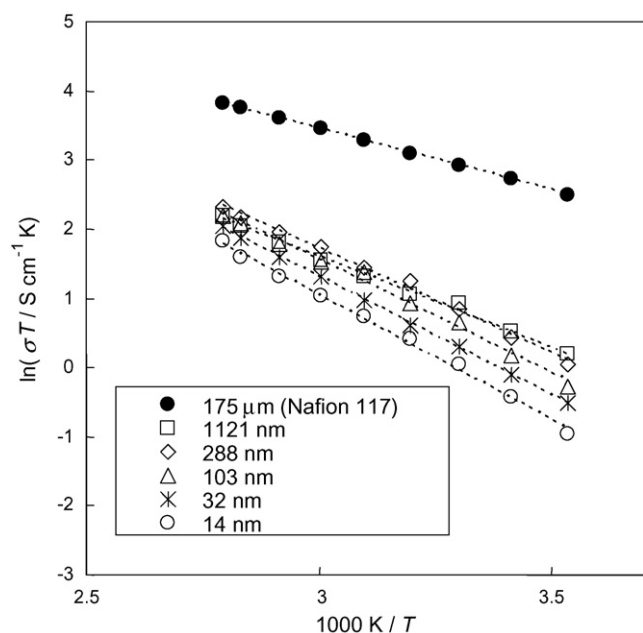
Fig. 7. Relation between the thickness and apparent activation energy for ionic conduction in recast films of Nafion®.

Fig. 6. Arrhenius plots for the conductivity of recast films of various thicknesses and bulk membrane (Nafion® 117) under a constant humidity (RH 85%).

the film is thinner than 100 nm). Initially, we suspected that we would find nonuniformity of the thickness or undesirable defects in the samples, since even a small number of defects, such as cracks, could seriously affect lateral conduction. However, AFM observations revealed that the surface of each sample was smooth and no defects were detected. Furthermore, the standard deviation of the thickness calculated using profilometer measurements at 10 different points on each sample did not exceed 10% of the average thickness. Therefore, the change in conductivity with a change in thickness is not caused by any morphological irregularity. Fig. 5 also shows that not only the cast films but also the bulk membranes show a thinning effect. Such phenomena have been previously reported in membranes of different thicknesses including Nafion® 112, 115 and 117 [26–28], albeit the mechanism has not yet been clarified.

If the change in conductivity was due to some intrinsic change in the material, the activation energy for conduction may also be affected by the thickness. Therefore, we measured the dependence of conductivity on the temperature in the range of 10–85 °C at a constant humidity (RH 60% or RH 85%). Fig. 6 shows Arrhenius plots of five samples of recast film and a bulk membrane, which indicate linear relations between the $\ln(T\sigma)$ and $1/T$ values in this temperature range. Furthermore, a thinner film has not only a lower conductivity but also a high apparent activation energy. The relation between the film thickness and the apparent activation energy obtained from the slope of the Arrhenius plots, including data in Fig. 6, is shown in Fig. 7. The apparent activation energy increases with a decrease in thickness. In Fig. 7, the apparent activation energy was obtained under constant RH condition. These values may contain some deviation from true activation energy, since the water content has a little dependence on the temperature. However, despite this restriction, difference in the apparent activation energy indicates difference in the material. Since morphological factors (defects or nonuniformity of the thickness) do not change the apparent activation energy, this phenomenon suggests that the decrease in conductivity is due to some intrinsic changes in the material that change the environment of the conducting ion (proton).

A dry membrane has a high activation energy [12,13]. In this study, we also confirmed the relation between the humidity and
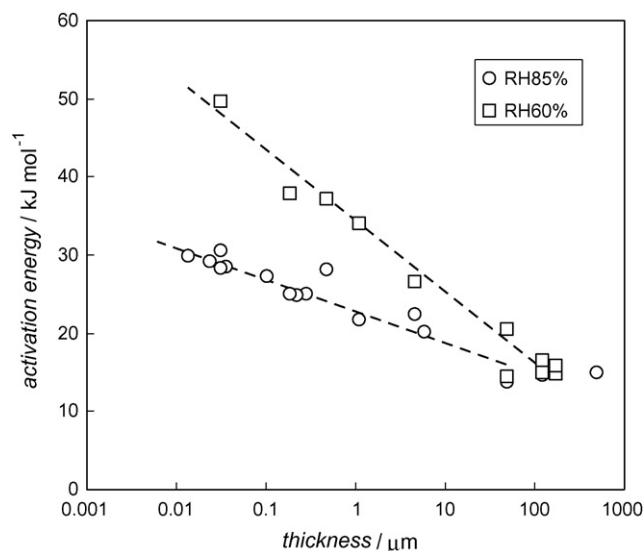
apparent activation energy for ionic conduction in the Nafion® 112 membrane, as shown in Fig. 8. The humidity range from 20 to 80% corresponds to a water content of from ca. 1.9 to 5.9 water molecules per sulfonyl group, based on the results reported by Hinatsu et al. [22]. The apparent activation energy rapidly increases when the humidity is reduced below 20%, due to a lack of water necessary for proton hopping. With regard to the bulk membranes, it has been reported that a thinner membrane (Nafion® 112) contains less water than a thicker membrane (Nafion® 117) [29]. Therefore, although this conclusion is still tentative, the dependence of the conductivity and apparent activation energy of the recast film on thickness is likely due to the dependence of the water content on thickness. It is difficult to measure the dependence of the water content on the film thickness, and this is now under investigation.
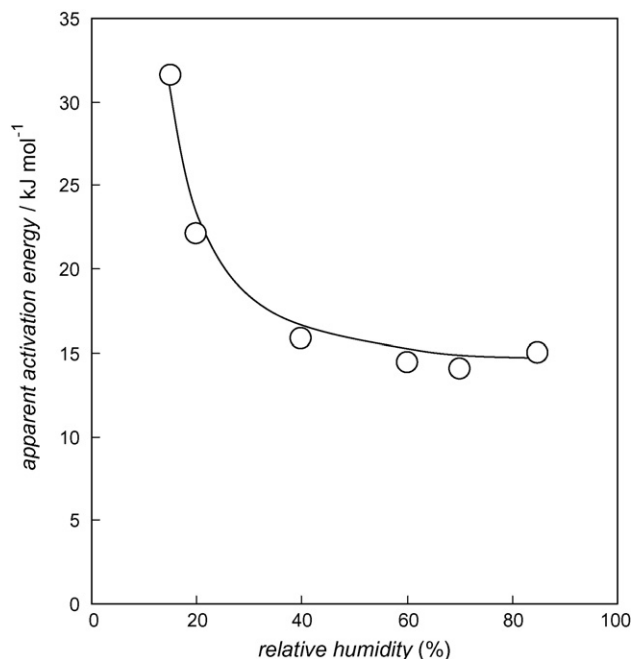

Fig. 8. Relation between the humidity and apparent activation energy for ionic conduction in Nafion® 112 membrane.

4. Conclusion

The proton conductivity and its dependence on the temperature of recast thin films of an ionomer (Nafion®) with various thicknesses was measured and compared with those of the bulk material (Nafion® 112, 115 and 117). The conductivity decreased and the apparent activation energy increased with decreasing thickness. Based on the finding that a dry membrane has a low conductivity and a high apparent activation energy, it is assumed that a thin film does not absorb sufficient water.

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