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Proton Conductivity Measurement Using A.C. Impedance Spectroscopy for Proton Exchange Membrane

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Abstract: The impedance and the subsequent proton conductivity of Nafion® membranes as standard samples were measured and compared *via* the two-probe method and the four-probe method using the prepared impedance measurement system. The different impedance behavior for the same membrane was observed at the fully hydrated state in the Nyquist impedance plot. The effect of the humidity and the temperature on the proton conduction through a membrane was investigated and compared with two different cell configurations.

Keywords: *proton conductivity, A.C impedance spectroscopy, four-probe method, two-probe method*

1. Introduction

In the cation-exchange membrane, the proton transports along with hydrated structure connected with negative charged fixed ions (sulfonic acid, phosphonic acid, and carboxylic acid groups, etc) or by aid of water molecules within the membrane. Actually the proton transport mechanism is very complex, and vehicle or hopping mechanism is well-accepted hypothesis for the transport. The achievement of high proton conductive materials has been strongly demanded in the field of fuel cell industry, expecting one of next-generation alternative energy sources. Therefore, many researchers have focused on the development of high proton conductive polymer membranes to realize early commercialization of PEMFC. There are many prerequisite factors in the research and development of proton exchange membrane but the exact measurement of proton conductivity through the membrane is significant first of all.

For this purpose, several measurement methods have been suggested and used to obtain the proton conductivity using voltage drop between electrodes. Although there was a new attempt to measure proton mobility as the diffusivity of mobile hydrogen ions using the pulsed field gradient spin-echo (PGSE) NMR, the proton transport behavior by Grotthus hoping mechanism, which are considerably significant at high water content but negligible at low water content, was not shown well, compared with the diffusivity by the estimation of the proton conductivity using the Nernst-Einstein equation [1].

The proton conductivity in a sample material with dielectric properties should be measured from the A.C impedance spectroscopic technique. In spite of the complexity in the interpretation of the spectroscopic diagram, the A.C impedance method has the higher accuracy if the polarization and electrode reactions were eliminated. The impedance, which takes phase difference into account, is a combined parameter to characterize electronic circuit, its components such as resistors, inductors and capacitors, and the component materials. The impedance can be expressed using the rectangular-coordinate form in Z' + jZ" (Nyquist plot) or in logarithm of the absolute magnitude of total impedance (log |Z|) to logarithm of the angular frequency

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($\log\omega$) (Bode plot).

In the practical electrochemical experiment, there are some methods to measure the impedance, which have advantages and disadvantages for purposes, the magnitude of measuring impedance and the measuring condition. Therefore, it is necessary to choose the most appropriate method, considering the frequency coverage, the measurement range, the measurement accuracy, and simple operation. Among some measurement methods, the auto balancing bridge method is most favorable for the general purpose measurement because of wide frequency coverage and high accuracy over a wide impedance measurement range[2]. The auto balancing bridge is equipped with four coaxial terminals (current Lo, voltage Lo, current Hi, voltage Hi). The impedance is measured by recording the voltage drop between reference electrodes (voltage Hi, voltage Lo), as constant current from working electrode (current Hi) to counter electrode (current Lo) is imposed.

Although there are several connection modes used to interconnect a sample material using the auto balancing bridge method, the four-electrodes set with four-terminal connection; *four-probe method* and the two-electrodes set with four-terminal connection; *two-probe method* are generally used to measure the impedance of a sample material. The key difference in two interconnection methods is the sameness of current flowing electrodes and voltage sensing electrodes. In two-probe method, the voltage drop is measured simultaneously at the same two electrodes as constant current flows. In the four-probe method, two different pairs of electrodes are used to impose a constant current and record the voltage drop as a response, respectively.

The two-probe method is the simplest mode and has been used to measure total, inherent impedance of the electrochemical cell, containing anode, cathode, electrolyte, and organic or inorganic fillers for its convenience. In spite of the simplicity of the two-probe method, it contains many error sources such as the lead inductance, the lead resistance, and the stray capacitance between two leads. The extra impedance derived from error sources has been added to the measurement result. Because of the existence of those error sources, the typical impedance measurement range is limited to 100 Ω to 10 kΩ. The four-probe method can eliminate the effects of the lead impedance due to the independence of the current path and voltage sensing cable. The measurement accuracy is improved not only in the high impedance measurement range but also in low impedance range down to 1 Ω. The low impedance is electrically regarded as the impedance below 10^6 Ω, compared with the high impedance.

In practice, many research groups have measured the impedance in proton conductive materials, using either the four-probe method[3-8] or the two-probe method [9-17]. However, the standard measurement method to measure exact proton conductivity has not been established yet. Additionally, many groups have confused even the concept of the probe configuration[9-11]. Inappropriate measurement methods result in imprecise and different proton conductivity even for the same material, which act as severe obstacles to development of effective proton exchange membrane with high performances.

Despite of different methodologies, most of all research groups have used the same following equation (1), which is generally applied to measure the ionic or electronic conductivity from the resistance of a sample material in D.C, to obtain a proton conductivity (σ) of proton exchange membrane materials with an impedance derived from the two-probe method or the four-probe method.

$$\sigma = \frac{1}{R_s \times S} = \frac{i}{X} \tag{1}$$

where R_s is the bulk resistance or ohmic resistance of membrane sample, l is the distance between reference electrodes, S is the cross-sectional area of membrane sample, i is the current density, and X is the electric field strength.

In this paper, an impedance analyzer was prepared to measure and compare impedances in membrane samples using both the two-probe method and the four-probe method in thermo- and hygro-controlled chamber. The proton conductivity of Nafion 112, 115 and 117 as reference membrane samples was obtained using the equation (1) from approximation of the measured impedance with two methods at constant humidity and temperature.

2. Experimental

The impedance of each proton exchange membrane as an proton conductor and dielectric was determined by using the electrode system, which contained both a two-probe cell and a four-probe cell depicted in Figure 1, connected with an electrochemical interface (Solatron 1287) in combination with an impedance/gain-phase analyzer (Solatron 1260). The impedance measurement system was designed and prepared in two part of the base plate for electrical connection and the electrode system. In the base plate for the electrical connection, four BPO coaxial sockets with slots in side of the socket were equipped to prevent the flooding effect by the condensation of water vapor and interconnected with low-noise coaxial cable. In the electrode system, four BPO plug connectors, which interconnected with platinum wire electrodes on Teflon plate, were established to assemble and disassemble the two-probe cell or the four-probe cell conveniently onto the base plate for the electrical connection in the way of plug-in and plug-out. The window was constructed to prevent the condensation of water vapor in high humidity and maintain the equilibrium state of the membrane with constant water content *in situ*. The membrane sample was fixed with six knurled nuts to keep its initial location without any movement for accurate impedance measurement. The whole structure was installed in a thermo- and hygro-controlled chamber which was shielded electrically for more stable measurement without any noise.

The maintenance of well-defined water content of membrane was required for more accurate impedance measurement, as the ion transport behavior of membrane was considerably affected in different hydrate states. To establish and maintain more accurate vapor pressure for the precise impedance measurement in a constant humidity, the hygrometer connected with a humidity controller in a thermo- and hygro-controlled chamber was calibrated by standard saturated salt solutions with well-known water activity.

The impedance of each Nafion® membrane was measured in the A.C impedance spectroscopic technique by using both the two-probe method and the four-probe method in the frequency range from 100 kHz to 0.1 Hz at constant current 1 mA. The impedance of a membrane sample at controlled humidity and temperature was indicated with both Nyquist plot and Bode plot. For Nyquist plot, both real part (Z') and imaginary part (Z") as components of impedance in the membrane sample were simultaneously measured over a defined frequency range. As imaginary component containing both the inductive reactance and the capacitive reactance converged into zero, a real Z' axis intercept was closely approximated and regarded as the bulk or ohmic resistance of a membrane sample without any effect of the reactance caused by the lead inductance, the stray capacitance and so on. For Bode plot, the change of impedance was observed over a wide frequency range. The ohmic resistance of the sample was derived from the invariable impedance within a reasonable frequency range, compared with approximation from the Nyquist plot. Finally, the proton conductivity was obtained by using the equation (1) with a measured ohmic resistance, the spacing distance between reference electrodes, and the cross-sectional area of a membrane sample.

3. Results and Discussion

The equilibrium water content of Nafion® membranes at a specific temperature was achieved by calibrating and setting up the hygrometer connected with a humidity controller by means of the saturated salt solution method and swelling membrane samples to the fully hydrated state. To confirm the equilibrium water content of membrane samples in isothermal and iso-

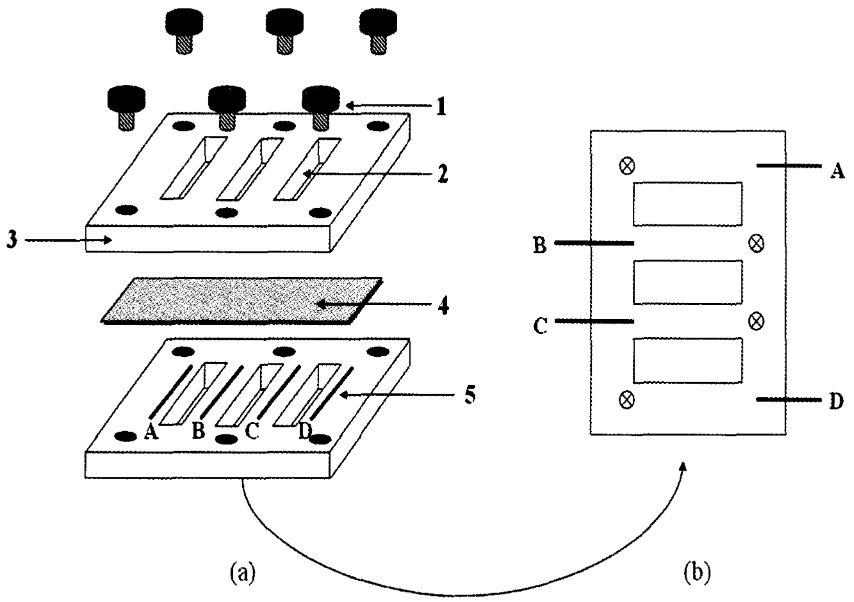


Fig. 1. Schematic diagram of electrode system: (a) 1. Knurled nuts 2. Window to prevent condensation of water and to absorb water vapor to membrane equilibration in situ 3. Teflon plate 4. A membrane sample for measurement 5. Platinum wire electrodes (b) Backside of electrode system: A electrode (working electrode): current Hi, B electrode (reference 2): voltage Hi, C electrode (reference 1): voltage Lo, D electrode (counter electrode): current Hi; Each electrode is connected with BPO plug connector.; In case of two-probe cell, electrode pairs of A and B at B electrode site, and C and D at C electrode site are combined, respectively.

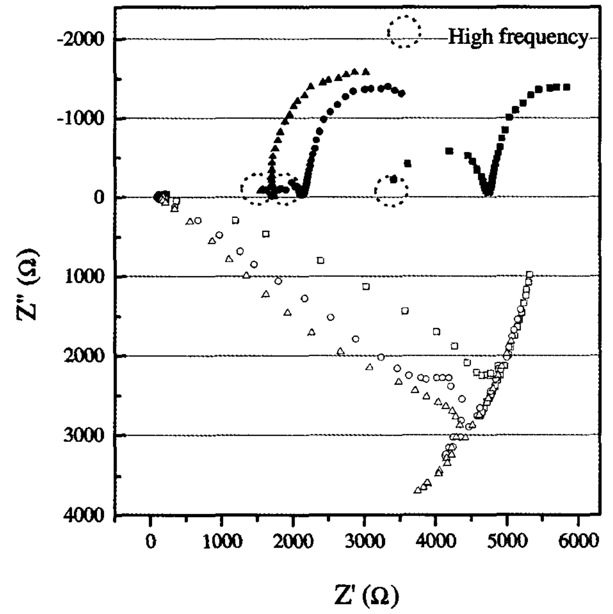
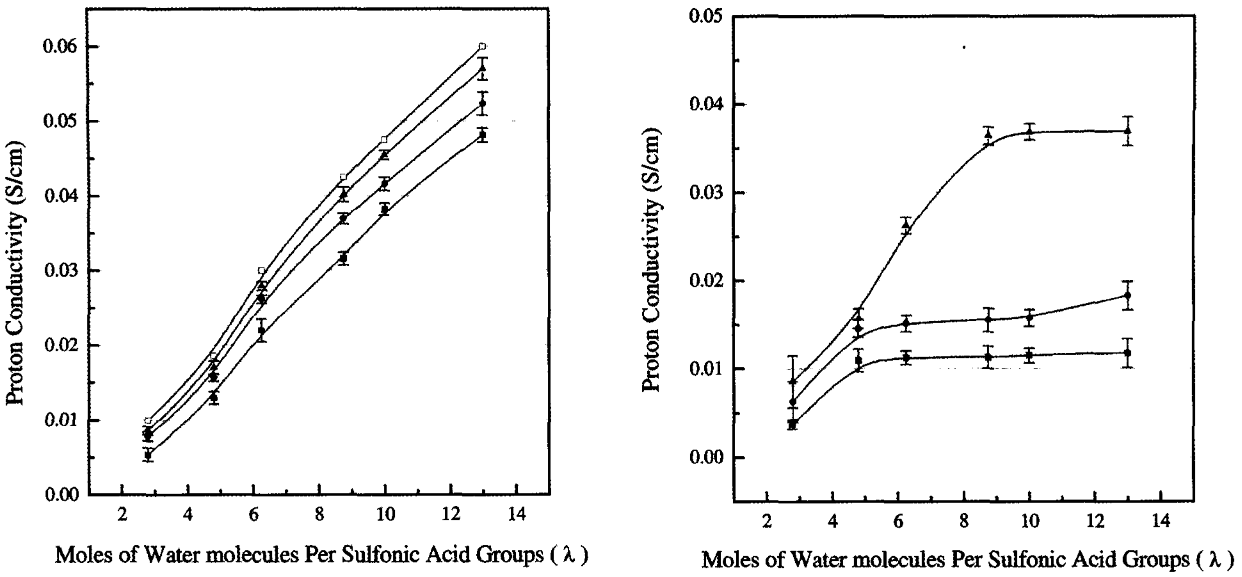


Fig. 2. The Nyquist plot for Nafion 112 (■), Nafion 115 (●), and Nafion 117 (▲) derived from four-probe method, and for Nafion 112 (□), Nafion 115 (○), and Nafion 117 (△) derived from two-probe method in a reasonable frequency range from 10^5 Hz to 0.1 Hz at temperature 60°C and 82% RH.

baric condition, repeated impedance measurements were conducted after the hydration for six hours to obtain the unchangeable impedance at a fixed frequency. The measured impedance was applied to the described equation (1) to obtain the proton conductivity in the sample. However, the equation (1) is generally utilized to derive the ionic or electronic conductivity from the resistivity in D.C circuit. In spite of the application in D.C, the equation (1) can be also used in the A.C impedance spectroscopy, as the ohmic resistance of a sample is theoretically the same in both D.C and A.C. The impedance measurement was accomplished by using two different electrode configurations, with Nafion 112, 115 and 117 in the fully hydrated state under thermo- and hygro equilibrium condition from high frequency 10^5 Hz to low frequency 0.1 Hz. As shown in Figure 2, the different impedance measuring methods resulted in more unique difference of impedance behavior in Nyquist impedance plot. For the two-probe method, all Nyquist plots for membrane samples within the controlled temperature and humidity range had



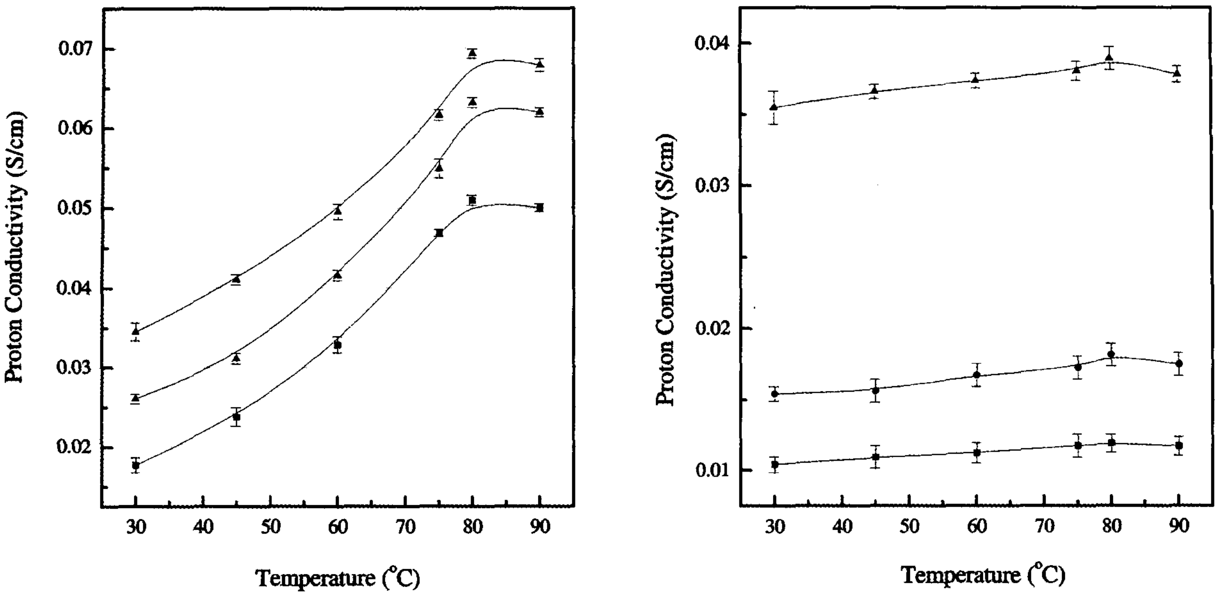
(a) (b)

Fig. 3. The proton conductivity of Nafion 117 (■), Nafion 115 (●), and Nafion 112 (▲) compared with that of Nafion 117 (□) reported by Zawodzinski, T. A. et al. as a function of water conten6t in membrane at 60°C, using (a) the four-probe method and (b) the two-probe method.

positive reactance values. It indicated that in the two-probe method, the inductive impedance derived from BPO connectors, Pt electrodes as well as leads including coaxial cables, was more predominant than the capacitive impedance between electrodes, although those components of the impedance measurement system to have relatively low impedance was designed and selected as inductors. Additionally, all Nyquist plots derived from the two-probe method were completely different from the typical Nyquist plot, as each Nyquist plot had two kinds of unusual arcs in the shape to induce entirely different approximation for the ohmic resistance measurement. Therefore, the 2^{nd} arc, which was likely to be convergent into real axis at lower frequency, was selected for approximation in this paper, as the 1^{st} arc indicated too small ohmic resistance up to 100 Ω.

Different from the two-probe method, the inductive impedance was disregarded in the total impedance due to the independence of the current path and voltage sensing cables in the four-probe method. In other words, only the capacitive impedance in reactance was considered as a component of the total impedance including the ohmic resistance. Practically, all Nyquist impedance plot in the four-probe method had negative reactance values in Z" axis, which indicate the predominant capacitive impedance, and had a semicircular arc and subsequent a rising curve similar to that of the typical Nyquist plot with approximation into the real axis intercept as the ohmic resistance. The first semicircular arc is related to complex impedance of Nafion® membranes and membrane-electrode interface and the second rising curve is attributed to the Warburg impedance by diffusion. The ohmic resistance in each membrane sample was obtained from approximation of the impedance in Nyquist plot measured by using two different cell configurations and the proton conductivity was derived from equation (1) with the ohmic resistance. The relationship between the conductivity and the water content in membrane was shown at 60°C as a function of proton conductivity and in Figure 3.

The λ value, which means the ratio of the mole number of water molecules to the fixed charged sulfonic acid groups, was just affected by the water content in a membrane at a specific humidity condition, as the ion exchange capacity (IEC) was constant value



(a) (b)

Fig. 4. The proton conductivity of Nafion 117 (■), Nafion 115 (●), and Nafion 112 (▲) as a function of temperature at 90% RH using (a) the four-probe method and (b) the two-probe method.

for the same membrane sample. The proton conductivity was measured not in water (λ= 14) but in water vapor condition. The range of λ was from 2.8 mole H_2O in the minimum water content to 13 mole H_2O per one mole sulfonic acid group in the maximum water content, as the increase of the relative humidity caused the water uptake into a membrane sample and the subsequent increase of λ. As the water content in membrane affects significantly the proton transport via both Grtthus hopping mechanism and vehicle mechanism, the increase of the proton conductivity was observed with the elevation of λ for all impedance measurement methods described in Figure 3. In practice, the proton conductivity of Nafion® membranes, mainly Nafion 117, have been measured by using several methods and reported differently by many research groups. The proton conductivity in Nafion 112, 115, and 117 derived from the four-probe method was almost consistent with that of Nafion 117 reported by Zawodzinski, T. A. et al. In addition, the unique behavior of Nafion® membrane, that the proton conductivity increased relatively fast at the low water content in membrane and then gradually at the high water content due to high ion density clusters to form ion-rich channels, was also shown well in the measurement using the four-probe method. The proton conductivity of Nafion 112 was somewhat higher than those of the other membranes and the proton conductivity of Nafion 117 was a little lower than the others. It is inferred that the nominal thickness of each membrane causes the difference of the proton conductivity, as a thicker membrane needs extra time to absorb water vapor to the fully hydrated state. In the two-probe method, it was shown that the proton conductivity of Nafion 117 was likely to be independent on the water content within membrane at high humidity condition, whereas the proton transport behavior of Nafion 112 with thin thickness was similar to the typical behavior of Nafion® at relatively low and moderate humidity condition. This unexpected, non-ideal behavior in the proton transportation was observed evidently in thicker membranes at the same impedance measurement condition using the two-probe method.

The temperature dependence on the proton transport behavior measured by using two different cell configurations at 90% RH for all perfluorinated membrane samples was shown in Figure 4. The proton conductivity of Nafion 112, derived from the four-probe method, increased continuously up to about 0.07 S/cm at 80°C. Although proton conductivities of both Nafion 115 and 117 were lower than that of Nafion 112 at the same measurement condition, their conductivity increased with the elevated temperature, showing the sigmoidal behavior. Additionally, at around 80°C, the drastic decrease of the proton conductivity of all Nafion® membranes was observed due to the fast vaporization rate of water from the Nafion® membrane in vapor condition. On the other hand, the proton conductivity obtained from the two-probe method just reached at about 0.04 S/cm for Nafion 112, although its proton conductivity also increased up to 80°C and decreased again above the temperature. This phenomenon was less prominent in the case of thicker membranes such as Nafion 115 and 117.

Comparing the impedance and the subsequent proton conductivity derived from the two-probe method and the four-probe method with Nafion® membranes as standard samples in different conditions (Figure 3, 4), it was found that the four-probe method was more suitable and extensively applicable to measure the inherent impedance and the specific proton conductivity of a membrane over a very large range of both temperature and humidity, even though the two-probe method was able to be utilized limitedly in low humidified condition. Moreover, it was found that all resistances of components such as leads, BPO connectors, electrodes, a potentiometer and so on were reflected in the impedance measured by the two-probe method.

Differently from the four-probe method, the additional interfacial contact resistance between the membrane sample and the measuring electrodes was also detected with the change of the clamping pressure in the two-probe method. This tendency has been well observed in both the fuel cell research and the stacking development. The contact resistance generally occurs on the interface between bipolar plate materials and the membrane electrode assembly (MEA) or current collectors and gas diffusion layers in application to either proton exchange membrane fuel cell (PEMFC) or direct methanol fuel cell (DMFC), and is pointed out as a critical reason of the decrease of the cell performance. The contact resistance is induced from the measurement geometry changes with the clamping pressure, as this applied pressure affects the water and fuel transport in the gas or liquid phase. The resistance derived from the two-probe method contains all resistance components in the path from electrodes to the potentiometer. Therefore, the two-probe method is suitable and applicable to the measurement of not the inherent impedance and subsequent proton conductivity of only a membrane, but the cell performance considering with even the contact resistance as well as impedances derived from other resistor, inductor, and capacitor, as all resistance components in the path of the measurement including leads, electrode, and so on is detected with the two-probe method.

4. Conclusions

The impedance measurement system was prepared to obtain the impedance and the subsequent proton conductivity of a membrane via the four-probe method and the two-probe method in the auto balancing bridge method. Three different kinds of Nafion® membranes were selected and utilized as standard samples to measure and observe the proton transport behavior at different measuring conditions. The impedance measurement was conducted, after each dried Nafion® membrane was made to reach equilibrium water content. The impedance measurement for the same membrane resulted in the different behavior, where the inductive impedance in the two-probe method and the capacitive impedance in the four-probe method were predominant, respectively. The proton conductivity derived from approximation of the Nyquist impedance plot was well identical to the reported proton conductivity in the four-probe method. Therefore, the proton transport behavior through the membrane over a wide range of humidity was much better observed by the four-probe method, whereas it was limitedly able to be observed in the relatively low and moderate humidity. The temperature dependence on the proton transport was shown with the degree of proton conductivity and the activation energy of each membrane sample. Although all resistance components in the path of the measurement were reflected in the two-probe method, the proton conductivity was much lower than that in the four-probe method and might be dependent on temperature. As a result, the four-probe method was applicable to measure the inherent impedance and the subsequent proton conductivity of a membrane over a wide range of not only humidity but also temperature, whereas the two-probe method was appropriate to measure total impedance of the electrochemical cell with the cell performance dependent on resistances of all components.

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