Report

Measuring Conductivity of Proton Conductive Membrane in the direction of thickness, part Ⅱ: using the 4-probe method in the direction of thickness

Shuhua Ma, Hirokazu Tanaka Technical Development Headquarters

Proton conductive membrane has been reported to exhibit anisotropic properties in its in-plane and thickness directions in such areas as crystalline structure, dimensional stability, and proton conductivity.1),2) Generally, the conductivity of proton conductive membrane is measured only in the in-plane direction due to the availability of well-developed methods. However, these measurements do not provide a complete and accurate grasp of the conduction properties of a membrane. As a result, methods of measuring ion conductivity in the direction of thickness are urgently required, especially with the successful use during recent decades of proton exchange membranes in polymer electrolyte membrane fuel cells (PEFCs). Unfortunately, an accurate and reliable method has yet to be established for measuring ion conductivity in the direction of thickness of the membrane.

Usually, higher accuracy is attained using the 2-probe and 4-probe methods to measure conductivity in the in-plane direction. At Espec, we have investigated the possibility of applying these methods for measuring conductivity in the direction of membrane thickness. Preceding reports2),3),4) have discussed the effects of interface complexity and contact quality between test membrane and electrodes, and have verified the feasibility of employing the 2-probe method for measuring ion conductivity in the direction of thickness. On the other hand, the 4-probe method can yield much more accurate measurements than the 2-probe method because it uses reference electrodes to sample electrical potentials on both sides of test membranes. This report will present results obtained using the 4-probe method in the direction of thickness for measuring the conductivity of ion exchange membranes.

1 Introduction

Compared to measuring in the in-plane direction, the 4-probe method of measuring in the direction of thickness features a much smaller cell constant (L/A in $\sigma = L/(RA)$)because the membrane is thinner and possesses a larger area. Consequently, the measured resistance, typically within the range of 0.1 to 50Ω, is significantly lower than that in the in-plane direction when using the 4-probe method, in which resistance can be as high as 10 to 10^4Ω according to the temperature and humidity environments used. When measuring in the direction of thickness with the 4-probe method, some new problems may hinder widespread practical application.

(1) Dispersion in measurement values may be incurred by unevenness of interlayers in membrane laminates and/or contact between the reference electrode and its adjacent membranes. Such dispersion may also be induced by the MEA (membrane/electrode assembly) from the much thicker wire diameter of the reference electrodes.

(2) A much larger contact area between the reference electrode (which samples electric potential on one face of the test membrane) and the test membrane, which may come from the exfoliation and/or the crumbling of the coating layer on the reference electrode, will

  (a) produce rather larger interface resistance than bulk test membrane and smaller interface capacitance between the test membrane and the reference electrodes. With these influences, some labile arc-like loops and/or semi-circles may arise in the Cole-Cole plot, which will make it impossible for the 4-probe method to avoid being influenced by effects related to interfaces.

  (b) cause the hemi-circles on the Cole-Cole plot to be unsteady due to changes in the contact area between the reference electrodes and membrane, and to be susceptible to the fluctuations of the temperature and the humidity in the operating environment. Furthermore, this mutability makes it impossible to measure bulk resistance of the membrane by intercepting on a real axis such as is done in 2-probe method.

(3) When MEA specimens are produced at higher temperatures and pressures using hot-pressing, reference electrodes frequently break off from the wires sandwiched between test membranes and current lead-in membranes, causing functional failure. This is caused by the creep property of the polymeric membranes that are liable to stretch and deform.

Because of these problems, input/output O/L (overload) error messages of current and voltage in the electrochemical measurement device (Potentiostat/Galvanostat) are much more likely to occur when using the 4-probe method in the direction of thickness than in the in-plane direction. The difficulties in manufacturing and measuring MEA specimens have greatly hindered the application of the 4-probe method in the direction of thickness in real ion conductivity measurements. Furthermore, a defective MEA specimen produced by improper temperature and pressure conditions will also lead to some failures and debase the accuracy of the measurements. For example, diffuse and scattered points with a poor convergence domain are brought about on the Cole-Cole plot, and/or completely singular resistance measurements may be obtained.

With the aim of overcoming the above failures and identifying the optimal specimen manufacturing conditions as well as conditions for accurately measuring proton conductivity in the direction of thickness of Nafion®-like membranes, we at Espec have developed the 4-probe technique in the direction of thickness. This report will discuss some important factors affecting the measuring performance of the MEA specimen, including the arrangement between the electric potential sampling electrodes and the electric current lead-in membranes, materials of the wire and its coating used as electric potential sampling electrodes, and the forming condition of MEA specimens. In addition, this report will also present measurement results from this 4-probe technique in the direction of thickness for Nafion117® membranes that underwent different temperature and pressure pretreatments.

2 Experimental method

2-1 Equipment and materials

Table 1 lists equipment and materials used in this research.

Table 1 Equipment and materials

Equipment/materials	Manufacturer	Model/registered product name
Ion exchange membrane	E. I. du Pont de Nemours and Company	Nafion117®
Cu/polyester coated wire, wire diameter: ϕ0.1mm	The Nilaco Corporation	CU-116167
Pt/Teflon coated wire, wire diameter: ϕ0.076mm	The Nilaco Corporation	PT-967353
Pt wire, wire diameter: ϕ0.10mm	The Nilaco Corporation	PT-351165
Insulating varnish	The Nilaco Corporation	Varnish, No. 7031
Impedance gain/phase analyzer	Solartron Instruments	SI 1260
Electrochemical interface	Solartron Instruments	SI 1287
Temperature & humidity chamber	Espec Corporation	PL-1KPH

2-2 Specimen preparation

2-2-1 Preparation of reference electrodes

Three types of coated wire with insulating layer were used as reference electrodes (also known as electric potential sampling electrodes) to examine effects of the coating and the conducting materials on the measuring performance of the MEA specimen.

(a) Cu/polyester coated wire: ready-made product used as listed in Table 1.
(b) Pt/Teflon coated wire: ready-made product used as listed in Table 1.
(c) Pt/insulating varnish coated wire: coating film formed on Pt wire by soaking bare Pt wire in Varnish No. 7031 solution diluted with solvent mixture of ethyl alcohol and toluene 50:50 by volume, and followed by drying in vacuum at 100℃ for 5 hours.

2-2-2 Manufacturing MEA specimens for the 4-probe method in the direction of thickness

Using the above three types of coated wires, reference electrodes were prepared by cutting one end obliquely to be used as the electric potential sampling electrode terminal and peeling the other end of the wire about 1 cm to be used as the connecting terminal into other external devices.

Two steps were involved in the manufacturing process of premium MEA specimens in this context.

First, the reference electrode was imbedded into the current lead-in membrane by placing one reference electrode on a 50μm-thick Teflon sheet with its bevel section exactly toward the film surface, covering that with a current lead-in membrane and another Teflon sheet in sequence, and then following with a hot-pressing treatment at 150℃ and 400 kgf cm^{-2}. Second, after removing the Teflon sheets, the MEA specimen was fabricated by sandwiching two current lead-in membrane units made above and one test membrane pretreated under the appointed temperature, pressure and chemical conditions, with the bevel sections situated opposite each other and located at equipotential positions, e.g., the center of the test membrane, and then hot-pressing them at 150℃ and 20 kgf cm^{-2}. The schematic construction of the MEA specimen as obtained above for the 4-probe method in the direction of thickness is shown in Fig.1.

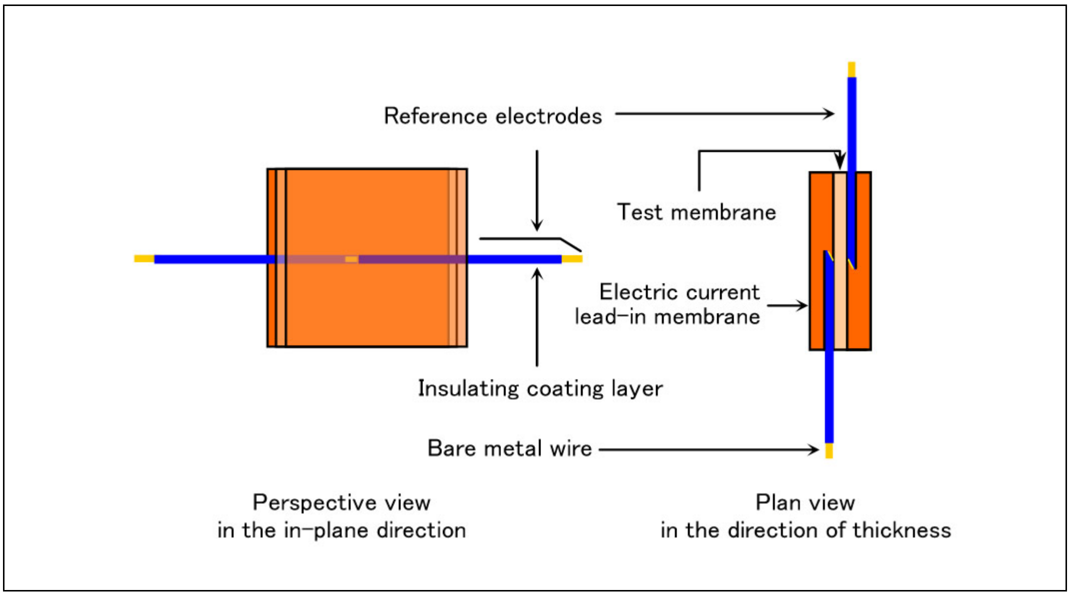


Fig.1 Construction of MEA specimen for the 4-probe method in the direction of thickness

2-3 Conductivity measurement of MEA specimens

A specimen fixed to the measuring cell was placed inside a temperature and humidity chamber under constant temperature and humidity (30℃, 30-90%rh). AC impedance measurements were taken using a computer-controlled impedance gain/phase analyzer and electrochemical interface measuring system, and Cole-Cole (Z’-Z’’) and Bode (log|*Z*|-log *Frequency* and *theta*-log *Frequency*) plots were obtained. The frequency limits of the sinusoidal signals were typically set between 5MHz and 0.01Hz, with an oscillation of 10 mV.

With test membrane bulk resistance R read out according to the center of gravity of the concentrated points on Cole-Cole plot, conductivity was calculated using the following formula.

$$\sigma = \frac{L}{R \cdot A} \quad \dots (1)$$

Where σ is conductivity (S cm^{-1}), R is resistance (Ω), L is test membrane thickness or interval between two electric potential sampling electrodes (cm), and A is electrode area (cm^2).

Equipment connection for the impedance gain/phase analyzer (IGPA), the electrochemical interface (EI) and the membrane/electrode assembly (MEA) was shown in Fig.2 for 4-probe conductivity measurements in the thickness direction used in this report.

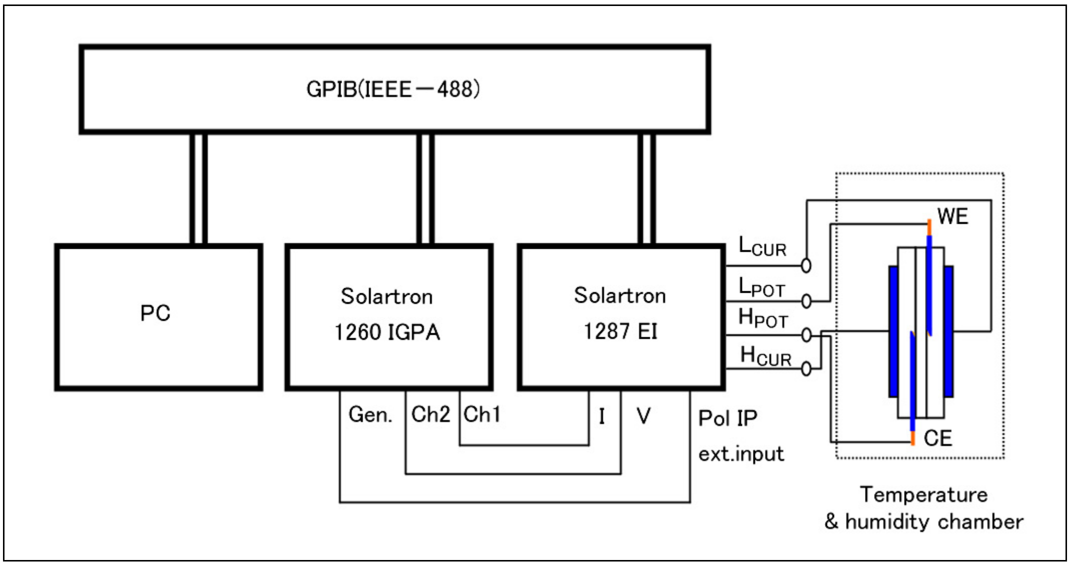
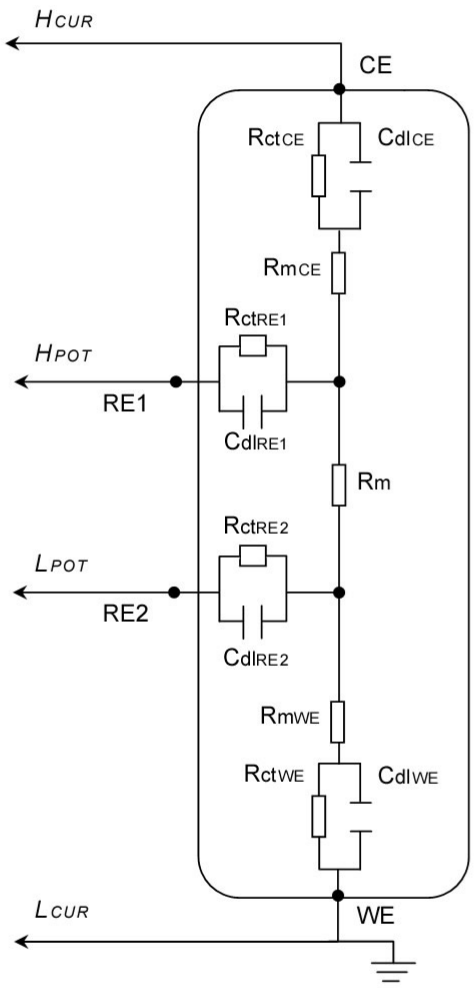


Fig.2 Block configuration for ion conductivity measurement using the 4-probe method in the direction of thickness

3 Considerations and discussion of measuring

3-1 Configuration of the 4-probe method in the direction of thickness

Using the 4-probe method in the direction of thickness, the simplest configuration is that which measures only a single test membrane, although theoretically multiple membranes can be measured unless the MEA stack is too thick to afford stable and sound internal contacts as well a dimensional evenness of the test membranes. As Fig.2 shows, a typical MEA specimen configuration consists of 4 electrodes, known as electric current lead-in electrodes and electric potential sampling electrodes, and 3 membranes as electric current lead-in membranes and test membrane. Considering the specimen as an active electrochemical system, the equivalent circuit5) and the connections into the external electrochemical device can be expressed in Fig.3.



R_{mCE}, R_{ctCE}, C_{dlCE}: denote resistance and capacitance related to the electric current lead-in membrane and the interface between that and the electric current lead-in electrode on the CE side.

R_m, R_{ctRE1}, C_{dlRE1}, R_{ctRE2}, C_{dlRE2}: denote resistance and capacitance related to the test membrane, and the interfaces between that and reference electrodes.

R_{mWE}, R_{ctWE}, C_{dlWE}: denote resistance and capacitance related to the electric current lead-in membrane and the interface between that and the electric current lead-in electrode on the WE side.

Where subscript CE stands for the electric current lead-in electrode or membrane on the CE side, RE1 for the electric potential sampling electrode on the CE side, m for the test membrane, RE2 for the electric potential sampling electrode on the WE side, WE for the electric current lead-in electrode or membrane on the WE side, respectively. Furthermore, ct and dl refer to charge transfer and double layer as conventionally for an electrochemical interface.

Fig.3 Connections and equivalent circuit for MEA specimen using the 4-probe method in the direction of thickness

Fig.3 demonstrates that the impedance pertaining to the electric current lead-in membrane and its interfaces with electric current lead-in electrodes, R_{mCE}, R_{mWE}, and R_{ctCE}, R_{ctWE}, C_{dlCE}, C_{dlWE}, are situated outside the electric potential sampling measurement system, and thus have little influence on measurement results. As a result, bulk membrane resistance R_m can be measured accurately using this method, provided the impedance related with R_{ctRE1}, R_{ctRE2}, and C_{dlRE1}, C_{dlRE2} are small enough. This impedance can be reduced by adjusting hot-pressing conditions and manufacturing processes of MEA specimens. Hence, we may infer that the electric current lead-in electrodes, CE and WE, may be omitted by substituting two electrode terminals of the measuring cell. Also, the electric current lead-in membranes of CE and WE do not affect the results even if different kinds and/or thickness of membranes are used, although they should possess the same current-conducting carriers as the test membrane, viz., either electron, proton, or other ions. In addition, test membranes can be pretreated by hot-pressing at various pressures and temperatures, or any chemical treatments may be applied before preparing MEA specimens. Thus, this method allows a wide range of membrane conditions.

However, it is necessary to prevent the thickness and the evenness of test membranes from being affected when the test membrane is combined into an MEA specimen. This means that temperature and pressure conditions must be neither too high nor too low when hot-pressing for successfully preparing MEA specimens. In this report, we have reported a two-step method by which reference electrodes were completely imbedded into electric current lead-in membranes in the first step. Because of this, we were able to use fairly reduced temperature and pressure conditions without markedly disturbing test membranes in the following second step. Consequently, the accuracy, reliability and reproducibility of the ion conductivity measurements using the 4-probe method in the direction of thickness have been significantly enhanced.

3-2 Identifying cause of failure of MEA specimens from O/L error messages in electrochemical measurement

When using the impedance gain/phase analyzer and electrochemical interface measuring system of Solartron Instruments to measure the proton conductivity in the direction of thickness of polymeric electrolyte membrane using the 4-probe method, RE1 O/L, RE1-RE2 O/L, and Current O/L and Current DVM O/L errors frequently occurred on the Potentiostat/Galvanostat electrochemical device (Model 1287, electrochemical interface).6) These messages, combined with the measuring principle of the electrochemical device used, may work as an informative guide for determining the failure cause of the MEA specimen, i.e., what defects have been observed and/or what failures have developed when measuring MEA specimens. For example, the appropriate conditions for the manufacture and measurement of MEA specimens can be found more effectively and rapidly based on analyses of these errors.

As mentioned in the connections and equivalent circuit of MEA specimen while measuring by the membrane thickness 4-probe method in Fig.3, the Potentiostat/Galvanostat was used to apply AC potential perturbation to the terminals of CE and WE while simultaneously sampling the electric potential signals between the terminals of RE1 and RE2. When error messages of RE1 O/L and/or RE1-RE2 O/L occur, they indicate that a higher voltage drop than the 14.5 V limit of the device has developed between the terminals of RE1 and the ground and/or the terminals of RE1 and RE2. An important phenomenon found while measuring is that the error messages RE1 O/L and RE1-RE2 O/L occurred simultaneously during the measuring period with a frequency range lower than 10 kHz. With the WE terminal as the ground for the instrument as shown in Fig.3, it can only be concluded that the impedance between the terminals of RE1 and RE2 rather than that between RE2 and WE was overloaded. This may have come from excessive interface resistance or insufficient interface capacitance (or both) for reference electrodes RE1 and RE2, as shown in Fig.3. Excessive interface resistance R_{ctRE1} or R_{ctRE2} is thought to have come from poor contact between the test membrane and reference electrode RE1 or RE2, or disconnected electrode wires. The following causes of failure can be expected: the snapping-off of electrode wires, the shielding of electrode terminals by the insulated coating tube or its fragments that may come from the stretching forward and/or the breaking up of the coating layer of the electrode wire, and unstable contact between the reference electrode and the test membrane.

4 Observations and discussion for measuring

4-1 Effect of manufacturing conditions of MEA specimens

Effects of hot-pressing conditions and reference electrode materials on MEA measuring performance are listed in Table 2 for measurements of proton conductivity of Nafion117® membrane using the 4-probe method in the direction of thickness using the AC impedance technique.

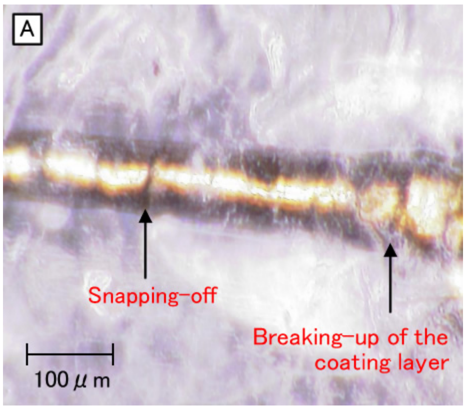
Table 2 Effects of hot-pressing conditions and electrode material on MEA measuring performance

Hot-pressing temperature / pressure — Forming method / electrode material		150℃			80℃		
		40 kgf cm^{-2}	200 kgf cm^{-2}	400 kgf cm^{-2}	40 kgf cm^{-2}	200 kgf cm^{-2}	400 kgf cm^{-2}
One-step	Teflon-Pt	Stretched coating	Wire break, Stretched coating	Wire break, Stretched coating	Stretched coating	Wire break, Stretched coating	Wire break, Stretched coating
	Varnish-Pt	Unstable performance	Wire break	Wire break	Unstable performance	Wire break	Wire break
	Polyester-Cu	Poor performance	Poor performance	Wire break	Good performance	Poor performance	Poor performance
Two-step*	Teflon-Pt	-	-	-	Stretched coating	Stretched coating	Wire break, Stretched coating
	Varnish-Pt	-	-	-	Good performance	Unstable performance	Poor performance
	Polyester-Cu	-	-	-	Excellent performance	Good performance	Unstable performance

*:Reference electrode wires were previously imbedded into electric current lead-in membranes by hot-pressing at 150℃ and 400 kgf cm^{-2} for 1 min in the first step

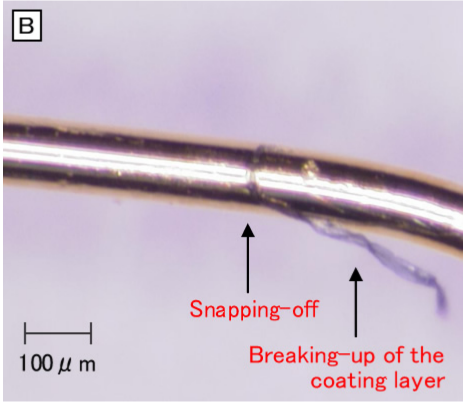
The one-step method in MEA manufacturing refers to a technique in which the MEA specimen is completed using a single hot-pressing process with the laminate stack sandwiched by two electric current lead-in membranes, two reference electrode wires, and one test membrane. Using the one-step method, shown in Table 2, MEA specimens prepared at relatively lower temperature or pressure afforded a comparatively higher measuring performance for all three reference electrode materials used, more obviously in the case of Cu/polyester coated wire. On the other hand, measuring performance of the MEA specimens was enhanced dramatically with the two-step method, which features a preceding hot-pressing process by which the reference electrode was imbedded into the electric current lead-in membranes. The results exhibited the marked effectiveness of the two-step method over the one-step method. Moreover, Table 2 also reveals an increase in the measuring performance of the MEA specimens with the use of electrode material in the following order: Pt/Teflon, Pt/varnish, and Cu/polyester.

Microscope analysis was used to clarify the mechanism of failure of the MEA specimens, observing and analyzing reference electrodes that underwent hot-pressing treatments. Typical failure examples of reference electrodes are shown in Photo 1. These failures occurred after first undergoing a hot-pressing process in the first step when using the two-step method.



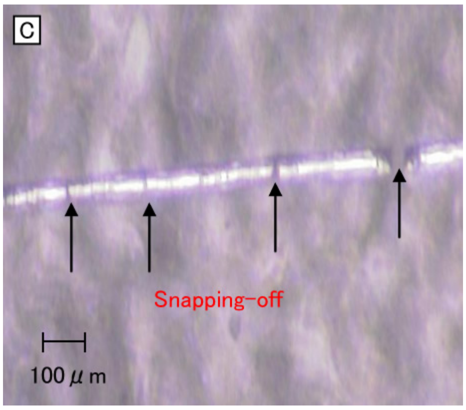
Polyester-Cu
Hot-pressing: 150℃, 400kgf cm^{-2}
10 min

Snapping-off of Cu wire and breaking-up of the coating layer can be observed due to the higher temperature and pressure, and the longer hot-pressing time.



Polyester-Cu
Hot-pressing: 150℃, 40kgf cm^{-2}
1 min

With lower pressure and shorter hot-pressing time, the integrity of the reference electrode was significantly improved. As less pressure than 40kgf cm^{-2} was applied, the adherence of the electrode into the electric current lead-in membrane degraded. However, shortened pressing time was viable.



Varnish-Pt
Hot-pressing: 150℃, 400kgf cm^{-2}
1 min

Identical conditions to (A) except time of hot-pressing. However, marked cutting was induced. The result is considered as due to poor malleability of Pt wire compared to Cu.

Photo 1 Typical failure examples of reference electrodes occurring after the first hot-pressing process in the two-step method

Photo 1 (C) exhibits an important conclusion to be drawn: a conductor with excellent malleability should be selected as the reference electrode, e.g., Au wire other than Pt should be used instead of Cu wire when a strongly corrosive environment is involved.

On the other hand, we also tried using Teflon-Pt-coated wire as the reference electrode and observed the MEA specimen. We found that besides causing the wire to snap off and breaking up the coating layer, the Teflon coating layer became badly elongated and covered the entire conducting tip of the electrode. This result is considered to stem from weaker adherence between the surface of the Pt wire and the Teflon coating layer when hot-pressed at the specified treatment temperature.

From the above observations, it has been confirmed that the stretching, breaking up and covering of the coating layer on the reference electrode as well as the cutting of the conducting wire have independently and/or jointly resulted in occurrences of O/L error messages in the electrochemical device.

In summary, the following measures are very important to a better measuring performance of the MEA specimen: adapting the two-step method, selecting the proper hot-pressing temperature, pressure, and time while taking into account both the firmness and the integrity of the reference electrode, and choosing the suitable conducting and coating materials for the reference electrode based on the applied membrane environment.

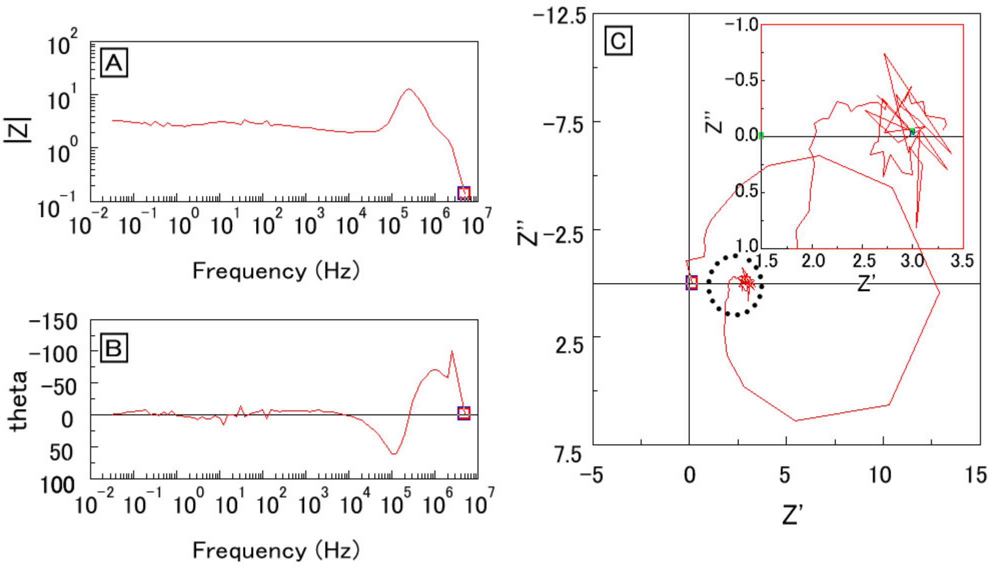
4-2 Influencing of the measuring cell

As described above, it is important to manufacture an MEA specimen free of any inherent defects. Furthermore, it is also necessary for a custom-designed measuring cell to be used to connect the ultra-fine reference electrode terminal of approximately 100 μm in diameter with external electrochemical devices, because connection reliability exerts a major influence on measurability and accuracy. A special measuring cell has been designed intended for exclusive use with the 4-probe method in the direction of thickness. This cell provides easy connecting operation, stable and unaffected internal contact in the MEA specimen while connecting, and the necessary external connection reliability.

4-3 Proton conductivity measurement in the direction of thickness with the Nafion117® membrane

The 2- and 4-probe methods in the direction of thickness and the 4-probe method in the in-plane direction were used to study the proton-conducting properties of the Nafion117® membrane pretreated by hot-pressing at 150℃ at various pressures. Fig.4 shows typical impedance spectra for membranes pretreated at 150℃ and 1200 kgf cm^{-2}. These were obtained using the membrane thickness 4-probe method in an environment of 30℃ at 60%rh.

Near constant resistance and almost 0° of phase angle were obtained in Bode plots (A) and (B) within the frequency range of between 0.01 Hz and 9000 Hz. Meanwhile, concentrated points with a narrow convergence domain were displayed in the Cole-Cole plot of Fig.4(C). These results indicate that the 4-probe method in the direction of thickness is viable in practice, exhibiting good measurement accuracy.

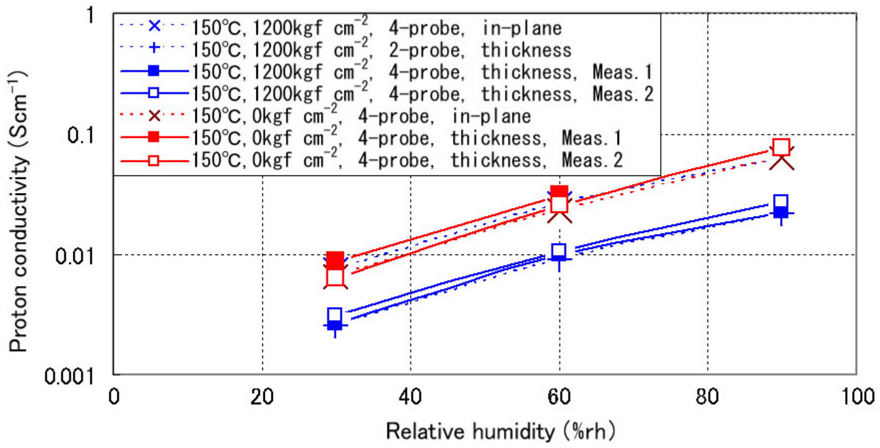


Measurement environment: 30℃, 60%rh
Membrane treatment: 150℃, 1200 kgf cm^{-2}
A and B: Bode plots, C: Cole-Cole plot
Inset shows detail of concentrated point.

Fig.4 Typical impedance spectra obtained using the 4-probe method in the direction of thickness for Nafion117® membrane

Fig.5 showed the measurement values for Nafion117® pretreated at 150℃ at various pressures using the membrane plane 4-probe method and membrane thickness 2- and 4-probe methods. Here, it should be noted that as a comparison standard, the measurements for these membranes were also carried out using the conventional 4-probe method in the in-plane direction and the 2-probe method in the direction of thickness. For membranes pretreated at 150℃ and 1200 kgf cm^{-2}, the proton conductivity values measured using the 2- and 4-probe methods in the direction of thickness fit very well, verifying the effectiveness of the 4-probe method in the direction of thickness. However, when compared to measuring in the in-plane direction using the 4-probe method, proton conductivity values in the direction of thickness were found to have significantly decreased. In order to make clear the actual causes, i.e., either from the immaturity of the measurement technology developed or from the degenerated property of the membrane, measurements were also carried out using the 4-probe methods in the in-plane and thickness directions to measure a membrane heat-treated at 150℃ but not pressurized.

As Fig.5 shows, good conformity exists for the measurements not only between the values in the in-plane and thickness directions for the membrane pressurized at 0 kgf cm^{-2} but also with those in the in-plane direction for the membrane treated at 1200 kgf cm^{-2}. These results indicate that after hot-pressing at higher temperature and pressure, proton conductivity in the direction of thickness of the Nafion117® membrane was significantly degraded. Merely a simple heat treatment with no pressurizing process did not induce the marked anisotropy in the proton conductance of the membrane.



Measurement environment: 30℃, 30, 60, and 90%rh
Membrane treatment: 150℃, 0 and 1200 kgf cm^{-2}

Fig.5 Proton conductivity measurements using the 4-probe method in the in-plane direction, and the 2- and 4-probe methods in the direction of thickness for Nafion117® membrane

From the above we may conclude that the 4-probe method may be employed in the direction of thickness and this method is conducive to the complete evaluation of the ion conductance of the electrolyte membrane with higher stability, accuracy and reproducibility.

5 Conclusions

(1) More attention should be paid to the following items as influencing factors in the 4-probe method in the direction of thickness: the species and characteristics of the conductor and the coating layer materials constituting reference electrodes, the method of fabricating MEA specimens, the temperature and pressure conditions in hot-pressing, and connections with external devices.

(2) Anisotropic ion conductance can be induced over the directions of thickness and in-plane for Nafion117®-like electrolyte membranes when pretreated at higher temperature and pressure.

(3) The 4-probe technique may be employed in the direction of thickness in real measurements of the ion-conducting electrolyte membrane.

6 Acknowledgement

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