
Report 2

Measuring conductivity of proton conductive membranes in the direction of thickness

Shuhua Ma, Akiko Kuse

Technical Development Headquarters, Espec Corp.

Zyun Siroma, Kazuaki Yasuda

National Institute of Advanced Industrial Science and Technology (AIST)

Proton conductive membrane is generally evaluated by measuring its conductivity along the planes of the membrane. However, in view of the possibility of this membrane exhibiting anisotropy in the direction of membrane thickness compared to measuring along the longitudinal and transversal planes, the need to measure its conductivity in the direction of thickness has recently been receiving greater attention. The research work for this report is aimed at finding a way to stably and precisely measure the conductivity of a Nafion^{®1} membrane in the direction of thickness. Measurements can be conducted with either 2- or 4-probe methods, but measuring with 2 probes is much easier than with 4, and this method yields more stable results as fewer inconsistencies occur with multiple specimens. This report presents the results with the 2-probe method for membrane conductivity measurements with an emphasis on the effect of interface complexity between membrane and electrodes and the feasibility of using this method for measurements.

1 Introduction

Polymer electrolyte membrane fuel cells (PEFCs) are promising energy systems for use as automotive power supplies and for stationary as well as portable applications, due to their low operating temperature, high energy density, and acceptable levels of miniaturization. Since it is one of the most important criteria, proton conductivity is always used to evaluate the practicability of newly-developed membranes as well as the cell performance of the perfluorosulfonic acid (PFSA) polymer membrane often used with PEFC.²⁾

Compared to the conductivity in the direction of thickness, the resistance measured in along the plane reaches as high as 1000Ω, which features a large cell constant^{*1}(L/A in $\sigma=L/(R \cdot A)$). The four-probe method^{*2} yields narrower data dispersion and smaller relative errors, thus this method is commonly used to measure the proton conductivity of the PFSA membrane^{*3} along the plane.

However, it is highly likely that treatments the membrane undergoes in the manufacturing and processing processes, such as stretching and hot-press, will change not only its crystalline structure and dimensional stability in the longitudinal, transverse, and thickness directions but also exert some influence on its proton conductivity. There is a high probability of anisotropy³⁾ in the proton conductivity of the membrane. On the other hand, PFSA membranes are being used in the direction of thickness for the solid polymer electrolyte fuel cells, and an anisotropically conductive membrane that was newly-developed must also be evaluated in various directions. Therefore, a reliable measuring technique with high stability, reproducibility and accuracy is required to evaluate proton conductivity in the direction of thickness of the membrane. The research for this report focuses on developing a stable and precise method of measuring conductivity in the direction of thickness for the proton-conductive polymer electrolyte membrane.⁴⁾

Measurements in the direction of thickness can be conducted with 2-probe*⁴ and 4-probe methods, but measuring with two probes is much easier than with four, and results are more stable as there are fewer inconsistencies with multiple specimens. This report presents the results obtained using the 2-probe method for conductivity measurements of ion exchange membranes.

2 Experimental method

2-1 Equipment and materials

Table 1 lists the equipment and materials used in this research.

Table 1 Equipment and materials

Equipment/materials	Manufacturer	Model/registered product name
Impedance gain/phase analyzer	Solartron Instruments	SI 1260
Electrochemical interface	Solartron Instruments	SI 1287
Temperature & humidity chamber	ESPEC Corporation	PL-1KPH
Ion exchange membrane	E. I. du Pont de Nemours and Company	Nafion®117

2-2 Specimen preparation

MEA specimens were made by hot-pressing electrodes to a Nafion®117 membrane. In a preliminary test, measurements were made with two kinds of MEAs. One type of MEA specimen was produced by hot-pressing two Pt foil electrodes, coated with Nafion® solution on one side each, to a membrane. The other MEA specimen was produced by hot-pressing two Pt foil electrodes to a membrane without using the Nafion® coatings. Results showed good reproducibility with the Nafion®-coated specimen, therefore, in this report specimens were prepared by coating a Nafion® solution onto one surface of the electrodes for voltage impression unless otherwise specified.

For 2-probe measurements in the direction of thickness, specimens were prepared by hot-pressing a Nafion® membrane sandwiched into electrodes consisting of two pieces of metal sheets (5 mm x 5 mm x 10 to 20µm) or carbon papers (5 mm x 5 mm x 190µm) situated opposite each other. On one face of the metal sheets, a coating was applied with 5 µl of 5 wt. % Nafion® dispersion solution in lower aliphatic alcohols followed by vacuum drying one hour at room temperature. No coating was used on the carbon paper electrodes. Photo 1 shows the configuration of the membrane/electrode assembly (MEA⁵) used in this report for the 2-probe measurements in the direction of thickness. The assembly is made of platinized Pt black sheets and Nafion®117 membrane.

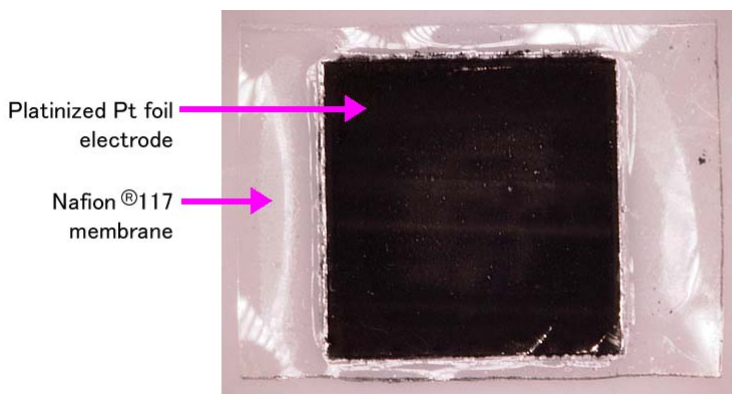


Photo.1 MEA of Pt black/Nafion®117 for 2-probe measurements in the direction of thickness

For 4-probe measurements in the direction of thickness, the specimens were prepared by sandwiching and hot-pressing platinum wire electrodes between three Nafion® membranes and then, as with the specimens for the 2-probe measurements, hot-pressing metal sheets that had been coated with Nafion® solution and vacuum-dried onto both outside faces of the assembly.

Since 4-probe measurements in the surface direction obtained results with better reproducibility, these measurements were used as comparison reference against the measurements in the direction of thickness of the membrane. The specimens for 4-probe surface direction measurements were prepared by press-fitting metal sheets to both ends of the Nafion® membrane and vertically piercing into the membrane near the center with platinum wires.

Fig. 1 (a) and (b) respectively show schematics of the specimens for the 2-probe and 4-probe measurements in the direction of thickness, while (c) shows the same for the 4-probe surface direction measurements.

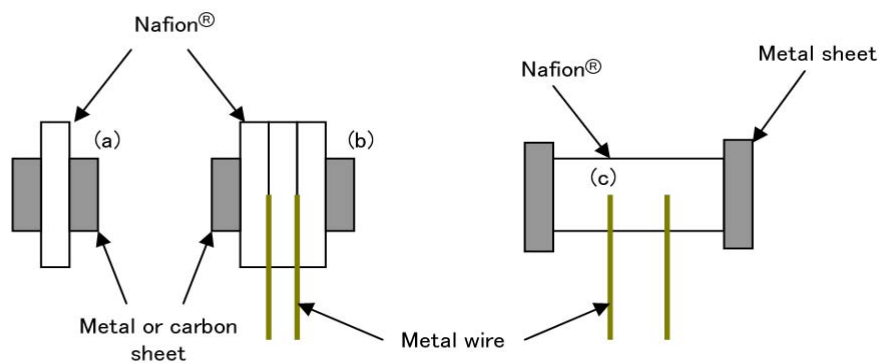


Fig.1 Sample arrangements for (a) the 2-probe method, (b) the 4-probe method in the direction of thickness, and (c) the 4-probe method in the surface direction

2-3 Conductivity Measurements

A specimen fixed to a measuring cell was placed inside a temperature and humidity chamber under constant temperature and humidity (80°C, 30 to 90% rh). AC impedance measurements were taken using a computer-controlled Solartron Instruments model 1260 impedance gain/phase analyzer and a computer-controlled 1287 electrochemical interface, 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 5 MHz and 0.01 Hz, with an oscillation of 10 mV. Assuming a circuit equivalent to the one shown in Fig.3, a best-fitting curve was overlaid onto the measurements taken by the 2-probe method. Conductivity was calculated from the obtained membrane resistance, R_{bulk} , using the following formula.

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

Where σ is conductivity (Scm^{-1}), L is membrane thickness (cm), A is electrode area (cm^2), and R is resistance (Ω).

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 2-probe conductivity measurements used in this report.

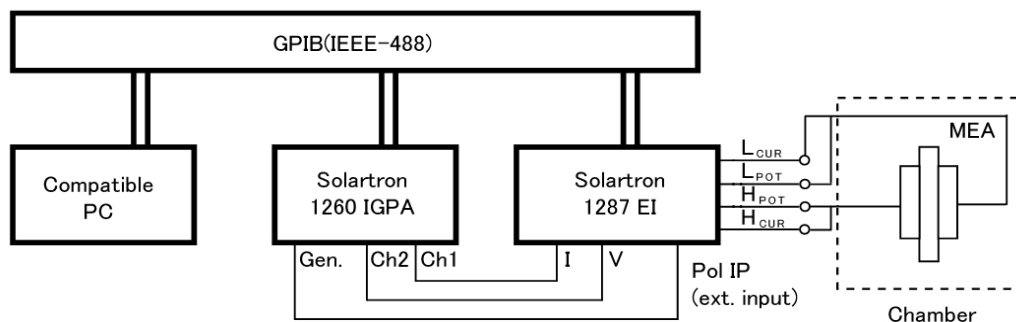


Fig.2 Connections for impedance measured by the 2-probe method, with an IGPA in combination with potentiostat/galvanostat (electrochemical interface) mode.

3 Results and observations

3-1 Humidity dependency of resistance and capacity components of impedance

In the Cole-Cole plot obtained from the 2-probe measurements, two loops appeared. They were named loop 1 and loop 2 in order of descending frequency and were treated as RY parallel circuits. The resistance and capacity components obtained from the fit were R1, R2, Y1 and Y2 (Y is a constant phase element and substituted for the equivalent capacity component in the fitting process). Fig. 3 shows a diagram of the equivalent circuit.

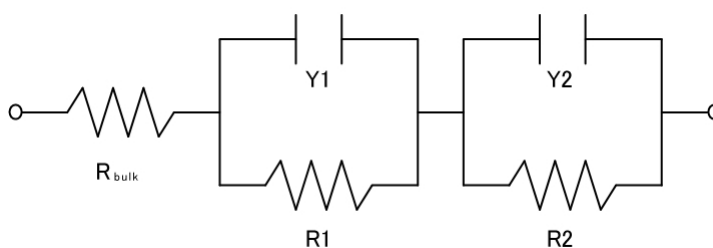


Fig.3 Equivalent circuit for the membrane/electrode interface studied

Measurements were taken at an ambient temperature of 80°C using 4 types of electrodes made of gold, platinum, platinum black and carbon paper. Fig. 4 shows the humidity dependency of R_{bulk} (membrane resistance), R1, Y1, R2, and Y2 using the various electrode materials.

As ambient relative humidity during measuring increased, R_{bulk} , R1, and R2 decreased. This phenomenon indicates that the conductivity of proton-conductive polymer materials such as Nafion® depend on their water content. In particular, minimum resistance was obtained for R1 and R2 when using the platinum black electrode with higher active surface area, suggesting that both loop 1 and loop 2 with R/Y parallel connections are strongly correlated to the interface between membrane and electrode. With capacitance components of Y1 and Y2, regular increases in electrical capacity were found to correspond to increases in ambient humidity. Increases in this electrical capacity can be considered to result from improved contact between membrane and electrode concurrent to the hygroscopic swelling of the moisture-absorbent membrane. Types and surface morphology of electrode materials also notably affect interface resistance and capacity due to their varied surface area and differences in membrane contact. However, with R_{bulk} membrane resistance, equivalent measurement values have been obtained for various electrode materials with no major influence based on material types found. Therefore, it can be concluded that membrane resistance (R_{bulk}) can be separated from interface elements (R1, Y1, R2, and Y2) regardless of electrode materials used, since the multi-layer complexity of contact of the interface between membrane and electrodes, e.g., multiple semicircles in Cole-Cole plot, can be removed by equivalent circuit fitting.

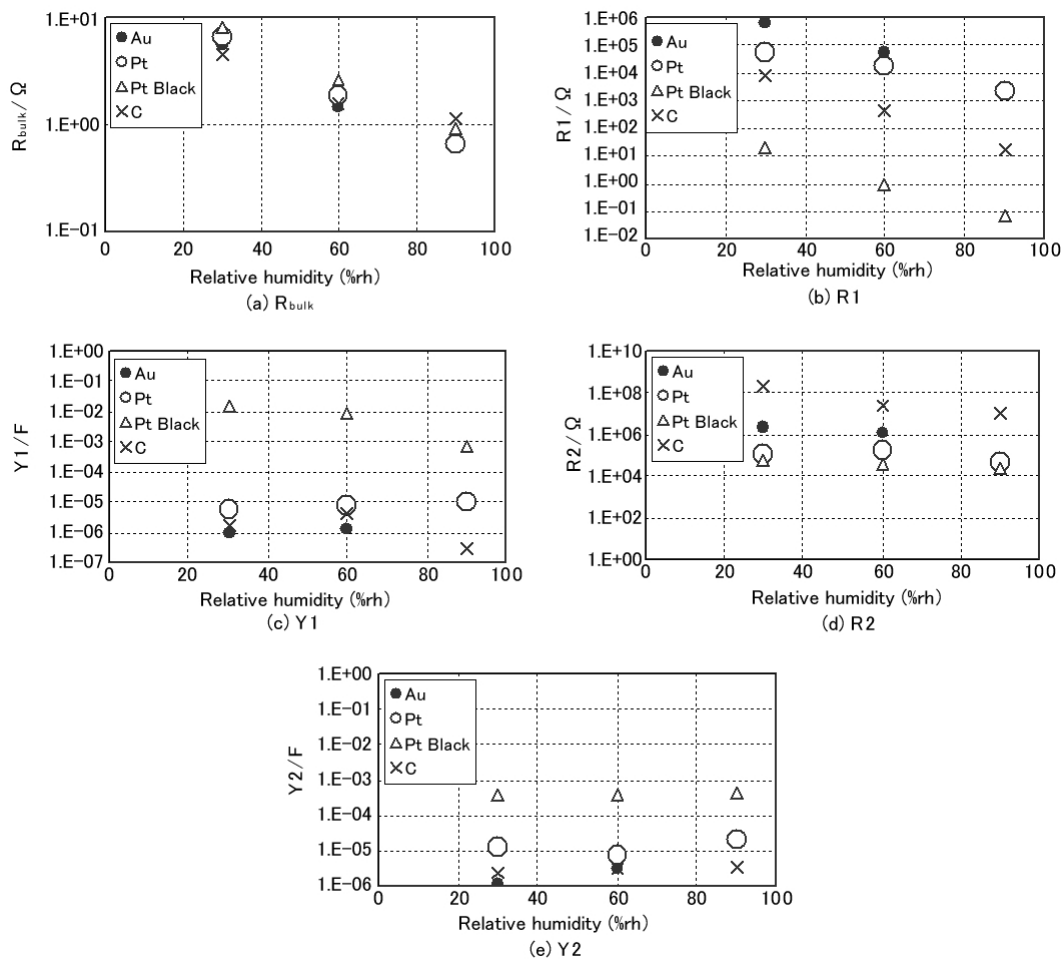


Fig. 4 Dependence on relative humidity of various electric elements in equivalent circuits at 80°C

3-2 Conductivity

Conductivity was calculated using R_{bulk} from Fig. 4 (a) and formula 1. Fig. 5 shows the conductivity values measured at an ambient temperature of 80°C and various humidity levels. For comparison, the results from 4-probe measurements in surface direction were also plotted. As shown in Fig. 5, conductivity results using 2-probe measurements in the direction of thickness were similar to those using 4-probe measurements in the surface direction for all electrode materials, demonstrating the validity of using the 2-probe method in the direction of thickness.

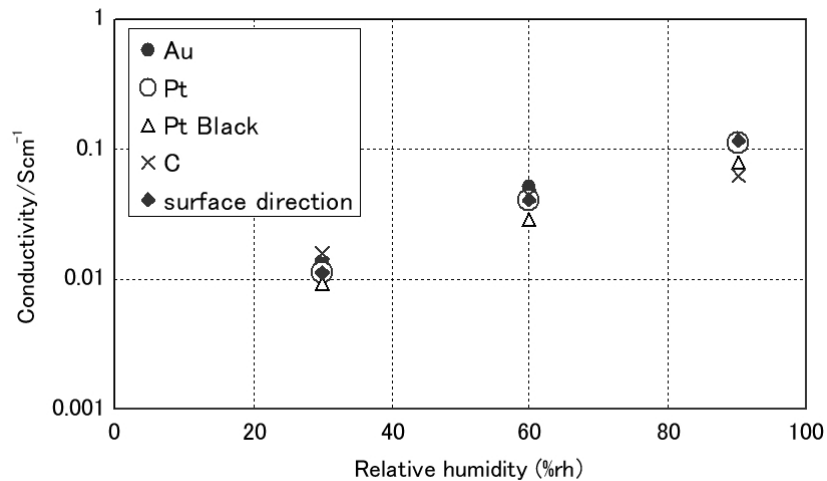


Fig. 5 Comparison of conductivity results at 80°C using the 2-probe Method in the direction of thickness and the 4-probe method in the surface direction.

4 Conclusions

Conductivity of Nafion® membranes in the direction of thickness was measured using the 2-probe AC impedance method. These experiments confirm that equivalent circuit fitting can separate membrane resistance from the interface components. Moreover, good contact at the interface between the membrane and electrode can be attained by coating the electrode with Nafion® solution, and conductivity results are similar to results using 4-probe measurements in the surface direction. These experiments demonstrate the validity and feasibility of using the 2-probe method for measuring in the direction of thickness.

[Terminology]

*1. Cell constant

Typically, electrical conductivity of a material can be expressed as $\sigma = L / (A \cdot R) = k / R$, where L is the length (cm) of the material in electronic flow, A is the sectional area (cm²) across the flow of the material, R is the measured resistance (Ω), and $k = L/A$, the proportionality factor, is called the cell constant. The electrical conductivity of the material is in direct proportion to the reciprocal of the measured resistance between the electrodes by the scale factor, k, which represents the influence of the dimensions of the measuring cell.

*2. Conductivity measurement using the 4-probe method

As one method for measuring the electrical conductivity of materials, the 4-probe method possesses much higher measurement precision than the 2-probe method. Two terminals are used to conduct a current through the sample, and another two terminals measure the potential drop across the sample.

*3. Proton-conductive membrane

When potential difference exists in a conductor, electrical charges move in the direction required to weaken the difference. The property of this conductor is called its electrical conduction. When protons exist in the conductor as the main current carriers, the material is referred to as proton conduction, and the quality or power of the conduction is called proton conductivity. Some membrane materials, typically consisting of such as inorganic compounds of ceramics and/or glass, organic polymer compounds, and inorganic/organic hybrid materials, exhibit high H⁺ ion conduction. Proton exchange membranes based on fluorinated polymers as typified by Nafion[®] have been widely used in solid polymer electrolyte fuel cells (PEFCs) due to their high proton conductivity (to 0.1 Scm⁻¹) and chemical stability.

*4. Conductivity measurement using the 2-probe method

As the simplest and most straightforward method for measuring electrical conductivity, the 2-probe method uses only two terminals that share the functions of both introduction of current (I) and measurement of voltage (V) across the sample. The electrical conductivity of a specimen can be calculated with the formula of $\sigma = (I \cdot L) / (V \cdot A)$, provided that sectional area (A) and length (L) of the specimen are measured.

*5. Membrane electrode assembly (MEA)

An electrode layer composed of platinum black or platinum-supporting carbon and a porous supporting collector layer composed of carbon paper or carbon cloth arranged in succession on both sides of a cation exchange membrane, with the assembly unified by hot-pressing, is called a membrane electrode assembly (MEA).

[Bibliography]

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