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Proton conductivity of Nafion® membrane in actual direct methanol fuel cell operation

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Abstract
This paper shows a comparison of proton conductivity measurement of Nafion® membrane for direct methanol fuel cell application. The experimental study was carried out in order to compare the proton conductivity of the polymer membrane using AC impedance technique, in which the specimens were under two different environments, under hydrated and acidic solution and under actual DMFC operation. Two methods were used in this study comprising of two-electrode method and measurement in DMFC a single cell. Experiments were carried out under temperature of 30 °C – 70 °C.

1. Introduction

Proton conducting membrane plays important role in direct methanol fuel cell operation as it functions as fuel and oxygen barrier and as proton transporting paths from anode to cathode in order to allow the reaction to complete. The methods typically used are four-point-probe method and two-electrode method, in which the electronic resistance of the membrane is measured by AC impedance technique. However, with the method mentioned above are typically done with the membrane was not under the DMFC operation but the membrane was under hydrated and acidic solution, from which the conductivity did not reflect the conductivity of the actual DMFC operation. Therefore, the measurement of conductivity of a membrane may be more accurate if it was carried out under DMFC operation. In this work, solution casting Nafion® membrane and Nafion117 membrane were used in the experiments.

2. Background and related work

The measurement of a polymer membrane conductivity for a DMFC application was typically determined by AC impedance techniques with two methods widely used, including four-point-probe method [1, 2] and two-electrode method [3, 4]. The four-point-probe method was reported to be more accurate in the measurement of the ionic resistance in a membrane because it is insensitive to the contact resistance between the surface of the measuring probes and membrane [5, 6]. Nevertheless, this method is typically used to measure the membrane conductivity in the longitudinal direction rather than the traverse direction [4] but in fuel cell applications, the conductivity in the transverse direction is more important than that in the longitudinal direction. Gardner C.L. and Anantaraman A.V. [7] have found a 70% decrease in conductivity for Nafion tested in the transverse rather than the longitudinal direction. Woo et al. [8] reported a typical schematic diagram of four-point-probe experimental setup. The two-electrode method is suitable for measuring the conductivity in the traverse direction. The system is much simpler than the four-point-probe method but it is more sensitive to the contact impedance of the electrodes [8].

3. Experimental

3.1 Measurement with two electrode method

In this work, the proton conductivity was characterized at different temperature. It was reported that the proton conductivity of a membrane usually increases with temperature [9] Therefore, the electrolyte container was surrounded by a water jacket ensuring a constant temperature during the measurement. The water jacket was connected to a temperature-controlled water bath with a pump used for water circulation was employed. The measurement apparatus is shown in Figure 1.

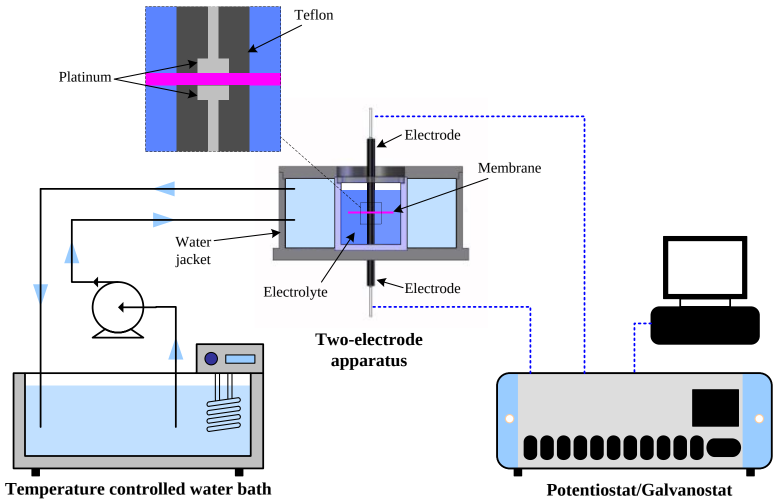

Figure 1 Schematic diagram of the two-electrode apparatus

As shown in Figure 1, two electrodes on opposite sides of the membrane hold a membrane sample in an electrolyte container. The electrodes used were platinum electrode with the diameter of 2 mm and the surfaces of both electrodes were polished by using 0.05µm alumina (Buehler, USA). By using this method, it was reported that the voltage applied to the cell had no effect on the measured resistance of the membrane [10]. Therefore, in this work the measurements were made with a voltage of 5 mV in the frequency range from 100 Hz to 1 MHz.

Before the measurement, the fabricated membrane specimens and Nafion117 were treated by boiling in 1 M of H_2O_2 and 1 M of H_2SO_4 solution and finally in deionised water. The membranes then were kept in deionised water under room temperature until their use. Prior to the test, the membranes were immersed in 1 M H_2SO_4 solution for at least 24 hours and during the measurement, the membranes were fully immersed in 1 M H_2SO_4.

3.2 Measurement in DMFC operation

This measuring method shares the same concept as the previous one but the platinum electrodes and membrane are replaced by an MEA in a DMFC. The advantage of this method is that the measurement can be done under an actual DMFC operation [11, 12]. By using this method, the overall ohmic resistance can be measured including the resistance of the membrane and of the ionomer in the electrodes and the electronic resistance. In this experiment, the assumption of the measurement is that the electronic resistance is negligible as it is reported that the main resistance in an MEA is in the membrane [13, 14].

The experimental setup of this experiment is schematically shown in Figure 2. The DMFC was directly connected to the galvanostat. The measurement was carried out at the open circuit voltage (OCV). The flow rate of 1 M methanol solution and air were 5 ml/min and 1000 ml/min respectively. The anode and cathode employed 1 mg Pt/cm^2.

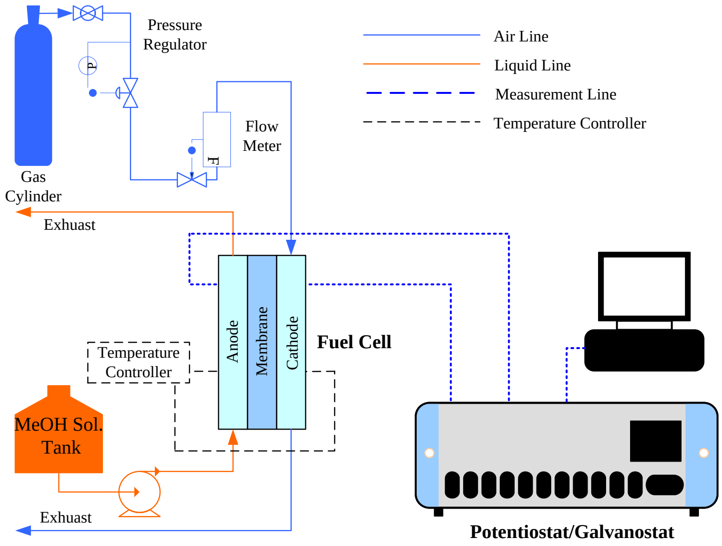

Figure 2 Experimental setup for the measurement of MEA resistance in a DMFC operation

4. Results and Discussion

4.1 Measurement with two electrode method

The results of proton conductivity measured by two electrode method are shown in Figure 3. The membrane with the higher proton conductivity is recast Nafion membrane. The conductivity of recast Nafion membrane at 30 °C and 70 °C are around 0.12 and 0.16 S/cm respectively. The Nafion117 membranes gave conductivity at 30 °C and 60 °C of 0.15 and 0.19 S/cm respectively.

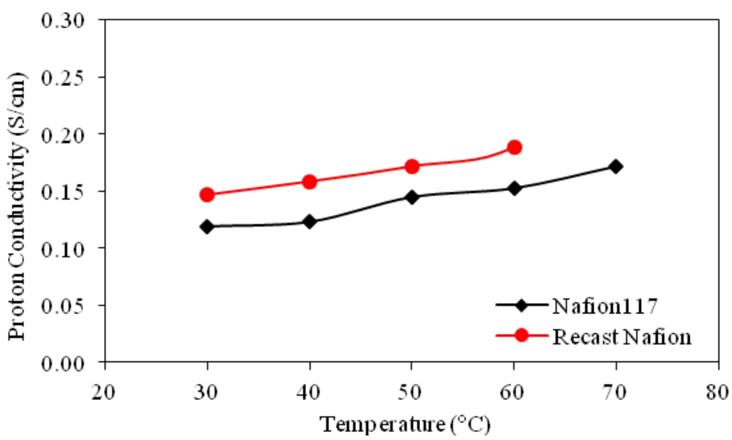

Figure 3 Proton conductivity of the membranes measured by two electrode method

4.2 Measurement in DMFC operation

The results of proton conductivity measured in DMFC operation are shown in Figure 4. The proton conductivity of the membranes increases with the temperature. The conductivity of Nafion117 membranes at 30 °C and 70 °C are around 0.045 and 0.06 S/cm respectively. The recast Nafion membrane gave conductivity at 30 °C and 70 °C of 0.038 and 0.05 S/cm respectively. The proton conductivity in Figure 4 is in contrast with that from the previous experiment in Figure 3 in which the conductivity of the recast Nafion membranes was measured in acid environment was higher conductivity.

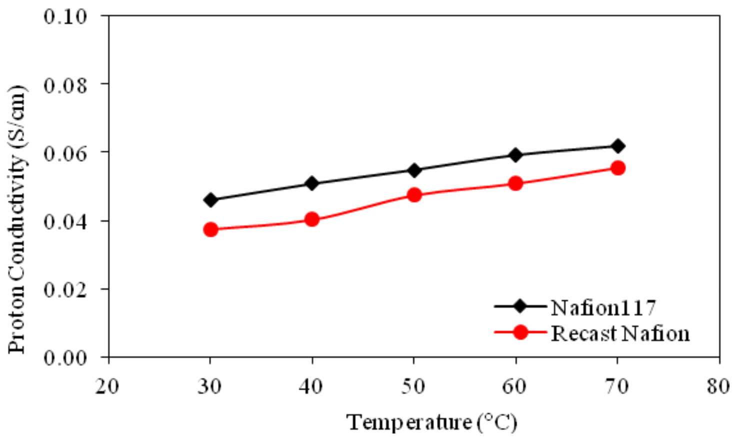

Figure 4 Proton conductivity of the membranes measured under DMFC operation

When comparing the results from an actual DMFC operation with 1 M to that from the H_2SO_4 solution, it shows that the acid solution containing H+ may have significant effect on the conductivity of the composite membrane. Hence, when the membranes were measured in H_2SO_4 solution, proton conductivity from both membranes was higher than that in a DMFC. Furthermore, recasting may also affect the conductivity of resulting membrane as can be seen that recast Nafion membrane gave higher conductivity in the measurement under H_2SO_4 solution but lower in DMFC operation.

5. Conclusions

From this study, it shows that the two techniques gave similar results of proton conductivity where conductivity of membrane increases with the increase temperature and it is in a good agreement reported in literatures. However, the measurement of conductivity under acidic environment gave higher conductivity than that from DMFC operation.

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