

Some Membrane Parameters Affecting the PEM Fuel Cell Performance

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Abstract

The effect of proton conductivity of a series of extruded Nafion membranes on the PEM fuel cell performance has been studied. In order to improve the proton conductivity of the polymer electrolyte membranes (Nafion), two basic parameters has been taken into account, the membrane thickness and the membrane equivalent weight (EW). The results showed that, the Nafion 1035 membrane can remain hydrated for longer than the Nafion 1135, or Nafion 112. In addition, a higher performance and longer life membrane electrode assembly can be manufactured using Nafion 1035 membrane as a solid electrolyte.

Keywords: PEM fuel cells, scanning electron microscopy, membrane electrode assemblies

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) 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 power density, and acceptable levels of miniaturization. The PEM is the vital component of a PEMFC, which makes it possible to attain high power densities. It serves as a physical barrier between the anode and cathode gases and also as the electrolyte (hence it's known as solid polymer electrolyte). A good membrane material for a PEMFC should have a high ionic conductivity, good chemical and mechanical stability, small water permeability, and low cost. In addition it should be electronically insulating and not permeable for H₂ and O₂ gases [1-4]. Gottesfield, et al. [5], suggest that perfluorosulfonic acid (PFSA) is the most commonly used membrane for PEM fuel cells. The PFSA membranes consists of poly-tetrafluoroethylene (PTFE)-like backbone, connected with ion clusters consisting of the sulfonic acid group (-SO₃H) via side chains of -O-CF₂-CF₂-O-CF₂-CF₂-. The PTFE backbone is hydrophobic and thus tends to minimize its interaction with water. The sulfonate head, however, is hydrophilic and thus has a strong affinity for water [6]. It is generally agreed that the hydrated membrane forms a bi-phase system will be formed, one phase containing the polymer matrix, and the other made up of water and the dissociated ions. These ions become mobile by bonding to the water molecules and moving between the sulfonic acid sites [6-8]. Nafion is a commercially available perfluorosulfonic cation membrane developed by E.I. DuPont de Nemours & Co. Inc. It is commonly used as the electrolyte in solid polymer electrolyte fuel cells. The structure of Nafion is shown in figure 1. The values of x and y can be varied to create materials with

different Equivalent Weights (EW). The equivalent weight is defined as the weight of dry polymer in grams containing one mole of exchange sites. The desired equivalent weight is achieved by varying the ratio of vinyl ether monomer to tetrafluoroethylene (TFE). 1100 EW is most commonly used though EWs of 900-1400 are available [9]. The two common strategies to improve the conductivity of the membrane are to raise the specific conductivity and to reduce the thickness. There is, however, a practical limit on the thickness since, much below 25 μm, mixing of the hydrogen and air (or oxygen) reactant gasses due to crossover through the ion-exchange material is too high for pure Nafion membranes and there is a loss of efficiency. Reducing the membrane thickness also increases the risks with respect to mechanical properties such as strength, raising concerns regarding the durability and ease of handling of the membranes. Many groups have previously studied the conductivity of Nafion membranes, predominantly using ac impedance spectroscopy [10-24] and dc techniques [15,25-27] Only one group appears to have considered both techniques in one paper.[15] A few groups have looked at the performance of the membrane in situ in the PEMFC using ac impedance[28] and a current pulse technique.[26] A variety of environments has been employed including 1 M H₂SO₄ ,[15,19,25,26] water, [11-14,15,16,23] water vapor,[11-14,17,20-22] and humidified gases [18,19] at temperatures from 20°C to 95°C. All the results of the above groups were summarized by Perez et. al., [17]. While reducing the membrane thickness is a common strategy to improve the performance of PEMFCs, a few papers have considered the proton conductivity of Nafion membranes of varying thickness. [15-18] Kolde et al. [15] found (using ac impedance) that for Nafion 117 (200 μm) and Nafion 112 (60 μm) the proton conductivity of the membranes immersed in water was

0.100 S cm⁻¹, this value being independent of the membrane thickness. This trend was also found by Nouel and Fedkiw, [17] but this time in air at 100% RH and 65°C. Again using ac impedance, conductivities of 0.140 and 0.144 S cm⁻¹ were reported for Nafion 117 (210 μm) and Nafion 112 (52 μm). Considering the experimental accuracy, this again reflects the independence of the conductivity on the membrane thickness as expected for materials that show ohmic behavior. This study has focused on the application of the Nafion range of cation-exchange membranes in proton exchange membrane fuel cells (PEMFCs).

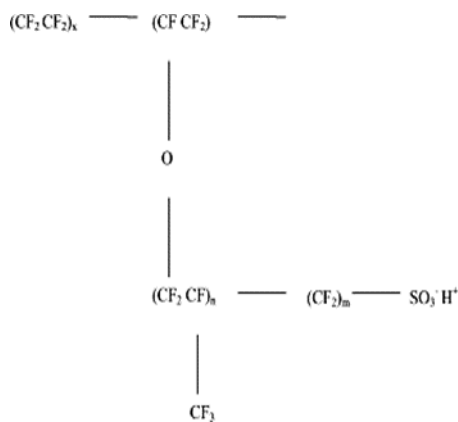


Figure 1 Structure of Nafion [31]

2. Experimental

Membrane Pre-treatment

Before being used in the membrane electrode assembly (MEA), samples of 5 cm diameter were cut from Nafion membranes type 112, 1135, and 1035 (Sigma-Aldrich UK,) and washed in various solutions to remove trace organic and inorganic contaminants and to change their form. The pre-treatment procedure involved boiling the polymer electrolyte membrane in 3 wt. % aqueous H₂O₂ solutions for 1 h at 85-90 °C, followed by boiling for 1 h in deionized water at 85-90 °C, and subsequently boiling for a further 1 h in a fresh sample of deionized water. The membrane was then boiled for 1 h in 0.5 M H₂SO₄ to get a fully H⁺-form exchanged membrane. After that, the membrane was boiled for 15 min. in pure water at temperature 85-90 °C to remove the remaining H₂SO₄ on the surface of the membrane, followed by storing in fresh deionized water until use

Membrane Thickness Measurements

Both the dry and the hydrated membrane thickness were measured at 20 random points over their surface to ±1 μm using a digital micrometer (Mitutoyo, Digimatic micrometer). Care was taken to ensure that the

micrometer jaws did not compress the membrane during thickness measurements. The membrane thickness inside the MEA was measured using the scanning electron microscope (SEM). Samples of dimensions 20 x 15 mm were cut from the middle of the MEA. Each section was placed in a fan-folded section of paper and the unit placed edge upright in a 25.4 mm diam nylon mold with Epoxy resin was poured into the mold to cover the upper edge of the section. The resin was allowed to dry at 60 °C for 48 h. The sample was removed from the mold and the two faces ground flat with 600 and then 1200 grit silicon carbide (SiC) paper. The sample edges were then polished using 6 and then 1 μm diamond pastes lubricated with an alcohol-based polishing fluid. The samples were then washed with distilled water to remove any traces of the polishing fluid. Finally, a carbon film (of approximately 20 nm thickness) was applied to a dried, polished face of the sample using a vacuum evaporation chamber. The fluorine line scan (F line scan) was principally employed to determine the membrane thickness using a Philips XL30 scanning electron microscope equipped with a thermal field emission gun (FEG- SEM) under the control of standard Philips data acquisition software. Typical operating conditions involved use of a 20 kV accelerating voltage. The scanning was repeated many times for different regions then the average thickness was taken as the membrane thickness.

MEA and Fuel Cell Tests

All of the Membrane Electrode Assembly (MEA) electrodes were prepared in-house by the decals process [22, 23], with some modifications [24]. The catalyst ink was prepared by using 30 % Pt supported on carbon catalyst (Sigma-Aldrich), and Nafion 20 wt % solution m(EW 1000, supplied by Sigma-Aldrich), diluted to 10 wt % in (25 % water, 37.5 % ethanol, and 37.5 % 1-propanol).the details of electrode preparation can be seen elsewhere [26]. PEM fuel cell was assembled by placing the MEA in a single cell test fixture (Electrochem Inc., USA) and connected to fuel cell test station (Nara Cell Tech Corp., Korea) provided with gas humidifier, mass flow controller, temperature indicator-controller etc. The current–voltage (I–V) characteristics of the cell was evaluated, using hydrogen and oxygen reactants at 1 atm, at 80°C using HPSCS1 high power potentiostat/galvanostat along with WBCS3000 battery cyclers system (WonA Tech., Korea).

3. Results

Membrane Thickness Measurements

Fresh circular samples of 5 cm diameter were cut from Nafion membranes type 112, 1135, and 1035, for use in membranes thickness measurements. The membrane thickness was measured before they were pre-treated and

the results are presented in Table 1. The membranes were then treated by boiling in H_2O_2 , H_2SO_4 , and deionized water, as described in section 2.1. The hydrated membranes thicknesses were measured, with the results presented in Table 1. The results show that the Nafion membranes swelled in the X-Y plane and in the thickness. The membrane thickness was increased by 15 to 20 % after the hydration. When the membranes were dried again for 48 h in an oven at 60 °C, the thickness measurement results, which are presented in Table 1, showed good agreement with the dried membrane thicknesses before the membrane treatments. The membrane thickness measurements inside the MEA were carried out following hot pressing of the membrane between two blank Teflon decals. A Nafion membrane was placed between two blank Teflon decals and pressed at 140 °C for 5 min; the thickness was then measured (Table 1). The results showed that the membranes are thinned by 16 to 20 % of their original thickness. Thus, when electrodes are assembled by hot pressing, the membrane thickness is decreased. When the membranes were rehydrated the membrane thickness was not significantly changed again. In the case of measurements using the SEM, a fluorine elemental line scan (SEM-EDX) scan was principally employed to determine the membranes thicknesses. The results are presented in Figure 2, 3 and 4, for the membranes of 1035, 1135 and 112, respectively. The fluorine line scan measurements were repeated 15 times for each sample and the average values are presented in Table 1. The results for the hot pressed membranes reflect some irreversible shrinkage of the ion cluster during the hot pressing. The results are in good agreement with the values reported by Slade et al. [31]. Therefore it is reasonable to consider that the membrane is well hydrated in the MEA although the hot pressing has lowered the water content a little, and the membrane thickness is considered the SEM measured thickness.

Membrane Thickness Effects

The effect of the Nafion membrane thickness on the optimum Nafion requirement to achieve a high MEA performance was investigated by preparing electrodes with different Nafion ionomer loadings ranging from 20 to 32.5 wt % and 5.0 mg/cm² catalyst loading [34]. These electrodes were assembled with Nafion 1135 and 112 membranes. Since these two membranes have the same EW. As shown from the results of Figure 4, the best performance is obtained for the MEA that use Nafion membranes type 112, and a Nafion loading of 25 wt %, as in the case of MEA with Nafion membranes type 1135. However, the current density monitored by the 1135 membrane was slightly higher than that monitored by 112 membranes. Thus, the optimum content of Nafion ionomer in the fuel cell electrode does not change with the thickness of the used membrane and

the higher current density obtained with the 1135 membrane may be attributed to the higher protonic conductivity of the 1135 membrane than that of the 112 membrane.

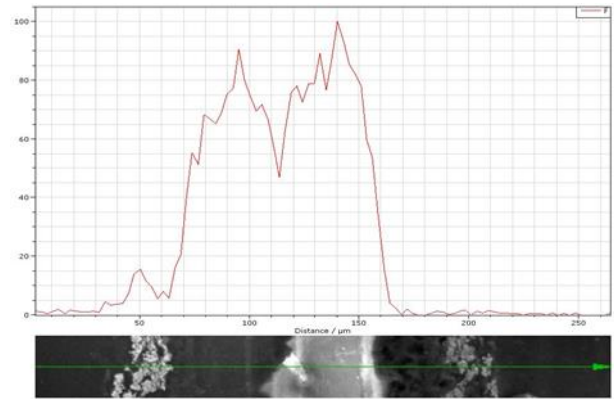


Figure 2 Profile of elemental fluorine line scan for MEA using Nafion 1035 as a membrane

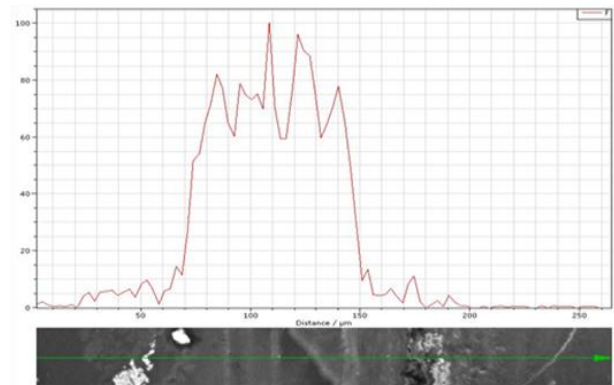


Figure 3 Profile of elemental fluorine line scan for MEA using Nafion 1135 as a membrane

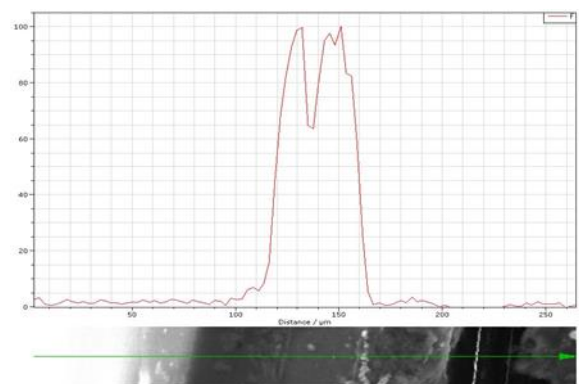
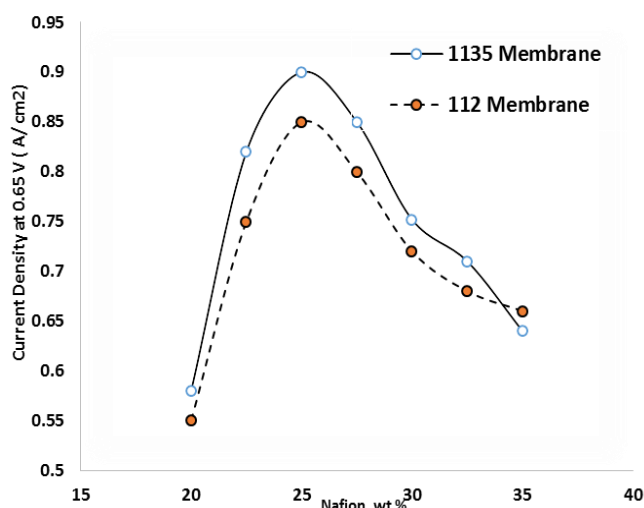


Figure 4 Profile of elemental fluorine line scan for MEA using Nafion 112 as a membrane

Membrane EW Effects

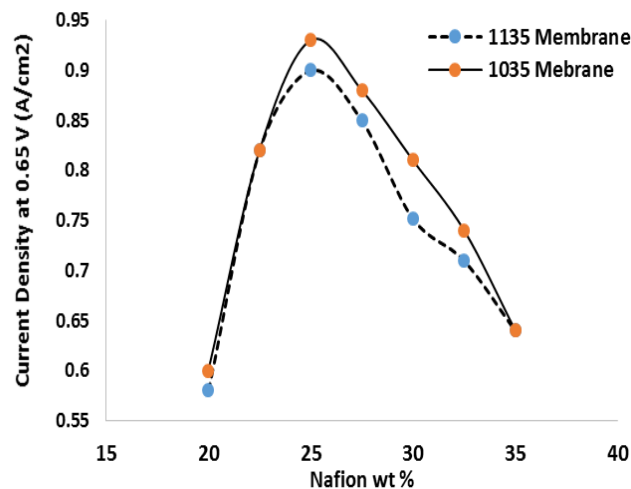
Electrodes with the same specifications as used above were used to study the effect of the Nafion membrane EW on the optimum Nafion requirement for high MEA performance. The electrodes were assembled with 1035 Nafion membrane and the MEA performance was compared with the performance of MEA assembled with 1135 membranes. Since these two membranes have the same thickness. From the results (Figure.5), it can be seen that, the best performance is obtained at 25 wt % Nafion loading, for electrodes with 5.0 mg/cm^2 catalyst loading, as in the case of Nafion 1035 and 1135 membranes.



Figure, 5 Effect of Nafion loading on the MEA performance using Nafion 1135 and Nafion 112 as membranes

Thus, the optimum Nafion ionomer percentage requirement does not change with the equivalent weight of the membrane used. The effects of the membrane thickness and EW on the MEA performance were studied by assembling electrodes with 5.0 mg/cm^2 catalyst loading and 25 wt % Nafion ionomer loading with Nafion 1035, Nafion 1135, and Nafion 112 membranes at 80°C temperature [34]. The results showed that there is no big difference in the MEA performance. This little difference could be attributed to the electrode parameters such as porosity, conductivity, etc. Moreover, the slightly better performance was achieved using 1035 Nafion membrane. These results clearly show a decrease in the membrane conductivity as the membrane thickness is reduced. Other factors such as the electrode structure, and the electrode parameters should be taken into account. In addition, the Nafion 1035 membrane can remain hydrated for longer than the Nafion 1135, or Nafion 112 membranes because its EW

is (1000) lower than the Nafion EW of Nafion 1135 (1100), and Nafion 112 (1100). Since the protonic conductivity of Nafion membranes is inversely proportional to their EW. Therefore, a higher performance and longer life MEA can be manufactured using Nafion 1035 membrane as a solid electrolyte.



Figure, 6 Effect of Nafion loading on the MEA performance using Nafion 1135 and Nafion 1035 as membranes

4. Conclusion

The proton conductivity of the membrane is particularly important since it plays an important role in controlling the MEA performance. High protonic conductivity allows high proton transfer from the anodic reaction zone to the cathode where the oxygen reduction reaction takes place. Two basic parameters were studied to improve the conductivity of the membranes, the membrane thickness and the membrane equivalent weight (EW). The results showed that the performance of the MEA containing Nafion 112 was lower than that of the MEA that assembled with Nafion 1135. Moreover, the best performance was achieved using 1035 Nafion membrane. It is clear that the ionic conductivity of the membrane is directly proportional to membrane thickness and inversely proportional to the membrane EW when fully hydrated membranes are used. Therefore, a higher performance and longer life MEA can be manufactured using Nafion 1035 membrane as a solid electrolyte. Finally, further electrochemical characterization of the membranes can be studied using other electrochemical techniques such as cyclic voltammetry, and the electrochemical impedance spectroscopy.

Table 1 Membrane thickness measurements

Nafion Membrane Type (μm)	Thickness as Supplied (μm)	Measured Thickness (μm)	Hydrated Thickness (μm)	Dried Membrane Thickness (μm)	Teflon Pressed Thickness (μm)	SEM Membrane Thickness (μm)
1035	89	89 ± 2	105 ± 3	91 ± 1	59 ± 2	85 ± 3
1135	89	90 ± 1	108 ± 2	91 ± 1	60 ± 3	76 ± 3
112	51	50 ± 1	59 ± 2	51 ± 1	41 ± 2	41 ± 2

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