The Effect of Nafion Ionomer Equivalent Weight (EW) on Polymer Electrolyte Membrane Fuel Cell Catalyst Layer Performance

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Abstract

Nafion ionomers with different Equivalent Weight (EW) 1000, and 1100 were incorporated with 4 mg/cm^2 commercial Palladium supported carbonof a 30% Pd/C (ETEK) catalyst, in the Polymer Electrolyte Membrane(PEM) fuel cell catalyst layers and their effects on the catalyst layer optimization and performance were evaluated by measuring the PEM fuel cell *i–V* characteristics. The results showed that, for 4.0 ± 0.1 mg/cm^2 of 30 % Pd/C loading, the optimum value Nafion ionomer percentage in the catalyst layer is 33 wt.% and this value is not change with the Nafion ionomer equivalent weight. Furthermore, it is possible to get high performance in PEM fuel cell under higher temperature (85°C) by employing the ionomers with 1000 EW.

Key words: PEM fuel cells, catalyst layer Performance, Renewable Energy, Nafion Equivalent Weight, Polarization Curve**.**

1. Introduction

Catalyst layer (CL) is one the key components for achieving a high performance with reducing costs of a polymer electrolyte membrane (PEM) fuel cell. The structure and elemental distribution of the composition in the catalyst layer determine a fuel cell efficiency, precious catalyst loading and a fuel cell durability [1-9]. The catalyst layer is a heterogeneous porous composite structure of carbon aggregations (electronically conductive), ionomer (transporting protons), catalytic nanoparticles to promote the electrochemical anodic hydrogen oxidation and/or the cathodic oxygen reduction. The Nafion ionomer incorporated in the catalyst layers acts both as a binder and a proton conductor and it should be moisturized properly to maintain its proton conductivity. Therefore, the membrane electrode assembly (MEA) hydration is a necessary step to maintain the protonic conductivity between the catalyst layer and the electrolyte membrane due to the presence of Nafion ionomer in their composition. The water uptake capability of the ionomer material is dependent on its equivalent weight and it could therefore influence the catalyst layer performance. The equivalent weight is defined as the weight of dry polymer in grams containing one mole of exchange sites [10-12]. It was reported that the ionic conductivity and water uptake capacity of the recast membrane with EW 1000 were 0.11 S/cm and 45 %, respectively, the values being about 1.1 and 1.3 times higher than those of the membrane with EW 1100 [13,14]. The better electrochemical properties of the recast membrane with EW 1000 are due to the larger population of sulfonic acid groups (about 1.1 times) in the ionomer than that of the membrane with EW 1100. The main objective of the present study is to evaluate the impact of the equivalent weight (EW) of Nafion ionomer on the performance of catalyst layers that include in PEM fuel cells using the *i*-V polarization curve under varies temperatures.

2. Experimental

Membrane Pre-treatment

Before being used in the membrane electrode assembly (MEA), the polymer electrolyte membranes made of Nafion 1035 (Sigma-Aldrich UK, 89 µm thickness, and 1000 EW) with a 3 cm diameter, were 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 H_2O_2 solutions for 1 h at 85-90℃, followed by boiling for 1 h in deionised water at 85-90℃, and subsequently boiling for a further 1 h in a fresh sample of deionised water. The membrane was then boiled for 1 h in 0.5 M H_2SO_4 to get a fully H^+-form exchanged membrane. After that, the membrane was boiled for 15 min. in pure water at temperature 85-90℃ to remove the remaining H_2SO_4 on the surface of the membrane, followed by storing in fresh deionised water until use.

Catalyst Layers Preparation and Membrane Electrode Assembly (MEA)

Catalyst inks were prepared by mixing 4.0 ± 0.1 mg/cm^2 of Palladium supported carbon (30% Pd/C, ETEK) with 5% Nafion_ solution (EW 1000, Solution Technologies, Inc., PA), and glycerol (Fisher Scientific, NJ). Different Nafion amount was used according to the calculation. The inks were ultrasonicated for 30mins and stirred vigorously overnight to achieve a uniform suspension. The formed catalyst ink was brush painted onto a 50 cm^2 Teflon discs. After painting the decals were left into dry air at room temperature for 30 min., and then weighed. The process of painting and drying was repeated until the desired catalyst loading was reached. The membraneelectrode assembly (MEA) was prepared by placing each pairs (cathode and anode) catalyst layers at both sides of the pre-treated Nafion 1035 membrane, followed by hot-pressing at 140℃ and

200 atm for 2 min. The formed MEA’s were then hydrated by boiling them in 0.5 M H_2SO_4 for 1 h, followed by boiling in pure deionized water for 10 min., with excess water subsequently being removed. When the catalyst layer is poorly bonded to the SPE, the catalyst particles detached during the boiling. Finally, the MEA was dried on a heated vacuum table at room temperature for 120 minutes.

Fuel cell Assembly and performance measurements.

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 85 °C using HPCS1 high power potentiostat/ galvanostat along with WBCS3000 battery cycler system (WonA Tech., Korea).

3. Results and Discussion

Fuel cell catalyst layers with a palladium loading of 4.0 ± 0.1 mg/cm^2 of 30% Pd/C were prepared with different Nafion ionomer (EW 1000) weight percentage ranging from 20 to 40 wt.% and assembled with Nafion 1035 membrane to form membrane electrode assembly (MEA). The cells performance was evaluated at 85 °C, with humidified hydrogen-oxygen reactants, at 1 atm pressure and the results are presented in Figure 1. It can be seen that; the catalyst layer performance is very low at 20% Nafion ionomer content. The performance increases as the Nafion ionomer percentage increased from 20 to 33%. Further increase to 35% Nafion content results in decrease in performance.

A new set of PEM fuel cell catalyst layers with the same palladium loadings of 4.0 ± 0.1 mg/cm^2Pd/C and different Nafion ionomer (EW 1100) weight percentage ranging from 20 to 40 wt.% were prepared and assembled with Nafion 1035 membrane to form membrane electrode assembly (MEA). The performance of these catalyst layers, were tested with humidified hydrogen-oxygen reactants at 85 °C, and 1 atm pressureto find the optimum Nafion ionomer content. It was found that the best catalyst layer performance is obtained at 33 wt.%Nafion ionomer content in the catalyst layer as shown in figure 2. Thus, optimum Nafion ionomer percentage which is needed in the PEM fuel cell catalyst layer to get the maximum cell performance is not change with the Nafion ionomer EW.

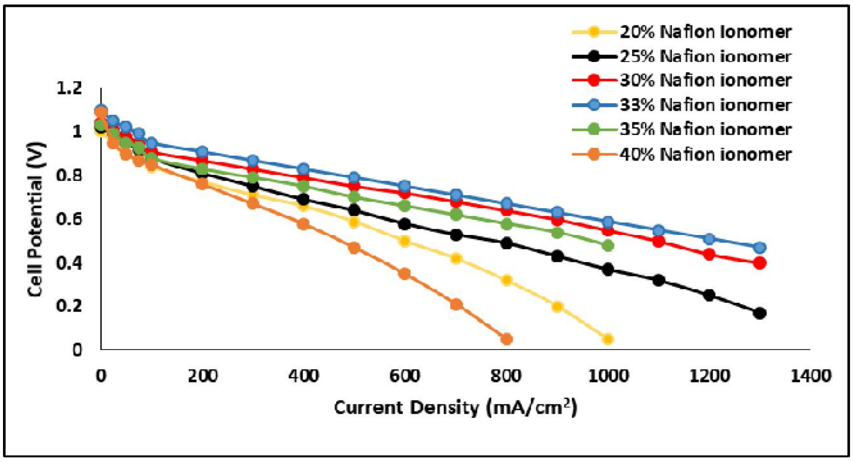

Figure 1: the current-voltage (*i*-V) characteristics of the catalyst layer with Pd/C of 4.0 ± 0.1 mg/cm^{2}and different Nafion ionomer (EW1000) contents, ranging from 20 to 40 wt.%, with humidified hydrogen-oxygen reactants at 85 °C, temperature and, 1 atm pressure.

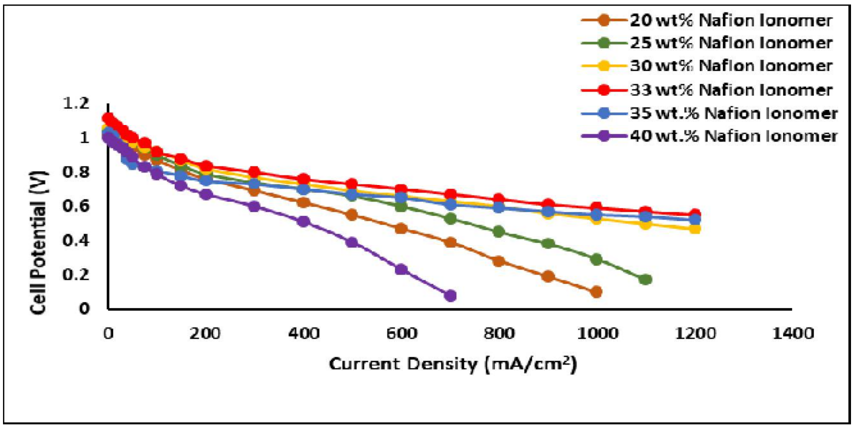

Figure 2: the current-voltage (*i*-V) characteristics of the catalyst layer with Pd/C of 4.0 ± 0.1 mg/cm^{2}and different Nafion ionomer (EW1100) contents, ranging from 20 to 40 wt.%, with humidified hydrogen-oxygen reactants at 85 °C, temperature and, 1 atm pressure.

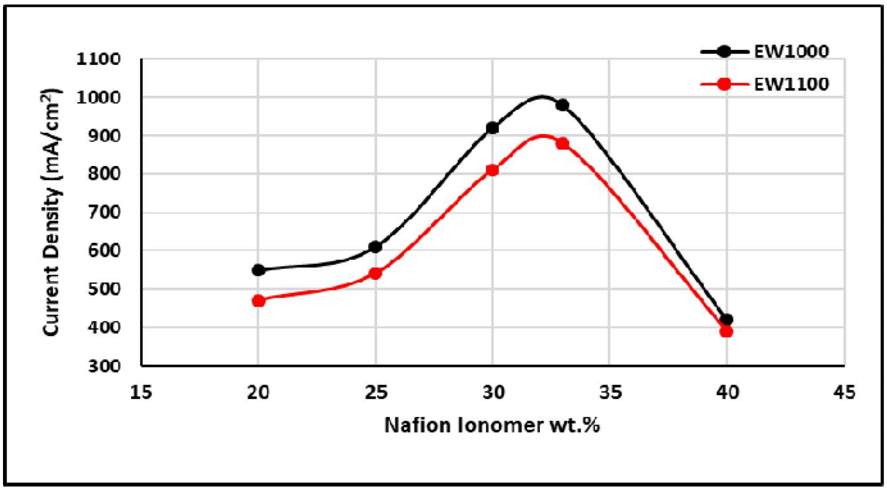

Figure 3, the effect of Nafion ionomer wt.% in the PEM fuel cell catalyst layer performance using Nafion ionomers of EW1000 and EW1100, at 95°C and 1 atm operating conditions.

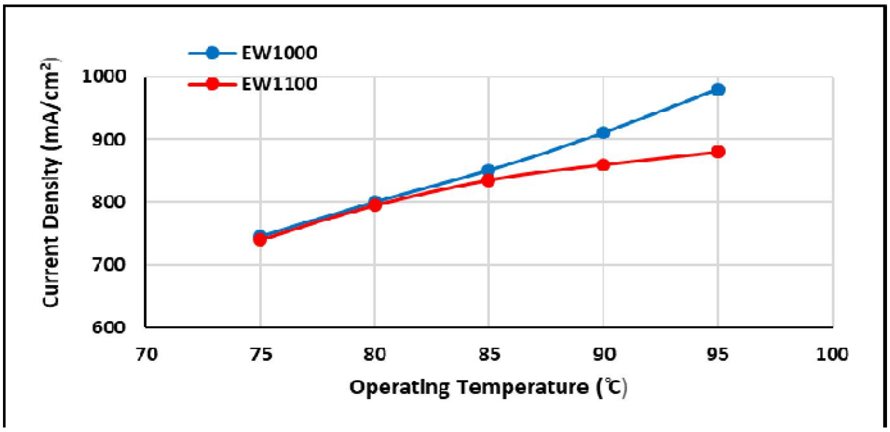

Figure 4: the effect of the cell operating temperature on the catalyst layers' performance with 4.0 ± 0.1 mg/cm2 30 % Pd/C and 33 wt.%of two different equivalent weight Nafion ionomers.

The same tests were carried out with humidified hydrogen-oxygen reactants at 95˚C and 1 atm. operating conditions, and the results are depicted in Figure 3. All the measurements were repeated at least four times at this temperature to confirm the reproducibility of the results. As can be seen in the figure, the optimum Nafion ionomer wt.% in the catalyst layer requirement does not change with the equivalent weight of Nafion ionomer used even at higher operating temperature. However, catalyst layers of EW1000 exhibit higher current density than that of EW1100. Figure 4. shows the effect of the cell operating temperature on the performance of the catalyst layers containing the same composition of 4.0 ± 0.1 mg/cm^2 30 % Pd/C and 33 wt.% of two different equivalent weight Nafion ionomers. The cells performance was evaluated at 1 atm pressure, with humidified hydrogen-oxygen reactants, and different temperatures ranging from 75 ˚C to 95 ˚C. The figure shows that at the temperatures below 85 ˚C, there was no appreciable difference in performance between two MEAs. However, at the temperatures 85 ˚C, the MEA with EW 1100 ionomer showed less performance than the MEA with EW1000. This behavior could be attributed to the ability and capability of the EW 1000 ionomer to capture and preserve moisture to maintain its proton conductivity under a sufficiently humidified condition [15]. This shows the effect of the lower EW ionomer (1000) which is more effective in preserving moisture and proton conductivity than the higher EW ionomer (1100).

4. Conclusions

The effects of equivalent weights of the ionomer involved in the catalyst layers on the PEM fuel cell performances have been investigated at different temperatures ranging from 75 ˚C to 95˚C and 1 atm operating conditions. Nafion ionomers with two different Equivalent Weight (EW) 1000, and 1100 were incorporated with 4.0 ± 0.1 mg/cm^2 of 30% Pd/C commercial Palladium supported carbon(ETEK) catalyst, in the Polymer Electrolyte Membrane(PEM) fuel cell catalyst layers and their effects on the catalyst layer optimization and performance were evaluated by measuring the PEM fuel cell *i–V* characteristics. The optimum value Nafion ionomer percentage in the catalyst layer requirement does not change with the Nafion ionomer equivalent weight. However, the effect EW1000 ionomer became more apparent as the cell operating temperature got far from 85˚C. This is because of the ability and capability of the EW 1000 ionomer to capture and preserve moisture to maintain its proton conductivity. In conclusion, it is possible to get high performance in PEM fuel cell under higher temperature (≈85˚C-95˚C) by employing the ionomers with EW1000.

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