

The Impact of Nafion Ionomer in Polymer Electrolyte Membrane (PEM) Fuel Cell Catalyst Layer Performance

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Abstract

Nafion ionomer content in the PEM fuel cell catalyst layer is the most important parameter in designing high performance PEM fuel cell. In this study, different catalyst layers were prepared by mixing numerous Nafion ionomer (EW 1000) weight percentage (wt.%) ranging from 20 to 40 wt.% with 3.2 ± 0.1 mg/cm² of palladium supported carbon ((30% Pd/C,) catalyst, and assembled with Nafion 1035 membrane to form membrane electrode assembly (MEA). The results showed that the best performance of the PEM fuel cell is obtained when 35 % of the Nafion ionomer is present in the catalyst layer. In addition, the microstructural study for the catalyst layers containing higher Nafion ionomer than 35 wt.% suggests that a very thin Nafion layer is produced on the outer surface of catalyst layer leads to blocking of the active sites of the palladium catalyst on the catalyst layer surface and decreased electrochemical reactions.

Key words: PEM fuel cells, catalyst layer, scanning electron microscopy, decal transfer method, optimum Nafion ionomer, renewable clean energy.

1. Introduction

With the growth of new energy economy, proton exchange membrane (PEM) fuel cell has great potential to be success as a clean and efficient electrochemical power sources for use in materials handling and transportation applications [1-4]. However, the lack of high-performance catalyst layer (CL) especially at cathode limits its applications [4]. The main components of the PEM fuel cell are a membrane electrode assembly (MEA) which is composed to the catalyst layers (CLs), and the proton exchange membrane (PEM), and gas diffusion media (GDM). The catalyst layer CL is a porous composite layer, consisting of the recast Nafion ionomer, and the nano-particle precious metal catalyst supported on micro-particle carbon. One of the key parameters in the manufacture of CLs is the content of Nafion_ ionomer. Incorporation of Nafion ionomer in the catalyst layer improves the performance of PEM fuel cells by increasing the three-phase boundary, so optimum Nafion content in the catalyst layer is important to achieve good performance [5]. An insufficient amount of Nafion ionomer in the catalyst layer results in poor contact of the membrane electrolyte with the catalyst and reduces the triple-phase boundary. Excessive quantities of Nafion ionomer also cause a decrease in the catalyst layer performance by blocking the active catalyst sites and reducing the gas permeability [6,7]. In this work, PEM fuel cell catalyst layers with different distribution and various weight percent's (wt.%) Nafion ionomer, and palladium supported carbon (30 % Pd/C) were prepared using the decals method [8], and examined for PEM fuel cell electrodes using The current-voltage(i -V) method in order to investigate the effect of Nafion ionomer on cell performance

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 $^\circ\text{C}$, followed by boiling for 1 h in deionised water at 85-90 $^\circ\text{C}$, 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 $^\circ\text{C}$ 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

Catalyst inks were prepared by mixing the carbon-supported catalyst (30% Pd/C, ETEK) with 5% Nafion_ solution (1000 EW, Solution Technologies, Inc., PA), and glycerol (Fisher Scientific, NJ). Different Nafion amount was used according to the calculation. The inks were ultrasonicated for 30 min. 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.

Membrane Electrode Assembly (MEA)

The membrane-electrode 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 °C and 200 atm. for 2 min. The formed MEA's were then hydrated by boiling them in 0.5 M H₂SO₄ 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 membrane, 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 cyler system (WonA Tech., Korea).

Scanning Electron Microscopy (SEM)

Samples of dimensions 12 x 12 mm were cut from the middle of the MEA and used for scanning electron microscopy (SEM) examinations. SEM analysis of surface and cross-sectional specimens was performed 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. Investigations were carried out in the secondary electron and backscattered electron modes. Typical operating conditions employed a 20 kV accelerating voltage. Prior to examination, the cross sectional samples were coated

with a carbon deposit (10-15 nm in thickness) to minimize problems associated with charging.

3. Results and Discussion

PEM fuel cell catalyst layers were prepared by mixing 3.2 ± 0.1 mg/cm^2 of 30% Pd/C 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 prepared catalyst layers' specifications are presented in table 1. All the measurements were repeated at least four times to confirm the reproducibility of the results and the polarization curves were taken after supplying dry gases to the anode and cathode of the cells at room temperature for 48h which had previously undergone a cell test at 1 atm. pressure, and 85 °C under fully humidified conditions.

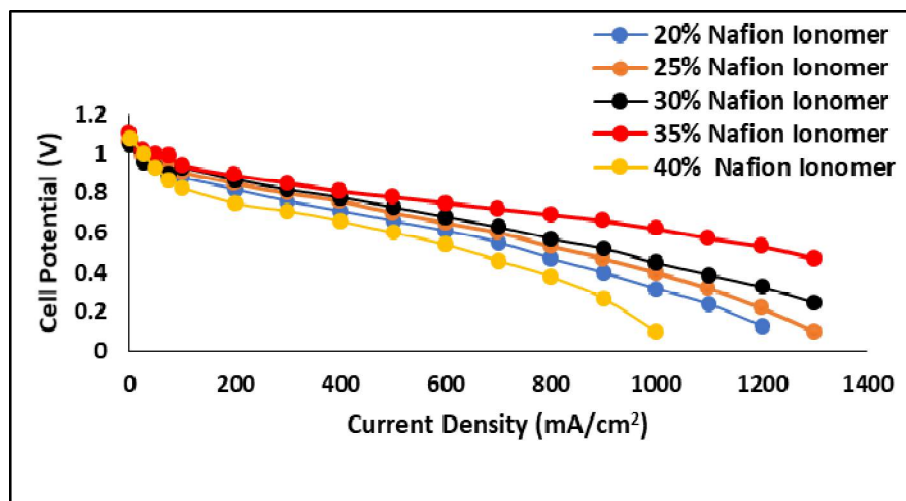


Figure 1: The current–voltage (i–V) characteristics of catalyst layers with catalyst loadings (30 % Pd/C) of 3.2 ± 0.1 mg/cm^2 catalyst loadings and various Nafion ionomer contents, at 85 °C, and 1 atm. pressure.

Figure 1, illustrates the current–voltage characteristics (i - V) of these catalyst layers. The catalyst layer performance is low when 20 wt.% of the Nafion ionomer is present in the catalyst layer. By increasing the Nafion ionomer amount from 20 wt.% to 35 wt.%, the catalyst layer performance improves. This result was expected since the increase in the amount of Nafion ionomer in the catalyst layer improves the proton conductivity of the catalyst layer [9-11]. The best performance of the PEM fuel cell is obtained when 35 % of the Nafion ionomer is present in the catalyst layer. However, a significant decrease in catalyst layer performance with further increase in the amount of Nafion ionomer (above 35 wt%) was observed. This behavior could be attributed to the high Nafion ionomer concentration in the catalyst layer, which then blocked the catalyst sites as an electronic insulator, reducing the electronic conductivity and gas permeability in the catalyst layer.

Further microstructural characterization studies of the catalyst layers (CL6) were carried out using SEM to gain more information about the impact of increase in the Nafion ionomer on the catalyst layer performance and the results are presented in figure 2, and figure 3. The SEM results suggest that during the catalyst layer preparation, the increase of Nafion ionomer concentration leads to a high dispersion of carbon aggregates in the catalyst ink. Nafion ionomer fills the gap between the carbon aggregates. Due to the geometry and the size of the carbon aggregates, large pores are formed when the catalyst layers are dried. In addition, a dense film, consisting of recast Nafion ionomer, forms on outer surface of the catalyst layer (arrow A in figure 2 and figure 3). The thickness of this film depends on the Nafion ionomer concentration in the catalyst layer. The Nafion film formation results in a decreased electronic conductivity between the catalyst layer and the gas diffusion layer, blocking of the palladium sites on the catalyst layer surface, and a decreased rate of the electrochemical reactions, which take place at the catalyst layer surface. Xie,*et. al*, [12]

proposed that when the catalyst ink is applied on the Teflon decal surface by the hand painting method, the polytetrafluoroethylene backbones (-CF-chains) of the Nafion ionomer in the ink layer adjacent to the decal surface are almost certainly more strongly attracted to the hydrophobic Teflon decal surface than the polar solvent system in which they are dissolved [12]. Because the majority of the Nafion ionomer backbone consists of -CF-chains, Nafion ionomer rod-like aggregates [13] in this ink layer are deposited onto the decal, forming a very thin layer of Nafion.

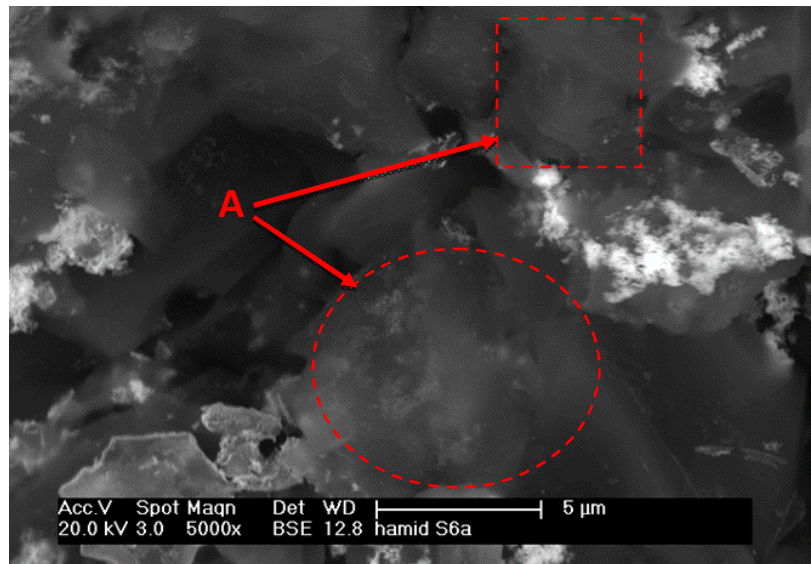


Figure 2: Backscattered electron surface image for the catalyst layer CL6 to explain the dense film formation process.

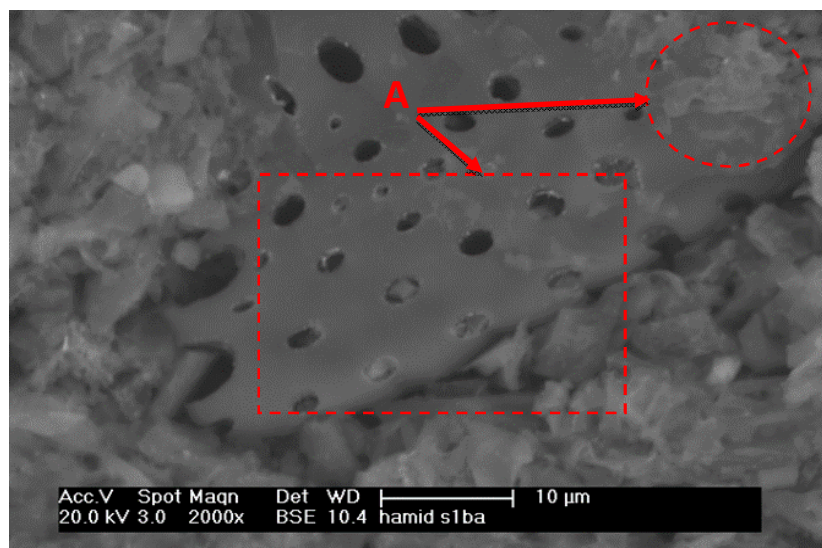


Figure 3: Backscattered electron surface image for the catalyst layer CL6 to explain the dense film and pores formation process.

As the rod-like aggregates are accumulated on the Teflon decal surface, the concentration of rod-like ionomer aggregates is reduced in the ink layer close to the Teflon decal surface and a concentration gradient of ionomer aggregates is produced. The concentration gradient of the Nafion ionomer enhances the diffusion of rod-like aggregates towards the Teflon decal surface as long as the ink is in the liquid state, resulting in Nafion ionomer segregation. When the catalyst layer is assembled with the membrane, to form the MEA, the inner layer becomes the catalyst layer outer surface. By applying this mechanism to the present system a clear picture of the impact of Nafion ionomer in the PEM fuel cell catalyst layer performance is gained. When the catalyst ink which contains higher Nafion ionomer (above 35 wt.%) is applied onto the Teflon decals, the rod-like Nafion ionomer aggregates are attracted by the strongly hydrophobic Teflon decal, diffuse to surface of the Teflon decal driven by the Nafion ionomer aggregate concentration gradient, accumulate on the decal

surface, and form a Nafion ionomer film on the outer surface of the PEM fuel cell catalyst layer. Because of the thickness of Nafion layer, it cannot be removed by boiling the MEA. Although the increase in the Nafion ionomer in the catalyst layer leads to an increase in the protonic conductivity between the catalyst layer and the membrane, it blocks the active sites of the palladium catalyst on the outer catalyst layer surface and electrochemical reactions are decreased. In addition, when the Nafion ionomer increases, a good dispersion of the carbon aggregates will be produced, and as a result the primary pores will be blocked or filled by the Nafion ionomer in the catalyst ink, due to the increase in the Nafion coverage on the carbon aggregates.

4. Conclusion

Optimum amount of Nafion ionomer in the catalyst layer is required for good PEM fuel cell performance. In the present study, catalyst layers were prepared by mixing $3.2 \pm 0.1 \text{ mg/cm}^2$ of 30 % Pd/C 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 PEM fuel cell performance was evaluated at 1 atm. pressure, and 85 °C. The results showed that the best performance of the PEM fuel cell is obtained when 35 % of the Nafion ionomer is present in the catalyst layer. However, a significant decrease in catalyst layer performance with further increase in the amount of Nafion ionomer (above 35 wt%) was observed. To gain more information about the performance of the catalyst layers that containing higher Nafion ionomer wt.% (above 35 wt.%) microstructural characterization studies of the catalyst layers (CL6) were carried out using SEM. The SEM analysis suggests that a very thin Nafion layer is produced on the outer surface of catalyst layer leads to blocking of the active sites of the palladium catalyst on the catalyst layer surface and decreased electrochemical reactions.

Table 1: Structural specifications of the catalyst layers with $3.2 \pm 0.1 \text{ mg/cm}^2$ of 30% Pd/C catalyst loadings and different Nafion ionomer (EW 1000) weight percentage ranging from 20 to 40 wt.%

Catalyst Layer Number	Catalyst Layer Weight (mg)	Nafion Ionomer Loading (wt.%)	Catalyst Layer Thickness (μm)	Catalyst Layer Composition Volume Fraction				
				C	Pd	Nafion	Pores	
CL1	Anode	12.8	20.0	20.0 ± 0.1	0.436	0.041	0.215	0.308
	Cathode	12.8	20.0	20.0 ± 0.1	0.436	0.041	0.215	0.308
CL2	Anode	13.2	25.0	20.5 ± 0.2	0.424	0.040	0.243	0.293
	Cathode	13.2	25.0	20.5 ± 0.2	0.424	0.040	0.243	0.293
CL3	Anode	13.7	30.0	21.1 ± 0.1	0.414	0.039	0.272	0.275
	Cathode	13.7	30.0	21.1 ± 0.1	0.414	0.039	0.272	0.275
CL4	Anode	14.2	33.0	21.7 ± 0.1	0.404	0.038	0.302	0.256
	Cathode	14.2	33.0	21.7 ± 0.1	0.404	0.038	0.302	0.256
CL5	Anode	14.7	35.0	22.2 ± 0.2	0.395	0.036	0.333	0.236
	Cathode	14.7	35.0	22.2 ± 0.2	0.395	0.036	0.333	0.236
CL6	Anode	15.0	40.0	22.7 ± 0.2	0.38	0.035	0.355	0.23
	Cathode	15.0	40.0	22.7 ± 0.2	0.38	0.035	0.355	0.23

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