한국신·재생에너지학회 2007년도 춘계학술대회논문집 pp.157~160

Experimental Investigation of the Effect of Composition on the Performance and Characteristics of PEM Fuel Cell Catalyst Layers

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Key words : PEM, PEMFC, Catalyst Layer, Polarization Curve, Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV)

Abstract : The catalyst layer of a proton exchange membrane (PEM) fuel cell is a mixture of polymer, carbon, and platinum. The characteristics of the catalyst layer play a critical role in determining the performance of the PEM fuel cell. This research investigates the role of catalyst layer composition using a Central Composite Design (CCD) experiment with two factors which are Nafion content and carbon loading while the platinum catalyst surface area is held constant. For each catalyst layer composition, polarization curves are measured to evaluate cell performance at common operating conditions, Electrochemical Impedance Spectroscopy (EIS), and Cyclic Voltammetry (CV) are then applied to investigate the cause of the observed variations in performance. The results show that both Nafion and carbon content significantly affect MEA performance. The ohmic resistance and active catalyst area of the cell do not correlate with catalyst layer composition, and observed variations in the cell resistance and active catalyst area produced changes in performance that were not significant relative to compositions of catalyst layers.

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PEM : proton exchange membrane
EIS : electrochemical impedance spectroscopy
CV : cyclic voltammetry
CCD : central composite design
RSM : response surface methodology

1. Introduction

A fuel cell converts reactants (hydrogen and oxygen) into water, and in the process produces electricity. Because reactants constantly flow into the cell, it is never exhausted like a battery. As long as reactants flow into the cell, electricity is produced. The Proton Exchange Membrane Fuel Cell (PEMFC) has received great attention because of its transportation applications and portable electronic power applications. PEMFCs are light, small, and exhibit good energy conversion efficiency and high power density at a relatively low operating temperature (Srinivasan, [1]).

The main goal of this research is to explore the effect of carbon and Nafion content on the performance and characteristics of the catalyst layer. To isolate the effects of these components, the platinum loading expressed as gross catalyst surface area is held constant. The main goal of this research is to explore the effect of carbon and Nafion content on the performance and characteristics of the catalyst layer. To isolate the effects of these components, the platinum loading expressed as gross catalyst surface area is held constant. A second goal of the research is to examine how catalyst layer characteristics such as physical characteristics are affected by composition.

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2. Experimental Procedures

2.1 Design of Experiment

A Central Composite Design (CCD) was chosen for the investigation of the carbon and Nafion contents. The CCD is one of the most common design tools for Response Surface Methodology (RSM) designs in statistical studies (Eriksson [2]). The following Table 2-1 shows the carbon loadings and the Nafion weight percent for fit into the CCD model.

Table 2-1. The Central Composite Design for the Carbon and Nafion contents

		Carbon Loadings L_c (mg/cm^2)				
		0.559	0.841	1.497	2.152	2.424
		Platinum Loadings L_{Pt} (mg/cm^2)				
		0.384	0.368	0.328	0.289	0.272
Nafion (%)	33			MEA8		
	30.7		MEA3		MEA4	
	25	MEA5		MEA9		MEA6
	19.3		MEA1		MEA2	
	17			MEA7		

2.2 Preparation of MEA Samples

The MEAs used in this experiment were constructed by means of the Wilson and Gottesfeld[3] techniques. Following Wilson and Gottesfeld, the catalyst inks were mixed the ink was painted onto Teflon coated decals and baked in an oven at 140 °C for 15-20 minutes, the decals were weighed and the process repeated to achieve the desired loading. Finally, decals were hot-pressed (at 70 atm for four minutes) onto a pre-treated Nafion membrane.

3. Experimental Results

3.1 Basis for Evaluation

To insure a fair comparison, all catalyst layers were subjected to the same conditions prior to testing and were tested at common conditions. After the MEAs were constructed, all of them were conditioned at least 24 hours or until a steady current density of 0.5 V was achieved. During the conditioning process, the cell conditions were maintained at the values presented in Table 3-1. These same conditions were maintained during the test procedure.

Table 3-1. Fuel cell operating conditions

Cell temperature	80 °C	
Reactant gas conditions	Anode	Cathode
Temperature	80 °C	80 °C
Pressure	200 kPa	200 kPa
Relative humidity	100 % RH	60 % RH
Mass flow rate	225 SCCM	550 SCCM

3.2 Evaluation of Polarization Curves

Polarization curves for all MEA samples are shown in Figure 3-1.

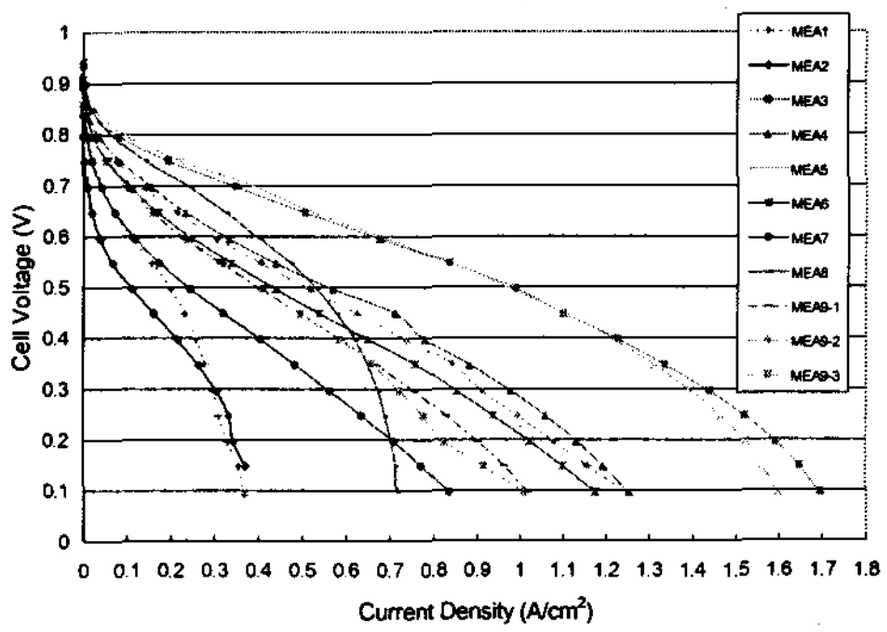

Figure 3-1. Effect of composition on cell performance

The best performing MEAs were MEA 3 and MEA 5. These MEAs exhibited low activation losses as demonstrated by the low slopes of polarization curves at low current density. These MEAs also had very little mass transport resistance, since the curve slowly and linearly declines as current density increases. For these MEAs, limiting current density values exceeded 1.5 A/cm^2. The worst performing MEAs were MEA 1 and MEA 2. These MEAs showed very poor performance with steep slope, in the activation region and limiting values for current density as low as 0.4 A/cm^2. The MEAs with low Nafion loadings (1, 2, and 7) were found to have the highest activation losses.

Overall, MEA 3 was the best MEA and contained 30.7 % Nafion and a carbon loading of 0.8406 mg/cm^2. This construction generated a maximum power density of 0.493 W/cm^2 and had a maximum current density of 1.59 A/cm^2 at 0.2V.

For this research, the repeatability of construction of the MEAs is very important factor because without repeatability, it is not possible to make a meaningful comparison of MEA performance. The repeatability reflects human error and test measurement error. In this research, three MEA samples were constructed with the same catalyst composition at the center point of the CCD model designated 9-1, 9-2, and 9-3. Comparison of the current density values at 0.5 V for these three MEA's indicates a repeatability of 8 %. This level of repeatability is sufficient for comparing MEA composition.

3.3 Effect of Carbon Loading and Nafion Content

Figures 3-2 shows the effect of composition on the performance of MEAs in this research. In this analysis performance is defined as current density at 0.5 V. MEAs constructed with medium-low carbon loadings performed best with 30.7 % Nafion in the catalyst layer. Performance for medium-low, medium, and medium-high carbon loadings all increased with Nafion

content, although at the higher Nafion loadings (33 %) the rate of increase diminished. This is consistent with the work of other researchers who found that medium carbon loading and 33 % Nafion loading were the best combinations in the catalyst layer.

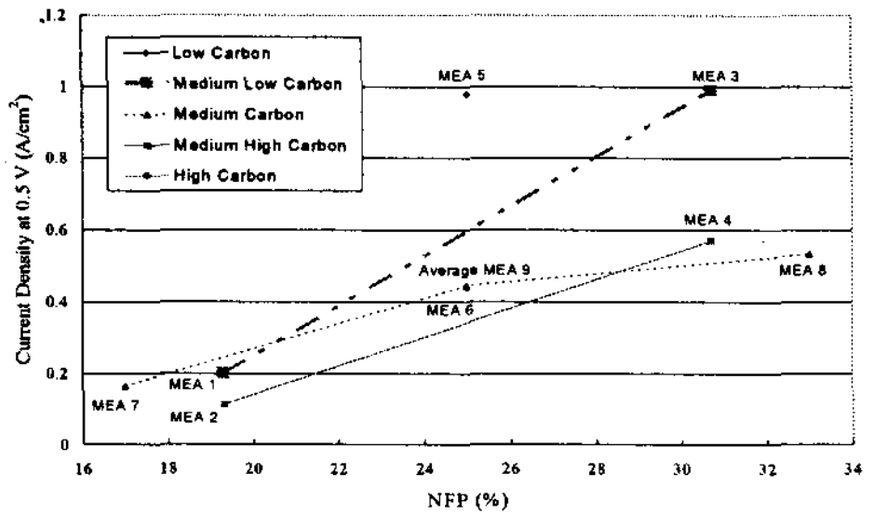

Figure 3-2. Effect of NFP on performance

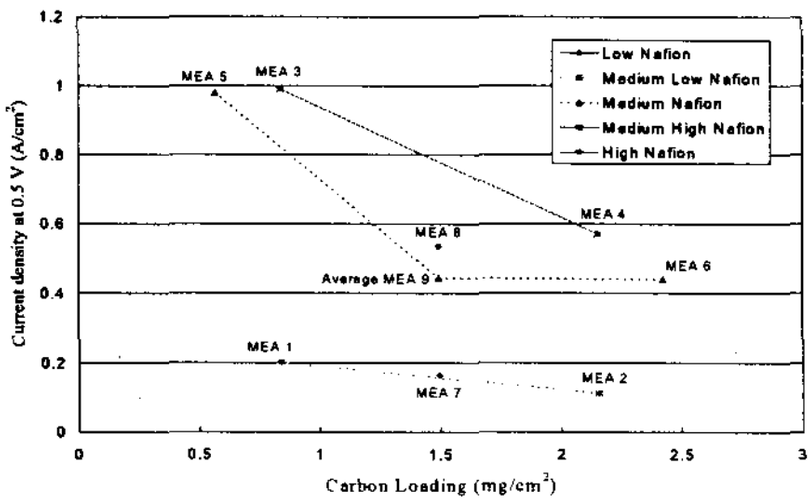

Figure 3-3. Effect of carbon loadings on performance

The results from Figures 3-3 show the effect of carbon loading in the catalyst layer. Carbon provides support for the platinum particles and provides electrical conductivity. On the other hand, too much carbon can reduce the catalyst layer porosity and inhibit reactant transport. For all Nafion loadings considered here, performance decreases with increasing carbon. A maximum in performance is shown at the lowest tested carbon loading, containing about 0.57 mg/cm^2

3.4 Response Surface

After completion of all performance tests, performance depended on two factors: carbon and Nafion loading. The MINITAB software was used to resolve the full fitted model equation. Equation 1 shows the fitted model from the analysis:

$$j = -1.62 + 0.17 \times N - 0.49 \times C \quad (1)$$
$$-0.0019 \times N^2 + 0.27 \times C^2 - 0.022 \times N \times C$$

where j is the current density at 0.5 V, N is the Nafion content, and C is carbon loading.

The plot for this equation is shown in Figure 3-4.

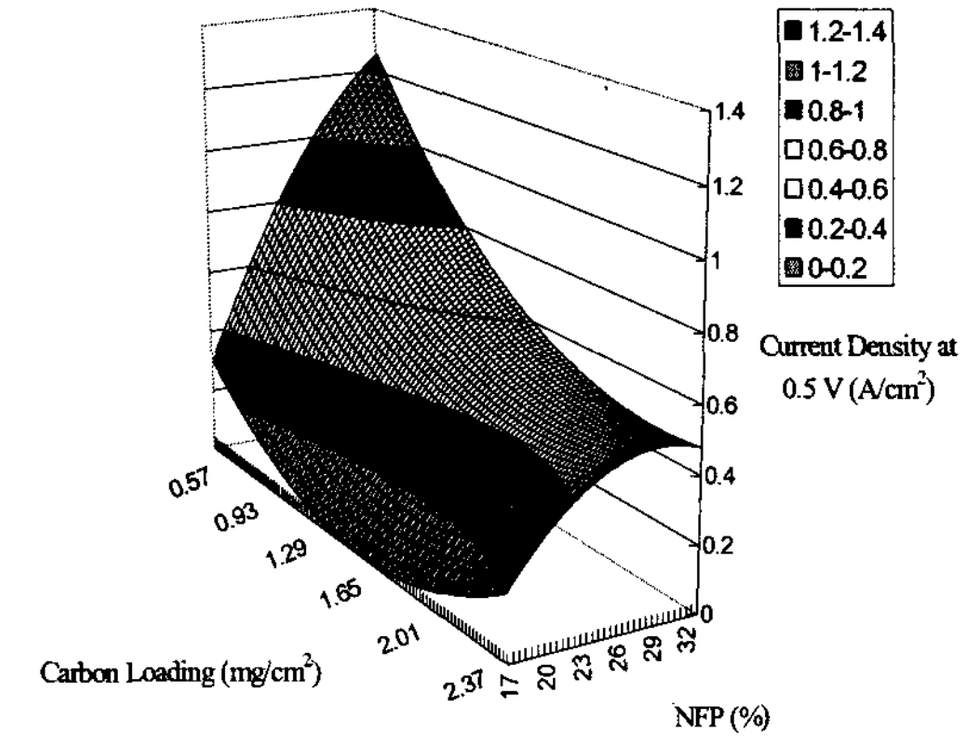

Figure 3-4. The performance plot for carbon and Nafion loading

3.5 Area Specific Resistance of Catalyst Layer

After completion of the performance tests, the MEAs were subjected to electrochemical impedance spectroscopy tests to determine their ohmic resistance. The current density of the cell was maintained at 0.1 A/cm^2 at which mass transport limitations were not significant. The high frequency resistance corresponds to the purely ohmic component of the cell resistance. The area specific resistance, ASR, in $\Omega \cdot cm^2$ was then determined by ohmic resistance times area.

The results show that there is no significant correlation between ASR and either NFP or carbon loading for the ranges considered here. This result suggests that the minimum values of NFP and carbon considered here are sufficient to insure that the ionic and electrical losses in the catalyst layer are small compared to losses in other cell components.

3.6 Active Platinum Surface Area

Cyclic voltammetry tests were conducted to calculate active platinum surface area for each MEA. In most cases, the difference between the adsorption and desorption charges was significant suggesting a relatively large uncertainty in the charge measurement. The average of the adsorption and desorption charges was used for the active area calculations.

The results shows that there is no relationship between the active platinum surface area and the Nafion or carbon loadings for the ranges considered here. Also results shows that there is no relationship between the active platinum surface area and the performance for the ranges considered here. Since the exchange current density is directly related to the active surface area, this result is consisted with the prior result indicating no correlation of composition with exchange current density. This result suggests that even at the minimum values of NFP and carbon loading, there is sufficient Nafion and carbon to

provide the minimal connectivity required to activate accessible platinum surface area for the cyclic voltammetry test. The reason for the generally low values of active surface area relative to the gross area is likely due to obstruction of platinum surface by the carbon support or by adjacent platinum particles.

3.7 Apparent Film Thickness

The catalyst layer can be modeled as a group of carbon particles with platinum catalyst deposited on the carbon particle surface and a film of Nafion surrounding the carbon particle. The Nafion film must be thick enough to provide continuity of ion transport to adjacent particles and/or the membrane. On the other hand, reactants and products must diffuse through the Nafion film to the platinum reaction sites, so the film represents a diffusive resistance. Thus, the thickness of the film surrounding the catalyst particles could be expected to influence performance and to exhibit an optimum value.

As suggested by Wilson and Gottesfeld[3], the volume ratio, R_V, of Nafion and carbon, is calculated by equation 2,

$$R_V = \frac{V_{Naf}}{V_c} = \frac{L_{Naf} \times \rho_c}{L_c \times \rho_{Naf}} \qquad (2)$$

Assuming that all of the Nafion in the catalyst layer exists only as a film surrounding carbon particles, a dimensionless apparent film thickness, t_{Naf}, can be determined by equation 3,

$$t_{Naf} = \frac{r_{Naf} - r_c}{r_c} = (R_V + 1)^{1/3} - 1 \qquad (3)$$

Figure 3-5 shows the effect of the apparent Nafion film thickness on the performance (expressed as current density at 0.5 V). For the range of thickness considered in this work, the current density increases as the apparent Nafion film thickness increases. The second line in Figure 3-5 reflects the results from Russell[4]. In this previous work, the current density is decreased as the apparent Nafion film thickness decreases.

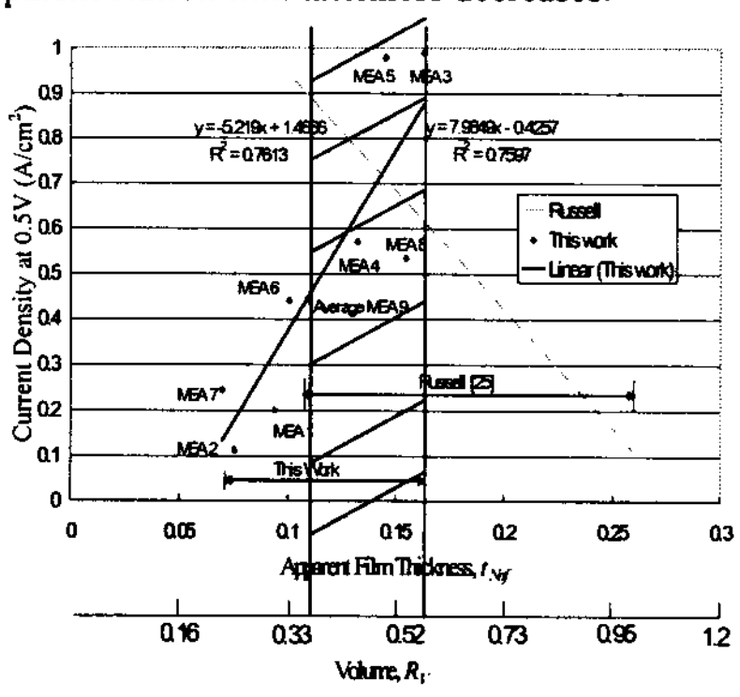

Figure 3-5. Effect of apparent film thickness on cell performance

Figure 3-5 is also presented in terms of the volume ratio. Wilson and Gottesfeld[3] concluded that increasing the volume ratio of the electrode is beneficial up to a critical volume ratio. However, their work does not report a particular value for this ratio. For this research, volume ratios ranged from 0.2 to 0.6, and from Russell[4] work, volume ratios ranged from 0.35 to 1.05. Combining these works suggest that the optimal volume ratio range is between 0.38 and 0.57 corresponding to an apparent film thickness of 0.113 and 0.163. With a carbon particle size of 30 nm this implies a film thickness of 4.5 nm.

4. Conclusions

This research investigated the effect of catalyst layer composition on the performance and characteristics of a PEM fuel cell. In this experiment, the gross catalyst surface area, 0.0384 m^2/cm^2, was held constant while the carbon and Nafion content of the catalyst layer were varied using a central composite design. The purpose of this experiment was to determine the optimum composition of catalyst layer and set up a full model equation.

The performance of a PEMFC catalyst layer was shown to be affected by both the carbon loading and the percentage of Nafion in the catalyst layer. The carbon loading was significant even when the gross platinum surface area was held constant. Lower carbon loadings with around 30 % of Nafion enhanced performance. Characteristics of the catalyst layer including porosity, area specific resistance, and active catalyst area were found to be either unaffected by the catalyst layer composition or insignificant factors in determining performance for the range of compositions considered here.

References

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