

The Correlation of Palladium Supported Carbon (Pd/C) Loading and Optimum Nafion Ionomer Weight Percent (wt.%) Content in the PEM Fuel Cell Catalyst Layer

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Abstract: The presence of Nafion ionomer as one of basic elements in the PEM fuel cell catalyst layer structure can extend the three phase contact between the reactant gases, electrolyte and the catalyst surface and make the catalyst layer active in three dimensions, since the proton can move throughout the entire catalyst layer, which would improve the PEM fuel cell performance. The main objective of this study is to examine the dependence of the optimum Nafion ionomer weight percent (wt.%), on the palladium supported carbon (Pd/C) loading in PEM fuel cell catalyst layer. The results showed that the optimum Nafion ionomer contents in the PEM fuel cell catalyst layer is dependent and inversely proportional to the amount of Pd/C loading. For catalyst layers with a Palladium supported carbon (Pd/C) loading of $4.0 \pm 0.1 \text{ mg/cm}^2$, $3.2 \pm 0.1 \text{ mg/cm}^2$, and $2.45 \pm 0.05 \text{ mg/cm}^2$, the best performance was obtained at about 33, 35, and 37 wt.% Nafion ionomer loading respectively.

ارتباط كمية الكربون المدعوم بالبلاديوم (Pd/C)
مع النسبة المثوية المثلى (wt.%) للنافيون في طبقة الحافز
لخلية الوقود ذات الغشاء البروتوني

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ملخص: وجود النافيون كعنصر أساسي من ضمن العناصر المكونة لطبقة الحافز في خلية الوقود ذات الغشاء البروتوني المبادل يؤدي الى اتساع مناطق اطوار الاتصال الثلاثة بين الغازات المتفاعلة والالكتروليت الصلب و سطح المحفز ويجعل طبقة الحافز أكثر نشاطا في ثلاثة ابعاد مما يمنح الايونات حرية الحركة خلال طبقة الحافز يؤدي بدوره الى تحسن أداء خلية الوقود ذات الغشاء البروتوني. ان الهدف الرئيسي من هذه الدراسة يتمحور في اختبار مدى اعتماد انسب كمية من النافيون على كتلة الحافز المتكون من عنصر البلاتينيوم المدعم بالكربون.

أظهرت نتائج هذه الدراسة أن القيمة المثلى لكمية النافيون الموجودة في طبقة الحافز تعتمد اعتمادا مباشرا وعلى صورة تناسب عكسي مع كمية الحافز في نفس الطبقة. فعندما تأخذ كمية الحافز المقادير 4.0 ± 0.1 و 3.2 ± 0.1 mg/cm^2 ، فإن النسب المثلى لكمية النافيون داخل طبقة الحافز والتي تمنح الخلية أعلى كفاءة هي 33 و 37 wt.% على الترتيب.

Keywords: PEM fuel cells, catalyst layer Performance, Nafion Ionomer, Polarization Curve, Renewable Energy

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1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are promising energy converters, especially in automobile applications, due to their high power density, zero emissions, rapid cold start-up, and system robustness [1-4]. Among the PEM fuel cell components, the catalyst layer (CL) is one of the most important component to achieve a high

performance with reducing costs and long lifetime of the PEM fuel cell. The synthesis of CLs has attracted a great deal of attention in terms of optimization to satisfy the twin demands of high performance and reduced costs. This component (CL) is a porous composite structure of carbon (electronically conductive), recast Nafion ionomer in order to provide a pathway for proton transport from the catalyst nanoparticle to the PEM. (transporting proton) and catalytic sites to promote the electrochemical reactions. Optimization of the Nafion ionomer content is essential step for production of high performance catalyst layer [5-13]. It's necessary to minimize ohmic and mass transport overpotentials in the catalyst layer. Very low Nafion ionomer results in poor contact of the membrane electrolyte with the catalyst layer and hence poor catalyst layer performance. Too high a concentration of Nafion ionomer causes reduction of catalyst layer performance due to blocking of the catalyst sites, blocking of the catalyst layer pores, reduction of gas permeability and increased mass transfer overpotential. Many related studies have been reported on the effect of Nafion ionomer content in the PEM fuel cell electrode performance [14-22]. Different researchers suggested that the different optimal Nafion ionomer loadings in the electrodes they studied were due to either the catalyst type [14-18] or the pre-treatment conditions [19-28]. Even though most of the researchers provided test results based on the same commercial catalyst (20 % Pt/Vulcan XC-72) [29-36,11], the electrodes providing the best cell performance and the highest power density comprised different optimal Nafion loadings. This paper aims to investigate the dependence of an optimum Nafion ionomer wt.% to the palladium loading in the PEM fuel cell catalyst layer prepared by the decals process using 30 % Palladium supported on carbon catalyst (Pd/C) and Nafion ionomers solution of EW 1000.

2. EXPERIMENTAL.

2.1. Membrane Pre-treatment

Before being used in the membrane electrode assembly (MEA), the polymer electrolyte membranes made of Nafion 1035 (Sigma-Aldrich UK, 89 mm 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 °C, followed by boiling for 1 h in deionised water at 85-90 °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 °C to remove the remaining H_2SO_4 on the surface of the membrane, followed by storing in fresh deionised water until use.

2.2. Catalyst Layers Preparation

All of the catalyst layers were prepared in-house by the decals process, with some modifications [7]. The catalyst ink was prepared by using of 30 % Palladium supported on carbon catalyst (Pd/C) (supplied by Sigma-Aldrich), and Nafion 20 wt.% solution (EW 1000, supplied by Sigma-Aldrich), diluted to 10 wt.% in (25 % water, 37.5 % ethanol, and 37.5 % 1-propanol). Catalyst mixtures were prepared in the following way: $4.0 \pm 0.1 \text{ mg/cm}^2$ of 30% Pd/C was wetted with a few drops of deionised water, and stirred for 10 min. After stirring, the required volume of 20 wt.% Nafion ionomer solution was added to the mixture and stirred for 30 min, followed by ultrasonication for 1 h. After ultrasonication process, the mixture was kept under stirring overnight to achieve a homogenous ink. The Nafion ionomer loading and the catalyst loading in the catalyst layer can be adjusted, according to the requirements of the parametric study [7]. The formed catalyst ink was brush painted onto a 3.14 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.

2.3. Membrane Electrode Assembly (MEA)

The membrane-electrode assembly (MEA) was prepared by placing catalyst layers at both sides of the pre-treated Nafion 1035 membrane, followed by hot-pressing at 140 °C and 200 atm for 3 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 deionised water for 10 min., with excess water subsequently being removed. Finally, the MEA's were placed between two glass strips, which kept it flat while slowly drying prior to use.

2.4. 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 HPSC1 high power potentiostat/galvanostat along with WBCS3000 battery cyclor system (WonA Tech., Korea).

3. RESULTS AND DISCUSSION

PEM Fuel cell catalyst layers with a 30 % Palladium supported carbon (30 % Pd/C) loading of $4.0 \pm 0.1 \text{ mg/cm}^2$, and $3.2 \pm 0.1 \text{ mg/cm}^2$, and $2.45 \pm 0.05 \text{ mg/cm}^2$ were prepared with different Nafion ionomer (EW 1000) weight percentage (wt.%) in the catalyst layer. The PEM fuel cell performance was evaluated at 85 °C, with humidified hydrogen-oxygen reactants, at 1 atm pressure. Figure 1, shows the current-voltage (i-V) characteristics of the catalyst layer with Pd/C of $4.0 \pm 0.1 \text{ mg/cm}^2$ and different Nafion ionomer contents, ranging from 20 to 40 wt.%. The catalyst layer performance is low at 20 wt.% Nafion content. The PEM fuel cell performance improved with an increase in the Nafion ionomer content from 20 to 33 wt.%.

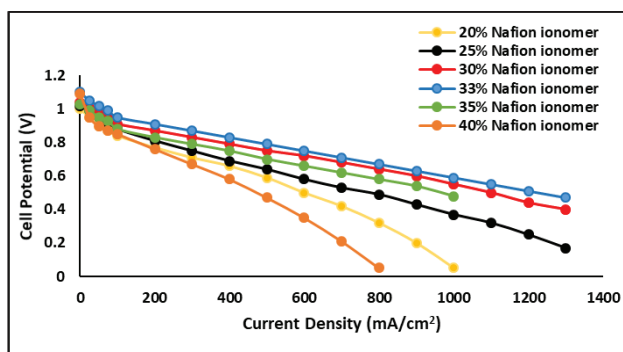


Figure (1). the current-voltage (i-V) characteristics of the catalyst layer with 30% Pd/C of $4.0 \pm 0.1 \text{ mg/cm}^2$ and different Nafion ionomer contents, ranging from 20 to 40 wt.%, with humidified hydrogen-oxygen reactants at 85 °C, temperature and, 1 atm pressure.

This was expected since the application of Nafion to the catalyst layer improves the proton transport between the catalyst layer surface and the membrane. The protonic conductivity of such a catalyst layer is proportional to the amount of Nafion ionomer in the composition mixture. However, a slightly decrease in the PEM fuel cell potential with a little further increase in Nafion ionomer content to 35 wt.% was found. When Nafion ionomer was increased to 40 wt% in the catalyst layer, the PEM fuel cell potential decreased to the minimum 0.21V at the same current density of 700 mA/cm². This behavior was due to the high Nafion ionomer concentration in the PEM fuel cell catalyst layer, which then blocked the catalyst sites, reducing the electronic conductivity, and gas permeability in the catalyst layer [6]. Therefore, the maximum catalyst layer performance was achieved at 33 wt. % Nafion loading, and the minimum catalyst layer performance was observed at 40 wt. % Nafion ionomer loading. In a similar way, the performance of the catalyst layers with $3.2 \pm 0.1 \text{ mg/cm}^2$ catalyst loading was tested using a Nafion 1035 membrane, and the results are presented in Figure 2. The performance was found to increase as the Nafion ionomer content increased from 20 to 35 wt. %. Further increase to 40 wt. % Nafion ionomer loading leads to a decrease in catalyst layer performance. The best catalyst layer performance is obtained at 35 wt.% Nafion. Figure 3, shows the current-voltage (i-V) characteristics of the catalyst layer with Pd/C of $2.45 \pm 0.05 \text{ mg/cm}^2$ and different Nafion ionomer contents, ranging from 20 to 45 wt.%. The best catalyst layer performance is obtained at 38wt. % Nafion.

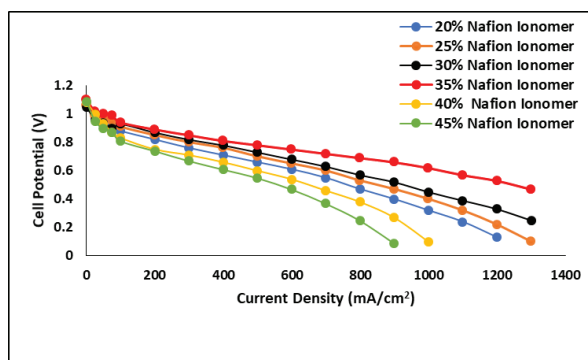


Figure (2). the current-voltage (i-V) characteristics of the catalyst layer with 30% Pd/C of $3.20 \pm 0.1 \text{ mg/cm}^2$ and different Nafion ionomer contents, ranging from 20 to 45 wt.%, with humidified hydrogen-oxygen reactants at 85 °C, temperature and, 1 atm pressure

Figure 4, shows how the Nafion ionomer wt.% correlates with Pd/C loadings for catalyst layers made using

30% Pd/C. Large amount of the Nafion ionomer 37 wt.% was observed at $2.45 \pm 0.05 \text{ mg/cm}^2$ Pd/C in the catalyst layer, and the low amount of Nafion ionomer which is needed to obtain the best PEM fuel cell catalyst layer performance was observed 33 wt.% when the Pd/C loading is $4.0 \pm 0.1 \text{ mg/cm}^2$.

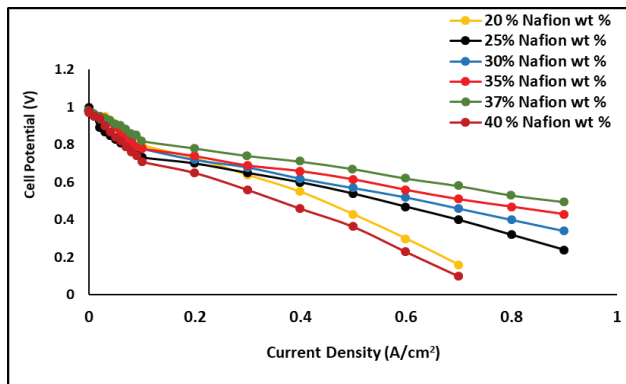


Figure (3). the current-voltage (i-V) characteristics of the catalyst layer with Pd/C of $2.45 \pm 0.05 \text{ mg/cm}^2$ and different Nafion ionomer contents, ranging from 20 to 45 wt.%, with humidified hydrogen-oxygen reactants at 85 °C, temperature and, 1 atm pressure.

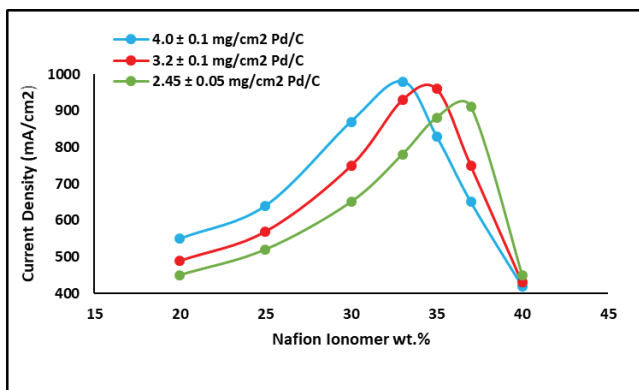


Figure (4). the effect of Nafion ionomer wt.% content in the catalyst layer on PEM fuel cell performance.

4. CONCLUSION

Optimum amount of Nafion ionomer in the catalyst layer is required for good PEM fuel cell performance. The present study has established that the optimum Nafion ionomer content in the PEM fuel cell catalyst layer should depend on the amount of Pd/C loading. The numerical values of the optimum amounts of Nafion may, however, depend on the fabrication method. It is also concluded that the optimum Nafion wt.% in PEM fuel cell catalyst layers' is inversely proportional to the Pd/C. For catalyst layers with a Palladium supported carbon (Pd/C) loading of $4.0 \pm 0.1 \text{ mg/cm}^2$, $3.2 \pm 0.1 \text{ mg/cm}^2$, and $2.45 \pm 0.05 \text{ mg/cm}^2$, the best performance was obtained at about 33, 35, and 37 wt.% Nafion ionomer loading respectively.

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