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Performance Evaluation of Single Cell and Stack of PolymerElectrolyte Fuel Cell by Using Transfer Printing Technique

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Abstract

The polymer electrolyte membrane fuel cell (PEMFC) system was developed. In order to enhance the performance of membrane electrode assembly (MEA), the transfer printing method of the electrocatalyst layer on membrane was developed. The H_2/O_2 single cell with an electrode area of 50 cm^2 was fabricated and tested using 20 wt.% Pt/C as an electrocatalyst and the commercial and hand-made MEA such as Nafion 115, Hanwha, Dow, Flemion T and Gore Select. The 100-cell PEMFC stack with an active electrode area of 300 cm^2 was designed and fabricated using 40 wt.% Pt/C and 30 wt.% Pt-Ru/C as a cathode and anode electrocatalysts, respectively. The performance of PEMFC system was obtained to be 7kW (250A at 28V) and 3.5kW (70A at 50V) at 80 °C by flowing H_2/air and methanol reformed fuel gas/air, respectively.

Key words : Fuel Cell, Polymer Electrolyte Membrane, Reformation, Methanol, PEMFC

Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is the most elegant of all fuel cell systems in terms of design and mode of operation because PEMFC offers several advantages: high power density, compactness, low temperature operation (room temperature to 100 °C), and nonelectrolyte leakage for applications of transportation, portable power generators, and stationary power plant[1,2]. Many researchers have concentrated on the development of the membrane electrode assembly (MEA), new catalyst and new polymer electrolyte, process of electrode and MEA fabrications, and H_2/O_2, H_2/air and methanol/air PEMFC stacks [3, 4]. The performance of PEMFC strongly depends on the properties of membrane and electrocatalysts, which are key parts of MEA. Since MEA is the heart of PEMFC, development of preparation mode of MEA provides the PEMFC stacks of high performance and reliability [4, 5]. Present PEMFC systems are usually using H_2, methanol or natural gas as the fuel and O_2 or air as the oxidant. H_2-O_2 and natural gas-air systems usually apply to space application and sited or fixed power plants, respectively, and methanol-air systems do to mobile power generators and transportation applications. The methanol and natural gas are steam-reformed to CO_2 and H_2 which is fed as fuel gas to the stack [3, 6]. In this work, we fabricated a large scale PEMFC system based upon the domestic technology of 2kW PEMFC stack. For this purpose, we developed construction technology of high performance electrode and MEA by using transfer printing method. The performance of H_2/O_2 single cell with 20 wt.% Pt/C and electrode area of 50 cm^2 was evaluated at 80 °C by using various commercial and hand-made MEAs. Furthermore, we built the 100-cell PEMFC stack with 40 wt.% Pt/C and 30 wt.% Pt-Ru/C as a cathode and anode electrocatalysts, respectively, and an active electrode area of 300 cm^2, and evaluated its performance under H_2/air and methanol reformed fuel gas/air.

Membrane electrolyte assembly fabrication

Figure 1 shows the procedure of MEA fabrication by using transfer printing method. In this work, the different polymer membranes (Nafion 115, Hanwha, Dow, Flemion T and Gore Select) were used for MEA manufacturing processes. The polymer membranes were washed in various treatment solution to remove organic and inorganic contaminants and to

change its form on propose. The membrane was pretreated in 3 wt.% aqueous H_2O_2 solution for 60 min at 90C, and washed repeatedly with de-ionized water. To obtain a membrane in the Na^+ form, the membrane was boiled in 20 wt.% NaOH solution, and washed in de-ionized water and then dried in a vacuum oven for 120 min at 80C.

For the performance test of H_2/O_2 single cell, the 20wt.% Pt/C was used as an electrocatalyst. In addition, for measuring the performance of methanol/air PEMFC stack, the 40wt.% Pt/C and 30 wt.% Pt-Ru/C were used as an electrocatalyst on cathode and anode, respectively. In order to increase the contact area between the polymer electrolyte membrane, platinum clusters and fuel or oxidant, the electrocatalyst slurries were prepared by thoroughly mixing with the Nafion solution in a small vial glass using a magnetic stirrer. The ratios of supported Pt and Pt-Ru catalysts to Nafion for the catalyst layer were typically in the range of 5 : 2 to 3 : 1 (in weight of solids).

In order to raise the stability of electrocatalyst, the protonated form of Nafion within the slurry was converted into the thermoplastic form by the addition of 1M tetrabuthylammonium hydroxide (TBAOH) in methanol containing hydrophobic anion of TBA^+. Since the addition of alkaline solutions directly to the solubilized Nafion results in some coagulation, the TBAOH solution was introduced into slurry after the electrocatalyst and Nafion solution were completely mixed (typically for a few hours). The paintability of the slurry was improved by the addition of glycerol, in the approximate ratio of 1:1 (in wt.%) with the Nafion solution.

The slurry was applied to one side of thin polymer film held in place on a vacuum table by using the screen printer. The content of electrocatalyst loading was controlled to be 0.2 $mgPt/cm^2$ and 0.2 $mgPt-Ru/cm^2$. And then, the coated layer was dried for 60 min in the vacuum oven at 140 °C. The Pt/C and Pt-Ru/C electrocatalysts coated on the polymer film were hot-pressed on each side of dried Na^+ type membrane for 1.5 min at 195 °C with a pressure of 77 bar. After hot pressing, the catalyzed membrane was rehydrated and ion-exchanged to the H^+ type by immersing into hot 0.5M H_2SO_4 for 60 min, followed by rinsing in deionized water. A separate teflonized carbon cloth was used as a backing for the thin film MEA to provide support and a hydrophobic distribution network for the gases. The carbon cloth backing was coated by the slurry containing carbon black powder and PTFE emulsion to decrease contact resistance.

Comparison of performance between commercial and hand-made MEAs

The single cell was fabricated using machined graphite blocks with rib-channel patterns on one side which facilitated the distribution of humidified fuel and oxidant gases to the porous gas-diffusion electrodes as well as collection of current from the electrodes. The graphite blocks were pretreated by impregnation of phenol resin to inhibit gas and cooling water leakage. The active cell area, represented by the rib-channel patterns, was $50cm^2$. Teflon-coated fiberglass gasket materials on both sides of the membrane provided sealing on bolting the cell components together. Copper endplates enabled test cell fixtures to be bolted together, and electrical cartridge heaters inserted into the walls of the copper plates allowed various operating cell temperatures to be selected.

Fuel cell test station used in this work consisted of several flow meters and temperature controllers. The former controls the temperatures and flow rates of the hydrogen and oxygen gases entering the fuel cell and the latter controls the temperatures of humidification vessels. The flow rates of hydrogen and oxygen depending on applied current density were controlled to be 1.2 and 2.0 stoichiometries, respectively. The pressure of hydrogen and oxygen was maintained at 1 bar. An electronic load with a maximum capability of 1 kW (Scribner Associates Inc.) was used to measure the performance of the single cells. All experiments were carried out at 80°C.

The performance of single cell with various MEAs such as commercial Gore PRIMEA 6000 and transfer printed Gore-Select and Nafion 115 membranes is demonstrated in **Fig. 2**. The performance of Gore PRIMEA 6000 and transfer printed Gore-Select MEA showed almost the same value of current density of 1200 mA/cm^2 at 0.6V and 80 °C (720 mW/cm^2). Furthermore, hand-made Nafion 115 MEA had a good performance of 800 mA/cm^2 at 0.6V (480 mW/cm^2), which is better performance under the same experimental condition than that previously reported [8]. This indicates that the fabrication method by using transfer printing method developed in this work is shown to be very appropriate. The difference of MEA performance between Gore PRIMEA 6000, Gore-Select and Nafion 115 MEAs is probably attributed to the different properties and thickness of membrane.

Performance comparison of MEAs using various membranes

Figure 3 shows the performance of MEAs fabricated by transfer printing method using various membranes such as Nafion 115, Hanwha, Dow, Flemion T and Gore-Select. The performance of MEA was increased in order of MEAs fabricated with Nafion 115 (120 m, equivalent weight(EW) 1100), Hanwha(130 m, EW 1100), Dow(115 m, EW 800), Flemion T(120 m, EW 1000) and Gore-Select(20 m, EW 1100). The Dow and Flemion T membranes had a similar performance of 950 mA/cm^2 at 0.6V. The Flemion T and Nafion 115 membranes with the same thickness showed some different performance of 950 mA/cm^2 and 850 mA/cm^2 at 0.6V, respectively. It is reported that the ionic conductivity of polymer membrane mainly depends on the EW, water uptake and thickness [5]. With decreasing membrane thickness and EW, the ionic conductivity is increased. Thus, the performance of MEA is strongly affected by the membrane thickness and EW.

It is remarkable that MEA with the Hanwha membrane developed by Hanwha Chemical Corp.(Korea, collaborative work with KIER) showed better performance (850 mA/cm^2 at 0.6V) than that with Nafion 115 membrane (800 mA/cm^2 at 0.6V) although Nafion 115 is thinner than Hanwha membrane. This means that the Hanwha membrane can be recommended as an alternative candidate membrane to the popular commercial membrane.

Fabrication and performance of 100-cell PEMFC stack

The 100-cell PEMFC stack with an active electrode area of 300 cm^2 was designed and fabricated using both Nafion 115 and Hanwha membranes as an electrolyte and 40 wt.% Pt/C and 30 wt.% Pt-Ru/C as a cathode and anode electrocatalyst, respectively. The PEMFC system was composed of the fuel cell stack, fuel reformer, system controller, electrical system, cooling system and fuel and air delivery systems. The stack section includes the plurality of MEAs, fluid flow field plates, gas diffusion layers and coolant flow plates. The hydrogen and oxygen gases were humidified by flowing each gas on one side of a water exchange membrane and by flowing the pure water on the opposite side of the membrane. The fuel reformer consisted of fuel evaporator, reforming reactor and CO concentration reducer by preferential oxidation. Methanol reformate is typically 75% H_2 and 25%CO_2 with about 1% Co. This CO level can be further minimized

by a subsequent catalytic oxidizer, reducing the CO level to the 1100 ppm level. In this work, CO level is reduced to significant low level.

Figure 4 illustrates performance of H_2/air PEMFC with 30 wt.% Pt-Ru/C and 40wt.% Pt/C catalyst at 80 °C. The flow rates of hydrogen or methanol reformate and oxygen were controlled to be 1.2 and 2.0 stoichiometries, respectively. The performance of H_2/air PEMFC stack was obtained to be 5kW (100 A at 50 V) and 7kW (200 A at 35 V) at fuel and air humidifier temperature of 70 °C and 60 °C, respectively. In addition, **Figure** 5 shows performance of the methanol reformate/air PEMFC under the same experimental condition in Figure 4. The performance was determined to be 3.5kW (70 A at 50 V) and much lower than that of H_2/air PEMFC. It is reported that significant PEMFC performance losses could arise because of two anode-related problems: local loss of water caused by electroosmotic drag of water and, most importantly, anode catalyst poisoning. Poisoning of the anode catalyst is caused primarily by CO, either brought into the cell with the fuel feed stream or generated in situ by the reduction of CO_2 [7]. This problem is therefore particularly with fuel feed streams derived from the stream reforming of methanol or other liquid fuels, and is of lesser concern when the PEMFC operates on pure hydrogen. Furthermore, recent reports have demonstrated better CO tolerance with higher loading Pt-Ru catalysts in PEMFC anodes, particularly at cell current densities lower than 200 mA/cm^2 [2, 6, 8]. The fuel gas was produced by methanol reforming process and purified by preferential oxidation reactor using the Pt-Ru catalyst layer in order to eliminate CO. The level of CO was successfully decreased to a significantly low level, but a small quantity of CO remained in fuel feed stream. Although CO-tolerant Pt-Ru alloy anode catalysts were used to inhibit the poisoning effect, the poisoning effect of CO was not completely reduced. Hence, the performance was determined to be 3.5kW (70 A at 50 V) and much lower than that of H_2/air PEMFC.

Conclusions

To develop PEMFC, elementary technologies such as MEA and stack design and fabrication were developed based upon the domestic technology of 2kW PEMFC stack by using single cell with large active electrode area. The transfer printing method was improved for manufacturing the qualified MEAs. The performance of single cell with transfer printed MEAs was obtained to be 800

mA/cm^2 (Nafion 115), 850 mA/cm^2 (Hanwha), 950 mA/cm^2 (Flemion T) and 1150 mA/cm^2 (Gore-Select) at 0.6V and 80 °C. This indicates that the transfer printing method is very appropriate to fabricate MEA. The large scale stack with control system and reformer was designed and constructed. It showed high performance of 7kW (250A at 28V) and 3.5kW (70A at 50V) by flowing H_2/air and methanol reformed fuel gas/air, respectively.

Acknowledgment

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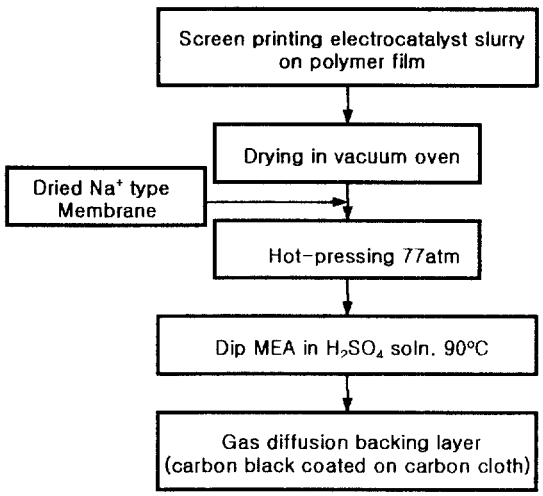

Fig. 1. Experimental procedure of MEA fabrication

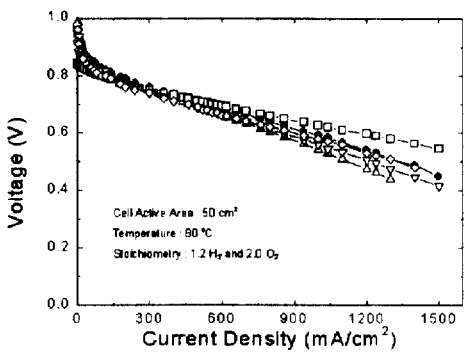

Fig.2. Performance of commercial and hand-made MEAs: , Gore PRIMEA 600; , MEA fabricated with Gore Select membrane by transfer printing method; , MEA fabricated with Nafion 115 membrane by transfer printing method, with 20 wt.% Pt/C.

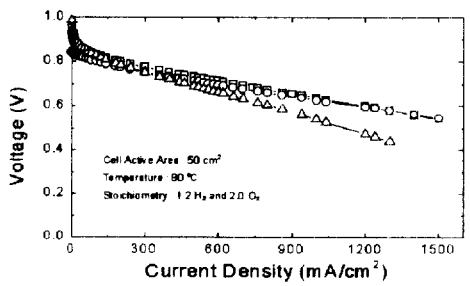

Fig.3. Performance of various MEAs fabricated by transfer printing method using: , Nafion 115; , Hanwha membrane; , Dow; , Flemion T; , Gore Select, with 20 wt.% Pt/C.

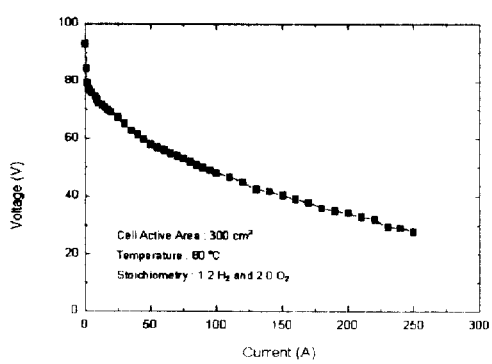

Fig. 4. Performance of H_2/air 100-cell PEMFC stack using 40wt.% Pt/C and 30 wt.% (Pt-Ru)/C as an electrocatalysts on cathode and anode, respectively.

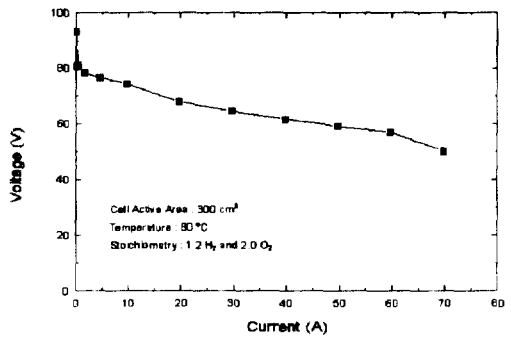

Fig. 5. Performance of reformed fuel gas/air 100-cell PEMFC stack using 40wt.% Pt/C and 30 wt.% (Pt-Ru)/C as an electrocatalysts on cathode and anode, respectively.