

고분자 전해질 연료전지에서 탄소복합 기체확산층의 제조와 특성분석

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Preparation and Characterization for Carbon Composite Gas Diffusion Layer on Polymer Electrolyte Membrane Fuel Cells

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Abstract >> Gas diffusion layers (GDLs) of carbon composite type in polymer electrolyte fuel cells were prepared by simple and cheap manufacturing process. To obtain the carbon composite GDLs, carbon black with polymer binder was mixed in solvent, rolled to make sheet, and finally heat-treated at 340°C. The performance of fuel cell using composite GDLs was changed by PTFE content. The physical properties of composite GDLs for pore, conductivity and air permeability were analyzed to compare with the variation of fuel cell performance. The conductivity of composite GDLs was very similar to carbon paper as commercial GDL but pore properties and air flux were considerably different. The porosity, PTFE content and conductivity for composite GDLs did not have an influence on the cell performance much. The increase of pore diameter and air flux led to enhance cell performance.

Key words : Polymer electrolyte membrane fuel cell(고분자 전해질 연료전지), Gas diffusion layer(기체 확산층), Carbon composite(탄소복합체), Electrode(전극), porosity(기공도)

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are good power sources for electronic devices because of their high efficiency, high power density, low

emissions, low operation temperature, and low noise¹⁾. Although PEMFCs have many advantages, there are still many obstacles to commercialization such as the high cost of materials and low durability. A membrane electrode assembly (MEA), which is the heart of a PEMFC, consists of a catalyst, a polymer electrolyte membrane and a gas diffusion layer (GDL).

The functions of the GDL are to act as a gas

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diffusion media, provide mechanical support, provide an electrical pathway, and channel product water away from the electrodes²). The GDL should have high conductivity³, appropriate hydrophobicity^{4,5}, high air permeability⁶ and sufficient mechanical strength⁷⁻⁹. GDLs are typically carbon-based materials, and usually in cloth or paper form^{10,11}. They are manufactured using huge and high-cost processes of carbonization or fabrication. Only a few researches studies on the preparation of GDLs without carbon paper or carbon cloth have been reported. Hayashi et al.¹² and Chen-Yang et al.¹³ reported a process for obtaining diffusion media from a combination of carbon materials and polytetrafluoroethylene (PTFE). They showed that the performance of a PEMFC containing such GDLs changed depending on the composition of the carbon materials and PTFE.

In this study, the carbon composite GDLs were prepared by mixing carbon black with a polymer binder, namely PTFE. The main properties of GDLs that affect fuel cell performance are hydrophobicity, electrical conductivity, pore size distribution, and air permeability. We investigated the role of each of these properties in cell performance.

2. Experimentals

To prepare the carbon composite GDL, carbon black (Vulcan XC-72, Cabot, Boston, MA, USA) and a PTFE suspension (60% solid, DuPont, Wilmington, DE, USA) were mixed in a water/isopropyl alcohol (IPA) solvent. The solution was agitated to make a paste-like gum, and then rolled on a glass plate until it formed a thin sheet. The carbon composite GDL sheet were dried at 80°C for 6h and then heat-treated at 340°C for 1h to remove surfactant contained in the PTFE suspension. The GDL thickness was from 150

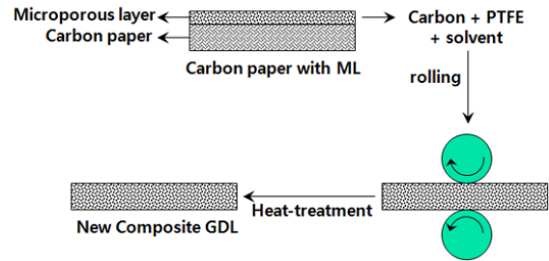


Fig. 1 Concept for manufacturing process of carbon composite GDL

to 200 mm and its PTFE content was from 20% (PF2) to 50% (PF5). Fig. 1 shows the manufacturing process for the carbon composite GDL.

The weights of carbon and binder were measured by thermal gravimetric analysis (TGA; SDT Q600, TA Instrument, New Castle, DE, USA), and the surface morphologies of the GDLs were observed by scanning electron microscopy (SEM; S-4800, Hitachi, Tokyo, Japan). The porosity and pore size distribution were measured using mercury porosimeter (AutoPore 9500, Micromeritics, Norcross, GA, USA).

Air flux through a plane (along the z direction) of the GDLs was measured with a laboratory-made instrument using the Gurley method (ASTM D737). This instrument, a permeometer, measured air flow per minute at 1.27 cm (0.5 inch) water pressure drop between the gas inlet and outlet. Single-phase flow through a porous medium is described by Darcy's law¹⁴:

$$-\nabla P = \mu v / K \quad (1)$$

where K is the absolute permeability of the porous material, μ is the viscosity (1.85×10^{-5} Pa·s for air) of the flowing fluid, v is the superficial velocity of the fluid and P is the pressure. Solution of Darcy's law for the one-dimensional flow of a compressible fluid results in the following equation¹⁵:

$$\frac{P_{in}^2 - P_{out}^2}{2LRT/MW_{air}} = \frac{\mu}{K} m' \quad (2)$$

where P_{in} is the inlet pressure, P_{out} is the outlet pressure, L is the length of the GDL, R is the universal gas constant, T is the temperature, MW_{air} is the molecular weight of air and m' is the mass flux through the GDL.

The through-plane resistance was measured using DC power supply (Jhp-1500A, Jin Heung Scientific Co, Korea) using Au-coated Cu plates. The GDL was set between the two plates which were connected to the power supply and a current-voltage multimeter (34401A, Agilent, Santa Clara, CA, USA). The measured resistance included the total resistance of the bulk material and the interface contact between the GDL and the metal plate. We measured the resistances of GDLs with two and four sheets compressed at 25 kgf/cm² and then, calculated the resistance, ρ (Ω cm), using the following equation, which was proposed by the New Energy and Industrial Technology Development Organization (NEDO) and Mitsubishi Electric:

$$\rho = (R_4 - R_2)A/2t \quad (3)$$

where R_4 and R_2 are the resistances for two and four sheets, respectively, A is the electrode area and t is the GDL thickness.

MEAs were prepared as follows¹⁶⁾, using a catalytic ink consisting of Pt/C (20%, Johnson Matthey, London, UK), Nafion (5% solution, DE521, DuPont, Wilmington, DE, USA) and IPA. The solid particles of Pt/C were dispersed uniformly by ultrasonication and the particles were connected by the Nafion polymer. The catalytic ink was sprayed on the GDL until the Pt loading reached 0.3 mg/cm². The electrode size was 25 cm² and dried at 60°C for 3h to remove solvents. To prepare

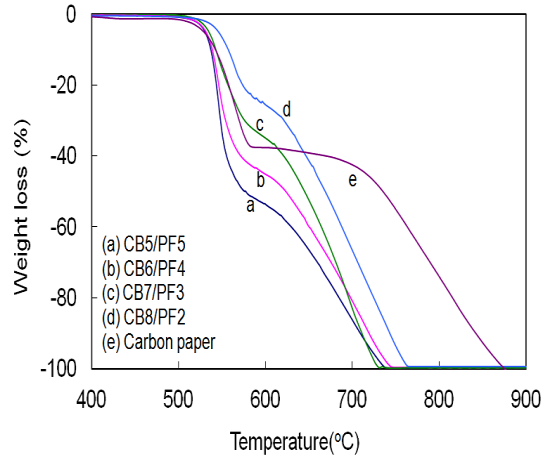


Fig. 2 TGA of carbon composite GDL and carbon paper in air

the MEA, two electrodes were sandwiched with a Nafion 112 membrane (EW 1100, DuPont, Wilmington, DE, USA) and hot-pressed at 120°C and 200 bar for 2min. Before hot-pressing, the Nafion 112 was treated using a well-known membrane cleaning procedure¹⁷⁾. The fuel cell was operated at 80°C and humidified hydrogen and air were supplied to the cell. The temperatures of the hydrogen and the air were 90 and 70°C, respectively, and the gas flows were controlled at 1.5 and 3.0 excess, respectively. The fuel cell performance was measured in constant current mode from open circuit voltage (OCV) to 0.3V.

3. Results and Discussion

The PTFE content of the GDL is a very important factor with respect to hydrophobic properties; these properties prevent water-flooding in the GDL and vent vapor to the outside of the GDL. As show in Fig. 2, TGA was carried out in an air atmosphere to determine the PTFE content and compare it with that in a commercial GDL. Weight loss for all the GDLs started at around 530°C, and this was assigned to

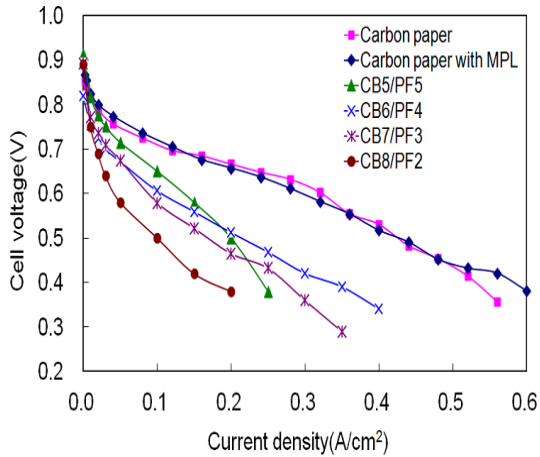


Fig. 3 Cell performance of carbon composite GDL and carbon paper as a function of mixing ratio

PTFE decomposition^{18,19)}. The second weight losses for the carbon composite GDLs were observed above 600°C, which is the region for carbon oxidation²⁰⁾. However, the second weight loss of carbon paper occurs above 700°C because its carbon material consists of graphitized carbon fibers. Finally all the materials were burned above 750°C for the carbon composite GDL and 850°C for the carbon paper. The PTFE loading in the GDL was confirmed from the weight loss induced by the decomposition of PTFE at around 550°C in air.

Fig. 3 shows the fuel cell performances of MEAs containing carbon composite GDLs and two commercial carbon papers. All the carbon composite GDLs showed lower performances than those of commercial carbon paper. The PTFE content in the carbon composite GDLs had a significant effect on cell performance.

The cell performance increased with increasing PTFE content until 40wt% PTFE. A low PTFE content may induce water-flooding phenomena in the GDL and prevent reactant gases from diffusing into the catalyst layer^{4,21)}. The performance of the GDL with 50% PTFE under the high current region, 0.3~0.5V of

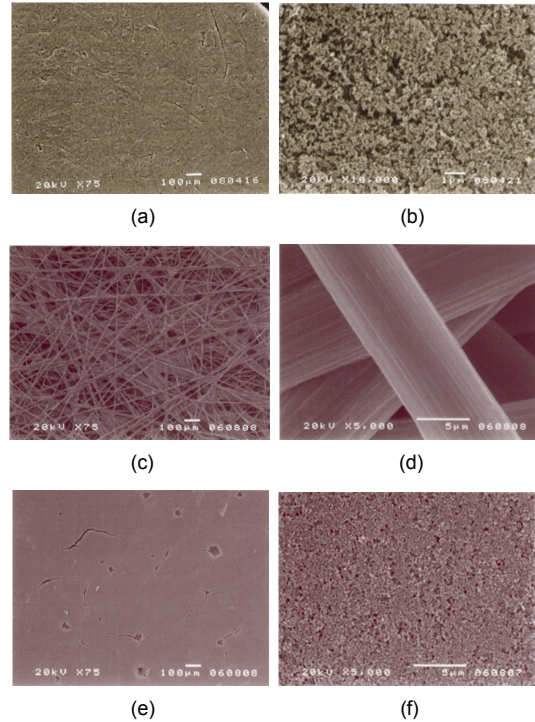


Fig. 4 SEM images of carbon composite GDL (CB8/PF2) (a,b), carbon paper (c,d) and microporous layer of carbon paper (e,f)

cell voltage, was lower than that with 40% PTFE because too high a PTFE loading may increase the resistance of the GDL.

SEM images of a carbon composite GDL (CB8/PF2) and carbon paper are shown in Fig. 4. The surface morphology of the carbon composite GDL looks very smooth and dense compared with that of the carbon paper. It seems very similar to the microporous layer (MPL) on carbon paper produced by E-TEK²²⁾. It was estimated that its pore size was much very smaller than that of carbon paper, and similar to that of an MPL.

Fig. 5 shows the pore size distribution of the carbon composite GDL, carbon paper and carbon paper with an MPL. The main pores of the carbon paper were in the range 10 - 100 µm, which were formed by the

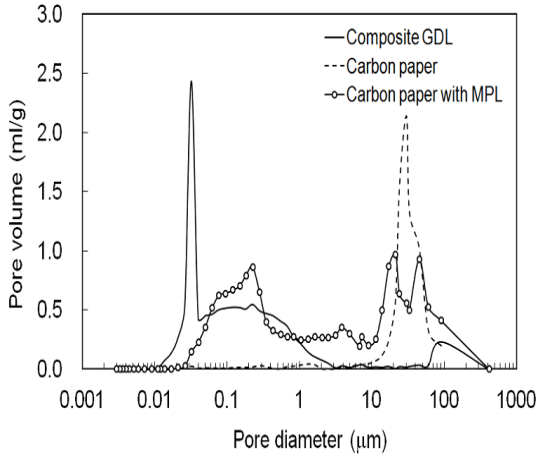


Fig. 5 Pore size distributions of carbon composite GDL, carbon paper and carbon paper with MPL

internal space between carbon fibers. The carbon paper with an MPL had two main pore types; pores in the range 0.04 - 0.5 μm in the MPL and pores in the range 10 - 100 μm in the carbon paper, the same as those in the other carbon paper. However, the carbon composite GDL had pores in the range 0.01 - 3.0 μm . Pore diameter above 50 nm is assigned to macro-pore, that of 2 - 50 nm is assigned to meso-pore and that less than 2 nm is assigned to micro-pore²³⁾. The sharp peak for the pore between 0.01 and 0.5 μm in the carbon composite GDL may be the result of pores formed by the spaces in agglomerated primary carbon particles, and the broad one in the range 0.5 - 3.0 μm may result from pores formed by the interspaces between the primary particles^{24,25)}. Diffusion of gas in porous media occurs mainly through Bulk and Knudsen diffusion processes. The effective diffusion coefficient in the Bulk diffusion regime, which is assigned to pore diameters above 7 μm , is three orders higher than that in the Knudsen diffusion regime for pores below 7 nm²⁶⁾. Larger pores therefore enhance mass transport through porous media. In the commercial carbon paper, pores above 10 μm were dominant in

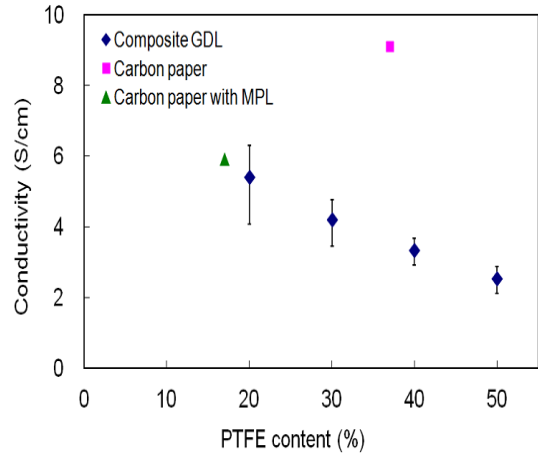


Fig. 6 Conductivity of carbon composite GDL, carbon paper and carbon paper with MPL at 25 kgf/cm²

the pore distribution, but the pores in the carbon paper with an MPL were well distributed in all ranges. However, the carbon composite GDL had pores in the micro-pore regions. This means that bulk diffusion for gas transport through large pores is deficient in the carbon composite GDL.

The role of the GDL with respect to electrical properties is to supply electrons, which will be produced or consumed at the catalytic layer, to or from a bipolar plate. The conductivity of the GDL is therefore a very important factor. Fig. 6 shows the through-plane conductivities of the carbon composite GDLs, carbon paper and carbon paper with an MPL; these were measured by the two-probe method. The GDL conductivity decreased with increasing PTFE content showing a linear relationship with the portion of non-conductor in the GDL. Carbon paper showed a very high conductivity as a result of the high conductivity of carbon fibers. However, the conductivity of carbon paper with an MPL was very similar to that of the carbon composite GDL with 20% PTFE despite the MPL on the carbon paper. This may be the reason for the composition of MPL being the same as that

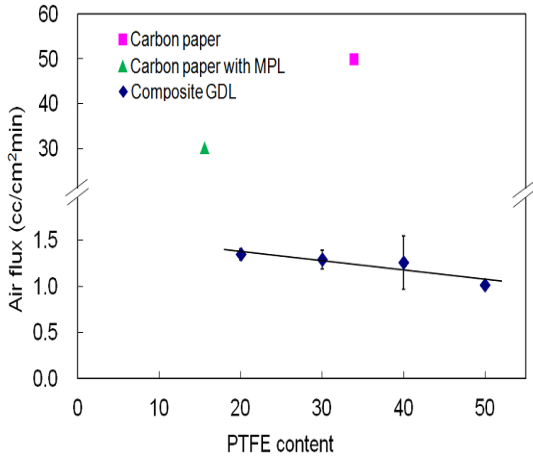


Fig. 7 Air flux of carbon composite GDL, carbon paper and carbon paper with MPL

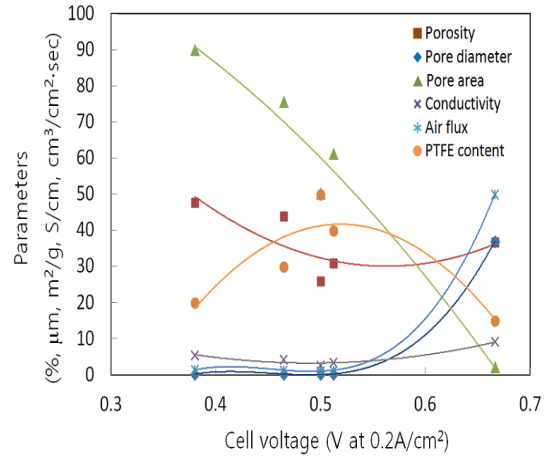


Fig. 8 Physical properties of carbon composite GDL as a function of cell voltage

of the carbon composite GDL.

The through-plane air fluxes of the carbon composite GDLs were measured using a laboratory-made apparatus. Fig. 7 shows the air fluxes of various GDLs as a function of PTFE content. Commercial GDLs, which are based on carbon fibers, had very high air fluxes compared with those of carbon composite GDLs. The PTFE binder decreased the air fluxes in the carbon composite GDLs because PTFE particles block the passage of gases through the GDLs²⁷⁾. The permeability coefficients of the GDLs were calculated using Darcy's law; the results are shown in Table 1. These results

are different from the values reported in the literature. Gostick et al.²⁸⁾ found the through-plane permeability coefficients for SGL, Ballard and Toray carbon papers to be in the range 5.7×10^{-12} to $37.4 \times 10^{-12} \text{ m}^2$, which are approximately 10 orders lower than those of the carbon composite GDLs. These differences may be caused by different measurement methods and apparatus.

Table 1 shows a summary of the physical properties for various GDLs and Fig. 8 shows the relationship between physical properties and cell performance (cell voltage at 0.2 A/cm²). The porosity, PTFE content

Table 1 Physical properties of carbon composite GDLs and carbon papers

	Carbon (%)	PTFE (%)	Pore size (μm)	Pore area (m ² /g)	Conductivity (S/cm)	Permeability coefficient ^c (m ²)	Current ^d (mA/cm ²)
CB5/PF5	50	50	0.13	50.31	2.55	7.38	200
CB6/PF4	60	40	0.16	61.35	3.34	9.11	215
CB7/PF3	70	30	0.18	75.66	4.21	9.36	170
CB8/PF2	80	20	0.21	89.97	5.41	9.77	100
Carbon paper ^a	63	37	37.03	2.22	9.10	362.8	425
Carbon paper -MPL ^b	83	17	5.04	22.60	5.92	218.6	425

a: Toray 060ST (E-TEK). b: LT 1200 (E-TEK), c: $\times 10^{-12}$, d: at 0.5V

and conductivity did not have much influence on the cell performance. Increase in pore diameter and air flux enhanced cell performance, but an increase in the pore area had the opposite effect. We concluded that increasing the pore diameter and air flux improved the fuel cell performance; Prasanna et al. also reported similar results²⁹⁾. If these carbon composite GDLs are used in fuel cells operated at high current ($>1 \text{ A/cm}^2$), the conductivity and PTFE content are also important factors with regard to cell performance^{30,31)}.

4. Conclusions

The characteristics of carbon composite GDLs for PEMFCs were investigated in terms of fuel cell performance and physical properties. The carbon composite GDLs were obtained by mixing carbon black and a polymer binder in a solvent, rolling to form a sheet, and finally heat-treating at 340°C . The performances of fuel cells using carbon composite GDLs were changed by changing the PTFE content. The conductivities of the carbon composite GDLs were very similar to that of a carbon paper, commercial GDL but the pore properties and air fluxes were significantly different. Macro-pores do not exist in the carbon composite GDLs, unlike the situation for carbon paper, and this may decrease mass transport through the GDL. The physical properties of the carbon composite GDLs were analyzed to determine their effects on fuel cell performance. The porosities, PTFE contents and conductivities for the carbon composite GDLs did not have much influence on the cell performance. Increase in pore diameter and air flux enhanced cell performance because of improved gas transport through the GDLs.

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