Effect of Carbon Content on the Physical Properties of Carbon Composite Gas Diffusion Layer in PEMFCs

Choonsoo Han[1,], In-Tae Kim[2], Ho-Jung Sun[3], Gyungse Park[4], Ji-Jung Lee[5], Hong-Ki Lee[5], Joongpyo Shim[1,]*

[1] Department of Nano & Chemical Engineering, Kunsan National University, Jeonbuk, 573-701, KOREA
[2] Fuel cell Nanomaterials Center, University of Yamanashi, Yamanashi, 400-8510, JAPAN
[3] Department of Material Science & Engineering, Kunsan National University, Jeonbuk, 573-701, KOREA
[4] Department of Chemistry, Kunsan National University, Jeonbuk, 573-701, KOREA
[5] Fuel Cell Regional Innovation Center, Woosuk University, Jeonbuk, 565-701, KOREA
*E-mail: jpshim@kunsan.ac.kr

Carbon composite gas diffusion layers (GDLs) containing carbon black and graphite for use in polymer electrolyte membrane fuel cells were prepared by a simple method. The physical properties of the carbon composite GDLs, such as air flux through a plane, porosity, pore diameter, pore area, and through-plane resistance, were investigated. Electrochemical measurements were carried out using a membrane electrolyte assembly prepared by hot-pressing a Nafion membrane and catalyst-coated GDLs. Graphite content was seen to have an effect on the physical properties of the carbon composite GDLs, and in turn, fuel cell performances. The effect of the variation in the physical properties of the carbon composite GDLs on fuel cell performance was investigated as a function of current density.

1. INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) are considered to be a clean power source for electronic devices because of their high efficiency, high power density, low level of emissions, low operation temperature, and low noise [1]. In spite of the many advantages of PEMFCs, commercialization remains a significant challenge owing to factors including the high cost of materials and low durability. The membrane electrode assembly (MEA), which is the most important component

of PEMFCs, consists of a catalyst, polymer electrolyte membrane (PEM), and gas diffusion layer (GDL). The GDL has the role of diffusing reactant gases, providing mechanical support, providing an electric pathway, and channelling product water away from the electrodes. The physical properties required of the GDL are high electrical conductivity [2], appropriate hydrophobicity as a water repellent sheet [3,4], high gas permeability [5], and sufficient strength [6,7].

The GDL is typically a carbon-based material, and usually produced in cloth or paper form using a carbonization or fabric process. Only a few studies on the preparation of GDLs without carbon paper or carbon cloth have been published [8,9]. We have previously reported a new and simple manufacturing process for synthesizing a porous carbon composite GDL for PEMFCs [10]. We compared the performance of fuel cells containing these carbon composite GDLs, which prepared using carbon black with polytetrafluoroethylene (PTFE) as the binder, in comparison with commercial GDLs. In this work, we investigate the preparation of composite GDLs with carbon black and graphite, and assess the relationship between their physical properties and cell performance.

2. EXPERIMENTAL

To prepare the carbon composite GDL, carbon black (Vulcan XC-72, Cabot), graphite (synthetic, ~20μm, Aldrich) and a PTFE suspension (60% solid, DuPont) were mixed in a water/isopropyl alcohol (IPA, Aldrich) solvent. The solution was agitated to make a paste-like gum, and then rolled on a glass plate until a thin sheet was formed. The carbon composite GDL sheet was dried at 80°C for 6 h and then heat-treated at 340°C for 1 h to remove the surfactant contained within the PTFE suspension. The GDL thickness ranged from 150 to 200 μm and its PTFE content was 40% with respect to carbon black and 10% with respect to graphite.

The porosity and pore size distribution were measured using mercury porosimeter (AutoPore 9500, Micromeritics, KBSI Jeonju Center), and the surface morphology of the GDLs was observed using scanning electron microscopy (SEM; S-4800, Hitachi).

Air permeability through a plane (along the z direction) of the GDLs was measured with a laboratory made instrument using the Gurley method (ASTM D737). The through-plane resistance was measured using a DC power supply (Jhp-1500A, Jin Heung Scientific Co) with a current-voltage multimeter (34401A, Agilent) using Au-coated Cu plates. The resistance, ρ (Ωcm), was calculated using the equation proposed by the New Energy and Industrial Technology Development Organization (NEDO), Mitsubishi Electric and elsewhere [11-14].

MEAs were prepared [15] using a catalytic ink consisting of Pt/C (20 %, Johnson Matthey), Nafion (5% solution, DE521, DuPont) and IPA. The solid particles of Pt/C were dispersed uniformly by ultrasonication and then connected by the Nafion polymer. The catalytic ink was sprayed on the GDL until the Pt loading reached 0.3 mg/cm^{2}. The electrode size was 25 cm^{2} and was dried at 60°C for 3 h to remove the residual solvent. To prepare the MEA, a Nafion 112 membrane (EW 1100, DuPont) was sandwiched between two electrodes and hot-pressed at 120°C and 200 bar for 2 min. The fuel cell was operated at 80°C under an atmosphere of humidified hydrogen and air. 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 0.3 V.

3. RESULTS AND DISCUSSION

The primary particle size of carbon black was approximately 0.02 μm; however, it is normally agglomerated to form bigger particles. The particle size of the graphite was around 20 μm which was significantly larger than that of carbon black. If the carbon black was well dispersed during mixing, it could cover the surface of the graphite particles. Fig. 1 shows the surface of the carbon composite GDLs prepared from the mixture of carbon black and graphite compared to that prepared from carbon black only.
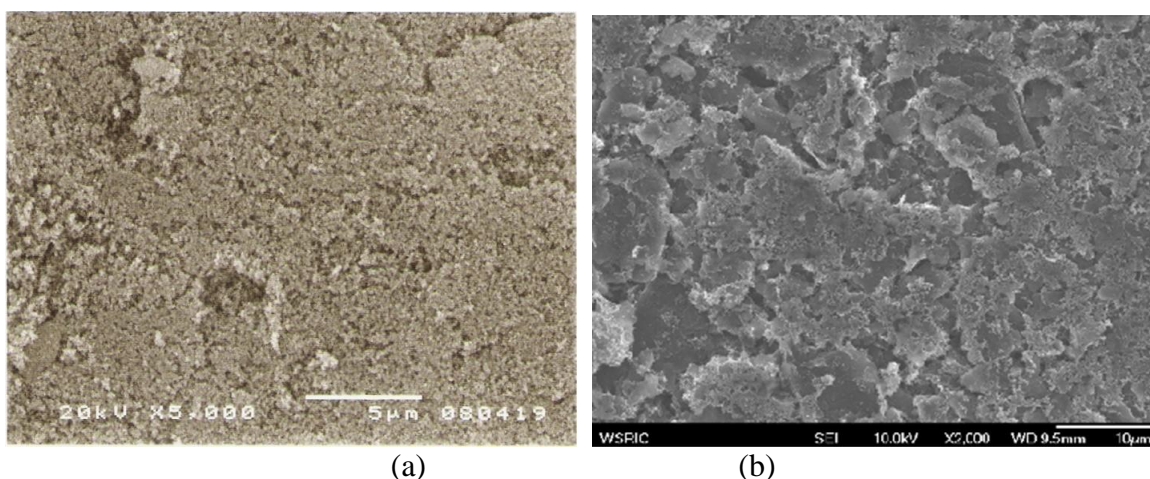

(a)   (b)

Figure 1. SEM images of carbon composite GDL. (a) CB 100% (G 0%), (b) CB 30% + G 70%.

The surface of GDL with only carbon black appears very smooth, whereas those containing graphite were seen to have particles that were covered with the carbon black (Fig. 1(b)). In addition, it was found that pore size of latter was significantly bigger than that of former. We expect that the addition of graphite could increase the air permeability of the GDL. In general, the resistivities of synthetic graphite through the *a* axis and *c* axis are 3.9×10^{-5} and 1.0×10^{-2} Ωcm, respectively [16]. However, the resistivity of carbon black varies widely depending on the sample manufacturing process. The Vulcan XC-72 carbon black has resistivities of 0.25 and 0.13 Ωcm at packing fraction of 0.3 and 0.4, respectively [17]. Fig. 2 shows that up to 25%, the conductivities of the carbon composite GDLs significantly decreased with increasing graphite content. It is considered that the contact area of the GDL is decreased by the increase in roughness due to the large particle size of the graphite, as seen in Fig. 1(b). However, at higher graphite contents, the conductivity of the carbon composite GDLs gradually increased. This is a reasonable result as the electric conductivity of graphite is much higher than that of carbon black. The measurement method for electric conductivity involves contact

resistivity between sheets, which is affected by surface roughness and difficult to eliminate from the original conductivity [18,19].
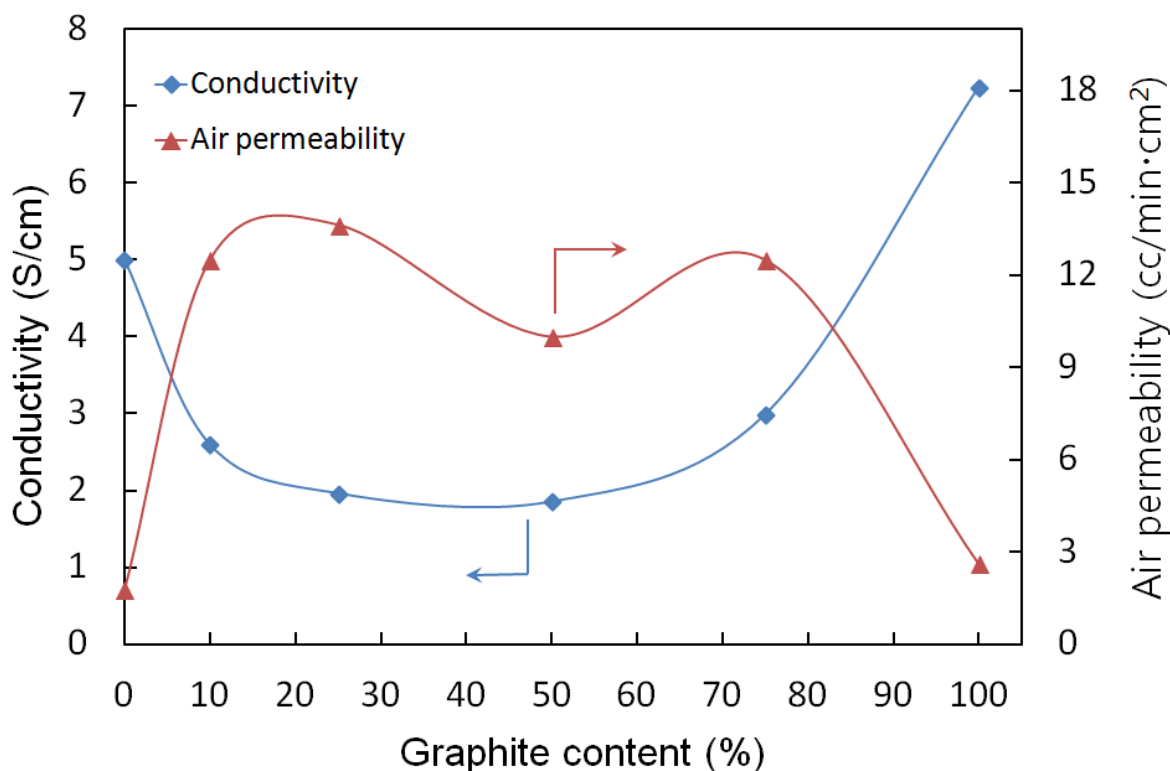

Figure 2. Conductivity and air permeability of carbon composite GDLs as a function of graphite content.

The air permeabilities of carbon composite GDLs are also shown in Fig. 2. The air permeability of these composite GDLs, apart from G 0 % and G 100 %, was approximately half that of other commercial GDLs made with a microporous layer (MPL) [10,20]. The lower air permeability of composite GDLs prepared using only carbon black or graphite is assumed to be due to the narrow pore channels formed by the small particles of carbon black, or the low number of large pore channels formed by the large graphite particles. Thus, the spaces or pores available for gas diffusion through composite GDLs consisting of solely carbon black or graphite might be insufficient in comparison to those formed from a mixture of the two materials.

To verify the results shown in Fig. 2, the pore size distribution for composite GDLs was analyzed using mercury porosimeter. As shown in Fig. 3, the pore size distribution of the composite GDLs was broadly spread in the range of 0.01 - 4.0 µm. The sharp peak at around 0.03 µm for the composite GDL without graphite was assigned to the spaces formed between the particles of carbon black [20-22]. As the content of graphite particles in GDL increased, this peak gradually became broad and shifted to a larger size. The composite GDL prepared from 100% graphite shows a single broad peak around 0.7 µm. The pore size in the composite GDLs can therefore be controlled by varying the content of carbon black or graphite. By considering the explanations by Wang and coworkers, larger pores are beneficial because of the increase in mass transport through the substrate by Bulk diffusion

and convection [23]. We assume that the gas diffusion through our composite GDL would occur via the Knudsen diffusion and the Bulk diffusion combined.
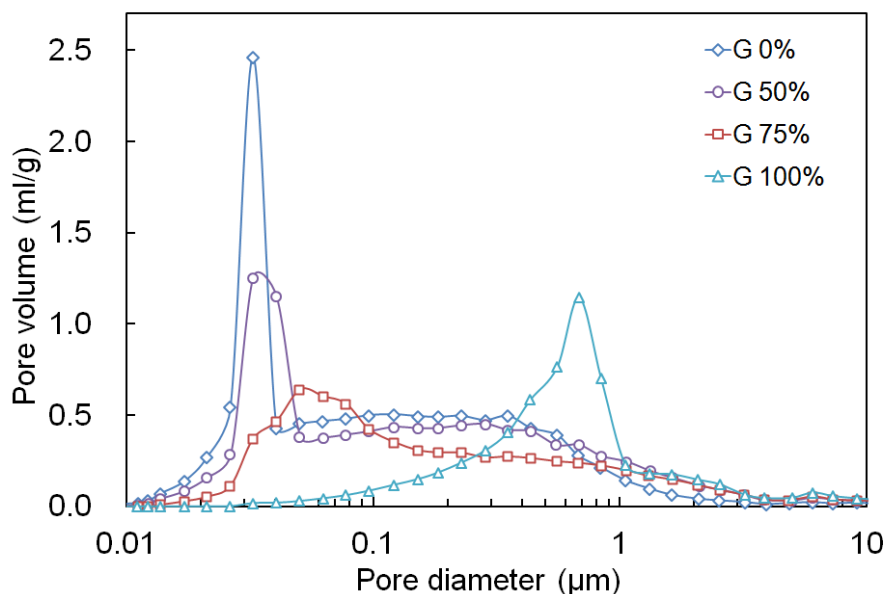

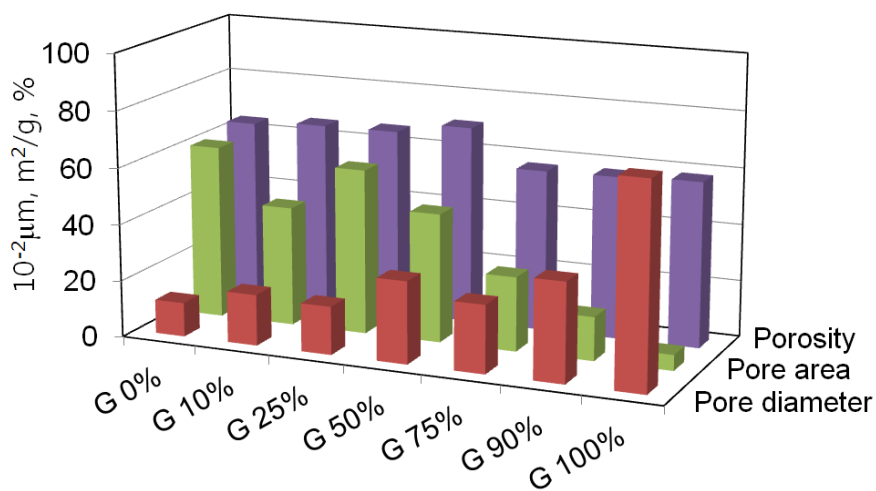**Figure 3.** Pore size distributions of carbon composite GDLs.

Figure 4. Porosity, pore area and pore diameter of carbon composite GDLs.

The porosity, average pore area, and pore diameter of all composite GDLs are shown in Fig. 4. It can be seen that the pore area increased with increasing carbon black content in the composite GDLs, opposite to the trend for pore diameter, with all GDLs showing similar porosities. Table 1 lists the physical properties of composite GDLs.

Electrochemical measurements were carried out for fuel cells containing MEAs with the composite GDLs. In the I-V polarization curves shown in Fig. 5, the composite GDL with high content of carbon black showed fairly good performance.

Table 1. Physical properties of carbon composite GDLs

	Porosity (%)	Pore size (μm)	Pore area (m²/g)	Conductivity (S/cm)	Permeability coefficient (cc/cm²min)	Current[a] (mA/cm²)	Tafel slope[b] (mV/dec)
CB100G0	64.44	0.12	61.31	5.00	1.76	151.1	77.5
CB75G25	66.21	0.17	58.30	1.96	13.6	156.8	71.6
CB50G50	69.98	0.29	45.45	1.85	10.0	123.4	81.8
CB25G75	57.05	0.24	26.25	2.98	12.5	99.5	84.8
CB0G100	58.45	0.72	5.55	7.24	2.63	152.0	58.0
a: at 0.6V. b: until 0.8V							

It is generally considered that the electric conductivity of carbon composite GDLs influences this. Nevertheless, the composite GDL with 100% graphite, which had high conductivity, showed poor performance. It is hypothesized that for the composite GDL containing solely graphite, other factors affected the cell performance.
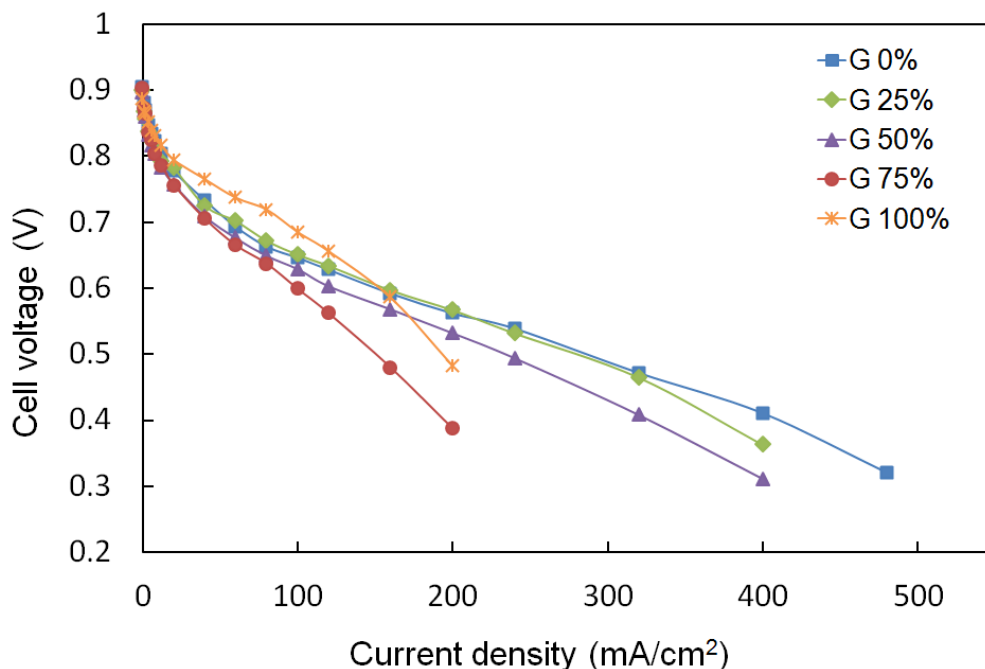

Figure 5. Fuel cell performances of MEAs with carbon composite GDL.

Fig. 6 shows the cell voltage with constant current as a function of graphite content in the composite GDLs. At the 100 mA/cm² of current density, the fuel cell performance dependence on the graphite content could not be seen.
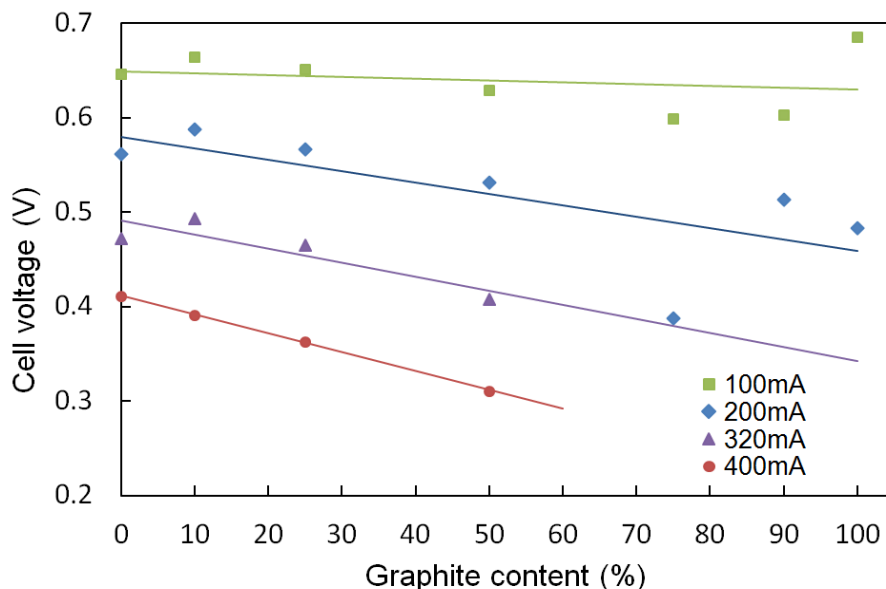
Figure 6. Cell voltage variation of MEAs with carbon composite GDL as a function of current.

However, at current densities above 100 mA/cm^2, the voltages of cells with the composite GDLs practically were seen to decrease with increasing graphite content. The graphite content had a significant influence on the physical properties, such as the pore properties, conductivity, gas permeability, etc. These physical properties affected the fuel cell performance by altering the mass transport of reactant gases and electric conductivity through the electrode. Therefore, it was important to examine the relationship between cell performance and the physical properties of the composite GDLs.
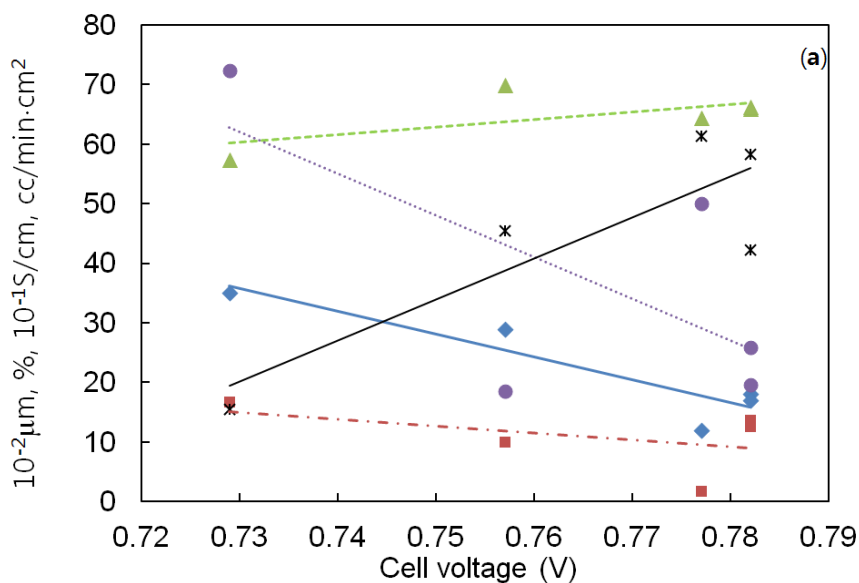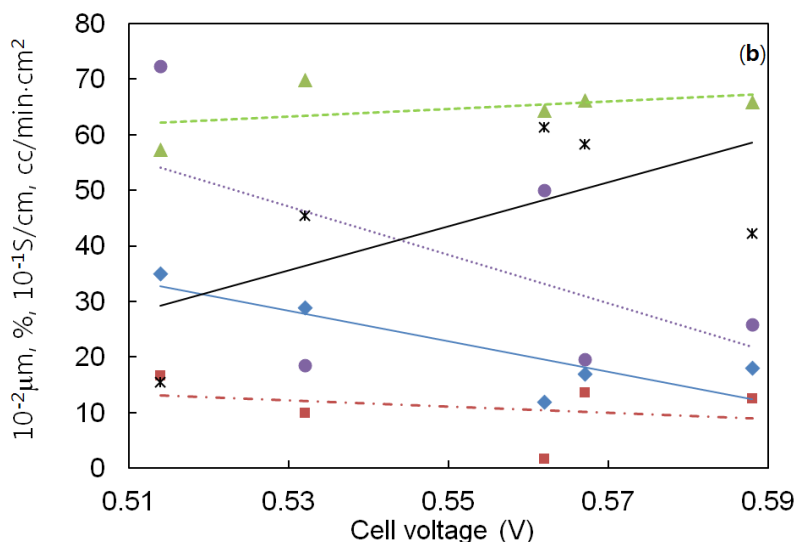
Figure 7. Physical properties of composite GDLs as a function of cell voltage at (a) 20 mA/cm^2 and (b) 200 mA/cm^2. ($\blacklozenge$, ———) Pore diameter, ($\blacktriangle$, - - - -) porosity, ($\ast$, ———) pore area, ($\bullet$, $\cdot\cdot$ $\cdot\cdot$) conductivity, ($\blacksquare$, — $\cdot$ —) air permeability.

Cell performance is known to be especially influenced by the mass transfer of the reactant gas and is directly related to gas concentration, which depends on pore area, air permeability. The ion conductivity of the electrolyte membrane is another contributing factor; however, in this work, the ion conductivity did not have any influence. Fig. 7 shows the relationship between fuel cell performance and the physical properties of the composite GDLs on the cell voltage at two constant current densities, one for an activation polarization region (below 50 mA/cm^2) and another for an ohmic polarization region (over 100 mA/cm^2). The changes in the Tafel slopes in the activation polarization region (listed in table 1) were small, being within about 10 mV, except for the GDL consisting of 100% graphite. This was because the same catalyst was used for all the composite GDLs and this affects the activation energy. In Fig. 7, both graphs show similar behavior as a function of the physical properties of the composite GDLs. The cell performance increased with increasing porosity and pore area, but pore diameter, conductivity and air permeability showed the opposite trend. Kannan and Munukutla reported that an increase in the pore diameter of a MPL on the GDL led to enhanced cell performance at higher current density without flooding [24]. The results of Kitahara et al. demonstrated a maximum cell performance at a pore diameter of 3 μm of the MPL on the GDL at the cathode side [25]. They assumed when the pore diameter was higher or lower than 3 μm, the performance tended to decrease by flooding or mass transport limitations. Usually, the introduction of a MPL on carbon paper or carbon cloth in GDLs improves gas transport and water management capabilities, and reduces ohmic resistance [26,27]. Chen et al. reported that the MPL on carbon paper increased the volume of micro-pores and meso-pores, but slightly decreased that of macro-pores [28].

The introduction of the MPL significantly decreased the air permeability and porosity of the GDLs but the cell performances were enhanced by certain properties of it [29]. Their simulation results for mass flow in the fuel cells showed that the increase in porosity of the GDL enhanced gas diffusion into the catalytic layer and led to the improvement in cell performance [30]. It may be assumed that the

mass transport in our GDLs might be controlled by Knudsen diffusion dominantly because of the low mean pore diameter. Therefore, the cell performance could be improved by the increase in gas diffusion (rather than Bulk diffusion) gained through the enlargement of pore volume, as shown in Fig. 7.

4. CONCLUSIONS

Carbon composite GDLs were prepared from carbon black and graphite using a simple method. Their physical properties and the fuel cell performances containing them were subsequently investigated. Graphite content was found to influence the physical properties (e.g. electric conductivity and air permeability) of the carbon composite GDLs. The pore size and conductivity of the composite GDLs increased with increasing graphite content but their porosity, pore area, and air permeability showed the reverse trend. The composite GDLs with high carbon black content showed better fuel cell performances than the others. Comparing the cell performances with the physical properties, it was observed that the cell performance increased with increasing porosity and pore area; but pore diameter, conductivity, and air permeability showed the reverse trend. It may be assumed that the mass transport in our GDLs might be controlled by Knudsen diffusion dominantly because of low mean pore diameter. Therefore, the cell performance could be improved by an increase in gas diffusion through an enlargement of pore volume.

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