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Short communication

Adoption of nano-materials for the micro-layer in gas diffusion layers of PEMFCs

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Abstract

Carbon nano-materials were applied to the gas diffusion layers of PEMFC. Gas diffusion layers consist of gas diffusion medium(carbon cloth or carbon paper) and micro-layers. Carbon blacks, such as Vulcan XC 72, have been widely used for the micro-layers. Main functions of gas diffusion layers are distribution of reactants to the active site of electrode, management of water supplied and/or generated and enhancement of electrical contact between the electrode and the bipolar plates. In this work, nano-fibers and nano-tubes are adopted to the micro-layer of gas diffusion layers. By applying nano-materials, thinner micro-layers can be fabricated. This newly made micro-layer showed higher gas permeability and good electric conductivity with similar degree of water management as well as enhanced performance.

Keywords: PEMFC; Gas diffusion layer; Micro-layer; Carbon nano-fiber; Carbon nano-tube

1. Introduction

Proton exchange membrane fuel cell (PEMFC) stacks consist of electro-catalysts, proton conducting membrane, gas diffusion layers (GDL), bipolar plates and so on. Among them, an assembly of membrane and electrodes (MEA) is one of core components for producing electricity. In general, because PEMFC operates under the temperature of 100 °C, liquid phase water coexists with reactants and gas phase water.

In PEMFC system, water plays a critical role in proton conduction. Though high water content in the membrane is desirable for high proton conduction, excess water can be easily condensed to liquid phase water in the electrode and gas diffusion layer. This liquid phase water can dramatically decrease the fuel cell performance by hindering gas diffusion as well as by covering the active sites of the electro-catalysts. To get stable and good fuel cell performance the water contents in the PEMFC system should be precisely controlled.

When PEMFC systems operate, hydrogen and air are usually supplied with relatively humid condition to the cells. The humid reactants can supply the desired water and reduce the excessive evaporation of water on both the anode and cathode sides. However, from an efficiency standpoint, it is difficult to supply fully hydrated air except in some specialized cases. Therefore, during operation of the fuel cells, the cathode side is generally in the relatively dry condition. This means that water-related research should be focused on effective water management under relatively dry cell operating conditions [1].

At the cathode GDL of PEMFC, the most amount of product water moves in the direction of the flow channel by gas-phase diffusion or liquid-phase transport. When the cathode air is humidified, the product water vapor is impeded from diffusing out of the GDL. As a result, partial or complete water condensation occurs when the humidified air is supplied at high electric load conditions. Therefore, the GDL is generally treated with PTFE to provide hydrophobicity to reduce water saturation and to aid in water transport. This means that the management of liquid phase water is important for high fuel cell performance [2,3]. The schematic diagram of water behavior in the PEMFC is shown in Fig. 1.

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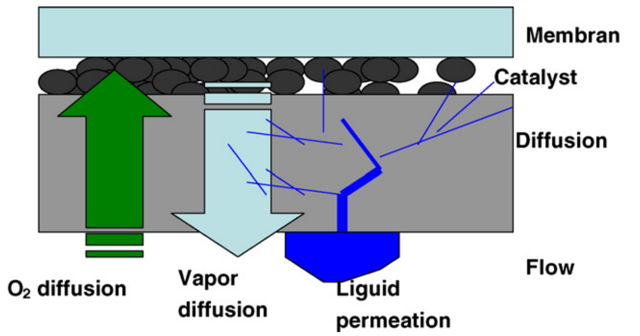

Fig. 1. Schematic diagram of water behaviors in a PEMFC cell. Reproduced from [1].

Carbon papers, carbon clothes and expanded and/or sintered metals have been widely used for the gas diffusion medium (GDM) materials [4,5]. The necessary conditions for the proper GDLs can be summarized with respect to an electric conductivity, water and gas transportations and corrosion resistance. In previous work, the GDM and micro-layer (ML) were investigated separately to determine which kind of driving forces (capillary, shear or evaporation) are more dominant for controlling water transport as well as affecting cell performance.

Table 1
Physical properties of carbon materials

Materials	Surface area ($m^2 g^{-1}$)	Dimension	Purity (%)
Vulcan XC 72	254	Diameter: 30 nm	–
Black Pearl 2000	1500	Diameter: ≤30 nm	–
Carbon nano-tube	196	Diameter: 20–30 nm Length: ≤10 μm	≥85
Carbon nano-fiber	113	Diameter: 70–100 nm Length: ≤30 μm	≥93

As seen in Fig. 2, Park et al. showed the effect of micro-layers on the PEMFC performance at various test conditions [6]. The micro-layer enhanced water management as well as cell performance.

In designing of GDLs, electric conductivity and gas permeability as well ability of water management should be considered simultaneously. The major roles of micro-layers which are applied to the GDM are lowering electric contact resistance, enhancing gas distributions and water management. As shown in Fig. 3, the mere GDM have the highest air permeability, but the ability of water management and electric conductivity is poor. In this figure, the area of each triangle can be interpreted as a

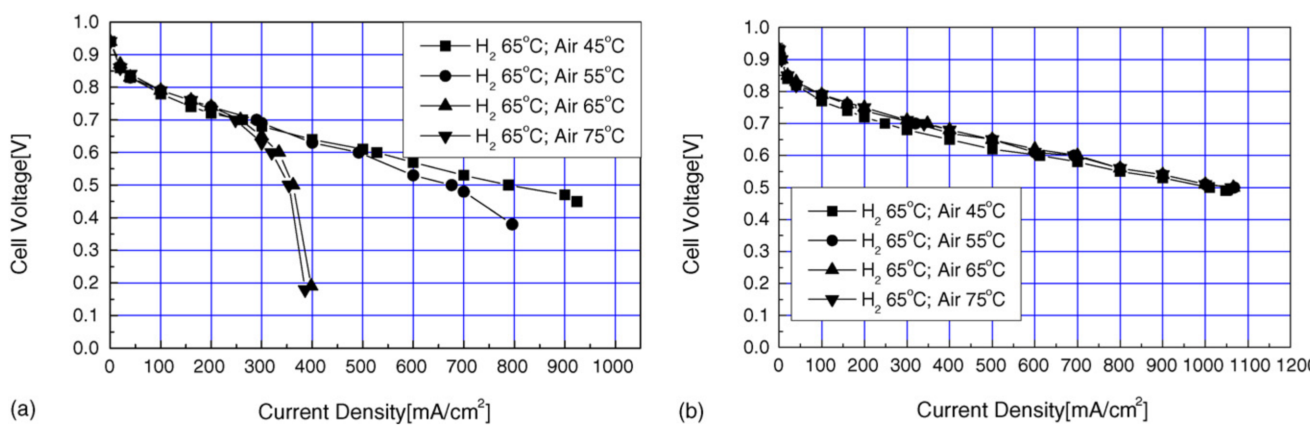

Fig. 2. Effect of micro-layer on the *I–V* performance of PEMFC. (a) GDM only, (b) GDM with micro-layer. Active area: 50 cm^2, cell temperature: 60 °C, fuel utilization: H_2 = 80%, air = 40%, Pt loading: anode = cathode = 0.3 mg cm^{-2}, operating pressure: anode = cathode = 0 psig. Legend means the temperature of humidifier [4].

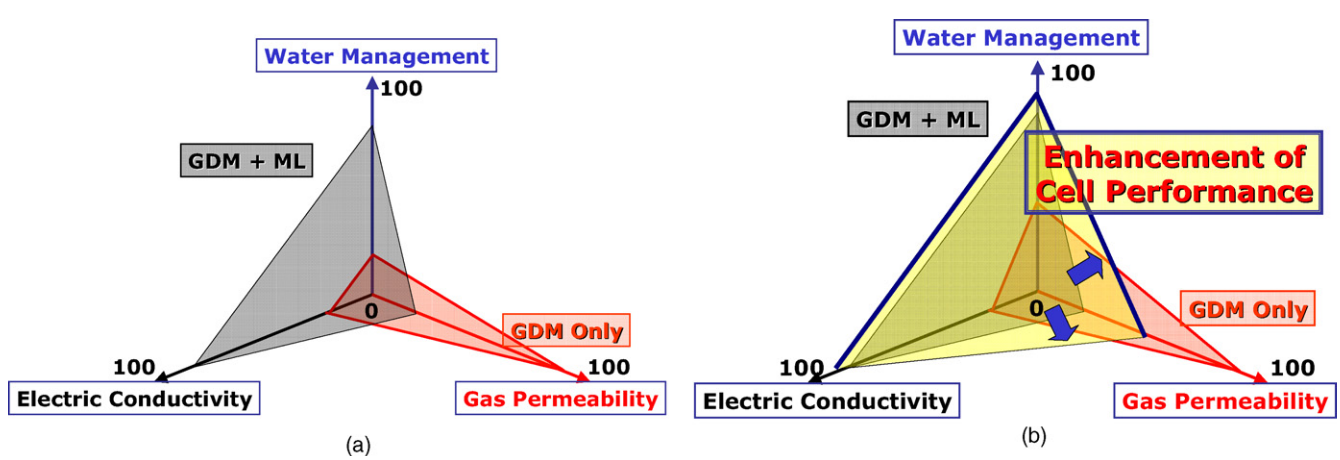

Fig. 3. Schematic diagram on the effect of micro-layers in GDLs. (a) comparison between GDM only and conventional GDL, (b) expected performance enhancement by adopting nano-materials for micro-layers.

cell performance. As comparisons, micro-layer coated GDMs show better electric conductivity and ability of water management revealing inferior gas permeability to mere GDM.

As shown in Fig. 3, optimized GDLs should be designed based on the three concepts, i.e. high electric conductivity with good water management as well as higher gas permeability. To get this property, micro-layer should be coated on the GDM as thin as possible keeping higher electric conductivity.

In this study, to make thinner micro-layers with similar electric conductivity, carbon nano-fibers and carbon nano-tubes were adopted. In general, carbon nano-fibers and carbon nano-tubes show higher electric conductivity about 10 times order of magnitude compared to ordinary carbon blacks. This intrinsic property makes it possible to expect that the prepared GDLs have thinner micro-layers with similar electric conductivity.

2. Experimental

Vulcan XC72 (Cabot) has been widely used for micro-layers in GDLs. In this work, Black pearl 2000 (Cabot), carbon nano-tube and carbon nano-fiber(Carbon nanotech, Korea) were selected for the raw materials of micro-layers. In Table 1, the physical properties of carbon materials were summarized. Black pearl 2000 has much larger surface area compared to Vulcan XC 72 with smaller particle diameter. Carbon nano-tube and carbon nano-fiber show smaller specific surface area than carbon blacks.

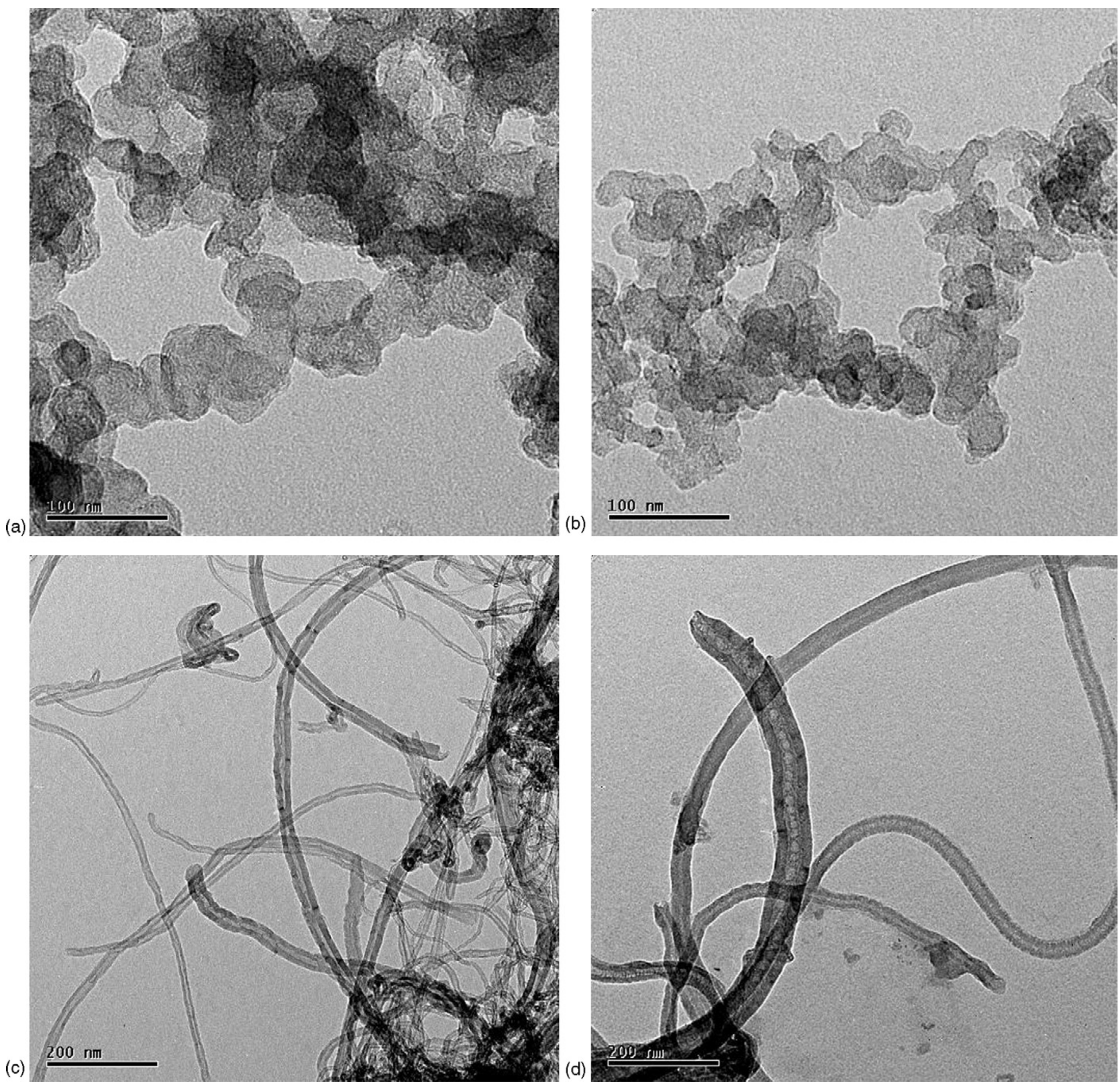

Fig. 4. TEM images of carbon materials. (a) Vulcan XC72, (b) Black pearl 2000, (c) carbon nano-tube, and (d) carbon nano-fiber.

Table 2
Physical properties of prepared GDLs

GDLs	ML Material	PTFE conc. in ML (%)	Thickness (μm)	Porosity (%)
CP 190-5	NO	–	195	77.5
V100	Vulcan XC72, 100%	25	320	77.0
BP2000	Black Pearl 2000, 100%	25	250	76.3
CNF100	CNF, 100%	25	330	70.1
CNF25V75	CNF: Vulcan = 25:75	25	215	74.2
CNF50V50	CNF: Vulcan = 50:50	25	230	73.0
CNF75V25	CNF: Vulcan = 75: 25	25	215	71.2

Where, all the micro-layers (ML) are coated on the CP190-5 GDM. Porosity = $(V_{total} - (V_{carbon} + V_{PTFE}))/V_{total}) \times 100$.

Their shape is linear and the carbon nano-fiber has longer chain than that of carbon nano-tube.

The dimensions of carbon materials can be seen by TEM in Fig. 4. Carbon black samples look like balls and Vulcan XC 72 shows larger diameter than that of Black pearl 2000. Carbon nano-tube and nano-fiber maintains a relatively uniform shape.

GDLs were fabricated by using carbon blacks, carbon nanotubes, nano-fibers and mixture of them. Carbon papers from Toray (TGP-H-060) was used for GDM material. As-received carbon papers were washed in aqueous acetone solutions to remove dusts or undesirable things. The dried carbon papers were dipped entirely in the PTFE solution for 30 s and dried again at room temperature for 5 h. After then, the samples were heat treated in four steps of temperature (80, 110, 290 and 350 °C) in air environment.

Carbon materials which have various combinations were made to slurry for the micro-layers of GDLs. In Table 2, physical properties of prepared GDLs were depicted for the several samples.

The prepared GDLs were evaluated by single cell in the various operating conditions. Prior to attaching the electrode

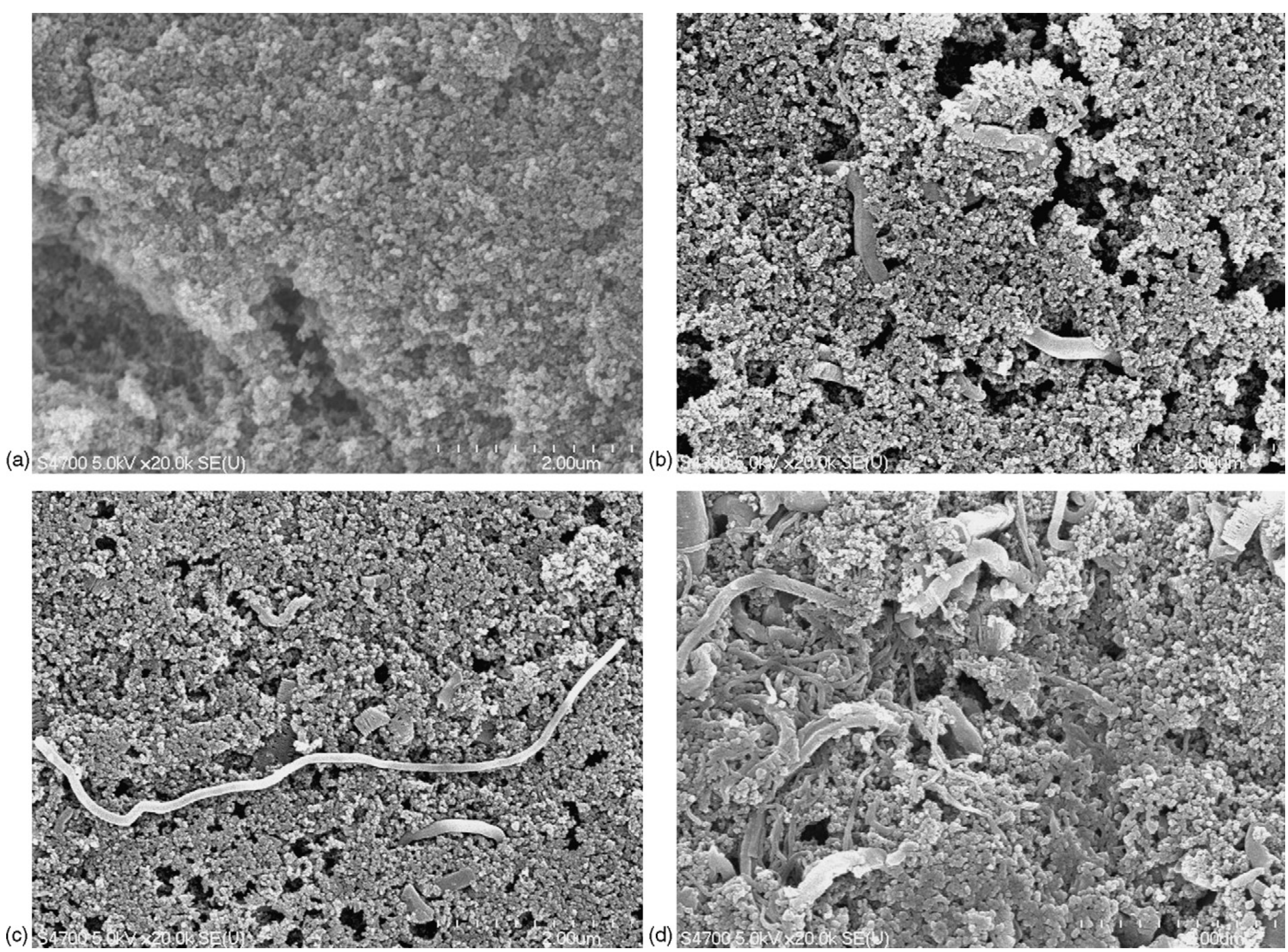

Fig. 5. SEM images of prepared GDLs; 20,000× magnification. (a) V100, (b) CNF25V75, (c) CNF50V50, and (d) CNF75V25.

layers, the Nafion 112 (Du Pont) membrane was pretreated with H_2O_2 and H_2SO_4 solutions step by step to remove the remaining organic and inorganic contaminants [7]. A 40 wt.% Pt/C electrocatalyst (Johnson Matthey) and 5 wt.% Nafion solution (Du Pont) were used to make electrodes for both the anode and cathode. The resulting membrane electrode assembly (MEA) had platinum loadings of 0.3 mg Pt cm^{-2} for the both sides of anode and cathode. The active area of MEA was 50 cm^2.

The water behavior in the prepared GDMs was analyzed by evaluation of PEMFC single cells. The assembled single cells were tested at the various relative humidity by changing the combination of cell and humidifier temperature. All tests were conducted at atmospheric pressure and the utilizations were controlled to 80% and 40% for hydrogen and air, respectively.

3. Results and discussion

The fabricated GDLs were investigated visually by SEM. In-pane SEM images of GDLs are shown in Fig. 5. Only ball shape carbon blacks are seen in (a) V100. When the carbon nanofibers are mixed with carbon blacks, wire-like carbon nano-fibers can be seen in the carbon black layers. In some parts of microlayers, kitting ball-like carbon nano-fibers which keep tangled are observed. As being expected, the highest population of carbon nano-fibers can be seen in (d) CNF75V25.

Air permeability of through-plane direction also measured for fabricated GDLs. In Fig. 6, the comparison of air permeability for the samples with and without micro-layers can be seen. CP190-5 showed much smaller pressure drop (ΔP) than microlayer containing GDLs. Even, at the flow rate of 10 L min^{-1}. the value differences of ΔP between them are exceed order of magnitudes. Among the micro-layer coated GDLs, CNF25V75 showed the highest air permeability. As summarized in Table 2, this result can be explained by higher porosity and thinner thickness of GDL. Commercially available SGL 31BC also compared at Fig. 6.

Single cell performances were evaluated by using prepared GDLs. In Fig. 7, the performance looks like that there exists much relationship between *I–V* performance and air permeability. CNF25V75 and SGL 31BC show the better performance than that of other GDLs. The two GDLs also showed higher air permeability in Fig. 6. Besides its good air permeability, CP 190-5 showed inferior performance to CNF25V75 and SGL 31BC. This is an evidence that not only air permeability but also electric conductivity as well as ability of water management can affect to the fuel cell performance.

For CNF25V75, the effect of relative humidity on the *I–V* performance was evaluated. The performance was evaluated from slightly dry to wet condition of cells. In this range of operating condition, there were no significant performance differences. This means that CNF25V75 does well water management in the whole operating range. The results of Figs. 7 and 8 can be understood that the carbon nano-fibers which are mixed with carbon blacks can be successfully applied to the micro-layers of GDLs.

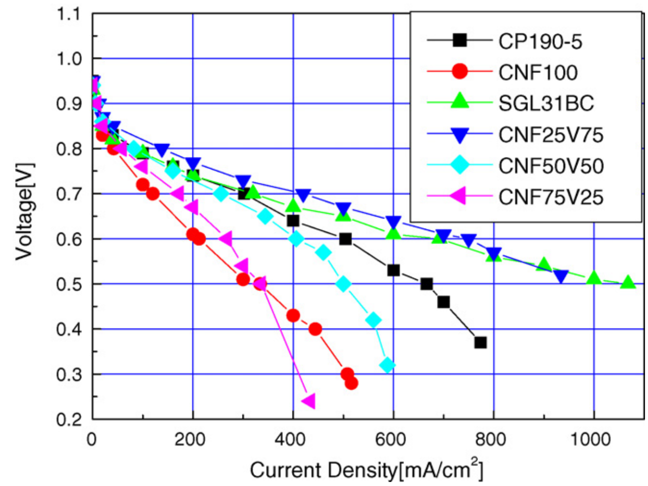

Fig. 7. Comparison of *I–V* performances for the different GDLs. Active area: 50 cm^2, cell temperature: 60 °C, fuel utilization: H_2 = 80%, air = 40%, Pt loading: anode = cathode = 0.3 mg cm^{-2}, operating pressure: anode = cathode = 0 psig.

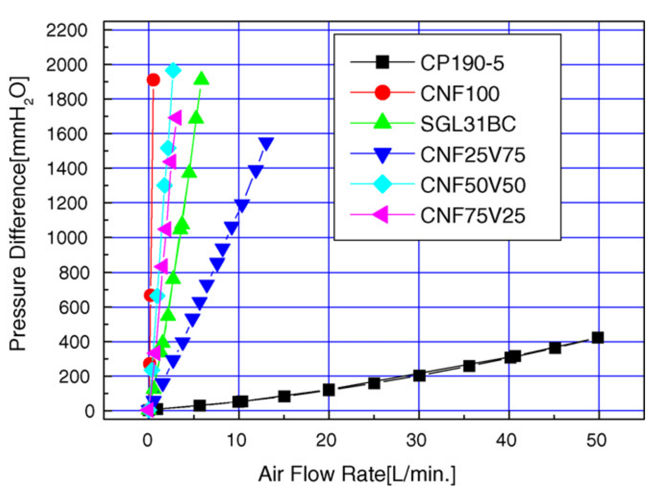

Fig. 6. Comparison of air permeability for the prepared samples.

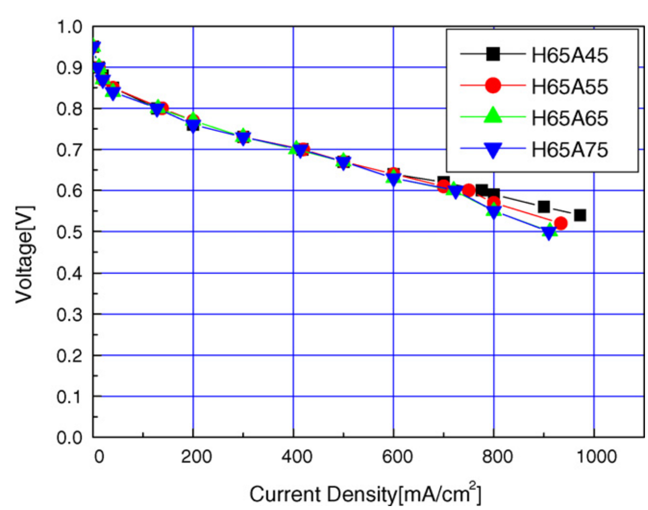

Fig. 8. *I–V* performance of CNF25V75 at the different relative humid condition. Legend means the temperature of humidifier.

4. Concluding remarks

Carbon nano-fiber and carbon nano-tube were adopted for the micro-layers of GDL. Various micro-layers which have different weight ratios of carbon nano-fiber to carbon black were coated on the PTFE treated carbon papers. The fabricated GDLs were investigated by visual measurements such as TEM and SEM. In the cell performance aspect, air permeability and *I–V* performance were analyzed to make the feedback information for finding out the optimum design parameters of micro-layer's structure. In this work, the 25% of carbon nano-fiber and 75% of Vulcan XC72 contained micro-layer case showed the best *I–V* performance. This result may be explained that the thinner micro-layers taken by adopting the carbon nano-fiber affect on the performance by enhancing the gas permeability and electric conductivity simultaneously maintaining the ability of water management.

Acknowledgements

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References

[1] J.H. Nam, M. Kaviany, Int. J. Heat Mass Transfer 46 (2003) 4595.
[2] J. Soler, E. Hontanon, L. Daza, J. Power Sources 118 (2003) 172.
[3] S. Gamburzev, A.V. Appleby, J. Power Sources 107 (2002) 5.
[4] T. Hottinen, O. Himanen, P. Lund, J. Power Sources 138 (2004) 205.
[5] J. Benziger, J. Nehlsen, D. Blackwell, T. Brennan, J. Itescu, J. Membr. Sci. 261 (2005) 98.
[6] G.-G. Park, Y.-J. Sohn, T.-H. Yang, Y.-G. Yoon, W.-Y. Lee, C.-S. Kim, J. Power Sources 131 (2004) 182.
[7] Y.-G. Yoon, T.-H. Yang, G.-G. Park, W.-Y. Lee, C.-S. Kim, J. Power Sources 118 (2003) 189.