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Effect of through-plane polytetrafluoroethylene distribution in gas diffusion layers on performance of proton exchange membrane fuel cells

Hiroshi Ito [a, *], Takuya Iwamura [a], Satoshi Someya [a], Tetsuo Munakata [a], Akihiro Nakano [a], Yun Heo [b], Masayoshi Ishida [b], Hironori Nakajima [c], Tatsumi Kitahara [c]

[a] *Research Institute for Energy Conservation, National Institute of Advanced Industrial Science and Technology (AIST), 1-2-1 Namiki, Tsukuba 305-8564, Japan*
[b] *Department of Engineering Mechanics and Energy, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan*
[c] *Department of Mechanical Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan*

HIGHLIGHTS

- We examined PTFE distribution in GDL substrate of polymer electrolyte fuel cells.
- The dependence of PTFE distribution on the drying conditions was examined with EDS.
- A uniform PTFE distribution in the GDL improved the performance at wet conditions.
- The effect of PTFE distribution in the GDL was important even when an MPL was coated.

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ABSTRACT

This experimental study identifies the effect of through-plane polytetrafluoroethylene (PTFE) distribution in gas diffusion backing (GDB) on the performance of proton exchange membrane fuel cells (PEMFC). PTFE-drying under vacuum pressure created a relatively uniform PTFE distribution in GDB compared to drying under atmospheric pressure. Carbon paper samples with different PTFE distributions due to the difference in drying conditions were prepared and used for the cathode gas diffusion layer (GDL) of PEMFCs. Also investigated is the effect of MPL application on the performance for those samples. The current density (i) – voltage (V) characteristics of these PEMFCs measured under high relative humidity conditions clearly showed that, with or without MPL, the cell using the GDL with PTFE dried under vacuum condition showed better performance than that dried under atmospheric condition. It is suggested that this improved performance is caused by the efficient transport of liquid water through the GDB due to the uniform distribution of PTFE.

1. Introduction

The critical component of a proton exchange membrane fuel cell (PEMFC) is the membrane-electrode assembly (MEA), which typically consists of a catalyst-coated membrane (CCM) and a gas diffusion layer (GDL) on both sides. In the CCM, a catalyst layer (CL) is coated and bonded on a proton exchange membrane (PEM) on both sides. The GDL is a critical component of a PEMFC, where its basic functions are effective transport of reactant gas to CL, drainage of liquid water into channels or keeping the PEM wet, high electric conduction between CL and the bipolar plates, and mechanical support of the CCM. In particular at the cathode, because water is produced by the reaction at the CL, the GDL functions related to water management, that is, attaining an appropriate balance of retention/exclusion of water, are essential for stable operation under a wide range of current density [1,2].

Relative humidity (RH) of the gases in the channel is an important parameter in evaluating the water management in a PEMFC. Recent commercialized fuel cell vehicles (FCV) [3] do not contain any individual humidifier due to cost reduction,

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* Corresponding author.
E-mail address: ito.h@aist.go.jp (H. Ito).

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conservation of parasitic energy, and simplifying and downsizing of the power system, when the inlet RH of cathode gas (air) might be relatively low. However, based on experimental results using fuel cells at a commercially available scale (50 cm^2), Mench et al. [4] and Yang et al. [5] revealed that the RH of cathode gas increases along the channel and sometimes reaches saturation near the exit even when the inlet RH is low (e.g., 20%), because product water is entrained in the flow channel. In particular, during the start-up period of FCVs, when the cell temperature is low and flooding tends to occur easily even at low current density, flooding should be carefully avoided at the cathode. Thus, the cathode GDL must retain its water management functions under a wide range of humidity conditions.

A basal substrate of GDL, called a gas diffusion backing (GDB), is made of materials that have high porosity and electric conductivity, such as woven carbon cloth, non-woven carbon paper, or non-woven carbon felt [6]. A GDL is generally composed of GDB coated with a hydrophobic microporous layer (MPL), which is usually a mixture of fine carbon particles and a hydrophobic agent. To improve their gas and water transport, GDBs are commonly treated with a hydrophobic agent such as polytetrafluoroethylene (PTFE) to increase the hydrophobicity.

The effect of PTFE content in carbon-paper GDLs without MPL (i.e., GDB) on the PEMFC performance has been experimentally examined [7–10]. In general, the addition of PTFE to the GDB reinforces the hydrophobicity of pores in the GDB, which can then improve the cell performance. However, excessive PTFE loading can reduce the pore size, making expulsion of liquid water from the pores more difficult. Those previous studies therefore concluded that there is an optimal PTFE content. Although the loading amount of PTFE was discussed in those studies [7–10], the PTFE distribution throughout the GDB in the through-plane direction was not examined.

Several recent works [6,11–15] have investigated the PTFE through-plane distribution in GDBs. Mathias et al. [6] reported that PTFE dispersion drying time can affect its distribution. Based on their measurements of PTFE through-plane distribution in relation to PTFE dispersion drying times, they reported that relatively slower drying times yielded higher concentrations in the interior of the GDB, whereas relatively faster drying times yielded higher concentrations near the surface. Quick et al. [11] prepared several carbon felt samples of PTFE treated with different drying times (the same drying times as those used by Mathias et al. [6]), and examined the effect of PTFE through-plane distribution on the water transport rate via GDB using an ex-situ measurement apparatus. Their results revealed that the GDB with PTFE that was dried slowly shows higher water transport rate than that with PTFE dried rapidly. Although their measurements were comprehensive, they did not present any observation of the PTFE distribution [11]. Fishman and Bazylak [12] measured the porosity through-plane distribution of carbon-paper GDB using micro-scale computed tomography (μCT) imaging. Based on comparison of porosity distribution between GDB samples with and without PTFE treatment, PTFE preferentially accumulated at the local area in the through-plane direction near the surface [12]. Rofaiel and Bazylak et al. [13] measured the heterogeneous through-plane PTFE distribution for different types of GDB (paper, felt, and cloth) using scanning electron microscopy (SEM)-based energy dispersive X-ray spectroscopy (EDS) imaging. They reported that the morphological features of untreated GDB significantly affect the PTFE distribution. Based on two-phase model calculation results, Kang et al. [14] correlated the profile of liquid water saturation with that of PTFE content throughout the GDB, and reported that the centrally located saturation peaks in the through-plane profile can be attributed to relatively fewer PTFE-coated pores in the inner GDB region. Our previous study [15] investigated the relation between the pressure condition during drying period of PTFE and the resulting through-plane PTFE distribution in carbon paper using SEM-EDS analysis. Our results revealed that PTFE-drying under vacuum pressure created a relatively uniform PTFE distribution, whereas PTFE-drying under atmospheric pressure created highly heterogeneous PTFE distributions in the through-plane direction.

It is well known that the application of MPL on GDB improves mass transport through the GDL [16–18]. Several hypotheses about the role of an MPL have been suggested. For example, Weber and Newman [19] hypothesized that a capillary barrier acts as a valve to repel water from the cathode GDL and to accelerate back diffusion of water from the cathode to the anode through the membrane. Wang et al. [20] pointed out that in hydrophobic meso-pores (pore diameter: 0.05–7 μm), liquid water does not easily penetrate into the pore because it needs to overcome the surface energy. Consequently, hydrophobic meso-pores are dry (i.e., “open”), and thus can act as a gas transport path. Gostick et al. [21] indicated that the MPL contributes to lower water saturation in GDL when the water breaks through the GDL. In addition, previous studies have experimentally examined the effect of MPL properties on the cell performance, focusing on the type of carbon powder [20,22–24], content of carbon powder [25], PTFE content [26], and fabricating process [27]. Ramasamy et al. [28] comprehensively studied the effects of interaction between GDB and MPL on the cell performance using different types of GDB such as carbon cloth (Gore) and carbon paper (Toray and Sigracet). Their results indicated a strong and complex interaction between GDB and MPL, although no distinct trend was observed in the nature of this interaction with respect to the bulk properties of the tested GDB [28]. Lee et al. [29] visualized liquid water distribution in GDL with and without MPL using synchrotron X-ray radiography, and their observations indicated that the presence of the MPL significantly reduced the water content at the interfacial region between CL and GDL.

In order to understand the dynamic behavior of liquid water through the GDL, different types of measurements of water injection into GDL samples have been attempted by several researchers as an ex-situ approach [18,21,30–35]. In those studies, the measurement apparatus was specially designed depending on each objective. Benziger et al. [30] measured hydrostatic water pressure at breakthrough and water flow rate through various types of GDL. Gostick et al. [31] measured the relationship between capillary pressure and liquid water saturation in GDLs, and detected the water saturation at breakthrough using GDLs with and without MPL [21]; their data demonstrated that liquid water saturation in a GDL at water breakthrough is drastically reduced due to the presence of MPL as noted above. Lu et al. [32] measured the water pressure and liquid water saturation at the breakthrough condition using GDLs with and without MPL, and also visualized water breakthrough from above of the sample surface. It has been reported by Lu et al. [32] that water saturation of GDLs with MPL is definitely lower than that of GDLs without MPL, and a dynamic change in water breakthrough locations has been observed in GDLs without MPL but not in GDLs with MPL. Santamaria et al. [33] investigated the breakthrough pressure, droplet adhesion force, and detachment velocity in Toray carbon papers. Mortazavi and Tajiri [34] also measured the breakthrough pressure at Toray papers with different amounts of PTFE loading. Kitahara et al. [18,35] evaluated the contact angle of GDLs with MPL by combining capillary flow porometry (CFP) [36,37] and water injection, and revealed that the contact angle obtained by this combined method clearly increased with increasing PTFE content in MPL, whereas the contact angle observed by the sessile droplet method was almost identical for different amounts of PTFE [18].