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Effect of through-plane distribution of polytetrafluoroethylene in carbon paper on in-plane gas permeability

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HIGHLIGHTS

- The through-plane PTFE distribution in GDB was analyzed by SEM–EDS.
- PTFE drying under vacuum condition yielded a relatively uniform PTFE distribution.
- In-plane gas permeability was influenced by the through-plane PTFE distribution.
- The binder distribution in carbon paper was greatly different in Toray and SGL.

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ABSTRACT

In-plane permeability of gas diffusion backing (GDB) of proton exchange membrane fuel cells (PEMFCs) was investigated experimentally. Toray-paper and SGL-paper were selected as GDB test samples. Several Toray-papers were treated in-house with polytetrafluoroethylene (PTFE) using the immersion technique, dried either under atmospheric or vacuum pressure, and then sintered. The dependence of PTFE distribution in the through-plane direction on the PTFE drying conditions was examined using scanning electron microscopy (SEM)-based energy dispersive X-ray spectroscopy (EDS) imaging. The EDS image maps revealed that the PTFE distribution strongly depended on the drying condition, and PTFE drying under vacuum pressure yielded a relatively uniform PTFE distribution. The measured in-plane permeability suggests that the homogeneous distribution of PTFE achieved by the vacuum drying produces a porosity-leveling effect. In addition, the relationship between the in-plane permeability and porosity of the Toray-paper samples followed the Kozeny–Carman relation, whereas due to non-fibrous solids such as binder, that of the SGL-paper samples did not.

1. Introduction

During operation of a proton exchange membrane fuel cell (PEMFC), the oxygen reduction reaction rate at the cathode is the limiting kinetic step and determines the maximum operating current density. This rate strongly depends on the transport rate of oxygen from the flow channel to the catalyst sites. Although the electrolyte membrane needs liquid water to retain proton conductivity, the oxygen gas transport can be greatly hindered when liquid water accumulates either in the catalyst layer (CL) or the gas diffusion layer (GDL) of the cathode. Consequently, for optimal water management and performance in PEMFCs, water retention/expulsion properties must be carefully balanced.

The GDL, which is a porous medium located between the CL and the bipolar (flow channel) plate, plays a vital role in this water management. A basal substrate of GDL, called a gas diffusion backing (GDB), is made of either woven carbon cloth or non-woven carbon paper due to their high porosity and electric conductivity [1]. 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

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examined [1–8]. Studies [2–8] report that adding PTFE to the GDB can enhance the hydrophobicity of pores in the GDB, which can then enhance the cell performance under high humidity conditions, although excessive PTFE loading can reduce the pore size, thus making expulsion of liquid water from the pores more difficult. However, although the loading amount of PTFE was discussed in those studies [2–8], the PTFE distribution throughout the GDB in the through-plane direction was not examined.

Recent several works [1,9–13] have focused on the PTFE through-plane distribution in GDBs. PTFE can be applied to the GDB in several ways. Most commonly, the GDB is dipped into an aqueous PTFE dispersion and excess dispersion is allowed to drip off, then the remaining solvent is removed by oven drying, and finally the PTFE is sintered at above 350 °C. The advantage of this immersion method is that the PTFE loading amount can be controlled by simply adjusting the dispersion concentration. However, uniform distribution of PTFE is difficult to achieve by any PTFE-coating method due to the complex micro pore structure of GDB. Mathias et al. [1] reported that PTFE dispersion drying time can affect its distribution. Based on 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. Inoue et al. [9] supported these observations based on numerical analysis of the evaporation and phase change of PTFE during the drying process. Fishman and Bazylak [10] measured the porosity though-plane distribution of carbon-paper GDB using microscale 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 through-plane direction near the surface [9]. Rofaiel and Bazylak et al. [11] 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. In addition, Kang et al. [13] focused on the liquid water saturation profile through the GDL (GDB + MPL) obtained by Turhan et al. [14] and Manahan et al. [15] using the neutron radiography (NR) technique. Based on two-phase model calculation results, Kang et al. [13] 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.

Mathias et al. [1] suggested that diffusion is typically dominant transport mode in the through-plane direction in a GDL, while convective transport is dominant in the in-plane direction. In particular, mass transfer in an interdigitated flow field is primarily driven by the in-plane permeability, which might also influence significantly the cell performance in a serpentine flow field. Pharoah [16] indicated that the convective transport via the GDB is relevant even when an MPL is added, suggesting that in-plane permeability is a crucial factor in the cell performance in serpentine flow fields. The analytical study of Feser et al. [17] reinforced the importance of the in-plane permeability at the serpentine flow fields. Feser et al. [18] also measured the in-plane permeability of various carbon papers as a function of porosity using either gas or liquid as the working fluid. Gostick et al. [19] examined the permeability of the in-plane and through-plane directions for various types of carbon paper and cloth, and found the in-plane permeability to be twice as high as the through-plane permeability, agreeing with the observation reported by Ihonen et al. [20]. Kitahara et al. [21] also measured the permeability of the in-plane and through-plane directions for carbon-paper GDL with and without MPL, and reported a correlation between the in-plane permeability and the thickness of the MPL penetrating the GDB. Banerjee and Kandlikar [22] reported the in-plane permeability of various GDBs at elevated temperatures up to 90 °C. They [22] also reported that in-plane permeability significantly decreases with PTFE loading. However, no previous studies have considered the correlation between in-plane permeability and the through-plane PTFE distribution.

Our goal in the present study was to verify the relationship between the in-plane permeability of a carbon-paper GDB and the through-plane distribution of PTFE. We did this by examining the effect of different drying conditions of PTFE dispersion on PTFE distribution in carbon-paper GDB by using EDS analysis. First, carbon-paper GDB samples were prepared using the immersion technique in which PTFE was loaded under different drying conditions, namely, vacuum pressure (vacuum-dried) and atmospheric pressure (air-dried), because previous studies pointed out [1,9] that this drying process is important for controlling the PTFE distribution in the through-plane direction of the GDB substrates. Then, the in-plane permeability of the samples was determined and compared with samples without PTFE loading. Finally, the relationship between in-plane permeability and porosity of the samples was evaluated based on the Kozeny–Carman relation.

2. Experiments

2.1. Sample preparation

Three commercial products available for carbon-paper GDBs of PEMFCs were selected for comparison and did not have any additional layer such as an MPL: Toray-paper (TGP-H-090) and SGL-paper (34AA and 34BA). A total of five samples were prepared as summarized in Table 1: (1) Toray-paper not treated with PTFE (sample CT0), (2) Toray-paper treated with PTFE under air drying conditions (CT1), (3) Toray-paper treated with PTFE under vacuum drying conditions (CT2), (4) SGL34AA not treated with PTFE (CS0), and (5) SGL34BA loaded 5 wt.% PTFE (CS1). Note that the PTFE treatment process for SGL34BA is unknown because PTFE was applied by the manufacturer. PTFE treatment for the Toray-paper samples (50 × 50 mm) was executed in-house as follows. Each sample was dipped into a 10 wt.% PTFE dispersion (D-210C, Daikin) for about 2 min, and then placed on a needle-point holder (Fig. 1). The size of PTFE particles in the dispersion is about 0.20 μm, which is sufficiently small compared with the fiber diameter (7–9 μm) or the pore diameter (>1 μm) of Toray-paper. The holder with the sample was immediately placed in a drying oven (VT220, Etak) at room temperature, and the oven was then heated immediately after the door was closed. (Due to its needle points, this holder allowed excess dispersion to drip off easily from the GDB during this drying process.) The oven was then heated to 100 °C in about

Table 1
GDB materials and properties in the present study.

Notation	Material	Initial porosity (ε_0)	Initial thickness (h_0) [μm]	PTFE loading [wt.%]	PTFE drying condition
CT0	Toray 090	0.762	305	–	–
CT1	Toray 090	0.724	305	14.6	Air
CT2	Toray 090	0.719	305	14.3	Vacuum
CS0	SGL34AA	0.812	283	–	–
CS1	SGL34BA	0.809	292	5	