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Application of a self-supporting microporous layer to gas diffusion layers of proton exchange membrane fuel cells

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HIGHLIGHTS

- A self-supporting MPL was fabricated and applied to a GDL of a PEMFC.
- The MPL thickness and interface of MPL/carbon paper could be controlled precisely.
- Carbon paper free MPL showed better performance than did the integrated GDB/MPL GDL.
- Low thermal conductivity of MPL would cause vapor diffusion through MPL.

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ABSTRACT

The intrinsic effect of properties of a self-supporting microporous layer (MPL) on the performance of proton exchange membrane fuel cells (PEMFCs) is identified. First, a self-supporting MPL is fabricated and applied to a gas diffusion layer (GDL) of a PEMFC, when the GDL is either an integrated sample composed of a gas diffusion backing (GDB, i.e., carbon paper) combined with MPL or a sample with only MPL. Cell performance tests reveal that, the same as the MPL fabricated by the coating method, the self-supporting MPL on the GDB improves the cell performance at high current density. Furthermore, the GDL composed only of the MPL (i.e., GDB-free GDL) shows better performance than does the integrated GDB/MPL GDL. These results along with literature data strongly suggest that the low thermal conductivity of MPL induces a high temperature throughout the GDL, and thus vapor diffusion is dominant in the transport of product water through the MPL.

1. Introduction

Due to their relatively low operating temperature (<80 °C), proton exchange membrane fuel cells (PEMFCs) have numerous advantages in their set-up and operation, such as ease of material selection for the cell components, fast start-up, and excellent transient characteristics. Conversely, because of this low operating temperature, PEMFCs also have drawbacks, such as requirement of noble metal catalysts and the presence of excessive liquid water in the cell.

When PEMFCs operate as vehicle power sources, special attention should be paid to water management during "start-up" periods. Because the cell temperature does not reach its rated temperature (~70 °C) during start-up, the produced water condenses and accumulates in the cell. This accumulated liquid water prevents continuous reaction in the cell before the cell can reach its rated operation. Thus, effective water management that enables stable operation under a wide range of current density even at lower temperature (<50 °C) is essential for stable operation of fuel cell vehicles (FCVs).

A gas diffusion layer (GDL) is a critical component in water management (i.e., an appropriate balance between retention and discharge of water) in PEMFCs, where its basic functions are (1) effective transport of reactant gas to the catalyst layer (CL), (2) either drain liquid water into channels or maintain a wet PEM, and (3) promote high electric conduction between the CL and bipolar plate. Particularly at the cathode, the GDL functions related to water management are essential for stable operation under a wide range

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Nomenclature

Symbols

D_{eff}	effective gas diffusion coefficient, $m^2\ s^{-1}$
d_p	pore diameter, m (μm)
i	current density, A m^{-2}
k	thermal conductivity, W $m^{-1}\ K^{-1}$
RH	relative humidity, %
R_{ohm}	ohmic resistance of cell, Ω cm^2
T_{cell}	cell temperature, K (°C)
T_{gas}	dewpoint of introduced gas, K (°C)
V	cell voltage, V
ΔP	differential pressure, Pa
ΔP_{BT}	water breakthrough pressure, Pa
ε_b	overall bulk porosity
ε_{MPL}	porosity of microporous layer (MPL)
γ	surface tension, N m^{-1}
θ	contact angle, ° (degree)

Abbreviations

BPD	bubble point diameter
CCM	catalyst-coated membrane
CFP	capillary flow porometry
CL	catalyst layer
GDB	gas diffusion backing
GDL	gas diffusion layer
IPA	isopropyl alcohol
MIP	mercury intrusion porosimetry
MPL	microporous layer
OCV	open circuit voltage
OPE	octylphenol ethoxylate
PEMFC	proton exchange membrane fuel cell
PSD	pore size distribution
PTFE	polytetrafluoroethylene
SEM	scanning electron microscopy

of current density [1,2]. A base substrate of GDL, called a gas diffusion backing (GDB), is made of either woven carbon cloth, non-woven carbon paper, or non-woven carbon felt, due to their high porosity and electric conductivity [3]. A GDL is generally composed of a 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 also treated with a hydrophobic agent such as polytetrafluoroethylene (PTFE) to increase their hydrophobicity [4,5].

In typical fabrication of MPLs, ink slurry is prepared by mixing fine carbon powder, PTFE dispersion, and a small amount of dispersant such as isopropyl alcohol (IPA) or octylphenol ethoxylate (OPE). This slurry is coated onto a GDB substrate using a doctor blade or spray method. Slurry-coated samples are dried and then sintered into a GDB/MPL assembly. Optimization of MPL properties has been extensively researched by focusing on carbon powder [6–10], PTFE content [11,12], thickness of the MPL [5,13], and fabrication process [14]. When the coating method is used in MPL fabrication, however, it is difficult to control and stabilize MPL properties such as thickness, pore diameter, and porosity. For example, MPL thickness strongly depends on the slurry and coating conditions, thus making it difficult to accurately determine this thickness because part of the slurry enters the pores in the GDB. In some cases, the GBD/MPL interface is extremely uneven and not clearly distinguishable [5,15–17]. As for pore diameter, it is well known that the surface of typical commercial products of MPL-coated GDL contain numerous cracks [3,15,18,19]. Because these cracks are randomly located and non-uniform in length and width, it is difficult to quantify the effect of cracks on the mass transport via GDL. Although directly measuring the porosity of MPL is also difficult, several researchers have estimated it [20,21].

Because a typical GDL is a GDB/MPL assembly, several studies have focused on the effect of GDB properties on the behavior of liquid water in a cell. Based on the output from a pore network modeling, Hinebaugh et al. [22] discussed the relation between the porosity distribution and liquid water saturation profile in GDB. Lee et al. [23] visualized liquid water distribution in a GDL with MPL using synchrotron X-ray radiography, and their results indicate that the amount of liquid water in the GDB region in GDL is higher than that in MPL. Our previous study [24] revealed that the uniform distribution of PTFE in the GDB facilitates the discharge of liquid water from the GDB even when MPL was applied to the GDB. Thus, to develop a robust GDL that is effective in a wide range of humidity conditions, the properties of both the GDB and MPL must be taken into account.

A recent noteworthy approach to develop a robust GDL is the application of a self-supporting MPL on the GDL. Bauder et al. [25] successfully manufactured a self-supporting MPL consisting of carbon particles and PTFE. Although details of their manufacturing procedure were not published, the mixture of carbon particles and PTFE was prepared without solvents or dispersants, and the dry-spraying technique was used to deposit the MPL onto the GDB. Researchers at Nissan Motor [26,27] also applied a GDL consisting only of MPL (i.e., GDB-free MPL) to the cell, and reported that the cell with GDB-free MPL showed significantly better performance than that with an integrated GDB/MPL GDL. Although again the details of the manufacturing procedure were not published, their MPL must be a type of self-supporting MPL. Here it should be noted that, in the case of Nissan Motor, the thickness of their GDB-free MPL (100 μm) was significantly smaller than that of the integrated GDB/MPL GDL (290 μm). The performance of a cell with GDB-free MPL whose thickness is comparable with that of a conventional integrated GDB/MPL GDL needs to be evaluated.

The crucial advantage of a self-supporting MPL is that its thickness can be accurately controlled during fabrication. In addition, because porosity and pore diameter of the MPL can be measured separately prior to being combined with a GDB, the uniformity of the MPL can be monitored and confirmed, thus reducing the variability among samples. Despite this advantage, concern exists that due to insufficient bonding between MPL and GDB, the ohmic resistance might increase or that significant amount of liquid water might accumulate at the interface between MPL and GDB.

The main motivation of this current work was to identify the intrinsic effect of MPL properties on cell performance, the same motivation behind the work of Bauder et al. [25]. First, a self-supporting MPL whose properties could be precisely controlled and accurately measured was fabricated and then combined with a GDB (i.e., carbon paper) to form a GDL. Based on reported excellent performance with GDB-free GDL [26,27], the thickness of the self-supporting MPL used as a GDL was set here as comparable with an integrated MPL/GDB GDL (~300 μm thickness). Second, several ex-situ measurements on the MPL were done to determine its porosity, pore size distribution, and water breakthrough pressure.