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Effects of hydrophobic agent content in macro-porous substrates on the fracture behavior of the gas diffusion layer for proton exchange membrane fuel cells

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HIGHLIGHTS

- Adhesion between MPS and MPL of a GDL has been measured for the first time.
- Adhesion enhancement mechanism was discovered by OM, SEM, and EDX.
- Higher PTFE contents in MPS led to better interaction between MPL and MPS.

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ABSTRACT

Although the adhesion between the macro-porous substrate (MPS) and micro-porous layer (MPL) of a gas diffusion layer (GDL) is a critical factor that affects the reliability and durability of proton exchange membrane fuel cells, systematic studies quantifying the interfacial fracture energy of GDL have not yet been reported. Therefore, in this study, the interfacial fracture energy of GDLs with different contents of hydrophobic agents in the MPS is quantitatively measured. GDL samples with 0, 5, 10, and 20 wt% of hydrophobic agent content are tested using double cantilever beam fracture mechanics tests. It is observed that the interfacial fracture energy of the GDLs increases as the content of hydrophobic agent increases, due to more favorable interactions between the hydrophobic agents of the MPL and MPS. Optical microscope, scanning electron microscope, and energy-dispersive X-ray spectroscope analyses are performed on the bare and delaminated surfaces in order to investigate the mechanism of the interfacial fracture energy increase of the GDLs.

1. Introduction

Due to the numerous advantages of proton exchange membrane fuel cells (PEMFCs), such as high power density, high efficiency, low operation temperature, low pollution, and low noise, they have been garnering significant attention for a wide range of applications including transportation, stationary, and portable applications [1–4]. Still, some issues must be resolved before PEMFC technology can be successfully applied in commercial uses. Researchers have focused on many PEMFC issues in order to improve its technology for better commercialization. These research topics have included performance improvement, durability, water management, and cost competitive materials [5–8]. More specifically, the membrane electrode assembly (MEA) and gas diffusion layer (GDL) are two critical components of PEMFCs that have been examined extensively in both academia and industry.

The GDL is typically composed of a micro-porous layer (MPL) and a macro-porous substrate (MPS) or backing [9–11]. In general, the MPL consists of carbon black powder and hydrophobic agent such as polytetrafluoroethylene (PTFE) or fluorinated ethylene-propylene [12,13]. The MPL provides better reactant gas transport and excessive water removal for PEMFCs and lowers the electrical contact resistance between the catalyst layer and GDL [14]. In contrast, the MPS is composed of hydrophobic agent and carbon fibers in the form of felt, paper, or cloth [15]. The MPS also has an important function in physically supporting the MEA, providing

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electron paths for flows between the catalyst layer and bipolar plate, and removing the excessive product water [16–18]. These GDL features should function well in order to improve the overall efficiency of PEMFCs, however, previous experiences in both academic and industrial fields have demonstrated that GDLs have weak fracture qualities and break very easily. Therefore, for the past decade, extensive studies have been conducted in order to investigate the long-term durability of the key components of PEMFCs, such as the MEAs and GDLs [19–22]. More efficient assessment of the critical parameters that affect the long-term durability of the fuel cell components under freeze-thaw or dry-wet cycling conditions is crucial to the commercialization of fuel cell vehicles because the conventional durability tests are costly and very time-consuming, i.e. up to several months. Thus, a deeper understanding of the fracture behavior of the MEA and GDL is very important in estimating the long-term durability of the components in actual fuel cells. Recently, Jia et al. [23] reported the effects of contamination and relative humidity (RH) on the fracture behavior of MEAs. On the other hand, systematic studies quantifying the adhesion strength between the MPL and MPS of the GDL in terms of interfacial fracture energy have not yet been undertaken and the primary factor in the fracture behavior has not been elucidated.

Therefore, in this study, a novel testing procedure for quantitatively measuring the interfacial fracture energy of the GDL is established using a double cantilever beam (DCB) fracture mechanics testing method. Then, this method is applied to several GDL samples in order to elucidate the effects of the hydrophobic agent content in the MPS on the interfacial fracture energy of the GDL.

2. Experimental

2.1. Materials and morphology characterization

In order to measure the interfacial fracture energy of the GDLs, four commercial carbon fiber felt-based GDLs (10AC, 10BC, 10CC, and 10DC) with different amounts of PTFE hydrophobic agent in the MPS (0, 5, 10, and 20 wt%, respectively) were obtained from SGL Technologies GmBH, Germany. An identical 'C'-type MPL was applied to all the four GDLs in this study and the PTFE content in the 'C'-type MPL is known to be 22.5 ± 2.5 wt% [24,25]. The thickness of each GDL sample was reported as the average and standard deviation values of 20 individual measurements using a digital micrometer (Mitutoyo Co., Japan). The key characteristics of the GDL samples, such as the GDL thickness, MPL presence, MPS type, and PTFE content in the MPS are listed in Table 1. Furthermore, in order to thoroughly examine the surface morphology of the GDLs, both an optical microscope (OM; Digital Microscope VHX-1000 Model, Keyence, Japan) and a scanning electron microscope (SEM; FE-SEM Sirion Model, FEI, USA) were used in this study.

All GDL samples in this study were composed of both MPLs and MPSs, and their morphologies for all GDLs used in this study were observed by SEM in Fig. 1(a–d). The same MPL that was also wet-proofed via a PTFE hydrophobic treatment was used for the four GDL samples. As explained in the introduction, the microstructure of the GDL is generally recognized as a combination of MPL and MPS. Technically speaking, however, there is an interfacial region between the MPL and MPS phases (i.e. a mixed layer) that is composed of mixed phases of both MPL and MPS as seen in Fig. 1(e) and (f). It was observed that the thickness of the mixed layer was relatively thick, and the border between the MPL and MPS phases was not clearly distinguishable.

Table 1
Key characteristics of the GDL samples.

GDL sample name	GDL grade name	GDL thickness (μm)	MPL presence	MPS type	Content of PTFE in MPS (wt%)
GDL-0	10AC	410 ± 8	Yes	Carbon fiber felt	0
GDL-5	10BC	436 ± 5	Yes	Carbon fiber felt	5
GDL-10	10CC	428 ± 5	Yes	Carbon fiber felt	10
GDL-20	10DC	425 ± 7	Yes	Carbon fiber felt	20

2.2. DCB test method

The DCB test is a fracture mechanics testing method that allows accurate quantitative measurement of the critical value of the strain energy release rate or fracture energy. In order to measure the interfacial fracture energy of the GDL specimens, the DCB test method was introduced in this study, and Fig. 2(a) and (b) present the schematics of the DCB specimen. The GDL samples were cut into the dimensions of 10 mm (width) by 40 mm (length) using a sharp razor blade. All GDL specimens for the DCB testing were cut carefully in order that the length direction of the GDL specimen was in parallel with the machine direction of the GDL roll. The rectangular GDL specimens were sandwiched by 3 mm thick polycarbonate (PC) substrates, as described in Fig. 2(a). Different adhesives were used to attach the GDL specimens to the polycarbonate, depending on whether the adjoining surface was MPL or MPS. For the MPL side, Epo-Tek 353ND (consisting of bisphenol F and imidazole; Epoxy Technology Co., USA) with a low viscosity was used, while 3M Scotch-Weld™ DP-420 (consisting of 2,4,6-tris((dimethylamino)methyl) phenol; 3M Co., USA) with high viscosity was used for the MPS side. The different adhesives were used due to the very different surface characteristics of the MPL and MPS. Compared with the MPL, the MPS surface contains relatively large pores (approximately several tens of micrometers) because it is primarily composed of carbon fiber felts, however, the MPL surface contains very small pores (less than micrometer-scale) and some small cracks. In order to induce a clear interfacial fracture path, the adhesives must penetrate into the MPL and MPS layers to a certain depth. Therefore, a low viscosity adhesive (353ND) is suitable for the MPL with small pores and cracks, while a high viscosity adhesive (DP-420) is suitable for the MPS with large pores.

Once the adhesives were applied to the PC substrates and the GDL specimen was sandwiched between the two PC substrates, a constant clamping pressure of 150 kPa was applied to the entire sandwiched unit followed by a curing process at 120 °C for 2 h in a convection oven. After curing the DCB test specimen, aluminum loading tabs were attached on top of the PC substrate surfaces using a commercial epoxy adhesive (DP-420), as illustrated in Fig. 2(b).

The DCB test was conducted using a high-precision micromechanical test system (Delaminator Adhesion Test System; DTS Co., USA). Fig. 3 presents the schematic of the DCB testing system used in this study. This test system was constructed of a linear actuator, loading grips, and a load cell (see Fig. 3(a)). The aluminum loading tabs attached to the DCB specimen structure were linked to the loading grip using steel pins (see Fig. 3(b)). This test procedure has been used extensively to measure the interfacial fracture energy of thin film structures [26–34]. During the DCB test, the specimen was loaded and unloaded under a constant displacement rate of approximately 2.5 μm s^{-1}. The constant displacement rate was determined using the range of other published papers [31,33].

3. Results and discussion

In the DCB tests of the GDL specimens, the crack length (a) and the interfacial fracture energy (G_c) can be calculated using the following equations [27,28]. In Eq. (2), G_c is defined as the critical value of the applied strain energy release rate (G):