



Investigation of the effect of a hydrophilic layer in the gas diffusion layer of a polymer electrolyte membrane fuel cell on the cell performance and cold start behaviour



Satoki Hirakata^a, Masanori Hara^a, Katsuyosi Kakinuma^b, Makoto Uchida^{b,*}, Donald A. Tryk^b, Hiroyuki Uchida^c, Masahiro Watanabe^{b,1}

^a Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4 Takeda, Kofu 400-8511, Japan

^b Fuel Cell Nanomaterials Center, University of Yamanashi, 6-43 Miyamae, Kofu 400-0021, Japan

^c Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu 400-8511, Japan

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ABSTRACT

The effect on PEFC performance of a gas diffusion layer (GDL) with a hydrophilic layer (HL) between the microporous layer (MPL) and the carbon paper (CP) was investigated at high and low humidity at normal operating temperatures and at subfreezing temperatures. Scanning electron microscopic examination and micro-Raman spectroscopic examination were carried out on the three-layer structure (MPL, HL and CP). In addition, high magnification SEM images of the samples showed that the HL had smaller pores than the MPL of the HL-GDL. Thus, we consider that the capillary pressure in the pores of the HL was higher than that in the MPL of the HL-GDL, which suggests that the HL can absorb more water. The performances of cells using the GDL with or without a HL were compared. The cell using a GDL with a HL showed a higher performance than a cell with a conventional GDL in the high current density region at both high and low humidity. At high humidity, the HL can absorb generated water, improving water removal from the catalyst layer (CL) to the GDL, and inhibiting the stoppage of gas diffusion by condensed water in the CL. At low humidity, the HL enhanced the water retention in the MEA, inhibiting the decrease of proton conductivity of the electrolyte by dehydration. A cell using a GDL with a HL also showed superior performance during cold startup from -10°C , due to water removal by the HL, inhibiting the blockage of gas diffusion by condensed or frozen water in the CL. These results indicate that an HL placed between the MPL and the carbon paper of the GDL can improve the PEFC performance over a wide range of operating conditions, including high and low humidity at normal temperatures and cold startup from subfreezing temperatures.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been focused upon as efficient power sources for electric vehicles, residential cogeneration systems, and portable devices. However, in order to popularize PEFCs, the improvement of performance over a wide range of operating conditions, including high and low humidities and cell temperatures ranging from subfreezing to normal operating temperature, is required.

The issue of water management at normal operating temperature (for example, 80°C) has been investigated intensively, and various improvements in cell construction have been proposed to

deal with the wide range of possible ambient humidities [1–8]. At high humidity, generated water can condense, blocking the air supply, while at low humidity, water loss can lead to membrane drying and decreased proton conductivity. Therefore, it has been necessary to design special types of gas diffusion structures that are immune to both flooding and drying [1,2].

Furthermore, during startup at subzero temperatures, the freezing of water generated by oxygen reduction in the cathode is an important issue, and various approaches have also been proposed to alleviate the problems caused by the resulting ice, which plugs the gas diffusion networks in the air cathode, leading to cell voltage degradation [8–15]. Since the PEFC should be able to be operated under all of these conditions, the development of better solutions for water management in the membrane-electrode assembly (MEA) are needed to cover all conditions.

The polymer electrolyte membrane, electrocatalysts, proton-conducting binder and gas diffusion layers (GDLs) constitute the MEA and work together to determine the PEFC performance. The

* Corresponding author. Tel.: +81 55 254 7095; fax: +81 55 254 7095.

E-mail addresses: uchidam@yamanashi.ac.jp (M. Uchida), m-watanabe@yamanashi.ac.jp (M. Watanabe).

¹ Tel.: +81 55 254 7091; fax: +81 55 254 7091.

GDL is the principal component used for the maintenance of reactant gas diffusion capability as well as the wetting of the proton-conducting electrolyte; thus, it can provide the key to improving the PEFC performance under various conditions such as high or low humidity and subfreezing temperatures.

Various types of useful information concerning GDLs have been summarized recently [1,2]. The most common type of GDL is composed of hydrophobically treated carbon paper (CP) and a microporous layer (MPL), which contains carbon powder. The carbon paper substrate can function as a gas diffuser and as a mechanical support for the electrode. The MPL can reduce the contact resistance between the catalyst layer (CL) and CP due to the fact that it forms a flat, uniform layer. The effects of various materials used for MPLs on PEFC performance have been examined. Jordan et al. [3] investigated the effect of carbon morphology in the GDL with Vulcan XC-72R and acetylene black on PEFC performance. For example, a cell using a GDL with a low pore volume acetylene black carbon exhibited better performance compared with a cell using a GDL with Vulcan XC-72R carbon black. These results show that the thickness, PTFE content and morphology are important for cell performance. Park et al. [4] examined the effect of carbon loading in the MPL on PEFC performance. Their AC impedance study also showed that an optimized MPL can lead to effective water management. Recent research on GDLs using hydrophilic and hydrophobic MPLs has focused on the improvement of removal and retention of generated water under high and low humidity conditions, respectively. Various researchers have investigated the effects of GDLs with hydrophilic/hydrophobic double MPLs [5–7]. Chun et al. [5] reported that a modified GDL, which contained a hydrophilic layer (HL) between the CP and a hydrophobic MPL, exhibited better performance than a conventional GDL at high and low humidity. However, there have been few reports concerning the effect of these GDLs on the PEFC performance under the full range of operating conditions, including both normal operating temperatures and subfreezing temperatures.

The understanding of the PEFC performance during cold startup is very important for applications for electric vehicles, and therefore many researchers have focused on this aspect. Degradation related to the GDL by the freezing of generated water is an important concern [16–22]. It was reported that the freezing of generated water can lead to increased ohmic and mass transport losses, due to delamination of the cathode CL and GDL, as well as the collapse and densification of the cathode CL [16]. Also, it was explained that freeze-thaw cycles between 20 and -30°C for fully hydrated MEAs caused cracks and catalyst domain segregation [17]. In order to understand the mechanism and location of degradation within the MEA during PEFC cold startup, various visualization approaches have been employed [13,23–25]. These experiments showed the locations of ice and the presence of super-cooled water.

Several experimental approaches for the improvement of PEFC cold start performance have been proposed [11,14,15,26]. However, there are few studies that have focused on the effect of the GDL on the improvement of PEFC cold start performance.

In our previous research, we have focused on such a strategy, examining the effects of the pore structure of the GDL on PEFC performance under standard and subfreezing temperature conditions [8]. A GDL with a smaller average pore diameter improved the anti-flooding performance under high humidity conditions and also improved the cold startup performance from -5°C . However, it did not improve the performance for cold startup from -10°C .

In the present research, we have focused on the effect of a GDL with a HL placed between the MPL and the CP. Because the HL can absorb the generated water from the CL, it was expected that this GDL could improve the performance of water removal and/or retention. Under both high humidity and subfreezing conditions, generated water can condense easily, and thus, the improvement

of water removal is expected to alleviate the blocking of gas diffusion by condensed water in the CL. Under low humidity conditions, water can vaporize easily, and thus, the improvement of water retention by the HL is expected to inhibit dehydration and decreased proton conductivity of the electrolyte. In this paper, the effect of the GDL with HL (HL-GDL) on the PEFC performance has been investigated, not only under standard temperature conditions but also under subfreezing conditions.

2. Experimental

2.1. Characterization of GDLs

The HL-GDL and conventional GDL (24BDL3 and 24BCH, MFC-Technology, Inc., SGL Group) were used in this research. The compositions of these materials are proprietary, but we have obtained permission from the manufacturer to analyze them. The cross-sections of these GDLs were observed by scanning electron microscopy (SEM, FEI Quanta 200 FEG, FEI Company).

In addition, the cross-sections were examined by Raman spectra recorded by a confocal micro-Raman instrument (LabRAM HR-800 spectrometer, HORIBA Jobin Yvon Ltd). The Raman spectra were obtained by excitation with the radiation from a He–Ne laser (632.8 nm) operated at approximately 2 mW. The Raman spectroscopic measurements were carried out with a 100 \times magnification objective and a 100- μm confocal aperture for the sample illumination. The collection of the scattered light was performed with a 600-line mm^{-1} grating and a Peltier-cooled CCD camera as a detector. The instrument control and spectral analysis were performed with the software programs Labspec 5 (HORIBA Jobin Yvon Ltd.) and GRAMS/AI 8.0 (Thermo Scientific).

2.2. Preparation of membrane-electrode assembly (MEA) and experimental cell

The catalyst pastes were prepared by the same method described previously [8]. Gas diffusion electrodes (GDEs) with a geometric area of 29.2 cm^2 were prepared by forming the catalyst layer on the MPL side of the GDLs, spraying the catalyst paste using a pulse-swirl-spray apparatus (Nordson), and then drying at 60°C for 12 h. The Pt loading amounts for the gas diffusion electrodes with and without an HL were 0.42 and 0.46 mg/cm^2 , respectively. The MEAs were prepared by hot-pressing a commercial Nafion membrane (NRE212, DuPont, 50 μm thick) sandwiched between two GDEs at 140°C and 10 $\text{kg}\cdot\text{f}/\text{cm}^2$ for 3 min. The MEA was mounted into a Japan Automobile Research Institute (JARI) standard cell, which has carbon separators for both cathode and anode, with serpentine flow channels. In this paper, cells with or without an HL will be denoted as HL-cells or conventional cells, respectively.

2.3. Fuel cell operation

2.3.1. Electrochemically active surface area measurement

The effects of the presence or absence of the HL in the GDL on the electrochemically active surface area (ECSA) of the Pt catalyst at the cathode catalyst layer were examined by use of cyclic voltammetry (CV, PGST30 Autolab System, Eco-Chemie) at $T_{\text{cell}} = 80^{\circ}\text{C}$. Hydrogen and nitrogen maintained at either 100% RH or 53% RH were supplied to the anode and the cathode, respectively, by use of a cold start-compatible fuel cell performance evaluation station (Panasonic Corporation). Prior to obtaining the cyclic voltammogram, hydrogen (100 ml/min) and nitrogen (150 ml/min) were supplied to the anode and cathode at each humidity condition, respectively, and the cathode potential was swept from 0.08 to 1.0 V vs. anode at 20 mV/s , until the voltammogram was reproducible, to ensure complete cleaning of the Pt surface in the catalyst layer.

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