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Impact of micro-porous layer on liquid water distribution at the catalyst layer interface and cell performance in a polymer electrolyte membrane fuel cell

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HIGHLIGHTS

- Liquid water distribution at the cathode catalyst layer (CL) surface is observed.
- Performance deteriorates due to the liquid water accumulated on the CL surface.
- The MPL reduces liquid water accumulation between the CL and the MPL.
- Cold startup induces much water accumulation and temporary performance deterioration.
- A gas diffusion electrode with fine CL to MPL contact mitigates the flooding.

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ABSTRACT

In polymer electrolyte membrane fuel cells, a gas diffusion layer (GDL) with a micro-porous layer (MPL) gives better anti-flooding performance than GDLs without an MPL. To investigate the function and mechanism of the MPL to suppress water flooding, the liquid water distribution at the cathode catalyst layer (CL) surface are observed by a freezing method; in the method liquid water is immobilized in ice form by rapid freezing, followed by disassembling the cell for observations. The ice covered area is quantified by image processing and cells with and without an MPL are compared. The results show that the MPL suppresses water accumulation at the interface due to smaller pore size and finer contact with the CL, and this results in less water flooding. Investigation of ice formed after −10 °C cold start shut-downs and the temporary performance deterioration at ordinary temperatures also indicates a significant influence of the liquid water accumulating at the interface. The importance of the fine contact between CL and MPL, the relative absence of gaps, is demonstrated by a gas diffusion electrode (GDE) which is directly coated with catalyst ink on the surface of the MPL achieving finer contact of the layers.

1. Introduction

The polymer electrolyte membrane fuel cell (PEFC) is a promising power source for automobiles and distributed cogeneration systems (the so-called combined heat and power; CHP) with high efficiency and clean emission characteristics. For practical uses of PEFC, water flooding at high current density conditions is one of the major issues to be improved, because flooding deteriorates efficiency and maximum power output due to limiting the supply of reactants to the reaction area by the water accumulated in the cell. It is generally known that a micro-porous layer (MPL) contributes to better water removal from the cathode catalyst layer (CL) and to improvements in the cell performance [1–4]. The MPL introduces a fine carbon layer between the CL and gas diffusion layer (GDL), and has smaller pore sizes than the GDL. However, the precise mechanism of water transport phenomena arising with the MPL is not fully understood.

Early computational studies reported that the MPL improves water removal from the cathode GDL by increasing the hydraulic pressure differential across the membrane [1], and that the MPL acts like a valve that pushes water away from the cathode and towards the anode through the membrane [2]. Gostick et al.

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estimated the water saturation and capillary pressure for GDLs with and without an MPL from the measured conditions of the liquid water breakthrough at the porous layers, and suggested that the efficacy of the MPL is due to finite-size effects related to invasion percolation in thin GDLs where liquid water percolation through the MPL results in limited access of water to the GDL inlet face [5]. Owejan et al. compared the cell performance using various types of GDLs with and without MPLs, analyzed the vapor flux driven by the saturation pressure gradient in the cathode diffusion layer due to the temperature gradient, and proposed that the primary role of the MPL is preventing condensed water from accumulating near the cathode CL surface [6]. The impact of interfacial gaps between the CL and the MPL was also noted, and it was indicated that these gaps may act as water accumulation sites and prevent the reactant gases from reaching active sites in the CL [7–9]. The morphology of the CL and MPL surfaces has been characterized in detail [7], and the effects of the interfacial morphology on the ohmic, thermal, and mass-transport losses were investigated numerically [8,9]. To elucidate the mechanism of water transport phenomena experimentally, some work has attempted to visualize the liquid water in a PEFC [10–14]. For the cross-sectional visualization of the liquid water inside porous structures like GDL, published studies have commonly used neutron radiography [10,11] and X-ray radiography [12,13]. Vapor condensation and liquid water breakthrough in the porous structures at the surface of the CL were observed by environmental scanning electron microscopy [14]. Here, the experiments indicated that an MPL reduces the saturation level of water on the CL surface [11,13,14], however the spatial resolution of the liquid water visualization has been inadequate and the structure of the cells investigated are different from commonly-used cells.

Recently, the authors observed the cross-sectional distribution of liquid water in the vicinity of a cathode MPL by the freezing method and by cryo-scanning electron microscopy. The freezing method immobilizes the liquid water in the cell as ice forms by decreasing the temperature in a short time, and the cryo-SEM visualizes the ice distribution in the MPL at high resolutions at −150 °C [15]. The research has however not resolved a number of issues, including the effects of the MPL on in-plane distribution of liquid water at the CL surface and the overall cell performance, a better understanding of which would enable further advances in the water management.

This study observed the liquid water distribution at the cathode CL surface using the freezing method, and quantified the amount of ice covered areas on the surface of the CL with image analysis for various operating conditions using GDLs with and without an MPL. The cell performance was also measured, and the role of the MPL in suppressing water flooding is discussed by comparing the observed water distribution on the CL surface and the measured flooding characteristics. Further, the following two phenomena related to the impact of the MPL and the liquid water distribution at the CL surface on the tolerance to flooding were investigated experimentally. The authors have reported that the shutdown at −10 °C cold startup induces a temporary performance deterioration in the subsequent operation at ordinary temperature, and that this is caused by the liquid water melted from the ice formed at the interface between the cathode CL and the MPL [16]. To validate that there is a larger ice covered area, which potentially makes much water accumulate at the interface after the cold startup, the ice distribution on the CL surface after the −10 °C cold start shutdown was quantified and compared with the ice distribution after operation at ordinary temperatures. As the second related phenomenon, the effect of the interfacial nature between the CL and the MPL was examined by comparing the polarization curves of two types of MEAs with different structures of the CL and MPL interface.

2. Experiments and image analysis

2.1. Experimental apparatus and methods

A small single cell with an active area of 1.8 cm^2 (0.9 cm × 2.0 cm) was used to ensure simple assembly and disassembly, and rapid cooling of the cell for the freezing method. A photo of a bipolar plate of the cell is shown in Fig. 1, together with a photo of the arrangements inside the thermostatic chamber used for the rapid cooling. The bipolar plate is made of copper overlaid with gold, and has five straight gas channels; the width of the channels and the lands were 1.0 mm, and the channel depth was 0.5 mm. The bipolar plates with stainless-steel end-plates for the anode and cathode sides sandwiched a catalyst-coated membrane (CCM) in the center and gas diffusion layers (GDLs) on both sides. The CCM was GORE-TEX (PRIMEA 5570), and two types of GDLs were used: 235 μm thick carbon paper with a hydrophobic MPL (SIGRACET®GDL 25BC), which was used for both of the anode and cathode sides, and 190 μm thick carbon paper without an MPL (SIGRACET®GDL 25BA) for the cathode side. Pure hydrogen as the anode gas and air as the cathode gas were supplied in the same direction, and the gas humidity was controlled by the bubbler temperature. The cell was set in a thermostatic chamber (HITACHI, EC-25MTP) with a controllable temperature range of −40 to 100 °C, and the temperatures of the cell and the supplied gas were controlled by the chamber temperature. The cell resistance was measured by an alternating impedance meter at 1 kHz. The cell voltage, cell resistance, and the temperatures of both cell and supplied gas were recorded digitally.

The procedures of the experiments are outlined in Fig. 2. After a conditioning process to enhance the performance of the CCM, a dry purge, lasting until the cell resistance reached 0.16 Ω cm^2, with dry nitrogen was conducted to remove all liquid water from the cell, and then the cell performance was measured at 35 °C. In the performance measurements, the flow rates of the anode hydrogen and the cathode air were 100 and 400 standard cc min^{-1} (SCCM) respectively, and the cell and humidification conditions of the gases were: a cell temperature of 35 °C and bubbler temperatures of 35 °C (relative humidity of gases 100%) and 30 °C (RH 76%). Then, for direct observations of the inside of the cell, the operation was stopped and the water distribution was investigated with the freezing method [15,17]. In this method, the cell is cooled to −30 °C in the thermostatic chamber for about 30 min to capture the liquid water in ice form. It took less than 4 min for the cell to be cooled to 0 °C. The authors have confirmed that the water moved little during the cooling process in an experiment limited to determine this [17]. Thus, the freezing method immobilizes the condensed water in the cell and makes it possible to observe the water distribution directly from the ice distribution. The cell was disassembled into its

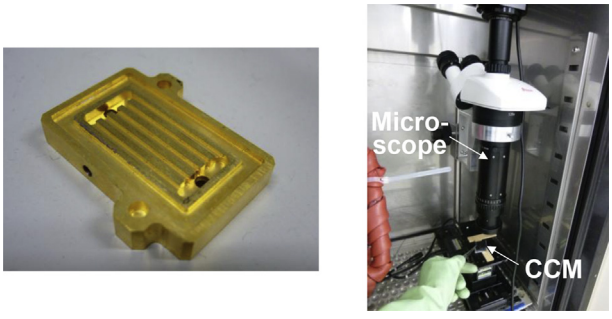

Fig. 1. The bipolar plate with straight channels used in the investigations here (left), and photo of the inside of the thermostatic chamber (right).