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Effect of glycerol on micro/nano structures of catalyst layers in polymer electrolyte membrane fuel cells

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Abstract

Effect of glycerol in catalyst ink on the micro/nano structures of polymer electrolyte membrane fuel cells (PEMFCs) catalyst layers was investigated. Catalyst layers were fabricated by the decal method for various mass ratios of glycerol to carbon in the catalyst ink r_{gc} (=m_g/m_c) from 0 to 20, and thus change the micro/nano structures of catalyst layer. The structures were evaluated by measuring the pore size with a mercury porosimeter and by observing the surface with a field emission scanning electron microscope (FE-SEM). At $r_{gc} < 5$, although the residual glycerol was almost zero, the cell performance decreased with decreasing r_{gc}, suggesting that the structure of the catalyst layers significantly depended on r_{gc}. At $r_{gc} > 5$, the remaining glycerol was proportional to r_{gc}. Because remaining glycerol blocks the pores and reduces the reaction sites, the cell performance decreased with increasing r_{gc}. If the remaining glycerol is removed by steam water, the performance is improved to the same level of the maximum performance for not steamed MEAs.

Keywords: MEA; Catalyst layer; Pore distribution; SEM; PEMFC

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered suitable candidates for power sources for transportation vehicles, either stationary or mobile applications, due to their high efficiency, high power density, and low operating temperature. The performance of PEMFCs is greatly affected by the properties of polymer electrolyte membranes (PEMs) and catalyst layers.

Significant effort has been expended to lower the platinum loading and to improve the performance of catalyst layers. In the mid 1980s, Ticianelli et al. [1] reduced the platinum loading to about 0.4 mg/cm^2 without degrading the cell performance by impregnating Nafion, perfluorosulfonate-ionomer (PFSI), into the gas diffusion catalyst layer. In the early 1990s, Wilson et al. [2,3] developed two fabrication methods for the electrodes of PEMFCs by mixing Pt-C particles and a PFSI solution into a catalyst ink. One method is to spray the ink directly onto a polymer membrane and then bake it, the other is the so-called decal method, where the catalyst ink is baked on a Teflon sheet and then assembled with a polymer membrane by hot-pressing. In both methods, the Pt loading is reduced to 0.12–0.16 mg/cm^2. Since then, numerous studies have reported further improvement in catalyst utilization. The ways to improve catalyst utilization could be divided into two categories. The one is to use new materials of catalyst layers, e.g. chemical modification of Pt-C [4,5], and the other is to optimize the structures of the catalyst layers by using different structured carbon particles [6], different organic solvents [7–9], different pore formers [10], different carbon/PFSI compositions [11–16], and fabrication methods [17–19]. In many of these studies, especially when the decal method was used, a viscous organic solvent such as glycerol was added to the catalyst ink to increase the paintability and stability. However, due to its high boiling point, the solvent apparently remains in the catalyst layers even after heat treatment [9]. If the solvent remains in the catalyst layers, it blocks the pores and prevents the continuity of carbon and PFSI, resulting in lowering gas access, proton access and electron access to the reaction sites.

The distribution of PFSI in catalyst layers and its effect on cell performance has been extensively studied [6–8,18,20–22], although few of these studies have experimentally studied the

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distribution of remaining glycerol or glycerol-like solvents, their effect on the structure of catalyst layers, and the resulting cell performance. Saab et al. [23] reported a difference in ionic and electronic resistivities of the catalyst layer before and after glycerol was extracted from the catalyst layers by water in the final fabrication process. Their experimental results showed that by extracting the glycerol, the ionic resistivity of the catalyst layer increased from 110 to 390 Ω cm, while the electronic resistivity decreased from 16 to 11 Ω cm. They attributed these results to the decrease in hydrophilicity. Chun et al. [24] investigated the effect of glycerol in catalyst ink on cell performance. They fabricated membrane electrode assemblies (MEAs) by the decal method combined with an ion exchange process and then hot-pressed the MEAs at 468 K for 1.5 min. The catalyst ink contained glycerol in the approximate ratio of 1/1 or 3/1 (wt.%) with 5% Nafion solution. Their experimental results showed that a catalyst ink containing highly concentrated glycerol decreases the cell performance, especially in the high current density region. They reported that glycerol reduces the contact area between the Pt electrocatalyst and Nafion, thus causing a decrease in charge transfer. Besides, if glycerol remains in catalyst layers, glycerol may cause a decrease in mass transfer. Although the amount of remaining glycerol and its effect on the structure of the catalyst layers remained unknown, they confirmed that the glycerol affects the cell performance. A US patent [25] claimed that a catalyst ink containing a catalyst, an ion exchange resin and high boiling solvent of which boiling point is not less than 373 K, valence is 1, 2 or 3, and mass is from one-fourth to four times larger than that of the ion exchange resin. The reasons of this mass range are reported that if below one-fourth of the solvent is employed, the pieces of the ion exchange resin are not sufficiently bonded so that no addition effects can be observed compared with complete drying, and if over four times of the solvent is employed, the amount of the solvent is excessive so that pores for gas diffusion are filled with the solvent when the catalyst layer is formed by pressurizing and sintering to lower electrode characteristics.

The effects of glycerol on the cell performance have already been known. However, the effects of the addition and extraction of glycerol on the structures of catalyst layers and the relation between the structures and cell performances have not yet been clarified, thus some additional learning is necessary. The purposes of the current study were to clarify (1) the effect of the addition and extraction of glycerol on the structures of catalyst layers, (2) the mass fractions of glycerol remaining in catalyst layers, and (3) resulting performance characteristics of a single cell. First, different MEAs were fabricated from catalyst inks that had different mass ratios of glycerol to carbon, r_{gc}, by using the decal method. It is noted that this fabrication process did not include ion exchange process and for the MEAs of which r_{gc} are larger than 5, two fabrication processes with and without glycerol extraction process were executed. Then, (a) the mass fraction of residual glycerol in the catalyst layers was determined by weighing samples at each preparation step, (b) the pore distribution in the catalyst layers was measured by using a mercury porosimeter, the surface structure was observed by using FE-SEM, and (c) the current density–voltage characteristics of a single cell with these MEAs were measured.

2. Experiments

MEAs were fabricated by the decal method proposed by Wilson and Gottesfeld [3]. The inks for the catalyst layers were prepared from Pt-C powder (30 wt.% platinum on Vulcan XC-72R, Tanaka Kikinzoku Kogyo), PFSI solution (5 wt.% Aciplex SS-910 solution in ethanol and water, Asahi Kasei Co.), and solvent (water and glycerol). For the experiment to clarify the distribution of PFSI in the catalyst layer, the mass fraction of PFSI in the catalyst layer x_p ranged from 0.1 to 0.4 and r_{gc} was kept constant at 10. For the experiment to clarify the effect of r_{gc} on the structure of the catalyst layer, r_{gc} ranged from 0 to 20 and x_p was kept constant at 0.3.

The ink was mixed by a stirrer until the ink became viscous, and then was ultrasonicated for 15 min. The ink was painted on Teflon sheets and baked at 403 K for 180 min. The active area for reaction was 9 cm^2. The catalyst-coated Teflon sheets were then hot-pressed onto both sides of a PFSI membrane (Aciplex SF-1002, Asahi Kasei Co.) at 9.8 MPa and 403 K for 4.5 min. After being hot-pressed, the resulting MEA was allowed to cool, and then the Teflon sheets were peeled away. Furthermore, to clarify the effect of glycerol extraction process, some of the MEAs of $r_{gc} = 10$ and 20 were steamed at 373 ± 5 K for 20 min to remove glycerol, and then dried at 353 K for 20 min to remove the absorbed water during steaming. An US patent [26] reported that the steaming process makes it possible to remove an organic solvent in a catalyst ink and fix an ion-conductive component while maintaining desired moisture content. The main claim of this patent is to maintain ion-conductive component under a constant humidified condition in the MEA fabrication process. However, in this study, the steaming process was used only for the removal of glycerol after the conventional fabrication of MEAs in the decal method.

For determining the masses of Pt-C, PFSI, and glycerol in the catalyst layer, the total mass of the catalyst layer was measured at different stages in the fabrication: (i) after painting the catalyst ink on a Teflon sheet, (ii) after baking, and (iii) after hot-pressing. The difference in mass between (i) and (ii) was assumed to be the mass of water, ethanol, and part of the glycerol, and that between (ii) and (iii) was assumed only due to the evaporation of part of the glycerol. For the steamed MEAs, the difference in mass before and after steaming and drying processes was also measured and it was assumed to be part of the glycerol. In the MEAs for measuring the pore size distribution and observing the surface, the total mass of the catalyst layers per unit area was kept constant, approximately 0.9 mg/cm^2. In contrast, in the MEAs for measuring the cell performances, the Pt loading was kept constant, approximately 0.08 mg/cm^2.

The pore distribution of the catalyst layers was examined by using a mercury porosimeter (AutoPore 9500, Micromeritics Co.), and the surface of the catalyst layers was observed by using a field emission scanning electron microscope (S-4700, Hitachi High-Tech Co.). The performance characteristics of the MEAs were investigated by using a single cell. An SUS plate with a