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The effects of Nafion® ionomer content in PEMFC MEAs prepared by a catalyst-coated membrane (CCM) spraying method

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ABSTRACT

We analyzed the effects of ionomer content on the proton exchange membrane fuel cell (PEMFC) performance of membrane electrode assemblies (MEAs) fabricated by a catalyst-coated membrane (CCM) spraying method in partially humidified atmospheric air and hydrogen. When high loading Pt/C catalysts (45.5 wt.%) were used, we observed that catalytic activity was not directly proportional to electrochemical active surface area (EAS). This suggests that ionic conductivity through ionomers in catalyst layers is also an important factor affecting MEA performance. In addition, the effects of mass transport were experimentally evaluated by manipulating the air stoichiometry ratio at the cathodes. MEA performance was more sensitive to flow rates under conditions of higher ionomer content. Due to the combined effect of EAS, ionic conductivity, and mass transfer characteristics (all of which varied according to the ionomer content), an MEA with 30 wt.% ionomer content at the cathode (25 wt.% at the anode) was shown to yield the best performance.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are clean and efficient electrochemical energy sources for use in mobile devices and transportation applications [1]. In order to achieve high performance and low cost for commercial applications, the development of membrane electrode assemblies (MEA), in which the electrochemical reactions actually occur, must be optimized. Expensive platinum is currently used as an electrochemical catalyst due to its high activity. Although various platinum alloys and non-platinum catalysts are under development, their stabilities and catalytic activities, especially in terms of the oxygen reduction reaction (ORR), render them currently unsuitable for practical use. Therefore, it is important

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to decrease platinum loading by optimizing the catalysts and electrode microstructure, as shown by the results of several studies [2–14].

MEAs have conventionally been fabricated by the catalyst-coated gas diffusion media (CCG) method, in which the catalyst layers are prepared on gas diffusion media (GDM) and the electrolyte membranes are then sandwiched between two catalyst/GDM layers [2–8,15–17]. In order to decrease the platinum loading weight through performance enhancement, the CCG process has been developed to utilize carbon-supported catalysts [2,3,15,16] and to incorporate Nafion® ionomer within the catalyst layers [2,3,16,17]. However, two technical problems, structural deformation due to the hot press step and catalyst loss through the porous GDM layers must be overcome to further enhance performance. The hot pressing step, which is required in the CCG method and enhances the electrolyte/catalyst interfacial properties, can induce structural changes in the porous catalyst layers [18] and the gas diffusion layers [19]. This results in slow gas transportation and increased electrical resistance. In addition, during preparation of the catalyst layer by either spraying or brushing, the catalyst particles can penetrate into the porous GDM [19–23]. The overall cell performance will then decrease due to both lower utilization of the platinum catalyst and pore blockage in the GDM.

As an alternative to the CCG process, the catalyst-coated membrane (CCM) method has been utilized. In this method, the catalyst layers are directly applied to both sides of the electrolyte membranes. It is believed that the CCM method yields higher cell performance, than the CCG method, due to higher catalyst utilization [22,24] and the establishment of a better electrolyte/catalyst interface [24,25]. With the CCM method, the interfacial characteristics between the electrolytes and the catalyst layers are greatly enhanced because the catalyst layers are directly coated onto the membranes. Therefore, the hot press step can be eliminated with the CCM method as reported by several authors [18,25–28]. However, some authors have included a hot press step in the CCM process [19,23,24,29]. When atmospheric air was used in cathodes, the current density of ca. 0.61 A/cm^2 (at 0.6 V) was reported for the CCM–MEA with a hot press step [24], while higher current densities (0.68–1.1 A/cm^2 at 0.6 V) were obtained when a hot press step was eliminated from the MEA fabrication procedure [18,26–28].

In addition, the decal transfer method, which is also called as indirect CCM method, has been developed [30–35]. In this method, the catalyst layers are prepared on decal substrates and then transferred to polymer electrolyte membranes after heat treatment. The decal transfer method is expected to be suitable for the mass production of PEMFC MEAs with film production processes. However, the heat treatment process, which can induce structural changes as in CCG methods, must be included to enable the transfer of catalyst layers.

In every MEA fabrication method, Nafion® ionomers are included in the catalyst layers. These ionomers act as: (i) proton conductors to expand the electrochemically active region into the bulk catalyst layer, (ii) binding materials to impart mechanical stability, and (iii) hydrophilic agents to retain moisture and prevent membrane dehydration. If the amount of Nafion® ionomer is insufficient to form a three-dimensional network, protons cannot access every part of the catalyst layer. Therefore, only part of the catalyst can be utilized as active sites for electrochemical reactions such as the oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR). In contrast, if a MEA contains too much ionomer, electronic conduction paths (Pt/C) and gas transport channels (pores) in the catalyst layers will be blocked by either the ionomer material or flooded water inside the more hydrophilic pores, especially at a high current density. [5,7,8,15–17]. For the CCG method, several studies where the catalyst layers were initially coated on GDM by brushing [2–4,8,16,17] or spraying methods [5,10,19] have reported optimum ionomer contents. The results of these studies indicate that the optimum ionomer content is highly dependent on the MEA fabrication parameters (platinum weight percent, platinum loading amount, and the solvent of the catalyst inks) and operating conditions (oxidant gas, reactant pressure, cell temperature, and relative humidity). For example, Lee et al. reported optimized ionomer contents of 49 wt.% and 23 wt.% under pressurized oxygen and air, respectively. These results demonstrate the effects of ionomer content on concentration overpotential [17]. Sasikumar et al. suggested that the optimum ionomer content in the catalyst layer gradually decreases with higher catalyst loading, from 50% (0.1 mgPt/cm^2) to 40% (0.25 mgPt/cm^2) to 20% (0.5 mgPt/cm^2), with the hydrogen/oxygen reactants at 80 °C [8]. For the decal transfer method, Xie et al. reported the ionomer content effect using Pt3Cr/C catalysts, focusing on the porous structures of catalyst layers [36].

For MEAs fabricated by the CCM method, optimum ionomer content has not been ascertained for practical preparation and operation conditions, even though the microstructure of the catalyst layers and the optimum amount of ionomer are expected to be different from those of CCG–MEAs. For example, Frey et al. reported that, at an ionomer content of 35 wt.%, the cell performance of a MEA fabricated by the CCM method including a heat treatment step was better than that of a CCG–MEA. However, at a higher ionomer content of 50 wt.%, CCG–MEAs outperformed hot-pressed CCM–MEAs [19]. It should be noted that the aforementioned flooding effect will be more severe in CCM–MEAs, as they are usually operated at higher current densities. Using a combination of the CCM method (cathodes) and the CCG method (anodes), Passos et al. reported the effects of ionomer content under oxygen (cathode) and hydrogen (anode) flows with low loading catalyst (20 wt.% Pt/C catalyst) [12]. However, considering that an atmospheric air reactant and highly loaded Pt/C catalysts are preferred for commercial PEMFC applications, the resulting optimum ionomer content estimate of 15 wt.% should be examined further for practical MEA development.

In this study, PEMFC MEAs were fabricated by the CCM spraying method without hot pressing. A high Pt loading catalyst was employed in the catalyst layers. The performance of the MEAs was examined under atmospheric air and hydrogen with partial humidification. For MEAs with various ionomer contents in the anodes and cathodes, the electrochemical activity (activation overpotential) and the mass transport properties (concentration overpotential) were analyzed and correlated with the single cell performance. For the MEAs fabricated by the CCM spraying method, an optimum ionomer content was suggested, providing practical information for commercial developments.