



Gradient Catalyst Coating for a Proton Exchange Membrane Fuel Cell Operation under Nonhumidified Conditions

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Operation under nonhumidified conditions was demonstrated with a membrane electrode assembly (MEA) for a proton exchange membrane fuel cell. The Pt catalyst was coated with a gradient on the active area of a MEA; the catalyst amount was reduced gradually from cathode inlet to outlet. The MEA with the gradient coating method produced more water near the inlet site than that with the uniform coating method. The water was used to mitigate dryness of the MEA. The cell performance was improved by 17% at 800 mA/cm² under nonhumidified conditions by effective water management of the gradient coating method.
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Manuscript submitted March 20, 2007; revised manuscript received June 4, 2007. Available electronically July 24, 2007.

The proton exchange membrane fuel cell (PEMFC) is an electrochemical device in which the chemical energy from fuel is converted to electrical energy. It has been spotlighted for its cleanliness and high energy efficiency compared to conventional power generation systems. The PEMFC uses a Nafion-type perfluorosulfonated polymer for an electrolyte membrane which must be humidified to maintain proton conductivity. To humidify the cell, a humidifier is equipped and a huge amount of water is supplied to the fuel cell.

Recently, PEMFCs have been demonstrated for portable electric devices.^{1,2} Because such portable devices seriously limit volume and weight of power sources, it is essential to minimize auxiliary components such as air supply and humidifier for the fuel cell. The reduction of volume and weight is the major challenge in the commercialization of PEMFCs for portable power sources. One of the most plausible ways to simplify the system is to remove the humidifier from the PEMFC system.

In order to operate a PEMFC without external humidification, several components in a fuel cell have been modified. The operations of PEMFC using a self-humidifying membrane by incorporating inorganic materials into the proton conducting membrane have been performed.^{3,4} Pt was incorporated into a Nafion membrane with inorganic compounds to operate the PEMFC under nonhumidified conditions.^{5,6} In this case, hydrogen and oxygen which cross over through the membrane combine and generate water by Pt catalytic activity, and the water is used to hydrate the whole MEA. Pt was dispersed in the middle of a Nafion/polytetrafluoroethylene (PTFE) composite membrane to improve cell performance under dry conditions.⁷ The operation under nonhumidified conditions was carried out by effective water management with modification of gas diffusion medium (GDM).⁸ Also, the electrode was modified with different amounts of ionomer to operate the PEMFC under nonhumidified conditions.⁹

Previously, we operated PEMFC under nonhumidified condition. We tested several different types of membranes and GDMs and found the best combination for the operation.¹⁰ In the case of the membrane, the thinner one showed better performance. The reduction of polymer electrolyte membrane (PEM) thickness reduces membrane resistance and improves proton conductivity in a PEM with effective back-diffusion of water from the cathode.¹¹ GDM with low porosity was used for the nonhumidified operation. Because of its high water-retaining ability, it showed better performance than that with high porosity.

In general, a catalyst is loaded uniformly for PEMFC operation. Therefore, the catalyst loading amount is the same over all the active area of MEA. However, actual conditions such as oxygen concentration, relative humidity, and amount of liquid water over the active area are very different. Therefore, we introduced the catalyst gradi-

ent coating method for the MEA to use the catalyst more effectively.¹² In this work, a higher amount of catalyst was loaded at the cathode inlet site for gradient catalyst coated MEA. In this case, more water was generated at the cathode inlet and the water was used to hydrate the MEA, resulting in high cell performance under nonhumidified conditions compared to uniform catalyst coated MEA. We report the fabrication of gradient catalyst coated MEA and its application for the operation under nonhumidified conditions.

Experimental

MEA preparation.—The catalyst ink was prepared by mixing the carbon-supported catalyst powder (40 wt % Pt/C, E-TEK), Nafion solution (EW 1100, 5 wt %, DuPont), and isopropyl alcohol (Baker, analyzed HPLC reagent). The ink was well sonicated and sprayed directly on the Nafion 111 membrane to fabricate MEA (active area: 5 × 5 cm). An automatic robot arm was utilized in order to guarantee constant spraying of the catalyst ink. The catalyst ink was sprayed not only on the membrane but also on a reference substrate simultaneously, for measurement of platinum loading. For the fabrication of the gradient catalyst coated MEA, the membrane was partially screened in order to spray a different amount of catalyst slurry. For instance, when type II MEA (Fig. 1c) was fabricated, a catalyst of 0.2 mg/cm² was loaded first on the whole area of the membrane. Then, a portion (5 × 1 cm) of the MEA whose catalyst loading was intended to be 0.2 mg/cm² was covered with a piece of plastic and a catalyst of 0.1 mg/cm² was additionally sprayed on the rest of the MEA (5 × 4 cm). Finally, additional spraying of 0.1 mg/cm² catalyst was performed on the area (5 × 1 cm) for the inlet site, while the remaining area was covered to get the gradient catalyst loaded MEA.

Performance measurement.—A single cell was assembled with a MEA, GDM (Sigracet 10BC, SGL Carbon Inc.), PTFE gaskets, and graphite bipolar plates which have a serpentine channel. First, the cell was activated under constant current mode (at 0.8 A/cm²) at 50°C with fully humidified hydrogen and air for 24 h before the performance test. Then, performance tests under fully humidified conditions were carried out. The cell temperature was maintained at 50°C and fully humidified hydrogen and air (or oxygen) was supplied with a stoichiometry of 1.25 and 2.5 for anode and cathode, respectively. After the tests, the cell was operated under nonhumidified conditions for 24 h before carrying out the performance tests under nonhumidified conditions.

To measure *I-V* characteristics, an electronic load (Daegil Electronics, EL 500P) was used. Also, a potentiostat (SI 1260, Solartron Inc.) was used for the impedance measurement, and the applied frequency was varied from 10 mHz to 10 kHz with an excitation voltage of 10 mV (peak to peak) at an applied voltage of 0.6 V. While impedance measurement was performed, hydrogen and oxygen was supplied with a stoichiometry of 1.25 and 2.5, respectively.

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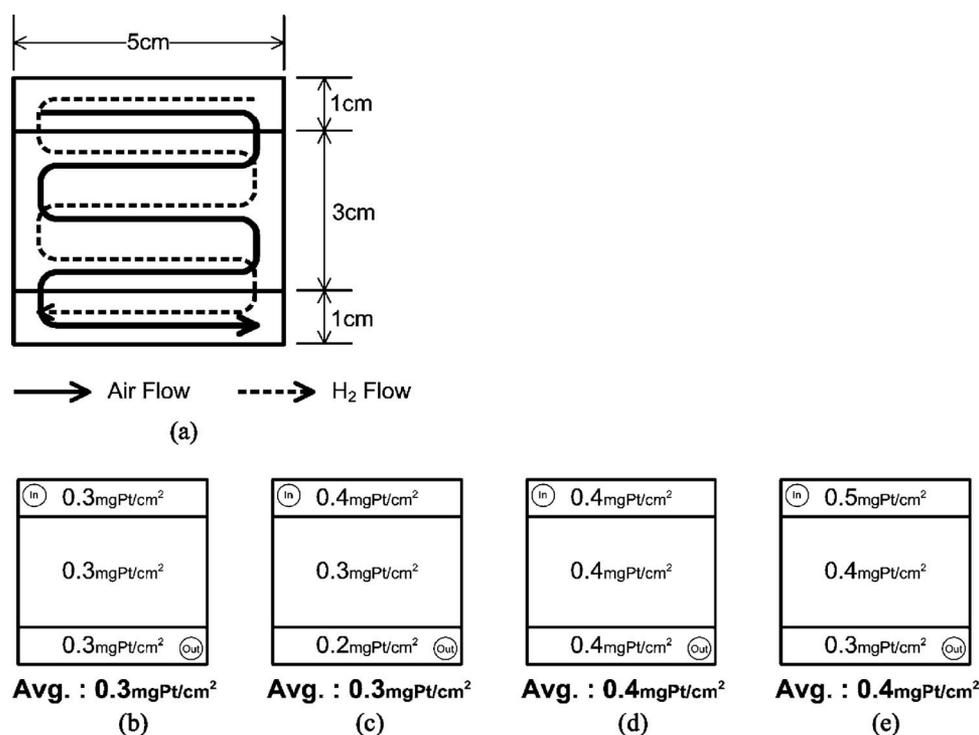


Figure 1. The specification of (a) flow pattern and cathode catalyst loading of (b) type I, (c) type II, (d) type III, and (e) type IV.

Results and Discussion

Four different kinds of MEAs were prepared to investigate the effects of gradient catalyst loading on the performance with dry fuel and oxidant. The specification of catalyst loading is shown in Fig. 1 [The arrow in (a) shows actual hydrogen and air flow.] At the anode of all MEAs, the catalyst was coated uniformly with 0.3 mg/cm² of Pt loading. Types I and II have the same platinum average loading of 0.3 mg/cm² for the cathode. The only difference between type I and II is whether the catalyst is coated with uniform distribution or the gradient one at the cathode. In the case of type II, the catalyst amount from inlet to outlet decreased gradually from 0.4 to 0.2 mg/cm². Type II MEA consists of three parts which have different platinum loading. The first part in which the catalyst loading is 0.4 mg/cm² has one-fifth of total area (5 cm²) at the air inlet. Areas of the second and third parts are 15 and 5 cm² and catalyst loading is 0.3 and 0.2 mg/cm², respectively. The MEAs denoted as type III and type IV are the same as type I and II except that the cathode electrodes have 0.4 mg/cm² of Pt catalyst loading.

The platinum loading was confirmed by scanning electron microscopy (SEM) image of MEA in Fig. 2. The thickness of the catalyst layer is linearly dependent on the catalyst loading because we used one kind of catalyst slurry. In the figure, it is observed that the expected catalyst loading is directly proportional to the thickness of the layer.

The main idea of the water management strategy by gradient coating methods is that water produced can be utilized efficiently to prevent MEA dryness if the profile of the water production rate along flow direction is optimized. For further comprehension, it is necessary to understand production and transport of water in the catalyst layer, GDM, and gas channels. When a PEMFC is in a steady state, the amount of water generated should be equal to the amount of water discharged at the outlet. First, water generated at the catalyst layer migrates to the gas channel through GDM by diffusion or capillary force. Then, water in the gas channel moves to the outlet by gas stream. Therefore, water generated near the gas inlet region might pass through the whole region of the cell along gas channels, whereas one generated near the gas outlet region passes only a short distance. In this respect, it can be conjectured that water generated near the inlet has more significant influence on

hydrating the MEA and hampering mass transport compared to water generated near the outlet. Therefore, it might be advantageous under nonhumidified conditions to generate water nearer the inlet rather than the outlet. To adjust the water production profile, catalyst gradient methods were applied; a larger amount of catalyst was loaded near the inlet, while the outlet region has a smaller amount of catalyst. The gradient method might help water to be generated nearer the inlet compared to the uniform coating method.

Figure 3 represents polarization curves under fully humidified conditions. The cell performance of gradient coated MEA was lower than that of the uniformly coated one when fully humidified hydrogen and air were supplied (Fig. 3a). A more significant difference is observed in the high current region. By contrast, the difference was relatively small under hydrogen and oxygen feeding conditions (Fig. 3b), which minimizes mass transport loss. These results agree well

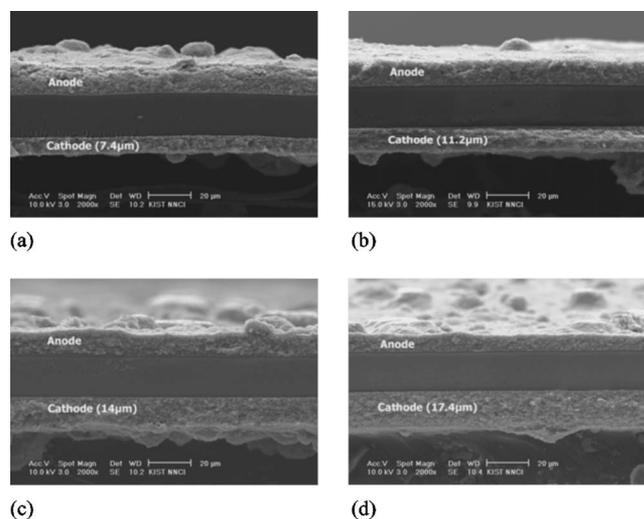
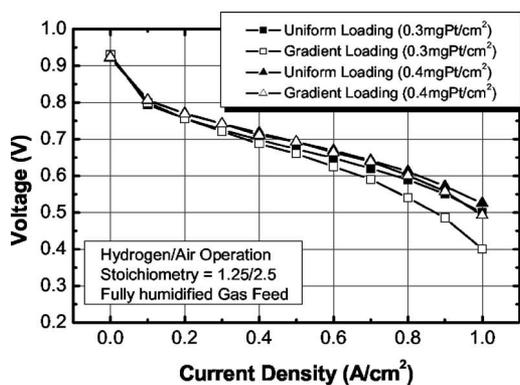
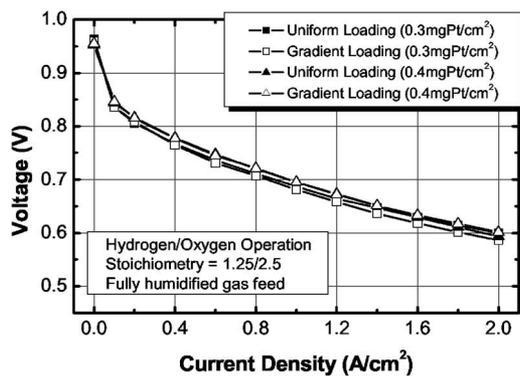


Figure 2. SEM cross-sectional images of MEA with different platinum loading: (a) 0.2 mg/cm², (b) 0.3 mg/cm², (c) 0.4 mg/cm², and (d) 0.5 mg/cm².

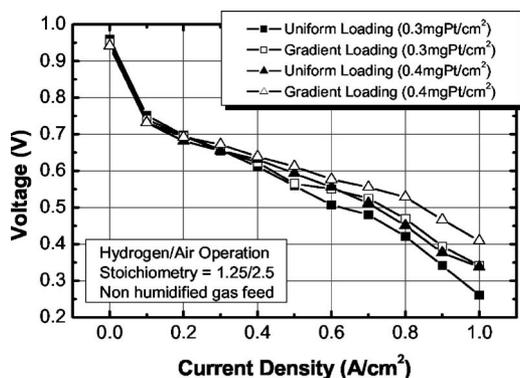


(a)

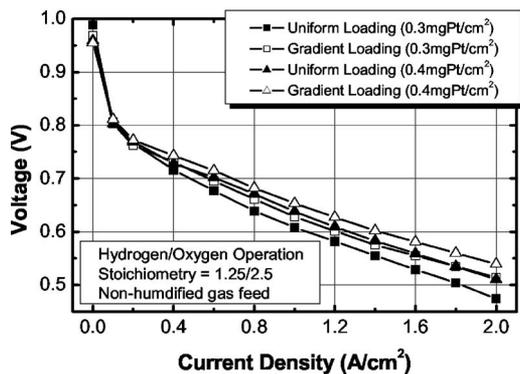


(b)

Figure 3. The polarization curves of the type I, II, III, and IV MEAs with fully humidified (a) hydrogen and air, and (b) hydrogen and oxygen.

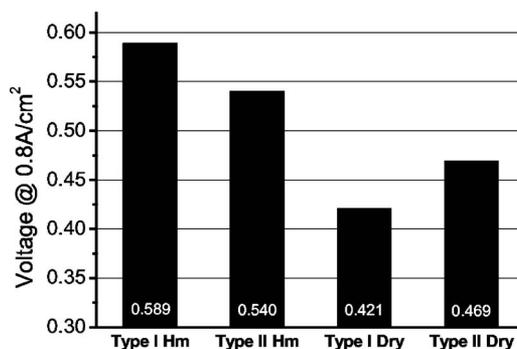


(a)

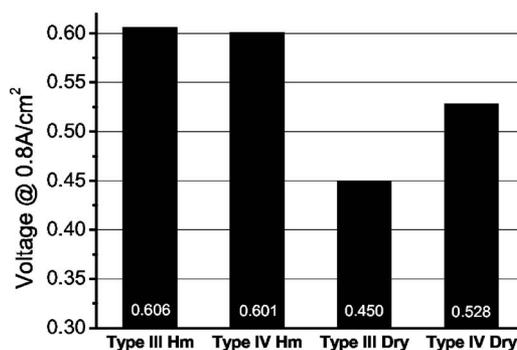


(b)

Figure 4. The polarization curves of the type I, II, III, and IV MEAs with nonhumidified (a) hydrogen and air, and (b) hydrogen and oxygen.



(a)



(b)

Figure 5. Effects of gradient coating on voltage at 0.8 A cm^{-2} of (a) type I and II and (b) type III and IV MEA under hydrogen and air feed conditions.

with the expectations mentioned above. Severe performance decrease when air is supplied means that the MEA with catalyst gradient has an innate weakness in mass transport under fully humidified conditions. Compared to the uniformly coated one, in the case of a MEA with gradient coating, a larger amount of water could be generated near the inlet and hamper air transport to the reaction site in the whole active region.

However, performance of gradient coated MEAs was higher than that with uniform coating under nonhumidified condition (Fig. 4). Figure 5 also shows performance enhancement at 0.8 A cm^{-2} . The gradient coating method improved cell performance by 11 and 17% at 0.8 A cm^{-2} in the case of 0.3 and 0.4 mg cm^{-2} Pt loading under nonhumidified condition, respectively. The enhancement of performance was rather significant in the high current density region, which supports the idea that gradient catalyst coating is suitable for managing water produced under nonhumidified conditions. Figure 6

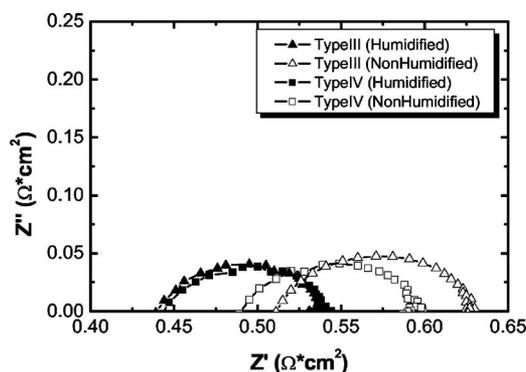


Figure 6. Nyquist plots at 0.6 V for type III and type IV MEA under humidified and dry reactants feed conditions.

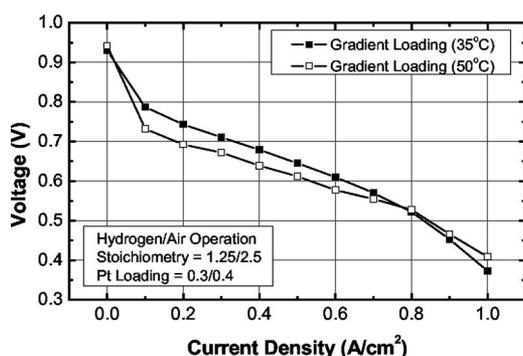


Figure 7. Effects of cell temperature on polarization curve of type IV MEA under nonhumidified hydrogen and air feed conditions.

shows impedance spectroscopy at 0.6 V of type III and type IV MEA with hydrogen and oxygen supply. When dry reactants were fed, ohmic resistance of the gradient catalyst coated MEA is smaller than that of the uniform catalyst coated one, while there is little difference between them at fully humidified conditions. Therefore, it can be concluded that the gradient coating method utilizes produced water more effectively to mitigate MEA dryness, resulting in the decrease of ohmic loss as represented in Fig. 6.

Comparison of cell performance at two different temperatures (35 vs 50°C) was carried out (Fig. 7). As in our previously reported results,¹⁰ the cell performance at higher temperature was lower than that at lower temperature due to severe water evaporation. However,

the cell performance was reversed in the high current density region. It could be related to the increase of mass transfer loss due to low saturated water vapor pressure at 35°C.

Conclusion

Performance enhancement under nonhumidified conditions was achieved by effective water management of a MEA with catalyst gradient loading. The gradient catalyst coating method improved cell performance by 17% at 0.8 A/cm² under nonhumidified condition, which is expected to be useful for system compactness. An optimization of catalyst distribution and long-term durability test will be carried out in future work.

Korea Institute of Science and Technology assisted in meeting the publication costs of this article.

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