

Utilization of Pt/Ru catalysts in MEA for fuel cell application by breathing process of proton exchange membrane

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Abstract

Small direct-methanol fuel cells (DMFCs) have recently been highlighted as possible power sources for applications ranging from cellular phones and wireless digital devices to autonomous sensors and micro-electro mechanical devices. One of the key issues in commercializing miniaturized DMFCs for portable applications is to improve the electrochemical performance of the cells with a small quantity of catalysts. Up to now, the spraying or brush method has been used to fabricate a catalyst layer, which uses a slurry of nano-sized Pt or Pt/Ru catalysts. However, these methods produce a poor electrochemical interface that reduces the catalytic activity and the reproducibility of their performance tests.

In this study, a unique process known as a “breathing process” was used to fabricate a catalytic electrode layer in a membrane-electrode-assembly (MEA) of DMFCs. The Pt/Ru nano-particles were loaded directly onto a proton exchange membrane using this breathing process. This process consisted of the following three steps: (1) the electrolyte membrane was fully swollen in water; (2) the swollen membrane was placed into an aprotic solvent, which induced the shrinkage of the membrane by driving the water out (“breathing out”); (3) the shrunken membrane was placed in an aqueous solution containing a suspension of Pt/Ru nano-particles. This induces the swelling of the membrane, and the suspended Pt/Ru nano-particles penetrate the membrane during this process (“breathing in”). It is possible to control the amount of catalysts loaded in the MEA by controlling the number of the cycles of such breathing processes.

Compared with the fuel cell adopting the MEA fabricated by a conventional spraying method with the same amount of catalysts, the performance of this novel fuel cell was enhanced by approximately 4.5 mW cm^{-2} in case of the passive-type fuel cell and by 9.0 mW cm^{-2} in case of the active-type.

This paper details the optimized process conditions along with other advanced fabrication processes to improve the electrochemical interface in a fuel cell system.

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1. Introduction

Most fuel cells are powered by hydrogen, which can be fed directly to the fuel cell system or be generated within the fuel cell system via a reforming process of hydrogen-rich fuels such as methanol, ethanol or hydrocarbon fuels. However, direct-methanol fuel cells (DMFCs) are powered by pure methanol and water, which is fed directly to the anode electrode of the fuel cell.

DMFCs do not have fuel storage problems because methanol has a higher energy density than hydrogen albeit less than that of gasoline or diesel fuel. In addition, methanol can be easily transported and supplied to consumers using existent infrastructures because it is a liquid. Despite these advantages, there are still some problems to be solved. These include the high cost of catalysts, the methanol crossover, the poor activity of catalysts, the poor contact between catalysts and the electrolyte membrane, and etc.

There are many procedures for fabricating an MEA: the indirect decal method, the diffusion layer-based method and the membrane-based method. These methods may be applied by impregnation, brush, or spraying with a catalyst solution. In

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the decal method, a transfer layer is brushed with a catalyst solution, dried and hot pressed onto the electrolyte membrane [1–3]. In the diffusion layer-based method, the catalyst solution is directly painted or sprayed onto the diffusion layer and then hot pressed onto the electrolyte membrane [4,5]. Fabrication of the MEA using a membrane-based method usually consists of spaying the catalyst solution onto a dried, heated and fixed electrolyte membrane, which is followed by a hot pressing process [6,7]. The application of the decal method to the preparation of electrodes has the risk of uneven or incomplete catalyst transfer from the transfer layer to the electrolyte membrane. The latter two methods have the advantage, in that the catalyst loading can be adjusted precisely by simply weighing the MEA or diffusion layer before and after loading the catalysts. However, these conventional methods have the following problems:

- (1) Formation of a non-uniform catalyst layer.
- (2) Poor contact between the catalyst and the electrolyte membrane.
- (3) Loss of the catalyst for the electrochemical reactions during catalyst loading.

None of the DMFCs reported so far has shown as high a performance as other types of fuel cells. Therefore, this study used a new method, a breathing process, to load catalysts more effectively in order to improve their efficiency [8]. The breathing process is one such method, which uses the breathing properties of polymers to disperse metal nano-particles. In particular, the dispersion method using polyacrylamide (PAM) hydrogels is well-known. The PAM hydrogels use highly swollen structures in water, but upon exposure to less polar solvents, such as acetone, there is a phase transition to collapsed states.

To achieve this aim, the new method must:

- (1) Produce a uniform catalyst layer.
- (2) Make a better dispersion of the catalyst particles onto the diffusion layer of electrode for electrochemical reaction.
- (3) Make better contact between the catalyst and the proton exchange membrane.

In this study, the new method to load catalysts, so-called “breathing process”, is introduced as a simple and organized concept for producing a catalyst layer showing maximum performance, compared with those of other MEA fabrication processes.

2. Experimental

2.1. Formation of the catalyst layer by breathing process

The catalyst layer was formed on a proton exchange membrane (PEM), which was used as the polymer electrolyte, via the breathing process. A Nafion® 115 polymer electrolyte membrane (thickness: 100 μm , equivalent weight: 1100 g mol^{-1} , conductivity: 0.059 $\Omega^{-1} \text{cm}^{-1}$) from DuPont was used as the PEM.

The Nafion® 115 membrane was cleaned and treated using the following method to ensure that the Nafion® 115 membrane is completely in the protonic form: 12 h swelling in D.I. water, boiling at 80 °C in 10% H_2O_2 for 1 h to remove organic impurities, cleaning in D.I. water for 1 h, boiling at 80 °C in 1 M H_2SO_4 for 1 h to remove the metal compound and to replace Na^+ ions with H^+ ions, and cleaning in D.I. water for 3 h.

Fig. 1 shows a schematic diagram of the breathing process. The breathing process was carried out using the Nafion® 115 membrane in an aprotic solvent, which was an acetone in this study, and aqueous solution containing highly dispersed Pt/Ru catalysts (A Johnson Matthey Co.).

First, the Nafion® 115 membrane was placed into an aqueous solution containing the Pt/Ru catalyst, and this polymer was then swollen in the aqueous solution (breathing in).

Second, the swollen Nafion® 115 membrane was placed into the aprotic solvent for 5 min, causing shrinkage after driving the aqueous solution out (breathing out). Third, the shrunken Nafion® 115 membrane was placed in the aqueous solution for 5 min where the Pt/Ru nano-particles were suspended.

Highly dispersed Pt/Ru particles were deposited on the Nafion® 115 membrane after several cycles (2–8 cycles). The loaded amount of catalyst can be precisely measured by simply weighing the Nafion® 115 membrane before and after loading the catalysts.

2.2. Fabrication of MEA

The electrode requires a diffusion layer to deliver the fuel to the anode and air to the cathode. In order to form a diffusion layer, Toray carbon paper TGPH-090 (thickness: 275 μm) was coated with a carbon slurry, which was made from Carbon black Vulcan XC-72 (E-tek), Teflon Emulsion PTFE 30 (Aldrich) and a solvent. The solvent was prepared from 1-propanol, 2-propanol and D.I. water (a volume ratio of 1:1:2).

The catalyst layer was formed by spraying a commercial Pt/Ru catalyst ink (a molar ratio of 1:1) onto the diffusion layer at the anode side; the diffusion layer of the cathode side was sprayed with a Pt catalyst ink containing Pt black (A John-

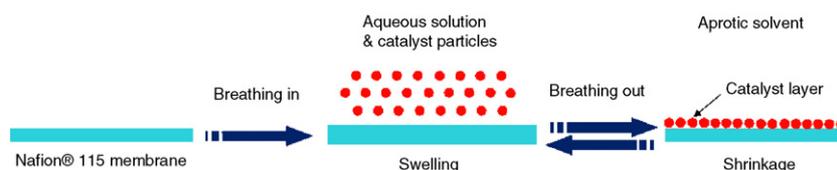


Fig. 1. The schematic illustration for loading the catalysts onto the proton exchange membrane by the breathing process.

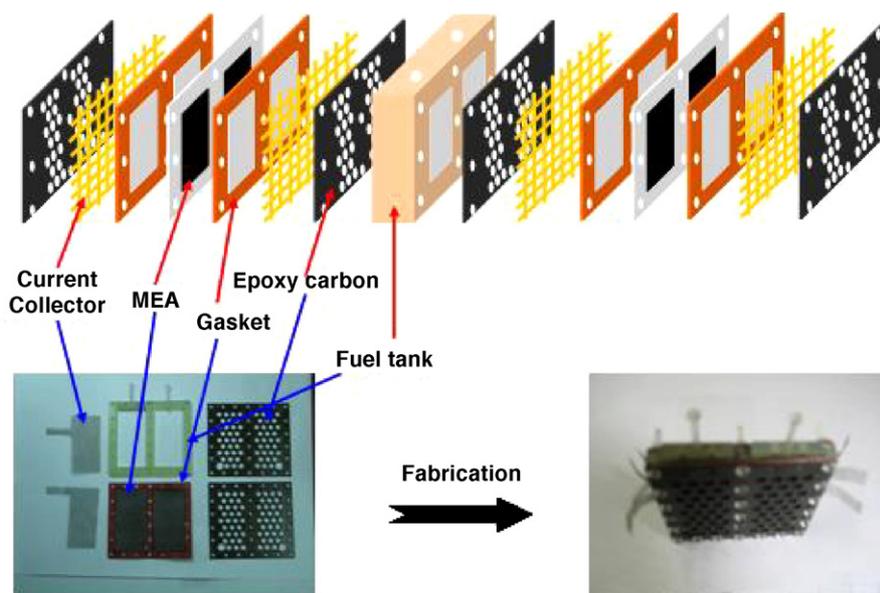
son Matthey Co.). The catalyst ink was prepared by adding a solvent to the catalyst, and adding a 15 wt.% Nafion solution (water-based 5 wt.% Nafion solution from Aldrich) to the solvent containing the catalyst. An airbrush gun was used to load the catalyst. Usually the catalyst ink is sprayed directly onto the diffusion layers until the desired catalyst loading is reached. The catalyst loading was adjusted to be 3.0 mg Pt/Ru catalysts cm^{-2} on the anode and 3.0 mg Pt catalysts cm^{-2} on the cathode.

Because the amount of catalyst, which can be loaded by breathing method on Nafion[®] 115 membrane to achieve a better contact between the catalyst layer and the diffusion layer on the electrode, is too small for it to be applied to the passive-type DMFCs, we need to form an additional catalyst layer on the diffusion layer with a spraying method. Consequently, the catalyst layer is formed on the diffusion layer with spraying and on the

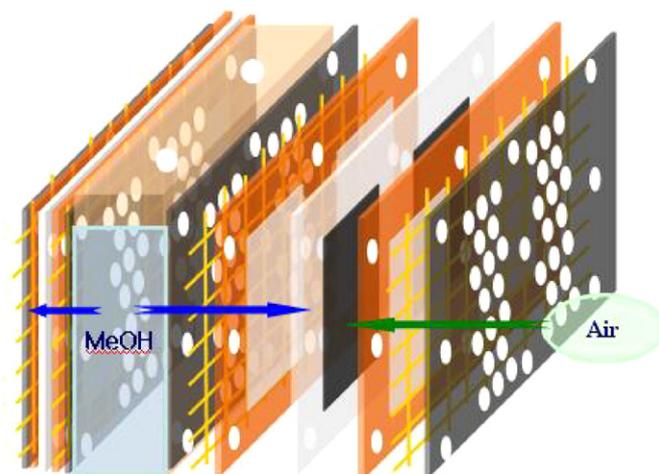
Nafion[®] 115 membrane using the breathing process. The electrode and Nafion[®] 115 membrane was hot-pressed at 135 °C, 2000 psi, 5 min to fabricate the MEA.

2.3. Cell performance test of passive- and active-type DMFCs

Passive-type DMFCs operate without the aid of external devices for pumping methanol and blowing air into the cell. Therefore, methanol is supplied to the anode by a concentration gradient between the anode and the fuel reservoir, and oxygen diffuses to the cathode from the ambient via air-breathing of the cell. A nickel mesh, which is used as a current collector, was electroplated with platinum, and then was located at both sides of the MEA. Fig. 2 shows a schematic diagram for fabricating the passive-type DMFCs.



(a)



(b)

Fig. 2. (a) A schematic diagram of the fabrication process and (b) the operating scheme of the passive-type flat-pack DMFCs.

After the swelling process with D.I. water, the cells were activated using a 2 M methanol solution for 2 h, and their performances were measured under passive-feed conditions.

In case of the active-type DMFCs, which use external devices for pumping methanol and blowing air into the cell, the MEA were installed in a single graphite cell. The activation of a single cell is similar to that of a passive-type DMFC, and the single cell test was performed using a 2 M methanol solution (feed speed: 50 mL min⁻¹) and air (feed speed: 500 mL min⁻¹) at 50 °C and ambient pressure. The performance of a single cell was measured using a potentiostat (WMPG-1000, Wonatech. Co.).

The unique method for forming a catalyst layer using the breathing process was developed in this study, and the performance of the breathing process is described below.

3. Results and discussion

In order to improve the efficiency of a catalyst layer in the MEA, highly dispersed catalyst particles were loaded onto an electrolyte membrane, and a uniform catalyst layer was formed to make a perfect three-phase interface between the catalyst layer, the electrolyte membrane and the electrode.

3.1. Effect of breathing process for catalysts loading

The breathing property of Nafion[®] 115 membrane was used to load the dispersed catalysts on the membrane. The Pt/Ru catalysts would penetrate the Nafion[®] 115 membrane when it is swollen in an aqueous solution containing catalysts. During the subsequent breathing out process, the dispersed catalysts remain on the Nafion[®] 115 membrane due to the physical entanglement of the polymer surface. Normally, the solvent used for the cat-

alyst ink preparation is water, and some organic solutions are also employed. Water is not harmful, cheap and do not react with the catalyst (no ignition, no poisoning). Therefore, water is used for an aqueous solution of breathing process. Acetone is an excellent aprotic solvent and highly volatile at low temperatures. No ignition was observed when it gets in contact with catalysts, neither during preparation nor loading of catalysts. With the acetone, used as an aprotic solvent for the breathing process, no congestion occurred during the breathing process, because of a self-cleaning effect.

Fig. 3 shows the morphology and distribution of the Pt/Ru catalysts on the Nafion[®] 115 membrane. The catalysts are in the form of somewhat spherical aggregates about 100–500 nm in size, with each aggregate being made of 200 nm sized elementary particles. An aggregation of catalyst layer has been the biggest problem in common spraying and brush method. However, as can be seen in ESEM picture, the aggregation of nano-size catalyst particles was suppressed when the catalyst was loaded by the breathing process, and the catalyst layer is also more uniform. Fig. 3(d) shows the ESEM picture of the catalyst layer when 0.51 mg cm⁻² of catalysts were loaded onto the Nafion[®] 115 membrane after eight cycles of the breathing process. This indicates that the quantity of catalysts can be controlled by the number of breathing cycles, and the catalyst loading can be determined precisely by simply weighing the Nafion[®] 115 membrane before and after loading the catalysts. Fig. 4 shows that the quantity of Pt/Ru catalysts can be adjusted as a function of the number of breathing cycles. This breathing process improved the contact between the Pt/Ru catalyst layer and the Nafion[®] 115 membrane compared with that of the conventional loading method, and formed a very uniform catalyst layer.

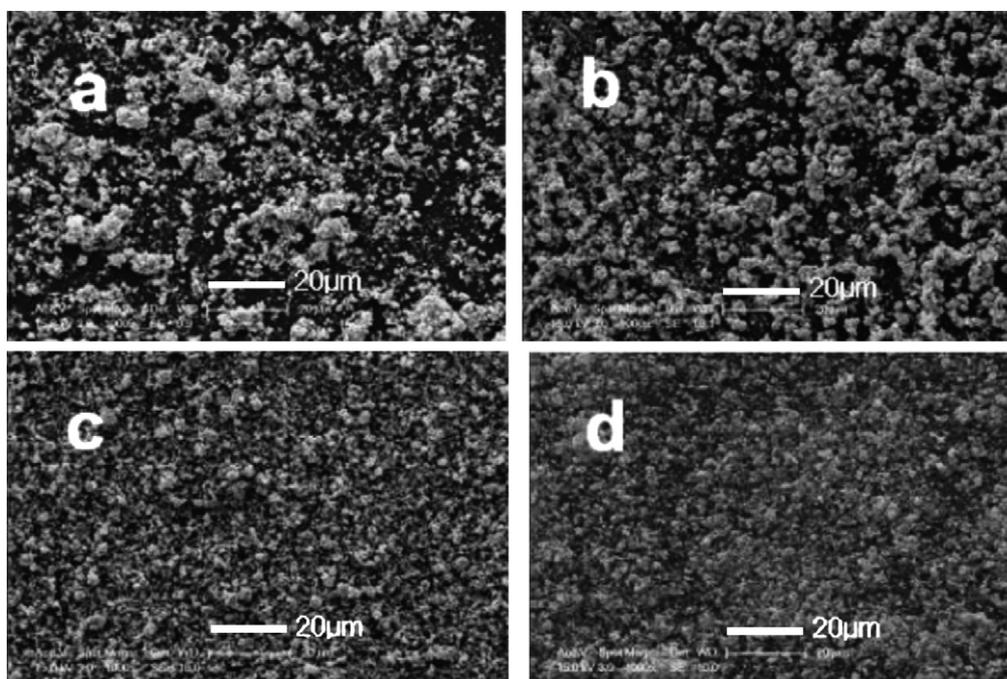


Fig. 3. SEM images of the Pt/Ru catalysts on the Nafion[®] 115 membrane using the breathing process: (a) two cycles, 0.21 mg cm⁻²; (b) four cycles, 0.35 mg cm⁻²; (c) six cycles, 0.46 mg cm⁻²; (d) eight cycles, 0.51 mg cm⁻².

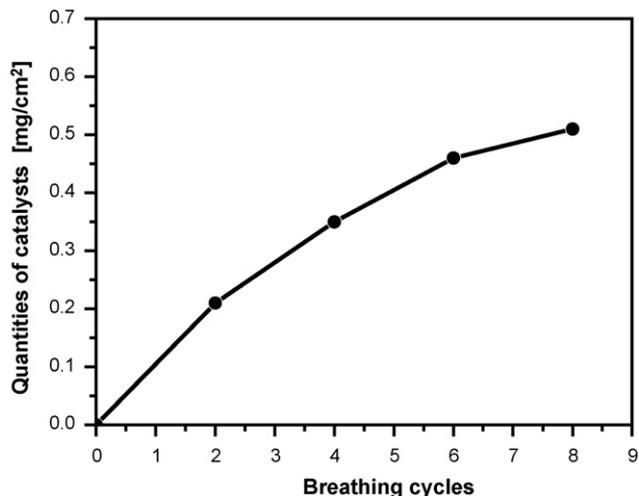


Fig. 4. The quantity of Pt/Ru catalysts adjusted by the breathing process.

3.2. Analysis of the catalyst layer of MEA

The basic unit, MEA, in terms of technology and economy, is the most important part of the fuel cell. The performance of the MEA is optimal only when the electrolyte membrane, the catalyst layer, and the electrode form an ideal connection for an electrochemical reaction. The catalyst layer is formed on diffusion layer with spraying and on Nafion[®] 115 membrane with the breathing process. Water has some drawbacks with regard to the ink application process for spraying, because the airbrush gun is particularly prone to congestion with a catalyst slurry when a water-based ink is used. So the solvent used for breathing process is water, but a mixing solution is employed for spraying.

Fig. 5(a) shows a crosssection of the MEA, which consists of a Nafion[®] 115 membrane, a catalyst layer and a diffusion layer. Fig. 5(b) shows that the uniformity of the catalyst layer. The catalyst layer in this study is formed by the breathing method, which utilizes the swelling properties of an electrolyte membrane. That is, the catalyst particles are entangled by the membrane, being well dispersed on the membrane surface, as shown in Fig. 3(d). Since, the catalyst layer is already well dispersed on

the membrane by breathing process, the catalyst layer and the membrane forms highly uniform (13.2 μm) contact with each other even after the hot pressing process, as shown in Fig. 5(b). Consequently, an enhancement of electrical contact between the electrode and the catalyst layer is also expected due to the uniform contact between these two.

3.3. Performance test

The performance test of an MEA fabricated using the breathing process of the Nafion[®] 115 membrane was compared with a MEA fabricated using the conventional diffusion layer-based method. Each MEA used a similar quantity of catalyst and was tested in our passive-type DMFC under the same operating parameters.

When the reservoir of the passive-type cell was fed with a 6 M methanol solution, the cell with MEA prepared using the breathing process had a maximum power density of 20.3 mW cm^{-2} , which was enhanced by 4.5 mW cm^{-2} , compared with that from the MEA produced using the diffusion layer-based method (Fig. 6(b)). Fig. 6(a) and (c), for the 4 and 8 M methanol solution shows that maximum power density of each “breathing method” cell was improved. Fig. 7 indicates that the temperature in the cell increases with increasing the methanol concentration. The rise in the temperature observed in Fig. 7 presumably originated from the methanol crossover as well as the catalytic reaction at the anode electrode. Usually the methanol crossover becomes significant at concentrations above 4 M methanol concentration in common passive-type DMFCs. However, if this increase in the temperature is only due to the methanol crossover, the difference in the performance of the cells should be lowered at higher concentrations, e.g. 6 and 8 M methanol solution, because, the efficiency of the cathode catalyst prepared by the breathing method is also high, this causes an increase in the mixed potential, thus lowers the overall cell performance. However, the difference in the performance of the cells at high fuel concentrations, e.g. 6 and 8 M methanol solution is even higher compared to that of 4 M methanol solution, as shown in Fig. 6. Therefore, the elevation of the cell temperature was not only caused by the fuel crossover, but it was also caused by the increase of the effective surface area of the catalysts due to the high dispersion of the

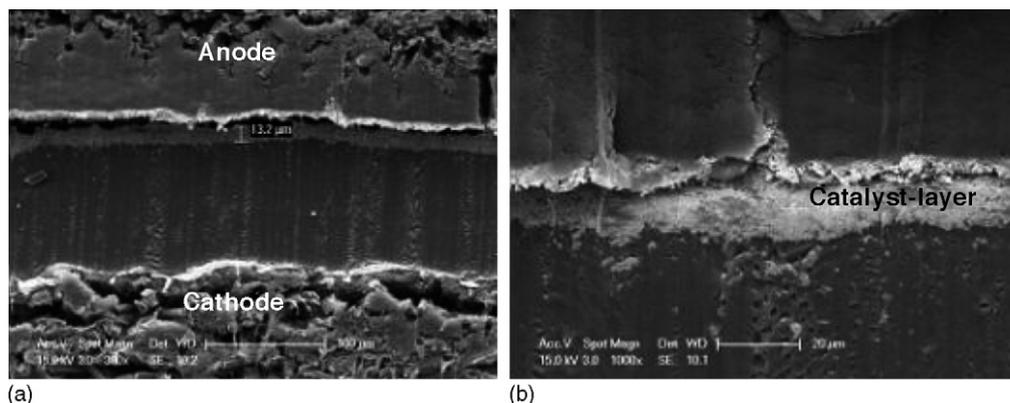


Fig. 5. SEM image of (a) MEA and (b) catalyst layer in the MEA.

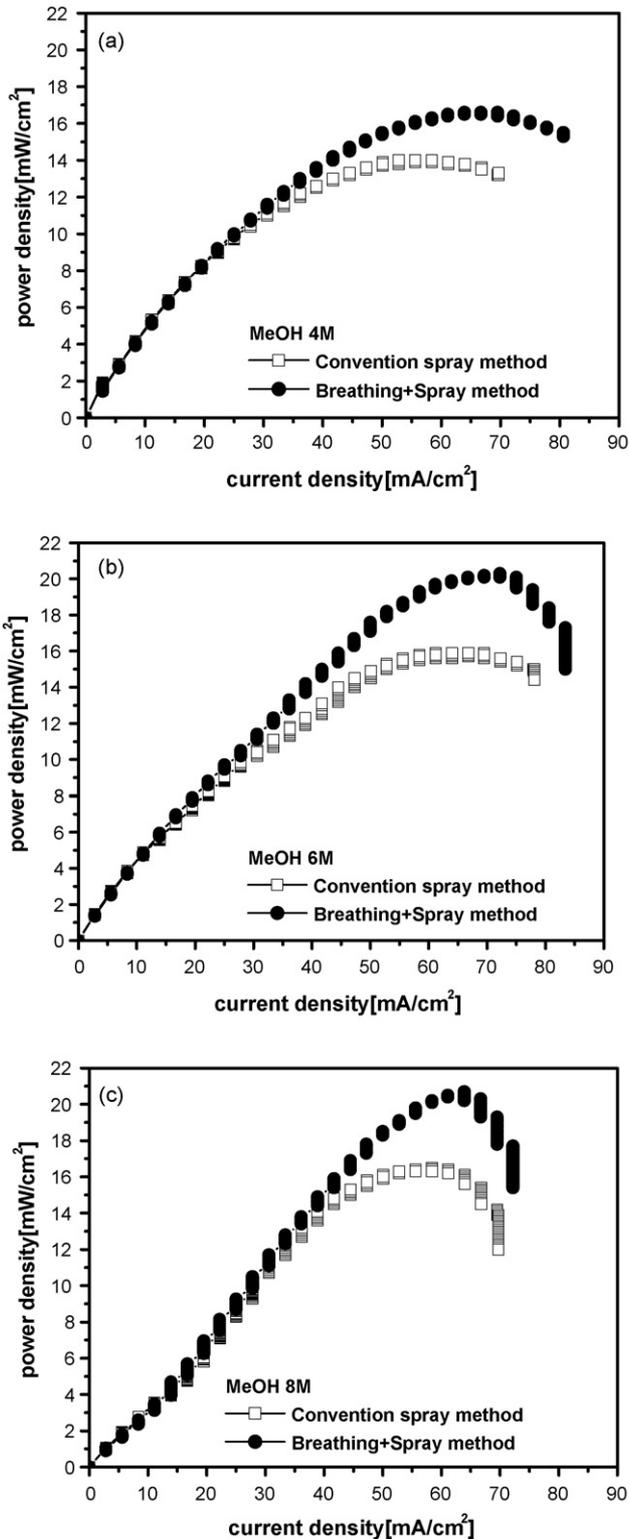


Fig. 6. The performance of the passive-type DMFC fabricated using the breathing process and the conventional method. Each cell performance was obtained with (a) 4 M methanol, (b) 6 M methanol and (c) 8 M methanol.

catalysts utilized by the breathing process (cf. Fig. 3). Furthermore, considering the cell performance in Fig. 6, the rise in the operating cell temperature is largely affected by the increase of catalytic surface area at the anode due to the high dispersion of the catalysts.

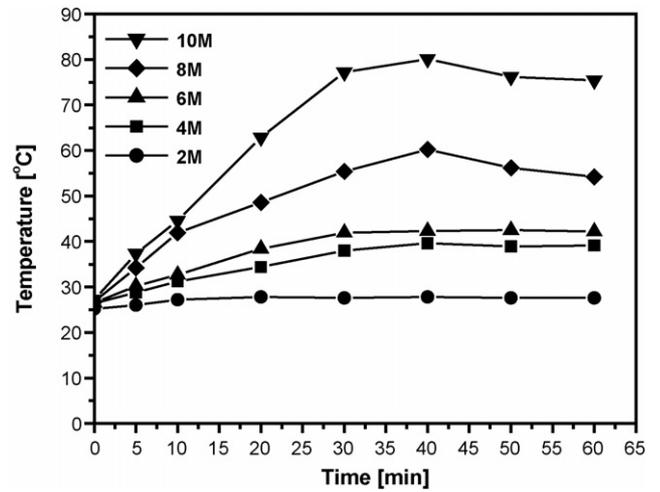


Fig. 7. Temperature in the cell according to increasing of methanol concentration.

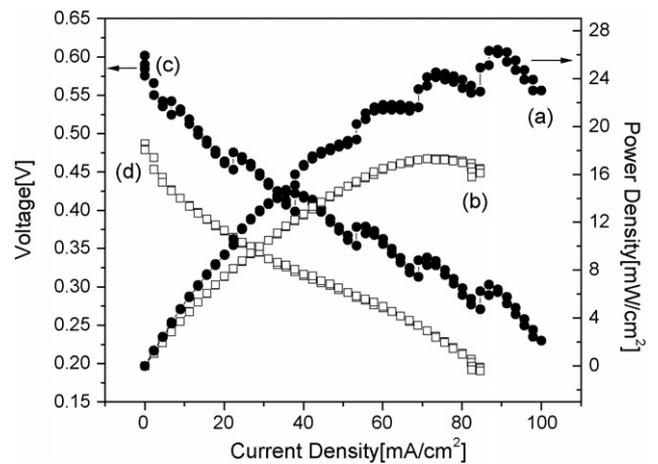


Fig. 8. The performance difference between the active-type DMFC produced using the breathing process and conventional method when the cell was fed with 2 M methanol by pump: (a) power density of breathing + spray method, (b) power density of spray method, (c) voltage of breathing + spray method and (d) voltage of spray method.

In the active-type DMFC, the performance test of the MEA was carried out by using the same quantity of catalysts as in the test of the passive-type, and an improvement in performance was observed in the DMFCs fabricated using the breathing process. Fig. 8 shows that when the cell was fed with 2 M methanol, the maximum power density was increased by 9.0 mW cm⁻² compared with the conventional MEA.

4. Conclusions

The characteristics of the catalyst layer that is formed on the diffusion layer with spraying and on Nafion[®] 115 membrane with breathing process have been analyzed with a view to developing a more effective catalyst layer for use as an MEA in DMFCs.

The results indicate the following:

- (1) A uniform distribution of catalyst particles on the electrolyte membrane is obtained by the breathing process, and this improves the catalytic properties of the catalyst layer.
- (2) The breathing process provides a good connection among the electrolyte membrane, catalyst particles, and conducting diffusion layer. Hence the MEA in DMFCs using the breathing process gives a superior performance.

In this study, the breathing process was used to fabricate a catalyst layer, and the performance of the MEAs prepared by this process was tested in the active- and passive-type DMFCs. These results show that the new method improves the catalyst layer contact with the Nafion[®] 115 membrane compared with the conventional loading method, and improves the performance of the MEA. The most improved performance of the new compared with the MEA fabricated using the conventional method was approximately 4.5 mW cm^{-2} at the passive-type and 9.0 mW cm^{-2} at the active-type. The sequence of this breathing process is based on a simple and a low cost process, which can

be used to produce an MEA for fuel cells that can be utilized as power sources for digital devices.

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