Short communication

Fabrication of catalyst-coated membrane-electrode assemblies by doctor blade method and their performance in fuel cells

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ARTICLE INFO

ABSTRACT

Membrane-electrode assemblies (MEAs) have been fabricated with a direct coating of the catalyst slurry by a doctor blade method on the pre-swollen Nafion membrane for proton exchange membrane (PEMFC) and direct methanol fuel cells (DMFC). The effects of various swelling agents with different boiling points such as ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TEEG), and glycerol in the swelling step of the membrane and the drying step of the coated catalyst have been investigated. Also, the use of dimethyl sulfoxide (DMSO) as a dispersing agent in the catalyst slurry has been investigated. Among the various swelling agents investigated, EG gives the best results with the dispersing agent DMSO offering further improvement. The MEAs fabricated with the EG-swollen membranes and DMSO as a dispersing agent in the catalyst layer show good performance in single fuel cells with hydrogen and methanol fuels.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) show great promise as power sources for a variety of energy needs owing to their high power density. However, the mass production of high-quality membrane-electrode assemblies (MEA) is critical for the successful commercialization of PEMFC. The current performances of PEMFCs are strongly influenced by the MEA fabrication methods due to variations in the catalyst utilization and the interfacial characteristics between the catalyst layer and the membrane [1–5].

The MEA fabrication methods could be categorized based on the substrate type and the technique used for the catalyst coating process. Currently, the CCM (catalyst-coated membrane) process offers higher performance than the CCS (catalyst-coated substrate) process due to the better interfacial properties [6]. Applying the catalyst layer to the membrane results in an efficient utilization of the catalyst material, as well as better contact of the catalyst and the ionomer with the proton-conducting membrane. In the CCS process, the loss of catalytically active sites could occur by an incorporation of the particles into the porous gas diffusion layer.

With the CCM process, the direct catalyst coating method is simpler and more efficient than the indirect coating method involving a transfer after coating on the substrate. However, the direct deposition of catalyst onto the membrane could be complicated by the swelling of the membrane during the coating process. The

hydration of membrane induces in-plane compression, and the membrane creeps to relieve these stresses. The membrane and catalyst layer could be deformed by fast volume changes occurring when the catalyst slurry is coated onto the polymer membrane. Therefore, controlling the swelling of the membranes is important in the direct catalyst coating method for the fabrication of high-quality MEAs. Hsu et al. suggested an innovative process by employing a pre-swollen Nafion membrane [7]. Nafion swells to a greater extent in a number of organic solvents than it does in water. Therefore, they soaked the Nafion membrane in ethylene glycol (EG) and sprayed the catalyst slurry onto the pre-swollen membrane. The MEAs thus prepared showed ∼16% improvement over a commercially available MEA due to a reduction of the stress problems by the pre-swelling process.

There are several methods for catalyst coating: spraying [5], screen printing [8,9] and rolling [10,11]. With these catalyst coating methods, doctor blade method is an efficient way for realizing a high precision in catalyst loading with high reproducibility. Bender et al. [12] coated the catalyst on a Teflon film by the doctor blade method and pointed out that this process is significantly more precise and faster than the hand painting process [12]. Accordingly, combining the doctor blade method and the pre-swollen membrane could offer an attractive way for the mass production of high-quality MEAs.

With this perspective, we present here the results of direct catalyst coating on the pre-swollen membrane with a doctor blade spreader. We investigate ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TEEG) and glycerol as swelling agents. To obtain a good compatibility between

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Table 1
Composition of the catalyst slurries.

	20 wt.% Pt/C	60 wt.% Pt/C or PtRu/C
Catalyst (mg)	200	200
Water (mg)	350	400
Nafion solution (mg)	857.14	500
DMSO (mg)	200	160
IPA (mg)	100	80
Solid wt.%	20	23
Pt wt.%	16	48

the pre-swollen membrane and catalyst slurry, dimethyl sulfoxide (DMSO) was used as a dispersing agent in the catalyst slurry.

2. Experimental

The Nafion-115 or Nafion-117 (H$^+$ form) membranes were prepared by the following procedure. The membrane was treated sequentially with a 3 wt.% H_2O_2, de-ionized water, 0.5 M H_2SO_4, and de-ionized water at 70 °C for 1 h [7]. The clean membranes were then stored in de-ionized water before use. For the swelling of the membranes, the pre-treated Nafion was cut into 3 cm × 3 cm pieces and dried at 60 °C for 1 h, and then dipped in each swelling solution at room temperature. The volume of the Nafion membrane before and after the treatment was obtained by measuring the dimensions (width, length and thickness) with a digital caliper.

As shown in Table 1, the catalyst slurry was prepared with carbon-supported Pt catalysts (20 wt.% Pt/C, 60 wt.% Pt/C or PtRu/C, E-TEK), Nafion solution (10 wt.%, Dupont), de-ionized water, dimethyl sulfoxide (DMSO), and IPA (isopropyl alcohol). The composition in the catalyst slurry was adjusted for optimized drying rate, concentration, and workability.

Doctor blading was performed on a smooth glass, which was used as a support for the substrate. For doctor blading, the pre-swollen Nafion-115 membrane was prepared by dipping the membrane, which was dried at 60 °C for 1 h, in the swelling agent solution for 1 h. The membrane was then wiped and dried at 60 °C for 5 min before doctor blading. The pre-swollen Nafion-115 membrane was put on the glass, and a 75 μL of the catalyst slurry was dropped on the membrane in front of the blade using a micropipette. A spreader with a height of 10 mil was driven through the catalyst slurry until the coat covered a sufficient area of the Nafion-115 membrane. With the Nafion-117 membrane, a similar procedure was used with a blade height of 15 mil and 100 μL catalyst slurry. The volume of the catalyst slurry, blade height, and drive speed were all adjusted for a given slurry composition until maximum reproducibility of a certain platinum loading was achieved. After drying at room temperature, the other side of the membrane was also coated using the same process. After coating and drying the catalyst slurry on both sides of the membrane, the coated membranes were dried in an oven at 60 °C for 4 h and then dipped into 0.5 M H_2SO_4 solution and de-ionized water at 60 °C for 2 h each. A hot-pressing step was used for assembling with the carbon cloth containing the gas diffusion layer (GDL, E-TEK) under 120 °C and 1200 pounds for 2 min.

The electrochemical evaluations of the MEAs were carried out with a single cell (5 cm^2 active area) at 80 °C, employing humidified hydrogen (150 mL min^{-1}, 14 psi) for the anode and oxygen (200 mL min^{-1}, 16 psi) for the cathode in PEMFC and 1 M methanol solution (5 mL min^{-1}) for the anode and oxygen (200 mL min^{-1}, 20 psi) for the cathode in DMFC.

3. Results and discussion

Fig. 1 shows the sequential volume changes found with the Nafion-117 membrane in the swelling and drying steps. The pre-
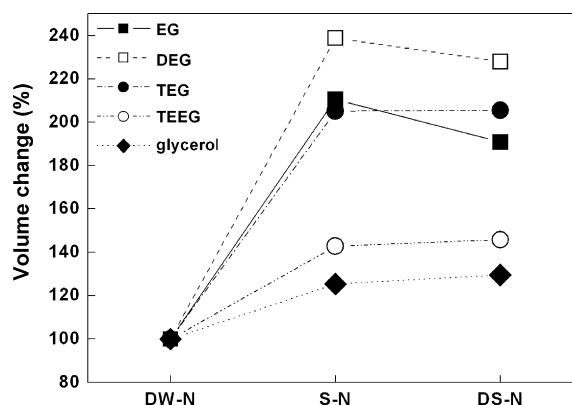

Fig. 1. Comparison of sequential volume changes observed with the Nafion-117 membrane in the swelling and drying steps carried out with different swelling agents. DW-N refers to dried Nafion obtained by drying at 60 °C for 1 h, S-N refers to swollen DW-N obtained by swelling in various solutions at room temperature for 1 h, and DS-N refers to dried S-N obtained after drying at 60 °C for 30 min.

treated membrane was dried at 60 °C for 1 h and is designated as DW-N. The DW-N was then swollen in the swelling agent solution at room temperature for 1 h to obtain S-N. The S-N was then dried at 60 °C for 30 min to obtain DS-N. After the swelling step in various swelling agents, the volume of the membrane varies depending on the swelling agent as DEG > EG > TEG > TEEG > glycerol. The membrane swollen in DEG shows a 140% increase in volume compared to DW-N. After the drying step at 60 °C for 30 min, the volume of each membrane varies as DEG > TEG > EG > TEEG > glycerol, and the degree of volume shrinkage varies as EG > DEG > TEG. The membranes swollen in TEEG and glycerol show a slight increase in volume after drying, which might be due to the humidity adsorbed from air. From the data in Fig. 1, EG, DEG and TEG were selected as swelling agent candidates as they exhibit appreciable volume expansion during swelling.

The time-dependent expansion/shrinkage rate of the Nafion-117 membrane was also investigated and compared with those of water. As shown in Fig. 2(a), the swelling rate and expansion are dependent on the swelling agents. After swelling at room temperature for 1 h, the volume of the membrane varies depending on the swelling agent as DEG > EG > TEG > water. However, the swelling rate at the initial time varies depending on the swelling agent as water > EG > DEG > TEG. With water, several minutes of dipping time is enough for complete swelling. As shown in Fig. 2(b), the shrinkage rate is also dependent on the swelling agent. After drying at 60 °C for 1 h, the decrease in volume varies depending on the swelling agent as EG > water > DEG > TEG. However, the drying rate at the initial time varies depending on the swelling agent as water > EG > DEG > TEG. The EG-swollen membrane displayed a considerable decrease in volume after drying for 1 h. Fig. 2(c) shows the shrinkage to expansion (S/E) ratio of the membranes [S/E = (100 − shrinkage)/(expansion − 100)]. The S/E ratio represents the stability of the swollen membrane during the catalyst coating process. In our study, TEG offers the most stability in volume change.

The swelling of Nafion could be explained by the polar interactions at the liquid/polymer interfaces [13,14]. It is well known that Nafion is composed of two incompatible segments, a hydrophilic vinyl ether side chain terminated with sulfonic acid groups and a hydrophobic perfluorocarbon backbone [15]. While the hydrophilic side attracts polar solvents, the hydrophobic side favors neutral or nonpolar solvents. Water is a polar solvent, so it strongly adheres only to the hydrophilic chain. On the other hand, the organic solvents are less polar than water, and the hydrophilic and hydrophobic sites of the organic solvents are absorbed,
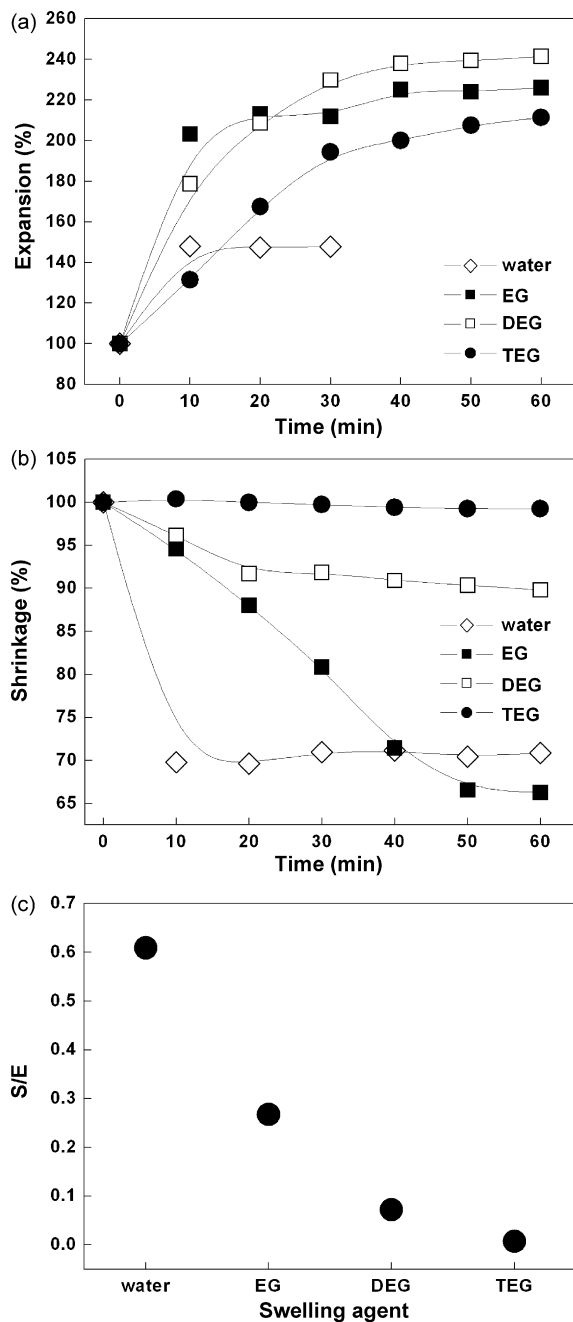
Fig. 2. Comparison of the volume changes versus time in swollen and dried Nafion-117 during 1 h: (a) expansion rate, (b) shrinkage rate, and (c) shrinkage/expansion (S/E) ratio [S/E = (100 − shrinkage)/(expansion − 100)].

Fig. 3. Optical microscopic images of the dried catalyst layer on the Nafion-117 membrane: (a) water-swollen membrane and (b) EG-swollen membrane.

respectively, by the sulfonic acid groups and the perfluorocarbon backbone. As a result, the swelling or liquid uptake of the membranes in organic solvents under steady-state condition is much higher than that in water [14,16]. Additionally, the expansion rate at initial time might be related to the diffusion properties, which could be influenced by the molecular size [17]. Therefore, the high volume increase observed for DEG might be due to its polarity and the molecular size. On the other hand, the drying rate might be determined by the boiling point of the swelling agents: water (100 °C), EG (197 °C), DEG (244 °C) and TEG (285 °C).

The effect of the swelling agent was then investigated in the doctor blading process. After the catalyst coating, the catalyst layer should be dried without any deformation in the catalyst layer and membrane. When DEG and TEG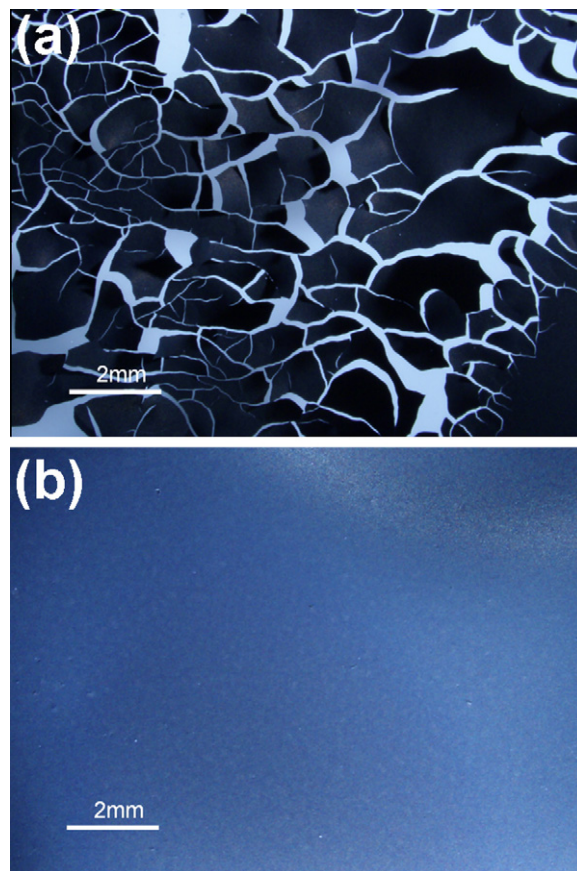 were used as swelling agents, the coated catalyst layers did not dry well at temperature below 60 °C, and wetting in the catalyst layer was observed after several days. This might be due to the slow drying rate and diffusion of the high boiling point DEG and TEG from the membrane into catalyst layer. In contrast, when water and EG were used as swelling agents, the catalyst layer could be dried. Fig. 3 shows the optical microscopic images of the dried catalyst layer on the water- and EG-swollen Nafion-117 membranes. As seen in Fig. 3(a), cracks and detachments were observed after drying the catalyst layer on the water-swollen membrane. This result might be due to the fast swelling/shrinkage rates occurring during the coating and drying processes. Fig. 3(b) shows the dried catalyst layer on the EG-swollen membrane. As seen in Fig. 3(b), a smooth and stable catalyst layer is formed when EG was used as the swelling agent. Also, the morphological property of the coated catalyst layer is improved considerably on the swollen membrane. This result indicates that an optimal drying rate for the swelling agent is important for obtaining a stable catalyst layer on the membrane.

Accordingly, the effect of DMSO in the coating process was investigated. The catalyst slurries with and without DMSO were applied onto the EG-swollen membrane and compared. It was found that the catalyst layer after drying was worse without using DMSO. The solution of Nafion ionomer in a mixture of water/IPA/DMSO will have a high dielectric constant ($\varepsilon > 10$) [18]. So the solution form of ionomer could assist the ink slurry in creating more attachments to the membrane. Also, the similar boiling point (189 °C) of DMSO with EG could eliminate the possible deformation in the catalyst layer during drying. These characteristics result in good compatibility between the swollen membrane and the catalyst slurry. For the fabrication of a stable catalyst layer on the membrane, the drying rate of the swelling agents and compat-
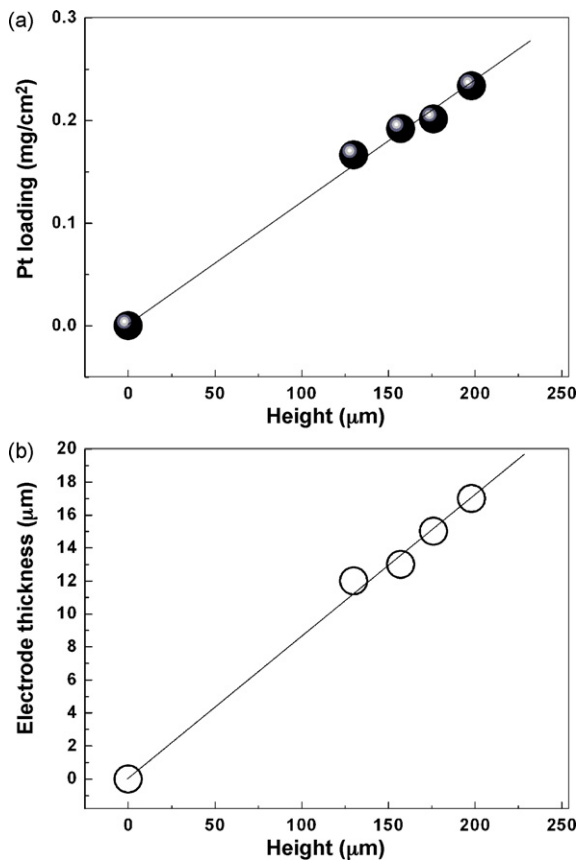
Fig. 4. Relation between Pt loading (or electrode thickness) and height (blade height–substrate thickness): (a) Pt loading and (b) electrode thickness in the catalyst coating.
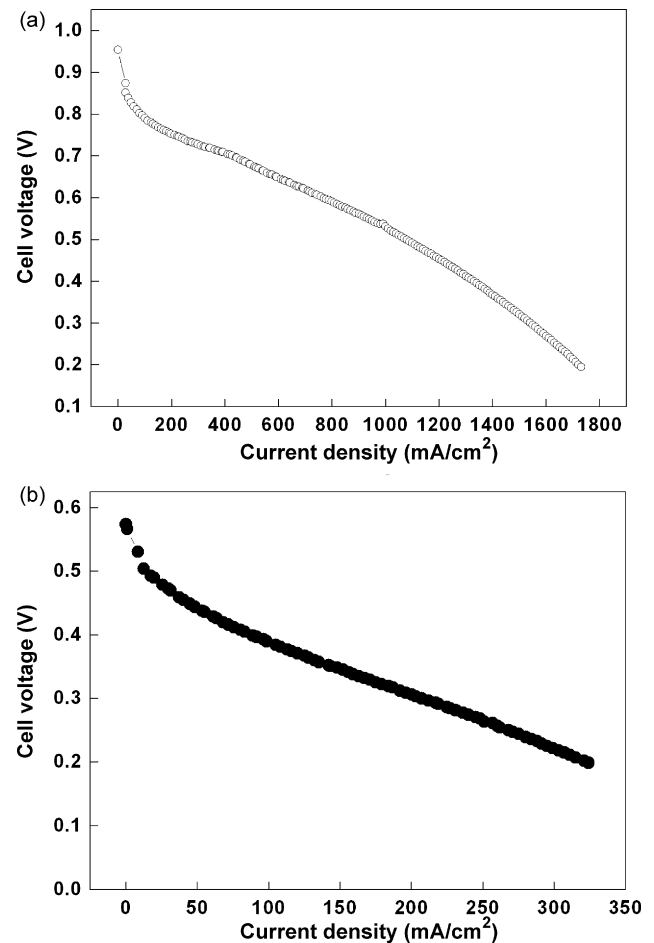

Fig. 5. Single-cell polarization curves of the MEAs prepared with EG-swollen membranes in (a) a hydrogen fuel cell and (b) a direct methanol fuel cell.

ibility between the catalyst slurry and the membrane should be optimized in the direct catalyst coating process.

The effects of Pt loading and electrode thickness were also investigated using 20 wt.% Pt/C catalyst and Teflon substrates with different thicknesses. Differences in the weight and thickness were measured after the catalyst coating. In this experiment, 10 mil height of doctor blade and 75 μL of slurry volume were used on Nafion-115 membrane. Fig. 4 shows the relation between Pt loading (or electrode thickness) and height (blade height–substrate thickness). As seen in Fig. 4, Pt loading and electrode thickness show a linear dependence on the height. This result indicates the high precision and reproducibility of the doctor blade method. From Fig. 4(a) and (b), the calculated Pt loading and electrode thickness were 0.125 mg cm^{-2} and 10 μm when the catalyst slurry was coated on the EG-swollen membrane. This Pt loading is in a similar scale to those of Bender et al. [12]. The real Pt loading and electrode thickness in MEAs could be estimated using their dependence on the height while keeping the other parameters constant.

The MEAs prepared with the EG-swollen Nafion-115 membrane were tested in single cells with hydrogen and methanol fuels. Fig. 5(a) shows the performances of the MEA (anode: 20 wt.% Pt/C, cathode: 60 wt.% Pt/C) in a hydrogen fuel cell, and a current density of 800 mA cm^{-2} is found at 0.6 V. Fig. 5(b) shows the performance of the MEA (anode: 60 wt.% PtRu/C, cathode: 60 wt.% Pt/C) in a direct methanol fuel cell, and a current density of 80 mA cm^{-2} is found at 0.4 V. These performances under the same operating temperatures are higher than those of the MEAs fabricated by conventional CCM. For a comparison, Xiong et al. reported 300 mA cm^{-2} (0.6 V) in hydrogen fuel cell using similar catalyst loading (0.1 mg cm^{-2}) and 25 mA cm^{-2} (0.4 V) in direct methanol fuel cell using a high catalyst

loading (1 mg cm^{-2}) [19,20]. The data thus illustrate the usefulness of direct catalyst coating on pre-swollen membrane using the doctor blade method.

4. Conclusions

The effect of various pre-swelling agents with different boiling points on the fabrication of MEAs with Nafion membranes has been investigated systematically with a doctor blade method. The results show that MEAs with high reproducibility and precision along with good electrochemical performance could be obtained by a direct coating of the slurry on the pre-swollen membranes obtained by using EG as a pre-swelling agent. Additionally, use of DMSO as a dispersing agent in the catalyst slurry offers smooth and dense catalyst layers on the pre-swollen membrane due to the optimal drying rate of ethylene glycol in the membrane and good compatibility between the catalyst slurry and the membrane. The doctor blade method presented here could be adopted for mass production of high-quality MEAs with reproducible properties.

Acknowledgements

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