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Development of a novel decal transfer process for fabrication of high-performance and reliable membrane electrode assemblies for PEMFCs

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ABSTRACT

To improve the performance of a polymer electrolyte membrane fuel cell (PEMFC), various membrane electrode assemblies (MEAs) were fabricated by the decal process. When peeling the decal films away from a Nafion membrane, a novel liquid nitrogen (LN₂) freezing method was employed. The results of a Fourier Transform Infrared (FTIR) analysis of the Nafion membranes demonstrate that this proposed method has no impact on the molecular structure of the Nafion polymer. In addition, the method makes it possible to achieve complete decal transferring under a wide range of hot-pressing pressures and temperatures: 9.8–15.7 MPa and 100–140 °C, respectively. Another approach to optimize the decal technique is to dry catalyst layers under vacuum. Catalyst layers dried under vacuum show better cell performances than atmospherically dried ones. Vacuum drying significantly facilitates the formation of small pores within Pt/C agglomerates on catalyst layers. Third, the use of Additive-A as a commercial dispersant in the catalyst ink has been investigated. From rheological characterizations, including thixotropy and catalyst ink viscosity, it is obvious that the additive plays an important role in elevating the dispersion stability of the ink. In addition, surface images of the catalyst layers revealed that the dispersing agent reduces cracks or fractures within the layers. Although adding Additive-A did not have an effect on the single-cell performance, the MEAs with the dispersant are expected to have better results for a long-term performance test of a single cell.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are attractive because of their low pollution and high energy density at low temperatures (50–90 °C). However, to successfully commercialize a PEMFC, mass production of the membrane electrode assembly (MEA), which consists of a polymer electrolyte membrane with catalyst layers on both sides and gas

diffusion layers (GDLs), is necessary. It is generally accepted that the MEA is the heart of PEMFCs and that it determines their performance. The MEA performance strongly depends on how the MEA is fabricated [1–4].

To date, several MEA fabrication techniques have been developed, such as decal, catalyst-coated membrane (CCM) and catalyst-coated gas diffusion layer (CCG) methods [5–11]. Among these MEA fabrication methods, the decal process is

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considered the most suitable method for mass producing MEAs. In this procedure, as shown in Fig. 1, the catalyst ink is first prepared with a Pt catalyst, an ionomer, and certain solvents. It is then coated over the decal substrate, such as Teflon film, by using a doctor blade in general. After spreading the catalyst ink on the substrate, the remaining solvent has to be evaporated to form an effective three-phase boundary where the catalyst, the reactants and the ionomer meet for electrochemical reactions to occur. In order to join the anode, the cathode and the membrane together, a hot-pressing process is subsequently carried out, and then the decal substrates are peeled away from both electrodes. In terms of the decal process, many researchers have been working to improve the performance of PEMFCs. However, several problems remain. First, the decal method causes uneven or incomplete transfer of the Pt catalyst from the decal substrate to the membrane [5]. In addition, we must find the optimum conditions for hot-pressing parameters such as the pressure and the temperature [1,5,11,15–19]. Second, in high-current regions, the microstructures of catalyst layers should be designed to eliminate the product water easily [10]. Third, the catalyst ink has to be prepared by dispersing appropriate amounts of catalyst and ionomer solution in a mixture of solvent, boosting Pt utilization and proton conduction [11].

In this work, we examined the three important factors mentioned above by optimizing a decal technique. To address the first problem, during the peeling-off process in Fig. 1, a liquid nitrogen (LN_2) treatment was employed to achieve complete decal transfer of the catalyst layers onto the membranes under a wide range of hot-pressing pressures and temperatures [12]. In addition, to address the second research topic associated with mass transfer problems at a high-current density, we applied a vacuum drying method when drying the catalyst layers on the decal films [13]. We compared the cell performances of MEAs fabricated by two different drying methods, atmospheric and vacuum drying. Even

though extensive studies have investigated decal processes, the effects of atmospheric and vacuum drying conditions on PEMFC performance have not yet been elucidated. Third, we chose to create a well-dispersed catalyst ink by adding a commercial dispersing agent into the catalyst ink [14]. The effect of the dispersant on the ink was examined through various experiments. We present here the results of these three categories of experiments that were focused on optimizing the decal process.

2. Experimental

2.1. Materials

As an ionomer solution, 20 wt% Nafion solution ($\text{EW} = 1100$, DuPont Co.) was adopted. The catalyst inks were prepared by mixing a carbon-supported Pt catalyst (Tanaka K. K., Pt 45.6 wt %), isopropyl alcohol (J.T. Baker, HPLC grade), deionized water (resistivity of $18.2 \text{ M}\Omega \text{ cm}$, Millipore, USA) and the Nafion solution. Additive-A, a commercial dispersant from BYK Additives & Instruments, was used for assessing the effect of a dispersing agent on the ink. A small amount of the additive was mixed with the catalyst ink. In this study, the Nafion ionomer content was adjusted to 30 wt% of the total solid content. In addition, Nafion 112 (thickness $\sim 50 \mu\text{m}$, DuPont Co.) was used as the polymer electrolyte membrane. As a gas diffusion layer, Sigracet 10BC was purchased from SGL Carbon, Inc.

2.2. MEA preparation by decal process

The catalyst ink was stirred for 30 min with a magnetic bar. Next, a homogenizer (ULTRA-TURAX, Younglin Corp.) was employed to ensure that all of the Pt particles came into contact with the other components uniformly. Table 1 shows

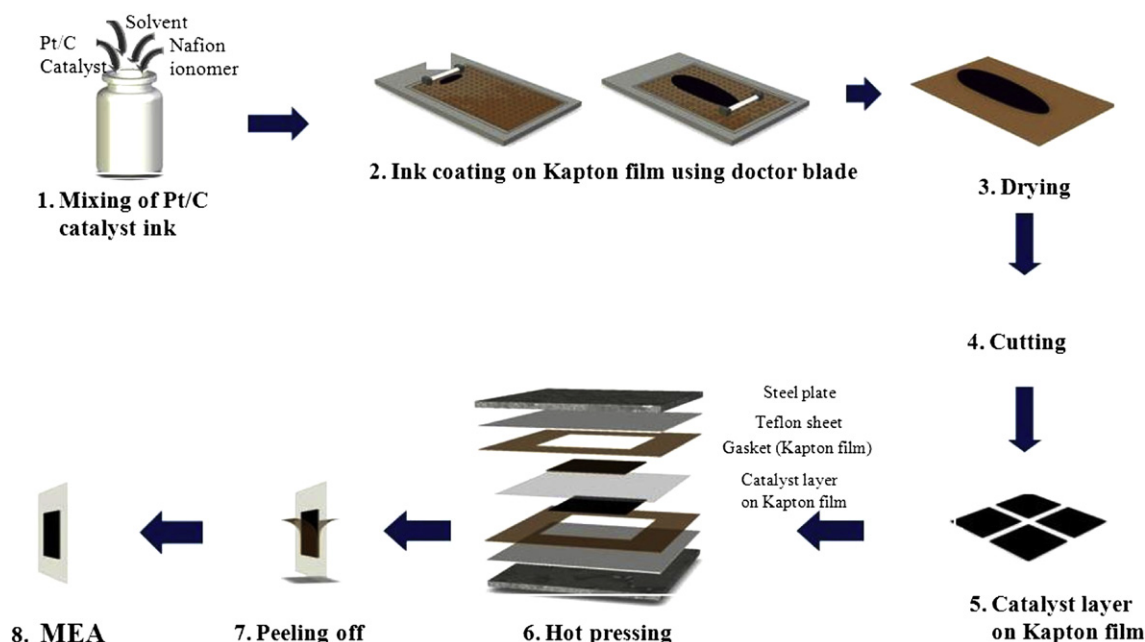


Fig. 1 – A schematic procedure for the MEA fabrication by the decal process.

the experimental conditions used for the homogenizer. All mixing processes were carried out at room temperature. After finishing this procedure, the prepared ink was coated on a substrate film with a doctor blade. Once coated, the decal films were dried overnight at 23 °C. The dried catalyst layers were hot-pressed onto both sides of a Nafion membrane. The bonding conditions of the hot-pressing step, such as the temperature, the pressure and the time, are reported in Table 1. Next, the decal substrates were released from two sides of the electrodes, leaving the MEAs. The Pt loading values were calculated by weighing the decal film before and after this releasing process. In addition, the transfer yield was defined as the weight of catalyst layer transferred to the membrane divided by the weight of catalyst layer coated to the decal substrate film.

2.3. Preparation of samples and their characterization

2.3.1. Decal transferring of catalyst layers onto the membrane by the LN₂ freezing method

Eight MEAs were made at the different hot-pressing temperatures and pressures given in Table 1. Four of them were treated with liquid nitrogen (LN₂) just before removing the decal films from the MEAs. In contrast, the conventional method was applied to the other samples, which means the decal films were peeled away from the MEA without additional treatment. To determine whether a complete transfer had been accomplished, the Pt loading of the cathode and the anode was measured. In addition, we investigated the effect of the LN₂ freezing method on the MEAs. To do this, the Nafion membranes were analyzed by Fourier Transform Infrared (FTIR) Spectroscopy in transmission mode before and after LN₂ treatment was applied to the MEAs, and then the cell performances of the MEA were evaluated.

2.3.2. Vacuum drying method

When drying the catalyst layers that were spread on substrate films, we fabricated two kinds of MEAs that were dried under either atmospheric or vacuum conditions. The Pt loading was kept at 0.3 mg/cm² for the cathode and anode electrodes. The pore structures of the catalyst layers were determined with a mercury porosimeter (AutoPore IV, Micromeritics). Subsequently, the single-cell tests of the corresponding MEAs were conducted.

2.3.3. Effect of Additive-A on the dispersion of catalyst ink

The catalyst ink mixed with the Additive-A was prepared. The rheological behavior of the ink was evaluated with a rotational

rheometer (MCR500, Rheoplus) to identify the dispersibility of the ionomer and the Pt catalyst in the ink. In order to verify if this ink was shear-stable or thixotropic, a thixotropic analysis was employed. The shear stress range (0–30 Pa) of this test was scanned forwards and then backwards, and the measuring program was run five times for each sample. In addition, the ink viscosity was measured at 23 °C with a cone-plate geometry under shear rates between 0.1 and 1000 s^{−1}. With the completion of the coating and drying procedures, a scanning electron microscope (SEM, XL-30 FEG-ESEM, FEI Co.) was used to observe the surface of the catalyst layers on the decal films. The Pt contents were controlled at 0.3 mg/cm² for the anode and the cathode. For comparison, the experiments with the conventional catalyst ink that did not include the additive were also conducted in the same manner.

2.4. Single-cell testing

The prepared MEAs, 25 cm² in active geometric area, were placed between two pieces of gas diffusion layers. Two graphite bipolar plates were used as current collectors and then assembled in a custom-made single-cell frame. A thermocouple was inserted into the graphite bipolar plates to measure the cell temperature. The single cell was then evaluated in a fuel cell test station (CES-F-S08008, CNL) equipped with an electronic load (ESL-300Z DC Electronic Load, Unicorn Co., Ltd). When testing the cell performance, the cell was operated at 65 °C under atmospheric pressure conditions. Using bubbler-type humidifiers, the relative humidity of two electrodes was fixed at 100%. The stoichiometries of hydrogen (anode) and air (cathode) were 1.5 and 2.0, respectively. After setting up the experimental conditions for the single-cell tests, each cell was activated under a constant voltage of 0.45 V for 48 h. The MEA performance was characterized by measuring the polarization curve, while the voltage was recorded at each current density.

After the polarization experiments (I–V curves), the single cell was characterized by electrochemical impedance spectroscopy (EIS). Under fuel cell operation conditions, EIS was performed at a dc potential of 0.85 V with an amplitude of 5 mV and an ac frequency range of 10 kHz–0.01 Hz.

3. Results and discussion

3.1. Decal transferring of catalyst layers onto the membrane by the LN₂ freezing method

In the first part of this work, the four MEAs, RT_1–RT_4, were made by the conventional method in which the decal films are peeled off of the MEAs without LN₂ treatment. For comparison with these samples, we applied the LN₂ freezing method to the rest of the MEAs, LN_1–LN_4, as seen in Table 2. The new technique we developed is to scatter liquid nitrogen over the MEAs just before releasing the foreign substrates from them. To prevent the MEAs from being frozen during this process, this developed method was applied at room temperature where liquid nitrogen is quickly changed into nitrogen gas. Table 2 represents the Pt loadings and the transfer yield according to the different release methods, pressures and

Table 1 – Experimental conditions for mixing the catalyst ink and for hot pressing.

	Condition
Mixing the catalyst ink (Homogenization)	Temperature: 23 °C Speed: 15000 rpm Time: 2 h
Hot pressing	Pressure: 15.7 and 9.8 MPa Temperature: 140 and 100 °C Time: 4 min

Table 2 – Pt loading and transfer yield according to the substrate releasing method and hot-pressing conditions.

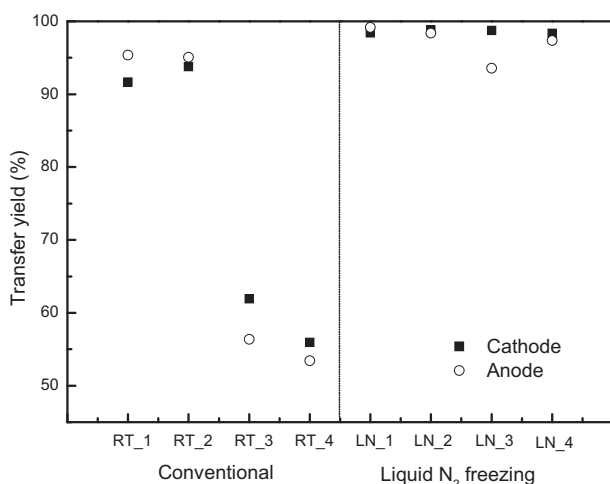
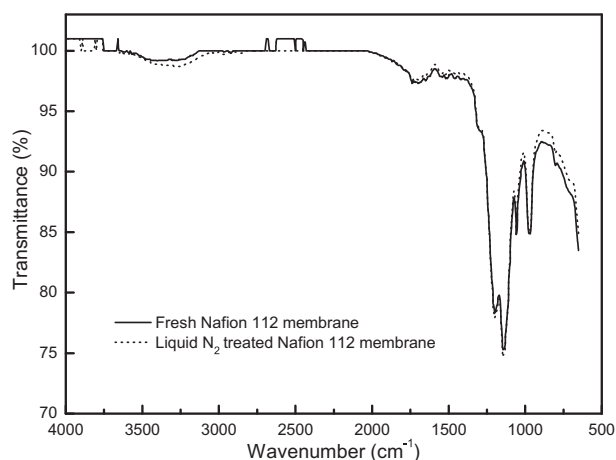
Substrate releasing method		Hot-pressing condition		Pt loading (mg/cm ²)		Transfer yield (%)	
		Pressure (MPa)	Temperature (°C)	Cathode	Anode	Cathode	Anode
RT_1	Conventional	15.7	140	0.307	0.325	91.7	95.4
RT_2	Conventional	15.7	140	0.309	0.298	93.8	95.1
RT_3	Conventional	9.8	140	0.191	0.172	61.9	56.4
RT_4	Conventional	9.8	100	0.170	0.154	55.9	53.4
LN_1	Liquid N ₂ freezing	15.7	140	0.320	0.303	98.4	99.2
LN_2	Liquid N ₂ freezing	15.7	140	0.319	0.315	98.8	98.4
LN_3	Liquid N ₂ freezing	9.8	140	0.302	0.311	98.7	93.6
LN_4	Liquid N ₂ freezing	9.8	100	0.307	0.285	98.4	97.4

temperatures of the hot-pressing conditions. As shown in Fig. 2, the differences in the transfer yield between two types of MEAs are pronounced, indicating that the LN₂ freezing method leads to much better results than the conventional method in terms of facilitating a high decal transfer rate.

From a closer look at the data in Table 2, it can be observed that in the new method, the measured transfer yield is most often greater than approximately 97% with an exception of 94% for the anode of LN₃. In contrast, without the liquid N₂ freezing process, the transfer yield was about 92–95% and 53–62% at hot-pressing pressure of 15.7 and 9.8 MPa, respectively. Typically, a high hot-pressing pressure results in a thinner catalyst layer, ensuring interfacial contact between the two electrodes and the membrane [11,15]. In spite of this advantage, mass transport is limited because of the decreased porosity of the electrodes. On the other hand, if low pressure is used, more porous catalyst layers are formed. However, after hot pressing at a low pressure, delamination between the electrodes and the membrane can occur [1,11]. Not only the bonding pressure but also the bonding temperature should be optimized. Because the glass transition temperature (T_g) of Nafion is approximately 125 °C, at temperatures lower than the T_g value, the Nafion resin in both the ionomer and the membrane will not melt. This indicates that it is difficult to

form good ionomeric contact between the catalyst layers and the membrane [1,11]. On the contrary, high temperature can cause some loss of the water retention properties of the Nafion membrane, degradation of the ionomer and partial delamination of the electrodes from the membrane [1,11]. Regarding the optimization of the hot-pressing parameters, many researchers have made efforts to obtain an optimum value [5,11,15–19]. With the help of this proposed approach, however, these burdens to find such optimal conditions can be reduced. The LN₂ freezing method provided us with nearly complete decal transferring over a wide range of hot-pressing pressures and temperatures, 9.8–15.7 MPa and 100–140 °C, respectively.

To investigate the effect of LN₂ treatment on a Nafion membrane, an FTIR analysis of the membranes was conducted. Fig. 3 shows FTIR spectra of fresh and LN₂-treated Nafion membranes. Four main peaks at 1197, 1142, 1056 and 969 cm⁻¹ were detected in the range of wavenumbers from 4000 to 500 cm⁻¹, corresponding to –CF₂– antisymmetric, –CF₂– symmetric, SO₃⁻ symmetric and C–O–C symmetric stretching of the Nafion polymer, respectively [2,20,21]. It can clearly be seen that the FTIR spectrum of a fresh membrane is identical to that of the LN₂-treated membrane. Thus, this result points to the fact that the LN₂ freezing method has no influence on the molecular structure of the membrane.

**Fig. 2 – Effects of the substrate releasing methods on the transfer yield.****Fig. 3 – FTIR spectra of the Nafion 112 membrane before and after the LN₂ freezing treatment.**

The polarization curves plotted in Fig. 4 also play an important role in showing that no alteration of the chemical structures of the MEAs fabricated with this method occurred. For the three MEAs with a similar amount of Pt loading ($\sim 0.3 \text{ mg/cm}^2$), RT_1, LN_1 and LN_4, there were no differences in the cell polarization data over the entire current density region. In the case of RT_4, it gave the lower cell performance than the other three, due to the low transfer yield around 55%. Accordingly, this leads to the conclusion that the LN_2 freezing method is very useful for enhancing decal transfer yield and hence reliability of the MEAs over a wide range of hot-pressing parameters while maintaining the same level of MEA performances.

3.2. Vacuum drying method

In this section, the single-cell performances of the MEAs using two different drying conditions were compared. Several research groups fabricated MEAs under the atmospheric drying condition [10,18,22,23]. Other researchers studied the performance of MEAs prepared with vacuum drying [17,24–26]. Komoda and coworkers fabricated MEAs by using a pressure-controlled drying technique that controls the drying rate [27]. However, they investigated how the PEMFC performance is affected by the mixing time of the catalyst ink, with the same drying condition. Despite extensive studies on MEA performance, the most suitable drying condition has not yet been clarified. In the present study, when drying catalyst layers on the substrate film at 23°C , two kinds of layers were prepared under atmospheric and vacuum conditions, respectively. In Fig. 5, the current density–voltage characteristics of two types of catalyst layers are presented. The cell performance levels of the four MEAs were similar at low current densities lower than 600 mA/cm^2 . However, as the current density increased, the difference in the cell voltages as a function of the drying condition was evident in the high-current region particularly higher than 1000 mA/cm^2 . The atmospherically dried samples show more rapid voltage drops than the vacuum-dried ones. At a current density of 1000 mA/

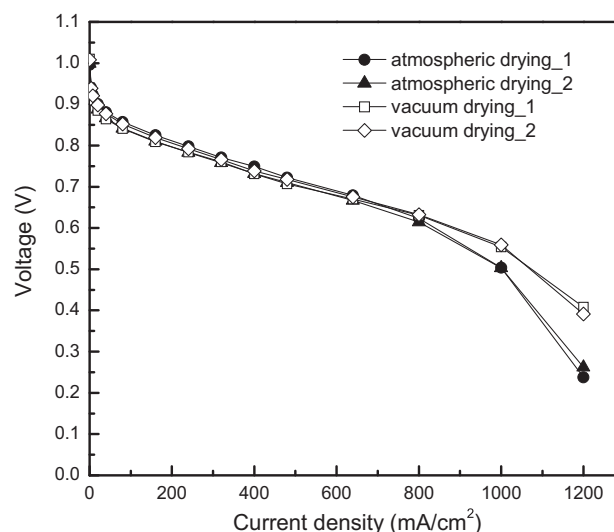


Fig. 5 – The effects of the drying conditions on the cell performance.

cm^2 , cell voltage of the MEAs prepared with vacuum drying was 0.56 V , which is approximately 12% higher than that of MEAs prepared with atmospheric drying (0.50 V). As the current density was increased, the differences in the cell performances were more pronounced. In a mass transfer region, this result can be explained in terms of the pore volumes of the catalyst layers. Various research groups have pointed out that the pore structures of catalyst layers have an impact on cell performance [10,25–28]. Because the catalyst layers are regions where electrochemical reactions occur, they must be porous enough to allow gas to diffuse to the reaction sites and liquid water to wick out. Watanabe et al. reported that both small and large pores can be found in the catalyst layer, and they correspond to the spaces within the Pt/C aggregates and the spaces between such individual aggregates, respectively [29]. In our analysis of pore size distributions of catalyst layers in Fig. 6, there were two categories of pores observed: small pores in the range of $0.01\text{--}1 \mu\text{m}$ in diameter and large pores in the range of $1\text{--}1000 \mu\text{m}$ in diameter. These graphs demonstrate that vacuum drying in particular promotes the formation of small pores in the MEA. The higher pore volume produces more reaction sites in the catalyst layer. In addition, according to the work reported by Chun et al. [30], capillary-driven liquid flow may predominate in fuel cell operation, especially in the oversaturated system. In the Young–Laplace equation, the capillary pressure can be related to the pore size by

$$P_c = \frac{2\gamma \cos \theta}{r}$$

where P_c is the capillary pressure; the contact angle of water with the surface of the pore; r the radius of pores; the surface energy of water. The above equation shows that small pores have an advantage over large pores for water removal. This is attributable to the fact that the capillary pressure increases as the pore diameter decreases [30]. Therefore, a higher performance for MEAs prepared by vacuum drying is to be expected.

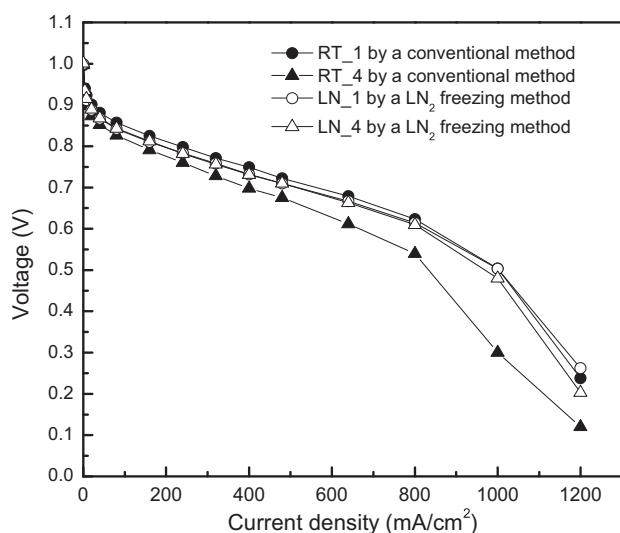


Fig. 4 – The effects of the substrate releasing methods on the cell performance.

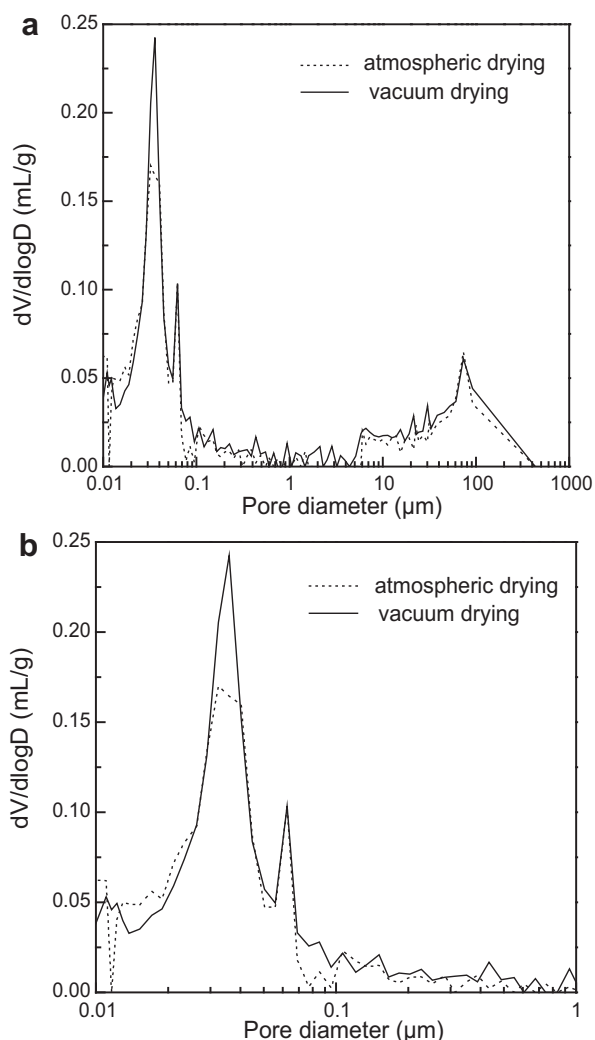


Fig. 6 – The pore size distribution within the catalyst layers for the following ranges of pore diameter: (a) 0.01–1000 μm and (b) 0.01–1 μm .

3.3. Effect of Additive-A on the dispersion of catalyst ink

A Nafion ionomer was used as a binder and a proton conductor to increase the reaction area, boosting Pt utilization. Thus, when the Nafion solution is mixed with Pt/C particles and other solvents, it is vital to extend the contact area between the catalyst and the ionomer and obtain a well-dispersed catalyst ink [11,27,31]. In this research, to achieve a uniform electrode, dispersant Additive-A was added to the catalyst mixtures. The catalyst ink can be classified as a suspension. Zhang and coworkers reported that suspension stability is important because unstable suspensions give rise to large shrinkage, surface cracking and precipitation [32]. In order to evaluate the suspension stability, a thixotropic analysis was conducted. In this test, ascending shear stress–shear rate diagrams have higher shear stress values at each shear rate than the descending diagram. This means that a breakdown of structure cannot be recovered immediately when the stress is removed. As plotted in Fig. 7, the catalyst ink has a thixotropic behavior in nature. The degree of

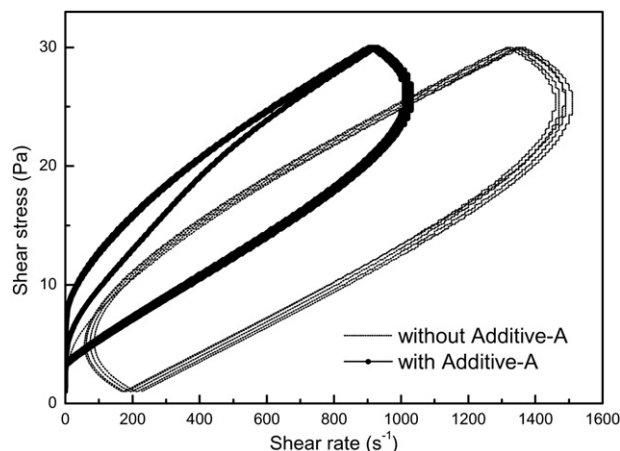


Fig. 7 – Shear stress vs. shear rate profiles for catalyst inks with and without Additive-A measured by the thixotropic analysis.

thixotropy is judged from the area between the up and down curves. The sample with Additive-A has a thixotropy of 9287.3 Pa s^{-1} , and that of the sample without Additive-A is $15,178.5 \text{ Pa s}^{-1}$. Hence, the ink containing Additive-A is more homogeneously dispersed and more stable than the other one because of its smaller thixotropy.

Fig. 8 represents the viscosity versus shear rate curves for the catalyst ink with and without Additive-A. Each viscosity value is significantly affected by particle aggregation in the ink. Two samples exhibit shear-thinning flow behavior over the shear rate range studied, as seen in Fig. 8. Generally, the viscosity of the suspension depends on the volume fraction of particles and the dispersion degree. It is believed that the viscosity of the suspension increases with the volume fraction of particles, and its viscosity is lower as the dispersion improves [33,34]. As presented in this graph, however, the catalyst suspension containing Additive-A shows a higher viscosity. A reasonable explanation for this result might be ascribed to settling of the Pt/C agglomerates. During the mixing of a catalyst ink, the ionomers adsorb on the

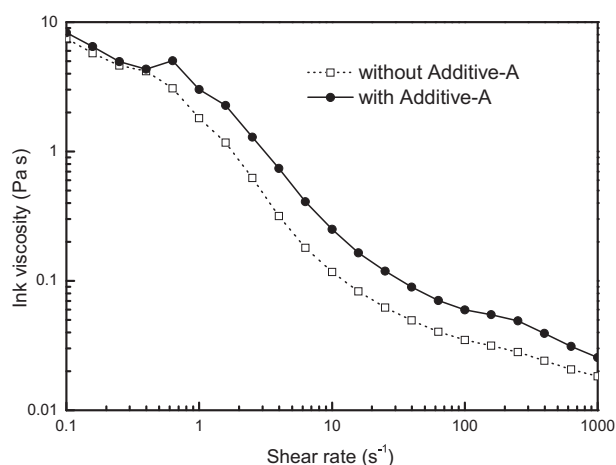


Fig. 8 – Viscosity vs. shear rate curves for catalyst inks with and without Additive-A.

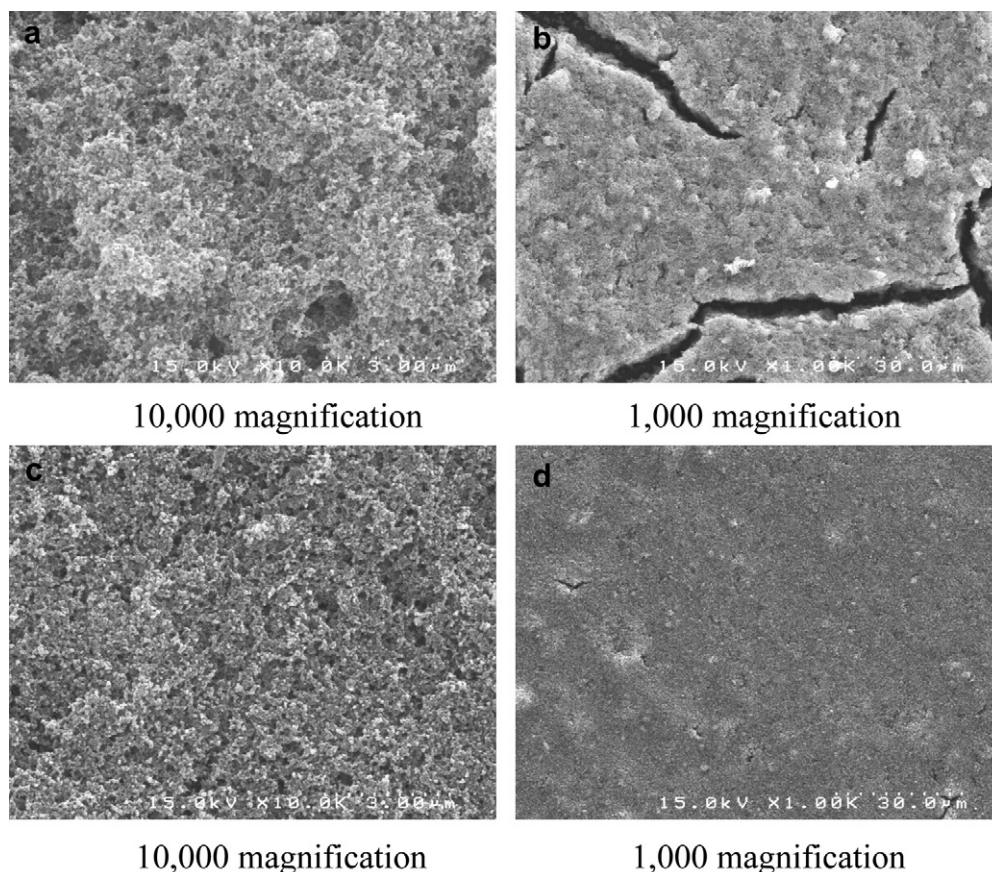


Fig. 9 – SEM images of the dried catalyst layer: (a) without Additive-A, 10,000 magnification; (b) without Additive-A, 1000 magnification; (c) with Additive-A, 10,000 magnification; and (d) with Additive-A, 1000 magnification.

aggregated Pt/C particles to form large Pt/C agglomerates. Some parts of the agglomerates might settle to the bottom. According to Fonseca et al. the particles in a well-dispersed suspension are weakly influenced by gravity, allowing the suspensions to remain homogeneous and stable for a longer time [35]. Therefore, for the ink without the additive, the volume fraction of the particles suspended in the catalyst mixtures decreased, and its viscosity was lower than anticipated. In contrast, it seems that Additive-A facilitates the dispersal of particles and suppresses the particle sedimentation. This leads to an increase in the total volume fraction of the agglomerates, which results in a higher viscosity.

To better understand the internal structures of two different catalyst layers, a surface image was obtained via SEM. Fig. 9 shows the SEM micrographs, which are magnified by factors of 1000 and 10,000. At 10,000 magnification, well-developed porous structures were identified in the surface images (Fig. 9a and c). However, at 1000 magnification, several cracks or fractures were observed on the surface of the catalyst layers containing no Additive-A. For the catalyst layer with Additive-A, cracks or fractures were rarely observed. Consequently, these images demonstrate that Additive-A promotes the formation of network structures of Pt/C agglomerates and allows the catalyst ink to achieve better dispersion stability.

In Fig. 10, the cell voltages for both types of MEAs are plotted as a function of the current density. The MEA with Additive-A was expected to show a higher level of

performance than that without the dispersant since there was no crack or fracture. Contrary to our expectations, the differences between the MEAs with and without the additive were not obvious. Even though the use of the agent reduces cracks and forms more reaction sites, it may block the path of protons and/or electrons that are essential for electrochemical reactions. As shown in Fig. 11, the EIS spectra for the MEAs with and without Additive-A were measured. The diameter of the semi-circle on the real impedance axis represents the charge transfer resistance (R_{ct}) across the electrode–membrane interface. The R_{ct} values for the MEA with and without the dispersant are found to be $0.999 \Omega \text{ cm}^2$ and $0.883 \Omega \text{ cm}^2$, respectively. This result indicates that the MEA with Additive-A has the larger resistance to charge transport. Therefore, it is likely that there is a trade-off between the advantages and disadvantages of the additive. For this reason, in spite of several cracks on the catalyst layer without Additive-A in Fig. 9, the performance of its corresponding MEA was nearly identical to that of the MEA with the additive. However, from the viewpoint of PEMFC durability, cracks on the electrodes may be a disadvantage. It is well known that during the long-term operation of fuel cells, the electrode materials are degraded [36,37]. As a result of electrode degradation, the interface between the catalyst and the ionomer is lost, consequently reducing the electrochemically active surface area of the electrode. Furthermore, the lifetime issues of the electrodes include the stability of the electrode their

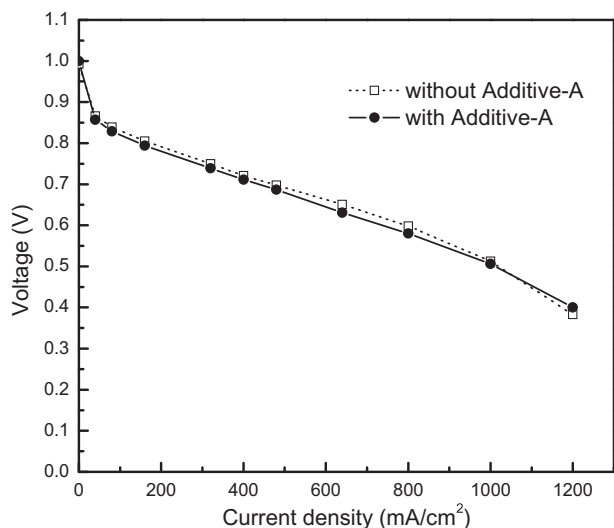


Fig. 10 – The effects of Additive-A on the cell performance.

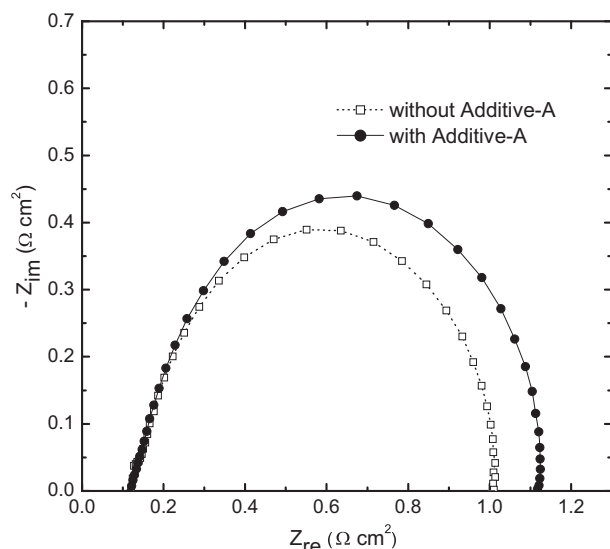


Fig. 11 – The effects of Additive-A on the electrochemical impedance spectra.

structures as well materials [37]. Accordingly, surface cracks on the MEA may cause a faster degradation of MEAs. In the case of the MEA with Additive-A, the electrode degradation can probably be retarded by the use of the additive. In the future, the influence of Additive-A on the durability of PEMFCs will need to be determined based on the long-term performance of a single cell.

4. Conclusions

With the aim of improving PEMFC performance by using a decal process, we have conducted research on three aspects of the decal technique. First, the LN₂ freezing method was used to enhance the transfer yield of Pt catalyst from decal substrates to a membrane, and it made it possible to provide a nearly

complete and reliable transferring under the pressure range of 9.8–15.7 MPa and for temperatures of 100–140 °C. In addition, the method had no influence on the molecular structure of the Nafion membrane, and the performance of the MEA was unchanged. Second, we investigated the effect of different drying conditions on MEA performance. At a current density of 1000 mA/cm², cell voltage of the vacuum-dried MEAs showed greater than 12% higher performances in comparison with the atmosphere-dried ones. This is attributable to the difference in the pore size distribution of the catalyst layers. The vacuum drying facilitated the formation of small pores within the Pt/C agglomerates. Finally, as a dispersing agent, Additive-A was added into the catalyst ink, ensuring better dispersion stability of the catalyst mixture and that there were no surface cracks or fractures on the catalyst layer. This was supported by the evidence based on the rheological behavior of the ink and its SEM images. In terms of the cell performances, there was no improvement from introducing the additive into the ink. However, it seems that use of the additive improves the durability of the PEMFC. Because the additive diminishes cracks and fractures in the catalyst layer, it is expected that MEAs without the additive will show more rapid voltage drops than their counterparts during the long-term operation of a cell.

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REFERENCES

- [1] Kocha SS. Principles of MEA preparation. In: Vielstich W, Lamm A, Gasteiger HA, editors. Handbook of fuel cells – fundamentals technology and applications, vol. 3. New York: Wiley; 2003. p. 538–65.
- [2] Prasanna M, Cho EA, Lim TH, Oh IH. Effects of MEA fabrication method on durability of polymer electrolyte membrane fuel cells. *Electrochim Acta* 2008;53:5909–12.
- [3] Bender G, Zawodzinski TA, Saab AP. Fabrication of high precision PEFC membrane electrode assemblies. *J Power Sources* 2003;124:114–7.
- [4] Bose AB, Shaik R, Mawdsley J. Optimization of the performance of polymer electrolyte fuel cell membrane-electrode assemblies: roles of curing parameters on the catalyst and ionomer structures and morphology. *J Power Sources* 2008;182:61–5.
- [5] Frey TH, Linardi M. Effects of membrane electrode assembly preparation on the polymer electrolyte membrane fuel cell performance. *Electrochim Acta* 2004;50:99–105.
- [6] Sun LL, Ran R, Wang GX, Shao ZP. Fabrication and performance test of a catalyst-coated membrane from direct spray deposition. *Solid State Ionics* 2008;179:960–5.
- [7] Hobson LJ, Nakano Y, Ozu H, Hayase S. Targeting improved DMFC performance. *J Power Sources* 2002;104:79–84.
- [8] Bevers D, Wagner N, Von Bradke M. Innovative production procedure for low cost PEFC electrodes and electrode/membrane structures. *Int J Hydrogen Energy* 1998;23:57–63.
- [9] Rajalakshmi N, Dhathathreyan KS. Catalyst layer in PEMFC electrodes - fabrication, characterisation and analysis. *Chem Eng J* 2007;129:31–40.

- [10] Xie J, More KL, Zawodzinski TA, Smith WH. Porosimetry of MEAs made by thin film decal method and its effect on performance of PEFCs. *J Electrochem Soc* 2004;151: A1841–6.
- [11] Zhang H, Wang X, Zhang J, Zhang J. Conventional catalyst ink, catalyst layer and MEA preparation. In: Zhang J, editor. *PEM fuel cell electrocatalysts and catalyst layers*. New York: Springer; 2008. p. 889–916.
- [12] Cho EA, Lim S, Oh IH, Lim TH, Lee SY, Kim HJ, et al. Korea Patent no. 10-2009-0040407.
- [13] Cho EA, Lim S, Lim TH, Oh IH, Nam SW, Yoon SP, et al. PCT Patent No. PCT/KR2009/0059.
- [14] Cho EA, Jang H, Lim TH, Nam SW, Oh IH, Kim SK, et al. Korea Patent no. 2010-0030003.
- [15] Kuver A, Vogel I, Vielstich W. Distinct performance evaluation of a direct methanol SPE fuel cell. A new method using a dynamic hydrogen reference electrode. *J Power Sources* 1994;52:77–80.
- [16] Krishnan NN, Prabhuram J, Hong YT, Kim HJ, Yoon K, Ha HY, et al. Fabrication of MEA with hydrocarbon based membranes using low temperature decal method for DMFC. *Int J Hydrogen Energy* 2010;35:5647–55.
- [17] Zhang J, Yin GP, Wang ZB, Lai QZ, Cai KD. Effects of hot pressing conditions on the performances of MEAs for direct methanol fuel cells. *J Power Sources* 2007;165: 73–81.
- [18] Saha MS, Paul DK, Peppley BA, Karan K. Fabrication of catalyst-coated membrane by modified decal transfer technique. *Electrochem Commun* 2010;12:410–3.
- [19] Cho JH, Kim JM, Prabhuram J, Hwang SY, Ahn DJ, Ha HY, et al. Fabrication and evaluation of membrane electrode assemblies by low-temperature decal methods for direct methanol fuel cells. *J Power Sources* 2009;187:378–86.
- [20] Fermamdez R, Ferreira-Aparicio P, Daza L. PEMFC electrode preparation: influence of the solvent composition and evaporation rate on the catalytic layer microstructure. *J Power Sources* 2005;151:18–24.
- [21] Liang Z, Chen W, Liu J, Wang S, Zhou Z, Li W, et al. FT-IR study of the microstructure of Nafion® membrane. *J Membr Sci* 2004;233:39–44.
- [22] Jeon S, Lee J, Rios GM, Kim HJ, Lee SY, Cho EA, et al. Effect of ionomer content and relative humidity on polymer electrolyte membrane fuel cell (PEMFC) performance of membrane-electrode assemblies (MEAs) prepared by decal transfer method. *Int J Hydrogen Energy* 2010;35:9678–86.
- [23] Park IS, Li W, Manthiram A. Fabrication of catalyst-coated membrane-electrode assemblies by doctor blade method and their performance in fuel cells. *J Power Sources* 2010;195: 7078–82.
- [24] Passos RR, Paganin VA, Ticianelli EA. Studies of the performance of PEM fuel cell cathodes with the catalyst layer directly applied on Nafion membranes. *Electrochim Acta* 2006;51:5239–45.
- [25] Zhao J, He X, Wang L, Tian J, Wan C, Jiang C. Addition of NH_4HCO_3 as pore-former in membrane electrode assembly for PEMFC. *Int J Hydrogen Energy* 2007;32:380–4.
- [26] Yoon YG, Park GG, Yang TH, Han JN, Lee WY, Kim CS. Effect of pore structure of catalyst layer in a PEMFC on its performance. *Int J Hydrogen Energy* 2003;28:657–62.
- [27] Komoda Y, Okabayashi K, Nishimura H, Hiromitsu M, Oboshi T, Usui H. Dependence of polymer electrolyte fuel cell performance on preparation conditions of slurry for catalyst layers. *J Power Sources* 2009;193:488–94.
- [28] Gode P, Jaouen F, Lindbergh G, Lundbald A, Sumdholm G. Influence of the composition on the structure and electrochemical characteristics of the PEFC cathode. *Electrochim Acta* 2003;48:4175–87.
- [29] Watanabe M, Tomikawa M, Motoo W. Experimental analysis of the reaction layer structure in a gas diffusion electrode. *J Electroanal Chem* 1985;195:81–93.
- [30] Chun JH, Park KT, Jo DH, Lee JY, Kim SG, Lee ES, et al. Determination of the pore size distribution of micro porous layer in PEMFC using pore forming agents under various drying conditions. *Int J Hydrogen Energy* 2010;35:11148–53.
- [31] Uchida M, Aoyama Y, Eda N, Ohta A. Investigation of the microstructure in the catalyst layer and effects of both perfluorosulfonate Ionomer and PTFE-loaded carbon on the catalyst layer of polymer electrolyte fuel cells. *J Electrochem Soc* 1995;142:4143–9.
- [32] Zhang L, Jiang SP, Wang W, Zhang Y. NiO/YSZ, anode-supported, thin-electrolyte, solid oxide fuel cells fabricated by gel casting. *J Power Sources* 2007;170:55–60.
- [33] Hsu CJ, Jean JH. Formulation and dispersion of NiCuZn ferrite paste. *Mater Chem Phys* 2002;78:323–9.
- [34] Lin HW, Chang CP, Hwu WH, Ger MD. The rheological behaviors of screen-printing pastes. *J Mater Sci Process Tech* 2008;197:284–91.
- [35] Fonseca CG, Basaglia RMF, Brant MC, Matencio T, Domingues RZ. Study of the rheological behavior of an anode slurry and the microstructural properties of an anode functional film obtained by spray coating. *Power Tech* 2009;192:352–8.
- [36] Fowler M, Mann RF, Amphlett JC, Peppley BA, Roberge PR. Reliability issues and voltage degradation. In: Vielstich W, Lamm A, Gasteiger HA, editors. *Handbook of fuel cells – fundamentals technology and applications*, vol. 3. New York: Wiley; 2003. p. 663–77.
- [37] De Bruijn FA, Dam VAT, Janssen GJM. Review: durability and degradation issues of PEM fuel cell components. *Fuel Cells* 2008;8:3–22.