Electrospray-assisted fabrication of porous platinum-carbon composite thin layers for enhancing the electrochemical performance of proton-exchange membrane fuel cells

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Article Info

Membrane electrode assembly (MEA) in proton-exchange membrane fuel cells (PEMFCs) have been fabricated using electrospray-assisted deposition of platinum-carbon composites on carbon-fiber-based paper substrate, because the technique is versatile, operated in atmospheric pressure, and easy to scale up for commercialization. In this study, we investigate the effects of electrospray-assisted platinum loadings from 0.1 to 0.5 mg cm$^{-2}$ on the electrochemical performance of PEMFCs. The PEMFCs with platinum loading of 0.3 mg cm$^{-2}$ generate the highest power density, which is ~35% higher than that of PEMFCs fabricated by traditional brush-deposited catalyst layers. Relatively high platinum loading ($>0.3$ mg cm$^{-2}$) enhances the pressure drop in MEA; therefore, the resulting power density is decreased due to low-reacting gas permeability. We also examine the effect of porous structures on the electrochemical performance of PEMFCs. Brij 58-based surfactant templates create micro- and nano-porous structures in the platinum-carbon composite thin layers via thermal removal. These porous structures in the platinum-carbon composite thin layers increase the reacting gas permeability and simultaneously lower the cell resistance, significantly enhancing the electrochemical performance of PEMFCs with porous structures.

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1. Introduction

Hydrogen fuel cells have been extensively developed as highly efficient, cost-effective, and less environmentally harmful energy conversion devices. Proton-exchange membrane fuel cells (PEMFCs) constitute one of versatile and useful fuel cell types because they are operated at relatively low temperatures and are constructed with relatively inexpensive materials. Therefore, PEMFCs are considered potentially important parts that can meet the stringent cost requirements in automobile and stationary power generation markets [1–5].

Generally, catalyst layers in PEMFCs are composed of relatively expensive platinum (Pt) or its alloys. Reducing the manufacturing cost and improving the utilization of catalytic materials are major issues for their applications in the energy industry. Various effective methods to fabricate optimized catalyst layers have been reported, which significantly improve the electrochemical performance of the PEMFCs [6–10]. To improve the utilization of catalyst layers, various catalyst deposition methods have also been developed, including cast [11,12], spray [13,14], and impregnation [15,16], which are known to be effective, but unable to provide a highly uniform catalyst distribution. Chemical vapor deposition [17,18] and sputter [19,20] are known as uniform catalyst deposition methods; however, they require the precisely controlled vacuum conditions and pressure controls, which are expensive, complex, and not easily adaptable to commercial scale-up.

On these grounds, an electrospray method can be considered as one of potential candidates for fabricating uniform catalyst layers in PEMFCs because of its various advantages of relatively simple experimental set-up, operability under atmospheric conditions, and easy commercialization by scale-up processes [21–23]. In addition, the amount of catalyst loading can be controlled more accurately by preparing the homogeneously dispersed catalyst...
Several research groups have attempted to employ the electrospray method to fabricate PEMFC electrodes, in which ultra-low Pt loadings (0.0125–0.1 mg cm$^{-2}$) were used. A linear relationship was commonly observed between the Pt loading amount and the obtained power density. However, Pt loadings much higher than 0.1 mg cm$^{-2}$ fabricated by electrospray deposition have not yet been explored to optimize the electrochemical performance of PEMFCs, which can be strongly affected by the stacking structures (e.g., catalyst layer thickness, catalyst amounts, etc.) of catalyst layers on carbon-fiber-based paper substrate [24–27].

In this study, we systematically investigated the effects of electrospray-assisted deposition of catalyst layers on the electrochemical performance of PEMFCs. Briefly, we fabricate PEMFCs with catalyst layers deposited on carbon-fiber-based paper substrates using electrospray method. The effect of various Pt loadings (0.1–0.5 mg cm$^{-2}$) on the electrochemical performance of PEMFCs was examined in terms of cell performance and resistance analyses. A traditional brush method was also used to fabricate catalyst layers for comparison with the electrospray method. We also examined the effects of porous structures in the Pt-carbon (C) composite layers on the electrochemical performance of PEMFCs. Briefly, surfactant templates (e.g., Brij 58) were added to the Pt-C composite thin layers followed by thermal removal, so that micro- and nano-sized pores were successfully created to improve the reacting gas permeability through the Pt-C composite thin layers.

2. Experimental

2.1. Preparation of catalyst suspension

The catalyst suspension for the electrospray process was prepared with Pt-C nanopowders (20 wt%, E-TEK), Nafion® solution (5 wt% in lower aliphatic alcohols) as the ionomer, and isopropyl alcohol (IPA) as the solvent. The aforementioned precursor-dispersed solution was sonicated in an ultrasonic bath with 200 W and 40 kHz for 1 h. For the catalyst suspension with surfactant templates, ~4.5 wt% non-ionic Brij 58 surfactant (polyethylene glycol hexadecyl ether, HO(CH$_2$CH$_2$O)$_{20}$C$_{16}$H$_{33}$, Sigma-Aldrich) was added to the total mass of Pt-C and Nafion®.
2.2. Electrospray-assisted deposition of Pt-C composite layers

Using both electrospray and brush deposition methods, Pt-C composite layers were coated on the surface of carbon-fiber-based paper substrates (area = 2.25 cm²) and were pretreated with polytetrafluoroethylene. Fig. 1a shows the electrospray device used for depositing Pt-C composite layer on the surface of carbon-fiber-based paper substrate.

The distance between the syringe nozzle and the substrate surface was fixed at ~2.5 cm, which was experimentally determined to be appropriate for covering the entire substrate area with Pt-C composite layers. The carbon-fiber-based paper substrate was heated at ~80°C using a heater (MSH 20-D, Witeg, Germany), which enabled complete evaporation of any residual isopropanol. The injection flow rate of the catalyst suspension was fixed at ~80 μL min⁻¹. The resulting Pt-C composite thin layers with various Pt loadings (0.1–0.5 mg cm⁻²) were obtained by controlling the total inject time of the catalyst suspension. In order to fabricate porous structures, Brij 58-added Pt-C layers were additionally heated at ~350°C for 30 min to thermally remove the Brij 58 surfactant templates from the Pt-C composite thin layers.

2.3. Fabrication and characterization of MEAs

To fabricate MEAs, firstly, Nafion® 212 membrane was inserted between the anode and the cathode, and was then pressed using a hot-press machine operated at 200 bar and 135°C for 10 min. The schematic and photograph of the components assembled for PEMFCs are presented in Fig. 1b and c. The morphological structures of the Pt-C composite thin layers were examined using scanning electron microscopy (SEM; S-4700, Hitachi, Tokyo, Japan). The current density-voltage (J-V) curve was obtained using fuel cell monitor pro 3.0 (FCM; U 103, H-TEC, Germany) feeding dry H₂/O₂ gases at the electrodes under room temperature and atmospheric pressure conditions. The cyclic voltammetry (CV; Reference 3000, GAMRY Instruments, USA) measurement was performed at 50 mV s⁻¹ under H₂/N₂ flow in the electrodes. Electrochemical impedance spectroscopy (EIS; Reference 3000, GAMRY)

![Fig. 3. Top-view and cross-sectional SEM images of brush-deposited Pt-C composite thin layer on carbon-fiber-based paper (a and b, respectively), and of electrospray-deposited Pt-C composite layer formed on carbon-fiber-based paper (c and d, respectively). (Pt loading was fixed at ~0.3 mg cm⁻²).](image)

![Fig. 4. (a) Current density-voltage (J-V) and (b) current density-power density (J-P) curves for PEMFCs composed of brush- and electrospray-assisted MEAs. (The Pt loading was fixed at 0.3 mg cm⁻²).](image)
Instruments, USA) was performed to analyze the internal resistance of the PEMFCs.

3. Results and discussion

3.1. Fabrication and characterization of Pt-C composite layers

We employed an electrospray process to generate fine Pt-C aerosol particles. The electrospray system consisted of syringe, liquid pump, high-voltage power supply, and electrically grounded collector. A high voltage was applied to a syringe nozzle tip, and then a liquid droplet was formed with a semi-spherical shape at the tip of the syringe. The positive charge carriers were moved from electrode to droplet. When the applied voltage was greater than the threshold, the liquid droplet turned into a Taylor cone, which resulted in forming small Pt-C-contained particles due to Coulombic explosion. Fig. 2 shows the various electrospray modes at different voltages at the syringe nozzle tip (2.5–12.5 kV) with a fixed Pt-C solution flow rate of ~80 μL min⁻¹ and a fixed distance of 2.5 cm between the syringe nozzle tip and the substrate surface. At applied voltages lower than 4.5 kV, large droplets were dripped directly on the substrate, while fine droplets were stably generated at voltages above 6.5 kV. At ~8.5 kV, an inverse cone shape was formed and very fine droplets were deposited homogeneously on the entire substrate surface. Multiple jet mode was obtained at applied voltages much higher than 9.5 kV, which resulted in non-

![Fig. 5. SEM images of electrospray-deposited Pt-C composite thin layers formed on carbon-fiber-based paper with Pt loadings of (a and b) 0.1 mg cm⁻², (c and d) 0.2 mg cm⁻², (e and f) 0.3 mg cm⁻², (g and h) 0.4 mg cm⁻², and (i and j) 0.5 mg cm⁻².](image-url)
uniform coating of Pt-C solution on the given substrate. Thus, in this study, the applied voltage was fixed at 8.5 kV for stably generating fine droplets on the substrate.

SEM analyses were performed to examine the morphological structure of the Pt-C composite layers formed by brush and electrospray deposition methods. Here, Pt loading was fixed at ~0.3 mg cm$^{-2}$. After simple brush deposition, the Pt-C composites were randomly located among the carbon fibers, and some carbon fibers were not fully coated with the Pt-C composites, as shown in Fig. 3a. In addition, Pt-C composites remained on the shallow region of carbon-fiber-based paper (Fig. 3b). On the other hand, the Pt-C composite layer prepared by the electrospray deposition method was uniformly distributed along the carbon fibers on the entire substrate surface as shown in Fig. 3c. This suggests that ion and electron transfers were easily made on the entire substrate surface, ensuring stable electrochemical reaction in the PEMFCs. Simultaneously, Pt-C composite layer was uniformly formed on the surface and inside of the carbon fiber paper (Fig. 3d), suggesting that the Pt-C composites present both surface and inside of the carbon fiber paper can also participate in improving the electrochemical reaction.

The current density-voltage ($J$-$V$) and current density-power density ($J$-$P$) curves of the PEMFCs fabricated by brush and electrospray deposition methods are presented in Fig. 4.

The Pt loading for the MEAs was fixed at ~0.3 mg cm$^{-2}$. The $J$-$V$ curves and $J$-$P$ curves were obtained after reaching steady state. For the PEMFCs fabricated by brush deposition method, the open cell voltage was 0.91 V, the short circuit current density was 90 mA cm$^{-2}$, and the highest power density was ~20 mW cm$^{-2}$. However, for the PEMFCs fabricated by electrospray deposition method, the open cell voltage was 0.95 V, the short circuit current density was 132 mA cm$^{-2}$, and the highest power density was ~27 mW cm$^{-2}$. The highest power density for the PEMFCs fabricated by the electrospray deposition method was ~35% higher than that for the PEMFCs fabricated by the brush deposition method. Thus, the PEMFCs fabricated by the electrospray deposition method shows much better electrochemical performance than that of brush-assisted MEA because uniform Pt catalyst thin layers are formed on the surface and inside the carbon fiber paper, which maximizes the utilization of Pt.

3.2. Effects of various Pt loadings on the electrochemical performance of PEMFCs

MEAs with various Pt loadings (0.1–0.5 mg cm$^{-2}$) were fabricated by the electrospray deposition method in this study. SEM analyses were performed to examine Pt-C composite structures for electrospray-assisted Pt loadings of 0.1, 0.2, 0.3, 0.4, and 0.5 mg cm$^{-2}$ on the carbon-fiber-based paper substrate (Fig. 5). When the Pt loading was 0.1 mg cm$^{-2}$, the Pt-C composites were mostly deposited along the carbon fibers, and pores were observed among the carbon fibers (Fig. 5a and b). When the Pt loading was increased to 0.2 mg cm$^{-2}$, some pores among the carbon fibers were filled with Pt-C composites (Fig. 5c and d). When Pt loading was increased to >0.3 mg cm$^{-2}$, compactly dense Pt-C composites were found to cover the carbon fiber paper (Fig. 5e–j).
The J-V curves were obtained for PEMFCs with various Pt loadings (Fig. 6a). The electrochemical performances of the PEMFCs increased upon increasing the Pt loading to 0.3 mg cm\(^{-2}\). However, at Pt loadings >0.3 mg cm\(^{-2}\), electrochemical performances were significantly decreased. Fig. 6b shows the CV analyses for MEAs with various Pt loadings. The electrochemically active surface area (EASA, in m\(^2\) g\(^{-1}\)) was calculated as follows:

![Fig. 8. (a) SEM image of Pt-C composite layers fabricated for Pt loading of 0.3 mg cm\(^{-2}\) without Brij 58 templates. SEM images of Pt-C composite thin layers fabricated with Pt loadings of (b) 0.3 mg cm\(^{-2}\), (c) 0.4 mg cm\(^{-2}\), and (d) 0.5 mg cm\(^{-2}\) after the thermal removal of the Brij 58 templates.](image-url)
where \( Q \) is the real adsorption of a hydrogen monolayer on the membrane surface (\( \mu\text{Ccm}^{-2} \)) and \( M \) is the catalyst loading on the electrode (\( \text{g cm}^{-2} \)). Here, the adsorption of hydrogen monolayer on the surface of polycrystalline Pt was normalized by a factor of 210 \( \mu\text{Ccm}^{-2} \) [28]. The EASA values for the MEAs were determined to be 31.7, 34.9, 47.6, 26.5, and 25.4 \( \text{m}^2\text{g}^{-1} \), for Pt loadings of 0.1, 0.2, 0.3, 0.4, and 0.5 \( \text{mg cm}^{-2} \), respectively. It is generally known that higher Pt loadings in MEAs result in larger EASA values [26]. However, for the electrospray-deposited catalyst layers fabricated in this study, the maximum EASA of 47.6 \( \text{m}^2\text{g}^{-1} \) is found for a Pt loading of 0.3 \( \text{mg cm}^{-2} \), and then it is considerably decreased to 25.4 \( \text{m}^2\text{g}^{-1} \) for the Pt loading of 0.5 \( \text{mg cm}^{-2} \). This suggests that the utilization of Pt is limited by the compactly dense Pt-C composite thin layer structures formed by the relatively high Pt loadings (>0.3 \( \text{mg cm}^{-2} \)), which restricts easy passage of the \( \text{H}_2/\text{O}_2 \) reacting gases, thus deteriorating the electrochemical performance of the PEMFCs.

Nyquist plots (Fig. 6c) present the internal resistances of the PEMFCs obtained by varying the Pt loadings. The first intersection point with the \( Z' \) axis and the size of semi-circle represent the ohmic resistance and the charge transfer resistance, respectively [29]. Both are significantly decreased upon increasing Pt loading amount up to 0.3 \( \text{mg cm}^{-2} \), and are suddenly increased upon increasing the amount of Pt loadings beyond 0.3 \( \text{mg cm}^{-2} \). The electrochemical impedance is initially large at relatively low Pt loadings (<0.3 \( \text{mg cm}^{-2} \)) due to the poor catalytic kinetics resulting from insufficient Pt loadings. However, too much Pt loading (>0.3 \( \text{mg cm}^{-2} \)) increases the electrochemical resistance due to formation of compactly dense Pt-C composite structures, which prevent easy passage of the reacting gases and simultaneously elongate the transfer paths of the generated ions and electrons through the Pt-C composite thin layer.

3.3. Effects of porosity of Pt-C composite layers on the electrochemical performance of PEMFCs

TGA analysis was performed to determine the appropriate calcination temperature for thermally removing the Brij 58 templates in the Pt-C composite layers as shown in Fig. 7. Pt-C composite can be significantly oxidized at higher than 400 °C. Therefore we precisely controlled the calcination temperature at ~350 °C to remove Brij-58 for minimizing the loss of Pt-C composite.

The presence of pores in the Pt-C composite layers can facilitate passage of the \( \text{H}_2/\text{O}_2 \) reacting gases, thus lowering the ion and electron transfer resistances [30–32]. In order to increase the porosity of the electrospray-deposited Pt-C composite layers, Brij 58 surfactant was added as a template to the Pt-C composite layers followed by their thermal removal by heating at ~350 °C. Fig. 8 shows the comparison of the microstructures of Pt-C composite thin layers before and after the thermal removal of Brij 58 templates for a Pt loading of 0.3 \( \text{mg cm}^{-2} \). The compactly dense Pt-C composite structures with large primary particles are shown in

![Fig. 9. Current density-voltage curves measurement for PEMFCs with various amounts of Brij 58 surfactant in the fixed amount of 0.3 mg cm\(^{-2}\) of Pt.](image)

![Fig. 10. (a) Pressure drops in MEAs as a function of the reacting gas flow rate. (b) Polarization curves and (c) Nyquist plots for various PEMFCs with electrospray-deposited Pt-C composite thin layers with and without using Brij 58 surfactant templates.](image)
Fig. 8a. However, after the thermal removal of the Brij 58 templates, the large primary particles disappeared and microstructured networks with micro- and nano-sized open pores were clearly observed in the Pt-C composite thin layers (Fig. 8b–d).

The effect of different mixing ratio between Pt and Brij 58 on the performance of PEMFCs was examined. The amount of Pt loading was fixed at 0.3 mg cm$^{-2}$, and then the amount of Brij-58 was varied at 0, 1, 5, and 10 wt%, which resulted in the porosity of 0.14, 0.71, and 1.42%, respectively. When the amount of Brij 58 was increased, the electrochemical performance of PEMFCs was improved as shown in Fig. 9. However, when the amount of Brij 58 was greater than 5 wt%, the electrochemical performance of PEMFCs was considerably deteriorated. This is presumably because the excessive Brij 58 resulted in serious damages in the Pt-C composite layer after calcination process. Therefore, we maintained the amount of Brij 58 at the fixed amount of 5 wt% throughout this study.

We examined the effects of porosity in the Pt-C composite layer on the pressure drop in the MEAs as a function of the reacting gas flow rate for various Pt loadings (0.3 – 0.5 mg cm$^{-2}$) (Fig. 10a). Upon increasing the Pt loading amount without Brij 58, the pressure drop in MEAs was significantly increased due to the formation of compactly dense Pt-C composite layers. However, after creating porous structures in the Pt-C composite layers, the pressure drops in MEAs were decreased at all flow rates compared with the pressure drops in MEAs without porous structures. The use of more Brij 58 templates was accompanied by lower pressure drops in MEAs. This suggests that the porosities of the Pt-C composite layers were successfully improved by thermally removing the Brij 58 templates and H$_2$/O$_2$ reacting gases easily passed through the thus-obtained porous Pt-C composite layers. J-V curves were obtained for various PEMFCs with and without using Brij 58-templated porous structures (Fig. 10b). The electrochemical performances of PEMFCs with porous Pt-C composite layers at Pt loadings of 0.3 – 0.5 mg cm$^{-2}$ were enhanced compared to the PEMFCs prepared without using Brij 58 templates (Fig. 10b). Finally, Nyquist plots for PEMFCs with and without using Brij 58 are shown in Fig. 10c. The size of the semi-circle for the PEMFCs decreased for Pt-C composite layers with Brij 58-templated porous structures. This suggests that the internal resistance of the PEMFCs was reduced by creating porous structures in the Pt-C composite thin layers so that the reacting gases can easily permeate, and the generated ions and electrons can rapidly transfer through the Pt-C composite thin layers.

4. Conclusions

In this study, we have investigated the effects of electrospay-deposited Pt-C composite thin layers on the electrochemical performances of PEMFCs. Upon increasing the Pt loadings up to 0.3 mg cm$^{-2}$, the electrochemical performances of PEMFCs were improved due to the formation of uniform Pt-C composite layers on the carbon fiber papers. However, increasing Pt loadings beyond 0.3 mg cm$^{-2}$ formed compactly dense Pt-C composite thin layers that restrict passage of the reacting gases through the MEAs, and simultaneously elongate the transfer paths for the generated ions and electrons. In order to enhance the reacting gas permeability, we employed Brij 58 surfactant templates to create porous structures in the Pt-C composite thin layers. The Brij 58 templates were added to the Pt-C composite thin layers, followed by thermal removal. The micro- and nano-porous structures created using the Brij 58 templates lowered the pressure drop in MEAs. As such, the reacting gas permeability was improved, which enhanced the electrochemical performance of the PEMFCs. This suggests that the creation of micro- and nano-porous structures in Pt-C composite thin layers play an important role in improving the electrochemical performance of PEMFCs in practical energy production applications.

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