

Fabrication of practical PEMFC electrode with ultralow mass loading of platinum via electro-spray deposition technique

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Various electrode deposition methods, such as air-brushing, decal transfer, screen printing and electrostatic spraying, have been explored to fabricate high-performance catalyst layer for proton exchange membrane fuel cells. Among them, the electrostatic spray deposition dragged a great attention due to the improved fuel cell performance at extremely low platinum mass loading. In this paper, we systematically investigated the effect of mass loading of platinum by using the electro-spray deposition. The electrode morphology of the electro-sprayed catalyst layer is compared with that of the conventional decal-transferred catalyst layer to highlight its unique microstructure. As a result, the electro-sprayed catalyst layer showed 2 times higher current density at 0.5 V as compared to the decal-transferred catalyst layer. Thus, it can be suggested that a great deal of efforts must put onto the microstructure of the catalyst layer to overcome the severe performance decrease at low platinum loading.

Key words: Electrostatic spray deposition, Catalyst layer, Membrane electrode assembly, Proton exchange membrane Fuel cell.

Introduction

Controlling the nano-sized structure created within the catalyst layer is the key factor that determines the proton exchange membrane fuel cell (PEMFC) performance. Besides the conventional slurry method, various approaches such as screen printing, ink-jet printing, physical vapor deposition and electro-spray deposition have been explored [1-4]. Among them, the electrode fabricated via electro-spray deposition has dragged a great attention due to the superior cell performance coming from its unique morphology [4].

Benitez et al. first developed an innovative electrode fabrication method based on the electrostatic spray deposition and employed it as the catalyst layer of PEMFC [4, 5]. By comparing with the impregnated and air-sprayed catalyst layers, they reported that the electro-sprayed catalyst layer may reach at least 2 times larger power density at a high platinum loading of 0.5 mg cm⁻². Subsequently, the optimal parameters of the catalyst ink composition, i.e. the dispersing solvents and Pt/C catalyst/Nafion ionomer contents are investigated by Chaparro et al. [6, 7]. The amount of the Nafion ionomer required was much lower than that of the conventional slurry method, indicating that the interaction between the Nafion ionomer and Pt/C catalyst has significantly

improved after the use of the electro-spray deposition. Later, the electro-sprayed catalyst layers are found to be highly efficient in utilizing the surfaces of the platinum catalyst. Martin et al. and Chaparro et al. both succeeded in fabricating the high-performance membrane electrode assemblies (MEAs), delivering approximately 600 to 700 mW cm⁻², at extremely low platinum loading of 0.02 mg cm⁻² [8-10]. Inspired by their works, many other researchers have demonstrated load platinum-loaded catalyst layer deposited directly onto the Nafion membrane instead of the microporous layer on the gas diffusion layer [11-14]. Despite these efforts, it is still under debate how the electro-sprayed catalyst layer results in larger power density at ultralow platinum loading.

In this paper, the electro-sprayed electrodes with different mass loading of the platinum catalyst have been fabricated and applied into PEMFC. In particular, we have investigated the relation between the platinum mass loading and mass transport resistance. SEM images of the electro-sprayed catalyst layer are compared with those of the conventional catalyst layer, showing the foundation of the improved mass transport at higher current densities. Furthermore, the cell performance of the electro-sprayed catalyst layer is evaluated with a decrease of the platinum mass loading.

Experimental

Composition of the catalyst ink

The catalyst ink was prepared with platinum

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supported on carbon powder (20 wt% Pt, HiSPEC 3000, Alfa Aesar). The commercial Nafion dispersion (5 wt%, DE521, DuPont) was first diluted with ethanol (99 wt%, Sigma Aldrich) and vigorously homogenized for 30 min. Subsequently, the Pt/C is added into the dispersion. The mixture was agitated for 24 hrs with magnetic stirring and then further sonicated over 2 hrs before the deposition.

Preparation of the membrane electrode assembly

The electrostatic spray machine (ESR200R2, NanoNC) is composed of a syringe pump, a DC high voltage generator and a conductive substrate. The metallic nozzle equipped has an internal diameter of 210 μm and external diameter of 410 μm . After the electrical voltage is applied, the catalyst ink flows at a rate of 0.4 mL hr^{-1} from the syringe pump into the nozzle and atomizes into the charged droplets. The droplet deposits onto the Nafion membrane by flying through the electrical field. The distance between the nozzle and the substrate is kept as 5 cm. During the deposition, the substrate temperature remained as 60 $^{\circ}\text{C}$. When the desired amount of the platinum is loaded, the membrane electrode assembly was rinsed with deionized water for 5 min and stored in the convection oven at 40 $^{\circ}\text{C}$ before characterization. For comparison, the conventional MEA was fabricated by the modified decal transfer method proposed by our group [15, 16]. The catalyst slurry was prepared by mixing 2.9 g of the Nafion dispersion into 3 g of the 1,2,3-propanetriol (99 wt%, Sigma Aldrich). After the slurry was physically stirred, a few drops of tetrabutylammonium hydroxide was added and intensively homogenized for 24 hrs. Teflon film was repeatedly painted with the ink and baked in a convection oven at 135 $^{\circ}\text{C}$ until the Pt loading reached the target. Finally, the catalyst layer was transferred onto the Nafion membrane by hot-pressing method.

Results and Discussion

Schematic illustration of the catalyst layer fabricated via the electro-spray deposition

Fig. 1 shows an illustration of the catalyst layer on the Nafion membrane fabricated via the electro-spray deposition. Here, the positively charged droplets composed of the Pt/C catalyst and Nafion ionomer travel onto the membrane, with an excellent distribution attributed to the repulsive interaction between the droplets. Accordingly, the Nafion ionomer is well distributed on the surfaces of the Pt/C aggregates. This may lead to the characteristic morphology, which provides higher electrochemically available surface area as well as larger accessible pore volume. As a result, the resultant catalyst layer is expected to have an improved cell performance in particular at lower Pt catalyst loadings. Although the amount of the Pt loading is decreased, the effective ionomer surface area

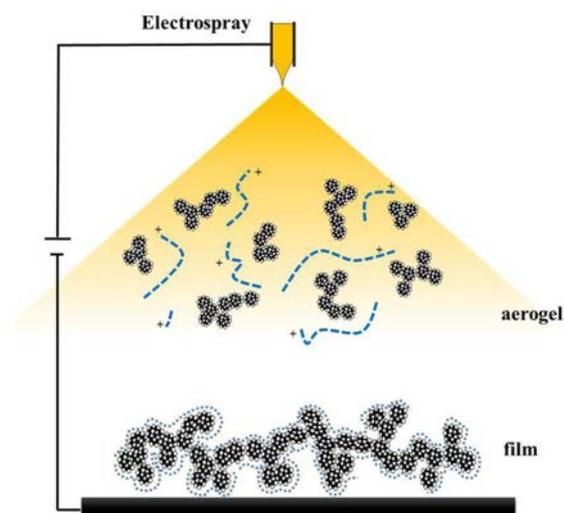


Fig. 1. Schematic illustration of the typical electrostatic spray deposition apparatus.

in the electro-sprayed catalyst layer is at least 2-3 times larger than that of the conventional decal-transferred catalyst layer, thus promoting the transportation of O_2 onto the catalytic surfaces.

Microstructure of the electro-spray deposition

To evaluate the characteristic morphology, the SEM images of the electro-sprayed catalyst layer are compared with those of the conventional decal-transferred catalyst layer, as shown in Fig. 2. Figs. 2A and 2B present the surfaces of the decal-transferred catalyst layer. It can be clearly seen that the Nafion ionomer is locally agglomerated. Accordingly, the catalyst layer structures are weakly connected to each other, coming from uneven distribution of the Nafion ionomer. Rough surface of the Pt/C aggregates are somewhat observable at higher magnitude (Fig. 2B). In contrast, the Nafion ionomer is well distributed on the surfaces of the electro-sprayed catalyst layer, as shown in Figs. 2C and 2D. As a result, the Pt/C-Nafion agglomerates are well connected to each other with a larger number of the accessible pores, as compared to the decal-transferred catalyst layer. Consequently, the catalyst layer structures fabricated via the electro-spray deposition would be quite beneficial in achieving an improved cell performance.

Fuel cell performance

Finally, we evaluated the cell performance of the MEA consisting of the electro-sprayed catalyst layer and compared it with that of the decal-transferred MEA. Fig. 3 shows the cell performance of the MEAs employing three different mass loadings of platinum, 0.05 mg cm^{-2} , 0.11 mg cm^{-2} and 0.18 mg cm^{-2} , in which the catalyst inks were electro-sprayed for 1.5 hrs, 3.0 h and 4.5 hrs, respectively. For comparison, the conventional decal-transferred MEA was fabricated

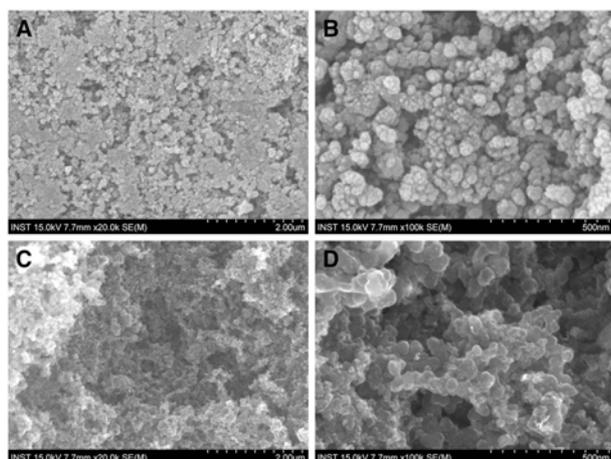


Fig. 2. SEM images of the decal-transferred catalyst layer (A and B) and electro-sprayed catalyst layer (C and D).

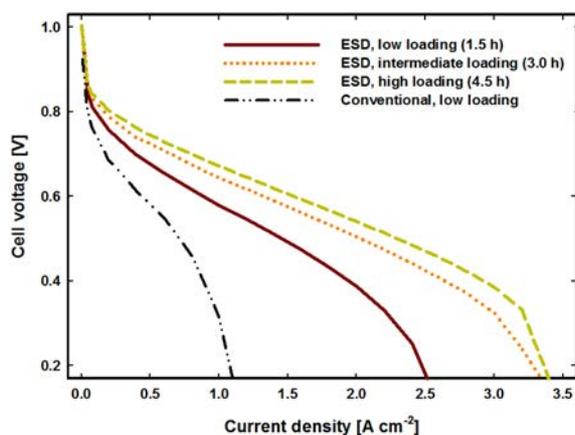


Fig. 3. Cell performance of the MEAs assembled with the electro-sprayed catalyst layers at different mass loading of platinum (0.05 mg cm^{-2} , 0.11 mg cm^{-2} and 0.18 mg cm^{-2}) and the conventional decal transferred catalyst layer at 0.05 mg cm^{-2} .

with the platinum mass loading of 0.05 mg cm^{-2} . As can be clearly seen, the mass transport resistance exponentially increases at higher current density when the mass loading of platinum has decreased from 0.11 to 0.05 mg cm^{-2} . However, as compared with the decal-transferred MEA, the electro-sprayed MEA reached 1.44 A cm^{-2} at the cell voltage of 0.5 V that is approximately 2 times larger. This can be mainly attributed to the following two reasons: The one is the unique structure of the electro-sprayed catalyst layer, which may lead to promotion of the O_2 transportation, and the other is the enlarged surface area of platinum covered by the Nafion ionomer. In particular, an increase in the effective surface area of the Nafion ionomer will deliver an efficient use of the platinum catalytic sites on the perspective of O_2 . Consequently, it is deduced that the electro-sprayed catalyst layer may mitigate the side effect of the reduction of platinum by facilitating the O_2 transportation rate.

Conclusions

In this work, we fabricated an electro-sprayed catalyst layer for PEMFCs, and conducted a systematical investigation on the mass loadings of platinum. The surface of the electro-sprayed catalyst layer is found to have the Nafion ionomer covering the Pt/C aggregates with an even distribution. By maintaining the repulsive interaction among the charged droplets, the highly accessible pores can be created after the use of the electro-spray deposition, thus forming less agglomerated structure. The fuel cell test showed that, as compared to the conventional decal-transferred catalyst layer, the electro-sprayed catalyst layer has the potential to reduce the O_2 transport resistance raised from the ultralow platinum loading. These results demonstrated that the MEA with the proposed catalyst layer structure fabricated via the electro-spray deposition has the ability to mitigate the sudden death of the cell performance at higher current density over 1.0 A cm^{-2} with a decrease of the platinum loading.

Acknowledgments

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