



Short communication

Comparative study of three different catalyst coating methods for direct methanol fuel cells

Hyung Joo Choi^a, Jinsoo Kim^{a,*}, Yongchai Kwon^{b,**}, Jonghee Han^c

^a Department of Chemical Engineering, Kyung Hee University, 1 Seocheon-dong, Giheung-gu, Yongin, Gyeonggi-do 446-701, Republic of Korea

^b Department of Chemical and Environmental Technology, Inha Technical College, 253, Yonghyun-dong, Nam-gu, Incheon 402-752, Republic of Korea

^c Fuel Cell Research Center, KIST, 39-1 Hawolgok-dong Seongbuk-gu, Seoul 130-650, Republic of Korea

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ABSTRACT

The performance of direct methanol fuel cells (DMFCs) with membrane–electrode assemblies (MEAs) made separately by three different catalyst coating methods, namely, air-spray, electro-spray and dual-mode spray, is evaluated. Platinum–ruthenium (PtRu) is incorporated as a catalyst for the anode. Several techniques (XRD, FE-SEM, and TEM) are used to examine whether the coating method affects the morphological features of the PtRu catalyst, whereas cyclic voltammetry is used to evaluate the active surface area. The cell polarization curves attained for the three coating methods that use different methanol concentrations are compared to determine the best method. It is found that the PtRu catalyst coated by the dual-mode spray shows the most uniform nanoparticle distribution and the highest active surface area. The DMFC performance is best when the dual-mode spray is employed (165 mW cm^{-2} at 2 M methanol).

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1. Introduction

There has been significant interest in developing power sources for portable electronic devices, electric vehicles, and other mobile applications. Nevertheless, attempts to reduce the size and the weight of power sources have not kept pace with the speed of miniaturization of portable devices [1–6].

To overcome these difficulties, liquid feed direct methanol fuel cells (DMFCs) based on a polymer electrolyte membrane (PEM) have been receiving much attention. Although there are some drawbacks to the extensive use of DMFCs, they offer the major advantages of high energy-conversion efficiency, easy delivery and storage of liquid fuel, ambient temperature operation, and simple construction. Accordingly, many attempts to create and commercialize DMFCs are in progress [7–11]. To maximize the advantages of the DMFC while reducing its drawbacks, the selection of suitable catalyst materials and the establishment of effective operational and manufacturing conditions are critical. To this end, platinum–ruthenium (PtRu) is a good catalyst material for DMFCs due to its ability to suppress the overpotential that occurs during the oxidation of methanol, and to promote oxidation of the adsorbed CO that acts as a poisoning agent to volatile CO₂ gas [12–20].

Air-spraying is a conventional method for depositing a catalyst on to an electrolyte [21,22]. It does, however, introduce problems such as agglomeration, loss of catalyst caused by large droplet sizes, and catalyst loss to the air, all of which lead to a degradation fuel cell performance and increased manufacturing cost. To avoid such problems, electro-spraying has been proposed [23,24]. The method uses a very fine liquid aerosol formed through electrostatic charging. A liquid passes through a nozzle and a plume of droplets is generated by electrically charging the liquid to a very high voltage. The charged liquid becomes unstable as it is forced to hold more and more charge. When the liquid reaches a critical point, at which it can hold no more electrical charge, it blows apart into a cloud of tiny, highly charged droplets at the tip of the nozzle. These tiny droplets fly about searching for an oppositely charged potential surface on which to land. Due to the electrostatic interaction between the charged particles, electro-spraying can prevent the formation of agglomerates and promotes adhesion to the substrate [23,24].

Based on the above descriptions, it is expected that a dual-mode spray that applies to both electro-spray and air-spray should be a more effective means of dispersing a catalyst. An experimental set-up for the dual-mode spray is shown schematically in Fig. 1.

In this investigation, a new catalyst coating method using the dual-mode spray for manufacturing the membrane–electrode assembly (MEA) of DMFCs is proposed. Through morphological and electrical analyzes, the best coating conditions for the dual-mode spray are determined, and the morphological and electrical performance of a PtRu catalyst coating on the anode using a dual-mode spray are compared with those of a PtRu catalyst coated

* Corresponding author. Tel.: +82 31 201 3674; fax: +82 31 202 1946.

** Corresponding author. Tel.: +82 32 870 2272; fax: +82-32 870 2514.

E-mail addresses: jkim21@khu.ac.kr (J. Kim), kwony@inhac.ac.kr (Y. Kwon).

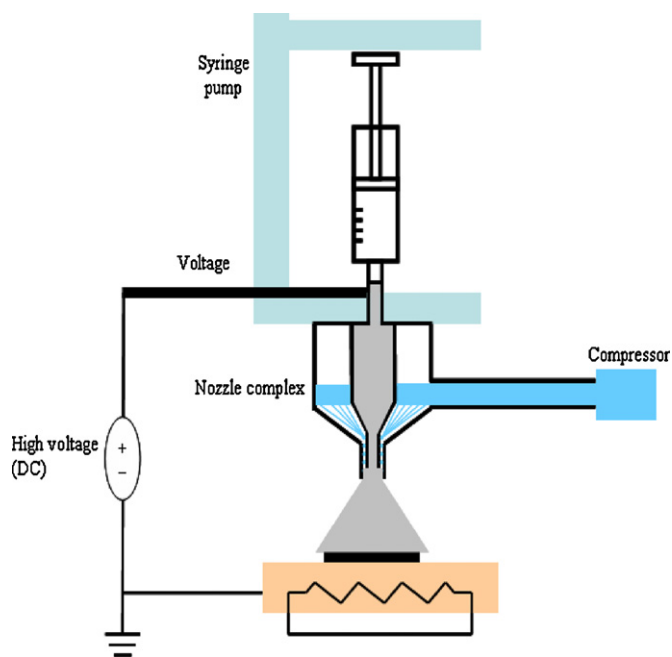


Fig. 1. Experimental set-up for dual-mode spray.

using either the electro-spray or air-spray techniques. The results obtained will help establish new protocols for catalyst coating using spray-type methods and provide useful information about the electro-oxidation mechanism of PtRu catalyst coatings on the anode of DMFCs.

2. Experimental

Nafion 117 (DuPont) was used for the proton-exchange membranes. They were cleaned by means of the following procedure: the membranes were boiled at 80 °C in a 5 wt.% H₂O₂ solution and deionized (DI) water for 1 h to remove organic impurities, rinsed twice in boiling DI water, boiled in a 1 M H₂SO₄ solution to obtain the H⁺ form, and rinsed twice in boiling DI water for 1 h. The membranes were subsequently immersed in DI water until ready for use. A solution of carbon powder (Vulcan XC-72), Teflon solution (60%), glycerol, and isopropyl alcohol (IPA) was screen-printed on carbon paper to form the diffusion layer, then annealed at 300 °C for 3 h.

A commercially available platinum (Pt) black (HiSPEC™ 1000 from Johnson Matthey) and a PtRu black (HiSPEC™ 6000 from Johnson Matthey), with a weight ratio of 50:50 were used as the cathode and anode catalysts, respectively. The catalyst ink was prepared by mixing the catalyst, the ionomer (Nafion, supplied by ALDRICH, 5 wt.% solution in a mixture of lower aliphatic alcohols and DI water) and IPA. Well-dispersed catalyst inks were obtained by stirring the mixture in an ultrasonic bath for at least 10 min. Appropriate amounts of anode and cathode inks were dispersed on a gas-diffusion layer (GDL) support of area 10 cm² using the three different methods, namely air-spray, electro-spray, and dual-mode spray. Catalyst loadings of about 3.0 mg cm⁻² were coated on each electrode. The pre-treated Nafion membrane was sandwiched between the two electrodes, and the resulting MEA was then hot pressed.

The MEA was coupled with gas-sealing gaskets and placed in a single-cell test station. All experiments were operated in fuel cell mode, and methanol concentrations of 0.5, 1 and 2 M were fed to the anode at a constant feed rate of 5 mL min⁻¹, while air at 250 sccm was provided to the cathode. All fuel cell tests were conducted at 80 °C. The methanol was used only once without recirculation to maintain a constant methanol concentration.

To analyze the pattern tendency of the nanoparticles in each catalyst coating method, X-ray diffraction (XRD) tests were performed with a M18XHF-SRA (Mac Science, Japan) X-ray diffractometer equipped with a Cu K α source. The diffractograms were scanned at a rate of 10° min⁻¹ over a 2 θ range of 30–90° at room temperature. The morphology of the catalytic layer was studied by means of FE-SEM (LEO SUPRA 55). TEM measurements were used to observe the distribution of the PtRu catalyst nanoparticles.

To determine the electrochemically active surface (EAS) area, a cyclic voltammetry was conducted on the PtRu black anode catalyst by using a single fuel cell station. Humidified H₂ was fed to the Pt black cathode at a flow rate of 200 mL min⁻¹, acting both as a counter electrode and as a dynamic hydrogen electrode (DHE). Deionized water was fed to the anode at a flow rate of 5 mL min⁻¹, serving as the working electrode. The Cyclic Voltammograms (CVs) were recorded over a potential range of 0–1.0 V versus a DHE at a scan rate of 20 mV s⁻¹.

3. Results and discussion

3.1. Material characterizations of PtRu catalyst

Prior to evaluating the cell performances of the DMFCs using three different catalyst coating methods, material characterization of the PtRu catalyst coating on the anode was performed to determine whether the cell performance would be affected by the characterization results of the catalyst. The characterizations might be also a clue to explaining the discrepancy in performance among the three different catalyst coating methods.

To determine the lattice structure and average particle size of the PtRu deposited by the three different catalyst coating methods, the XRD patterns were analyzed and the results are presented in Fig. 2. The XRD patterns show that all the PtRu/Cs have a face-centered cubic (fcc) structure with major peaks of (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) [22]. The average particle sizes were determined from the broadening in the Pt (2 2 0) reflection of the Pt fcc lattice using the Debye-Scherrer equation [25]. The (2 2 0) peak in the Pt region shows no contribution from the carbon support [26]. The average particle sizes obtained from the XRD patterns of the PtRu catalysts coated using the three coating methods are estimated to be 2.2, 2.4 and 2.5 nm, respectively.

To evaluate the surface morphology of the electrodes made using the different coating methods, FE-SEM inspections were undertaken. The photographic images are shown in Fig. 3. When air-

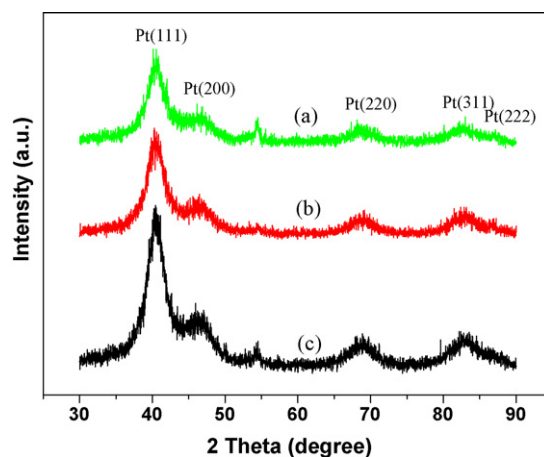


Fig. 2. X-ray diffraction patterns of PtRu catalysts on anode electrodes coated by: (a) dual-mode spray, (b) electro-spray, and (c) air-spray. XRD tests performed using an X-ray diffractometer equipped with a Cu K α source. Diffractograms scanned at 10 °C min⁻¹ in a 2 θ range of 30–90° at room temperature.

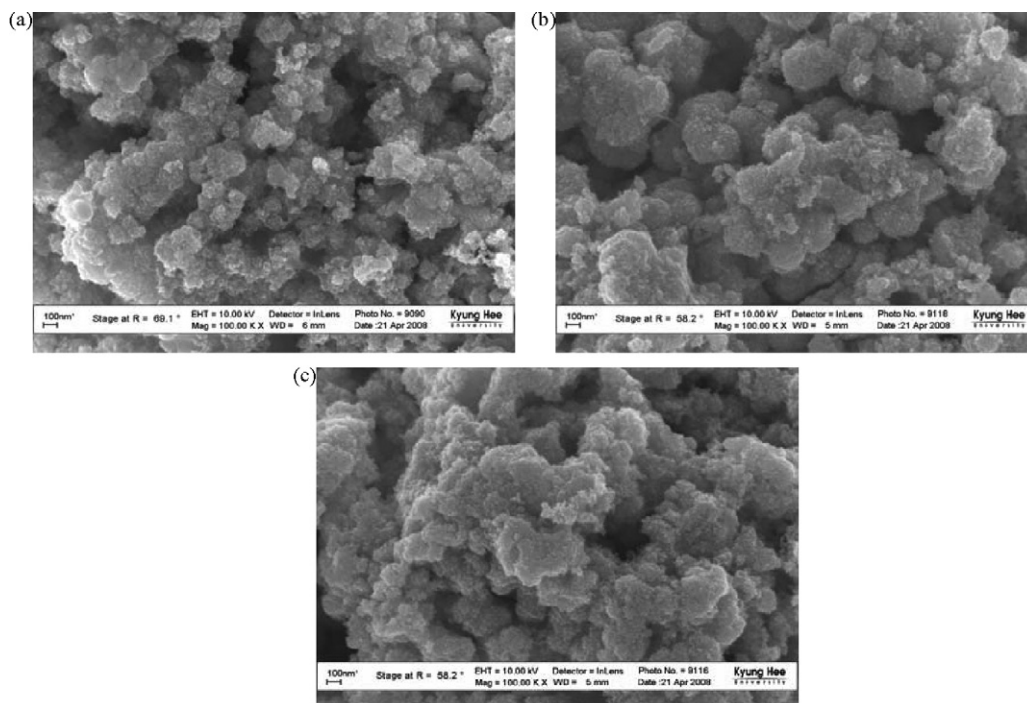


Fig. 3. FE-SEM images of PtRu catalysts on anode electrodes coated by: (a) dual-mode spray, (b) electro-spray, and (c) air-spray.

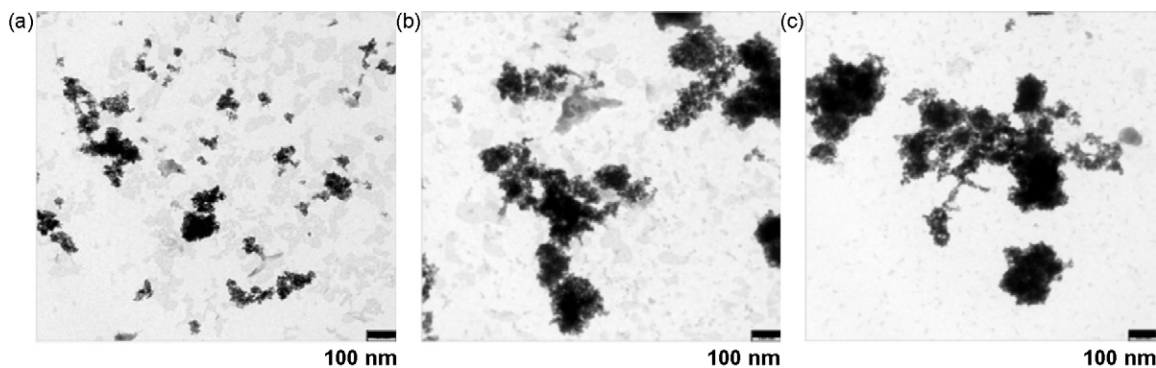


Fig. 4. TEM images of PtRu catalysts on anode electrodes coated by: (a) dual-mode spray, (b) electro-spray, and (c) air-spray.

spray and electro-spray are used, the PtRu nanoparticles are largely agglomerated during the coating process, and some large, round particle chunks remain (Fig. 2(b) and (c)). By contrast, with the use of the dual-mode spray, the particles are smaller in size and more porous. It is predicted that these differences in particle size and the degree of porosity promote access of methanol to the catalyst layer as well as a higher ionic–electronic transfer rate, followed by better utilization of the catalyst and higher DMFC performance. In this regard, the FE-SEM results also match well with the XRD analyze.

To examine the degree of particle dispersion in the PtRu catalyst, TEM measurements were used. The results are shown in Fig. 4. The PtRu nanoparticles coated using the dual-mode spray are found to be the most uniformly dispersed.

3.2. Effect of catalyst dispersion method on active surface area

Differences in the PtRu catalyst coating method for the anode may affect both the active surface area and DMFC performance because it is understood that smaller and more uniformly dispersed particles lead to a larger EAS area and better DMFC performance.

To examine the EAS area, CV tests were conducted; the results are given in Fig. 5. The cathodic and anodic peaks that appeared in

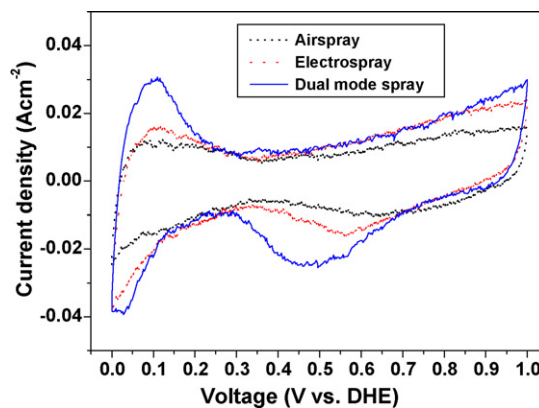


Fig. 5. Cyclic Voltammograms of PtRu catalysts on anode coated by: (a) dual-mode spray, (b) electro-spray, and (c) air-spray. Humidified H_2 is fed to the cathode at a flow rate of 200 mL min^{-1} , acting both as the counter electrode and as a DHE. DI water is fed to the anode at a flow rate of 5 mL min^{-1} , serving as the working electrode. Measurements conducted over a range of 0–1.0V versus DHE at a scan rate of 20 mV s^{-1} .

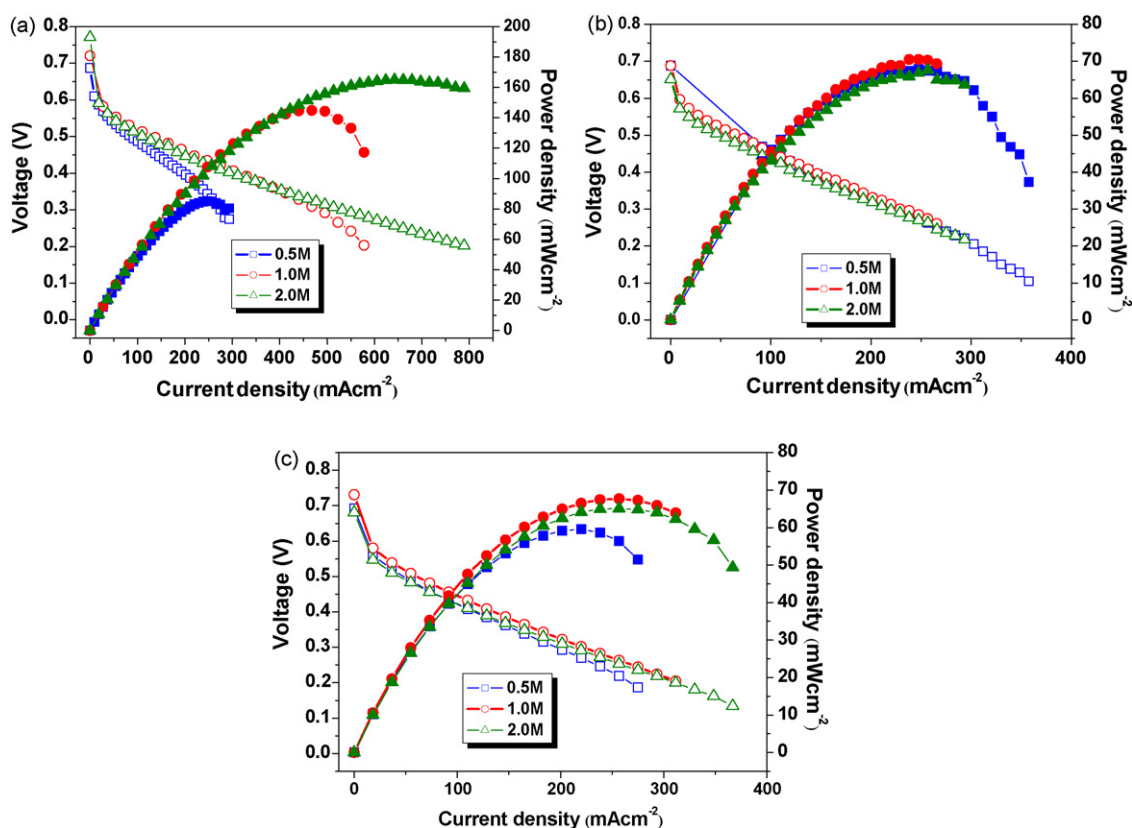


Fig. 6. Polarization curves of DMFCs using catalysts coated by: (a) dual-mode spray, (b) electro-spray, and (c) air-spray with different methanol concentrations of 0.5, 1.0, and 2.0 M. In all tests, methanol is fed to the anode at a constant feed rate of 5 mL min^{-1} and air at 250 sccm is provided to the cathode. All tests were conducted at 80°C .

the range from 0.05 to 0.4 V are considered because they related to the adsorption and desorption reactions of hydrogen on the catalyst surface. The average area between the hydrogen adsorption and desorption peaks is used to calculate the EAS area [27–29].

The average area is the largest in the MEA prepared using the dual-mode spray and the smallest in that prepared using the air-spray. The difference in area between the electro-spray and the air-spray is not significant. A large area indicates that a greater amount of catalyst is involved in the hydrogen adsorption and desorption reactions, that is, the MEA prepared using the dual-mode spray may have more efficient electrocatalytic reactions and better DMFC performance.

3.3. Effect of catalyst dispersion method on DMFC performance

The effect of the catalyst coating method on the DMFC polarization curve was investigated and the results are presented in Fig. 6. Three methanol concentrations, namely 0.5, 1 and 2 M, were fed to the anode at a constant feed rate of 5 mL min^{-1} , while humidified oxygen at 250 sccm was supplied to the cathode. There is no significant difference in power density difference for the DMFCs prepared using air-spray and electro-spray. In the cell prepared using air-spray, the maximum power density is 62 mW cm^{-2} at 1 M methanol, whereas the value obtained by electro-spray is 71 mW cm^{-2} at 1 M methanol.

By comparison with the maximum power density obtained by the above two methods, the power density achieved with the dual-mode spray is 165 mW cm^{-2} at 2 M methanol, i.e., 240% better than the value attained when using the electro-spray. Ranking cell performance in terms of maximum power density is reasonable because the DMFC prepared using the dual-mode spray already shows (1) smaller particle size, (2) more uniform particle disper-

sion, (3) more porous particle connection, and (4) a greater EAS area. It is concluded that the dual-mode spray gives to the highest utilization of the PtRu catalyst coated on the anode.

When spray-type coating methods are used for the coating of catalyst, there is no significant correlation between methanol concentration and cell performance; the methanol concentrations showing the best performance profile from each coating method are different. When using air-spray and electro-spray, 1 M methanol yields the best performance, while 2 M methanol yields the best performance when the dual-mode spray is used. Related experiments are underway to understand the reasons why there is little correlation between methanol concentration and the performance of DMFCs.

4. Conclusions

The cell performance of DMFCs that include MEAs created using three different catalyst coating methods (air-spray, electro-spray, and dual-mode spray) have been evaluated. It is found that the PtRu catalyst coated on the anode via a dual-mode spray has a more uniform nanoparticle distribution and a higher EAS than those prepared by the other two methods. With the dual-mode spray, the cell performance is the best and gives a maximum power density of 165 mW cm^{-2} at 2 M methanol.

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