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Description	

Effects of Nafion impregnation using inkjet printing for membrane electrode assemblies in  
polymer electrolyte membrane fuel cells

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**Abstract**

We present a method of using inkjet printing to deposit Nafion ionomer as the transport media onto catalyst layer made into membrane electrode assemblies (MEAs) for polymer electrolyte fuel cells (PEMFCs). This method provides a more suitable mode of controlling the solution deposition than the existing deposition methods such as spray painting. The cyclic voltammetry results also show that the inkjet printing method has better performance than spray painting by improving catalyst efficiency. Using the appropriate Nafion loading of  $0.64 \text{ mg cm}^{-2}$  by inkjet printing, we have demonstrated that this technique can be used to improve the performance of the MEA for PEMFCs.

Keywords: Polymer electrolyte membrane fuel cell (PEMFC); Inkjet printing technology; Membrane electrode assemblies; Catalyst layer; Nafion impregnation

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## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have received much attention because of their unique properties and their ability to create an efficient and clean source of energy [1-3]. The heart of a PEMFC is the membrane electrode assembly (MEA), which comprises of a proton exchange membrane, catalyst layers (CLs), and gas diffusion layers (GDLs). MEA requires catalyst as an active material of electrodes, for which it is important to increase the reaction sites in the catalytic layer to improve the electrode performance. Preparation of more efficient and cheaper electrodes has become an important research and development direction of PEMFCs in recent years [4,5].

It is known that catalyst particle as an effective reactive site connects with Nafion solution as a proton conductor to ensure high catalyst utilization and cell performance in Fig. 1. This fact suggests that proton conductivity through ionomer in catalyst layers is an important factor affecting MEA performance. The catalyst layer is impregnated with a dilute solution of electrolyte, thereby extending the three-phase boundary region. Aiming to improve three-phase boundary region of catalytic layer and catalyst utilization, several studies have specifically examined novel methodologies for MEA development [6,7]. An adequate dispersion of Nafion ionomer must be present within catalyst layer to ensure efficient proton conduction. Numerous studies have demonstrated that the ionomer network formed in catalyst layer can optimize the electrode structure and can improve catalyst utilization in PEMFCs.

Many deposition methods (such as spraying [8,9], screen-printing [10,11], electro-deposition [12,13], and sputtering [14,15]) have been developed recently to disperse the Pt content close to the electro-membrane interface, where electrochemical reactions take place. Inkjet printing techniques show great potential for increasing Pt efficiency by reducing amount

of ionomer and by controlling Pt content. Inkjet printing cannot be regarded as a conventional process for MEA fabrication. Recently however, great interest has arisen with respect to inkjet printing technology for manufacturing catalyst layers onto the MEA [16-18]. Taylor et al. demonstrated a method of inkjet printing to deposit catalyst materials onto GDLs that are made into membrane electrode assemblies for PEMFCs [18]. He reported that inkjet printing had been demonstrated as a catalyst application method for PEMFCs and that high-precision of inkjet printing allows for controlled catalyst deposition, especially for ultra-low Pt loadings.

Therefore, inkjet printing technology was used here to prepare a solution that should be impregnated in catalytic layer to increase Pt utilization for proton exchange membrane fuel cells. However, Nafion solution as the transport media in the solutions and within catalyst layer generally exists as aggregated states, thereby leading to an insufficient Nafion utilization. To provide close contact between Nafion membrane and Pt catalyst, a Nafion solution is usually added to catalyst electrode. The appropriate loading of Nafion necessary for the best performing MEAs was investigated previously for electrodes prepared using ink processes [19-22]. A previous study by Kim et al. analyzed the effects of ionomer contents on the proton exchange membrane fuel cell performance of MEA fabricated using a catalyst-coated membrane spraying method in partially humidified atmospheric air and hydrogen [23]. That report described that the best MEA performance was obtained by an MEA containing 30 wt% ionomer in the cathode and 25 wt% ionomer in the anode.

Inkjet printing can be regarded as an efficient method for catalyst deposition due to its excellent control of Pt loading which results in better utilization of Pt than that by conventional catalyst deposition methods such as screen printing and spray painting. However, the effect of Nafion loading in catalyst layer by inkjet printing is not discussed.

This report describes demonstration of a new method for depositing Nafion ionomer as the transport media onto catalyst layer to increase the contact surface area using inkjet printing. The objective of this work is to study the effect of Nafion loading by assessing the performance of fuel cell using inkjet printing and spray painting method. The results showed that this method consumes a markedly lower amount of Nafion ionomer as the primary liquid media, which can be favorable for the fabrication of high-performance PEMFCs.

## **2. Experimental**

### **2.1. Preparation of Nafion membranes**

Nafion 117 membrane as the proton exchange membranes was first pre-treated step-by-step with  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  solutions to remove the remaining organic and inorganic contaminants [24,25]. The pre-treatment of the Nafion membrane was accomplished successively by treating the membrane in boiling 3% (v/v)  $\text{H}_2\text{O}_2$  solution, distilled water at 100 °C, boiling 1 mol l<sup>-1</sup>  $\text{H}_2\text{SO}_4$  solution and then in distilled water at 100 °C again, for 30 min each step. The pretreated membranes were kept in water before the MEA fabrication.

### **2.2. Formation process of inkjet printing technology**

Fig. 2 shows the schematic illustration of the formation and evolution process of Nafion droplets on the hydrophobic substrate using inkjet printing. The typical inkjet printing process is based on a drop-on-demand printing method. It is necessary to understand the formation process of the printed ink droplet for effective design and fabrication of catalyst layer for PEMFCs. The printed dot is produced from the nozzles of the inkjet printer, which ejects ink onto the substrate. The nozzles are mounted about 1 mm over the substrate, and ink ejection velocities are in the range of 5 to 10 meters per second. Drops are formed by propagating a pressure pulse in a

chamber behind the printing nozzle. The liquid drop hits a substrate, and this process is controlled by a number of physical processes and can be driven by inertial forces, capillary forces, and gravitational forces. Generally, the impact behavior of a drop can be divided into impact driven and capillary driven [26,27]. Therefore, the vertical speed and droplet gravity force play important roles in impregnating Nafion ink into the catalyst layer to improve the performance of the MEA. Furthermore, the droplets fabricated by inkjet printing have better orientation character than spray painting which enhances the impregnation of the Nafion ionomer in the catalyst layer. Subsequent phase change will transform the liquid into solid after solvent evaporation [27]. Fig. 2 also shows a clear illustration of the shape of ink droplet. The droplets fabricated by inkjet printing are impregnated into the catalyst layer, following the rapidly evolution process which resembles a Nafion channel improving the Nafion ionomer distribution. Considering the viscosity limit for the inkjet printer, the inkjet printing ink was prepared by mixing Nafion ionomer (5 wt% dispersion solution DE521 CS type; Wako Pure Chemical Industries, Japan) and 1-Propanol with a volume ratio of 1:19. The most important parameter for inkjet printing equipment (LaboJet-500; MICROJET Co., Japan) is the distance between the two droplets, which is 200  $\mu\text{m}$  in this study. The vertical speed of the droplet is 6  $\text{m s}^{-1}$  as the optimal condition for the inkjet printing equipment. As a reference in this study, using a spray gun, Nafion ionomer was sprayed as the spray painting ink on the catalyst layer. In a manual operation method the gun sprayer is held about 15cm to the substrate as the spray distance. The diameter of spray nozzle size is about 150  $\mu\text{m}$ .

### **2.3. Fabrication of the membrane electrode assembly**

A standard catalyst layer with Pt loading of 1  $\text{mg cm}^{-2}$  for both the anode and the cathode (EC-20-10-7; TOYO Co., Japan) was also prepared for MEA. It is made with 20 wt.% Pt/C

catalyst on carbon paper without Nafion loading. For the preparation of MEA, the above Nafion inks were deposited using inkjet printer and a spray gun onto the catalyst layer. Three MEAs by inkjet printing with different Nafion loadings (0.35, 0.64, and 1.49 mg cm<sup>-2</sup>) and one MEA by spray painting (0.35 mg cm<sup>-2</sup>) as a reference sample were prepared. The MEA was fabricated with the pre-treated Nafion membrane and catalyst coated GDL by hot embossing. Hot pressing was maintained at 130 °C and 5 MPa for 5 min on both sides of pre-treated Nafion 117 [28]. The same hot pressing condition (temperature, pressure, time) was used to fabricate the MEA for different Nafion impregnation method. It is used to demonstrate that the inkjet printing can deposit a well-distributed dispersion of the Nafion ionomer in the catalyst layer.

#### **2.4. Testing of cell performance**

The MEA performance was evaluated in a single cell with an active cross-sectional area of 5 cm<sup>2</sup>. All assemblies were inserted between two graphite plates with serpentine flow fields and were then placed in a single-cell test fixture. The experiments were conducted at a cell temperature of 40 °C. The humidified hydrogen and oxygen gases were fed, respectively, into the cell at the anode and at the cathode. The flow gas flow rate for anode and cathode was 100 sccm. The mass multi-purpose mass flow controller was used to control the constant flow-rates for the fuel cell. The current density – potential (I–V) properties were measured by an Electronic Load unit (PLZ164WA; Kikusui Electronics Co.).

#### **2.5. Electrochemical measurement**

The catalytic activity of MEA was investigated using cyclic voltammetry (CHI 711 electrochemical analyzer; BAS Inc.) to determine the electrochemical surface area (ESA) and catalyst utilization. The electrochemical active surface area of the electrode was obtained from the charge required for hydrogen desorption from the Pt electrocatalyst. In these measurements,

the potential was swept from 0.1 V to 0.6 V at a scan rate of  $0.01 \text{ V s}^{-1}$ . Humidified hydrogen and nitrogen were used in a half cell. The working electrode (WE) was connected to the nitrogen side and the counter (CE) and reference (RE) electrodes were connected to the hydrogen side in the cell. Cyclic voltammetry measurement was conducted at  $40 \text{ }^\circ\text{C}$  on a  $5 \text{ cm}^2$  single cell fixture to determine the electrochemically active surface area.

### **3. Results and discussion**

In this study, the effects of Nafion ionomer content on the performance of MEA for PEMFC using inkjet printing and spray painting methods were investigated. In addition, the appropriate condition was attained after several composition ratios. To accomplish this, two sets of experiments were performed. In the first set of experiments, we used the same catalyst layer but a different deposition method for the fuel cell. For the next set of experiments, we measured the performance of the single cell with various Nafion loading using inkjet printing to ascertain the appropriate condition for MEA.

The I–V curve of a single PEMFC using inkjet printing and spray painted MEA were evaluated in Fig. 3. The I–V plots were obtained by decreasing the cell voltage stepwise at intervals of  $0.05 \text{ V}$ . A visible difference is apparent between two Nafion loading method by the same weight of the Nafion ionomer ( $0.64 \text{ mg cm}^{-2}$ ). The peak power density of the cell produced by inkjet printing is  $113 \text{ mW cm}^{-2}$ , which is higher than the  $53 \text{ mW cm}^{-2}$  measured on the cell produced by spray painting. In other words, the MEA produced by the inkjet printing method shows better catalyst utilization, more intimate membrane/electrode interface, and a greater number of three-phase boundary sites those produced than the spray painting method using the same Nafion loading value. The inkjet printing method for the catalyst layer significantly improves the performance of the PEMFCs, suggesting that a better contact between Nafion

ionomer and catalyst particle was obtained when the Nafion ionomer was impregnated into the catalyst layer using inkjet printing. The performance comparison with Nafion loading of  $0.35 \text{ mg cm}^{-2}$  is shown in the supplementary information. From figure S1, it also demonstrates that the fuel cell using inkjet printing has better performance than spray painting.

Fig. 4 shows cyclic voltammograms for the inkjet printing and spray painting. The CV results were measured for inkjet printing and spray painting with Nafion loading  $0.64 \text{ mg cm}^{-2}$ . The cyclic voltammograms showed the range of potential from 0.1 to 0.6 V. The utilization of platinum in the catalyst layer is 3.9 % for spray painting and 8.3 % for inkjet printing. The much higher Pt catalyst utilization efficiency of the cell prepared by the inkjet printing method could be due to the close contact between the Pt particles and membrane. So it might have more efficient electrocatalyst reactions and better performance.

The I–V technique has been studied extensively in the case of PEMFC to evaluate the appropriate Nafion loading which is necessary for the highest electric power output. It is evident from Fig. 5 that the PEMFC performance is determined by the Nafion loading. Figure 5 shows I–V curves at  $40 \text{ }^\circ\text{C}$  for PEMFC fabricated with different loadings of Nafion ionomer. Among the curves in Fig. 5, the single-cell with a Nafion loading of  $0.64 \text{ mg cm}^{-2}$  demonstrated the best performance for any discharging current. The peak power density of the cell increases from  $85 \text{ mW cm}^{-2}$  to  $113 \text{ mW cm}^{-2}$  when the Nafion loading in the cell increases from  $0.35$  to  $0.64 \text{ mg cm}^{-2}$ , which means that the reactive region of catalyst increases with Nafion loading. With increased Nafion loading from  $0.64$  to  $1.49 \text{ mg cm}^{-2}$ , the performance decreases from  $113 \text{ mW cm}^{-2}$  to  $78 \text{ mW cm}^{-2}$ , because the addition of Nafion blocks the reactant gases and the hydrophilic Nafion is likely to trap water in the catalyst layer. The maximum power density of  $113 \text{ mW cm}^{-2}$  is reached with the Nafion loading of  $0.64 \text{ mg cm}^{-2}$ . We used Nafion loading of  $0.64 \text{ mg cm}^{-2}$  for

the repeatability experiment in the supplementary information. Figure S2 shows that the result of PEMFCs performance using inkjet printing has acceptable repeatable capability. For the MEA fabricated by the inkjet printing method, appropriate ionomer content is suggested, providing practical information for commercial development.

Proton conduction in the catalyst layer of PEMFC is affected by the loading and distribution of Nafion ionomer. Nafion, as a good adhesive, can help to produce a close contact between the Pt particles and Nafion membrane for a reduced contact resistance [29,30]. Figure 6 is a schematic view of the catalyst layer that depicts the effect of Nafion loading using different deposition methods. We infer that the Nafion ionomer was adsorbed randomly into the catalyst layer in Fig. 6 (a). Furthermore, if the volume of the Nafion solution is small, it is just adsorbed in the catalyst layer surface. Most of the Pt particles cannot be connected to the membrane with a low Nafion content by spray painting. It will reduce the performance of the cell fabricated using spraying method. In Fig. 6 (b), the proper amount of Nafion within the electrode can greatly expand the electrolyte distribution. At the appropriate Nafion content, using inkjet printing makes good connections of proton and electronic conduction for most of the Pt particles. The Nafion ionomer is fabricated by inkjet printing in which the droplet is set in the same place. It resembles a Nafion channel in the catalyst layer, which will improve the Nafion ionomer distribution. Furthermore, it is readily understood that it will improve the reaction region for the three-phase boundary region. For that reason, we obtain the result in Fig. 3 that the fuel cell fabricated by inkjet printing demonstrates better performance than that fabricated by spray painting using the same Nafion content. In Fig. 6(c), the mass volume of Nafion ionomer is impregnated in the catalyst layer using inkjet printing. It might also block gas diffusion inside the catalyst layer, and it results in decreased fuel-cell performance. The results in Fig. 5 demonstrate

that, with the increase of Nafion loading from 0.64 to 1.49 mg cm<sup>-2</sup>, the performance decreases obviously. It also indicates that it is important to ascertain the appropriate Nafion loading content for the catalyst layer, which will improve the MEA performance.

#### **4. Conclusions**

We have studied the inkjet printing method for depositing the Nafion ionomer as the transport media onto a catalyst layer for PEMFC application. The inkjet printing method can provide better catalyst utilization than spray painting with the same Nafion loading for the MEA. The PEMFC performance and the catalyst activity determined by different Nafion loadings using inkjet printing method have been investigated intensively. Nafion loading that is too low will engender a poor contact between the electrolyte and catalyst layer and thereby lead to poor cell performance. On the other hand, very high Nafion content is expected to decrease cell performance because of blocking of the catalyst sites, blocking of the electrode pores, reduction of gas permeability, and increase in the mass transfer resistance. The maximum power density of single-cell is obtained at Nafion loading of 0.64 mg cm<sup>-2</sup>. Using the appropriate Nafion content, we have demonstrated that inkjet printing can deposit a well-distributed dispersion of the Nafion solution in the catalyst layer. This method can be used to improve MEA performance for PEMFCs with a small amount of Nafion.

#### **Acknowledgements**

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## ***Figure Captions***

**Fig.1** Schematic diagram of microstructure in the catalyst layer for single typical proton exchange membrane fuel cell.

**Fig.2** Schematic illustration of the formation and evolution process using inkjet printing.

**Fig. 3** PEMFCs performance comparison of inkjet printing to spray painting. Nafion loading of inkjet printing and spray painting was  $0.64 \text{ mg cm}^{-2}$ .

**Fig. 4** Cyclic voltammograms for the different Nafion impregnation method.

**Fig. 5** Cell polarization curves of PEMFC with various values of Nafion loading. The Nafion loading values for inkjet printing were  $0.35 \text{ mg cm}^{-2}$ ,  $0.64 \text{ mg cm}^{-2}$ , and  $1.49 \text{ mg cm}^{-2}$ .

**Fig. 6** Schematic views of the catalyst layer cross-section. Red shows Pt particles. Blue shows Nafion ionomer. Black shows carbon aggregates. (a) Low Nafion content using spray painting for which not all catalyst particles are connected to the membrane by Nafion ionomer. (b) Appropriate loading of the Nafion ionomer condition using inkjet printing. (c) Mass volume of Nafion loading condition using inkjet printing.

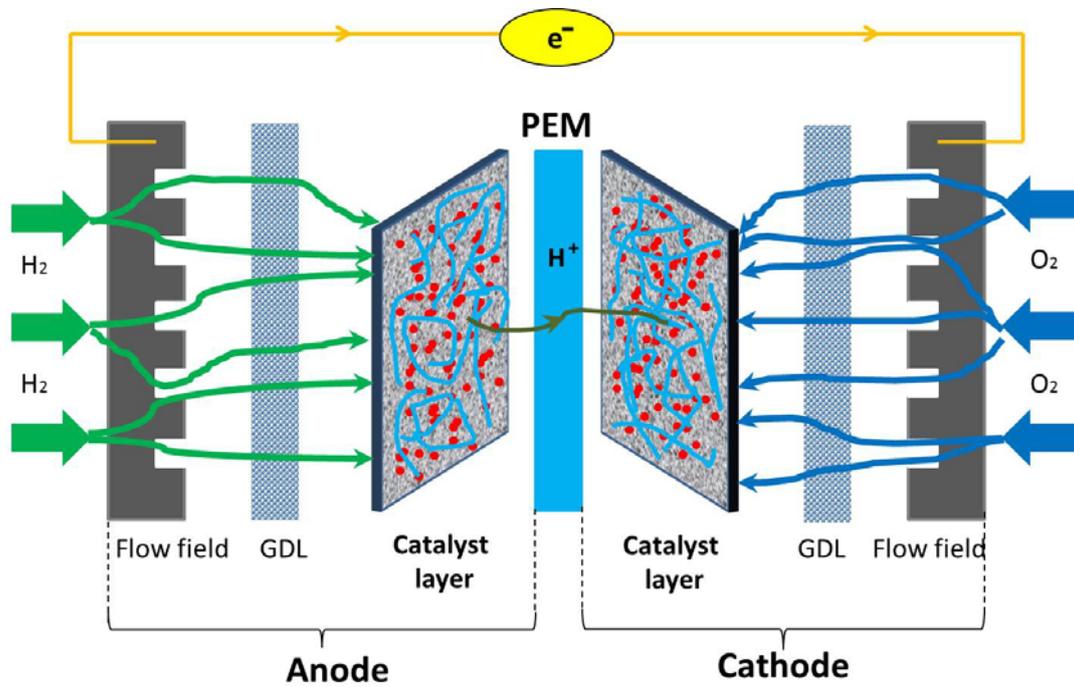


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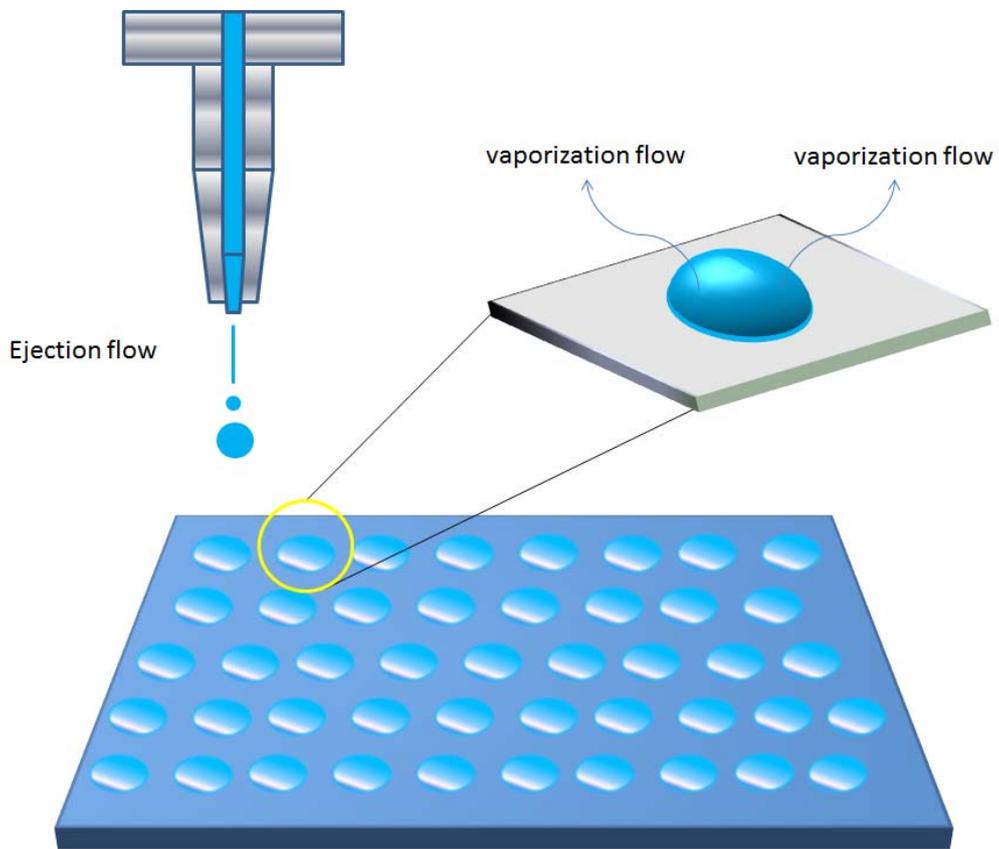


Fig.2. Schematic illustration of the formation and evolution process using inkjet printing

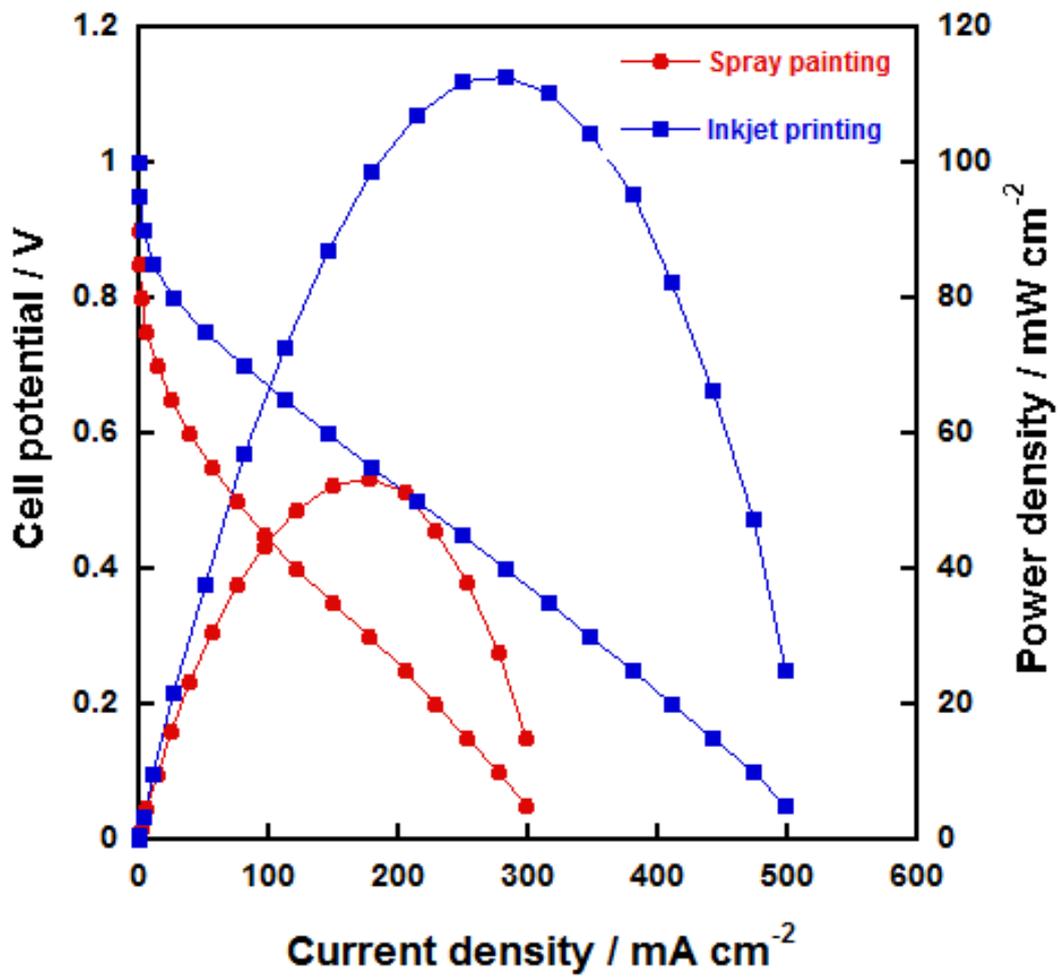


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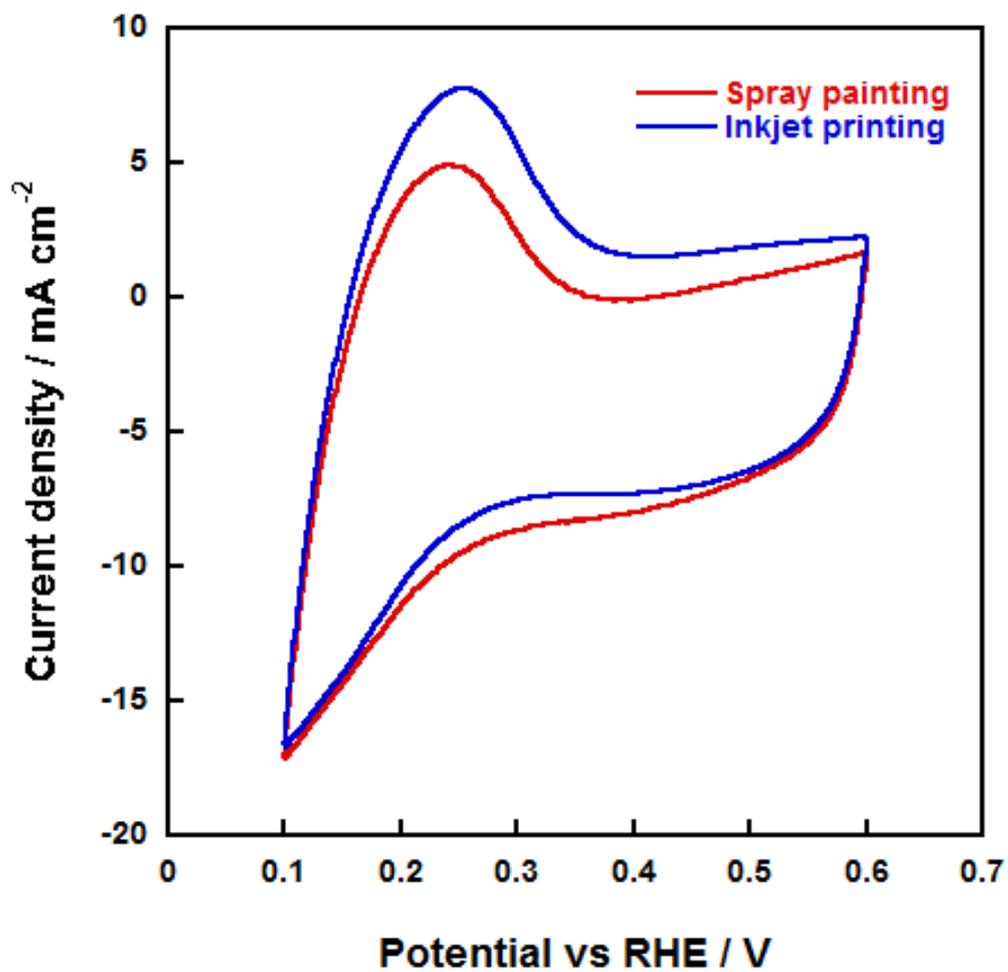
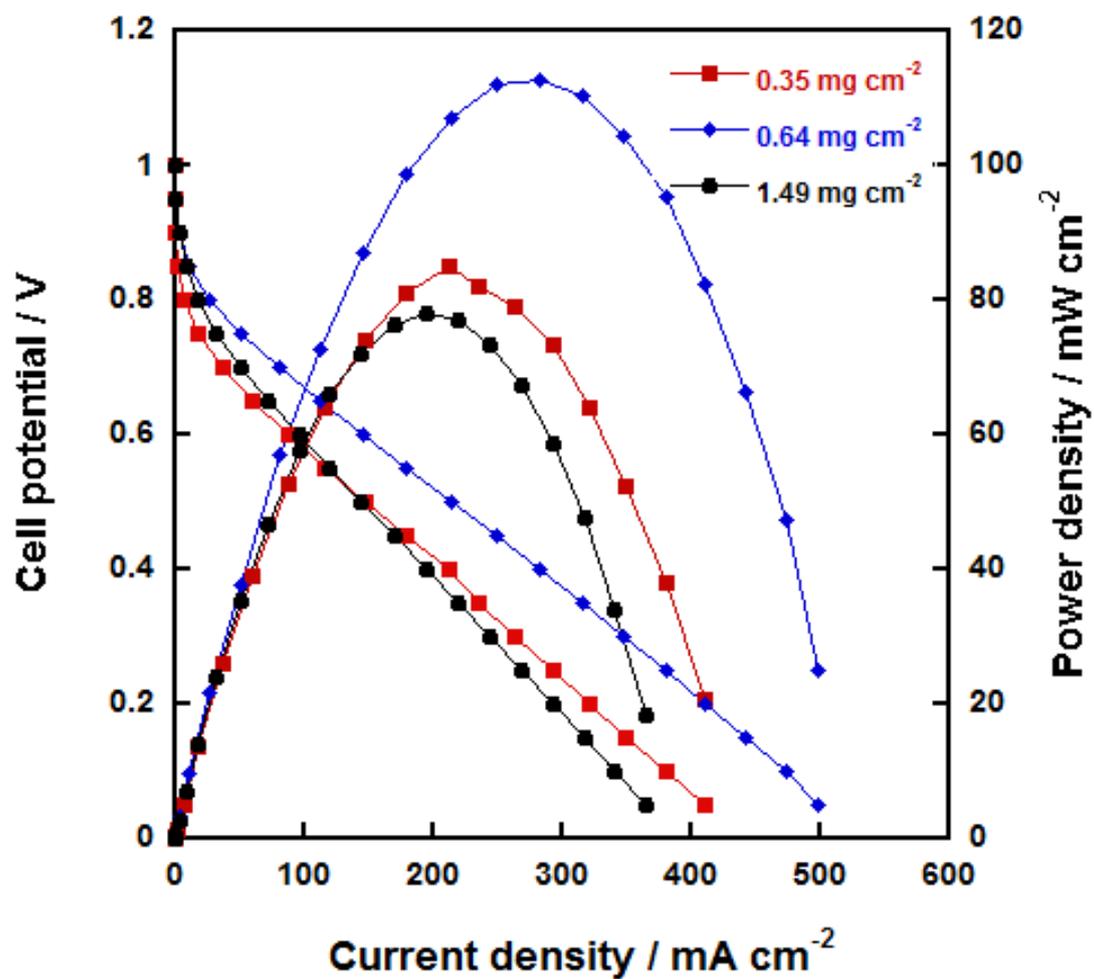
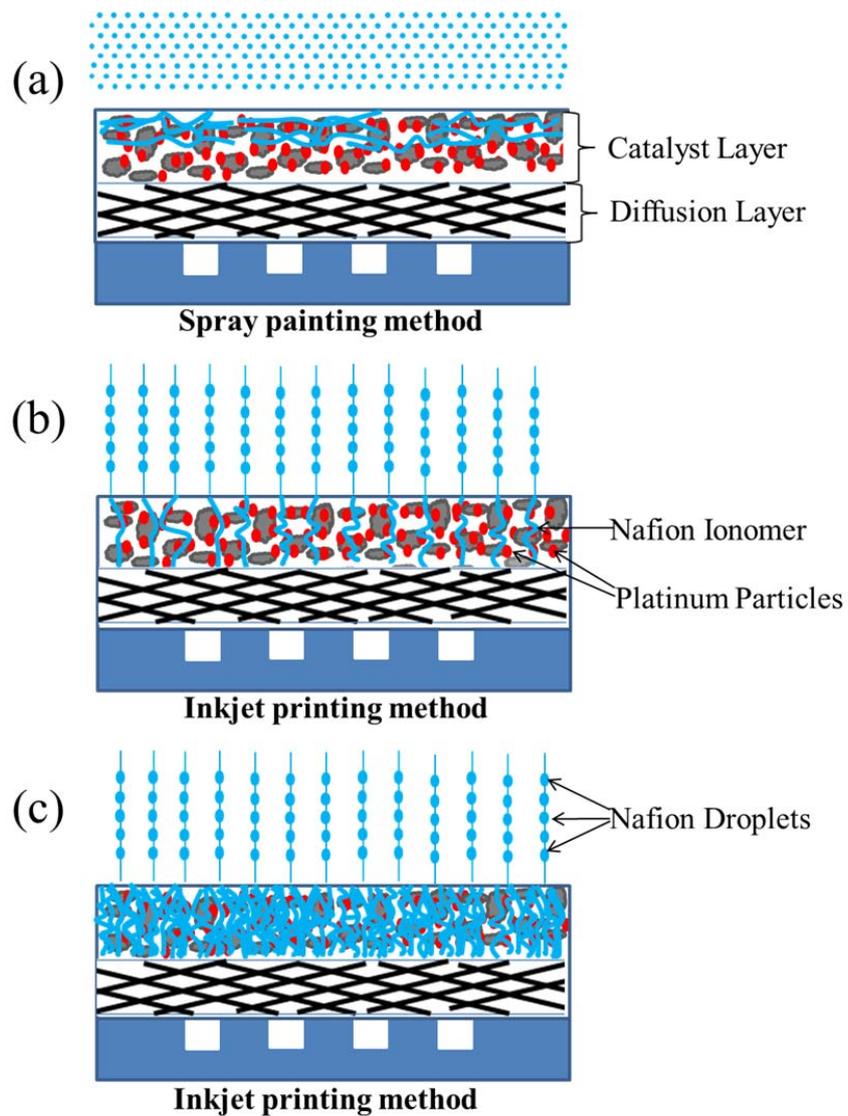


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