

Highly optimized MEA for direct methanol fuel cell prepared by sedimentation method

침전법을 이용한 직접 메탄올 연료전지용 고성능 MEA 제조

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1. Introduction

Direct methanol fuel cell (DMFC) is attracting more attentions due to its flexible applications [1-10]. However, when the conventional methods are used to fabricate the DMFC anode, it is difficult to produce a perfectly homogeneous catalyst layer due to that large systematic errors exist in the preparation process.

In this work the DMFC electrode was fabricated using sedimentation method in which the manual work was reduced to the minimum. A planar and homogeneous catalyst layer was obtained. The systematic errors were reduced and thus good reproducibility was achieved. Higher power density was obtained using the sedimentation method.

2. Experimental

1) Fabrication of membrane electrode assemblies (MEA) by sedimentation method

The substrate for the catalyst layer was wet-proofed Toray carbon paper with a gas diffusion layer. The gas diffusion layer for cathode and anode comprised XC-72 carbon and 20 wt% of PTFE, and XC-72 carbon and 7 wt% of Nafion ionomer, respectively. Pt and PtRu black (Johnson Matthey Co.) were used as the cathode and anode catalyst, respectively. The electrode preparation method reported by Sun [11] was modified and procedure of sedimentation method for fabricating the electrode is given as follows:

The catalyst powder was suspended in water in an ultrasonic bath until homogeneous ink was formed. Using a vacuum-filtering device, the suspension was filtered through a polycarbonate filter film containing the average pore size of 1 micron and thus an even and planar layer of catalyst remained on one side of the filter film. The catalyst loaded filter film was then removed from the filtering device and a thin layer of glycerol was applied to the backside of the film. The catalyst layer was then transferred from the filter film to the gas diffusion layer by pressing the assembly of the catalyst loaded filter film and the gas diffusion layer with a hydraulic press, and then polycarbonate filter film was peeled off. The obtained electrode was vacuum dried

at 110 °C for 24 hours. The 3 % H₂O₂ and 0.5 M H₂SO₄ treated Nafion 115 membrane was sandwiched between the prepared anode and cathode assembly. This assembly was hot pressed at 130 °C for 90 seconds under a pressure of 100 atm. The PtRu and Pt loadings of both anode and cathode are 5 mg/cm².

2) Single cell test

The tests of polarization curves were carried out using a single cell with the working area of 4 cm². Unless otherwise specified, PtRu and Pt blacks were used as the anode and cathode catalysts, respectively. The MEA was sandwiched between two graphite plates with straight channel flow fields. Two pieces of rubber gasket were used for sealing the MEA. The single cell was heated to the required temperature by two electrical heaters attached to the outer surface of the end plates. 2 M aqueous methanol solution was fed to the anode side using a peristaltic pump at a flow rate of 2 ml/min. O₂ was supplied to cathode chamber under ambient pressure.

3. Results and Discussion

1) Comparison of power densities of MEAs prepared by sedimentation method and brushing method

The power density curves of the single cell operated at various temperatures were presented in Fig. 1. In Table 1, a comparison of power densities was made between the MEA fabricated by sedimentation method and that by the conventional brushing method. At the cell temperature of 40 °C, the power density of MEA prepared by sedimentation method was only 10 % higher than that by brushing method. At a higher temperature of 60 °C and 80 °C, the power densities of MEA prepared by sedimentation method are 70 % and 180 % higher than that prepared by brushing method, respectively.

Various methods have been developed to prepare the electrode for H₂-O₂ PEMFC and DMFC, such as brushing, doctor blade, rolling, spraying, screen printing, decal method, etc. However, there exist common disadvantages in these methods, which are the requirement for skilled hands and the inevitable large systematic errors. Therefore a fabrication method without the influence of manual work is needed. Using the sedimentation method developed in this study, the catalyst layer was formed under the force of gravity and vacuum suction. As a result, a very homogenous and planar catalyst layer can be produced with the least systematic errors. In addition, During the sedimentation process, a perpendicularly oriented network of pores in the catalyst layer was generated though the spontaneous accumulation of the catalyst particles and the filtering process, which facilitated the mass transport of the reactants and the products.

Fig. 2 shows the durability test of the MEA prepared by sedimentation method when operated at a constant current density of 0.16 A/cm². After 30 hours of operation, the cell voltage decreased from 0.406 V to 0.4 V. The degradation of cell voltage was

0.25 mV/h, which was smaller than the 0.3 mV/h reported by Waidhas [12] and 2.5 mV/h reported by Shukla [13]. Therefore, the MEA prepared by sedimentation method showed good stability in the long-term operation.

Table. 1. Comparison of power densities of MEA fabricated by sedimentation and brushing method operated at the cell voltage of 0.4 V. Pt and PtRu loading: 5 mg/cm², P₀ = ambient pressure, O₂ flow rate: 500 ml/min, CH₃OH: 2.0 M, CH₃OH flow rate : 2 ml/min

	40 °C	60 °C	80 °C
Sedimentation	30 mW/cm ²	68 mW/cm ²	123 mW/cm ²
Brushing	27 mW/cm ²	40 mW/cm ²	44 mW/cm ²

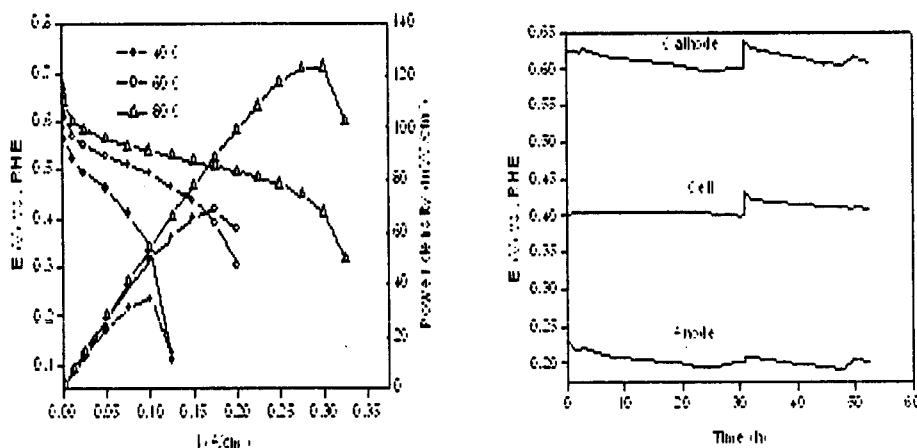


Fig. 1. Power density curves of the single cell at various temperatures. Pt and PtRu loading: 5 mg/cm², P_{O₂} = ambient pressure, O₂ flow rate : 500 ml/min, CH₃OH: 2.0 M, CH₃OH flow rate: 2 ml/min

Fig. 2. Durability test of the single cell under load current density of 0.16 A/cm². Pt and PtRu loading: 5 mg/cm², T = 60 °C, P_{O₂} = ambient pressure, O₂ flow rate: 500 ml/min, CH₃OH: 2.0 M, CH₃OH flow rate : 2ml/min

2) The order of adding Nafion to the catalyst layer

The order of adding Nafion to the cathode catalyst layer was studied. Compared

were two methods, of which one is dissolving the Nafion solution into the catalyst suspension before the sedimentation process and the other is impregnating Nafion solution after the catalyst layer was fabricated by sedimentation method. The Nafion loadings of both methods were 20 wt%. As shown in Fig 3, with the second method the cathode gave better performance than with the first one. When using the impregnation method, the Nafion solution flowed along the network of pores in the catalyst layer in a direction perpendicular to the surface of the electrode and did not block the pores which situated farther from the outer surface of the catalyst layer. Thus, there existed enough diffusion pathways for the reacting agents. The electronic conduction among the catalyst particles was not affected by the impregnation of Nafion. Furthermore, a very thin layer of Nafion formed on the surface of the catalyst layer which improved the bonding between the catalyst layer and the Nafion membrane after the hot pressing process.

3) Optimized amount of PTFE

The effect of PTFE content on the cathode performance was studied. The emulsion of PTFE was added into the catalyst suspension and then catalyst layer containing PTFE was prepared by sedimentation method. The experiments optimizing the content of PTFE were carried out in a half-cell, of which the electrolyte was 2 M H_2SO_4 or 2 M $\text{H}_2\text{SO}_4 + 2 \text{ M CH}_3\text{OH}$. As shown in Fig. 4, cathode containing 15 wt% PTFE in the catalyst layer showed a better performance than that without PTFE when 2 M H_2SO_4 was electrolyte at 28 °C. While the cathode containing 30 wt% of PTFE showed the worst performance. When 15 wt% PTFE was added to the catalyst layer, an optimal network of pores in the catalyst layer formed due to the hydrophobic property of PTFE, which made the mass transport of oxygen and water more efficiently without flooding. As the PTFE content was further raised to 30 wt%, the insulation of PTFE caused the increase of inner resistance of the cell, which compensated its favorable effect and even worsened the cell performance.

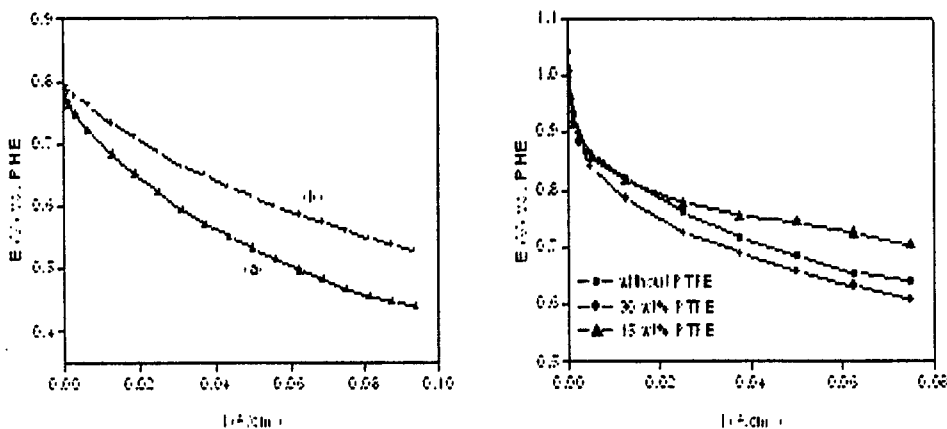


Fig. 3. Comparison of the methods of adding Nafion to the cathode catalyst layer. (a) Nafion was added to the catalyst suspension before the sedimentation process; (b) Impregnating the Nafion into the catalyst layer which was prepared by sedimentation method. Pt loading : 5 mg/cm², T = 28 °C, P_{O2} = ambient pressure, O₂ flow rate: 500 ml/min, Electrolyte: 2.0 M H₂SO₄ + 2.0 M CH₃OH, Flow rate: 2 ml/min

Fig. 4. Effect of PTFE content on the cathode performance. Pt loading: 5 mg/cm², T = 28 °C, P_{O2} = ambient pressure, O₂ flow rate: 500 ml/min, Electrolyte: 2.0 M H₂SO₄, Flow rate: 2 ml/min

4. Conclusion

The DMFC electrode was prepared by sedimentation method. Reducing the manual work to the minimum, this method greatly decreased the systematic errors and a planar and homogeneous catalyst layer was produced. Operating at 60 °C, the power density of the MEA prepared by sedimentation was 70% higher than that prepared by a conventional brushing method. The preparation process and the operating condition were optimized. Using the impregnation method to introduce Nafion into the catalyst layer, the MEA prepared by sedimentation method gave better performance. It is found that the addition of PTFE to the cathode catalyst layer improved the methanol tolerance of cathode. The optimal methanol concentration was 4 M.

5. References

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