

A multi-layer structured cathode for the PEMFC

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Abstract

Multi-layer structured cathodes for PEMFC were prepared by a spray-drying method to provide more efficient oxygen reduction in the cathode. The catalytic layer is, in general, composed of electrolyte for proton conduction and of Pt/C for both the electrochemical reaction and electron conduction. Although the presence of electrolyte is essential for proton conduction, the electrolyte phase retards the electron conduction through the catalytic layer because the electrolyte is electronically insulating. For the Pt/C part, vice versa is valid. In an attempt to develop a cathode possessing superior properties both in the proton and electron conduction, double catalytic electrolyte-rich and -poor layers were coated on the polymer electrolyte membrane (PEM). Performances of the double layered cathodes were evaluated from the current–voltage (I – V) characteristics of single cells. In addition, pressure drops across the fabricated cathodes were determined by using permeability measuring apparatus. From the experimental results, the rate of electrochemical reaction in the cathode was discussed in terms of proton transport and electronic conduction along with oxygen transport.

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1. Introduction

It has been generally noticed that the rate of cathodic reaction occurring in the cathode catalyst layer determines the cell voltage, while the rate of the electrochemical reaction in the anode catalyst layer is relatively fast by comparison [1–3]. Hence, the characteristics of the cathode catalytic layer in a PEMFC has significant impact on the overall performance of the cell.

Many works [4–13] have been done to improve the performance of the cathode. These involve optimization of electrolyte content [4], inhomogeneous catalyst layer [5], vacuum deposition [6–8], homogenization of catalyst slurry [9], introduction of pore former [10,11], increasing interface area between membrane and catalytic layer [12], impregnation of cathode with electrolyte phase [13], and so on.

Catalytic layer is, in general, composed of an electrolyte phase for proton conduction and of carbon supported Pt catalyst for both the electrochemical reaction and electron conduction. Although the presence of electrolyte is essential for proton conduction, the electrolyte phase retards the electron conduction through the catalytic layer because the electrolyte is electronically insulating. For the Pt/C part, vice versa is valid. Reactant transport through the catalytic layer is another important factor to be considered.

The microstructure of a catalytic layer strongly affects the gas transport rate in the catalytic layer. Springer et al. [1] pointed out that oxygen could diffuse fast along grain boundaries of the catalytic layer. Gloaguen et al. [2] suggested that oxygen is first transported through gas pores and then diffuses through the electrolyte phase of the catalytic layer, from the comparative study of macro-homogeneous and agglomerate models for the oxygen reduction in the thin catalytic layer.

In an attempt to develop a cathode possessing better performance both in the proton and electron conduction, double catalytic electrolyte-rich and -poor layers were coated on the polymer electrolyte membrane (PEM). Performances of the double layered cathodes were evaluated from the current–voltage (I – V) characteristics of single cells, along with pressure drops across the fabricated cathodes. From the experimental results, the rate of electrochemical reaction in the cathode was discussed in terms of proton transport and electronic conduction along with oxygen transport.

2. Experimental

2.1. Membrane electrode assembly fabrication

Prior to fabricating MEAs, the polymer electrolyte membranes, Nafion 112 (DuPont) were treated in various solutions to remove trace organic and inorganic contaminants and to change its form. The pretreatment procedure involved

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boiling the membrane in 3 wt.% aqueous H_2O_2 solution for 1 h, followed by boiling the membrane for 1 h in pure water. Then, the membrane was boiled for 24 h in 1 M H_2SO_4 solution to make the membrane into H^+ form. After that, the membrane was boiled for 2 h in pure water to remove the remaining H_2SO_4 on the surface of the membrane, followed by drying the membrane at ambient temperature.

In order to fabricate double and single layered cathode structures, several kinds of catalytic layers having different Nafion contents were deposited onto the poly-imide transfer film and carbon paper by using the spray-drying method. A 40 wt.% Pt/C (HiSPEC 4000 Fuel Cell Catalyst, Johnson Matthey) was used as an electrocatalyst on both the cathode and anode.

The electrocatalyst slurry mixed with 5 wt.% solubilized Nafion was made to increase the contact area between the membrane and the platinum clusters. The Nafion and Pt/C slurry was prepared by first thoroughly mixing the Nafion solution and Pt/C using a magnetic stirrer. The Nafion content in the supported Pt catalyst was varied from 10 to 60 wt.% (in weight of solids).

Catalytic layers were fabricated by spray-drying of catalyst-containing slurries onto the poly-imide transfer film and teflonized carbon paper (TGP-H-060, Toray), used as a gas diffusion media backing. Prior to spraying, the carbon paper backing was coated by PTFE emulsion to provide hydrophobic properties to the gas diffusion media. Two slurry formulations were used. One was composed of only electrocatalyst and solvent. The other contained electrocatalyst, solvent and additional Nafion ionomer. For the former formulation, Nafion ionomer was sprayed onto the dried catalyst layer.

After the spraying, electrocatalyst-coated poly-imide transfer film and gas diffusion media were dried for 2 h in the vacuum oven at 80 °C. Then, a double layered cathode structure was achieved by using two steps of hot pressing. The first step involved the transfer of catalytic layer from catalyst-coated poly-imide transfer film to the H^+ type Nafion membrane of 90 μm thick by hot pressing for 180 s at 135 °C with a pressure of 75 atm, thereby forming the first layer of the double layered cathode. In the second step, the second layer was fabricated by hot pressing of catalyst-coated diffusion media with previously hot pressed membrane at the same pressing condition. Nafion contents in the first and second catalyst layers were varied from low (10 wt.%) to high (60 wt.%). For comparison, single layered cathodes were also prepared. The Pt loading for the anode was 0.4 mg/cm^2 and that for each layer of the cathode was maintained to be 0.2 mg/cm^2 . The single cell was operated at 60 °C, humidifier temperature of 70 °C and ambient pressure of H_2/O_2 or H_2/air with the stoichiometry of 1.25/2.5.

2.2. Permeability measurement of catalytic layers

In order to determine the ease of oxygen transport through the catalytic layers, pressure drops across the catalytic layers

were measured. Two pieces of carbon papers that were coated with catalyst were hot pressed at the same condition for the MEA fabrication. In the permeation apparatus, the exposed area was 10 cm^2 and the flow rate of oxygen was 6 cm^3/s .

3. Results and discussion

Table 1 presents the pressure drops for the various catalyst-coated carbon papers under the application of 6 cm^3/cm^2 s, oxygen gas. In fact, catalyst slurry or Nafion ionomer was penetrated into the pores of diffusion media more or less, during the spraying. So, the measured pressure drop across the catalyst-coated carbon paper might be influenced by the degree of solvent penetration into the pores. However, it seemed to be obvious that the catalytic layers containing higher Nafion content showed higher pressure drop. In addition, spraying of Nafion ionomer onto the catalytic layers increased the pressure drop across the catalytic layers.

Nafion ionomer coating onto the catalyst layer seemed to block the pores located between the catalyst particles, thereby increasing the pressure drop across the catalytic layer. The catalytic layer is, in general, composed of electrolyte for proton conduction and of Pt/C for both the electrochemical reaction and electron conduction. Although the presence of electrolyte is essential for proton conduction, electrolyte phase retards the electron conduction through the catalytic layer because the electrolyte is electronically insulating. In addition, higher content of electrolyte phase seems to be detrimental to the oxygen transport through the cathode due to the blocking of pores by the excess electrolyte phase, resulting in reduction of the cell performance. This detrimental effect seems to be enhanced especially in the case of spraying of Nafion ionomer onto the catalytic layers. However, the performance of a cell was not always decreased with increasing pressure drops across the cathode layers as expected.

The I - V characteristics of fabricated single and double catalytic layers measured under the application of H_2/O_2 and H_2/air are presented in Fig. 1. Comparing the two double layered cathodes, the cathode which had the membrane

Table 1
Pressure drops measured from the various catalyst-coated carbon papers under the application of 6 cm^3/cm^2 s, oxygen gas

Nafion content (%)	EW of Nafion	Nafion coating method	ΔP [mmH_2O]
0	Carbon paper	None	5
10	1100	Mixing before spraying	11
35	1100	Mixing before spraying	11
60	1100	Mixing before spraying	40
35	1100	Spraying on to catalytic layer	27
35	1000	Spraying on to catalytic layer	36
60	1100	Spraying on to catalytic layer	71
60	1000	Spraying on to catalytic layer	80

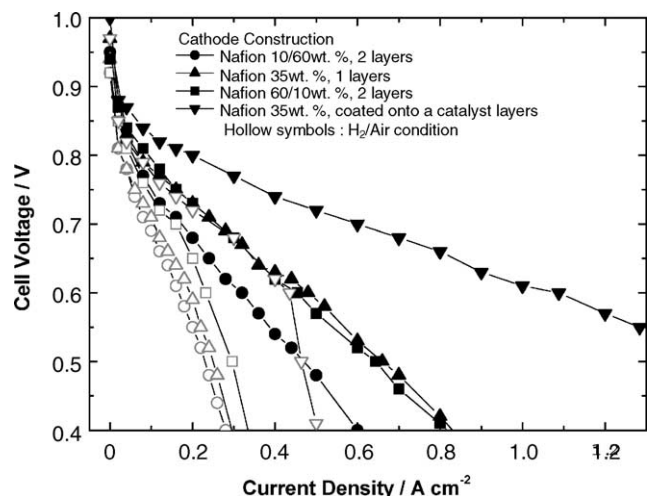


Fig. 1. *I*-*V* characteristics of single and double catalytic layers measured under the application of H₂/O₂ and H₂/air.

contacting the first layer possessing 60 wt.% of electrolyte phase showed higher performance at both H₂/O₂ and H₂/air conditions. The cathode which was electrolyte phase coated onto the catalyst layer presents the best performance.

Let us first consider the two double layered cathodes. In this case, Nafion ionomer was mixed before the catalyst spraying. Considering the two layers, while one layer having the lower electrolyte content (10 wt.%) is conjectured to be favorable to oxygen transport and electronic conduction, the other layer containing a higher content of Nafion ionomer (60 wt.%) seems to be advantageous in proton conduction to the cathode and unfavorable to oxygen transport. Therefore, the result of higher performance of the cathode having an inner layer of higher electrolyte content seems to indicate that sufficient electrolyte phase is required to support proton conduction in the cathode, at least in the vicinity of the interface between the membrane and the catalyst layer.

Comparing the performance of the single cells, the electrolyte phase-coated cathode (35 wt.%) showed the best performance, in spite of the highest pressure drop across the cathode. It indicates that oxygen transport through the cathode is not a rate-determining step in the oxygen reduction reaction, at least in the range investigated. This kind of cathode which is fabricated by coating the Nafion ionomer onto the catalytic is not a new idea and it was previously suggested by Cheng et al. [13]. They pointed out that electron passage is blocked by the electrolyte phase and therefore, the electrolyte phase reduces the utilization of the catalyst. One way to provide the sufficient proton and electron transfer simultaneously was suggested to be impregnating the catalytic layer with Nafion ionomer [13].

Because the single cell adopting the cathode impregnated with electrolyte phase showed much higher performance, more attention has been paid to this type of cathodes. In order to determine the suitable Nafion content impregnated in the catalytic layer, three kinds of cathode layers impregnated

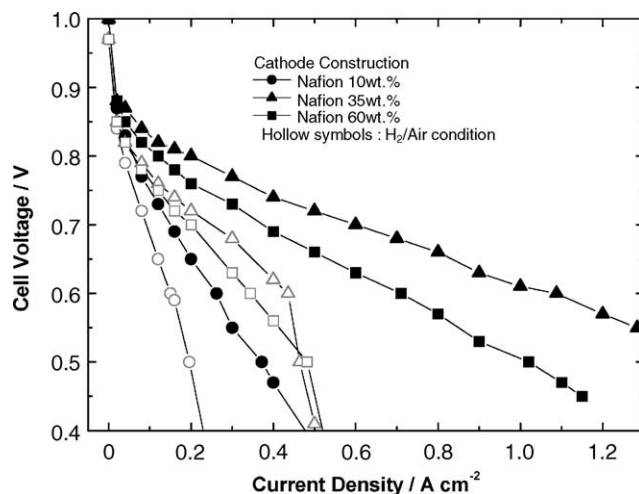


Fig. 2. *I*-*V* characteristics of catalytic layers impregnated with electrolyte content of 10 wt.% (●), 35 wt.% (▲) and 60 wt.% (■). Equivalent weight of Nafion is 1100.

with 10, 35 and 60 wt.% Nafion ionomer were prepared and measured the performances of the single cells. The results are plotted in Fig. 2. The cathode impregnated with 35 wt.% electrolyte phase showed the best performance. The higher (60 wt.%) and lower (10 wt.%) impregnation levels resulted in worse performance, probably due to the limited oxygen transport and insufficient proton passage, respectively.

In an attempt to enhance the cathode performance, double layered cathodes which were composed of catalytic layers impregnated with high (60 wt.%) and low (35 wt.%) Nafion contents were fabricated by using Nafion of equivalent weight of 1100 and 1000. It was expected that proton passage would be enhanced by using Nafion ionomer of equivalent weight 1000, thereby increasing the cell performance. However, the measured single cell performances were not consistent with the expectation. The single cells

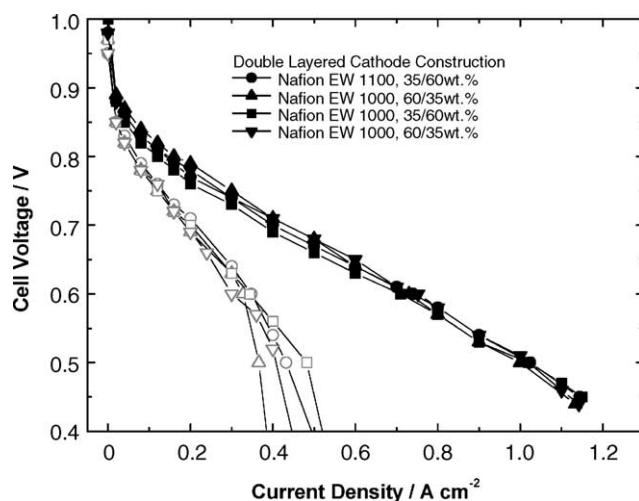


Fig. 3. *I*-*V* characteristics of double layered cathodes impregnated with 35 wt.% (●) and 60 wt.% (▲) of Nafion 1100, and 35 wt.% (■) and 60 wt.% (▼) of Nafion 1000.

adopting four kinds of double layered cathodes showed almost the same performance, irrespective of equivalent weight of Nafion, and Nafion content of the inner and outer layers. The results are depicted in Fig. 3. It seems that the addition of lower equivalent weight of Nafion ionomer is not so beneficial to the cell performance, at least in the range investigated.

4. Concluding remarks

In an attempt to provide more efficient oxygen reduction in the cathode, double layer structured cathodes were prepared. Performances of the double layered cathodes were evaluated from the I - V characteristics of single cells along with the pressure drops across the fabricated cathodes.

Although the pressure drop of the cathode impregnated with electrolyte phase was higher, it showed the best performance, due to the formation of both sufficient electron and proton passages.

The single cells adopting four kinds of double layered cathodes showed almost the same performance, irrespective of the equivalent weight of Nafion, and Nafion content of the inner and outer layers, at least in the range investigated.

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