Effect of the catalytic ink preparation method on the performance of polymer electrolyte membrane fuel cells

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Abstract

The effect of the preparation method of the catalytic inks on the electrode structure and, thus, on the performance of polymer electrolyte membrane fuel cells (PEMFCs) was investigated. Since the catalytic inks, which are a mixture of Pt/C powders, solvent, and ionomers, change into one of the three states: (i) solution; (ii) colloids and (iii) precipitates, according to the interaction between the ionomers and solvents, two different catalytic inks have been prepared for comparison, the solution inks based on *iso*-propyl alcohol (IPA) and the colloidal inks based on normal butyl acetate. Performance evaluation, electrochemical analyses, and physical property examination revealed that the electrode prepared by a colloidal method showed better results compared to those of the solution method. The former appeared to secure continuity of the ionomer network and higher porosity in the catalytic layer, resulting in higher proton conductivity and less mass transfer resistance.
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Keywords: Catalyst inks; Solution method; Colloidal method; Ionomer impregnation

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been receiving attention on account of their highly attractive properties as a power source for both stationary and mobile application. Their significant advantages are their ability to eliminate electrolyte leakage, lower corrosion, simplify stack design and increase ruggedness [1,2]. As PEMFCs require platinum (Pt) catalyst as an active material of electrodes, it is important to increase the reaction sites in the catalytic layer and, thus, to improve electrode performance and reduce Pt loading. Since the polymer membrane used for electrolyte is a solid phase, it does not penetrate deeply into the electrode as does a liquid one, therefore the reaction area is limited to the contact surface between the electrode and membrane.

To increase this contact surface area, an ionomer like Nafion should be impregnated in the catalytic layer. The Nafion ionomer, which is the perfluorosulfonate-ionomer (PFSI), has two functional groups; hydrophilic and hydrophobic. When the Nafion ionomer is mixed with organic solvents, the mixture may become one of three states: (i) solution; (ii) colloids and (iii) precipitates, according to the different dielecric constant ε of the organic solvents and the corresponding interaction between the ionomers and

solvents. It is well known that the Nafion solution forms a solution in the solvents with $\varepsilon > 10$, a colloidal solution with ε between 3 and 10, and a precipitate with $\varepsilon < 3$ [3]. For example, in the conventional "solution method" where *iso*-propyl alcohol (IPA; $\varepsilon = 18.3$) is used as a solvent, the ionomer totally dissolves and forms a solution state; whereas the ionomer forms colloids in the "colloidal method" where normal-butyl acetate (NBA; $\varepsilon = 5.01$) is used.

In the solution method, however, it is considered possible for an ionomer to block the conduction of electrons as a result from covering the surface of carbons by ionomers and decreasing platinum utilization when ionomers cover the surface of carbon excessively, because an ionomer is an electron insulator. In the colloidal method, however, ionomer colloids adsorb the Pt/C powders and the size of the agglomerate of Pt/C powders increases. Then the porosity of the electrode will increase and, accordingly, the mass transfer resistance will be diminished. The continuous network of ionomers throughout the catalytic layer will be also increased, which will improve the proton movement from the electrode to the membrane. Fig. 1 represents the schematic diagram of the microstructure of the catalytic layers prepared by such solution method and the colloidal one. In this study, the effect of the solution and colloidal method on the electrode performance was investigated through single cell performance evaluation, electrochemical analyses, and physical property examination.

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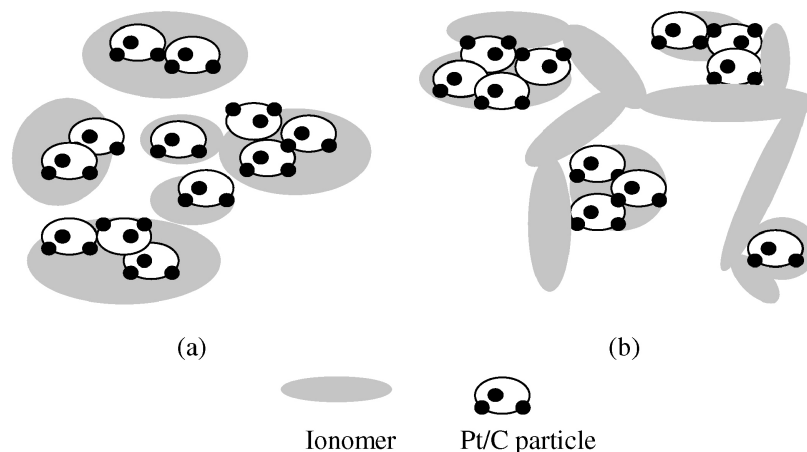*E-mail address:* oih@kist.re.kr (I.-H. Oh).

Fig. 1. Schematic diagram of the microstructures in the catalytic layer according to the catalyst ink preparation method; (a) ionomer solution method and (b) ionomer colloidal method.

2. Experimental

The inks for the catalytic layers were prepared from the Pt/C powders (40 wt.% of Pt), Nafion solution, and solvent. In the colloidal method, the inks were dripped drop by drop in NBA solvent [4] and the ionomer colloids formed were forced to adsorb the Pt/C powders by ultrasonic treatment; whereas in the conventional solution method, the inks were fully suspended in the IPA solvent. The above inks were then sprayed by air-brushing over the carbon papers which had a carbon layer in advance to produce the electrodes. When the inks on the carbon paper were dried up, the extra Nafion solution in IPA was sprayed on the surface of the electrode. The MEA was prepared by placing the above electrodes on the both sides of the pre-treated Nafion 115 membrane, followed by hot pressing at 140 °C and 200 atm for 1.5 min. The MEA fabrication procedure is represented in Fig. 2.

The MEA with an active area of 25 cm^2 was constructed with a cell frame which consisted of graphite plates with rib channels of series-parallel type for gas flow and the
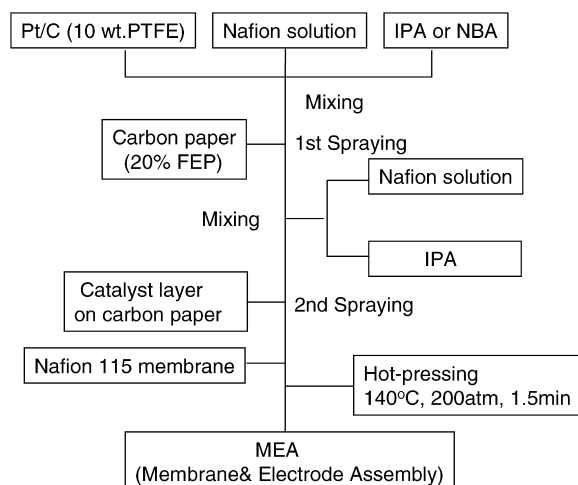

Fig. 2. Procedure of the MEA fabrication.

aluminum end plates. The electronic loader (Daegil Electronics, EL 500P) was used to measure the cell potentials as a function of current density. The cell temperature was held at 80 °C throughout the experiments for hydrogen and oxygen. The reactant gases were fed to the cell at a flow rate of 270 cc/min and they were humidified by bubbling through water contained in stainless steel bottles under atmospheric pressure prior to being provided to the cell.

Cyclic voltammetry measurement was conducted at 80 °C on a 5 cm^2 single cell fixture to determine the electrochemically active surface area. The measurement involved hydrogen and nitrogen atmospheres at the counter electrode (anode) and the working electrode (cathode), respectively, and was conducted with a potential range of 0.01–1.4 V versus NHE and a sweep rate of 50 mV/s. The electrochemical active surface area of the electrode was obtained from the charge required for hydrogen desorption from the Pt electrocatalyst. The coulombic charge for the oxidation of atomic hydrogen (area under the anodic peak minus the double layer charge at 0.4 V versus NHE) was used to evaluate the roughness factor of the electrode assuming a value of 220 μC/cm^2 for the oxidation of atomic hydrogen on a smooth Pt surface.

An impedance analyzer (EG&G 5210 lock-in amplifier) measured the resistance of the MEA (5 cm^2 geometric area) at 0.9 V under operating cell conditions. The reference and counter electrode were connected to the hydrogen electrode, and the working electrode, to the oxygen electrode. The current response with respect to the 5 mV sine wave was evaluated in a frequency range from 1 mHz to 50 kHz.

3. Results and discussion

When the electrode is fabricated, the Nafion ionomer solution is usually brushed on the electrodes and then the solvent in the electrodes is evaporated. A pair of electrodes is hot-pressed on both sides of an electrolyte membrane to

produce a MEA. Through this step, the ionomers penetrate into the catalytic layer [5], providing a path for proton transfer. The penetration, however, is rather difficult because most of the ionomers are located near the electrode surface. In another method, the catalytic inks made of a mixture of ionomers, Pt/C powders, and solvent are used for constructing the catalytic layer. The ionomer solution is additionally sprayed on the surface of the catalytic layer to increase proton conductivity at the interface between the catalytic layer and the electrolyte membrane.

Uchida et al. [6] made a paste mixed with ionomers and catalysts and utilized a filtration method to fabricate the catalytic layer. In this case, the total Nafion amounts impregnated in the catalytic layer were contained in the catalytic inks. If Nafion is impregnated excessively in the catalytic layer, however, the performance of the electrode would decrease due to reduction of porosity, Pt utilization, and electronic conduction in the catalytic layer. From the previous study on the effect of the Nafion ionomer distribution in the catalytic layer on the electrode performances, therefore, ionomers with 8 wt.% of the Pt/C weight were impregnated inside the catalytic layer and those with 25 wt.% of the Pt/C weight were coated on the surface of the catalytic layer for all the electrodes in this study, even though the different catalyst ink preparation methods were applied.

The fabrication of the electrode through spray coating or screen printing on the carbon paper produced an unintentional problem. Some catalyst particles penetrated into the carbon paper, blocking its pores. The catalyst particles then reduced the rate of reactant transfer and were more difficult to participate in the electrochemical reaction than catalysts near the electrolyte membrane. To prevent penetration, it is necessary to increase the size of agglomerates of catalysts by means of the enhanced interaction between catalysts and ionomers. This can be done by the ionomer colloidal method when the catalyst inks are prepared. Other than the increase in the agglomerate size, the advantage in the proton conductivity may be achieved.

For those purposes, ionomer colloids are forced to adsorb the Pt/C powders by ultrasonic treatment in order to increase the interface area between ionomers and supported catalysts [3] and the continuous network of ionomers through the catalytic layer. This method can also be used to increase the size of Pt/C powder and ionomer agglomerate and, thus, to diminish the resistance of mass transfer resulting from the rise of catalytic layer porosity and reduction of penetration phenomena in the carbon paper.

Fig. 3 shows the cell performances according to the different catalyst ink preparation methods and Fig. 4 represents the corresponding cyclic voltammograms for the evaluation of the electrochemical reaction areas. The electrode made by the colloidal method showed nearly 30% increase in the electrochemical reaction area and, therefore, about 20% improvement in the cell performance compared to the solution method, with a current density of 928 mA/cm^2 at 0.6 V under the condition of 80 °C and 1 atm using hydrogen
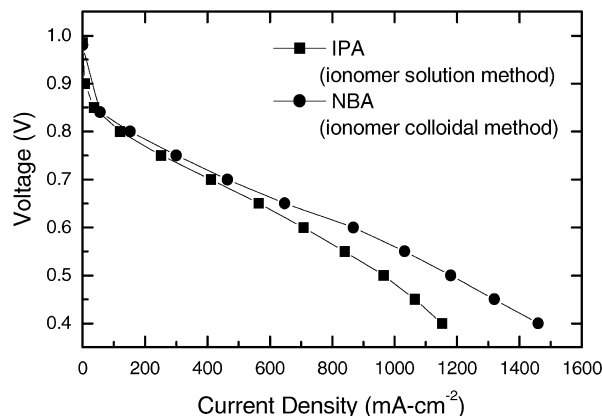

Fig. 3. Effect of the catalyst ink preparation method on the cell performance, Pt loading = 0.4 mg/cm^2, H_2/O_2 = 1/1 atm, and T = 80 °C.
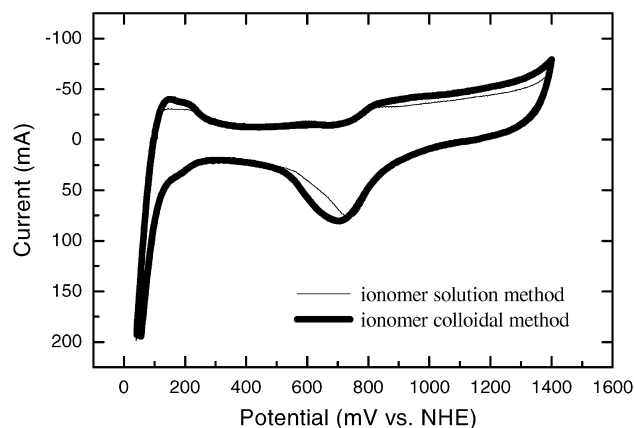

Fig. 4. Cyclic voltammograms for the different catalyst ink preparation methods. Scan rate = 50 mV/s, Pt loading = 0.4 mg/cm^2, Ca./An. = N_2/H_2, T = 80 °C, and P = 1 atm.

and oxygen. Fig. 5 presents the results of impedance analysis to measure polarization resistance for the different catalyst ink preparation methods. When a colloidal method was applied, it is seen that a polarization resistance, which is
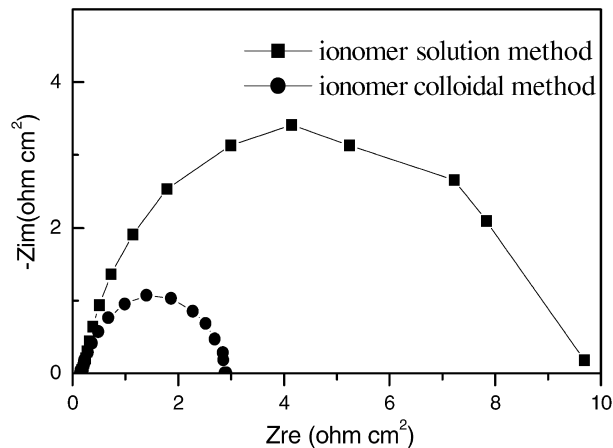

Fig. 5. Nyquist plots of electrodes at 0.9 V for the different catalyst ink preparation methods.

Table 1
Physical properties of the electrodes

Preparation method	Properties	
	Size of Pt/C and ionomer agglomerates (nm)	Thickness of catalytic layer (μm)
Ionomer solution method		
Average size	550	20
Polydispersity	0.044	20
Ionomer colloidal method		
Average size	736	40
Polydispersity	0.487	40

the combination of electron transfer resistance and diffusion resistance, was diminished by $7\,\Omega\,cm^2$ compared with a solution method. It seems that the colloidal method for the fabrication of the catalytic layers leads to the formation of thinner Nafion films on the carbon surface than the solution method.

The effect of the ionomer impregnation method on the electrochemical activity of electrodes is closely related to its physical properties as shown in Table 1. It was found that the agglomerate of catalysts impregnated with ionomers in NBA was 180 nm bigger than the size of those in IPA. Also, the catalytic layer by the colloidal method was 20 μm thicker than the one by the solution method using IPA. Therefore, the introduction of a colloidal method in the preparation of catalytic inks increased the size of agglomerates of catalysts. As the size of agglomerates grew, the amount of catalysts which penetrated into the pores in the carbon paper diminished and the supply of reactant gases improved. This finding can be confirmed by reducing mass transfer limitation in the region below 0.5 V (refer Fig. 3).

Fig. 6 shows the results of mercury porosimeter analysis for pore size distribution electrode. Watanabe et al. [7] reported that the catalytic layer had two distinctive pore distributions with a boundary of about 0.1 μm. The primary pore was identified with the space in and between the primary particles in the agglomerates, and the secondary pore, between the agglomerates. In the case shown in Fig. 6, the boundary of pore size distribution was at 0.07 μm. Therefore, the pores in 0.02–0.07 μm were the "primary pores", and those in 0.07–1.0 μm were the "secondary pores" in the electrode. It is seen from Fig. 6 that the pore size distribution below 0.07 μm in the electrode made by a colloidal method remained unchanged compared with the standard electrode which was not impregnated with ionomers. However, pores between 0.07 and 1.0 μm were not measured due to the blocking of ionomers in them and pore size distribution which ranged in the region above 1 μm was similar to that in the standard electrode. Therefore, it is concluded in the colloidal method that the ionomers penetrated into the large pores between 0.07 and 1 μm and blocked these; whereas small pores below 0.07 μm were not blocked by ionomers. In the case of the solution method, however, it is clearly seen from Fig. 6 that all pores below 0.07 μm were blocked by ionomers.

In the case of the colloidal method, big ionomer colloids penetrated into and blocked the secondary pores only, with the primary pores not being impregnated by ionomers. Therefore, the ionomer colloids play a role of the binders for the agglomerates between the Pt/C powders. Instead of being spread all over the catalyst powders as in the solution method, the ionomers gather each other to make the catalyst powders form agglomerates. The primary pores which were not filled with ionomers during the preparation of catalytic layers were later exposed to, and filled with, the extra
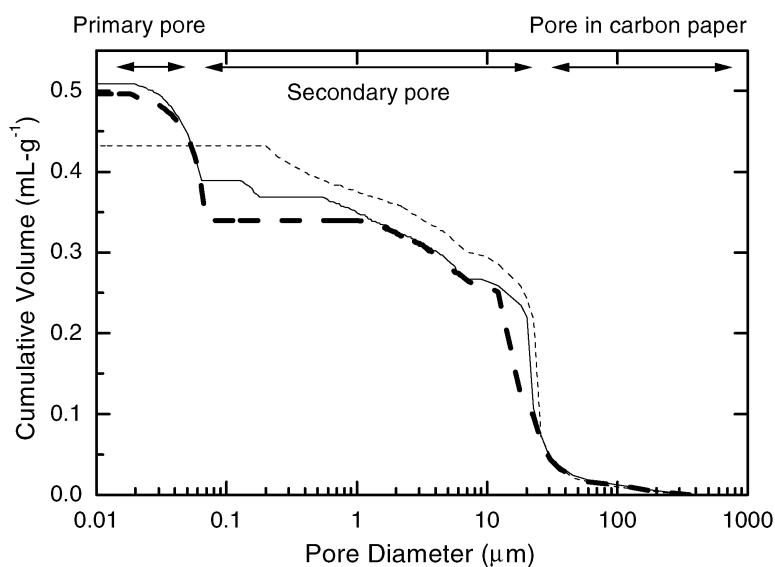

Fig. 6. Cumulative pore volume distribution of the electrodes. (——): Pt/C electrode without ionomers, (- - -): ionomer impregnated Pt/C electrode by solution method, (– – –): ionomer impregnated Pt/C electrode by colloidal method.

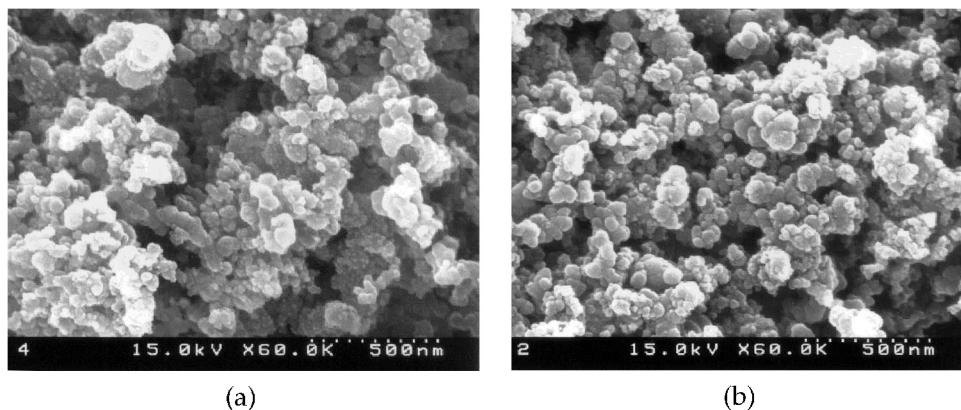(a)   (b)

Fig. 7. Surface morphology of the electrodes for the different catalyst ink preparation methods; (a) ionomer colloidal method and (b) ionomer solution method.

ionomers when the Nafion solution in IPA was sprayed on the dried electrode surface to improve the adhesion between the electrode and the membrane. In the colloidal method, therefore, the utilization of Pt in all the pores is larger compared to the solution method, due to the increased agglomerate size, resulting in the better performance.

Also, from Fig. 7, which shows the surface morphology of the electrodes made by the different catalyst preparation methods, it could be discerned that the electrode surface made by a colloidal method had bigger pores and Pt/C agglomerates than that made by a solution method. Considering these results, it can be verified that the catalytic layer with larger pores can be made through the increase of agglomerates of Pt/C powders and ionomers in size by a colloidal method. Fig. 8 compares the TEM images for ionomer solution, pure Pt/C powders, agglomerates by a solution method, and agglomerates by a colloidal method. It can be seen that the agglomerates prepared by a colloidal method show more dispersed structure as depicted by Fig. 1(b); whereas the one by a solution method appears to be in a dense phase.

To investigate the effect of the electrode microstructure on the conductivity of protons and the mass transfer rate of the reactant gases, the electrode with a resistance layer was fabricated, as shown in Fig. 9 [8]. The existence of the resistance layer may influence the cell performance by changing the proton conductivity and mass transfer rate. As the resistance layer is made of the carbon particles and the Nafion ionomers, without any catalysts, it will provide only the paths for proton and reactant gas movement and no electrochemical reaction will take place. When the resistance layer was fabricated, the amount of the carbon powders was the same as that of the catalytic layer, excluding the catalysts, and the amount of the ionomers was also the same as that in the catalytic layer. Two different resistance layers were fabricated; the one by the solution method with IPA and the other by the colloidal method with NBA. But, the catalytic layers for the both cases were fabricated by the colloidal method with NBA. When such a resistance layer is

located between the electrolyte membrane and the catalytic layer as in Fig. 9(a), the performance of the electrode is controlled by proton conductivity through the resistance layer. When the resistance layer is located between the carbon paper and the catalytic layer as in Fig. 9(b), the performance will be controlled by the diffusion rate of the reactant gases through the resistance layer.

Fig. 10 shows the cell performance for the different resistance layer preparation methods, with the resistance layer located between the catalytic layer and the electrolyte

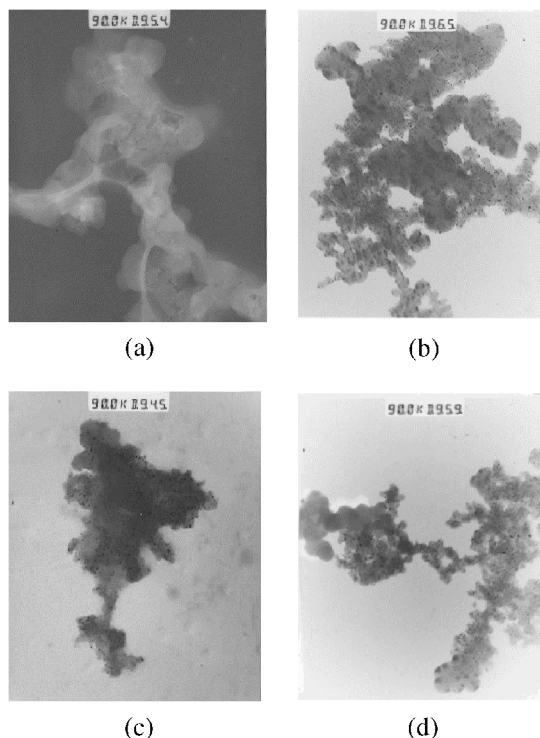(a)   (b)

(c)   (d)

Fig. 8. TEM images of the ionomer solution and the Pt/C catalysts with ionomers; (a) ionomer solution; (b) pure 20 wt.% Pt/C powders; (c) 20 wt.% Pt/C + powders from solution method; (d) 20 wt.% Pt/C + powders from colloidal method.
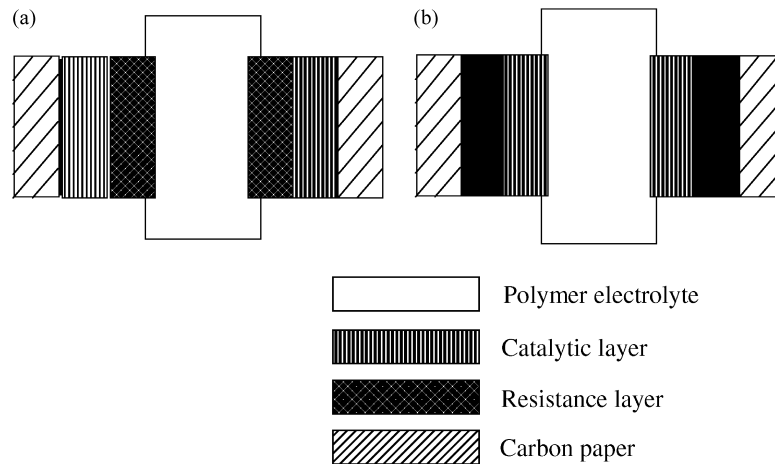
Fig. 9. Schematic diagram of the multilayer electrode system; (a) system for proton conductivity and (b) system for mass transfer.

membrane. As the resistance layer prohibits the proton conductance from the catalytic layer to the electrolyte membrane, the cell performances in this case are seen to be considerably lower than those of the cell without the resistance layer, which are usually 350–400 mA/cm^2 at 0.7 V. For example, the cell fabricated with a resistance layer by the solution method showed 16 mA/cm^2 at 0.7 V; whereas the cell fabricated with the one by the colloidal method showed 36 mA/cm^2. But, it should be noted that the colloidal method produced higher cell performance compared to the solution method. This is because the proton conductivity increased due to the interconnection of the ionomers in the catalytic layer.

Fig. 11 shows the cell performance for the different resistance layer preparation methods, with the resistance layer located between the catalytic layer and the carbon paper. Because of the existence of the resistance layer, the mass transfer of the reactant gases will be a rate-determining step and, thus, the cell performance is controlled by the mass transfer through this layer. It is seen from the figure that the cell performance was not significantly affected by the

resistance layer at low current density region, but the influence increased as the current density became higher. Particularly, the effect of the colloidal method was prominent at high current density region, where the cell performance was 864 mA/cm^2 by the solution method and 1044 mA/cm^2 by the colloidal method at 0.4 V. The colloidal method appeared to secure a higher porosity in the catalytic layer, resulting in higher mass transfer.

Based on these results, it is seen that the catalyst ink preparation method and, thus, the structure of the electrode have much influence on the cell performance. As shown in Fig. 1, where the microstructures in the catalytic layer are schematically represented according to the catalyst ink preparation methods, ionomers cover the Pt/C particles in a different manner. In the solution method (see Fig. 1(a)), the ionomer solution penetrates into the pores of the agglomerates, covering the platinum catalysts. It is considered to be possible for the ionomers to block the conduction of electrons and cause the decrease of catalyst utilization. In the colloidal method (see Fig. 1(b)), however, the ionomer colloids form before the ionomers penetrate into the pores
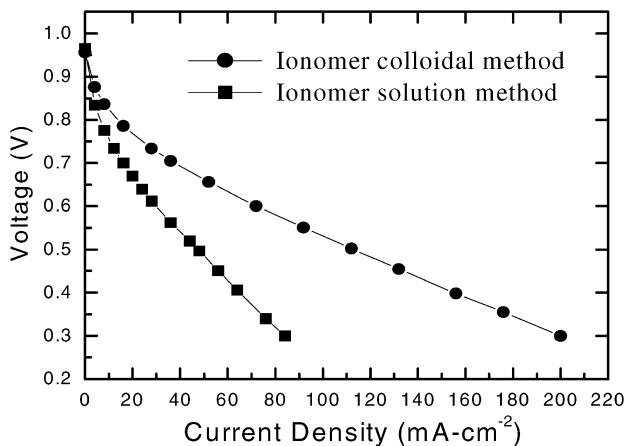

Fig. 10. Effect of the resistance layer to proton conductivity on the cell performance.
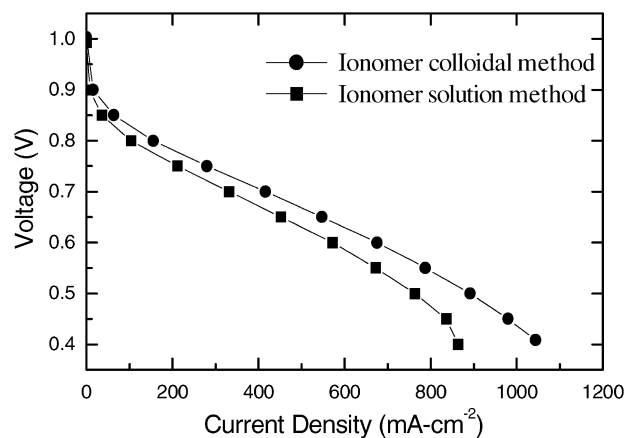

Fig. 11. Effect of the resistance layer to mass transport on the cell performance.

of the catalyst agglomerates. Therfore, the ionomers outside the agglomerates secure the continuous electrolyte network, improving the proton conductivity. The higher porosity of the agglomerates also results in the increase of mass transport, providing the higher platinum utilization. It is due to these effects that the performance of the cell made by a colloidal method was about 20% higher than the one by the conventional solution method.

4. Conclusions

The effect of the preparation method of the catalytic inks on the electrode structure and, thus, on the performance of PEMFCs was investigated. In the conventional "solution method" where IPA is used as a solvent, the ionomer totally dissolves and forms a solution state; whereas the ionomer forms colloids in the "colloidal method" where NBA is used.

The electrode made by the colloidal method showed nearly 30% increase in the electrochemical reaction area and, therefore, about 20% improvement in the cell performance compared to the solution method, with a current density of 928 mA/cm^2 at 0.6 V under the conditions of 80 °C and 1 atm using hydrogen and oxygen. The polarization resistance, which is the combination of electron transfer resistance and diffusion resistance, was also diminished by 7 Ω cm^2 compared with the solution method.

To examine the advantages of the colloidal method, the physical properties of the electrodes were examined. It was found that the agglomerate of the catalysts impregnated with ionomers in NBA was 180 nm bigger than the size of those in IPA. Also, the catalytic layer prepared by the colloidal method was 20 μm thicker than the one by the solution method using IPA. It was also seen in the colloidal method

that ionomers penetrated into the large pores between 0.07 and 1 μm and blocked these; whereas small pores below 0.07 μm were not blocked by ionomers. In the case of the solution method, however, all pores below 0.07 μm were blocked by ionomers.

Therefore, in the solution method, the ionomer solution penetrates into the pores of the agglomerates, covering the platinum catalysts. It is considered to be possible for the ionomers to block the conduction of electrons and cause a decrease of catalyst utilization. In the colloidal method, however, the ionomer colloids form before the ionomers penetrate into the pores of the catalyst agglomerates. It is concluded that the ionomers outside the agglomerates secure the continuous electrolyte network, improving the proton conductivity. The higher porosity of the agglomerates also results in an increase of mass transport, providing higher platinum utilization.

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