

Process and Characteristics of High Power Catalyst Electrode for PEM Fuel Cell

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Abstract

Novel process for high power catalyst electrode for PEM fuel cell has been developed. MEA having this catalyst electrode showed 0.5 W/cm² with 0.2 mg/cm² of Pt loading at atmospheric humid hydrogen and oxygen condition. In this process, platinized carbon and plain carbon powders were coated with ionomer (Nafion) and hydrophobic polymer (PTFE), respectively and it could maximize two roles of catalyst electrode, *i.e.*, reaction and gas supplying component. Those polarization characteristics proved the improved performance by reducing potential drop especially in the concentration polarization region.

Key words : PEM fuel cell, Catalyst electrode, Polarization

1. Introduction

The application potential is high for proton exchange membrane (PEM) fuel cell to the power source of the zero or near zero emission vehicles, stationary stand-alone utilities and the portable electronics. Especially, it is concerned that a technology meets environmental criteria, and indeed advances beyond combustion altogether, is the fuel cell.¹⁾ This is due to its several features such as abundant and environmentally benign energy source of hydrogen, high efficiency and portable operation at ambient temperature. With many of key technologies for the commercializing PEM fuel cell including low cost membrane, light weight bipolar plate material and compact design, the membrane and electrode assembly (MEA) of high power density is one of the main concerns. And the catalyst electrode is where the most of the cell reaction occurs in the MEA.

Catalyst electrodes consist of catalyst layer and gas diffusion electrode normally utilizing platinized carbon (Pt/C) and substrate composed of wicks of carbon, respectively. It is most important to have effective catalyst layer in order to increase the power density and the durability of the PEM Fuel Cell. Porous electrode structure is also important in order to have free path of gas and water, which is achieved by carbon powder. Of all these, each of the followings is the dominant factor for high power catalyst electrode: (i) reaction component that drives the electrochemical catalytic reaction with fuel gas and transfer the protons and (ii) gas supplying component that makes path for fuel gas.

Uchida et.al. reported good performance data utilizing a method of mixing Pt/C and PTFE/C powder in a PFSI colloidal solution.²⁾ Another unique method for preparation of

PTFE/C and different mixing process for the slurry was introduced in this study and it could improve the interface characteristics of the catalyst electrode. This novel process was applied for maximizing two roles of catalyst electrode, reaction and gas-supplying. Platinized carbon and plain carbon powders were coated with PFSI (perfluoro-sulfonic ionomer, Nafion) and hydrophobic polymer (polytetrafluoroethylene, PTFE), respectively. It was able to produce high power catalyst electrodes by coating the slurry mixed with Nafion/Pt/C and PTFE/C on a gas diffusion electrode. Polarization characteristics were studied on the MEAs assembled with these catalyst electrodes. Transmission Electron Microscopy (TEM) examinations were followed on the active materials of Nafion/Pt/C and PTFE/C. The MEA was also investigated by TEM on its cross section.

2. Experimental

2.1. Reaction Component

Nafion solution (5% Nafion powder in Isopropyl Alcohol, IPA) mixed with Etylene Glycol (EG) was stirred at room temperature so that the IPA can be substituted with EG. With this EG treated Nafion solutions, the rest of the process turned out to be more easy because that the solvent is not evaporated at room temperature and the viscosity is managed the same during the whole process.³⁾ This Nafion solution was mixed again with 30 wt.% Sodium Hydroxide where the Na⁺ amount equivalent to 2 stoichiometric of proton in Nafion. The IPA in this solution was dried at 80°C so that this ionomer solution could be exchanged with Na⁺ ion in Sodium Hydroxide. This solution (2.5 g) was mixed with 0.25 g of 40% Pt/C resulted in the Nafion/Pt/C.

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2.2. Gas Supplying Component

The PTFE coated carbon (PTFE/C) powder was prepared. The PTFE powder having hydrophobicity was coated on the surface of carbon (Vulcan XC 72R) powders and the PTFE contents were varied from 10 to 40%. The PTFE powders, firstly, dispersed in the solution of Fluorotrichloromethane (CFC) resulting in an emulsion and then mixed with carbon powders in ultrasonic bath until it is fully dried. Those PTFE could be uniformly coated on the surface of carbon by sintering this mixture at 350°C for 30 min. in an inert gas condition. If water was utilized for the dispersing agent, milling in liquid nitrogen mortar should be required after sintering in order to break the agglomerates with preventing fiberization of PTFE.

2.3. Catalyst Electrode

Reaction components and gas supplying components were mixed as slurry, which is ready for coating on a gas diffusion electrode. In this study, the slurry contained the solution of Nafion/Pt/C (2.5 g) and 40% PTFE/C power (0.25 g). The ideal composition here was 20% Pt, 20% PTFE, and 60% C, where Pt/C to Nafion amount was controlled as 2 : 1. As finishes the stirring, the slurry was coated on the gas diffusion electrode (TGPH 090, Toray) by utilizing tape casting method. Spray coating method was also tried and different viscosity of slurry was prepared for this application. Catalyst layer was dried in the convection oven at 180°C for evaporating the inorganic solvent, EG. Process for catalyst electrode was completed with the protonation of Nafion in the catalyst layer dipping in a 0.1 M H₂SO₄ solution at 80°C.

2.4. MEA Bonding and Polarization Test

Fully rinsed and dried catalyst electrodes were cut in square of 25 cm² and assembled with wet Nafion 115 membrane. They were pressed at 125°C for 3 min with 200 kgf/cm² of pressure with the aid of hydraulic press (Model 2699, Carver). The MEA was assembled with single cell fixture and tested by fuel cell test station (GT500, Globetech) combined with electric load (Model 890, Scribner). Humid hydrogen and oxygen was applied and all the MEAs were also tested with air. Polarization characteristics were studied after the MEA shows saturated property after proper activation process.⁴⁾

2.5. Microscopy

Particles of Nafion, PTFE, Pt/C, Nafion/Pt/C and PTFE/C and the interface between the membrane and catalyst layer in the MEA were examined by TEM (H-9000NA, Hitachi) and their morphologies were characterized. Particles were diluted in liquid media and dried on the carbon coated copper grid. Cross section of MEA was prepared by ultramicrotomy method.⁵⁾ Specimens of 60 nm thickness could be prepared at the stroke rate of 1 mm/sec during the sectioning.

3. Results and Discussion

3.1. Process Development

The rates of the catalyst electrode reactions depend on a number of factors, but the most important is the total effective surface area of the catalyst present at the interface between the reactant gas and the electrolyte. Very little of Pt catalyst surface is present at the three phase interface, where the membrane electrolyte is in direct contact with Pt catalyst surface and an adjacent gas pore. This occurs most readily at the front surface of the electrode where it contacts with membrane. The catalyst electrode is not fully used because the electrolyte does not penetrate into the thickness of the catalyst layer. It also has to be concerned that a water content of the membrane and PFSI in the catalyst layer increased with an increase of current density due to the water product diffused in.⁶⁾

Fig. 1 shows the novel process developed in this study. This process enabled the close contact of Pt catalyst with electrolyte material that is PFSI since this was pre-coated with Pt/C before the MEA bonding process. Previously, the most popular approach was that a PFSI solution dissolved in an alcohol solvent impregnated into catalyst layer to increase the contact area between Pt particle and PFSI. This enabled the low Pt loading down to 0.35 to 0.5 mg/cm².⁷⁻⁹⁾ In another conventional method, Pt/C and PTFE/C were mixed up and hot pressed onto the carbon paper at 360°C¹⁰⁻¹²⁾ followed by spreading PFSI on the hot pressed electrode. Limitation of this process is that a certain amount of active Pt particles are coated with PTFE and it decreases utility ratio of Pt. It also causes that impregnated PFSI solution is not only coated on Pt particles but on the PTFE particles.

The novel process (Fig. 1) developed in this study controlled the microstructure of catalyst layer and made each component of Pt/C, PTFE and Nafion in the catalyst electrode to play their roles effectively. Contact between Pt cata-

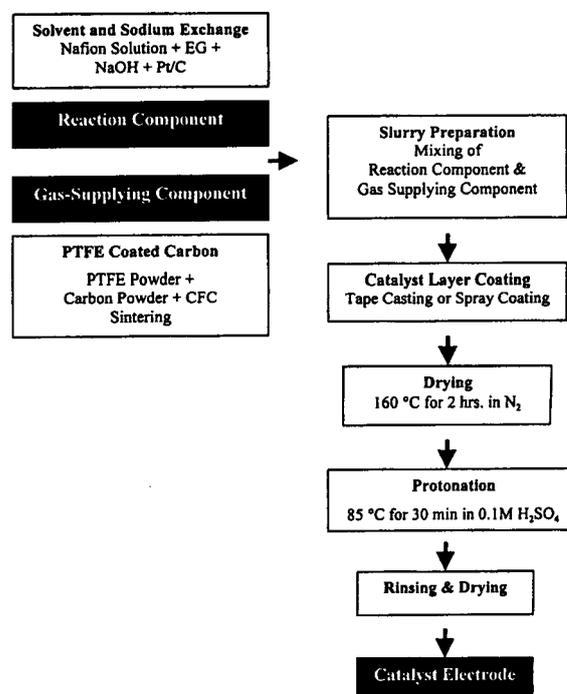


Fig. 1. Catalyst electrode process

lyst and Nafion was maximized so that the Pt utilization ratio could be increased. PTFE did not cover the Pt particles but dispersed on the carbon powders so that a gas-supplying path could be cleared and also helped water management in the electrode.

3.2. Polarization Characteristics

As the hydrogen electrode (anode) faces hydrogen fuel, it requires the energy for breaking chemical bonds of hydrogen. It drives the activation polarization causing a potential drop at a low current. Since it is developed as soon as the electrodes are connected through an external load, and electrons then start to be depleted.¹³⁾ Cathodic activation polarization at the oxygen electrode (cathode) during the oxygen reduction is more severe than the one at the anode. Thus, the overall potential drop is mostly coming from the cathode in this range. Fig. 2 shows the typical polarization curve of MEA processed with PTFE bound and Nafion impregnated catalyst electrodes.

It is presented in logarithm of current density in order to show each polarization region more effectively. In this way, the slope of each region shows that they are practically governed by the relation as expressed by a Tafel equation. Ohmic polarization is also shown and it is due to the resistance of the cell. Concentration polarization is owing to the mass transport of gases to the reaction site. As this continues, lower quantity of fuel gas at the catalyst electrode causes the decrease of the number of chemical reaction at the electrode so that the MEA voltage reduced. Also, the fuel gas is diluted by the building up of product water resulting in a reduction of the effectiveness of the reaction site at the catalyst electrode.

When the load reaches the transient current value of I_{OC} , its cell potential changes from ohmic polarization region to the concentration polarization region and the potential drop starts to be controlled by diffusion process. Increase of this value means the electrodes are well managed in the matter of product water and fuel gas and it occurred as applying novel

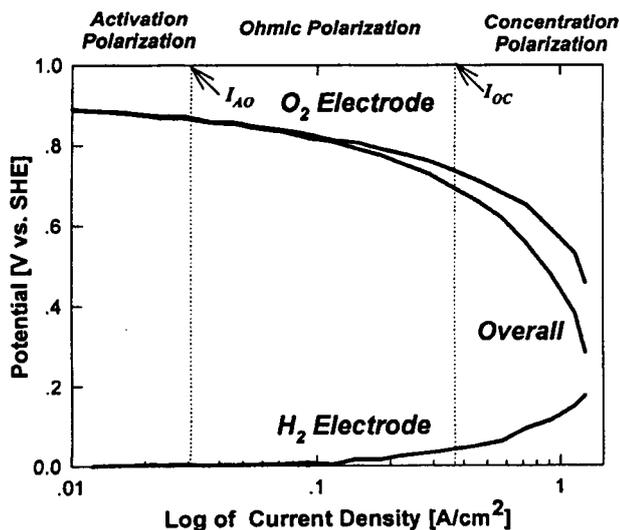


Fig. 2. Typical polarization curve of PEM fuel cell.

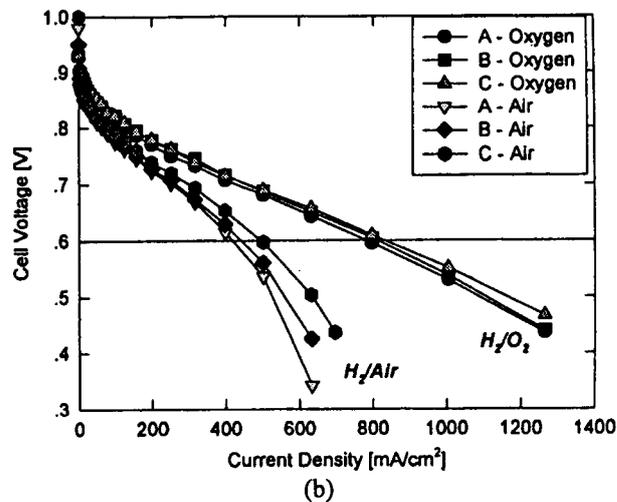
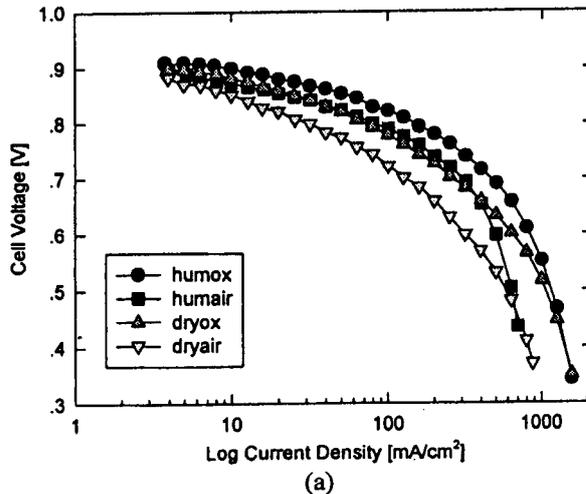


Fig. 3. Polarization characteristics of MEA made of catalyst electrodes having Nafion/Pt/C and PTFE/C; (a) H₂-All humid, O₂ or air-humid and dry, Pt 0.4 mg/cm², PTFE 20 wt.% (presented in Logarithm) (b) All humid fuel (A-Pt 0.3 mg/cm², PTFE 6.7 wt.%; B-Pt 0.3 mg/cm², PTFE 13 wt.%; C-Pt 0.4 mg/cm², PTFE 20 wt.%)

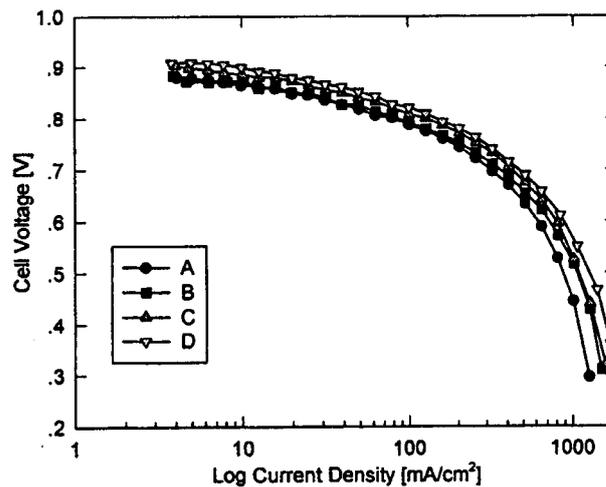


Fig. 4. Polarization characteristics of MEA made by various catalyst electrode processes (Catalyst electrode are made with A-PFSI bound Pt/C; B-PFSI bound with PTFE layer; C-PTFE bound Pt/C with PFSI impregnation; D-PFSI/Pt/C and PTFE/C).

catalyst electrode process developed in this study.

The MEAs with catalyst electrodes made by process as in

Fig. 1 were tested and their polarization characteristics are shown in Fig. 3. Hydrogen was humidified at all the cases

Table 1. Cell performances of MEAs made by various catalyst electrode processes

Process	Tape Casting				Spray Coating
	PFSI Bound	PFSI Bound PTFE Layered	PTFE Bound PFSI Impreg.	PFSI/Pt/C PTFE/C	PTFE Bound PFSI Impreg.
I_{oc} [mA/cm ²]	550	560	550	600	560
Current Density* [mA/cm ²]	600	650	720	840	700
Nominal Power Density* [W/cm ²]	0.36	0.42	0.43	0.50	0.42

* measured at 0.6 V

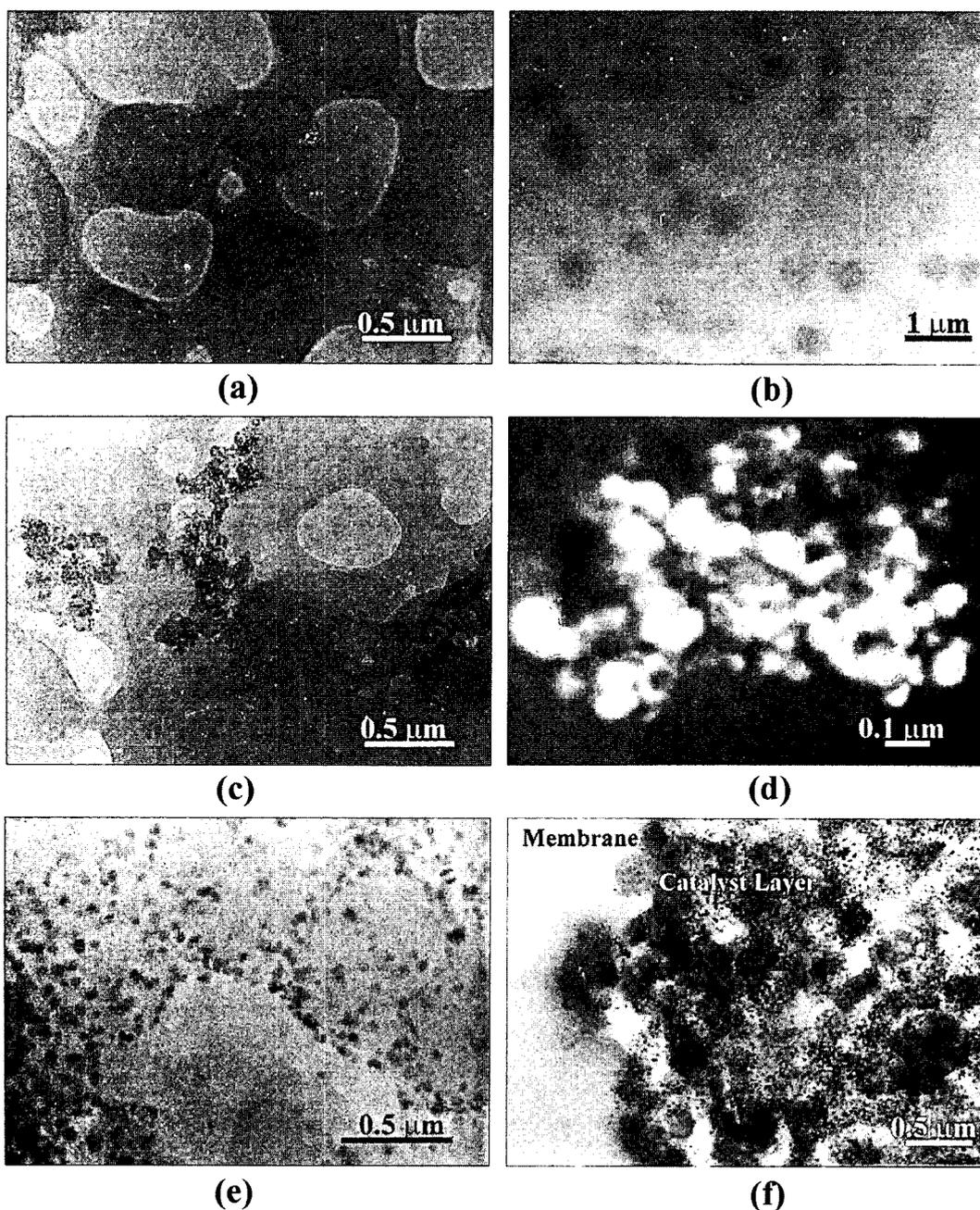


Fig. 5. TEM images of catalyst electrode components and MEA; (a) Nafion particles ($d = 0.3 \mu\text{m}$) (b) PTFE particle ($d = 0.5 \mu\text{m}$) (c) Nafion/Pt/C particles (Pt $d = 3\text{-}10 \text{ nm}$, Carbon $d = 50\text{-}70 \text{ nm}$) (d) Darkfield image of PTFE/C particles (diffracted from crystalline carbon) (e) Nafion/Pt/C PTFE/C particles (f) Membrane and catalyst electrode interface at the cross section of MEA.

and oxygen and air were used in dry and humid state in order to confirm the effect of PTFE coated carbon. Catalyst (Pt) and PTFE amount were also varied. Overall potential showed 0.5 W/cm^2 at 0.6 V at humid hydrogen and oxygen at ambient pressure. Humid air or oxygen decreased the I_{OC} more severely because of excess water in the catalyst electrode. The PTFE coating on carbon also could reduce the potential drop in the concentration polarization region so that the I_{OC} increased.

Other conventional catalyst layer process was tried and they were compared with the novel process developed in this study as shown in Fig. 4. The slopes of ohmic polarization regions are almost the same in all the processes because cell hardware was all in the same condition. The reaction components are different and they controlled the activation polarization, but the effect did not determine the power density since it used to be decided in the concentration polarization region.

However, Nafion coating on Pt/C assisted to reduce the potential drop in this region. Especially, when the PTFE is away from blocking reaction component the energy for the activation polarization reduced. The MEA D in the Fig. 4 has larger value of I_{OC} (600 mA/cm^2) than those of MEA A, B and C ($550\text{--}560 \text{ mA/cm}^2$) which are processed with conventional method and the effect of PTFE coated carbon is well explained here. This is due to the higher Pt utilization was enabled since the binder, PTFE, did not block the interface between the catalyst and ionomer.

The I_{OC} , current density and nominal power densities are presented in Table 1. Catalyst electrode process affected these values very much as shown and another technique of spray coating is also compared. Data presented in this table were the results tested at cell temperature of 80°C with atmospheric humid H_2 and O_2 . These data showed the improved performance of the novel process. Less potential drop in the concentration polarization region was found and the MEA could achieve higher power density than the MEAs made by other conventional processes.

3.3. Microscopy

Morphologies of catalyst electrode components and cross section of MEA are shown in Figs. 5. Nafion particles in the Nafion solution and PTFE dispersoids could be found in Figs. 5(a) and (b). Shown in Figs. 5(c), (d) and (e), reaction component process turned out to be successful indicating Pt/C particles are well dispersed in Nafion particles without any blocking by PTFE particles. Pt catalysts supported on carbon was shown as 3 to 10 nm size particles. Carbon particles of 50 to 70 nm in diameter are mixed uniformly with PTFE as

the image of dark field (Diffraction from crystalline carbon particles) from PTFE coated carbon, which could act as gas supplying component in the catalyst electrode. Membrane had nice contact with catalyst layer at the interface as shown in Fig. 5(f), that is the cross section of MEA. Also shown in these micrographs, reaction components and gas supplying components are individually dispersed enhancing the power characteristics of catalyst electrode.

4. Conclusions

Platinized carbon and plain carbon powders were coated with ionomer (Nafion) and hydrophobic polymer (PTFE), respectively. MEA assembled with these catalyst electrodes showed 0.5 W/cm^2 with 0.2 mg/cm^2 of Pt loading at atmospheric condition. This novel process maximized two roles of catalyst electrode, *i.e.*, reaction and gas supplying so that it could increase the catalyst utilization ratio and made easy for proton transfer. Humid fuel gas path was formed more effectively so that the polarization characteristics were improved especially at the high current range of concentration polarization region. Further studies of utilizing this technique to a catalyzed membrane could improve the PEM fuel cell performance.

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