Morphological control of PEMFC electrode by graft polymerization of polymer electrolyte onto platinum-supported carbon black

Hirotaka Mizuhata, Shin-ichi Nakao, Takeo Yamaguchi*

Department of Chemical System Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

Abstract

An increase in platinum catalyst utilization in polymer electrolyte fuel cells is necessary to improve performance and reduce costs. In the present study, a novel electrode preparation method was developed, based on the process of graft polymerization of electrolyte polymer onto a carbon black support. In this method, the electrolyte polymer is graft polymerized from monomer solution, which is able to penetrate into the small pores in the agglomerate of the carbon supports. This ensures that most of the platinum particles loaded can be accessed with electrolyte polymer and results in an increased platinum–electrolyte–polymer interface in the agglomerate. Although the improvement of polymer electrolyte fuel cell (PEFC) performance was not large, the analysis by the Tafel plot verified that the electrochemically active area for the oxygen reduction reaction increased significantly, compared with the conventional process.
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Keywords: PEFC electrode; Carbon black support; Graft polymerization; Monomer solution; Polymer electrolyte fuel cell; Tafel plots

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have received much attention on account of their attractive properties as a power source for portable, automobile, and home electricity applications. However, as PEFCs require a platinum catalyst as an active material for the electrodes, the high cost of that catalyst has restricted their commercialization [1].

Therefore, several studies have been made on lowering the platinum loading in the electrodes. First, a major breakthrough was accomplished by the method based on impregnation of the traditional gas diffusion electrode with a solubilized Nafion ionomer [2]. Further improvements on the electrode were made by Willson and Gottesfeld [3,4], they mixed solubilized ionomer with a carbon-supported catalyst to form a catalyst layer. A process called the "colloidal method" that features a cross-linking carbon-supported catalyst with perfluorosulfonate ionomer, during its coagulation

from colloid also achieved a low-platinum loading [5,6]. The electro deposition of platinum has been studied by a number of researchers [7–9]. The underlying concept of these studies is to enhance catalyst utilization in the electrode by extending the so-called three-phase boundary. It is worth noting that only platinum particles in contact with both electrolyte and reactant are electrochemically active. Although several efforts have been made to optimize this three-phase boundary structure, and various methods for producing it have been reported [10–15], still the substantial mass of the platinum catalyst may not be utilized [7].

One feasible explanation for low-platinum utilization was presented by Uchida et al. [16], who studied the microstructure of the catalyst layer. Usually, nanometer-sized platinum catalysts were dispersed on the surface of 30–40-nm carbon substrates to enhance the platinum catalyst surface. However, such small carbon particles always make an agglomerated structure as shown in Fig. 1, and the platinum inside the agglomerate cannot be utilized for the fuel cell reaction because of the lack of a path for the proton conduction, since the perfluorosulfonate ionomer, which added to the catalyst layer,
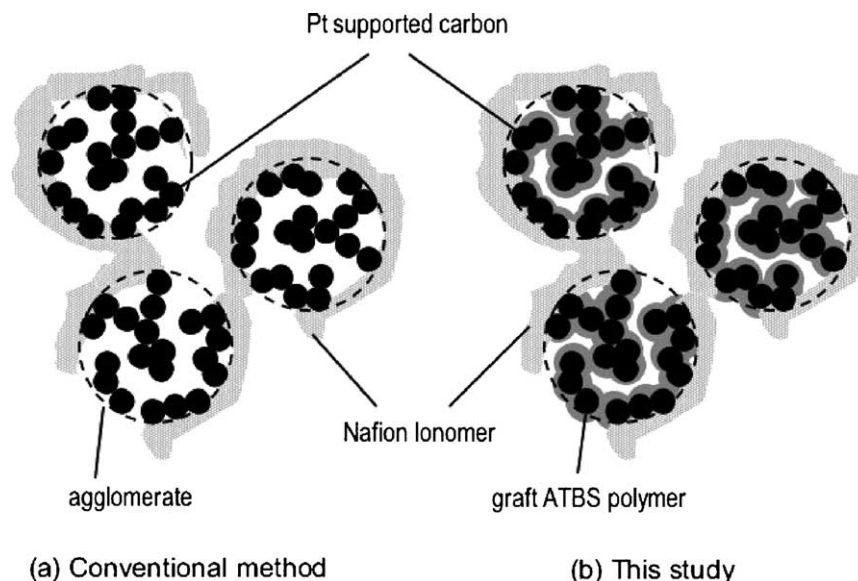
Fig. 1. Schematic illustration of the internal structure of the catalyst layer. Nanometer-sized platinum catalysts are dispersed on each 30–40-nm sized carbon black surface, and the carbon black particles are agglomerated. Nafion ionomers are partly covered on the agglomerated structure. (a) Catalyst layer made by Pt/Ketjenblack without graft polymerization. (b) Catalyst layer made by PATBS grafted Pt/Ketjenblack.

could not penetrate into the pores in the agglomerate during the preparation step.

In this study, we propose a new electrode preparation method to achieve an ideal structure of the reaction field in the catalyst layer. This is performed by graft polymerization of an electrolyte polymer onto carbon black support. In this method, the electrolyte polymer is graft polymerized onto carbon black supports from monomer solution. The monomer is able to penetrate into the small pores in the agglomerate in contrast to the perfluorosulfonated polymer because of its small molecular size. This ensures that most of the reacted protons at the platinum surfaces can access the electrolyte polymer formed, and results in increasing the platinum–electrolyte–polymer interface. The concept is shown in Fig. 1 and compared with the conventional method. By the conventional method, it is likely that the electrolyte polymer is not uniformly distributed throughout the catalyst layer as shown in Fig. 1 and the platinum particles not in contact with the electrolyte polymer cannot be utilized for the fuel cell reaction. Conversely, a small monomer can penetrate into the small pores in the agglomerated structure and the polymer electrolyte can grow on the surface of the carbon support. The polymer can be covalently bonded with the carbon surface. The protons produced at the platinum catalyst can access the grafted polymer electrolyte and utilize the platinum surface for reactions.

2. Experimental

2.1. Grafting on catalyst-supported carbon

The method used to prepare polymer-grafted carbon was based on the method reported by Tsubokawa [17,18]. We uti-

lized that method for the fuel cell catalysts. First, alcoholic hydroxyl groups were introduced onto a carbon black support by treatment with formaldehyde. Next, a radical graft polymerization of electrolyte polymer from a carbon black support was performed, initiated by a redox system consisting of ceric ion and alcoholic hydroxyl groups.

The reaction schemes are as follows:
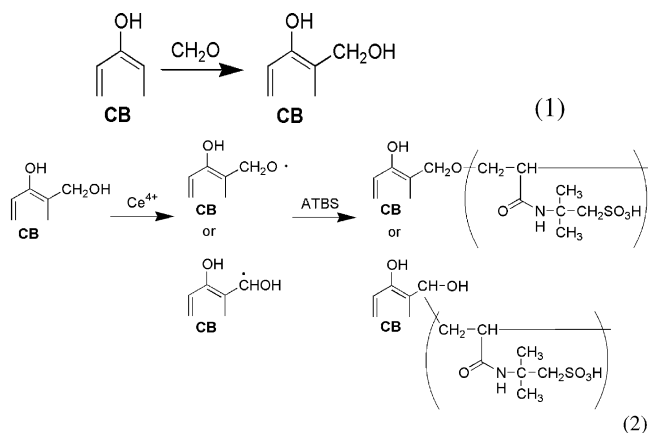
We used 46.1 wt.% platinum on Ketjenblack (Tanaka Kikinzoku Kogo, Pt/Ketjenblack) and 20 wt.% platinum on XC-72 (E-TEK, Pt/XC-72) as the carbon-supported catalyst. Acrylamide tertiary butyl sulfonic acid (ATBS, Toagosei Co. Ltd.) was used as the monomer material. ATBS was recrystallized from methanol and sublimed under reduced pressure. A 36–38% formaldehyde aqueous solution, sodium hydrate, ceric ammonium nitrate, and 1N nitric acid were used without further purification.

The introduction of an alcoholic hydroxyl group onto the carbon black support was achieved as follows [18]: in a flask,

3.0 g of carbon-supported catalyst was added to 12 mL of pure water. Subsequently, 45 mL of formaldehyde aqueous solution and 0.36 g of sodium hydrate were added. After 5 min of supersonic treatment, the mixture was heated at 70 °C with stirring. After a 24-h reaction time, the resulting catalyst was filtered and dried at 100 °C under nitrogen.

Graft polymerization of ATBS onto the carbon black support was carried out [17]. The typical experimental condition was as follows: in a flask, 0.6 g of carbon-supported catalyst was added to alcoholic hydroxyl groups and 9 mL of 0.47 mol/L aqueous solution of ATBS. After the de-aeration of the mixture by bubbling nitrogen, 1.0 mL of 0.2 mol/L solution of ceric ammonium nitrate in 1N nitrate acid was added. The polymerization was conducted at 30 °C with stirring. After the reaction, the resulting catalyst was filtered and extracted with methanol using a Soxhlet apparatus to fully remove ungrafted polymer and monomer. In the present study, the carbon particles had platinum catalysts and there was a risk of fire if catalyst particles directly contacted an organic solvent, so the catalyst particles had to be adequately wetted with water before and after contacting organic solvent.

Graft polymerization of ATBS onto the carbon black support was confirmed by Fourier transform infrared (FTIR) spectroscopy using a Magna IR 560 (Nicolet) spectrophotometer and by elemental analysis using a Perkin Elmer 2400 II (PE). Wafers of KBr containing a small amount of sample were used to obtain the transmission FTIR spectra in the range of 400–4000 cm^{-1}. The pore size distribution and the specific pore volume of the catalyst were determined by using a mercury intrusion porosimeter (Auto Pore 9520, Micromeritics).

2.2. Preparation of MEA

To prepare the electrode layer, the following materials were used: Nafion solution (Aldrich, 5 wt.% in 15–20% water/low aliphatic alcohols), PTFE suspension (Aldrich, 60 wt.% in water), and carbon-supported catalyst (46.1 wt.% platinum on Ketjenblack, Pt/Ketjenblack, Tanaka Kikinzoku Kogyo). For the H_2/O_2 PEMFC cases, most of the losses are IR loss, and loss at the cathode and the loss at the anode is negligible. Thus, polyacrylamide tertiary butyl sulfonic acid (PATBS)-grafted Pt/Ketjenblack was used to prepare the cathode layer. The same cathode layer made with nongrafted catalyst carbon was also prepared for a comparison. For the anode, Pt/Ketjenblack without graft polymerization was used.

First, the diffusion layer was formed on a polytetrafluoroethylene (PTFE)-treated carbon paper obtained from ElectroChem, Inc. [19,20]. The inks for the catalyst layers were prepared from the grafted or non-grafted carbon-supported catalyst, the Nafion solution, and the PTFE suspension with water as the solvent. The weight ratio of carbon-supported catalyst, Nafion, and PTFE was fixed at 60:25:15 in the dry state. The platinum loading in the catalyst layer was fixed at 0.4 mg/cm^2.

The membrane electrode assemblies (MEAs) were prepared by placing the above electrodes on both sides of the pretreated Nafion 112 membrane, followed by hot pressing at 130 °C for 1 min.

2.3. H_2/O_2 fuel cell experiments

The MEAs obtained were characterized in a 5 cm^2 single cell (ElectroChem, Inc.) at 60 °C in H_2/O_2. The gases were passed through humidifiers before being fed into the cell. The temperatures of the humidifiers were fixed at 58 and 40 °C for H_2 and O_2, respectively. The reactant gases were fed to the cell at a flow rate of 100 and 500 mL/min for H_2 and O_2, respectively. Measurements of cell potential as a function of current density were made galvanostatically using an electronic load (890B Fuel Cell Load Unit, Scribner). The ohmic loss of the cell was also determined by the current interruption method. Before performing any measurements, the cell was conditioned by running it for ca. 6 h under various loads.

3. Results and discussion

3.1. Preparation of electrolyte-grafted carbon with catalyst

Graft polymerization of PATBS was performed onto various carbon-supported catalysts. Table 1 shows the results of the elemental analysis. It is clear that the weight percentage of sulfur has risen by graft polymerization of PATBS. Since PATBS contains sulfur, this increase in the sulfur content may result from the graft polymerization of PATBS.

For Pt/Ketjenblack, the FTIR spectrum subtracted before, from after graft polymerisation, is shown in Fig. 2. The FTIR spectrum of PATBS is also shown in Fig. 2. There is a band near 1037 cm^{-1}, which can be assigned to a SO_2 symmetric stretching vibration, that must correspond to the PATBS polymer. On the other hand, the SO_2 symmetric stretching vibration band was not clearly observed for Pt/XC-72. By increasing the polymerization time, to increase the amount of graft polymer, the SO_2 symmetric stretching vibration was also detected for Pt/XC-72.

We have therefore verified that the ATBS polymer was successfully graft polymerized to various carbon-supported catalysts using our technique. Given that the increase in the

Table 1
Sulfur content in the catalyst particles before and after graft polymerization

	Sulfur content (wt.%)	
	Before polymerization	After polymerization
Pt/XC-72	0.22	2.5
Pt/Ketjenblack	0	0.67

Polymerization conditions are as follows: 0.6 g catalyst particles having alcoholic hydroxyl groups, 9 mL of 0.47 mol/L aqueous solution of ATBS, 1.0 mL of 0.2 mol/L solution of ceric ammonium nitrate in 1N nitrate acid, 30 °C, 48 h.
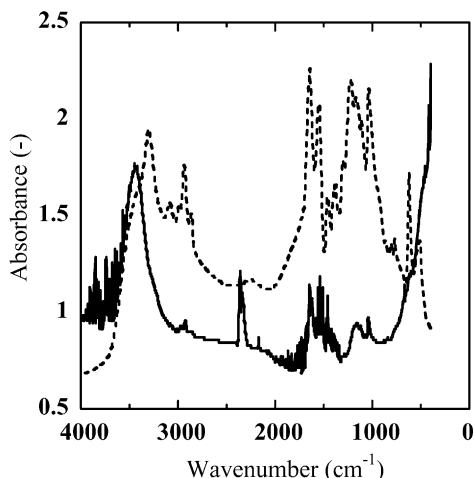
Fig. 2. FTIR spectra of the samples. The broken line shows the FTIR spectrum of PATBS. The continuous line shows the subtraction FTIR spectrum from before and after graft polymerization onto Pt/Ketjenblack. The polymerization condition is the same as for sample 5 shown in Table 2.

sulfur content results from the grafted ATBS polymer, we can also calculate the weight percentage of PATBS in the sample. As for Pt/Ketjenblack, the weight percentage of PATBS was controlled in the range 1–10 wt.% by varying the experimental conditions, such as the polymerization time and the concentration of Ce ions.

3.2. Morphology analysis of the grafted carbon

Fig. 3 shows the results of the mercury porosimeter analysis for pore size distribution of the Pt/Ketjenblack catalyst before and after graft polymerization of PATBS. The log differential intrusion is expressed per weight of Pt/Ketjenblack in the sample. The weight of Pt/Ketjenblack was determined from elemental analysis. Uchida et al. [16] reported that the
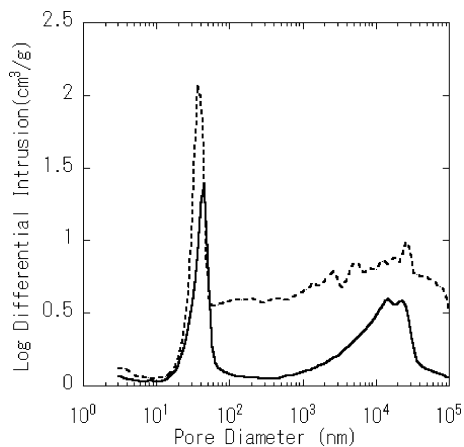

Fig. 3. Pore size distribution curves for the catalyst particles. The dashed line shows the pore size distribution curve for the Pt/Ketjenblack without graft polymerization. The continuous line shows the pore size distribution curve for the Pt/Ketjenblack after graft polymerization of PATBS. The polymerization condition is the same as for sample 2 in Table 2.

catalyst layer had two distinctive pore distributions with a boundary of about 0.04 μm. The smaller pore (primary pore) was identified with the space between the primary particles in the agglomerate, and the larger pore (secondary pore) was that between the agglomerates. In the case shown in Fig. 3, there is a distinctive peak in the pore size distribution at 0.02–0.06 μm. Therefore, we define the pores from 0.02 to 0.06 μm as the "primary pores". From Fig. 3, it is evident that the primary pore volume is decreased by graft polymerization of PATBS. From the above results, we can say that polymer electrolyte is introduced into primary pores using our technique.

On the other hand, Uchida et al. [16] reported that the perfluorosulfonic ionomer added to the catalyst layer exists only in the secondary pores, and the secondary pores act as reaction sites because the polymer electrolyte exists there only. The above difference between our results and Uchida's arises from the preparation method. To prepare the three-phase boundary in the catalyst layer, we performed a graft polymerization of electrolyte polymer from the monomer solution. Conversely, they mixed the carbon-supported catalysts with the perfluorosulfonic ionomer. It seems that the monomer solution is able to penetrate into the primary pores, in contrast to perfluorosulfonic ionomer, because of its molecular size in accordance with the concept.

From the decrease in the primary pore volume, the filling ratios of PATBS into primary pores were determined. The filling ratio of PATBS was controlled in the range 2–30 wt.% by varying the experimental conditions, such as polymerization time and concentration of Ce ions. Table 2 summarizes the various polymerization conditions, the weight percentages of PATBS in the sample, and the filling ratios of PATBS into the primary pores.

3.3. Fuel cell performances

Fig. 4 shows the polarization curves of the MEA made by the conventional method (by Pt/Ketjenblack without graft polymerization) and of the MEA made by PATBS grafted Pt/Ketjenblack, for comparison. The relationships between the current density and the overvoltage at the cathode are also shown in Fig. 4. The overvoltage at the cathode is determined by the result of the current interruption measurement. The cell potential E is expressed by the following equation:

$$E = E_r - (\eta_{anode} + \eta_{IR} + \eta_{cathode}) \qquad (3)$$

where E_r is the reversible potential for the reaction, which can be calculated from thermodynamic data, η_{anode} is the overvoltage at the anode, $\eta_{cathode}$ is the overvoltage at the cathode, and η_{IR} represents the ohmic overvoltage that was directly determined by the current interruption method. Given that the overvoltage at the anode is comparatively very small and negligible, and the overvoltage at the cathode can be separately determined.

Table 2
Graft polymerization of PATBS onto Pt/Ketjenblack

	Polymerization condition[a]			Results of evaluation	
	Ce(IV) ion concentration (mol/L)	Time (h)	ATBS content[b] (wt.%)	Primary pore volume[c] (cm^3/g)	Filling ratio[d] (%)
Pt/Ketjenblack	–	–	–	0.49	–
Sample 1	0.05	48	1.2	0.43	13
Sample 2	0.1	48	2.5	0.46	7.0
Sample 3	0.2	76	9	0.33	33
Sample 4	0.2	12	4.1	0.49	1.9
Sample 5	0.8	48	10	0.40	20

[a] Polymerization conditions were fixed as follows: 0.6 g Pt/Ketjenblack having alcoholic hydroxyl groups, 9 mL of 0.47 mol/L aqueous solution of ATBS, 30 °C.

[b] ATBS content in the samples was determined from elemental analysis.

[c] Primary pores are those in the range 0.02–0.06 μm. Pore volume is expressed per the weight of Pt/Ketjenblack in the sample.

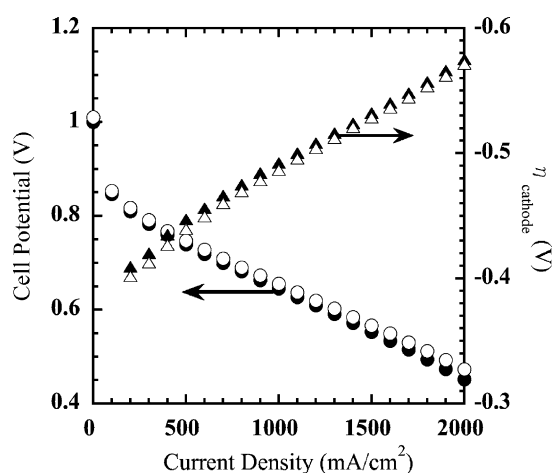[d] Filling ratios of PATBS into primary pores were determined by the decrease in the primary pore volume.

Fig. 4. Polarization curves and the over voltages at the cathode of the MEA made by Pt/Ketjenblack without graft polymerization ((●), (▲)) and MEA made by PATBS grafted Pt/Ketjenblack ((○), (△)). Polymerization condition is the same as for sample 1 in Table 2. Operating conditions: cell temperature 60 °C; atmospheric pressure.
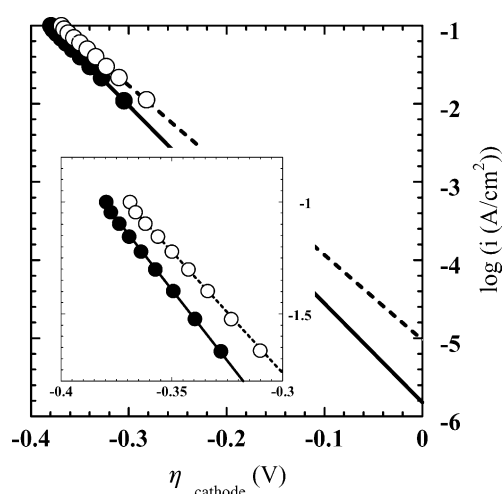

Fig. 5. Tafel plots for MEAs made by Pt/Ketjenblack without graft polymerization (●) and PATBS grafted Pt/Ketjenblack (○). Enlarged view is also shown in inset. The polymerization condition is the same as for sample 1 shown in Table 2. Operating conditions: cell temperature 60 °C; atmospheric pressure.

As indicated in Fig. 4, the performance of MEA made by the PATBS grafted Pt/Ketjenblack is slightly superior to that of MEA made by the conventional method. The overvoltage at the cathode is also slightly reduced over the range of current densities. Therefore, this improvement may be due to the reduction in the overvoltage at the cathode.

However, this improvement is not very clear, so the lower current-density region was focused upon because electrochemical reaction can be examined without the mass transfer effect. The Tafel equation was used:

$$\eta = b \log_{10} i_0 - b \log_{10} i \tag{4}$$

where b is the Tafel slope and i_0 represents the exchange current density for the oxygen reduction reaction. Fig. 5 shows the Tafel plot for the MEAs made by the conventional method and by PATBS grafted Pt/Ketjenblack in the low-current-density region (0–100 mA/cm^2). In this region, the Tafel plots show a good linear relationship and are controlled by a charge transfer process. The above equation was fitted to the exper-

imental data by least squares, and the derived parameters are reported in Table 3. The exchange current density should be proportional to the effective catalyst area because the same catalyst supported carbon was used for the comparison.

The influence of the graft polymerization of PATBS is evident from Table 3. When the Tafel plots were extrapolated to the theoretical equilibrium potential, the exchange current

Table 3
Calculated Tafel parameters

Catalyst	b (V/dec)	$\log_{10} i_0$ (–)	i_0[a] (A/cm^2)
Pt/Ketjenblack without graft polymerization	0.079	−5.8	1.5E−06
PATBS grafted Pt/Ketjenblack[b]	0.092	−5.0	9.5E−06

[a] i_0 is the exchange current density that is obtained from the extrapolation of Tafel plot. i_0 is expressed per geometrical electrode area.

[b] The polymerization condition is the same as for sample 1 shown in Table 2. Operating conditions: cell temperature 60 °C; atmospheric pressure.
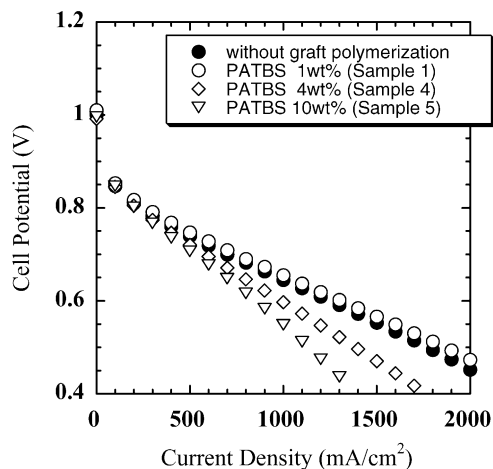
Fig. 6. Polarization curves of the MEA made by Pt/Ketjenblack without graft polymerization (●) and MEAs made by PATBS grafted Pt/Ketjenblack ((○), (◇), (▽)). Polymerization conditions are shown in Table 2. Operating conditions: cell temperature 60 °C; atmospheric pressure.

density was six times larger compared with the conventional method. Since this extrapolation would include errors, there is no definitive multiplier. However, this result means that the reaction area in the electrode increased by the graft polymerization in accordance with the concept illustrated in Fig. 1.

Fig. 6 shows the polarization curves of the MEAs made by different amounts of PATBS grafted Pt/Ketjenblack. Higher amounts of graft polymer would increase the number of platinum particles effectively used in the electrode reaction, and superior fuel cell performances could be expected. However, the results indicated that higher amounts of graft polymer result in inferior cell performance at the high-current-density region. It seems that the excess graft polymer electrolyte inside the pores of the catalyst layer introduces mass transport problems either by retarding the access of reactant gas to the active sites or by flooding the electrode. The above results lead to the conclusion that the graft polymerization of electrolyte polymer onto the carbon black supports increases the reaction area; however, an optimum graft polymer content may exist because of a trade-off between the oxygen gas diffusion to the polymer–electrolyte-covered platinum catalysts and proton access to the platinum catalysts.

Further work is goingon, to clarify the detailed mechanism of increased catalyst utilization by investigating the structure of the catalyst layer and the oxygen reduction reaction at the catalyst/graft polymer interface.

4. Conclusions

A new approach in the development of a catalyst layer for a PEFC application has been proposed. This is achieved by graft polymerization of electrolyte polymer onto a carbon-supported catalyst. The following conclusions can be drawn from the experimental data.

1. Graft polymerization of electrolyte polymer has been successfully performed onto various catalyst particles.
2. The presence of electrolyte polymer in the primary pores of catalyst particles was confirmed by the pore volume distributions obtained from mercury intrusion porosimetry.
3. The catalyst layer made by the present study showed higher electrochemically active catalyst area to the conventional method. Thus, there is a possibility that the catalyst loading is significantly reduced compared with the conventional method.

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