EFFECT OF CONTACT PRESSURE
AT Pt-POLYMER ELECTROLYTE INTERFACE
ON OXYGEN REDUCTION REACTION

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In order to clarify the interface reaction between electrode/solid polymer electrolyte, the effect of the contact pressure between Pt electrode and polymer electrolyte(Nafion®) on oxygen reduction reaction(ORR) on Pt electrode has been studied at room temperature by the electrochemical methods (cyclic voltammetry, potential sweep and chronoamperometry) using a strain gauge.

The current of ORR at a fixed potential depended on the contact pressure. At low oxygen overpotential where the activation controlled the reaction the ORR current increased with the increase of contact pressure because of the suppression of the formation of Pt oxide. On the other hand the limiting current of ORR where the reaction was controlled by the diffusion of reaction species decreased with the increase of the contact pressure owing to the suppression of oxygen flux in the polymer electrolyte.

INTRODUCTION

The polymer electrolyte fuel cells(PEFC) are started again to develop extensively since they can operate at relatively low temperature(close to room temperature) and have high power density and are easy to handle compared to other fuel cells1). This was originally developed for the space use(Gemini Program). At that time the ability of PEFC is not enough compared to other fuel cells. Several years ago the announcement of Dow membrane changes the situation of PEFC for its high power density(current density)2). The breakthrough of basic material causes the great technical innovation. The special attention is paid for the application of PEFC to the moving power source, especially to the automobiles.

However, they have several technical problems to be solved before commercialization. The decrease the usage of Pt amount in catalyst, the water management in the polymer electrolyte, and the poisoning of the electrode by carbonaceous materials(especially CO) are thought to be primary major technical problems. Besides them the large overpotential of the oxygen reduction reaction(ORR) at the cathode exists. Oxygen electrodes generally causes this kind of problem in any electrochemical system especially at
low temperature. The active electrode material for the oxygen reduction is inevitable for a high performance PEFC. Presently, Pt or Pt based alloys on dispersed carbon are used since they are relatively active for oxygen reduction and stable with the polymer electrolyte that is thought to be a strong acid.

The catalytic activity of ORR at the cathode is affected by several other factors. The contact pressure between the cathode and the polymer electrolyte is one of them, since the characteristics of polymer electrolyte would be affected easily by the pressure(force) from outside. If the pressure were weak, the ORR could not proceed thoroughly since enough reaction interface could not be obtained. If the contact pressure were very strong, the reaction would be affected by the deformation of the polymer electrolyte. The deformation might cause the changes of the ionic conductivity or the diffusivity of the reaction species in the electrolyte.

In this work the effect of the contact pressure(or force) between the polymer electrolyte and the Pt cathode has been studied fundamentally by the electrochemical method using the pressure controlling devise.

**EXPERIMENTAL**

The solid state electrochemical cell that was used for the reaction cell\(^3\). Figure 1 shows the schematic drawings of the experimental cell where the contact pressure between the working electrode and polymer electrolyte can be controlled. The working electrode and the counter electrode were contacted on both sides of the polymer electrolyte. The electrolyte was Nafton® 117. The polymer electrolyte was washed in 5 wt% H₂O₂, 0.5 M HCl, and ultra pure water at 80°C before use. The contact pressure was changed by the turning of the screw of the micrometer head that was connected to the working electrode. The pressure was measured with the straingauge transducer that was placed on the top of the micrometer head.

At first spherical Pt electrodes were used for the working electrodes whose diameter were 0.45, 0.80 and 1.7mmØ that were made by melting Pt wires. The surface of the electrodes were polished with alumina polishing powder and washed in pure water with ultrasonic washer. In order to minimize the effect of oxygen diffusion through the polymer electrolyte, Pt microelectrode(0.3mmØ disk) was used for the cathode working electrode that was made by mounting Pt wire in acrylic housing with epoxy resin. The surface of Pt cathode was coated by polymer electrolyte using 10μl of 5% Nafton®- alcohol solution and dried in air at room temperature. The counter electrode was Pd plate with small holes with the current collector of Pt mesh. The reference electrode was the dynamic hydrogen electrode(DHE)\(^4\) that was made by the thermal decomposition of Pt salt on 1.5 mmØ Ti. The current density for the DHE was 1 mA/cm².
The oxygen gas was humidified by bubbling through the water whose temperature was kept same as the reaction cell. The ORR on the Pt electrode was studied at room temperature using the apparatus by the potential sweep method, the cyclic voltammetry and the chronoamperometry\(^5,6\).

**RESULTS AND DISCUSSION**

Figure 2 shows the dependence of the net current of ORR on the spherical Pt electrodes at the potential of 0.3V vs.DHE on the contact force between Pt electrode and the polymer electrolyte. The current was obtained by the potential sweep from 1.3 V at the sweep rate of 0.01 V/s. The current increases on larger size Pt electrode and becomes constant value at high contact force. Figure 3 shows the dependence of the contact area of the Pt electrodes on the contact force that was obtained from the peak current of the Pt oxide reduction at the cyclic voltammogram from 1.5 V to 0.05 V at the sweep rate of 0.1 V/s in nitrogen atmosphere. The contact area increases sharply at small contact force. At high contact force the increase of the area becomes small, where the deformation of the polymer electrolyte would take place.

Combined the results of Fig.2 and Fig.3, the real current density of ORR can be calculated and plotted in Fig.4. With 0.45 and 0.80 mmØ electrodes the current density increases at small contact force and gets the maximum at 100 gf and 200 gf, respectively. At higher contact force the current density decreases gradually. If the ORR at Pt/polymer electrolyte interface were independent of the contact force, the current density should stay constant and be independent of contact force. The result of this work is different. The ORR would be affected by the contact force not only by the reaction area but by the other factors.

The surface of Pt electrode might be divided into two regions. One is active for ORR and the other is inactive. On Pt electrode Pt oxide is present as well as Pt metal in oxygen containing atmosphere. Generally, Pt oxide is inactive for electrode reactions compared to Pt metal. In the polymer electrolyte both the hydrophobic area and the hydrophilic area exist. The hydrophilic area would be more active for ORR. These phenomena were mixed and the current density got the maximum in Fig.4. The inactive area increases gradually at higher contact force in this case.

Figure 5 shows the results of the potential sweep (1.1 ~ 0.3 ~ 1.1 V vs. DHE) in oxygen atmosphere on the 0.3mmØ Pt microelectrode that was mounted in epoxy resin. The sweep rate was 2 mV/s and the contact pressures were 0, 1.4, 2.8, 4.2, 5.7 and 7.1 kgf/cm\(^2\). These results are in the same figure. The starting and the terminal potential of each sweep was 1.1V. The reduction current starts about 1.0 V and gets the limiting around 0.7 V in each sweep. Since this kind of reduction current did not appear without oxygen, this reduction current would correspond to the oxygen reduction current. Although the shape of the curves are almost same, the absolute values (current) of sweeps are different.
Namely, the oxygen reduction current increases as the contact pressure increases in the low oxygen overpotential region (1.0 ~ 0.9 V). On the other hand, the limiting current that is controlled by the diffusion process of the reaction species in the polymer electrolyte decreases as the contact pressure increases.

Figure 6 shows the relation between contact pressure and the peak potential and the peak current of Pt oxide reduction on the Pt microelectrode that were obtained by the cyclic voltammograms in nitrogen atmosphere. The peak potential is independent of the contact pressure. However, the peak current decreases as the contact pressure increases. The ohmic contact between the Pt electrode and the polymer electrolyte did not change since the peak potential does not change. The electric quantity of hydrogen desorption peak at the cyclic voltammogram on Pt micro electrode is independent of the contact pressure. That means the reaction area did not change with the contact pressure.

Taking into account of these facts, the reduction of the Pt oxide reduction current with the contact pressure does not owe to the reduction of the active reaction area but to the increase of the hydrophobic area of the polymer electrolyte at the electrode surface. The increase of hydrophobic area causes the decrease of water content in the polymer and suppress the Pt oxide formation at the electrode/polymer interface. The oxide free Pt is more active for ORR than Pt oxide. This would be the reason for the increase of ORR current at higher contact pressure at low oxygen overpotential.

In order to obtain the transport properties of reaction species the chronoamperometry was studied using the Pt microelectrode in oxygen atmosphere. The initial potential was 1.1 V vs. DHE that was stepped to 0.3 V and the response current was measured up to 10 s. The obtained current decreased with time. The current was proportional to \((\text{time})^{-0.5}\) and the diffusion coefficient and the solubility of oxygen in the polymer electrolyte were obtained. Figure 7 shows the dependence of these factors on the contact pressure. As the contact pressure increases, the diffusion coefficient of oxygen decreases and the solubility increases.

Considering these results the water concentration gradient might be formed in the polymer electrolyte. The diffusion characteristics of oxygen in the polymer electrolyte would be affected by the water content. In this work the diffusion coefficient of oxygen was also measured with semi-dried electrolyte and with the electrolyte in water using the same method. The diffusion coefficient is highest in water and lowest with semi-dried membrane. The diffusion of oxygen in phosphoric acid increased at higher content of water owing to the increase of the viscosity of the electrolyte7). The decrease of water content in the polymer electrolyte means the decrease of the diffusivity of oxygen in the electrolyte. This might be a reason for the decrease of the limiting current on the Pt microelectrode at higher contact pressures.
CONCLUSION

The oxygen reduction kinetics on Pt electrode at the polymer electrolyte interface were studied in relation to the contact pressure between electrolyte and electrode. At low oxygen overpotential the ORR current increased at higher contact pressure due to the suppression of the formation of Pt oxide. At high oxygen overpotential the limiting current of ORR decreased at higher contact pressure because of the decrease of the diffusivity of oxygen in the polymer electrolyte.

In order to apply these concepts to the polymer electrolyte fuel cell, the results of low oxygen overpotential are important. In this sense, the catalytic activity of oxygen cathode might increase at higher contact pressure. However, the polymer electrolyte deforms or is destroyed easily at high contact pressure. A suitable contact pressure should be found by studying the wider range of contact pressure.

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Fig. 1 Schematic drawings of the cell.
Fig. 2 Dependence of net ORR current at 0.3V on contact force.

Fig. 3 Dependence of Pt active surface area on contact force.
Fig. 4 Dependence of net ORR current density at 0.3 V on contact force.
Fig. 5 Potential sweep curves of ORR at Pt micro electrodes at various contact pressure.
Fig. 6 Dependence of peak potential and current of Pt oxide reduction on contact pressure.

Fig. 7 Dependence of diffusion coefficient and solubility of oxygen in polymer electrolyte on contact pressure.