Improvement of MEA Performance for PEFC by using High Oxygen Permeable Ionomers

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Asahi Glass Co., Ltd. has been developing a variety of perfluorinated ion exchange polymers (ionomers) in order to improve the performance, durability and robustness of membrane electrode assembly (MEA) for polymer electrolyte fuel cell (PEFC). In the present report, the effect of high oxygen permeable ionomers on MEA performance is described. At first, the oxygen permeability of some ionomers was determined by means of potential step chronoamperometry with a Pt microelectrode. It was confirmed that the newly developed ionomers had higher oxygen permeability compared with reference ionomer, and the permeability strongly depended on ionomer density. Then, the MEA performance was improved by using the high oxygen permeable ionomers in cathodes. These results also suggested that the high oxygen permeable ionomers would be available for the reduction of Pt loading in MEA cathodes.

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1．Introduction

Significant cost reduction of MEA is required for the widespread commercialization of PEFC systems for fuel cell vehicle (FCV) and residential use. Especially, the reduction of Pt loading in MEA cathode is thought to be effective for the purpose. At the cathode, the oxygen reduction reaction (ORR) proceeds on a Pt electrocatalyst supported on carbon in a porous gas diffusion electrode. Although the kinetics and mechanism of the ORR have been investigated with a various kinds of electrocatalyst materials and electrolytes [1-6], the Pt or Pt-alloy have been the best electrocatalyst up to now. However, the ORR on Pt electrocatalyst is very irreversible, and in addition the mass transport of reactive species dominates the ORR at high current density. Therefore, as the cathode Pt loading is reduced, flux of oxygen near the Pt electrocatalyst surface should be increased, that is, the Pt specific current density should be improved. In the present report, the new perfluorinated ion exchange polymers having higher oxygen permeability (HOP ionomers) than the reference ionomer were evaluated. Additionally, the effect of the HOP ionomers on MEA performance was investigated.

2．Experimental

2.1　Ionomers tested

At first, new perfluorinated HOP ionomers were prepared for the present study. The characteristic features of the ionomers showed the lower density compared with the reference ionomer. **Table 1** shows the density and the ion exchange capacity (IEC) of the HOP ionomers. Here, the density was measured as a precursor form without hydrolysis. The IEC of these ionomers were fixed at 1.5 meq.·g^{-1}. In the case of the measurements of oxygen permeability and MEA performance, these ionomers were used after hydrolysis treatment to H-form.

Table 1　Properties of ionomers tested.

Ionomer	Density g·cm^{-3}	Ion exchange capacity (IEC) meq.·g^{-1}
Reference	2.07	1.5
HOP-1	1.94	1.5
HOP-2	1.91	1.5

2.2　Oxygen permeability and solubility in ionomers

The oxygen permeability and solubility were determined by means of potential step chronoamperometry (PSCA) using a Pt microdisk electrode and a dynamic hydrogen electrode (DHE), which was similar technique written in the published papers [7,8]. The working electrode was a Pt microdisk electrode of the diameter of $50\,\mu$m which was sealed in a glass rod. The counter electrode was a Pt wire of the diameter of 1mm and the length of 50mm. A DHE, which was a pair of $300\,\mu$m Pt wire in a glass rod, was used as a reference electrode. The electrode reactions for DHE were hydrogen evolution and oxygen evolution on each electrode from water electrolysis [9]. A small current of 3 μA was applied, and electrode side of hydrogen evolution was used as a reference electrode. In order to obtain good contact between electrodes and ionomer samples, each electrode was pressed on the sample which was the membrane of the thickness of $200\,\mu$m prepared by casting the ionomer solutions.

The measurement cell, which was similar to that in the literature [7], was placed in an electric oven, and the temperature was maintained at 80℃ under an atmospheric pressure. The humidified air was flowed into the cell, and relative humidity (RH) was controlled between 30% and 80%.

As for electrochemical measurements, cyclic voltammetry and PSCA were carried out by using a potentiostat ALS Model 720D. Prior to electrochemical measurements all the electrodes were pretreated by scanning repeatedly between 0.0 and 1.4V vs RHE in 0.1 mol·l^{-1} H$_2$SO$_4$ at a rate of 0.2 V·sec^{-1}. In order to *in-situ* clean up and activate Pt microdisk surface in the cell, the potential of the working electrode was repeatedly scanned between 0.05 and 1.5 V vs. DHE at 0.1 V·sec^{-1} before each electrochemical measurements.

From the PSCA measurements, mass transport parameters of oxygen in ionomers (C, D and CD) were obtained (C: solubility, D: diffusion coefficient, and CD: permeability). The potential of working electrode was stepped from 1.2 to 0.5 V vs. DHE, at which ORR is under diffusion limiting conditions, and the transient currents were monitored in the period of 20 sec. In general, the transient current for PSCA using a microdisk electrode is described by the following equation [10,11]:

$$I = \frac{nFAC\sqrt{D}}{\sqrt{\pi}\sqrt{t}} + \pi nFCDr \qquad (1)$$

Here, *n*, *F*, *A* and r are the number of electrons transferred (4 for ORR on Pt), the Faraday constant, the geometrical area of the microdisk electrode, and

the radius of the microdisk, respectively. The mass transport parameters were calculated from the slope and the intercept of the I vs. $t^{-1/2}$ plots.

2.3 Evaluation of MEAs

In order to investigate the effect of the HOP ionomers on MEA performance, MEAs were fabricated as follows. Firstly, catalyst inks were prepared by mixing Pt/C catalyst (TEC10EA50E, TKK), solvent and the ionomer listed in **Table 1**, so that the weight ratio of the ionomer content was 0.8 relative to the carbon support (I/C=0.8). Secondly, the cathode catalyst layers of Pt loading of 0.2 mg·cm^{-2} were obtained by casting and drying the inks on a transfer sheet. Next, the cathode catalyst layers were decal-transferred on a perfluorosulfonic ion exchange membrane with an anode catalyst layer. All the anode catalyst layer was consisted of Pt/C catalyst (TEC10EA50E, TKK) and perfluorinated ion exchange ionomer (Flemion®) of I/C=1.0. The Pt loading of the anode catalyst layer was kept at 0.05 mg·cm^{-2}. Finally, MEAs were assembled with gas diffusion layers (GDL) on both sides of the catalyst-coated membranes. The GDLs used in this study were non-woven type carbon fiber substrates with microporous layer. The geometric area of the MEAs was 6.25 cm^2.

The IV performance of the MEAs was measured under the condition of H$_2$/air of 0.75/2.0 L·min^{-1} of gas flow rate, at a cell temperature of 80℃, 40% RH and 150 kPa-abs. In addition, cyclic voltammetry measurements were also carried out under a similar condition of H$_2$/air of 0.3/0.3 L·min^{-1} of gas flow rate, at a cell temperature of 80℃, 40% RH and 150 kPa-abs. The potential scan rate of 20 mV·sec^{-1} was used.

2.4 Evaluation of Low Pt Loading MEAs

The low Pt loading MEAs were fabricated by the same method described above, except for the followings. The Pt/Co alloy catalyst (TEC36F62, TKK) was used for the cathode ink, and the Pt loading of the cathode catalyst layers was reduced to 0.10 and 0.15 from 0.2 mg·cm^{-2}. The weight ratio of the ionomer content to the carbon support was 1.0 (I/C=1.0). The geometric area of the MEAs was 25 cm^2. The IV performance of the MEAs was obtained under the condition of H$_2$/Air of 1.43/2.0 stoichiometry, at a cell temperature of 80℃, 20% RH and 150 kPa-abs.

3. Results and Discussion

3.1 Oxygen Permeability and Solubility in Ionomers

Figure 1 shows the oxygen permeability of the ionomers at 80℃ in air from 30% to 80% RH. The permeability was around the order of 10^{-12} mol·cm^{-1}·sec^{-1}, and increased with raising the relative humidity. These values and RH dependence were similar to the earlier report [8]. As a result, it was found that the permeability strongly depended on the kinds of ionomer, and increased with the reduction of the ionomer density. The permeability of HOP-2 ionomer having the density of 1.91 showed ca. twice higher CD values compared with that of the reference ionomer. **Figure 2** shows the oxygen solubility in ionomers obtained from the analysis using equation (1). It was clear that the oxygen solubility increased with decreasing the ionomer density. These results indicated that the oxygen dissolution and transport in ionomers strongly depended on the ionomer density, which was thought to be related to the free volume of ionomers.
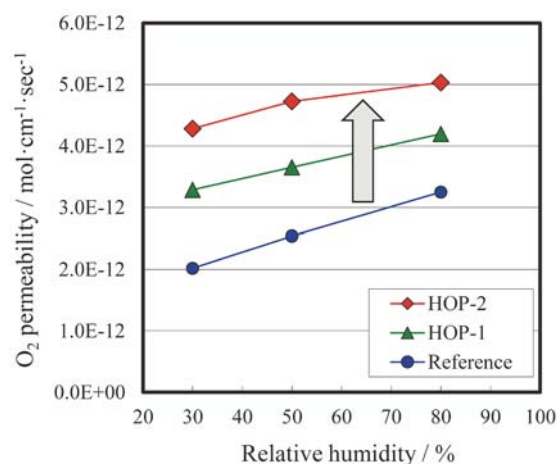

Fig.1 Oxygen permeability CD of ionomers as a function of relative humidity at 80℃ in air.
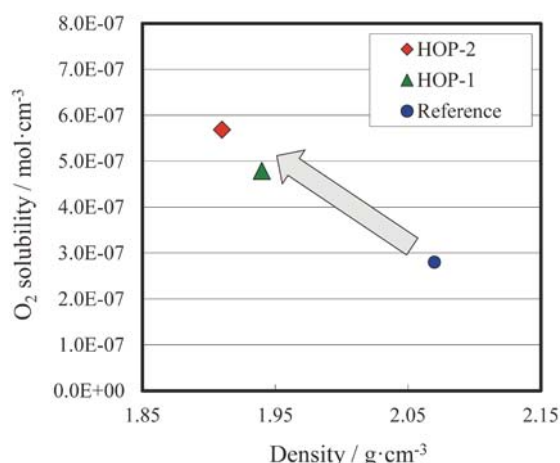

Fig.2 Oxygen solubility C of ionomers as a function of ionomer density at 80℃ in air.

3.2　Evaluation of MEAs

Next, the effect of the HOP ionomers on MEA performance was investigated. **Figure 3** shows the effect of ionomer in cathode on MEA performance at 80℃, 40% RH. The cell voltage and the IR free voltage depended on the ionomer, and was drastically improved with increasing the oxygen permeability of ionomer in the entire range of current density. In **Fig.4**, the effect of ionomer on cyclic voltammograms under similar condition to the measurement of MEA performance is shown. The oxygen reduction current was clearly observed, and the absolute value of the current was increased with the oxygen permeability of ionomer. Therefore, one of the reasons for the improvement of MEA performance by using HOP ionomers was thought to be the low mass-transfer loss of oxygen near Pt surface in cathodes, although the thermodynamic potential gain was not corrected yet.
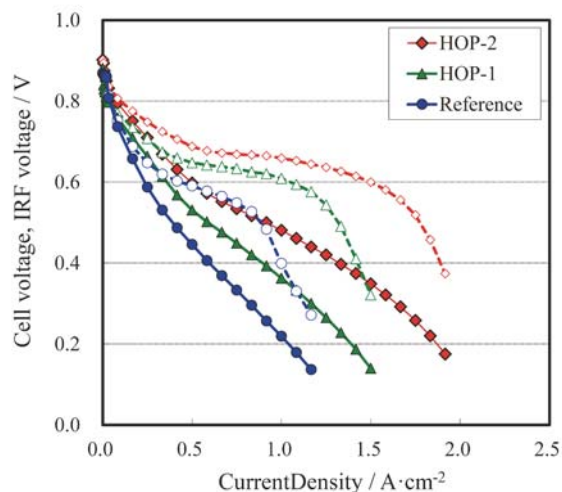

Fig.3 Effect of ionomer on MEA performance at 80℃, 40% RH, 150 kPa-abs, H$_2$/air=0.75/2.5 L·min^{-1}, solid: cell voltage, broken: IR free voltage.
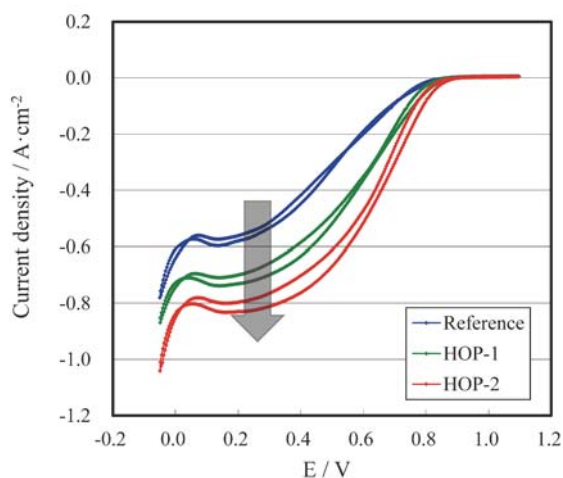

Fig.4 Effect of ionomer on cyclic voltammograms at 80℃, 40% RH, 150 kPa-abs, H$_2$/air=0.3/0.3 L·min^{-1}, scan rate=20 mV·sec^{-1}.
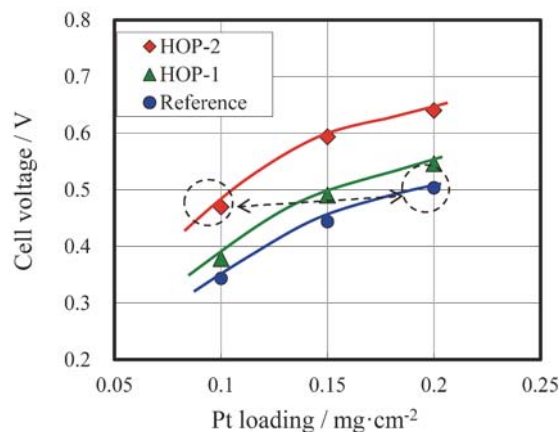

Fig.5 Cell voltage at 1.6 A·cm^{-2} as a function of Pt loading at 80℃, 20% RH, 150 kPa-abs, H$_2$/air=1.43/2.0 stoich.

3.3　Evaluation of Low Pt Loading MEAs

Figure 5 shows the cell voltage at 1.6 A·cm^{-2} as a function of Pt loading. As shown in the figure, the lower cell voltage was obtained in the case of MEA of low Pt loading. Then, it was found that the cell voltage of MEA assembled with the catalyst layer of Pt loading of 0.1 mg·cm^{-2} and HOP-2 ionomer was almost similar to that with Pt loading of 0.2mg·cm^{-2} and the reference ionomer. This result suggested that the HOP ionomer would be available for the reduction of Pt loading in MEA cathodes, which is required for widespread commercialization of PEFC system.

4．Conclusion

The mass transport parameters of oxygen in the newly synthesized perfluorinated ionomers were evaluated by means of electrochemical techniques. As a result it was confirmed that the permeability strongly depended on the ionomer density. Then, the IV performance was found to be improved by using the HOP ionomers in MEA cathodes. These results indicated that the high oxygen permeable ionomer would be available for the reduction of Pt loading in MEA cathodes.

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