Polymer electrolyte fuel cells (PEFCs) have been receiving intensive attention as power generation units for automotive and residential co-generation applications, due to their low level of exhaust emissions and high energy efficiency. However, for the large-scale commercialization of PEFCs, two main problems must be solved, i.e., durability and cost reduction. In particular, the Pt loading must be reduced, which is also related to the performance and the lifetime. In order to reduce the amount of Pt, it is very important to develop highly efficient cathode catalyst layers (CLs) that increase the number of reaction sites on the Pt particles and ensure an effective reactant supply, because the cathode CLs require an appreciable amount of costly platinum or its alloys due to the slow kinetics of the oxygen reduction reaction (ORR) in an acidic environment at low operating temperatures (<100 °C). In previous work, we demonstrated the importance of two factors for the design of high performance cathode CLs. The first is a higher effective Pt surface area (S(\text{ePt})) which practically contributes to the ORR performance; the AB250-supported Pt catalyst (n-Pt/AB250), for which all of the Pt particles exist only on the exterior surface of acetylene black (AB) with 219 m²/g specific surface area, is the most attractive in order to generate the large current densities required by actual fuel cell operation. The second is the optimized distribution of ionomer on the surfaces both of Pt particles and carbon particles; short-side-chain (SSC) perfluorosulfonic acid (PFSA) ionomers with high ion exchange capacity (IEC) showed better continuity and uniformity on the Pt and graphitized carbon black (GCB) particles than the conventional ionomer, which might have led to the improvement of both the mass transport and the proton-conducting network in the cathode CLs. There has been a lot of recent research on catalyst layer compositions, which has focused on ionomer content, catalyst porous structure, equivalent weight, and so on.

We believe that there is still much room for further increasing the cathode performance by making the best use of the n-Pt/AB250 catalyst with the higher effective Pt surface area, for example, by means of improvement of ionomer coverage; specifically, we found that the ionomer was not covered on the Pt catalyst as uniformly as for the commercial Pt loaded carbon black (Pt/CB) catalyst. The ionomer distribution is an important factor in order to improve both the oxygen mass transport and the proton conductance within the cathode CLs. As reported in our previous study, the ionomer should be thick enough for good proton-conducting networks and also should be thin enough for effective gas transport. However, it is practically difficult to optimize the thickness of the ionomer on the carbon-supported Pt catalyst for maximum utilization during the membrane electrode assembly (MEA) preparation process.

Instead of focusing on the control of ionomer thickness, we have investigated the effects of high oxygen permeability ionomers as binders on the cathode performance of PEFCs in this study, which will be able to be easily implemented in practical CLs. The high oxygen permeability ionomers are expected to increase the flux of oxygen near the Pt surface of the three-phase boundary, which is particularly important in the case of extremely low Pt loadings. At the same time, we have focused on the effect of the IEC values of ionomers, in order to investigate the combined effects of oxygen permeability and ionomer content on cell performance and Pt catalyst. Also, we investigated the durability of cells in which various values of both the oxygen permeability and IEC were used in the ionomers in catalyst layers during load cycle testing (Fuel Cell Commercialization Conference of Japan (FCCJ) 2011 protocol), in comparison with the standard Nafion ionomer.

**Experimental**

**Oxygen permeability, water content of ionomers.**—Oxygen permeability of regular oxygen permeability (ROP) ionomer developed by AGC (IEC = 1.13 meq g⁻¹; ROP 1.1) and two high oxygen permeability (HOP) ionomers (IEC = 1.17 meq g⁻¹; HOP 1.2 and IEC = 1.50 meq g⁻¹; HOP 1.5) were measured with a gas permeation measurement apparatus (100XFAG, GTR-Tech Inc.), and the concentrations of the permeated gases were quantified with a gas chromatograph (GC, G2700, Yanaco) with a thermal conductivity detector. Helium was used as the carrier gas for the measurement. Membranes were placed in the center of the permeation cell, and the test gas was
introduced into the chamber on one side of the membrane at a flow rate of 20 mL min$^{-1}$. The carrier gas was introduced into the chamber on the other side of the membrane at the same flow rate and was analyzed by the GC. The membrane was equilibrated until stable permeation data were obtained.

The ROP 1.1 ionomer developed by AGC is equivalent product to DE521 developed by Du Pont (IEC $= 0.91$ meq g$^{-1}$; ROP 1.0). The parameters of both ionomers were similar (ROP 1.1 $\approx$ ROP 1.0).

Water uptake of the regular oxygen permeability ionomer (ROP 1.0) and two high oxygen permeability ionomers (ROP 1.2 and HOP 1.5) was measured with a solid electrolyte analyzer (MSABAD-MSBAD,BEL Japan Co.) equipped with an environmental chamber and a magnetic suspension balance. First, ionomer solutions were cast onto a flat glass plate to prepare the membranes. Then, the membrane sample (40–60 mg) with a thickness of 20 $\mu$m was placed in the chamber and dried at 80 °C under vacuum for 3 h, until constant weight was reached; this was used as the dry material. The membrane was then equilibrated with N$_2$ gas at a given temperature and humidity for 1 h before the gravimetric measurement was done.

**MEA preparation.**—The cathode CLs were prepared from Nafion ionomer (ROP 1.0) or PFSA ionomers developed by AGC; two high oxygen permeability ionomers (ROP 1.2 and HOP 1.5), with the AB250-supported Pt catalyst, which was loaded by means of an in-house method developed with Tanaka Kikinzoku Kogyo K. K.26 (n-Pt/AB250: $S_{\text{Pt}} = 107$ $\text{m}^2 \text{g}^{-1}$, specific surface area of AB250: 219 $\text{m}^2 \text{g}^{-1}$; Denki Kagaku Kogyo Co., Ltd.). Scanning transmission electron microscope (STEM, HD-2700, Hitachi High-215 Technologies Co.) images and Pt distributions at both interior and exterior surfaces of the AB250 support are shown in Figure 1; characteristics of the AB support and supported Pt catalyst were reported in our previous paper.10 In contrast, all of the anode CLs were prepared with the CB-supported Pt catalyst (Pt/CB, TEC10E50E, 46.7 wt%-Pt, Tanaka Kikinzoku Kogyo K. K.) and Nafion ionomer (DE521, E.I. Du Pont de Nemours & Co., Inc.).

The Pt catalyst inks were prepared from the Pt/CB or n-Pt/AB250 catalysts, four different types of ionomers, ethanol and pure water by use of a planetary ball mill for 30 min. The mass ratio of the binder to carbon black (ionomer/carbon I/C) was adjusted to 0.7, which was the optimized ratio for the ROP 1.0 ionomer. In the future, for more accurate investigation to it will be desirable to optimize the I/C ratio for each ionomer. However, we believe that the general trend observed is valid. To prepare uniform catalyst-coated membranes (CCM), the catalyst paste was directly sprayed onto the Nafion membrane (NRE 212, Du Pont, 50 $\mu$m thickness) by the pulse-swirl-spray technique (PSS, Nordson Co.). The PSS method, although not easily scalable, is sufficient for the present single cell evaluation. However, for manufacturing, the fabrication method for the CL must either be modified or replaced for scalability. Then CCM was dried at 60 °C in an electric oven. The CCMs were annealed by hot-pressing at 140 °C and 2.8 MPa for 3 min, and then they were assembled with two gas diffusion layers (GDLs, 25BCH, SGL Carbon Group Co., Ltd.) and a single serpentine pattern cell (Japan Automobile Research Institute (JARI) standard cell) with an active geometric area of 29.2 $\text{cm}^2$. The Pt loading of the cathode CLs was 0.05 ± 0.003 mg Pt $\text{cm}^{-2}$, and that of the anode CLs was 0.5 ± 0.01 mg Pt $\text{cm}^{-2}$. For experimental convenience, we used the high loading anode catalyst in order to evaluate cathode performance differences, because this made the polarization of the hydrogen anode relatively small.

**Electrochemical measurements.**—The current-potential (I-E) polarization curves of the MEAs were measured by supplying hydrogen and oxygen/air to the anode and cathode, respectively, at 80 °C under ambient pressure (1 atm), which were pre-humidified at 30, 53, 80 and 100% relative humidity (RH) by bubbling through water reservoirs. The flow rates of all gases were controlled by mass flow controllers. The utilisations of the reactant gases were 70% for H$_2$, 40% for O$_2$ and 40% for air. The cell potentials were measured galvanostatically as a function of current density by use of an electronic load (PLZ-664WA, Kikusui electronics Co.) controlled by a measurement system (FCE-1, Panasonic Production Engineering Co., Ltd). The cell resistance was measured at 1 kHz under load by use of a digital ac milliohmmeter (Model 3566, Tsuruga Electric, Co.) in order to determine mainly the bulk membrane resistance. The I-E curves were measured under steady-state operation, with a measurement time of 5 min for each point. We also calculated the O$_2$ gain, which is the difference between the potentials measured during O$_2$ supply and air supply at constant current density, in order to evaluate the oxygen mass transfer ability of the cathode CL.

Cyclic voltammetry (CV) measurements were performed at 40 °C and 100% RH and 80 °C and 100% RH, 30% RH by use of a potentiostat (HZ-5000 Automatic Polarization System, Hokuto Denko Co.) in order to evaluate the electrochemically active surface area (ECSA) of the Pt catalyst in the cathode CLs. The cathode compartment was purged with N$_2$ (100 mL min$^{-1}$, 100% RH or 30% RH), while H$_2$ gas (100 mL min$^{-1}$, 100% RH or 30% RH) was supplied to the anode. Prior to the potential sweep, the potential was maintained at 0.075 V for 3 s to ensure that the Pt was in a reproducibly reduced state. Then, the potential was swept from 0.075 V to 1.000 V at 20 mV s$^{-1}$ and reversed back to 0.075 V. The N$_2$ flow was stopped during the entire CV measurement to avoid perturbing the H$_2$ partial pressure. The values of ECSA were determined from the hydrogen adsorption charge referred to $\Delta Q_{\text{H}_2} = 0.21$ mC cm$^{-2}$, the conventional value for a monolayer of adsorbed hydrogen on clean polycrystalline platinum.
Durability test using stimulated load cycling modes.—The durability of cathode catalysts was evaluated by the use of potential cycling protocols by the FCCJ 2011 protocol. To measure the effect with a wide range of ionomer IEC values for durability, an ionomer with unenhanced (“regular”) oxygen permeability, with IEC = 1.8 meq g⁻¹ (ROP 1.8 XSS500/10, Asahi Kasei Co.), was also subjected to this test. The load cycling was operated with H₂ (anode, 100 mL min⁻¹) and N₂ (cathode, 100 mL min⁻¹) at 80°C and 100% RH. In the first step, the initial performance test (I-E curve) and CV were measured. Then, the durability tests were conducted by use of square wave cycling. The cell voltages were stepped between 0.6 and 1.0 V with a holding time of 3 s at each voltage. During the course of the durability tests, the ECSA values of the cathode side were examined by CV. In the final step, the performance degradation of the MEAs was evaluated by comparing the initial I-E curve with the final I-E curve.

Ionomer and particle distribution and cross-sectional images by use of TEM and STEM.—The distributions of the ionomers coated on the n-Pt/AB250 catalyst were obtained by use of Transmission electron microscope (TEM, HT7700S, Hitachi High-technologies Co.) at a low acceleration voltage (80 kV), in order to obtain images with high contrast and high resolution. The low acceleration voltage can minimize the beam damage of soft materials. The TEM, which was equipped with a special high-resolution objective lens, allowed us to achieve high resolution observation with high contrast at the low acceleration voltage, and also enabled us to carry out a simultaneous evaluation of the nanometer-sized soft organic ionomer, and inorganic carbon materials. The catalysts were also observed by use of STEM. These images were used to obtain the particle size distribution and the average particle diameter. The cross-sections of the interface of CLs and membrane were observed using STEM; small sections of the samples prepared with a focused ion beam (FIB) apparatus (FB2200, Hitachi High-technologies Co.).

Results and Discussion

Ionomer properties.—Figure 2a shows the oxygen permeability for the ROP 1.1, HOP 1.2 and HOP 1.5 ionomers. The oxygen permeabilities were 3.6, 5.0 and 4.5 x 10⁻⁹ cc cm cm⁻² s⁻¹ mHg⁻¹ for ROP 1.1, HOP 1.2 and HOP 1.5, respectively. The oxygen permeabilities for HOP 1.2 and HOP 1.5 were 1.4 and 1.2 times higher, respectively, than that of ROP 1.1. Figure 2b shows the water uptake values for the ROP 1.0, HOP 1.2 and HOP 1.5 ionomers. The HOP 1.5 ionomer exhibited the highest water uptake over the full range of RH conditions. Also, the HOP 1.2 ionomer exhibited higher water uptake than ROP 1.0 under all RH conditions. Figure 2c shows that the dependence of λ (H₂O / SO₃H) on RH was nearly the same for all of the ionomers. These results indicate that high IEC values induced high water uptake, especially at high RH. High water uptake induced swelling due simply to the volume of water, leading to increased thickness of the ionomer coating. To be accurate, the water uptake of the coated ionomer film is not necessarily the same as that of the bulk membrane. However, at least, the results of water uptake for the thin membranes suggest that the coated ionomer film with high IEC values would undergo more severe swelling.

Cell performance of ionomers.—Figure 3a shows the CVs for the ROP 1.0, HOP 1.2 and HOP 1.5 cells at 40°C and 100% RH at the beginning of life. The CVs of all cells exhibited nearly identical
voltammmograms. The values of ECSA determined from the hydrogen adsorption peak were 75, 73 and 72 m² g⁻¹ at 40°C and 100% RH (59, 55 and 57 m² g⁻¹ at 80°C and 30% RH) for ROP 1.0, HOP 1.2 and HOP 1.5, respectively (Figure 3b). This result indicates that the proton-conductive paths were well formed for all cells under these conditions.

Figures 4a and 4b show the I-E curves at 80°C and 100% RH under H₂/O₂ conditions and H₂/air conditions. In the case of the H₂/O₂ condition, the potentials obtained for the HOP 1.2 and ROP 1.0 cells were comparable in the high current density region. The mass activities for each cell at 0.85 V (low current density region) were 202, 250 and 233 A g⁻¹ for ROP 1.0, HOP 1.2 and HOP 1.5, respectively (Figure 4d). Under O₂ gas supply conditions, the use of the high oxygen permeability ionomers improved the mass activity, but there was little effect in the high current density region. On the other hand, under H₂/air conditions, the potential of the HOP 1.2 cell was higher than those of the others, especially in the high current region. The order of mass activity was the same as that for the H₂/O₂ condition (HOP 1.2 (62 A g⁻¹) > HOP 1.5 (50 A g⁻¹) > ROP 1.0 (40 A g⁻¹)). This meant that the HOP 1.2 ionomer led to improved cell performance, not only in the low current density region but also in the high current density region under H₂/air conditions, compared with the ROP 1.0 ionomer.

Figure 4c displays the results for O₂ gain, in which the ROP 1.0 and HOP 1.5 cells exhibited nearly the same values over a wide current density region. The change of O₂ gain in the high current density region was larger than that in the low current density region due to the influence of generated water. The O₂ gain of the HOP 1.2 cell was much lower than those of the others. This result clearly means that the use of the HOP 1.2 ionomer led to improved cell performance under air supply condition. Under these conditions, the cells require a much higher gas flux reaching the reaction zone due to the low oxygen partial pressure in air. Therefore, this result may be attributed to the high oxygen permeability of the HOP 1.2 ionomer. However, the HOP 1.5 ionomer showed the same level of O₂ gain and low cell performance in the high current density region, as did ROP 1.0, even though it had higher oxygen permeability. We will discuss these phenomena in the next Section.

Considering future commercialization, the cell performances for various RH conditions are very important, and therefore, we also measured the cell performance at 80% RH, 53% RH and 30% RH. The I-E curves are shown in Figures 5a–5c. In the case of 80% RH, in the low current density region, the HOP 1.5 cell showed the highest potentials of the three cells. Also, the potential of the HOP 1.2 cell was higher than that of the ROP 1.0 cell in the low current density region. In the high current region, the HOP 1.2 cell exhibited the highest potential, which was also higher than that for the 100% RH condition. The HOP 1.5 cell exhibited a higher potential than that for 100% RH. However, the ROP 1.0 cell maintained a cell performance similar to that for 100% RH. Figure 5b shows I-E curves at 53% RH, at which the HOP 1.5 cell exhibited higher performance, not only in the low current density region but also in the high current region. The potential of the HOP 1.2 cell was still higher than that of the ROP 1.0 cell. Finally, in Figure 5c (30% RH) the HOP 1.5 cell exhibited the highest performance over a wide range of current density among the three cells. The HOP 1.2 cell had higher performance than the ROP 1.0 cell in the low current density region, whereas, in the high current density region, the ROP 1.0 cell exhibited nearly the same behavior.

The RH dependence of mass activity, which was based on the performance at 0.85 V, reflecting the low current density region, and maximum mass power, reflecting the high current density performance, display the differences between the cells more clearly, as shown in Figures 5d and 5e, respectively. In Figure 5d, in which the mass activities at 0.85 V are plotted versus RH, the two HOP ionomer cells showed higher mass activity than the ROP ionomer cell for all RH. At 100% RH, the order of mass activity was HOP 1.2 > HOP 1.5 > ROP 1.0. For 80% RH and lower, the HOP 1.5 cell had the highest mass activity, higher than the HOP 1.2 cell. This result indicates that

Figure 4. IR-free polarization curves for the n-Pt/AB250 catalyst utilizing the ROP 1.0, HOP 1.2 and HOP 1.5 ionomers under (a) H₂/O₂, (b) H₂/air conditions, (c) O₂ gain as a function of current density and (d) mass activities obtained from both O₂ and air conditions at 80°C and 100% RH.
the high IEC and high oxygen permeability led to high performance in the low current density region. Figure 5e shows plots of the maximum mass power values, which were obtained from the high current density region for each cell. The maximum mass powers of the two HOP ionomer cells showed higher values than that of the ROP 1.0 cell at high RH. Especially at 80% RH, the HOP 1.2 cell had a 1.6 times higher value than that of the ROP 1.0 cell. At low RH, the values of the HOP ionomer cells remained high but were comparable to that of the ROP 1.0 cell. The maximum mass power of the HOP 1.2 cell increased markedly going from 53% to 80% RH but then decreased at 100% RH. In the case of the HOP 1.5 cell, the mass power also increased between 53% and 80% RH but decreased again between 100% and 80% RH; the mass activity also showed a similar tendency.

We hypothesized that these results were related to water uptake (Figures 2b, 2c). The water uptakes of all of the ionomers increased significantly from low to high RH. The water uptake of the HOP 1.5 ionomer exhibited a much higher value at 100% RH than those of the HOP 1.2 and ROP 1.0 ionomers. The increase of the water uptake value indicates increased ionomer swelling, which leads to increasing thickness of the ionomer layers in the CL. These results suggest that the high IEC and high oxygen permeability led to high performance in the low current density region. Figure 5e shows plots of the maximum mass power values, which were obtained from the high current density region for each cell. The maximum mass powers of the two HOP ionomer cells showed higher values than that of the ROP 1.0 cell at high RH. Especially at 80% RH, the HOP 1.2 cell had a 1.6 times higher value than that of the ROP 1.0 cell. At low RH, the values of the HOP ionomer cells remained high but were comparable to that of the ROP 1.0 cell. The maximum mass power of the HOP 1.2 cell increased markedly going from 53% to 80% RH but then decreased at 100% RH. In the case of the HOP 1.5 cell, the mass power also increased between 53% and 80% RH but decreased again between 100% and 80% RH; the mass activity also showed a similar tendency.

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Figure 6. (a) Mass activities and (b) maximum mass powers as a function of ionomers oxygen permeability at 80°C, 80% RH with H2/air supply.

for the two factors (IEC and oxygen permeability) of these ionomers for mass activity (Figures 5d and 6a) and maximum mass power (Figures 5e and 6b) suggest that the ionomer needs both high oxygen permeability and an appropriate water uptake value (nearly equal to IEC) in order to improve the cell performance.

The morphologies of the ionomers on the carbon-supported Pt catalyst were observed by use of TEM with a low acceleration voltage (Figure 7), in which the carbon support and ionomer are distinguishable. It can be seen that the ROP 1.0 ionomer (Figure 7a) did not cover the surface of the n-Pt/AB250 support catalyst homogeneously and continuously at several points. In comparison, the HOP 1.2 and HOP 1.5 ionomers covered the catalyst uniformly and continuously (Figures 7b, 7c). However, the ECSA values obtained from the CV measurement at 40°C and 100% RH were nearly the same for all of the ionomers (Figure 3). This indicated that under hydrated conditions, even an extremely thin ionomer layer would be sufficient to contact the Pt particles, but these might not be visible under the ultra-dry TEM conditions. Thus, we were able to observe the problem under low RH conditions for the ROP 1.0 ionomer by use of TEM. However, from only TEM observation, it is difficult to be conclusive. We are continuing to investigate tomographic images30 for a deeper understanding.

In Figure 8, we propose models for the ionomer coverage structures at 100% RH. In this work, we used the AB250 support, whose particles do not contain nanopores. All of the Pt particles were supported on the exterior carbon particle surfaces (Figure 1). In the case of the CL using the ROP 1.0 ionomer (Figure 8a), the coverage of ionomer was nonuniform, i.e., at some points, the ionomer layer thickness was small, whereas at other points, it was large. In the thin ionomer regions, the oxygen gas can easily reach the reaction zone. In the thick regions, only a small fraction of the oxygen gas can reach the reaction zone, due to the low oxygen permeability. Therefore, the ROP 1.0 cell exhibited low cell performance, especially for air supply conditions at high current density. In the case of the HOP 1.2 ionomer (Figure 8b), the coverage of ionomer was very uniform. The ionomer also had high oxygen permeability, which led to effective oxygen transport for all of the ionomer-coated areas. These effects also led to high cell performance over the full range of current density and humidity conditions. In the case of the HOP 1.5 ionomer, the coverage of ionomer was uniform; however, even though the water uptake of the coated ionomer films might be different from those of the bulk membranes, the results of Figure 2 suggest that the coated ionomer films with high IEC values would also undergo more severe swelling, which might lead to increased oxygen transport distances. This impeded the O2 supply to the catalyst, despite the high oxygen permeability.

Thus, we suggest that the ionomer properties that are most important are (1) high oxygen permeability, in order to improve cell performance in both low and high current density regions, and (2) high IEC values for low RH conditions for uniform coverage on the catalyst surfaces, and (3) low IEC values for high RH conditions, in order not to experience severe swelling.

Effect of oxygen permeability and IEC of ionomers for load-cycle durability evaluation.—The cells using the HOP 1.2 and HOP 1.5 ionomers and the ROP 1.0 ionomer were subjected to an accelerated stress test (AST) that simulates practical electric vehicle load cycles (FCCJ 2011 protocol, depicted in Figure 9a). To measure the effect on durability with a wide range of ionomer IEC values, an additional ROP ionomer with IEC = 1.8 meq g⁻¹ (ROP 1.8) was also subjected to this AST protocol. Figure 9a shows the change of the ECSA during the
Figure 8. Schematic illustrations of ionomer coverages on n-Pt/AB250 catalyst and oxygen and proton transport for ROP 1.0, HOP 1.2 and HOP 1.5 ionomers at 80°C, 100% RH with H2/air supply.

AST cycling, and Figure 9b shows the ECSA values at the beginning of life (BOL, 0 cycles) and end of life (EOL, 5000 cycles). At 80°C and 100% RH, the HOP 1.2 cell had the highest ECSA value at the BOL. All cells nearly maintained their initial ECSA values up to 200 cycles. After 200 cycles, the ECSA values for all cells decreased continuously and approximately linearly versus the logarithm of the number of cycles. The percentages of ECSA decrease at the EOL (5000 cycles) were 53%, 52%, 68% and 68% for ROP 1.0, HOP 1.2, HOP 1.5 and ROP 1.8, respectively (Figure 9b). This result indicates that the higher IEC values led to greater degradation at the EOL. Based on the high initial ECSA value and lower percentage of ECSA decrease, the HOP 1.2 cell exhibited the highest ECSA value after the AST cycling.

This tendency was also shown in the I-E curve at 80°C and 100% RH under air supply conditions before and after the AST cycling (Figure 10a). The cell performances of all cells had degraded at the EOL. The HOP 1.2 cell still exhibited the highest performance at EOL of all of the cells. This can also be clearly seen in the O2 gain shown in Figure 10b. The order of O2 gain values was HOP 1.2 < ROP 1.8 < ROP 1.0 < HOP 1.5 at the BOL. At the EOL, the order became HOP 1.2.
Figure 11. TEM images of the uncycled n-Pt/AB250 catalyst and that utilizing the ROP 1.0, HOP 1.2, HOP 1.5 and ROP 1.8 ionomers after AST cycling, with average Pt particle size.

1.2 < ROP 1.0 < HOP 1.5 < ROP 1.8. The HOP 1.2 cell maintained a lower O₂ gain at the EOL. In the case of the ROP 1.8 cell, the O₂ gain had increased significantly at the EOL. These results also suggest that the high ionomer IEC value caused severe degradation during the AST cycling. However, in terms of the oxygen permeability of the ionomers, there was little effect on degradation for the AST cycling.

Based on the above results, we focused upon the effect of IEC value on the durability. We examined the catalyst using TEM (Figure 11). Comparing the initial image and those obtained after AST cycling, the Pt particle sizes increased in all cathodes. The Pt particle size of the initial catalyst was 2.8 ± 0.6 nm. After AST cycling, the sizes were 5.0 ± 1.5, 5.4 ± 1.3, 5.8 ± 1.8 and 6.2 ± 1.9 nm for the ROP 1.0, HOP 1.2, HOP 1.5 and ROP 1.8 cells, respectively. In Figure 12, the Pt particle sizes obtained from the TEM images are plotted versus the ionomer IEC values, with a nearly linear plot, the Pt particle size after AST cycling increasing with increasing IEC, in agreement with the ECSA changes (Figure 9). Mitsushima et al. reported that higher H₂SO₄ concentration is associated with higher Pt solubility and enhanced dissolution of Pt particles. These results suggest that the increased acid concentration of the ionomer can cause more severe Pt agglomeration during the cycling.

We also examined each of the cross-sectional images of the CLs and membrane interfaces (Figure 13). For all cells, Pt particles were observed in the membrane near the cathode CL region after cycling. In the HOP 1.5 and ROP 1.8 cell images, the Pt particles in the membrane were larger than those for the ROP 1.0 and HOP 1.2 cells. These results indicate that the increase of the ionomer IEC values led to increased dissolution of Pt into the ionomers and subsequent redeposition of large numbers of Pt particles in the membranes. Therefore, the high IEC ionomers caused both the severe Pt agglomeration in the cathode CL and the thicker Pt band in the membrane near the cathode CL.

Finally, based on the evaluation results of both the initial cell performances and durability test cycles, we propose that the ionomer needs to have high oxygen permeability and suitable IEC values. The high oxygen permeability of the ionomers resulted in improved cell performance, without any adverse effects. However, high IEC caused severe swelling under high RH conditions, which impeded oxygen transport and also caused Pt dissolution, which led to the Pt agglomeration and Pt band formation. The low IEC ionomer led to decreased cell performance under low RH conditions due to low proton conductivity and poor ionomer coating. Therefore, the selection of a suitable IEC value is necessary in order to improve the cell performance and durability.

For a more detailed understanding of ionomer coverage and local oxygen transport, further investigation of the ionomer thin film...
characteristics, as well as optimization of the I/C ratio, which may vary from ionomer to ionomer is required. We will focus on these aspects in future work.

Conclusions
We investigated the effects of high oxygen permeability ionomers on the cathode performance of PEFCs. The low Pt loading cathode CLs were prepared from the n-PE/AB250 catalyst and high oxygen permeability ionomers. The cell performances of the high oxygen permeability ionomer cells were increased in the low current density region over a wide RH range. The order of mass activity under H2/air permeability ionomers. The cell performances of the high oxygen permeability ionomer cells were increased in the low current density region under 100% RH. Also, the O2 gain for HOP 1.2 was much lower than those of the others. This is also attributed to the high oxygen permeability of the HOP 1.2 ionomer. However, the HOP 1.5 cell at 100% RH experienced impeded O2 supply due to the excessive ionomer swelling. On the other hand, the HOP 1.5 cell showed high performance under low RH conditions.

We found from the AST cycling durability evaluation that the Pt particle size observed after cycling increased with increasing ionomer IEC value. The increase of the ionomer IEC value led to increased dissolution of Pt into the ionomer and redeposition of large numbers of Pt particles in the membrane. Consequently, we propose that the ionomer needs to have high oxygen permeability and suitable IEC values. The high oxygen permeability of the ionomers led to improved cell performance, without any adverse effects. The high IEC caused severe proton swelling under high RH conditions, which impeded oxygen transport and Pt dissolution. The low IEC decreased cell performance under low RH conditions due to low proton conductivity and poor ionomer coating. Therefore, selection of a suitable IEC value is necessary in order to improve the cell performances and durability.

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