

Durability Evaluation of Polymer Electrolyte Membrane for Fuel Cells by Molecular Weight Analysis

Atsushi HIRAIDE*

Akira NAKAHARA*

ABSTRACT

As molecular weight analysis of polymer electrolyte membrane for fuel cells has an advantage in sensitivity of membrane damage detection, it can detect slight changes in membrane damage even in a short-term durability test. Modelizing the relationship between the molecular weight of polymer and the probability that the polymer will react with a radical allows calculation of molecular weight reduction as an approximation to a curve. Hydrogen peroxide exposure testing was carried out on a membrane to experimentally confirm that the decrease in molecular weight due to degradation of the membrane follows the molecular weight reduction curve. It was also experimentally confirmed by a real fuel cell durability test that the reduction in molecular weight of membrane under the fuel cell operating conditions follows the molecular weight reduction curve. With the molecular weight reduction curve, it becomes possible to predict the degree of degradation in long term durability tests from degradation in short term tests, thereby shortening the test time necessary for evaluating the durability of the polymer electrolyte membrane to around one fifth or less.

1. Introduction

A fuel cell is a power source characterized by the use of electrochemical reactions to generate power without burning fuel. The advantages are that energy conversion efficiency is good because there are no waste heat losses, and that there are few reaction by-products because the reaction does not reach high temperatures. If hydrogen is used as fuel, power is generated by the reaction between hydrogen and the atmospheric oxygen, and water is produced as the reaction product (Fig. 1). Since fuel cells produce energy with a low environmental burden, fuel cells are increasingly being used as the power source for electric vehicles.

Reducing size and cost are requirements in the fuel cells developed for vehicles, and it is also important to optimize designs to balance those needs against durability, which is in a tradeoff relationship with them. However, it has been necessary to perform long-term testing that takes from several months to a year, in order to evaluate the durability of fuel cells. That has previously been a factor lengthening the development period for fuel cell vehicles.

Power generation in a fuel cell occurs in the membrane electrode assembly (MEA) (Fig. 1). It is generally known that the polymer electrolyte membrane (PEM), which is interposed between the anode electrode and the cathode

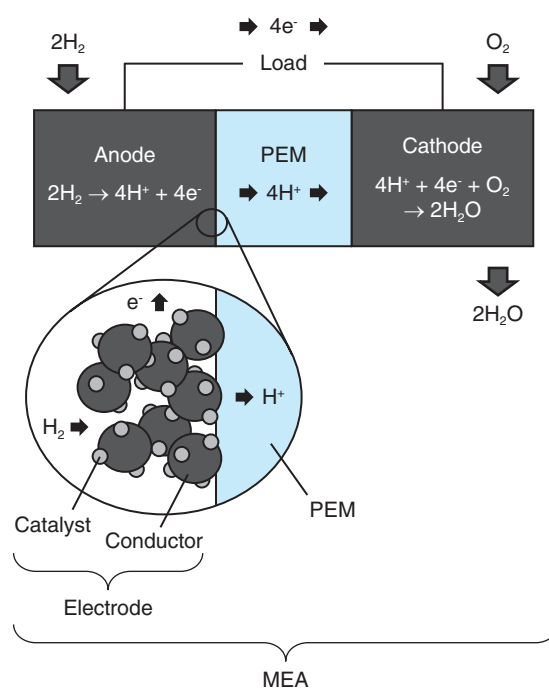


Fig. 1 Schematic cross section of typical fuel cell

* Automobile R&D Center

electrode, gradually degrades during the operation of the fuel cell. It is necessary to design fuel cells with sufficient durability, but the PEM is generally manufactured to be just a few tens of μm thick, in order to enhance fuel cell power generation performance. The main PEM material now is perfluorosulfonic acid (PFSA), a fluorine resin electrolyte which features a polytetrafluoroethylene backbone ($-\text{CF}_2-$), known as Teflon®. Figure 2 shows the chemical structure of Nafion®, a typical PFSA polymer molecule. The degradation mechanisms of PFSA, as shown in Fig. 3⁽¹⁾, are thought to involve two reactions: Polymer scission (indicated by the green scissors in Fig. 3), and the unzipping reaction (indicated by the blue arrows in Fig. 3), in which breakdown proceeds from the carboxyl groups ($-\text{COOH}$) at the ends of the polymer molecule. Hydroxyl radicals are thought to be the causative agent of both reaction mechanisms, and when scission of PFSA polymer molecules occurs, the new ends are carboxyl radicals, which become new starting points of the unzipping reaction⁽²⁾,⁽³⁾. The chemical reactions in the unzipping reaction are as stated below⁽²⁾.

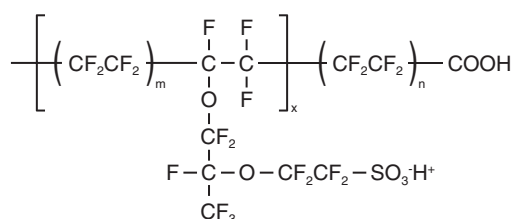
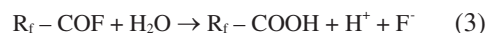
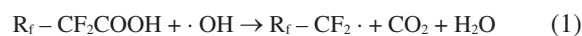


Fig. 2 Chemical structure of Nafion®

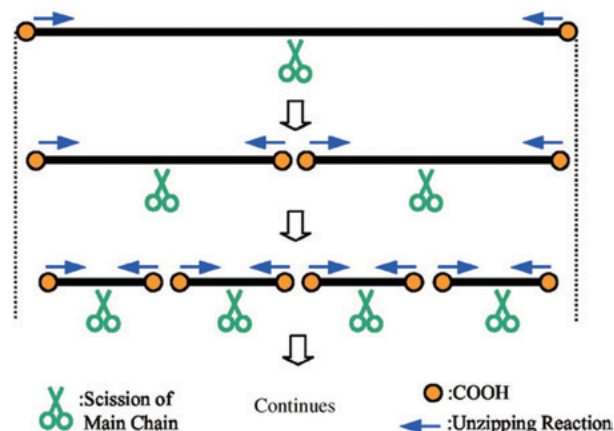


Fig. 3 Degradation mechanism of PFSA polymer

The PEM thickness should decrease during the unzipping reaction, because the carbon and fluorine, which are constituents of PFSA, are emitted from the PEM in the forms of CO_2 and fluoride ions⁽⁴⁾. The degradation rate of PFSA can be identified by measuring the quantity of emitted fluoride ions at that time, and that is termed “fluoride release.”

Before 2016, no method had been established for quantitative evaluation of the durability of the PEM made from PFSA. Therefore, to ascertain the PEM lifetime, it was necessary to perform long-term durability tests running until the end of the PEM lifetime. As reported previously⁽⁵⁾ on this subject, a method for PEM lifetime prediction has been developed that focuses on the behavior of increasing fluoride release. The starting points of unzipping reactions should increase exponentially, because two new ends are created when the PFSA polymer chain scission reaction occurs as shown in Fig. 3. A method that can calculate a fluoride release that increases exponentially was established by modeling the two reaction mechanisms of PFSA degradation, and mathematizing the amount of fluoride release as a function of durability time (Fig. 4). As a result, the degradation rate can be evaluated quantitatively, before the PEM reaches the end of its lifetime and even during the durability test, based on the behavior of increasing fluoride release. However, a long-term durability test of at least several months was still required to identify PEM degradation with adequate sensitivity, because the behavior of a fluoride release that increases exponentially shows little variation in the early stages of the durability test.

Therefore, a new evaluation method was developed as a substitute for fluoride release that was able to detect PEM degradation with high sensitivity even during a short durability test period, in order to evaluate PEM durability in a shorter period.

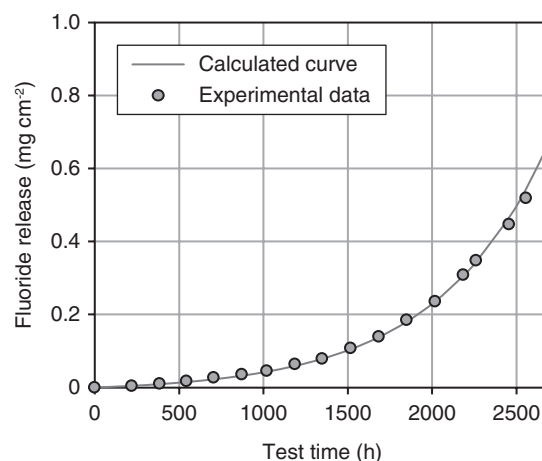


Fig. 4 Non-linear behavior of fluoride release in durability test

2. Modelization of Molecular Weight Reduction

In the degradation mechanism shown in Fig. 3, focusing on one polymer molecule, the number of polymer end groups double, and the molecular weight that represents the length of the polymer molecule is reduced to around half after one scission reaction occurs. Therefore, the amount of fluoride release increase from polymer end groups is small in the initial stage, but that growth increases exponentially with the passage of time. In contrast, the behavior of molecular weight decreasing could show exponential decay, similar to a half-life, which would mean a molecular weight decrease significantly at the initial stage, and the amount of the decrease becomes smaller with the passage of time. Focusing on this point, analyzing molecular weight should be better than analyzing fluoride release in order to detect PFSA degradation with high-sensitivity in a short term, because its variation is greater in the initial stages of PFSA degradation.

As a theoretical approach, the first step was modeling the reduction of molecular weight, in order to learn how molecular weight is reduced by polymer molecule degradation. The Monte Carlo simulation was used to modelize polymer molecular degradation due to a chain scission reaction caused by random reactions with hydroxyl radicals, in order to create an equation that can calculate the molecular weight reduction rate. The following assumptions were employed for modelization. For the two reaction mechanisms shown in Fig. 3, a single scission reaction between the polymer molecules causes a major reduction in molecular weight, while the molecular weight reduction due to the unzipping reaction, as shown in Eqs. (1), (2) and (3), is very slight. Therefore, only the scission reaction is considered in the model to simplify this study. The gel permeation chromatography method was used for molecular weight measurement. Regarding the principle that separating polymer molecules based on the size of polymer molecules in solvent, the measurement results mainly reflect the main chain length of the polymer molecule, and are affected little by the presence of side chains. Therefore, the model assumes that polymer molecules are linear, with no branching, and that the molecular weight is proportional to the length of the polymer molecule.

Next, a scission reaction that occurs through a reaction with hydroxyl radicals was modeled. As the reactivity of hydroxyl radicals is extraordinarily high, the model assumes that scission occurs at the point where a hydroxyl radical comes into contact with a polymer molecule. According to the lattice model by Flory⁽⁶⁾ and Huggis⁽⁷⁾, the volume that is occupied by a polymer molecule is proportional to its molecular weight, so the probability of contact between hydroxyl radicals diffusing randomly in space and any given polymer molecule is thought to be proportional to the molecular weight. Therefore, the probability of the scission reaction is assumed to be proportional to

its molecular weight, which is to say, to its length in the simplified model. Figure 5 shows the algorithm for computer implementation. Firstly, as shown in Fig. 5(a), the initial lengths and number of polymer molecules to be handled by the model was determined from previously measured PEM molecular weight distribution information. To simplify representation, the distribution of molecular weight was plotted as a histogram with the molecular weight range 10^3 g/mol to 10^7 g/mol divided into 16 equal intervals on the logarithmic axis, then with the number of polymer molecules in each interval determined. Next, as shown in Fig. 5(b), the aggregate of all polymer molecules with lengths and numbers determined was joined into a single chain. Then the scission points were determined by generating uniform random numbers against that total length. The scission points determined by random numbers were indicated by green scissor symbols in Fig. 5(c). This method expressed the probability of contact and reaction between randomly diffusing hydroxyl radicals and each polymer molecule, which is to say, it expresses the fact that probability of scission of a polymer molecule is proportional to its length. Finally, as shown in Fig. 5(d), the lengths and numbers of polymer molecules after scission are plotted in a histogram, to obtain the molecular weight distribution after degradation. Figure 6 presents calculation results produced by the created molecular weight reduction model. The scission count N is indicated as the number of scissions per molecule when averaged by the original number of polymer molecules.

$$N = (\text{scission count}) / (\text{original number of polymer molecules}) \quad (4)$$

Figure 7 presents the relationship between scission count N and molecular weight reduction. The vertical axis expresses the molecular weight retention rate, relative to the initial molecular weight as 100%. Calculating with $N=1$

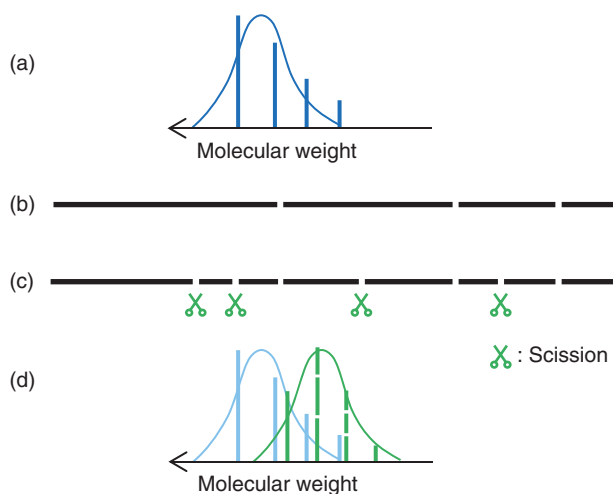


Fig. 5 Modelization of random polymer scission and molecular weight reduction

means that all polymer molecules have one scission, on average, so the molecular weight retention rate is around 50%, approximately half.

From the above results, it was anticipated from the created molecular weight reduction model that when a polymer material is degraded at a constant rate, the average molecular weight would decline along the curve shown in Fig. 7. Therefore, this curve was named the molecular weight reduction curve. The horizontal axis shows the polymer molecule scission count, so in a durability test in which the generation rate of hydroxyl radicals is constant, this curve can be used by replacing the horizontal axis with test time.

In Fig. 4, the amount of fluoride release followed exponential growth, so the initial change was the smallest, whereas the molecular weight reduction curve shown in Fig. 7 follows exponential decay, so the initial change is the largest. Therefore, it can be stated that measuring molecular weight rather than fluoride release is a more suitable method

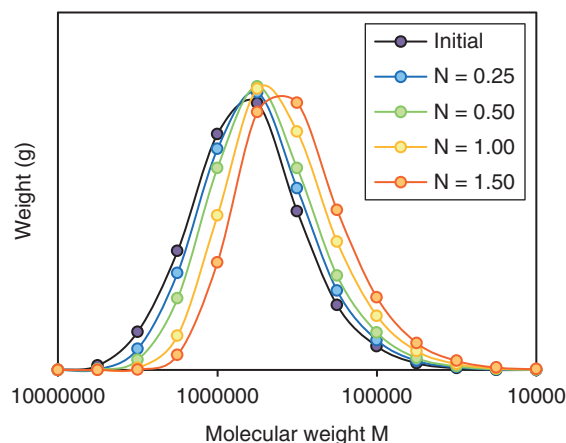


Fig. 6 Calculated shift of molecular weight distribution using random polymer scission model

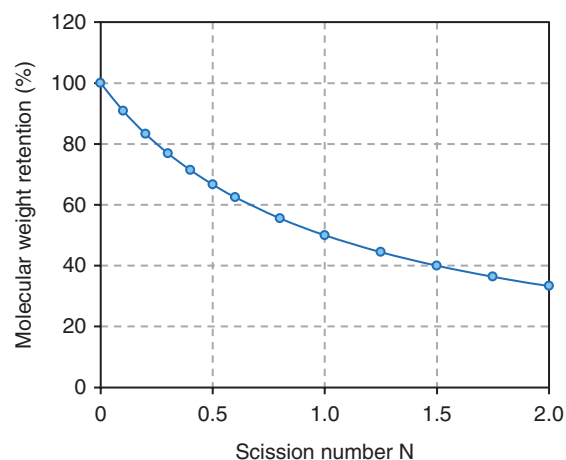


Fig. 7 Calculated molecular weight reduction curve using random polymer scission model

for high-sensitivity detection of material degradation in an early diagnosis.

3. Experiments and Observations

In Chapter 2, the molecular weight reduction when polymer material is degraded at a fixed speed was modeled and the molecular weight reduction curve was obtained. In the process of creating the model, some assumptions were set for the purpose of simplification, and the accuracy of the created model is validated experimentally in this Chapter 3.

3.1. Validation of the Model in Single-material Testing

This model was created by simplifying the structures and reactions of polymer molecules, but the PFSA polymer molecules used in the PEM for actual fuel cells differ from the simplified model in the following three points. (1) The model assumes that the polymer molecules are linear and the scission reactions occur at random positions, but actually they have a main chain structure as shown in Fig. 2, so the positions where the scissions occur could be limited to certain positions⁽³⁾. (2) The model assumes that the polymer molecules are linear with no branching, but actually they have side chains as shown in Fig. 2. (3) The model only considered polymer molecule scission, but actually polymer molecules are degraded by two reaction mechanisms, scission and unzipping. Therefore, to confirm the accuracy of the model, the question of whether molecular weight reduction of PFSA polymer molecules follows the molecular weight reduction curve was validated experimentally in a test that causes PEM degradation in isolation. If the experimental molecular weight reduction follows the molecular weight reduction curve, even a model that has been simplified in the three points stated above can be said to be practically applicable to the prediction of molecular weight reduction in PFSA polymer molecules.

The test method was a hydrogen peroxide exposure test⁽⁸⁾. The hydrogen peroxide exposure test is a test that simulates the environment in which PEM is degraded during fuel cell operation, in order to evaluate PEM durability. The PEM is exposed to steam containing hydrogen peroxide at a constant concentration, so that it is exposed to hydroxyl radicals supplied at a constant rate. Provided the generation rate of hydroxyl radical is constant, the number of reactions degrading the PEM is thought to be proportional to the exposure time. In order to confirm that the relationship between exposure time and molecular weight reduction in the hydrogen peroxide exposure test follows the molecular weight reduction curve in Fig. 7, samples were prepared at five levels of varied exposure time, and their molecular weights were measured. The conditions for the exposure test were set at a temperature of 90°C and with 30% humidity, based on operation conditions expected for fuel cells.

First, the water used for washing the PEM after the test was analyzed with ion chromatography, confirming the generation of fluorine ions, which confirmed that the

unzipping reaction occurred in the hydrogen peroxide exposure test. Figures 8 and 9 present the molecular weight measurement results. Figure 8 shows the molecular weight distribution after testing for each exposure period. The vertical axis shows the refractive index detector output of the molecular weight measurement instrument. The refractive index of the polymer molecule solution is known to be proportional to the mass concentration of the solute. Similar to the calculation results from the model shown in Fig. 6, it has been confirmed that the peak of the molecular weight distribution maintains its shape as it shifts to the low molecular weight side. Also, Fig. 9 plots the average molecular weight after the test for each exposure time, with the horizontal axis adjusted, superimposed on the molecular weight reduction curve from Fig. 7. The relationship between exposure time in the hydrogen peroxide exposure

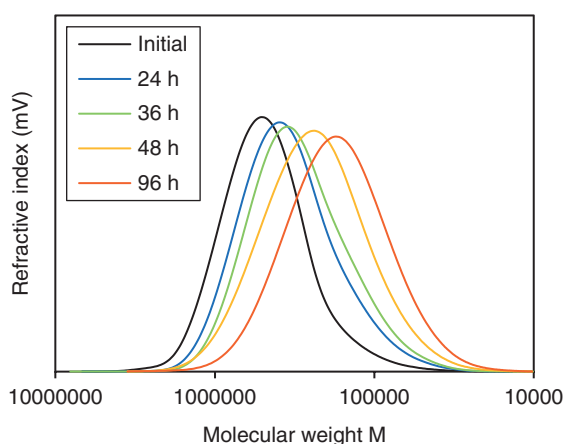


Fig. 8 Membrane degradation detected by shift of molecular weight distribution in hydrogen peroxide exposure test

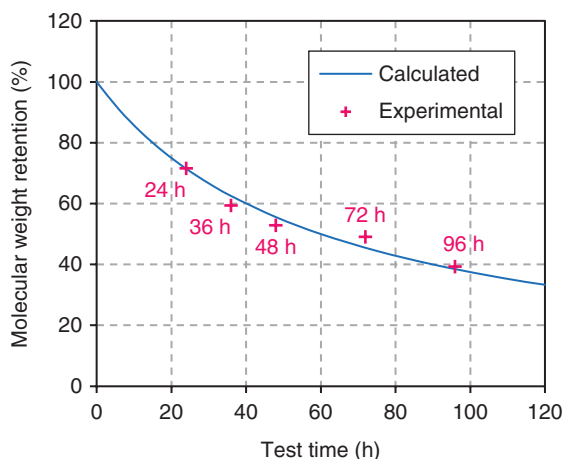


Fig. 9 Relationship between exposure time and molecular weight reduction follows model-calculated curve

test and molecular weight reduction matched the molecular weight reduction curve, underlining the correctness of the three assumptions stated above.

- (1) Even in a PFSA polymer molecule with a main chain structure as shown in Fig. 2, the positions at which scission of the polymer molecule occurs are distributed with a level of evenness such that positions may reasonably be assumed to be random.
- (2) Even in a PFSA polymer molecule having side chains as shown in Fig. 2, the probability of the scission reaction of a polymer molecule is proportional to its length, and by extension, to its molecular weight.
- (3) Even for PFSA polymer molecules degraded by the two reaction mechanisms of scission and unzipping reaction, the reduction of molecular weight follows the molecular weight reduction curve, which only consider scission reactions because the influence of unzipping on molecular weight reduction is smaller than that of a scission reaction.

From the above results and observations, it was confirmed that when a PFSA polymer molecule is degraded at a constant rate, the reduction of its molecular weight follows the molecular weight reduction curve.

3.2. Validation of the Model in a Fuel Cell Operation Environment

In the preceding section, it was confirmed in the hydrogen peroxide exposure test on the PEM alone that molecular weight reduction due to degradation of PFSA follows the molecular weight reduction curve. However, in a real fuel cell operation environment, the following three points differ from the hydrogen peroxide exposure test on the PEM alone: (1) In an MEA which electrodes including catalysts are placed on both sides of the PEM, there is the possibility that multiple side reactions, other than the main reaction shown in Fig. 1, could contribute to membrane degradation⁽³⁾. (2) Changing the electrical potential during power generation could influence the reaction rate and reaction pathway, so that the two reaction mechanisms of polymer molecule scission and unzipping reaction may occur in different ratios from the hydrogen peroxide exposure test performed on PEM alone. (3) There is the possibility that the generation rate of hydroxyl radicals may not be constant, due to factors such as degradation of the constituent materials of the MEA.

Therefore, the question of whether molecular weight reduction of PFSA polymer molecules follows the molecular weight reduction curve, even in PEM degradation during real fuel cell operation, was validated experimentally in a fuel cell durability test. If molecular weight reduction during a power generation test follows the molecular weight reduction curve, the modeled molecular weight reduction curve can be said to be practically applicable to the prediction of molecular weight reduction in fuel cell operation. The durability test has a further objective, to experimentally associate the number of scission reactions

of the polymer molecule on the horizontal axis of the molecular weight reduction curve shown in Fig. 7 with the operation time of the fuel cell. As durability testing of fuel cell materials requires a long period, durability testing is generally performed under accelerated stress⁽³⁾. In this case, the accelerated test was performed at a temperature of 90°C and relative humidity of 30%. These are severe conditions for chemical degradation within the range of operational environment conditions expected for fuel cells^{(3), (4)}. In order to confirm that the relationship between fuel cell operation time and PEM molecular weight reduction follows the molecular weight reduction curve in Fig. 7, durability tests were performed at five levels of varied operation time, and the molecular weight of PEM was measured after the end of the durability test.

The results are as shown in Figs. 10 and 11. Figure

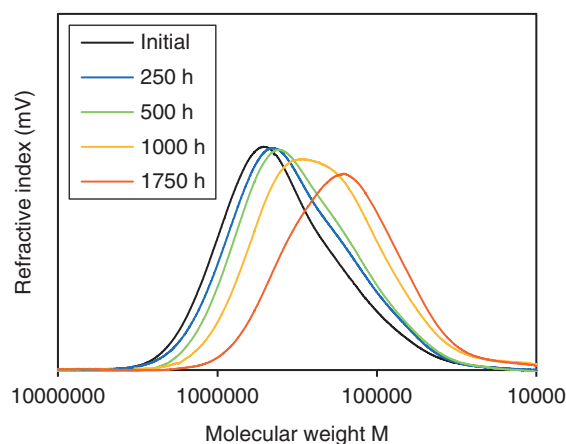


Fig. 10 Membrane degradation detected by shift of molecular weight distribution in real fuel cell test

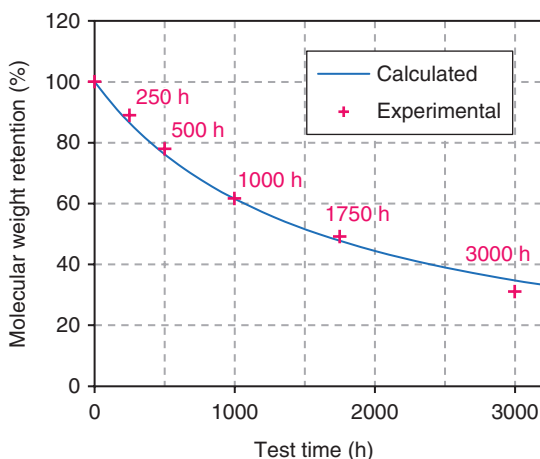


Fig. 11 Relationship between accelerated test time and molecular weight reduction follows model-calculated curve

10 shows the molecular weight distribution after testing for each durability period. Similar to the calculation results from the model shown in Fig. 6, it has been confirmed that the peak of the molecular weight distribution largely maintains its shape as it shifts to the low molecular weight side. Also, Fig. 11 plots the average molecular weight after the test for each durability time, with the horizontal axis adjusted, superimposed on the molecular weight reduction curve from Fig. 7. As the relationship between fuel cell operation time and molecular weight reduction matches the molecular weight reduction curve, it is confirmed that molecular weight reduction in PFSA follows the molecular weight reduction curve in PEM degradation occurring in the real fuel cell operation environment. This result also supports the constant-rate generation of hydroxyl radicals during fuel cell operation under constant conditions. Furthermore, based on the modeled molecular weight reduction curve, it was possible to predict the amount of PEM degradation in a long-term durability test by analyzing the molecular weight reduction of the PEM in a short-term durability test.

Figure 12 is a graphical representation comparing the molecular weight reduction curve with membrane thickness reduction and fluoride release behavior. In conventional methods for measuring membrane thickness and fluoride release, the amount of degradation exhibits exponential growth, so a long-term durability test was necessary before degradation could be detected. With the new focus on molecular weight reduction in this research, it is now possible to detect PEM degradation with high sensitivity, even in a short-term durability test in which almost no change appears in membrane thickness or fluoride release. Specifically, if an approximately 10% change is needed to detect PEM degradation accurately in both membrane

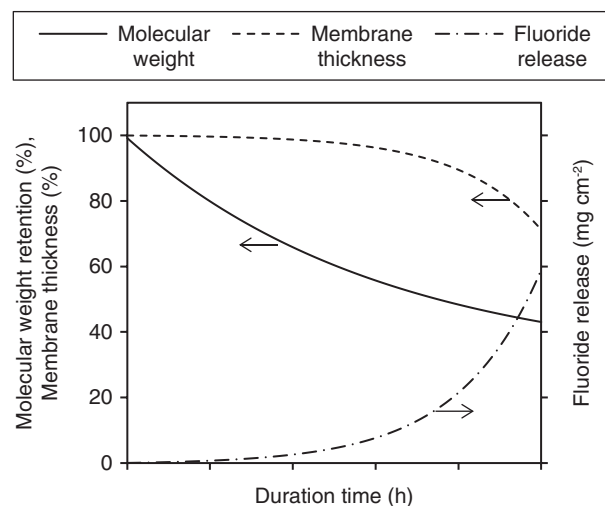


Fig. 12 Non-linear behavior of molecular weight reduction, membrane thickness loss, and fluoride release in durability test

thickness and molecular weight in Fig. 12, the required durability time can be shortened to one fifth or less using a modeled molecular weight reduction curve. This has made it possible to shorten the time of durability testing required to detect PEM degradation accurately to a period of several weeks, rather than the several months or more previously.

4. Conclusion

Until now, the development of fuel cells has faced the challenge that evaluation of PEM durability required long-term durability testing for at least several months. By focusing on molecular weight reduction in PFSA polymer molecules, this research has found that PEM degradation can be detected with high sensitivity, even in short-term durability testing. By modeling the relationship between molecular weight and the probability of a polymer molecule reacting with a radical in a polymer degradation reaction, this research has predicted the reduction of molecular weight through calculation, and created a molecular weight reduction curve for polymer materials. The accuracy of the created model has been validated by experimental confirmation that molecular weight reduction in PFSA polymer molecules used in the PEM follows the molecular weight reduction curve, and molecular weight reduction of the PEM occurring in a fuel cell operation environment also follows the molecular weight reduction curve. Creating and using the molecular weight reduction curve has made it possible to predict the degradation amount in long-term durability tests based on the molecular weight analysis result for the PEM after short-term durability tests, achieving as a result a reduction of the test period required for PEM durability assessment to around one fifth or less.

References

- (1) Hommura, S., Kawahara, K., Shimohira, T., Teraoka, Y.: Development of a Method for Clarifying the Perfluorosulfonated Membrane Degradation Mechanism in a Fuel Cell Environment, *J. Electrochem. Soc.*, 155(1), p. A29-A33, (2008)
- (2) Curtin, D. E., Lousenberg, R. D., Henry, T. J., Tangeman, P. C., Tisack, M. E.: Advanced Materials for Improved PEMFC Performance and Life, *J. Power Sources*, 131, p. 41-48, (2004)
- (3) Coms, F. D.: The Chemistry of Fuel Cell Membrane Chemical Degradation, *ECS Transactions*, 16 (2), p. 235-255, (2008)
- (4) Li, J., Wang, K., Yang, Y.: Membrane Durability and Degradation under Dry Fuel Cell Operation Conditions, *ECS Transactions*, 25 (1), p. 385-394, (2009)
- (5) Hiraide, A: Life Prediction Model Estimating Chemical Degradation of Polymer Electrolyte Membrane for Fuel Cells, *Honda R&D Technical Review*, Vol. 28, No. 1, p. 50-58
- (6) Flory, P. J.: *Thermodynamics of High Polymer Solutions*, *J. Chem. Phys.*, 10, p. 51-61, (1942)
- (7) Huggins, M. L.: Some Properties of Solutions of Long-Chain Compounds, *J. Phys. Chem.*, 46(1), p. 151-158, (1942)
- (8) Hommura, S., Kawahara, K., Shimohira, T.: Degradation Mechanism of Perfluorinated Membrane in Polymer Electrolyte Membrane Fuel Cell Environment, *Polymer Preprints, Japan* 54(2), p. 4517-4518, (2005)

■ Author ■



Atsushi HIRAIDE



Akira NAKAHARA