

Life Prediction Model Estimating Chemical Degradation of Polymer Electrolyte Membrane for Fuel Cells

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ABSTRACT

A calculation method was developed that can predict the lifetime of polymer electrolyte membrane for fuel cells. The chemical degradation of polymer electrolyte membrane is caused by two reaction mechanisms, scission of polymer main chains and unzipping reaction. It was made clear by both experimental and theoretical approaches that the degradation behaviors can be closely approximated with exponential function. By defining the coefficient of the exponential function as the accelerating factor of membrane degradation, the size of the effect of factors accelerating or mitigating chemical degradation could be evaluated quantitatively, and the influence of multiple factors could be represented by a single variable. With the development of a method for predicting membrane lifetime, it became possible to estimate the durability of the polymer electrolyte membrane under the specific fuel cell control as envisioned in the actual operation of an FCV. As a result, polymer electrolyte membrane design values related to the trade-off between fuel cell performance, efficiency, cost, and durability could be optimized.

1. Introduction

A fuel cell is a power source that utilizes electrochemical reactions. The power generating part is termed the membrane electrode assembly (MEA) (Fig. 1). An MEA is composed of two electrodes — the anode and cathode — and a polymer electrolyte membrane (PEM) that is positioned between the electrodes. The hydrogen that is the fuel is decomposed into protons and electrons on the anode catalyst. PEM is an electrical insulant to transmit protons selectively between the two electrodes without conducting electrons. Protons that come from the anode are used for reaction on the cathode catalyst with oxygen that is taken from the atmosphere, and the water is then produced as the reaction product. Because the two electrodes are insulated by a PEM, electromotive force is generated between the electrodes. The electrons are parted from the protons to travel between the electrodes, causing a current to flow in the circuit. The number of electrons flowing in the circuit is equal to the number of protons moving through the PEM, so that the performance of the fuel cell is mainly determined by the activity of the catalyst on the two electrodes and by the proton conductivity of the PEM.

In order to produce high power output, a fuel cell installed in a fuel cell vehicle (FCV) has hundreds of MEAs

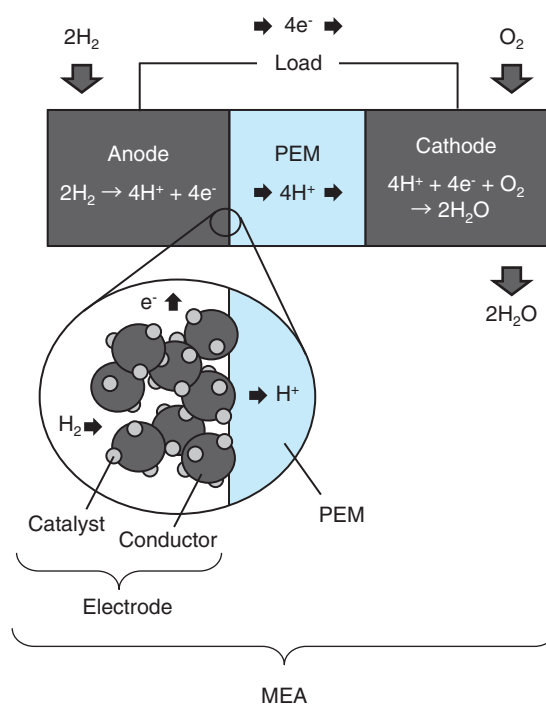


Fig. 1 Schematic cross section of typical fuel cell

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stacked in layers, thus it is referred to as a fuel cell stack. Development of fuel cell stacks for FCV use always seeks to achieve greater compactness by means of higher power density and greater driving range by means of enhanced energy efficiency. At the same time, stacks also require endurance reliability comparable to internal combustion engines and need to achieve cost reduction to enable widespread use by consumers (Fig. 2).

Characteristics of the fuel cell stack are related to design parameters of the PEM, including membrane thickness, ion exchange content, and the amount of additives. For performance of a fuel cell stack, higher ion exchange content and a thinner membrane are better for increased PEM proton conductivity. For durability, a thicker membrane and lower ion exchange content are preferable. In many cases, the additives used to assure PEM durability impede proton transportation, so that performance is sacrificed. For efficiency, a membrane that is too thick will resist proton transportation, while one that is too thin will allow hydrogen, which is the fuel, to permeate through to the cathode side. In either case, energy efficiency is reduced.

As this indicates, PEM design parameters are related to several fuel cell stack characteristics. Changing one PEM design parameter will cause interlinked changes in multiple fuel cell stack characteristics. Furthermore, these fuel cell stack characteristics involve trade-offs, so that PEM design necessitates optimization of the required fuel cell stack characteristics. Every time a PEM design is changed, it is necessary to evaluate the balance of performance, energy efficiency, and durability, so optimization of the PEM design is not readily achieved.

A particular issue that used to be faced in optimization of PEM design was the amount of time it took to estimate PEM durability. PEM degradation includes mechanical degradation due to fatigue caused by mechanical stress as well as chemical degradation in which molecules are

decomposed by chemical reactions⁽¹⁾. Regarding mechanical degradation, there have been reports of design using computer-aided engineering (CAE) for material strength calculations. PEM durability is estimated based on the fatigue limits of polymeric material determined from the mechanical properties of the membrane^{(2), (3)}. In other words, model-based approaches have been employed to estimate PEM durability in a shorter period of time by the use of CAE, in the case of mechanical degradation. As for chemical degradation, however, there have been issues with quantitative evaluation of the degradation rate because chemical degradation tends to occur locally or suddenly, so that former reports have been confined to clarification of reaction mechanisms⁽⁴⁾ and development of highly durable materials⁽⁵⁾. The only method that has been available for estimating PEM durability or lifetime, therefore, has been to implement durability testing over extended periods of time, and this has been a factor in lengthening the process of fuel cell development.

2. Purpose of Development

In order to optimize the PEM design within a brief period in the development of fuel cells for FCV use, new technology capable of estimating the durability of a designed PEM without implementing durability testing needs to be developed.

A model-based development approach was employed in this report as a method for quantitative evaluation of chemical degradation. Quantitative evaluation of degradation speed and PEM durability enable the computational prediction of the PEM lifetime.

3. Modelization and Mathematical Description of Chemical Degradation

3.1. Ascertaining Degradation Behavior

The chemical degradation of PEM does not occur at a fixed rate⁽⁶⁾. Prediction of PEM lifetime therefore requires a grasp of how the rate of degradation changes. The reaction mechanism of chemical degradation was therefore modeled and the rate of degradation was formulated in the mathematical description as a function of operating time, thereby enabling prediction of the estimated PEM lifetime.

The 2016 model FCV adopts a perfluorosulfonic acid (PFSA) membrane with the goal of chemical stability. PFSA molecules feature a fluorocarbon backbone ($-\text{CF}_2-$) that is well known as Teflon[®]. The typical chemical structure of PFSA is shown in Fig. 3. The causative agent of chemical degradation of PFSA membrane is thought to be a radical species represented by hydroxyl radical, which is a side reaction product of fuel cell operation. Radicals are highly reactive reagents, and are known to be causative agents that generally attack and degrade polymeric material. It has been suggested that the following reaction formulas describe the main PFSA membrane degradation reactions⁽⁴⁾.

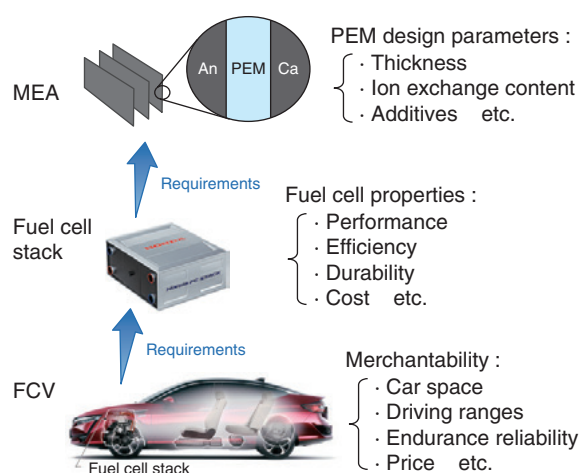
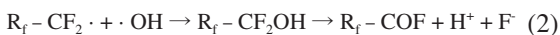
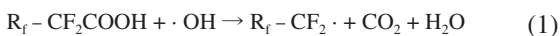


Fig. 2 Hierarchy of requirements from vehicle to materials



It is known that as chemical degradation causes the PFSA membrane to decompose, the membrane grows thinner. The reason is that the carbon (C) and fluorine (F) that are component substances of the PFSA membrane are released from the PEM in the form of CO₂ and fluoride ions.

An example of a report of PFSA membrane durability testing is shown in Fig. 4⁽⁵⁾. The vertical axis shows the amount of hydrogen crossover through the PEM in terms of the crossover current value. The permeation volume of the gas is in inverse proportion to the thickness of the membrane, so when the PEM degrades and grows thinner, the hydrogen permeation volume increases. However, the chemical degradation of a PEM generally occurs locally, so the increase in hydrogen permeation volume that accompanies reduction in membrane thickness is hardly observed at all. A sudden increase takes place at the stage of reaching pinhole failure of the PEM. Thus, there are no conspicuous signs that warn of impending PEM failure, and this is the issue for prediction of membrane lifetime.

The release of fluoride ions that occurs with chemical degradation of the PFSA membrane is termed fluoride release, and comparisons of the amounts or rates of fluoride

release are sometimes made when evaluating PEM's stability against chemical degradation. However, the fluoride release rate does not remain constant in durability testing even when tested under steady-state conditions⁽⁶⁾. It had been thought, therefore, that PEM lifetime could not be predicted from the fluoride release rate. Another consideration was that evaluation of fluoride release involved measurement of the total quantity of fluoride ions and averaging it out over the electrode area, so that correct evaluation could not readily be carried out when local degradation existed.

Previously, therefore, chemical degradation of PEM occurring locally interfered with the quantitative evaluation of the degradation speed. The present research examined methods for evaluating chemical degradation under conditions that would not cause local degradation in the PEM. Conceivable causes of local chemical degradation would be inhomogeneous environments, such as temperature and humidity inside the cell used for durability testing, as well as flow rate and pressure of reaction gas. This was addressed by devising a cell heater capacity and heater shape, and arranging the proper placement of thermal insulator in order to maintain an appropriate balance of heating and heat release in order to achieve homogeneous temperatures. For the reaction gas, the shape of gas flow channels and the gas flow rate were also determined properly so that gas would be homogeneously distributed throughout the cell interior.

Evaluation of chemical degradation was carried out by open circuit voltage (OCV) testing. By placing the fuel cell in a particular state in which it is supplied with fuel but is not generating electricity, the fuel cell tends to produce many radical species that are a side reaction product of fuel cell reaction, as shown in Fig. 1. Since the radical species promotes the PEM degradation reaction, this is a prevalent method of accelerated testing for evaluation of PEM durability against chemical degradation⁽⁶⁾.

The results for fluoride release quantity during OCV testing are shown in Fig. 5. When the temperature or gas in the fuel cell are not homogeneously distributed (shown by box-shaped points in Fig. 5), the released fluoride quantity increases rapidly. This behavior matches with the former generally accepted view. The results of analysis confirmed that local degradation originating from the fuel cell structure was occurring. On the other hand, when the internal environment of the cell was made homogeneous, and when homogeneity and high reproducibility of chemical degradation of the PEM were achieved (shown by round points in Fig. 5), the fluoride release rate could be seen to increase smoothly.

The PEM thickness was measured after OCV testing, which clearly indicates that the size of the reduction in membrane thickness and the fluoride release quantity are correlated, as shown in Fig. 6. If calculation of fluoride release behavior were to become possible, therefore, the lifetime of PEM could be predicted by converting fluoride

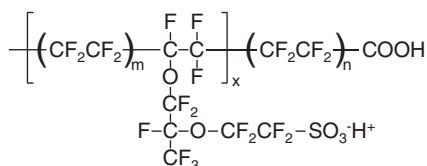


Fig. 3 Chemical structure of PFSA (Nafion®)

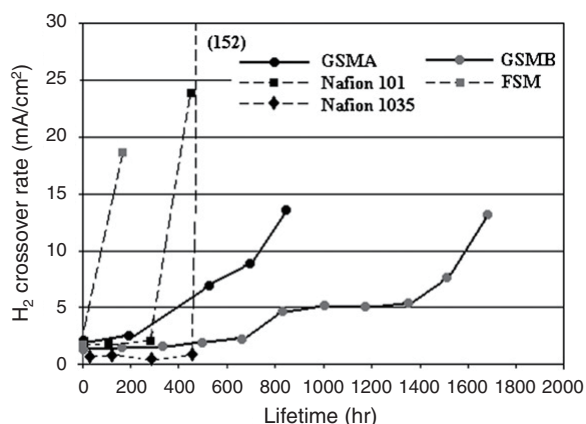


Fig. 4 Comparison of Nafion®, GORE-SELECT® membranes (GSM A, B) and their comparative non-reinforced membrane (FSM)

release quantity into the reduction in membrane thickness using the relationship shown in Fig. 6.

3.2. Modelization of the Degradation Mechanism

A proposed mechanism of the chemical degradation of PFSA membrane is shown in Fig. 7⁽⁷⁾. There are thought to be two reaction mechanisms involved. One is scission of the main chains of polymer (shown by green scissor symbols in Fig. 7) and the other is an unzipping reaction in which the end groups of the main chains progressively degrade (refer to Eqs. (1) to (3) in the previous section; shown by blue arrows in Fig. 7). When scission of the main chain occurs, the location of the cleavage becomes two new end groups, which suggests that number of points of origin for the unzipping reaction increases exponentially. The reaction mechanism for chemical degradation of the PFSA membrane was therefore modeled and the fluoride release behavior calculated, and it was confirmed that the experimental results shown in Fig. 5 could be explained by

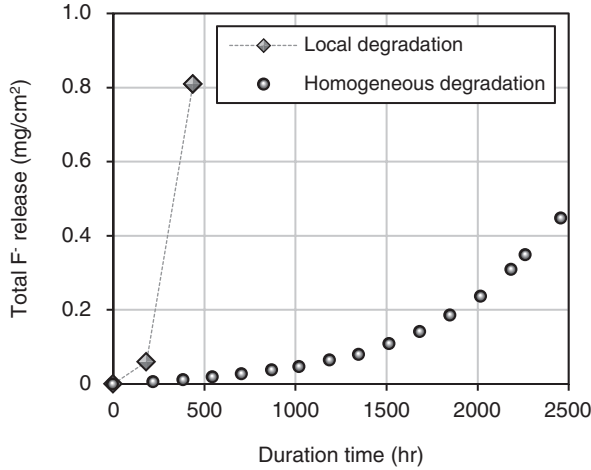


Fig. 5 Fluoride release behavior during stable condition durability test

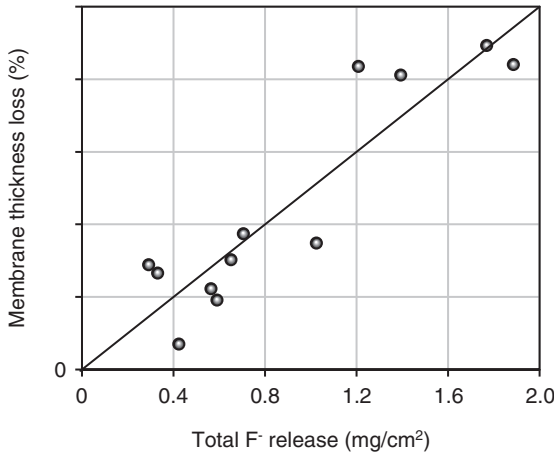


Fig. 6 Correlation between total amount of fluoride release and reduction of membrane thickness

these two reaction mechanisms of chemical degradation.

In creating the model, the formation rate of the radical species per unit time that is a causative agent of chemical degradation was set as v_{Rad} . The number of $-\text{CF}_2-$ bonds in the polymer main chain was set as N_{Main} , with the end group number set as N_{End} , and the initial values of these were set by the average molecular weight of the polymer. The probability that the radical species would encounter the main chain or the end group was determined with reference to the general diffusion model for polymers, and it was presumed to be in proportion to the ratio of N_{Main} and N_{End} . The main chain degradation probability R_{Main} was taken as the probability that when the radical species encountered the polymer main chain, scission of the main chain would occur. The probability R_{Main} was determined in consideration of the chemically stable structure of the fluorocarbon backbone ($-\text{CF}_2-$) of the PFSA polymer molecule. Since the main chain degradation number D_{Main} is in proportion to v_{Rad} , R_{Main} , and the abundance ratio of the main chain unit number N_{Main} , it can be described as follows:

$$D_{\text{Main}} = v_{\text{Rad}} R_{\text{Main}} \left(\frac{N_{\text{Main}}}{N_{\text{Main}} + N_{\text{End}}} \right) \quad (4)$$

In the same way, when the radical species encounter an end group of the main chain, the probability that degradation will occur due to the unzipping reaction is set as the end group degradation probability R_{End} . Since the end group degradation number D_{End} is in proportion to v_{Rad} , R_{End} , and the abundance ratio of chain end group number N_{End} , it can be described as follows:

$$D_{\text{End}} = v_{\text{Rad}} R_{\text{End}} \left(\frac{N_{\text{End}}}{N_{\text{Main}} + N_{\text{End}}} \right) \quad (5)$$

Next, since the N_{Main} is reduced by the scission of the main chain and degradation of end groups, this becomes:

$$N_{\text{Main } t+1} = N_{\text{Main } t} - (D_{\text{Main } t} + D_{\text{End } t}) \quad (6)$$

Since the N_{End} has two end groups created at each scission location, this becomes:

$$N_{\text{End } t+1} = N_{\text{End } t} + 2D_{\text{Main } t} \quad (7)$$

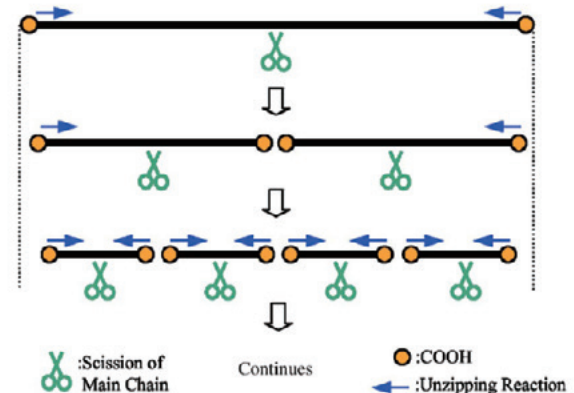


Fig. 7 Degradation mechanism of PFSA membrane

Given Eqs. (1) to (3), the degradation of one end group produces two fluoride ions. Therefore the fluoride release quantity F over time t can be described as follows:

$$F = \sum_t (c D_{\text{Main } t} + 2D_{\text{End } t}) \quad (8)$$

c is a constant that is determined by the chemical structure of the PFSA polymer molecule, an example of which is shown in Fig. 3. Figure 8(1) shows the results of the fluoride release quantity calculation. The experimental results shown in Fig. 5 are also shown in this figure (marked as “Experimental data” in Fig. 8), and the scale of the axes is adjusted to fit the experimental results. Modeling of the two reaction mechanisms of chemical degradation of PFSA membrane — main chain scission and the unzipping reaction — enabled confirmation that the calculated fluoride release quantity formed a smoothly increasing curve that is similar to the curve of the experimental results.

It was also confirmed that when either the degradation probability R_{Main} or R_{End} in the created model is defined as zero, in either case the fluoride release behavior becomes a straight line and does not match the experimental results (Fig. 8). Case (2) supposes occurrence only of the unzipping reaction, and case (3) supposes occurrence only of scission of the main chain. These calculation results from modeling of the chemical degradation reaction not only substantiate the notion that chemical degradation of the PFSA membrane consists of the two reaction mechanisms of main chain scission and unzipping reaction, but also corroborate the notion that the fluoride release rate increases continuously and the graph of fluoride release amount describes a smooth curve.

3.3. Mathematical Description of Fluoride Release Behavior

It was confirmed by both experimental and theoretical approaches that the fluoride release quantity shows

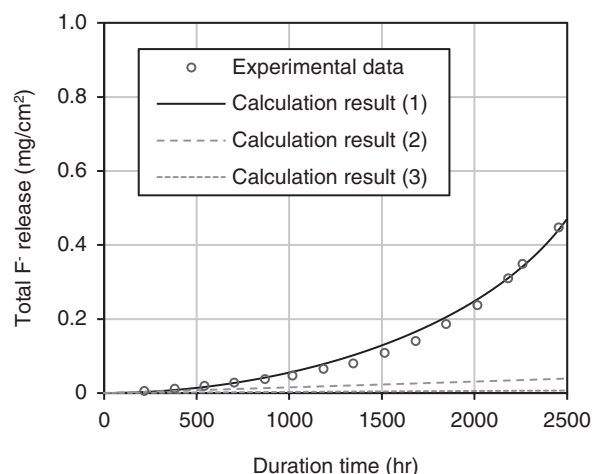


Fig. 8 Fluoride release behavior, calculated by PFSA membrane degradation model

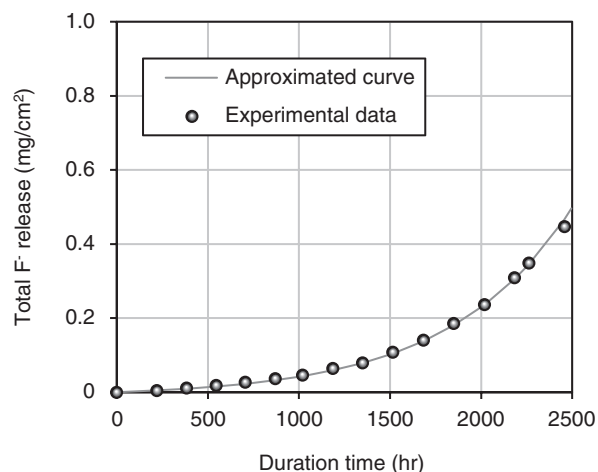


Fig. 9 Experimental data of fluoride release behavior, approximated by exponential function

smoothly increasing behavior. In order to describe the fluoride release quantity F as a function of OCV test time t , Eq. (9) was formulated as an experimental equation that closely matches the experimental results.

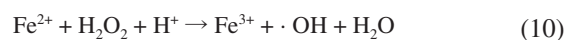
$$F(t) = a[\exp(bt) - 1] \quad (9)$$

Figure 9 shows the experimental result that was shown in Fig. 5, being fitted with Eq. (9). Coefficient a and coefficient b include information on the degradation speed and chemical stability of PEM.

4. Evaluation by the Accelerating Factor of Chemical Degradation

4.1. Acceleration of Degradation by Metal Ions

One of the factors that influence the PFSA membrane chemical degradation rate is contamination by metal ions. Among metal ions, ferrous ions in particular are known to act powerfully to accelerate PFSA membrane degradation. This is because ferrous ions have catalytic activity of the Fenton reaction that decomposes hydrogen peroxide. In fuel cells, there is a side reaction to the fuel cell reaction shown in Fig. 1, whereby there is a certain probability that hydrogen peroxide will be formed. Ferrous ions decompose the hydrogen peroxide by the Fenton reaction shown in Eq. (10), forming a highly reactive hydroxyl radical. Fe^{3+} reacts with hydrogen peroxide or other such active species and reduces to Fe^{2+} , and is thought to function repeatedly as a catalyst⁽⁷⁾.



Ferrous ions were mixed into a PEM and carefully kept in a homogeneous concentration in order to confirm the relationship between the concentration of ferrous ions and their accelerating effect of chemical degradation. An OCV test was then carried out, with the result shown in

Fig. 10. As the concentration of ferrous ions increases to 0.2, 0.3, and 0.5 $\mu\text{g}/\text{cm}^2$, the slope of the fluoride release quantity curve grows steeper, confirming that the chemical degradation is being accelerated by the ferrous ions.

At the same time, Fig. 10 also shows the results of fitting the exponential function of Eq. (9) to fluoride release quantity during the OCV test. The data for a ferrous ion concentration of 0.0 $\mu\text{g}/\text{cm}^2$ (below the lower detection limit) is the same as shown in Fig. 9. The fitting results show that the fluoride release behavior can be represented by fixing coefficient b and varying only coefficient a . Coefficient a is therefore defined as the accelerating factor of chemical degradation. The accelerating factor can be obtained by fitting Eq. (9) with the experimental fluoride release data, and it can be used as an indicator of the severity of chemical degradation. At the same time, the accelerating factor is also an indicator of the size of the effect of factors that accelerate chemical degradation. Since the accelerating factor increases as the ferrous ion concentration in the PEM increases, the accelerating factor is a function of ferrous ion concentration.

4.2. Degradation Mitigation by Radical Quencher

In order to mitigate chemical degradation of PEM, adding a radical quencher is a well-known method to assure the durability of the PFSA membrane. A radical quencher is an additive that actively reacts with a radical species and renders it harmless. This function is frequently fulfilled by metal ions or organic molecules with conjugated systems. When metal ion X is used as a radical quencher, for example, the reaction can be described by Eq. (11)⁽⁸⁾.

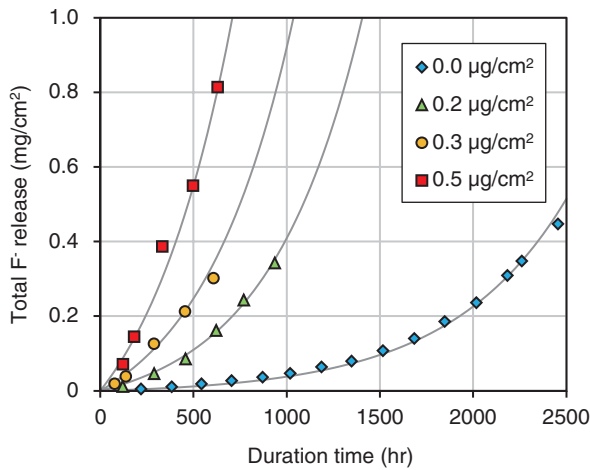
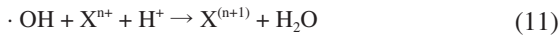


Fig. 10 Comparison of fluoride release behavior between membranes with different amounts of Fe ion contamination

$\text{X}^{(n+1)+}$ ions oxidized by hydroxyl radical are reduced to X^{n+} ions by hydrogen or some other means so that they function repeatedly as a catalyst. The effect of radical quencher in mitigating the rate of chemical degradation can also be indicated by the accelerating factor. As in the case of ferrous ion, the accelerating factor is a function of the amount of radical quencher.

Moreover, when using a radical quencher as an additive, accelerating factor becomes a function of the two factors of ferrous ion concentration and amount of additive in the PEM. In order to decide the amount of additive required to assure sufficient durability of the PEM relative to the assumed amount of ferrous ion contamination during FCV operation, it is necessary to know the relationship between the quantities of these two factors and the value of accelerating factor. There is an interaction here between the acceleration effect of ferrous ions and the mitigation effect of the radical quencher. This means that a map of the value for accelerating factor that is determined by the two factors needs to be created experimentally by combination testing.

Figure 11 shows the map of accelerating factor obtained through testing. The ferrous ion contamination amount and radical quencher additive amount are placed on horizontal axes and the blue points are experimental data of the accelerating factor obtained by OCV testing. Based on these test results, the three-dimensional map was created to represent the accelerating factor as a function of the ferrous ion contamination amount and the radical quencher additive amount. The introduction of the concept of the accelerating factor in order to represent the degree of the fluoride release rate has made it possible to not only deal quantitatively with the effect of factors that accelerate or mitigate chemical degradation, but also to indicate the size of the effect of multiple factors by a single variable.

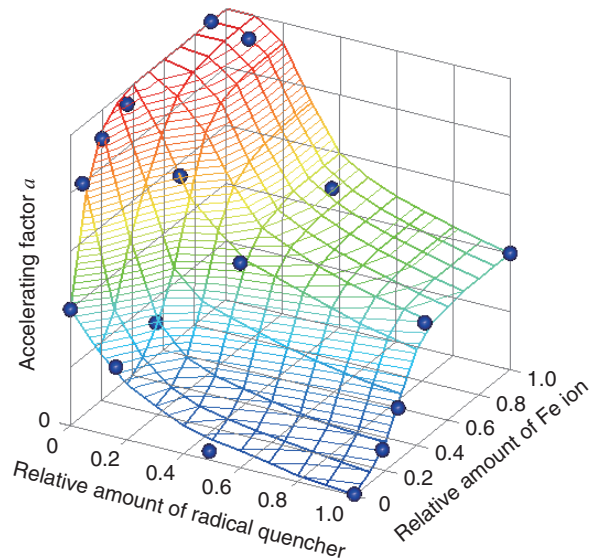


Fig. 11 3D visualized map of accelerating factor a

5. Technology for Predicting PEM Lifetime

5.1. Predicting Lifetime in a Non-Steady State

In Chapter 4, the OCV test aiming to evaluate the accelerating factor was carried out in a steady state. In order to fit the exponential function to the behavior of fluoride release quantity, it was necessary for the factors being studied, the environment in the cell, and other conditions to be kept constant during testing.

During FCV operation, however, the operating environment, the operating conditions, the amount of metal ion contamination, and other such factors that influence the rate of chemical degradation are constantly changing. Therefore the values of accelerating factor will be constantly changing. Consequently, the PEM lifetime prediction method considering actual FCV operation necessitates confirmation of whether the degradation behavior represented by the exponential function in Equation (9), which was set by OCV testing in a steady state, can also be applied in a non-steady state.

Figure 12 presents an example of non-steady state testing. As a model case, the accelerating factor was arranged to change by adding metal ion contamination in PEM, at a certain time of OCV testing. In this case, the behavior of the fluoride release cannot be represented by the single accelerating factor. Based on the experimental test results shown in Fig. 12, it is necessary to consider how to handle the mathematical formulas for non-steady states in which the accelerating factor changes during OCV testing. Figure 12 shows that the behavior of fluoride release according to test conditions (1) and (2) can be approximated by the two exponential functions in which the accelerating factor is expressed as a_1 and a_2 . Accelerating factors a_1 and a_2 are inserted into Eq. (9), Eqs. (12) and (13) below are the result.

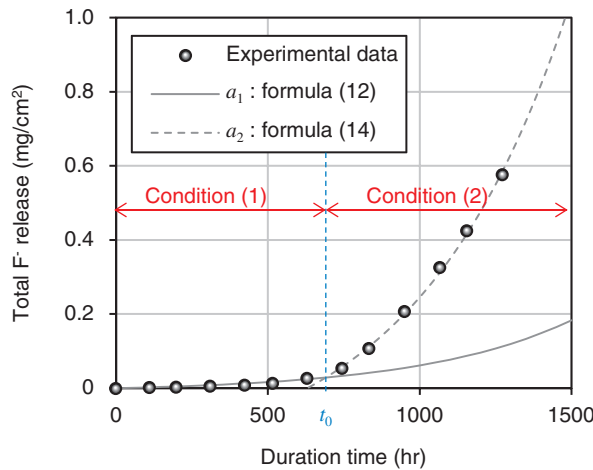


Fig. 12 Fluoride release behavior in case of non-steady state in which test condition was changed at 700 hr

$$F_1(t) = a_1[\exp(b \cdot t) - 1] \quad (12)$$

$$F_2(t) = a_2[\exp(b \cdot t) - 1] \quad (13)$$

Since Eqs. (12) and (13) both pass through the origin, Eq. (13) is fitted into Fig. 12 by shifting just the time difference Δt in the direction of the x axis. If this function is $F_2'(t)$, then:

$$F_2'(t) = a_2\{\exp[b \cdot (t - \Delta t)] - 1\} \quad (14)$$

Next, consideration was given to expressing Δt by the accelerating factors a_1 and a_2 . In Fig. 12, the time at which the testing conditions are changed so that the accelerating factor changes from a_1 to a_2 can be expressed as $t = t_0$. In that case, at t_0 it will be the case that $F_1(t_0) = F_2'(t_0) = F_2(t_0 - \Delta t)$, so that:

$$\begin{aligned} F_1(t_0) &= a_1[\exp(b \cdot t_0) - 1] \\ &= a_2\{\exp[b \cdot (t_0 - \Delta t)] - 1\} = F_2'(t_0) \end{aligned} \quad (15)$$

Solving this equation (15) for Δt results in:

$$\Delta t = t_0 - \frac{\log\left\{\frac{a_1}{a_2}[\exp(b \cdot t_0) - 1] + 1\right\}}{b} \quad (16)$$

Thus, in the case that the accelerating factor changes during durability testing at ($t = t_0$), the exponential function (13) with new accelerating factor should be displaced toward the x axis for the size of the Δt determined in Eq. (16). Then the fluoride release behavior can be expressed by connecting the exponential functions while keeping the fluoride release quantity the same at time t_0 .

In this way, it was confirmed from the test result shown in Fig. 12 that fluoride release behavior can be calculated as a function of the accelerating factor even in a non-steady state in which the value of accelerating factor changes over time. This indicates that lifetime of PEM can be predicted in the kind of non-steady state envisioning an actual FCV operating environment.

5.2. PEM Lifetime Design

A calculating method considering non-steady state was developed in order to predict PEM lifetime envisioning actual FCV operation. The results can be used to estimate excesses or deficiencies in PEM durability. Optimization of PEM design and fuel cell stack operation control was carried out according to the calculation result. This process is shown in Fig. 13. The PEM thickness is indicated by the black line, while the accelerating factor is indicated by the red line. The solid lines and the broken lines are in respectively corresponding relationships.

In order to predict PEM lifetime that envisions actual FCV operation, it is necessary to grasp the changes in accelerating factor that occur during FCV operation. The operating conditions, the amount of metal ion contamination, and other such factors that affect chemical degradation of the PEM are constantly undergoing change during FCV operation. For example, since the fuel cell

stack uses many parts that contain steel, the amount of ferrous ions that contaminate the PEM gradually increases during FCV operation. As described in section 4.2., the introduction of the accelerating factor makes it possible to represent the effects of multiple factors affecting the chemical degradation of the PEM by a single variable. The effects of these factors were confirmed using the results from bench testing that demonstrate the driving modes of an actual vehicle using a fuel cell stack with the same specifications as stacks installed in actual vehicles (the red broken line in Fig. 13).

Next, a calculation method that was developed to consider a non-steady state shown in section 5.1. was used to calculate the fluoride release quantity from the accelerating factor. Then the relationship between membrane thickness and fluoride release quantity shown in Fig. 6 was used to convert the fluoride release quantity into the amount of reduction in membrane thickness. This allowed calculations predicting a decrease in membrane thickness during FCV operation (the black broken line in Fig. 13). In the calculations, past user data was used for reference to devise an operating method sufficiently demanding in terms of chemical degradation of the PEM. The calculation results confirm that, with the initial design shown by the broken lines in Fig. 13, the accelerating factor starts increasing immediately after the FCV starts operating, and that the membrane thickness decreases at a rapid rate. These results show clearly that PEM durability is insufficient.

Because the method for predicting lifetime by calculation makes prolonged durability testing unnecessary, the durability and the lifetime of the PEM can be readily designed. Also, because it becomes possible to seek out parameters that will effectively increase PEM durability without degrading performance or energy efficiency, PEM design can be readily optimized.

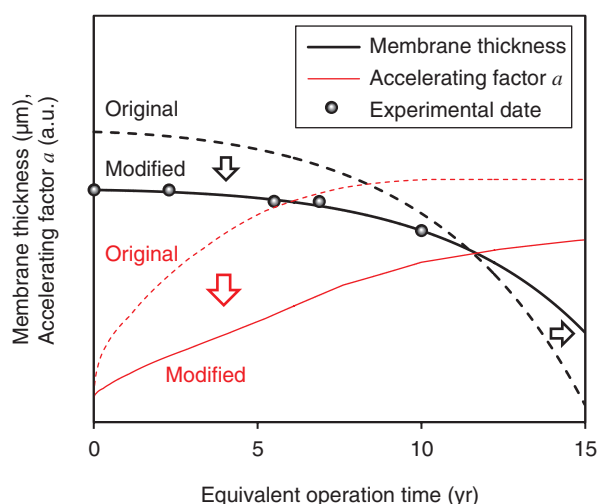


Fig. 13 Achievement of satisfying lifetime without reducing FC performance and efficiency.

As a result of this investigation of durability enhancement, the PEM design and fuel cell stack operation control were modified. The calculation results for the modified specifications are shown in Fig. 13 by the solid lines. Changes to PEM design included an increase in the amount of radical quencher added with consideration of the map in Fig. 11 obtained in section 4.2. This made it possible to hold down the increase in accelerating factor that occurred when ferrous ions contaminated the PEM. Changes made in fuel cell stack operation control also achieved control of the water content in the fuel cell stack⁽⁹⁾. This made it possible to help prevent the release of ferrous ions from metal parts and their contamination of the PEM as well as to limit the increase in the accelerating factor.

As a result of measures like these, the accelerating factor was found to increase at a lower rate than with the previous specifications, as shown by the solid red line in Fig. 13. It was also confirmed from the results for calculation of membrane thickness, as shown by the solid black line in the figure, that the rate of decrease in membrane thickness was suppressed. These results further confirm that sufficient durability is assured by the specifications incorporating the measures, and that there is an available margin for further reduction of the initial PEM thickness to improve fuel cell performance.

In Fig. 13, the experimental results of durability testing carried out with specifications incorporating the measures are also plotted. As was the case with the calculations, past user data was used for reference to devise an operating method sufficiently demanding in terms of chemical degradation of the PEM. The horizontal axis shows the equivalent years to actual vehicle operation. The test results match closely with the calculation results, confirming that the lifetime prediction method developed in the present research is highly predictive. This method has enabled quantitative evaluation of PEM durability. As a result, PEM lifetime can be predicted by calculation, without implementing durability testing over long periods of time, and the results can be provided as feedback for PEM design. This technology was applied to the 2016 model FCV, and the optimization of PEM design contributed to the balance of performance and durability achieved in the fuel cell stack.

6. Conclusion

In this report, a calculation methodology for predicting PEM lifetime was developed. The chemical degradation behavior of PFSA membrane is modeled as a function of operating time of fuel cells, which enable quantitative estimation of chemical degradation speed and durability of PEM.

- (1) It was confirmed that chemical degradation of the PFSA membrane causes the fluoride release and its quantity increases smoothly due to the two reaction mechanisms of chemical degradation — the scission of polymer main

chain and the unzipping reaction. It was also confirmed by both experiment and modeling that those behaviors can be approximated by exponential functions.

- (2) By defining the coefficient of the exponential function that approximates fluoride release behavior as the accelerating factor, it became possible to quantitatively estimate the effect of factors that accelerate or mitigate chemical degradation of the PEM. This also made it possible to represent the size of the effects of multiple factors by a single variable.
- (3) It became possible to calculate fluoride release behavior as a function of the accelerating factor even in non-steady states in which the value of the accelerating factor changes with time. This enabled PEM lifetime prediction that envisions actual FCV operation.

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