

Fuel-Cell Performance of Multiply-Crosslinked Polymer Electrolyte Membranes Prepared by Two-Step Radiation Technique

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A multiply-crosslinked polymer electrolyte membrane was prepared by the radiation-induced co-grafting of styrene and a bis(vinyl phenyl)ethane (BVPE) crosslinker into a radiation-crosslinked polytetrafluoroethylene (cPTFE) film. We then investigated its H₂/O₂ fuel-cell performance at 60 and 80°C in terms of the effect of radiation and chemical crosslinking. At 60°C, all the membranes initially exhibited similar performance, but only the cPTFE-based membranes were durable at 80°C, indicating the necessity of radiation crosslinking in the PTFE main chains. Importantly, cell performance of the multiply-crosslinked membrane was found high enough to reach that of a Nafion112 membrane. This is probably because the BVPE crosslinks in the graft component improved the membrane-electrode interface in addition to membrane durability. After severe OCV hold tests at 80 and 95°C, the performance deteriorated, while no significant change was observed in ohmic resistivity. Accordingly, our membranes seemed so chemically stable that an influence on overall performance loss could be negligible.

Introduction

Radiation-induced graft copolymerization, sometimes shortened to “radiation grafting”, is an attractive method of preparing polymer electrolyte membranes for proton exchange membrane fuel cells (PEMFCs); typically, the radiation grafting of styrene is followed by a sulfonation step. Often, in this technique, the grafted polymer chains are bridged and linked together by the addition of monomers with two or more vinyl groups to the reaction monomer solution. This so-called chemical crosslinker, e.g., divinylbenzene (DVB) or triallylcyanurate (TAC), has been investigated using various fluoropolymer substrates since the early 1990s. The optimum conditions of styrene/DVB grafting were carefully evaluated for poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)- or poly(ethylene-*alt*-tetrafluoroethylene) (ETFE)-based membranes, in terms of the balance between conductivity, mechanical properties and actual PEMFC performance, and durability (1,2). As a result, a long-term stable operation in an H₂/O₂ single cell was achieved over 4,000 or 2,100 h at a temperature of 80°C, respectively (3,4).

Independently of these ongoing studies, Yamaki et al. at JAEA reported the preparation of novel membranes by the styrene grafting into radiation-crosslinked polytetrafluoroethylene (cPTFE) films (5,6), while commercially-available non-crosslinked fluoropolymer films have mainly been considered as a base material for the grafting. This work provides the first successful example of the membranes composed of the crosslinked perfluorocarbon main chain, which is absent in Nafion and other pre-existing membranes. As the previous papers demonstrated, cPTFE was found to represent many interesting property changes from original non-crosslinked PTFE; for example, it exhibited remarkable improvements in radiation resistance and thermal or mechanical properties, and the crosslinking lowered crystallinity of PTFE with decreasing the crystallite size (7,8). Such uniqueness of the base polymer film resulted in electrolyte membranes endowed with good bulk properties. In fact, the membranes had an ion exchange capacity (IEC) higher than that of the conventional ones and, however, they showed moderate osmotic swelling properties in water and a water/methanol mixture (6).

The JAEA group then tried to combine the cPTFE main chain with the grafts crosslinked via the above-mentioned crosslinker method, expecting that the resulting “multiple” crosslinking structure will effectively improve the membrane performance and durability for PEMFC applications. A similarly named concept, “double” crosslinking was previously introduced for a membrane preparation procedure, where two types of crosslinkers, such as DVB and TAC, were simultaneously grafted with styrene in the same grafting solution (9). On the other hand, the strategy of “multiple” crosslinking is very different from this method. Figure 1 shows a schematic structure of the copolymers comprising our “multiply”-crosslinked polymer electrolyte membranes. The term “multiple” refers to a combination of a crosslinker-based graft network with a radiation-crosslinked fluoropolymer substrate: the crosslinking in both the main and side chains. Indeed, the recent paper dealt with the radiation grafting of styrene and a new crosslinker bis(vinyl phenyl)ethane (BVPE) using the base film of cPTFE (10). The important result is that the BVPE-based crosslinks in the graft chain improved chemical stability more than the conventional DVB-based ones, as well as decreased water uptake and kept reasonable proton conductivity. It follows that the BVPE crosslinker was highly compatible with radiation grafting into cPTFE films for the development of high-performance electrolyte membranes. This is probably because, in contrast to DVB, BVPE should crosslink the graft chains rather uniformly and densely even when co-grafted into a diffusion-limited, crosslinked polymer (10).

Thus we investigated here H₂/O₂ PEMFC performance of this multiply-crosslinked membrane, which comprises the cPTFE main chain and styrene/BVPE-based grafts. The membranes based on non-crosslinked PTFE or cPTFE, and grafted without any crosslinker were also obtained and compared for elucidating how the radiation or chemical crosslinking (in the main or graft chain, respectively) affected the characteristics of the membrane-electrode assembly (MEA), intermittently characterized by polarization experiments, the auxiliary current-pulse (C-P) method, electrochemical impedance spectroscopy (EIS), and H₂ permeation measurements. In addition to the initial performance, the cell operation was continued at a fixed current density for preliminary durability experiments. Finally, since the single cell tests were not long enough to assess durability of the MEA, much more severe open circuit voltage (OCV) hold tests were carried out for accelerating its performance deterioration.

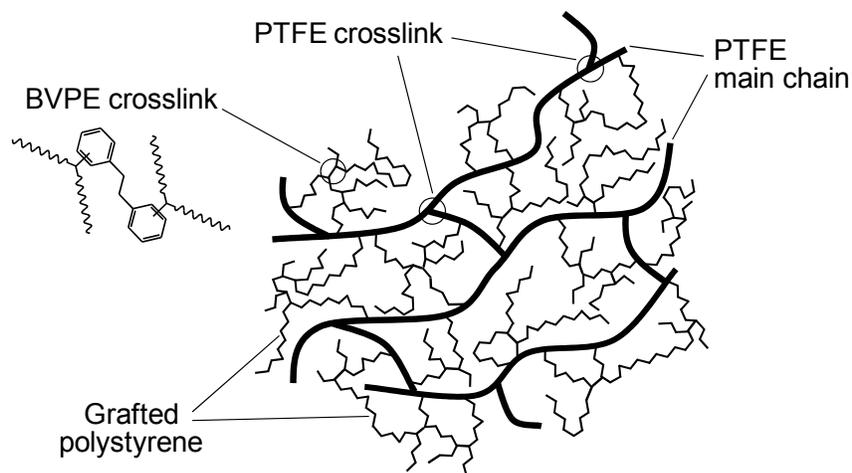


Figure 1. Schematic structure of the copolymers comprising our multiply-crosslinked membrane, indicating crosslinks in the base polymer (thick lines) as well as in the graft component.

Experimental Details

Membrane Preparation and *Ex Situ* Characterization

The multiply-crosslinked membrane was prepared by the established procedure (10). We used, as a substrate, 50 μm -thick cPTFE films obtained by irradiating PTFE films with an electron beam at $340\pm 5^\circ\text{C}$ in its molten state just above the melting temperature (327°C). The irradiation was done at a dose of 100 kGy in an O_2 -free atmosphere. The cPTFE film was irradiated again with ^{60}Co γ -rays at 15 or 60 kGy in a glass ampoule filled with Ar at room temperature. Immediately after the pre-irradiation, grafting was performed at 60°C in a deaerated mixture of styrene and BVPE (a *m,m*-, *m,p*-, and *p,p*-isomer mixture free of an inhibitor) without exposure to air. The molar fraction of BVPE in the grafting solution was 20mol%; the DVB crosslinker at such a high concentration was unable to be grafted with styrene into the cPTFE film under the present conditions (10). The degree of grafting or graft level is given by the following expression:

$$100(w_g - w_o)/w_o (\%), \quad [1]$$

where w_g and w_o are weights of the grafted and original base films, respectively. The grafted membranes were sulfonated in a 0.2 mol dm^{-3} chlorosulfonic acid/1,2-dichloroethane mixture at 50°C for 6 h. Finally, the resulting membranes were hydrolyzed and rinsed with pure water.

For comparison, styrene grafting without any crosslinker was also carried out using both the non-crosslinked PTFE and cPTFE base films. The non-crosslinked PTFE-based, BVPE-crosslinked membrane was not included in our performance test because a sufficient graft level was not achieved under the same irradiation and grafting conditions.

Table I lists the membranes for the performance test, together with their IEC, dry-state thickness, and proton conductivity. The method used for characterization of these *ex situ* membrane properties was reported elsewhere (10). Please note that the

prepared membranes were a little thicker than a Nafion112 membrane, and were twice as thick as those investigated in the recent studies, in which 25- μm thick FEP and ETFE were used as the base film (1-4).

TABLE I. List of membranes for our performance test, together with their *ex situ* properties such as IEC, dry-state thickness, and proton conductivity. A Nafion112 membrane is included for comparison.

| Membrane | Base Polymer | Grafting Monomer | Degree of Grafting (%) | Ion Exchange Capacity (mmol g^{-1}) | Dry-State Thickness (μm) | Proton Conductivity ¹ (S cm^{-1}) |
|-----------|--------------|------------------|------------------------|--|---------------------------------------|---|
| #1 | cPTFE | styrene/BVPE | 24 | 1.6 | 73 | 0.084 |
| #2 | cPTFE | styrene | 36 | 2.0 | 67 | 0.16 |
| #3 | PTFE | styrene | 26 | 1.7 | 74 | 0.12 |
| Nafion112 | – | – | – | 0.91 | 51 | 0.13 |

¹ measured at a temperature of 80°C and relative humidity of 95%.

Single Cell Testing

An MEA with the respective membranes was fabricated by sandwiching the membrane between two ELAT gas diffusion electrodes with 0.5 mg cm^{-2} Pt (type LT140EWSI, E-TEK/BASF Fuel Cell, Inc.) and with an active area of 30 cm^2 . It was assembled into a single cell comprising a serpentine flow field machined into graphite plates. We maintained a constant temperature of 60 and then 80°C for the cell, to which pure H_2 and O_2 were supplied in a counter-flow mode through a bubbler humidifier at the same temperature (in other words, the gases were fully humidified). The gas stoichiometry was 1.5 for each reactant with minimum flow rates of 60 and 30 ml min^{-1} for H_2 and O_2 , respectively. The steady-state cell operation was done at a current density of 0.5 A cm^{-2} .

Electrochemical Impedance Spectroscopy (EIS)

The EIS previously provided information on ohmic and interfacial resistances in an MEA (1-4). EIS spectra were recorded using a Zahner IM6 or IM6e system at a DC current density of 0.5 A cm^{-2} in a pseudo-galvanostat mode with a perturbation signal of 3.4 mA cm^{-2} (100 mA absolute) amplitude, in a frequency range between 0.1 Hz and 25 kHz. The resulting spectra were semi-circle like, intercepting the real axis at the low- and high-frequency end, respectively. As in the previous analysis, the high frequency intercept was interpreted as ohmic resistance, R_Ω , of the MEA, which would be governed by the resistance of the electrolyte membrane. The diameter of the semicircle, obtained by subtracting R_Ω from the resistance at the low-frequency intersection, represented the polarization resistance, R_p . The analysis of various MEAs based on radiation-grafted membranes demonstrated that the polarization resistance was a measure for assessing the quality of the membrane-electrode interface.

H_2 Permeation

In order to evaluate the reactant permeation via *in situ* measurement of the H_2 crossover rate, the cell was operated at 80°C in the H_2/N_2 mode. Fully humidified N_2 and H_2 gases were fed at a flow rate of 200 ml min^{-1} to the cathode (working electrode) and anode (reference and counter electrode), respectively. After about 1 h, a stable equilibrium potential of around 0.1 V was reached. Using a DC power supply (E3633A

DC Power Supply, Agilent Technologies) the cathode potential was increased from 0.2 to 0.8 V in steps of 0.1 V, with an equilibration time of 60 s per setpoint, and decreased again to 0.2 V. H₂ crossing over to the cathode was oxidized at the prevailing high potentials. The resulting current, i.e., the limiting current for H₂ permeation through the membrane, was recorded at the end of the equilibrium time. The H₂ crossover rate was obtained from the intercept of the linear regression line of a current vs. cell potential plot, i.e., as the current density extrapolated to 0 V.

OCV Hold Test

After the above steady-state operation, OCV hold tests were performed at different temperatures for accelerating deterioration. Both pure H₂ and O₂ were humidified at 80°C and were fed to the anode and cathode, respectively, at 200 ml min⁻¹ each and at atmospheric back-pressure.

Results and Discussion

Before testing was started, the cells were initially maintained at 60°C and conditioned at a constant current density of 0.5 A cm⁻² until stable performance was attained. After this conditioning period, the MEAs with grafted membranes #1 to #3 exhibited basically similar performance, obviously depending on their cell resistance measured by a C-P method. Thus, all the membranes were found to work well at such lower temperatures.

When a cell temperature was increased to 80°C, only the MEA based on membrane #3 exhibited lower performance than at 60°C, and thus it was not considered for further testing. The performance deterioration observed here was accompanied by an increase in the ohmic cell resistance, indicative of substantial membrane degradation due to poor chemical stability of the non-crosslinked PTFE-based membranes. Because both of non-crosslinked PTFE and cPTFE are chemically and mechanically very stable, radiation sensitivity must reasonably make a large difference between these substrate materials. Non-crosslinked PTFE undergoes a main-chain scission upon room-temperature irradiation even at relatively low doses; for example, exposure of a PTFE film to a dose of 10 kGy of γ -rays in vacuum resulted in roughly 70% loss of initial elongation at break and 60% loss of tensile strength (7). This disadvantage should justify the rationale that low-dose pre-irradiation for the grafting reaction is likely to have a tremendous impact on the properties of the resulting electrolyte membrane. On the other hand, radiation resistance of cPTFE is high enough to reach the same level as that of other less sensitive partially-fluorinated polymers such as ETFE and poly(vinylidene fluoride) (PVDF), which was explained by the depression of crystallization of polymer segments in the crosslinked chain matrix (7). Accordingly, the crosslinking of PTFE for lowering radiation sensitivity would be essential for keeping the membrane endowed with PEMFC electrolyte properties.

Figure 2 shows polarization curves and the corresponding C-P method-determined ohmic resistance values for the cell with membranes #1 and #2 at a cell temperature of 80°C in comparison to a Nafion112 membrane. The performance characteristics of the same cells are also presented in Table II. Apparently, membrane #1 exhibited the best performance among our grafted membranes, that was high enough to reach that of a

Nafion112 membrane; the cell voltages at 1.0 A cm^{-2} were 0.571 and 0.603 V for membrane #1 and Nafion112, respectively. This finding is in agreement with the similar ohmic resistance observed for both the membranes over almost the entire measured current densities (for example, 0.099 and $0.102 \text{ } \Omega \text{ cm}^2$ at 0.5 A cm^{-2} , respectively). In Nafion112, we noticed a dramatic resistance increase at high current densities starting from 1.4 A cm^{-2} as was reported in our quite recent paper (4), although it did not seem to affect so much the cell performance. In line with the discussion there, this may be ascribed to a stronger dehydration on the anode side by the effect of electro-osmotic drag and insufficient water back-diffusion, leading to an increase in the area resistance. In any case, if we can obtain thinner multiply-crosslinked membranes, we expect improved performance, exceeding that of the Nafion112 membrane-based MEA, because of their reduced ohmic resistance.

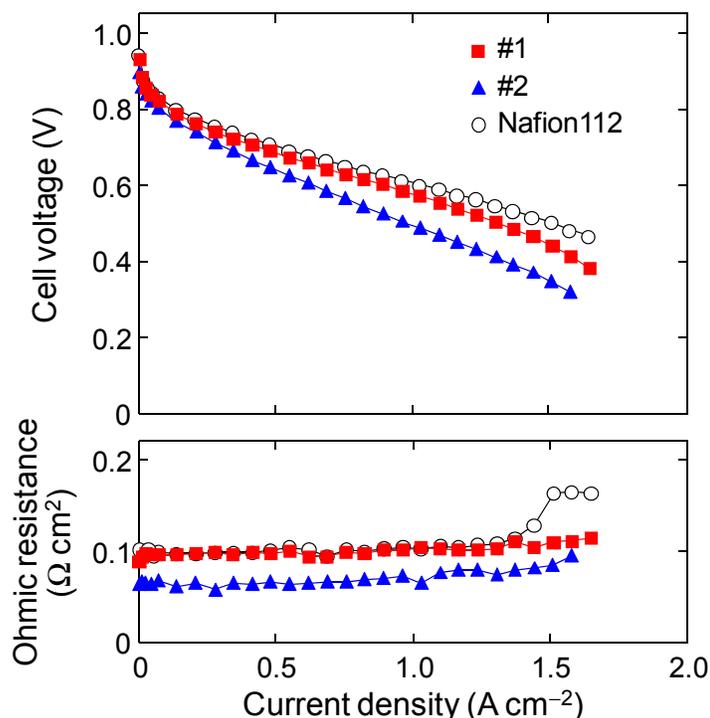


Figure 2. Single-cell performance data of the MEA with membranes #1 and #2 compared to the results of a Nafion112 membrane. The cell temperature was maintained at 80°C . The ohmic resistance was measured via the auxiliary C-P technique.

TABLE II. Performance characteristics of the MEAs based on membranes #1 and #2, which was tested in a single cell at a temperature of 80°C . The results of the Nafion112 membrane-based MEA are included for comparison.

| Membrane | OCV (V) | Cell Voltage @ 1.0 A cm^{-2} (V) | Ohmic Resistance (C-P) ¹ ($\Omega \text{ cm}^2$) | Ohmic Resistance (EIS) ² R_{Ω} ($\Omega \text{ cm}^2$) | Polarization Resistance (EIS) R_P ($\Omega \text{ cm}^2$) |
|-----------|---------|--|---|--|---|
| #1 | 0.933 | 0.571 | 0.098 | 0.105 | 0.193 |
| #2 | 0.895 | 0.487 | 0.066 | 0.084 | 0.258 |
| Nafion112 | 0.947 | 0.603 | 0.100 | 0.104 | 0.152 |

¹ determined via the auxiliary C-P method at a current density of 0.5 A cm^{-2}

² obtained by EIS at a current density of 0.5 A cm^{-2}

The OCV values extracted from Fig. 2 were 0.933, 0.895, and 0.947 V for membranes #1, #2, and Nafion112, respectively. The high value obtained for membrane #1 undoubtedly means lower H₂ crossover across the multiply-crosslinked membrane (see the second last paragraph). A Finnish group observed no significant decrease in the solubility and diffusion coefficient of H₂ and O₂ gases for the PVDF-based, styrene/BVPE-grafted membranes (11). Still, it has remained unclear so far whether this apparent crosslinker inefficiency is due to the inherent nature of BVPE itself or not. In our case, however, we found an increase in the OCV by the introduction of the BVPE crosslinker at a higher concentration. Thus, a combination with crosslinking in the PTFE main chains, i.e., the multiple-crosslinking structure, as well as the high extent of crosslinking must be considered as a good reason for the effectively reduced permeation properties. From the EIS results, we can resolve the different losses occurring in the MEA, R_{Ω} and R_p . The ohmic resistances recorded via the C-P method and EIS had a similar trend and, however, the latter consistently gave the higher values because it can still include a non-ohmic contribution, probably due to finite cable inductance at high frequencies. Compared to a Nafion112 membrane, a higher R_p value was seen for membranes #1 and #2. This tendency was observed in several previous studies on FEP- or ETFE-based grafted membranes (2-4), indicating higher interfacial losses in the grafted membranes-based MEA. It is reasonable to consider that the quality of the membrane-electrode interface is influenced to a great extent by the surface properties of the membrane. The surface of the grafted membranes could be less chemically compatible to the Nafion ionomer in the catalyst layer of the gas diffusion electrode in contrast to the both-Nafion-based membrane-electrode combination.

Next, let us compare the results between the two cPTFE-based, grafted membranes to discuss the effect of BVPE graft-chain crosslinking. The MEA with membrane #2 showed lower performance than that with membrane #1; the cell voltage at 1.0 A cm⁻² was 0.487 V. This is seemingly surprising because the BVPE-free membrane had by far the lowest cell resistance (0.066 Ω cm² at 0.5 A cm⁻²), which originates from its highest proton conductivity. Yet, there were a few similar observations for FEP- or ETFE-based, styrene/DVB-grafted membranes with various contents of crosslinking (1,2). Very clearly in Table II, the MEA with membrane #2 exhibited the highest overall impedance ($R_{\Omega} + R_p$) of 0.342 Ω cm², which can account for the lowest observed performance. Recovery from the poor membrane-electrode interface properties was similarly found for the styrene/DVB-grafted but other fluoropolymer-based membranes. The BVPE crosslinker in the graft component appeared to change the state of the membrane surface so that we could achieve improved contact giving higher cell performance. Further improvement in performance is fully expected when the interface is optimized by impregnation in a Nafion solution and/or hotpressing, which were successful for the other grafted membranes.

Figure 3 shows the cell performance as a function of time over 500 h for the MEA with membranes #1 and #2. After approximately 150 h of the 0.5 A cm⁻² operation from the beginning (including the conditioning at 60°C), the cell performance of the membrane #2-based MEA deteriorated gradually, with a concomitant increase in ohmic resistance as shown in the figure; the cell voltage and resistance changed from 0.630 V and 0.070 Ω cm² at its best (after around 113 h) to 0.576 V and 0.115 Ω cm² toward the end. On the other hand, there were no signs of degradation in membrane #1; the ohmic resistance and cell voltage were stable for the entire testing period. Membrane #1 denoted the distinct

decrease in the resistance and increase in the cell voltage after 50 h, most probably in relation to membrane proton conductivity enhanced by the temperature rise to 80°C, while membrane #2 appeared to be unaffected. This implies that the BVPE-free membrane might experience some degradation in the early stage of 80°C operation, even if it has a crosslinking structure in the PTFE main chain. It follows that the BVPE crosslinking would also be effective in enhancing membrane durability during the operation.

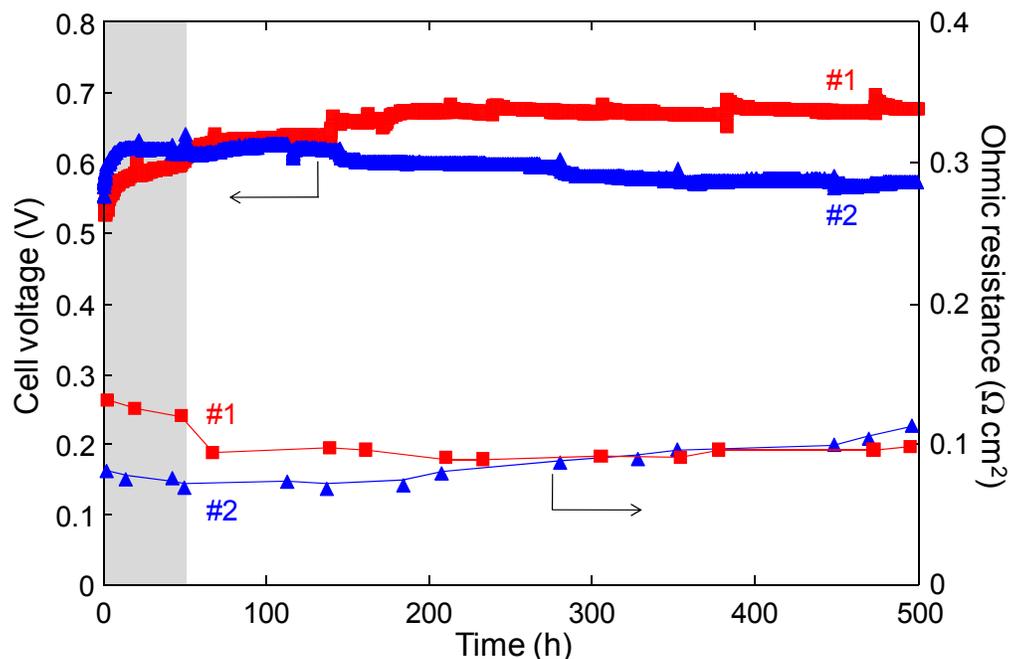


Figure 3. Single-cell durability for 500 h at a current density of 0.5 A cm^{-2} of the MEA with membranes #1 and #2, along with the cell resistance at 0.5 A cm^{-2} measured by the C-P method. The cell was conditioned at 60°C during the first ca. 50 h (colored in gray area) and then maintained at 80°C for actual operation.

The resistance values extracted from the EIS results are depicted in Fig. 4. The R_{Ω} increased continuously as also clarified by the results from the C-P method (Fig. 3). Yet, we saw a much larger increase in R_p , which would be a main reason for performance deterioration observed for the MEA with membrane #2. Please note that we cannot exclude the possibility that the increase in these two resistances might be correlated with each other; degradation of the membrane might change its surface state to make the membrane-electrode interface less compatible. The high stability of the membrane #1-based MEA over the testing period was confirmed by this figure as well. Moreover, the OCV value was 0.933 and 0.868 V for the membranes #1 and #2 at the end of steady-state operation. A comparison with the values shown in Table II could give another aspect of performance deterioration: an increase in the H_2 crossover rate, which certainly lowers OCV, must be taken into account, in other words, loss of mechanical integrity is one of the crucial factors.

Following the above stable operation for 500 h, the MEA with both the membranes were subjected to the OCV hold tests. At first, we found considerable drop in performance in the membrane #2-based MEA after the OCV hold at 80°C for a duration

of approximately 60-70 h; the maximum current density of the cell fell below 0.2 A cm^{-2} . According to the subsequent characterization, the ohmic resistance, determined via the C-P method, was increased to almost $3 \text{ } \Omega \text{ cm}^2$, which is nearly 30 times higher than that before the test (a little over $0.1 \text{ } \Omega \text{ cm}^2$ as discussed above), concurrently with poor polarization characteristics. According to these findings, the OCV conditions would be extremely severe so that the membrane degradation accelerated dramatically.

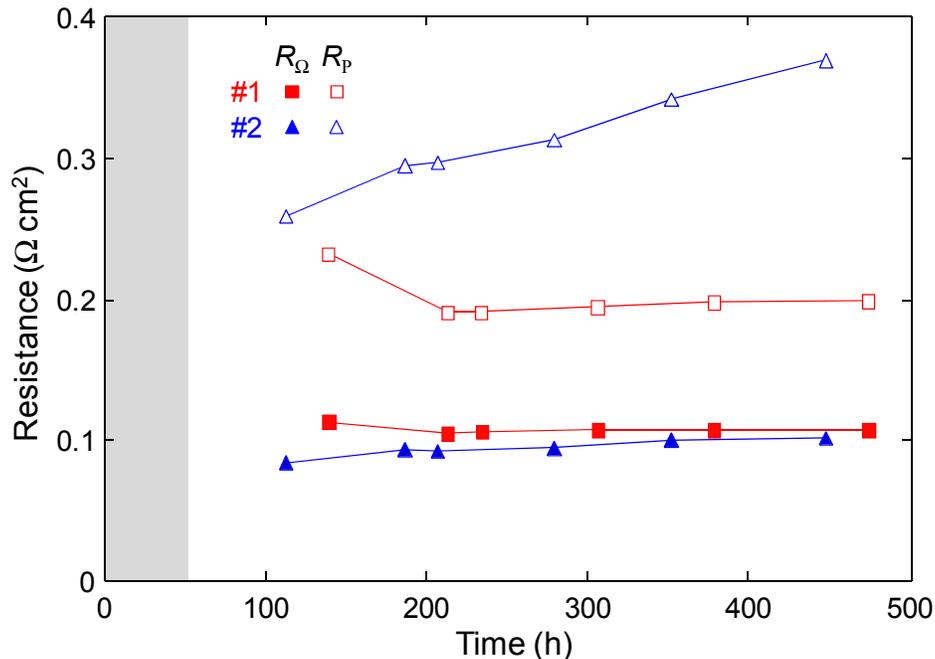


Figure 4. Ohmic (R_{Ω}) and polarization (R_p) resistance values for the MEA with membranes #1 and #2 as a function of operating time. These were extracted from the EIS results at a current density of 0.5 A cm^{-2} . The cell was conditioned at 60°C during the first ca. 50 h (colored in gray area) and then maintained at 80°C for actual operation.

Figure 5 presents polarization curves and the corresponding ohmic resistance values for the cell of the MEA with membrane #1 during the course of OCV hold tests. In contrast to membrane #2, the ohmic resistance of membrane #1 was not affected by two of the identical OCV holds, although the single-cell performance deteriorated notably. The EIS spectra obtained after each OCV hold period are shown in Fig. 6. We are able to make sure by both the measuring methods that almost no change in the ohmic resistance occurred in the MEA based on the multiply-crosslinked membrane. This indicates negligible chemical degradation of the membrane. As also seen in the figure, however, the R_p value was increased substantially at the same time, implying that a certain deterioration in the electrodes, conceivably thereby lowering the quality of membrane-electrode interface, should be a main origin of the observed performance deterioration. Very strikingly, a similar trend of deterioration was observed even after additional OCV hold was tested under much more severe OCV-hold conditions to further accelerate degradation. A 234 h OCV hold test at a cell temperature of 95°C then lowered the performance and, still, no increase in the ohmic resistance was observed, i.e., no chemical degradation took place in the membrane. Meanwhile, the performance decrease was due to a further increase in R_p .

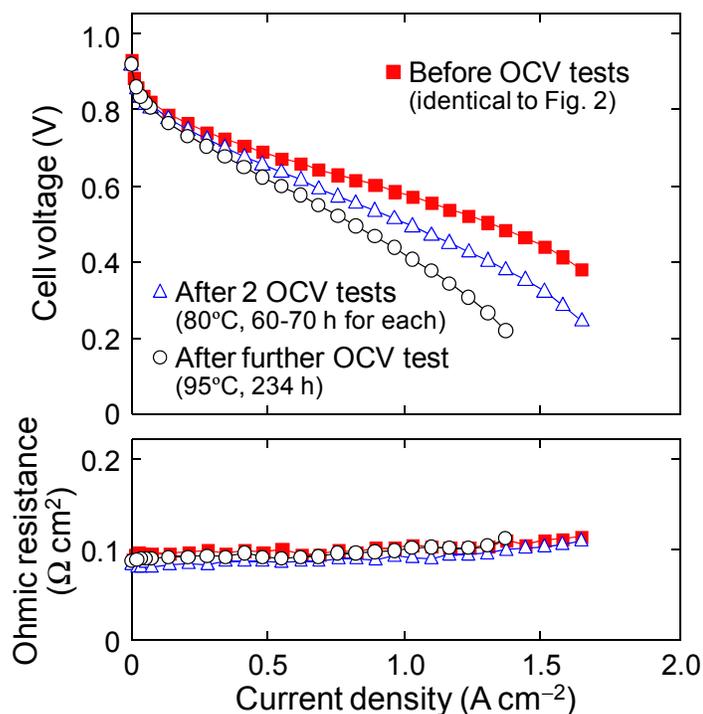


Figure 5. Change in single-cell performance of the MEA with membrane #1 during the course of OCV hold tests. The performance test was done at a cell temperature of 80°C. The ohmic resistance was measured via the auxiliary C-P technique.

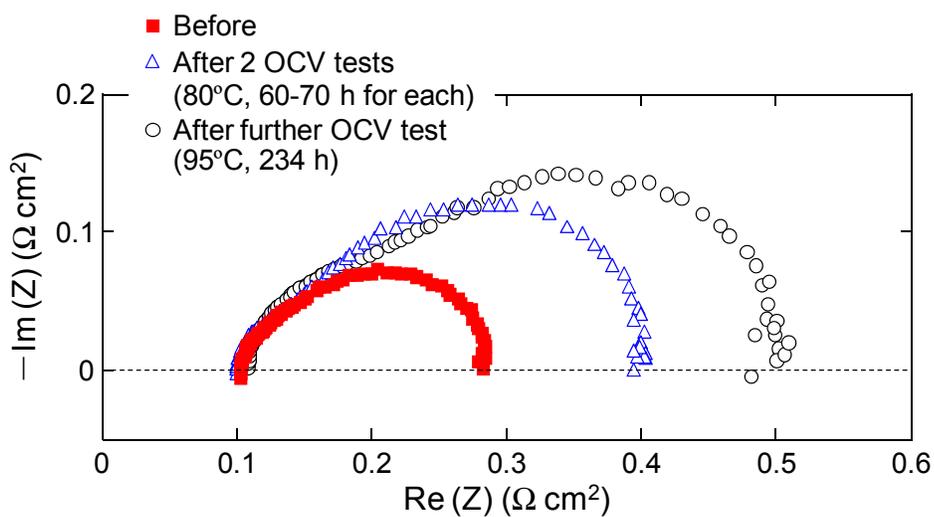


Figure 6. Change in the EIS spectra of the MEA with membrane #1 during the course of OCV hold tests. Each measurement was done at a cell temperature of 80°C.

Table III shows the results of *in situ* measurement of the H₂ crossover rate as well as variation of the OCV value, both of which can assess the reactant permeability of the electrolyte membrane. Some researchers pointed out that the permeability of the membrane for reactant gases was correlated with the rate of membrane degradation because hydrogen peroxide and radical species, likely contributing to chemical membrane degradation, are known to form through the interaction of H₂ and O₂ on the Pt catalyst surface (12,13). In this sense, it is important to investigate the H₂ crossover rate during the course of the OCV hold test for specifying the mechanism of performance deterioration. From Table III, the multiply-crosslinked membrane was found to have a 10 times lower H₂ permeability compared to a Nafion112 membrane exhibiting 1.14 mA cm⁻² under the same measurement conditions. Such a relatively low permeability has never been reported in the previous studies on the FEP- or ETFE-based, styrene/DVB-grafted membranes (1-4). Accordingly, one of the reasonable explanations is that this unprecedented superiority will give the high chemical stability to membrane #1. The H₂ permeation steadily increased after each OCV hold test, which did not correspond entirely to, but is consistent with a change in the OCV value. Considering that the crossover rate is represented by the limiting current for H₂ permeation through the membrane from the H₂ to the N₂ side, we assume that morphological changes of the membrane arising from loss of its mechanical integrity, rather than from its chemical degradation, may be responsible for the increasing H₂ crossover. Still at the end of the tests, the H₂ crossover rate was as low as 0.875 mA cm⁻².

Of particular interest is the stability improvement observed here agrees with our previous result of *ex situ* chemical stability tests using a 3% H₂O₂ aqueous solution at 60°C (10). The BVPE-based crosslinks were found to possess a higher stability even if the crosslinker concentration was the same as the DVB; at 5mol%, their degradation onset time was twice as long as DVB-based ones. The distribution of the crosslinks in the membrane is considered to be the most significant factor for determining the stability. In the case of DVB, the crosslinks were formed in the concentrated form only near the membrane surface (10,14), where the graft chains were susceptible to the attack of the reactive oxygen species. In contrast, a synergetic effect is expected as a joint result of the homogeneous crosslinking structures in the PTFE main chain and styrene/BVPE-based grafts. The satisfactory multiple crosslinking system here can allow not only for decreasing the reactant permeability but also for strengthening the chemical stability itself directly. The BVPE concentration was 20mol% in the grafting solution, and thus the achieved higher-density crosslinking is likely to bring about further stability.

TABLE III. Results of *in situ* measurement of the H₂ crossover rate as well as variation of the OCV value during the course of OCV tests for the MEA with membrane #1. The cell was kept at a temperature of 80°C during the measurement.

| | OCV (V) | H ₂ Crossover (mA cm ⁻²) |
|---|---------|---|
| Before OCV tests | 0.933 | 0.122 |
| After 2 OCV tests at 80°C for ca. 60-70 h | 0.919 | 0.482 |
| After further OCV test at 95°C for 234 h | 0.919 | 0.875 |

Conclusions

We prepared the multiply-crosslinked membrane by radiation grafting of styrene/BVPE into a cPTFE base film and then investigated its H₂/O₂ PEMFC

performance concerning the effect of the radiation or chemical crosslinking in the main or graft chain, respectively, and actual durability of the MEA by intermittent characterization using polarization experiments, the auxiliary C-P method, EIS, and H₂ permeation measurements. Only the cPTFE-based membranes were durable at 80°C, indicating that radiation crosslinking in the PTFE main chains would be absolutely essential to lower radiation sensitivity, thereby keeping PEMFC electrolyte properties. It is important that cell performance of the multiply-crosslinked membrane was found comparable to that of a Nafion112 membrane. This is probably because the BVPE crosslinks in the graft component improved not only the quality of the membrane-electrode interface but also membrane durability. Over 500 h, there were no signs of degradation, in other words, the membrane resistance and cell voltage were stable. Instead of extended operations over thousands of hours, much more severe OCV hold tests were carried out at 80 and 95°C for accelerating its performance deterioration and then assessing its durability. Strikingly, any significant change was not observed in the ohmic resistance, while a steady increase in the polarization resistance R_p occurred in the MEA. This implies that chemical degradation in the multiply-crosslinked membrane should be small enough to have a negligible influence on overall performance loss. Another advantage of the membrane was its low H₂ permeation rate, which seemed to correlate with the observed high chemical stability.

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