# A Mechanical Durability Comparison of Various Perfluocarbon Proton Exchange Membranes

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**ABSTRACT:** Mechanical endurance and degradation mechanism of Nafion211 proton exchange membrane and ePTFE/PFSA composite PEMs were investigated in this article. It was found that the shrinkage stress caused by the water-uptake is the primary source to induce the mechanical decay. The Nafion 211 is more stable when cycle-stress is lower than 1.5 MPa, while the water-uptake generating stress can reach to 2.23 MPa soaked in surroundings with condition of 25% RH and temperature at 25°C. The study also found that the ePTFE/PFSA composite PEMs are more durable than the Nafion membrane mostly due to the lower water-uptake generating shrinkage stress of 0.34–0.4 MPa (25% RH@ 25°C) but not the high yield strength or breaking strength. The PFSA/ ePTFE composite membranes can keep stable for more than 5000 cycles, which is about 40% higher than that of the pure Nafion membrane (about 3500 cycles.). For preparing durable proton exchange membrane, it is necessary to improve the proton exchange resin impregnation in the ePTFE matrix. Chemical bonding of the PTFE and the PSFI by modification of the PTFE matrix is also very effective to enhance the mechanical durability of the composite PEMs. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2671–2678, 2008

**Key words:** proton exchange membrane; mechanical degradation; mechanism; ePTFE/PFSA composite membrane; impregnation; chemical modify

## INTRODUCTION

Fuel cells using perfluorosulfonate acid proton exchange membranes (PFSA PEMs) have received much attention for reasons that they provide high power density at relatively low operating temperatures. These fuel cells are promising candidates for portable and stationary power sources, and in the future, for electric vehicle applications.[1–5] Durability issues are critical for fuel cell commercialization because the fuel cells are required to demonstrate durability of about 5000 h for automotive applications and 10,000–40,000 h for stationary applications.[6,7] Over the past decades, most degradation of the fuel cell performance has been ascribed to the decay of the membrane-electrode-assembly materials.[8–10] Hydrogen peroxide remains the most likely culprit for membrane chemical degradation, which can be readily homolyzed into peroxide radicals capable of breaking of the polymer constituent bonds.[11,12] As a result, fluorine ions release and proton conductivity lose were always appeared in the long-term testing of PEM fuel cells.[13–15] Besides, mechanical durability is also very important to the

PEM because mechanical fission of membranes in the form of pinholes and tears has been frequently observed in the decomposed PEMs.[16] By now, extensive research have been performed to study the stress behaviors of the generally used Nafion proton exchange membrane in fuel cell.[17–19] However, detail studies of the mechanical degradation mechanism of Nafion membrane, together with the high-strength ePTFE/PFSA composite PEMs should be further investigated.

Our recent studies revealed that the decomposition of Nafion polymer originating from the defect ends of the main chain, resulting in the loss of the polymer repeat units. With the increase of repeat unit loss, slim voids, and pinholes would appear in the body of proton exchange membrane. These little voids and pinhole can be enlarged by the RH-induced stress and then make the membrane high permeated to reactant gas and failure.[20] As a result, highly durable PEMs can be fabricated by fixing the polymer ionomers in the PTFE matrix micropores to increase the membrane physical stability and followed by heat-treating the polymer at 270°C after converted the polymer to Na+ form to decrease the defect groups in the polymer.[21]

This article mostly compares the durability issues of ePTFE/PFSA membrane to the widely used Nafion membrane. The ePTFE/PFSA membranes are typically fabricated by impregnating PFSA ionomers

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into porous poly (tetrafluoroethylene) membranes (expanded PTFE, or ePTFE for short).[22–32] Because of the high strength of the ePTFE matrix, the thickness of the composite membranes can be reduced greatly, resulting in the salient reduction in the loading of the expensive PFSA resin and higher area conductance.

## EXPERIMENTAL

### The proton exchange membranes

Nafion proton exchange membrane and ePTFE/PFSA composite PEMs were used in this study. Nafion® NRE 211 membranes (Nafion is a registered trademark of DuPont), fabricated with chemically stabilized perfluorosulfonic acid/PTFE copolymer were purchased from DuPont without further treatment.

The ePTFE/PFSA composite PEMs were prepared by impregnating surfactant Nafion solutions into porous PTFE membranes (ePTFE). The Nafion solutions containing Triton-100 for ePTFE impregnation were prepared by mixing 95 vol % part of as-received Nafion DE 520 solutions (5 wt %, EW 1000, Du Pont) with 5 vol % part of Triton X-100 (p-tertiary-octyl-phenoxy polyethyl alcohol, a nonionic Surfactant, Aldrich). The ePTFE membranes with 85% porosity were purchased from Shanghai Dagong Corporation. After impregnation, the membranes were soaked in distilled water for 24 h, and in isopropanol for 5 min to dissolve Triton X-100, followed by washing with distilled water. Finally, the membrane was treated with 0.5$M$ sulfuric acid and distilled water for 4 h respectively to obtain the H-form PFSA/ePTFE composite PEMs.

There are three types of ePTFE/PFSA composite PEMs used in this study. The first is the standard ePTFE/PFSA composite PEMs prepared by the method prepared elsewhere.[22–24] For the preparation, an as-received ePTFE membrane was mounted on a 15- × 15-cm plastic frame and immersed in the Nafion/Triton X-100 solution for 5 min. Then the impregnated membrane was dried at 120°C for 5 min. The impregnation and drying steps were repeated thrice to eliminate the voids or pinholes in the composite membrane.

The second ePTFE/PFSA composite PEM is prepared by a namely high impregnation method. For this preparation, the porous ePTFE membranes were mounted on 15 cm × 15 cm plastic frames and placed into a home-made impregnation system, then the impregnation system had been pumped to 5 × 10² Pa to remove the gas inner the porous PTFE. After 3-min quiescence with locking the gas pump, the ePTFE membrane was immersed into the Nafion/Triton X-100 solution. Then the air pump was unlocked to give the Nafion solution an atmospheric pressure. Then the membranes were dried at 140°C

for 150 s. The impregnation and drying steps were also repeated thrice to make the porous PTFE a complete impregnation.

The third ePTFE/PFSA composite PEM is prepared with chemical modified ePTFE membranes and high impregnation method.[33] Before the PEMs preparation, pressing, the ePTFE membranes treated with sodium-naphthalene complex solution and following with grafting N-methyl acrylamide (NMA, EMA) ionomers. Then the chemical modified ePTFE membranes were mounted on 15 cm × 15 cm plastic frames and placed into a home-made impregnation system, and then the impregnation system had been pumped to 5 × 10² Pa (absolute pressure) to remove the gas inner the porous PTFE. After 3-min quiescence with locking the gas pump, the ePTFE membrane was immersed into the Nafion/Triton X-100 solution. Then the air pump was unlocked to give the Nafion solution an atmospheric pressure. Then the membranes were dried at 140°C for 150 s. The impregnation and drying steps were also repeated thrice to make the porous PTFE a complete impregnation.

### Characterization of the proton exchange membrane

Surface and cross sections of the proton exchange membranes were examined by scanning electron microscopy (SEM, JEOL JSM-5610LV). Cross section specimens of the composite membrane were prepared by breaking the membrane under liquid nitrogen (77 K). The samples were Au-sputtered under vacuum before the SEM examination.

Mechanical strength of membranes was measured with an Electromechanical Universal Testing Machine (WDW-1C) using a Chinese Standard QB-13022-91. The samples were measured at a strain rate of 50 mm/min.

The shrinkage stresses generated by humidify or temperature change was tested by Electromechanically Universal Testing Machine with an environment chamber. The chamber was fitted on the horizontal rail of the machine load frame and had independent T/RH control. The RH control was achieved by circulating a low speed water vapor saturated gas stream with a controlled dew point. If an absolute dry condition (~ 0 RH %) is needed, the gas stream will be dehydrated with three bottle of anhydrous $CaCl_2$ before entering the clamber. The temperature was achieved by placing electric heating wires inside the chamber, and the control is achieved by placing a platinum thermoelectric couple close to the sample. During the test, the samples were cut to spindle shape (2 cm × 6 cm, with elliptical ends) and two ends of the sample were clamped by the claws of the Electromechanical Universal Testing Machine.

## Accelerated experiment and durability evaluation of the proton exchange membrane

A stress-cycle accelerated experiment was introduced to investigate the endurance of the proton exchange membrane under the mechanical stress. These experiments were performed by cutting the PEMs to spindle shape and clamped the two ends of the sample with the claws of the Electromechanical Universal Testing Machine. Then the samples were tensed with different strength interval of 60 s.

The humidity-cycle accelerates experiment and temperature-cycle was performed by mounting the PEMs on a single-cell clamp. In the humidity-cycle accelerated experiment test, the temperature inside of the single cell was kept as 90°C. Water vapor with a temperature of 90°C was purged into the flow fields for 2 min. The dry and wet cycle was repeated every 10 min. The limiting oxidation current of $H_2$ crossover through the PEMs was measured every 300 cycles. In the temperature-cycle accelerated experiment test, the single cell was cycled between 90 and 40°C every 30 min. Two type of conditions of dehumidified environment and vapor saturated environment (100 RH %) were carried to take into account of the water content on the temperature-cycle experiment. The dehumidified environment performed by dehumidified the inlet gas. And the vapor saturated environment performed by humidified the gas to 100 RH% at corresponding temperature before the gas entering the cell.

## Electrochemical characterizations of the proton exchange membranes

The electrochemical characteristics of the membranes were measured in a single PEM fuel cell. The fuel cell was fabricated as follows. First, catalyst layer consisting of Pt/C catalysts (40 wt % Pt/C, Johnson Matthey) and Nafion ionomers were transferred to the membrane surface to obtain a catalyst coated membrane (CCM).[34] Pt catalyst loadings of both electrodes were 0.2 mg Pt/cm$^2$, and the dry loadings of Nafion were 0.4 mg/cm$^2$. The GDL was placed on the anode and cathode side of the CCM to form membrane-electrode assembly (MEA). The MEA was mounted in a single-cell test fixture with serpentine flow field and a fuel cell clamp (with an active area of 25 cm$^2$). For the purpose of comparison, MEA with Nafion 211 (28.4 μm thick) membrane was also prepared and tested under the same conditions.

The proton conductance of the proton exchange membranes was measured by using an impedance analyzer (Autolab PG30/FRA, Eco Chemie, The Netherlands) under the condition of 100% RH and 60°C. The membrane (2.2 cm × 2.2 cm) was sandwiched between two Pt sheets (2 cm × 2 cm) under pressure. One Pt sheet was used as the working electrode and the other as the reference and counter electrodes. EIS was measured in the frequency range of 10 Hz and 100 kHz and the signal amplitude is set as 10 mV.

The gas permeability or crossover of the composite membranes was evaluated by measuring the limiting oxidation currents of the crossovered $H_2$ at 80°C, using the Autolab PG30/FRA. $H_2$ gas (300 sccm) was fed to the anode side of the cell while $N_2$ was fed to the cathode. The anode (i.e., DHE) was run at 0.5 mV/s and the limiting $H_2$ oxidation current was measured by applying a dynamic potential varying from 0 to 0.6 V versus SHE. The anode side, where hydrogen evolution took place, served as the counter electrode as well as the DHE reference electrode.

## RESULTS AND DISCUSSION

### The possible stress that make the proton exchange membrane mechanical decay

The frequent appearance of mechanical decay, such as pinholes and cracks, reveal that the PEM have survived much of the stress until it becomes useless. However, it is well known that the proton exchange membrane has a significantly mechanical improvement because the perfluocarbon Nafion PEM have been developed and used in the fuel cell area. Therefore, a stress-cycle experiment was introduced to investigate the stress-resistance ability of the Nafion membrane. The result (Fig. 1) reveals that the PEM was stable when the cycling stress is less than 1.5 MPa. However, when the cycling stress is larger
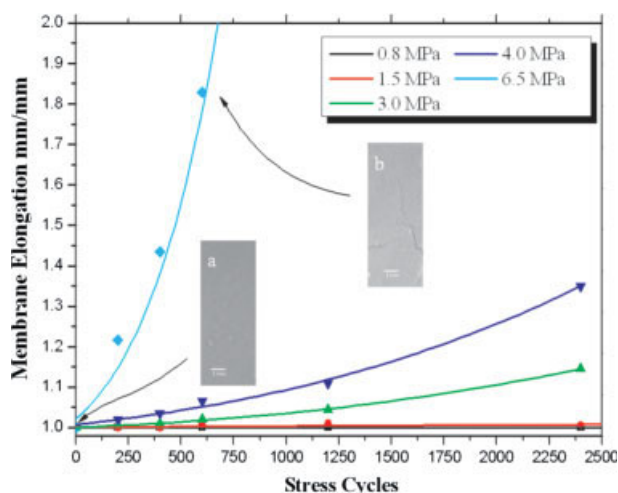


**Figure 1** Elongation of Nafion 211 membranes as a function of various fatigue stress cycles. The insert pictures are the surface SEM of: (a) as-received Nafion 211 membrane, (b) the Nafion 211 membrane after 540 cycles under stress switched between 0 and 6.5 MPa. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

## TABLE I
### Shrinkage Stress of Nafion 211 Membranes Generated by Water-Uptake and Temperature Change

| | Soaking, 25°C | 80°C, ~ 0% RH | 100RH%@80°C |
|---|---|---|---|
| Initial state | Soaking, 25°C | 80°C, ~ 0% RH | 100RH%@80°C |
| Finial state | 25% RH, 25°C | 25°C, ~ 0% RH | 100RH%@25°C |
| Shrinkage stress (MPa) | 2.23 ± 0.01 | 0.14 ± 0.01 | 1.76 ± 0.01 |

than 3.0 MPa, the dimensional changes emerges and microstructures destruction appears to the surface of proton exchange membrane. After 1000 cycles with the 4.0 MPa, the membrane was elongated and the membrane thickness change obviously. When the stress increased to 6.5 MPa, many of the cracks appeared on the surface of the PEM, which revealed that the microstructure had been greatly destroyed. Considered that the Nafion 211 membrane is mechanical strong with tensile strength of about 23–28 MPa,[35] the stability in this cycle-stress test is not satisfied. The comparison obviously mentioned that the PEM can be destroyed under lower stress during the stress fatigue than on the conditions of direct tension. For the fatigue stresses condition, the Nafion PEM can only survive under stress of about 1.5 MPa.

It is well known that the cycling stress in the fuel cell can be induced from the gas and water, which passes through the gas-diffusing layers and may introduce force vertically to the PEM. However, the impulsive pressure generated from gas and water fluid would no greater than 1 MPa based on the air compressor supplied fuel cell stacks.[36,37] Hence the mechanical destruction of the PEM is unlikely generated from the gas and water fluid.

The stress of the PEM also can be generated from dimensional extension and shrinkage of the membrane because of stress–strain pertinence. Excepting for the excessive extent of the PEM during the cell assembly, this dimension change can also be induced by the change of the cell temperature and membrane water uptake during the fuel cell performance. The shrinkage stress from water saturated to 25% RH at temperature of 25°C was shown in Table I. During the test, the samples with a spindle shape were picked up form DI water and clamped by the claws of test machine at room temperature of 25°C. Then, humidity in the chamber was reduced from original state to 25% RH. The result shown that the shrinkage stress of the PEM (at condition of 25°C, from water soaking to 25% RH) is 2.23 MPa. This value is higher than the safe fatigue stress of 1.5 MPa obtained in Figure 1.

To probe the mechanical stress induced by the temperature, an experiment of the shrinkage stress was tested by giving the PEM a temperature change under absolute dryness condition. The test was performed under the conditions of ~ 0 RH%. The value of the shrinkage stress is about 0.14 MPa (shown in Table I), which is very less than that of the humidifying change. This result mentioned that the temperature-induced shrinkage stress is not the reason of the mechanical destruction. However, in the fuel cell performance condition, the inlet humidification and the production water always provide water to the PEM. Hence it is necessary to investigate the stress behavior of the PEM induced by the temperature under the moister condition. In this study, a condition of 80°C humidified gas inlet was considered to the temperature-induced shrinkage stress research. As shown in Table I, a notable shrinkage stress about 1.76 MPa appeared under this condition. The results show that the temperature change can generate stress only with the sole condition of water involved. And this stress is most likely generated by the water uptake in the PEMs, which varies with the change of the environment temperature.

### Mechanical comparison between the homogenous PEM and the ePTFE enhanced PEM

The ePTFE/PFSA composite proton exchange membrane have been developed by W. L. Gore and Los Alamos National Laboratories in the middle of 1990s and attracted much of the attention, because it can provide desired physical strength and allows thinner membrane with lower resistance to improve the fuel cell performance.[38,39] Over the past decades, Gore also reported the long-time performance of the ePTFE-enhanced PEM, and the results demonstrated that the composite PEM is superior to the homogenous PEM, such as Nafion membrane. Because the ePTFE-enhanced PEMs and the Nafion membrane use the same proton conductive resin, the variation of the lifetime maybe generated from the promising mechanical stability of the PTFE matrix. However, the investigations on mechanical durability or mechanical properties, which related to the durability comparison between the two kind of the perfluocarbon PEMs are still rare.

Figure 2 shows the stress–strain responses of the Nafion 211 membrane and ePTFE-enhanced PEMs. The shape of the stress–strain curves can be approximately divided into two linear segments. The front of it reveals the yield strain, and the tail segment
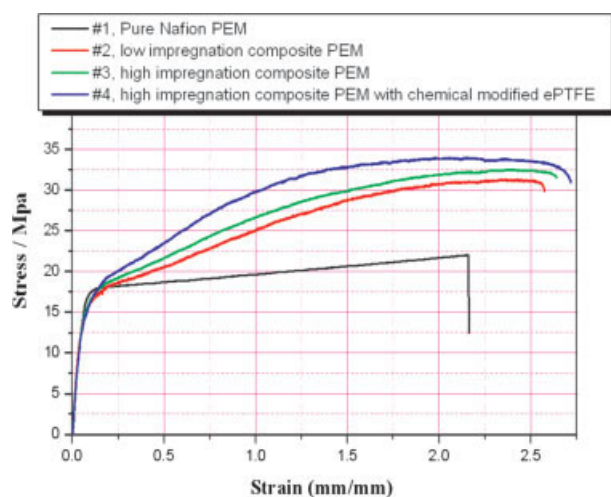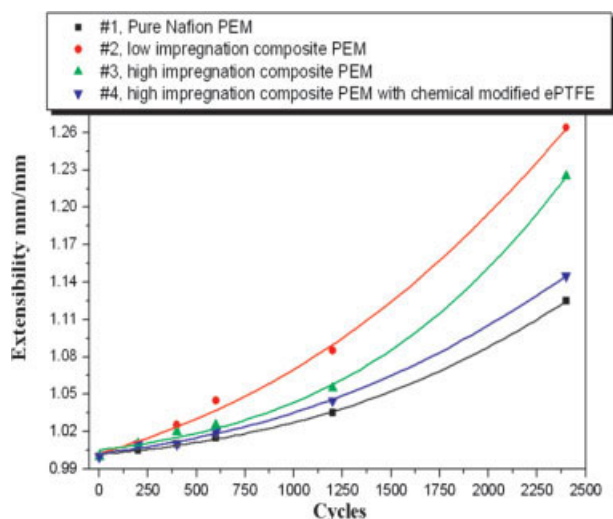
**Figure 2** Stress–strain curves of the Nafion 211 membranes and various ePTFE/PFSA composite PEMs at 25°C and 50% RH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

reveals the stress-to-failure. It is found that the ePTFE-enhanced PEMs have larger stress-to-failure and strain-to-failure than the homogenous Nafion PEM. The breaking strength of the composite PEMs is larger than 30 MPa. The increase of the Nafion impregnation improves the membrane strength (sample 3). The close bonding between the PTFE fiber and Nafion polymer by using the chemically grafting ePTFE also increases the strength of the composite PEM (sample 4). The ePTFE-enhanced PEMs tested in the series are also found to be very ductile and have the excellent strain-to-failure of more than 130% compared to the original state. The virtues of the strain-to-failure are very helpful for the PEMs by giving the PEM a potential resistibility when the membrane is exceedingly extended during the cell assembly or the fuel cell running. The other notable difference between the homogenous Nafion membrane and the composite PEMs is that the former is more stable than the latter under very low stress. It can be found from Figure 2 that there still a slight extend of all PEMs under the low stress region. In this region, the dimensional change slope of Nafion PEM is less than those of the composite PEMs. This high stability will reasonably help the membrane keeping away from mechanical decay when the membranes are affected by a low stress.

A stress-cycle experiment was introduced to compare dimensional stability of the composite PEMs with the Nafion 211 membrane under low stress (below the stress of the yield stress). A cycle stress of 2.23 MPa was selected to perform the test, which is the shrinkage stress of Nafion 211 PEMs induced by water-uptake under temperature of 25°C. As shown in Figure 3, the stability of the composite

PEMs is less than that of the Nafion 211 membrane at the same cycling stress of 2.23 MPa. This is reasonably contributed to the unsatisfied strain–stress stability of PTFE-enhanced PEMs. The improvement of the Nafion impregnation in the porous matrix (3) and the crosslinking of the matrix fibers with the impregnating Nafion polymer (4) are also effective to improve the stability of the composite PEMs may be due to the improvement of the composite structure between the PTFE and the Nafion polymers.

As mentioned earlier, the shrinkage stress induced by water-uptake change is the most probable reason that results in mechanical degradation of the proton exchange membrane. Hence, it is very necessary to investigate the stress behavior generated by the water-uptake change. Figure 4 is the stress change of the various PEMs as a function of dry time at the air-dry condition of 25°C and 40 RH%. At the beginning of the test (0 s), the PEMs are water saturated by soaking in the 25°C DI water for 2 h and then removing the liquid water on the PEMs surface. The peak stress of Nafion PEM is 2.23 MPa, and the stress can maintain above 2.1 MPa at the later of the test. This result is approximately confirmed with the shrinkage stress of reinforced PEM reported by DuPont.[40] For the composite PEMs, the peak stress at this condition is about 0.34–0.4 MPa, which is no more than a quarter of the value of Nafion PEM. The decrease of the water-uptake-generated stress in the composite membranes can be contributed to the stabilization of porous PTFE fibers in the ePTFE matrix. PTFE is water hydrophobic and does not absorb water when the membrane swells in the water.



**Figure 3** Elongation of Nafion 211 membranes and various ePTFE/PFSA composite PEMs as a function of fatigue stress cycles switched between 0 and 2.23 MPa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
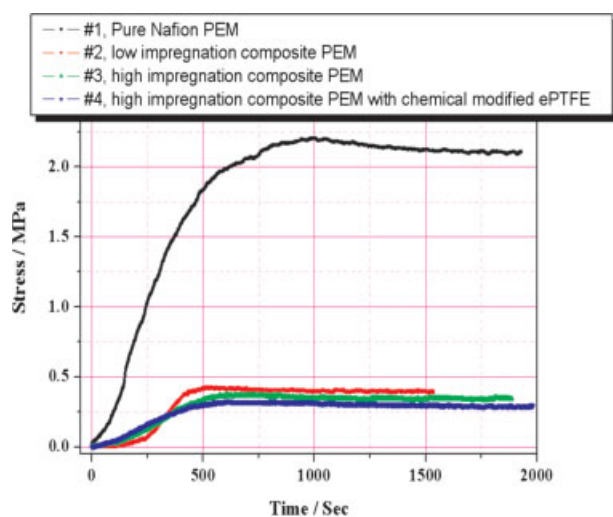
**Figure 4** Shrinkage stress of Nafion 211 membranes and various ePTFE/PFSA composite PEMs generated by water-uptake change at 25°C. The samples were picked up form DI water and clamped by the claws of test machine at room temperature of 25°C. Then humidity in the chamber was reduced to 25% RH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Hence the framework of porous PTFE can reasonably restrict the dimensional change of the membrane and resulting in low shrinkage stress due to the strain–stress relationship.

The water-uptake-generated stress durability of the composite membranes was investigated under an accelerated wet/dry cycling test. Figure 5 shows the limiting oxidation currents of the crossovered $H_2$ of the membranes as the function of the dry/wet cycles. At the early stage of the cycling experiments, the $H_2$ crossover current was in the range of 1–2 mA/cm$^2$ and the change in the $H_2$ crossover current is negligible. In the case of Nafion 211 membrane, the significant increase in the $H_2$ crossover current started after the cycling for more than 3500 times. In the case of the PFSA/ePTFE composite membranes, except for the sample 2 with low Nafion impregnation, the stability of the 3 and 4 had an obvious improvement and the significant increase of the $H_2$ crossover currents started around more than 5000 cycles. As is shown in Figure 2, the composite PEMs have lower stability at the same stress when the stress is lower than the yield stress. This improvement of the stability under the dry/wet cycles is reasonably contributed to the low-water-uptake-generated stress of the composite PEMs. In the case of Nafion 211 membrane, the membrane is under the stress cycles of about 2.1 MPa during the dry/wet cycles. However, for the composite PEMs, this stress is only about 0.34–0.4 MPa. The test also reveals a rapid crossover of the composite when the crossover

increases start. Such sudden increase in the $H_2$ crossover current indicates the formation of through and open pores of the composite membrane, indicating the debonding of the PFSA phase and ePTFE matrix. The debonding of the PFSA and ePTFE is most likely due to the incompatibility of the hydrophilic PFSA and hydrophobic PTFE.

Another important conclusion of the Figure 5 is the stability difference of the various composite PEMs. Sample 4 composite PEM, which was prepared with high PFSA impregnation and chemical-modified PTFE matrix, had the best stability in the dry/wet cycles. Sample 3 composite PEM, which was prepared with high PFSA impregnation without chemical modified PTFE matrix, also had promising stability but lower than that of sample 4. The high durability and stability of the composite PEMs prepared with chemical-modified ePTFE may come from the much better interface contact between ePTFE and PFSA resin because of the strong bonding between PFSA and ePTFE phases. The strong bonding not only decreases the hazard of interface break at the ePTFE-PFSA interface, but also slightly decreases the shrinkage stress generated by the water uptake due to the dimensional changes resistance of the PTFE fibers (Fig. 4). The sample 2 composite PEM, which was prepared by the conventional method and had low PFSA impregnation, is relatively weak in the dry/wet cycles because most exists in the surface of the membrane, and not form a composite structure in the membrane. Hence the water-uptake-generated stress is not much higher
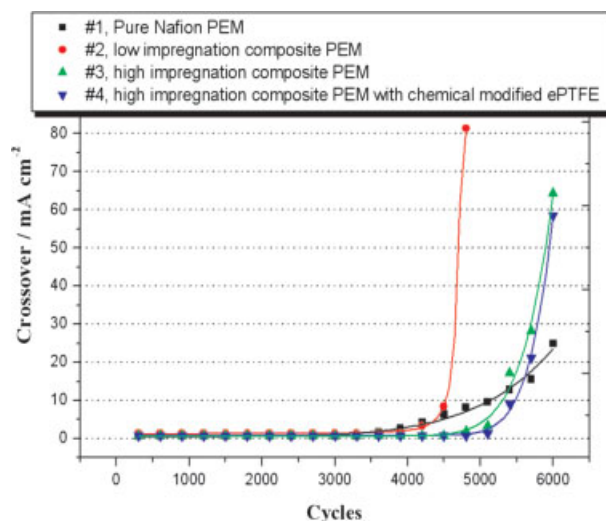


**Figure 5** $H_2$ crossover currents of Nafion 211 membranes and various ePTFE/PFSA composite PEMs as a function of the dry–wet cycles. The limiting $H_2$ oxidation current was measured at 60°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

than other two composite PEMs. But the stress mostly exists on the sides of the membrane due to the uptake-generated dimensional change. This stress should be similar to the stress value of the homogenous Nafion PEMs. And the PFSA layer should decay more rapid because the porous PTFE matrix cannot effectively prevent the resin from dimensional change and decay.

## CONCLUSIONS

Mechanical endurance of the homogenous Nafion211 PEM was investigated by an ex situ accelerated experiment, and the results indicate that PEM can be destroyed under lower stress during the stress fatigue than on conditions of direct tension. For the fatigue stresses condition, this kind of membrane is very stable under stress of lower than 1.5 MPa. Hence this homogenous PEM is reliable under normal-state water and gas fluids in the fuel cell work condition. However, the shrinkage stress generated by the water uptake is higher than the safe stress, and the value from soaking to 25% RH@ 25°C can be high to 2.23 MPa. In a wet/dry cycling test, the physical structure of PEMs can be destroyed and gas crossover have a significant increase after 3500 cycles. Hence the water-uptake-generating shrinkage stress can be viewed as the reason for mechanical decay in Nafion, which is generally used in the fuel cell. Temperature changes also may give a stress on the Nafion membrane. But the stress is very little when the membrane is absolutely dry (0.14 MPa from 80 to 25°C). The temperature change can only have a large stress on the membrane by chemical factors like the water content in the membrane (0.14 MPa from 100 RH, 80°C to 100 RH, 25°C).

The mechanical durability of ePTFE/PFSA composite PEMs was also systematically investigated, with a comparison of Nafion211 PEM. The composite PEMs are more durable than the homogenous PEM mostly due to the lower water-uptake-generating shrinkage stress of 0.34–0.4 MPa (25% RH@ 25°C) but not the high yield strength or breaking strength. Under a same cycling strength of 2.23 MPa, the structure destruction investigated by gas crossover of the composite PEM is more rapid than that of the Nafion membrane. However, in the wet/dry accelerated cycling test, the PFSA/ePTFE composite membranes can keep stable for more than 5000 cycles, which is about 40% higher than that of the pure Nafion membrane. The durability improvement cannot be achieved if the PFSA resin does not impregnate into the PTFE matrix. If most PFSA resin coated on the PEM surface, the PEMs can only survive for lower than 3500 cycles and have a sudden increase in the following cycles. Chemical bonding of the PTFE and the PSFI by modification of the PTFE matrix is also very effective to enhance the mechanical durability of the composite PEMs. With chemical-modified ePTFE, the durability of the ePTFE/PFSA composite PEMs has obvious increase in the accelerated test.

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