Durability of Perfluorosulfonic Acid Membranes for PEM Fuel Cells

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Introduction

One of the key challenges facing the commercialization of fuel cells is developing membrane electrode assemblies (MEAs) that can meet industry durability targets. Polymer electrolyte membranes (PEMs) are the most promising membranes for automotive applications. These membranes serve to conduct protons from the anode electrode to the cathode electrode of the fuel cell while preventing crossover of the reactant gases, H_2 and O_2. State of the art PEM fuel cells for high power density operation utilize perfluorosulfonic acid (PFSA) membranes that are typically no more than 25 microns thick. To be successful in automotive application, these membranes must survive 10 years in a vehicle and 5,500 hours of operation including transient operation with start-stop and freeze-thaw cycles. The requirements on the chemical and mechanical stability of these thin membranes are significantly more demanding compared to the thick membranes (100-200 μm) used in the past. Fuel cells cannot operate effectively if even small amounts of gas are able to permeate the membrane through microscopic pinholes. Ultimately, fuel cells fail because such pinholes develop and propagate within the polymer membranes. It is critical that these membranes are mechanically and chemically durable over the range of conditions experienced during fuel cell operation.

During operation, PEM fuel cells will see temperatures ranging from sub-zero to 100^oC and a variety of humidification levels including exposure to liquid water. As the PFSA membranes absorb water they undergo significant volumetric swelling. Nafion® NR-111 (25 μm solution-cast) adsorbs 50 wt% of water at 100^oC, and undergoes 10 and 15% linear expansion at 23^oC and 100^oC respectively[1]. Upon dehydration, PFSA membranes shrink to smaller than their original size. For example, Nafion® shrinks by about 7 and 11% from its initial area upon dehydration after soaking in water at 80^oC and 100^oC, respectively [2,5]. These membranes will experience tensile, compressive and shear stresses as their dimensions change in a constrained fuel cell architecture with fluctuations in temperature and humidity level. The membranes also experience other stresses during fuel cell operation. For example, the membranes are compressed between sheets of carbon based diffusion media at pressures up to 3.5MPa. As in other engineering materials, mechanical fatigue can reduce the membrane strength over time, leading to mechanical membrane degradation and reduced fuel cell durability.

Further complicating matters, the glass transition temperature of perfluorosulfonic acid membranes such as Nafion occurs within fuel cell operating temperature range, $60\text{-}100^oC$[3,4,5]. Thus, the polymer experiences structural as well as dimensional changes during fuel cell operation. Furthermore, perfluorosulfonic acid membranes are susceptible to chemical attack by peroxide radicals, which subsequently impacts the mechanical integrity of the membrane.

An *in situ* test has been developed to study the mechanical durability of fuel cell membranes by cycling the humidity of the membrane in the absence of electric potential or reactive gases. Previously reported results show that the stresses imposed solely by cycling between wet and dry operating conditions can create membrane failure leading to gas crossover[5,6]. This paper discusses the impact of the severity of the humidity swing and also the compounding effects of chemical degradation on membrane mechanical durability. We also investigate the impact of varying membrane types, including the effects of membrane processing method and mechanical reinforcement. Finally, we will discuss the impact of humidity cycling on the mechanical durability of hydrocarbon and partially-fluorinated hydrocarbon proton exchange membranes.

Experimental

In this study we subject membranes to cyclic stresses by intermittently flowing wet and dry inert gases over the membrane in a non-operating fuel cell. Membrane electrode assemblies (MEAs) with anode and cathode Pt loadings of 0.4 mg/cm_2 were built into $50cm^2$ cells using flow fields with 2mm wide straight channels separated by 2mm lands. The MEAs were compressed between two pieces of commercially available carbon fiber gas diffusion media. The cycle consisted of flowing 2.0 SLPM of 150%RH air over both the anode and cathode sides of the MEA for 2 minutes followed by flowing 2.0 SLPM of dry air over both sides of the cell for 2 minutes. The tests ran isothermally at 80^oC with no back pressure. To ensure that any failures that occurred were induced solely by mechanical stresses, no H_2 was used and no current was drawn from the cell during the test. Membrane failure was determined by periodically measuring the flow of air crossing the membrane when a 3 psi pressure was applied to one side of the cell.

The mechanical properties of the membranes used in this study were also evaluated. Data was collected for both the machine (MD) and transverse (TD) direction for all samples. Tensile tests were conducted using ASTM method D882. The tests were conducted at 23^oC and 50% RH using a 25 mm wide sample with 50 mm between the grips and a loading rate of 500mm/min. Tests were also conducted submerged in deionized water at 80°C. Tear tests were conducted using ASTM method D624 (Die B). The tests were conducted at 23^oC and 50% RH with a loading rate of 50mm/min. The peak loads and the energies to break are determined as described in the ASTM procedures. Averages and standard deviations for both the tensile and tear tests are based of five replicate samples.

The dimensional stability of the PFSA membranes was measured as well. The membranes were cut into 200mm by 125mm sheets. The membranes were equilibrated at 23^oC and 35% RH overnight before recording the initial dimensions. The membranes were then dried at 80°C for 1h and the dimensions were measured. The membranes were subsequently soaked in deionized water at 80°C for 2h and the dimensions were measured again. The membranes were then dried again at 80°C for 1h and the dimensions were measured. Finally, the membranes were allowed to equilibrate at 23^oC and 35% RH overnight before recording the final dimensions.

Effect of Membrane Type

There are a variety of types of PFSA membranes available. Equivalent weights typically range from 700 to 1100. The membrane processing method can also vary. DuPont™ manufactures a solution-cast form of hydrolyzed Nafion 1100 EW 25μm membrane as NR-111 (currently sold as NRE-211). Ion Power™ manufactures an alternate form of hydrolyzed Nafion® 1100 EW 25μm membrane as N111-IP. Both of these Nafion® membranes are homogeneous and are made using 1100 EW Nafion®. There are also methods to mechanically reinforce PFSA membranes. For example, Gore™ manufactures expanded polytetraflouroethylene (ePTFE) micro reinforced composite PFSA membranes under the Gore™ Primea® MEA product line. These reinforced membranes have been shown to have improved tear resistance and dimensional stability compared to homogeneous membranes[7].

The homogeneous DuPont™ NR-111, the homogeneous Ion Power™ N111-IP and the composite Gore™ Primea® Series 57 membranes were tested for durability under inert RH cycling conditions described above. Two cells were run for each type of MEA. The progression of crossover leak as a function of the number of humidity cycles is shown in Figure 1. Failure in these tests is defined as 10 sccm crossover. The NR-111 fails after about 4500 cycles, whereas after 10000 cycles there was no detectable leak in the N111-IP membrane. The composite Gore™ Primea® MEA fails due to crossover between 6000-7000 cycles. These results indicate that mechanical reinforcement is not sufficient to prevent mechanical failure caused by humidity cycling.

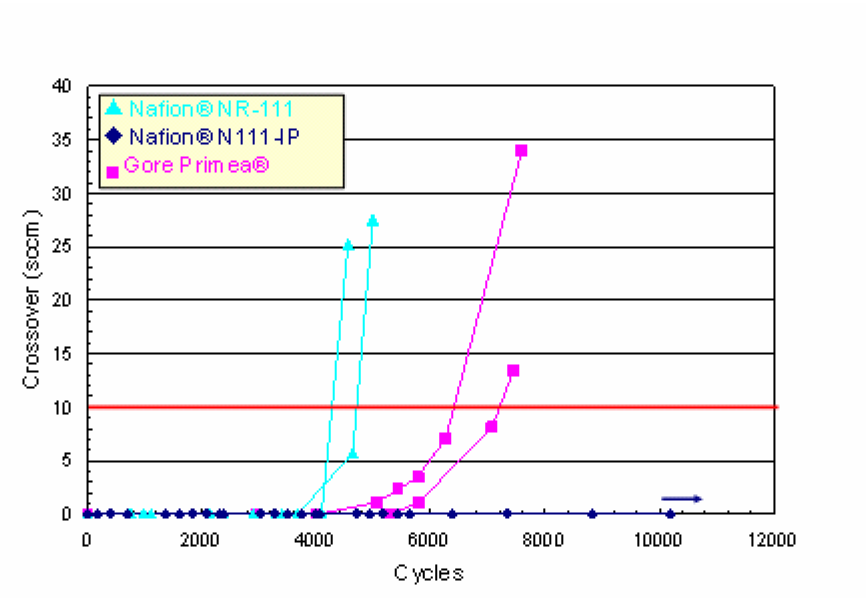

Figure 1. Crossover leak as a function of number of humidity cycles during inert RH cycling of NR-111 (▲) , N111-IP (◆), and Gore™ Primea® (■) PFSA membranes. The N111-IP tests were stopped before any crossover was measured. Line at 10 sccm indicates test failure criteria.

The mechanical properties of the membranes used in this study were measured to determine if there was any correlation between these properties and the results of the humidity cycling tests. The tensile test results of NR-111, N111-IP and Gore™ Primea® membranes are shown in Table 1. Tensile Strength, Yield Strength, Elongation at Break and Young's Modulus are reported. None of these properties stands out as significantly different for the N111-IP compared to the other two membranes that suggest it would exhibit superior durability in the humidity cycling test.

The tear test results are summarized in Figure 2. The peak load and the energy to break for the membranes are recorded. It was found that the Nafion® N111-IP exhibits the lowest peak load and the smallest energy to break of the three membranes tested. Thus, its superior durability in the humidity cycling test cannot be attributed to better tear resistance. Also, as shown previously[7], the composite Gore™ Primea® membrane is the most tear resistant. This enhancement in tear resistance has been attributed to the ePTFE reinforcement[7].

Table 1 Tensile Test results for PFSA membranes at 50% RH and 23°C and submerged in deionized water at 80°C. MD = machine direction, TD = transverse direction, +/- = standard deviation

Membrane		NR-111				N111-IP				Gore™ Primea®			
	unit	MD	+/-	TD	+/-	MD	+/-	TD	+/-	MD	+/-	TD	+/-
50% RH, 23°C													
Tensile Strength	MPa	30.5	3.9	28.0	3.0	32.6	3.6	37.5	4.0	35.0	1.4	32.3	3.3
Yield Strength (2% offset)	MPa	14.4	0.0	14.0	0.2	14.1	0.6	14.9	0.2	18.0	0.5	15.6	0.8
Elongation	%	253	49	235	36	176	19	141	20	196	37	147	29
Young's Modulus	MPa	272	21	253	17	304	8	319	7	324	51	340	19
submerged, 80°C													
Tensile Strength	MPa	8.9	2.9	9.5	2.1	17.2	5.5	16.1	8.4	18.4	0.7	15.1	0.8
Yield Strength (2% offset)	MPa	4.4	0.3	4.6	0.2	5.0	5.0	5.3	0.4	5.2	0.2	4.1	0.1
Elongation	%	159	127	188	117	193	81	127	90	153	22	157	26
Young's Modulus	MPa	23.9	3.8	25.1	5.1	45.0	5.6	51.5	4.2	58.0	2.7	28.3	1.7

The results of the dimensional stability testing are shown in Figure 3. The % swelling is defined as the area change from the initial dimensions to those measured after soaking for 2h at 80°C. The % shrinking is defined as the area change from the initial dimensions to those measured after drying for 1h at 80°C after the soak. Note that these values are negative. The % Swollen – Shrunken is defined as the area change from the swollen dimensions after soaking for 2h at 80°C to the shrunken dimensions after drying for 1h at 80°C. The Nafion® N111-IP exhibits the smallest amount of swelling when submerged at 80°C and also the smallest difference in area changed between the swollen and shrunken states. More work is required to determine if this smaller dimensional change leads to better mechanical durability during humidity cycling. One can hypothesize that the smaller the dimensional change of a membrane upon cycling between wet and dry, the lower the stress on the membrane would be when constrained in a fuel cell.

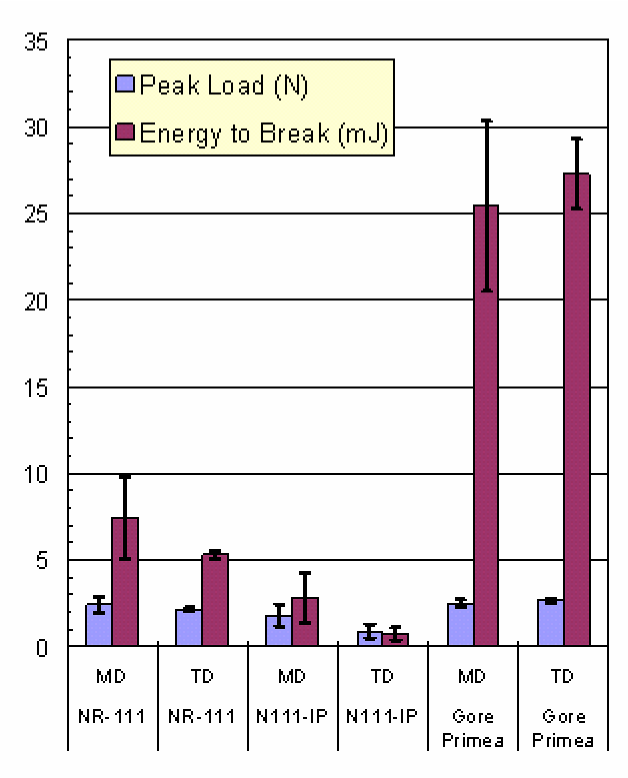

Figure 2 Tear test results for PFSA membranes at 50% RH and 23°C

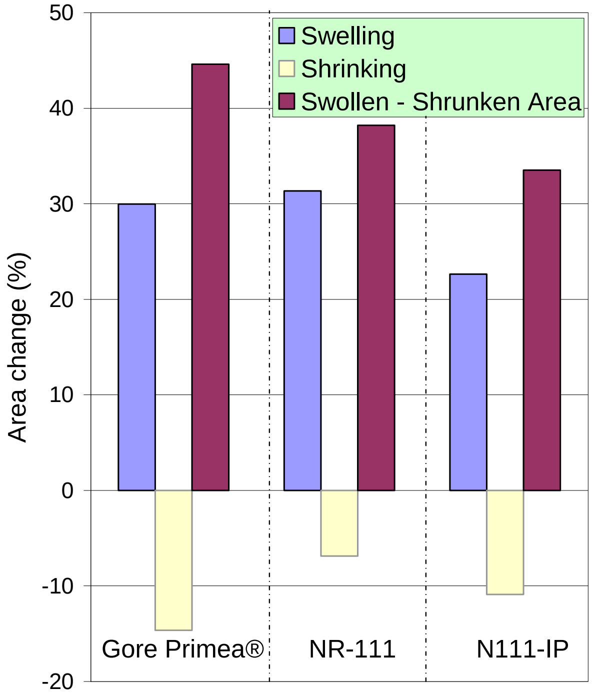

Figure 3 Dimensional Stability of PFSA membranes.

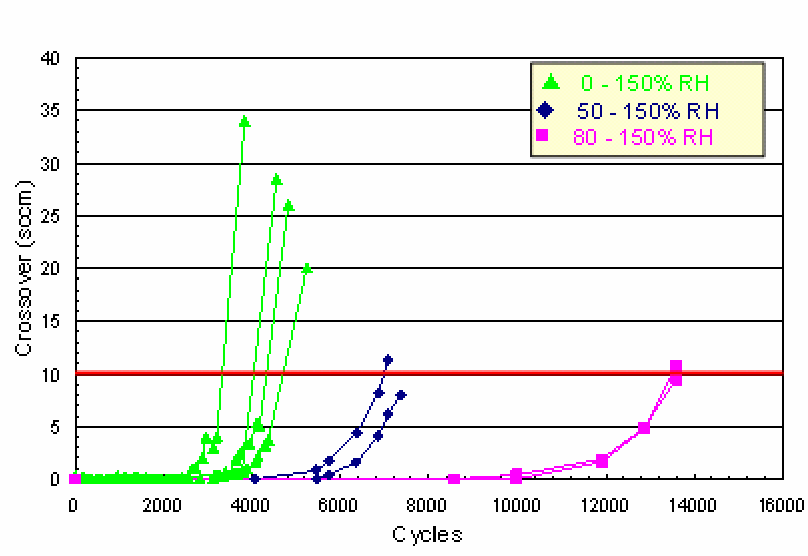

Figure 4. Crossover leak as a function of number of humidity cycles of Gore™ Primea® MEAs during inert RH cycling tests. Cycle: 2.5 min at 150%RH/ 3.5 min at 0% (▲) , 50% (◆), and 80% RH (■). Line at 10 sccm indicates test failure criteria.

Effect of RH Swing

Thus far we have shown that cycling between bone dry operation and exposure to liquid water causes mechanical failure of PFSA membranes. However, under expected operating conditions, the membranes may never be completely dried out. Therefore we have studied the impact of humidity cycling without completely drying out the membrane. Figure 4 shows results of humidity cycling of Gore™ Primea® MEAs from either 0%, 50%, or 80% RH to supersaturated conditions. In these tests the RH cycle consisted of 2.5 minutes at 150% RH followed by 3.5 minutes at drier conditions. All tests were conducted at 80°C and no back pressure. The time to crossover failure increases from about 4000 to 7000 to 14,000 cycles and the magnitude of the RH swing is decreased. These results indicate that the smaller the magnitude of the humidity swing, the longer the life of the membrane. However, even relatively small RH swings, such as from 80% RH to liquid water, will eventually leady to mechanical membrane failure. These types of RH swings would certainly be expected during fuel cell operation.

Effect of Electrochemical Potential

While PFSA membranes are chemically very stable, they are known to degrade in the fuel cell environment via peroxyl-radical attack [7], strongly enhanced in the presence of trace iron contamination[8]. The mechanism is quite complicated, depending on ionomer structure, iron level, catalyst components, electrode design, relative humidity, temperature and other factors. Fortunately, several research groups are focused on understanding this mechanism, and good progress is being made[9].

To evaluate the impact of chemical degradation on membrane mechanical failure, we have run our in-situ 50 cm^2 RH cycling test with reactive gases (H_2 and air) and at a constant current density of 0.1 A/cm^2. In these tests both the anode and cathode stoichiometries were 20 to enable essential uniform relative humidity throughout the cell. The other conditions were identical to our inert gas tests (2 minute 0% RH feed/2 minute 150% RH feed, 80ºC, 0 kPag). Failure in these tests was again defined at 10 sccm crossover leak. The results for both homogeneous 25 µm Nafion® 1100EW membranes and the reinforced Gore™ Primea® MEAs are shown in Table 2.

Table 2 Comparison of RH cycling with inert gases vs. at 0.1A/cm^2

MEA	Cycles to Failure w/o load	Cycles to Failure @ 0.1 A/cm2
DuPont™ Nafion® (NR-111)	4500	800
Ion Power™ Nafion® (N111-IP)	10000+	1800
Gore™ Primea®	6000-7000	1300

For all membranes, operation at 0.1 A/ cm^2 significantly accelerates membrane failure. The failure times for the both the DuPont™ NR-111 and the Gore™ Primea® MEAs are reduced by at least a factor of five relative to the inert humidity cycling tests. Note that the Ion

Power™ N111-IP did not run to failure in the inert tests, but developed crossover leaks after 1800 humidity cycles at 0.1 A/cm^2, indicating at least a fivefold lifetime reduction. Clearly, chemical degradation of these PFSA membranes causes mechanical weakening. Further investigation is required to fully understand the interaction between chemical and mechanical degradation.

Hydrocarbon Membranes

There has been significant research recently on alternatives to perfluorinated membranes. The primary motivations are: 1) the possibility of decreased membrane cost at lower automotive volumes and 2) the elimination of fluoride to decrease metal plate corrosion problems, thus enabling the use of more affordable plate materials. The most common family of materials under investigation is hydrocarbon sulfonic and phosphonic acid polymer membranes. Most of this work has focused on membrane performance, particularly conductivity at high temperatures and low relative humidity. However, little attention has been given to the durability of these materials.

We have tested a wide variety of hydrocarbon and partially-fluorinated hydrocarbon proton-conductive membranes for mechanical durability. The results from the *in-situ* humidity cycling (0-150% RH) tests at 80ºC are shown in Figure 5. None of the hydrocarbon or partially-fluorinated hydrocarbon polymer membranes lasted for more than 400 cycles before developing a crossover leak. This is an order of magnitude lower than the least durable of the PFSA membranes. While the development of proton conductive hydrocarbon membranes is in its early stages relatively compared to PFSA membranes, these results suggest that those developing these materials must do so bearing in mind their susceptibility to mechanical failure caused by humidity cycling.

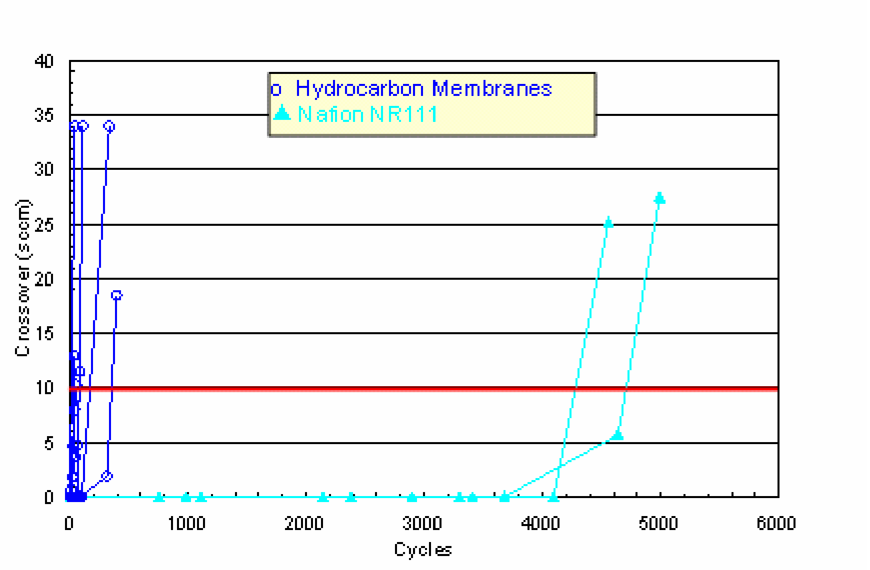

Figure 5. Crossover leak as a function of number of humidity cycles during inert RH cycling of Nafion® NR-111 (▲) and hydrocarbon and partially-fluorinated hydrocarbon (o) membranes. Line at 10 sccm indicates test failure criteria.

Conclusions

We have shown that repeated cycling between wet and dry conditions in a fuel cell environment can generate failure of PFSA membranes. The ability of these membranes to withstand humidity cycling is extremely dependent of the processing conditions, as membranes manufactured from the same base ionomer can have significantly varying durability results. While mechanical reinforcement with expanded PTFE can extend the lifetime of PFSA membranes, it is not sufficient to prevent mechanical failure in the presence of humidity cycling. Characterization of the mechanical properties and dimensional stability of PFSA membranes has been conducted, but no direct correlation has been found between these measurements and the membrane's ability to withstand humidity cycling.

The rate of mechanical failure in fuel cell humidity cycling tests is inversely related to the magnitude of the humidity swing. Humidity swings as small as 80-150% RH can still generate mechanical failure after thousands of cycles. Accelerated testing by cycling between fully dry and wet conditions can be used as an indication of mechanical durability under milder humidity swings that occur during fuel cell operation. We have also shown the mechanical failure is significantly further accelerated by the presence of an electrochemical load. Operating at $0.1A/cm_2$ during humidity cycling reduces lifetimes by a factor of five or more relative to inert conditions.

Finally, we have shown that hydrocarbon and partially-fluorinated hydrocarbon membranes are extremely susceptible to mechanical failure during humidity cycling and that the durability of these materials must be considered during their development. In order to accelerate the development of both new membrane materials and new processing methods, direct testing of membrane durability under humidity cycling conditions is necessary, as *ex-situ* measurements of membrane mechanical properties are not sufficient to predict mechanical durability.

Acknowledgements

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