V.I.1 Materials and Modules for Low-Cost, High-Performance Fuel Cell Humidifiers

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Subcontractor:
dPoint Technologies, Inc.
Vancouver, British Columbia, CANADA

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Fiscal Year (FY) 2012 Objectives

- Demonstrate a durable, high-performance water transport membrane.
- Build and test a compact, low-cost, membrane-based module utilizing that membrane for use in an automotive stationary and/or portable fuel cell water transport exchangers.
- Model and show high volume costs associated with membrane and module.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan in Task 7, "Develop balance of plant components":

(A) Durability
(B) Cost
(C) Performance

FY 2012 Accomplishments

- Humidifier operating conditions for stationary, automotive and portable fuel cells have been established using input from original equipment manufacturers (OEMs) and other stakeholders.
- A range of humidifier membrane materials have been prepared and characterized.
- Permeance, air permeability and membrane durability testing for a range of humidifier membranes have been performed. One class of membranes, GORE™ M311.05[1*], has been identified as particularly promising.
- A room temperature static water vapor transport test protocol has been developed for rapid permeance testing and/or quality control of humidifier membranes.
- Performance and durability testing of the GORE™ M311.05 membrane indicate that it has acceptable performance for automotive humidifier modules, with a projected loss in performance of 20-25% in 5,000 hours.
- Humidifier membrane and module cost modeling have shown that the humidifier module using the preferred Gore humidifier membrane has projected a module cost at a volume level of 500,000 vehicles per year of less than $150 per module.
- A high-performance humidifier module has been designed and sub-scale prototypes indicate that all automotive specifications can be met with the full-scale module. The initial full-scale modules are under construction, and will be tested in the final stages of the program, prior to delivery of a prototype to DOE.

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Introduction

Today it is essential to humidify the gases supplied to the fuel cell inlets for automotive and many stationary fuel cell stack designs. In this work, we are providing a new, inexpensive, composite membrane capable of very high water vapor transport and low air cross-over. The composite structure has been designed to allow lower total cost while still meeting automotive and stationary humidifier water transport and durability targets.

Because the transport rates of these new materials are so high, current planar membrane humidifier designs are not capable of fully utilizing the high rates. Therefore, the project is using an innovative, low-cost humidifier module with customized channel geometries that can take advantage

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of the high water transport rates. By having a materials development effort integrated with a humidifier module-system design and build project, we will be able to effectively exploit the improved material properties in an actual device.

Approach

Perfluorosulfonic acid (PFSA) membranes fulfill most of the requirements for the water transport media at the heart of the planar membrane water exchanger. They fall short primarily on cost, and secondarily on durability, especially when they are made thin to increase performance and lower cost. Gore has developed a composite water vapor transport membrane that has overcome both of these limitations [1]. The basic composite structure consists of a very thin ionomer layer sandwiched between two microporous polymer layers. The ionomer layer provides the active water transport and provides an impermeable layer to prevent gas cross-over. The water transport rate can be engineered to be very high either through the use of a material that has very high inherent water transport rates (e.g., PFSA polymers), or by making it extremely thin (e.g., <5 µm). The microporous layer provides three critical features: first it protects the thin ionomer layer from mechanical damage during handling; second, it confers strength to the thin layer allowing it to be more durable during use. Third, it offers a strong, protective support layer for placement of a macroporous gas diffusion layer.

Our subcontractor, dPoint Technologies, has developed an innovative pleated planar membrane humidifier that is able to achieve automotive OEM water transport and pressure drop requirements. The pleated design utilizes existing low-cost, high-volume pleating equipment that is used to manufacture air filters for automotive and heating, ventilation and air conditioning applications. The pleated humidifier is a proven technology that dPoint has been developing in cooperation with several major automotive OEMs. Further improvement in humidifier size, cost and performance is possible through the use of the Gore membrane and optimizing the flow field channel design to take full advantage of this new membrane.

Results

During the past year, the membrane focus of the work has been on developing and testing a polymer composite structure of a thin PFSA polymer sandwiched between two expanded polytetrafluoroethylene layers. This membrane was selected for further work after an extensive selection process of various composite materials prepared by Gore [2]. The ability to prepare very thin layers of an ionomer allows very high permeances to be achieved with these materials. For example, by using an ~5 micron PFSA layer in this sandwich structure, described as GORE™ M311.05, permeances of close to two times a 25-micron homogeneous PFSA membrane are achieved. The work in this project year has been aimed at characterizing this membrane for the key properties for use in a humidifier module in automotive or stationary fuel cell systems. These properties include performance durability after extended high temperature soaks, performance after relative humidity (RH) cycling, and performance after freeze-thaw cycling. A high-temperature test for water transport has been developed to allow rapid testing of water transport characterization [3], and has been used exclusively during testing in this project year. This test is a modified version of International Organization for Standardization standard 15496 for room moisture transport measurement of fabrics [3].

Initial studies of the durability of the sandwich M311.05 composite microstructures, e.g., showed virtually no performance degradation with time at 65ºC [2]. We have now extended these studies to 80ºC, where a degradation of ~20-25% in water transfer capability is observed after a ~4,200 hour hold in a module (Figure 1). There appears to be two major causes of this degradation: contamination by ionic species, and the thermally driven reaction of the PFSA polymer to cross-link at high temperature with the loss of water and the formation of a sulfonic anhydride [3,4]. The former mechanism can be minimized in operation by maintaining a clean system. The anhydride formation on PFSA polymers has been confirmed by infrared spectroscopy (Figure 2) and nuclear magnetic resonance [4], and is driven by thermodynamics so occurs faster in drier conditions and at higher temperatures [3]. The anhydride has lower water sorption, and lower water transport than the acid form of the polymer. Thus, the loss of performance of the M311 membrane after extended holds at high temperature arises from these chemical changes in the PFSA polymer. The anhydride formation of PFSA polymers is reversible by treatment with acid [3,4], or under active fuel cell operation [5].

Durability under freeze-thaw cycling and RH cycling has also been performed. The former shows no effect on performance [2]. When RH cycling is performed at 80ºC there is no effect on performance beyond that expected from temperature holds at 80ºC (Figure 3). The water transport loss is driven by anhydride formation just as it is with high-temperature holds [3]. The gas cross-over does not change after 20,000 cycles, the equivalent of ~5,500 hours of automotive use [3].

In summary, the testing results of the M311 membrane show some degradation of performance that arises from the chemical formation of anhydrides with the concomitant water loss. The performance loss is significant, but the magnitude should not prevent the use of this membrane in automotive humidifier applications since it is on the order of only 20% over the expected fuel cell system lifetime. In stationary applications, which operate at lower temperatures, there is much less degradation so the membrane should be acceptable for use in those applications as well.

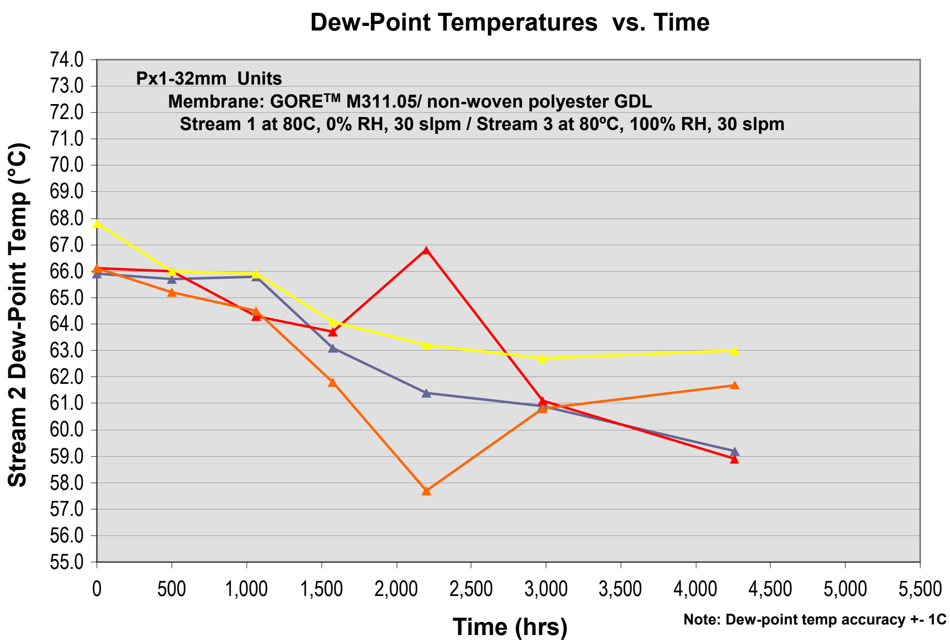

FIGURE 1. The performance of the M311 humidifier membranes made in this project degrade with time at 80°C in the conditions shown in the figure. (The Stream 2 dew point temperature is the dew point of the dry outlet.) The water transport degradation, on the order of 25% over the >4,000 hours, is likely acceptable for automotive fuel cell life times

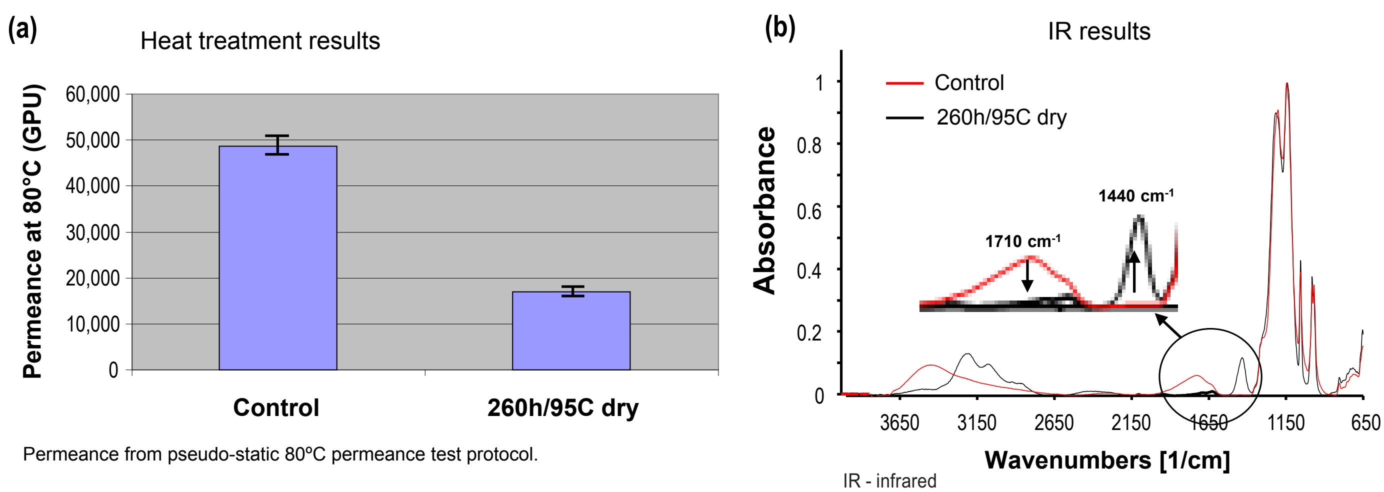

FIGURE 2. (a) An ex situ dry soak at elevated temperatures of 95°C leads to accelerated water transport degradation compared to testing at 80°C shown in Figure 1. (b) The degradation in both wet and dry conditions is driven by the loss of water and the concomitant formation of anhydride, which has lower water sorption and lower water transport. The formation of the anhydride is confirmed by infrared spectroscopy.

The design and prototyping of humidifier modules by dPoint Technologies is proceeding according to plan. Using a finite element model, the module flow field and other design parameters have been optimized, and a housing design has been chosen (Figure 4a and 4b). Several subscale modules, have been built using the designs identified by the modeling. The initial results from these subscale modules indicate that the high permeance Gore composite materials will allow modules to be built that have the requisite size and water transport characteristics required in demanding fuel cell automotive humidifier module applications.

A high-volume cost model for module production has been completed [3]. At volumes of 500,000 units per year, the projected module cost is less than $100. Further reductions are possible depending on final module design, system performance and size. This easily meets the automotive targets for humidifier modules.

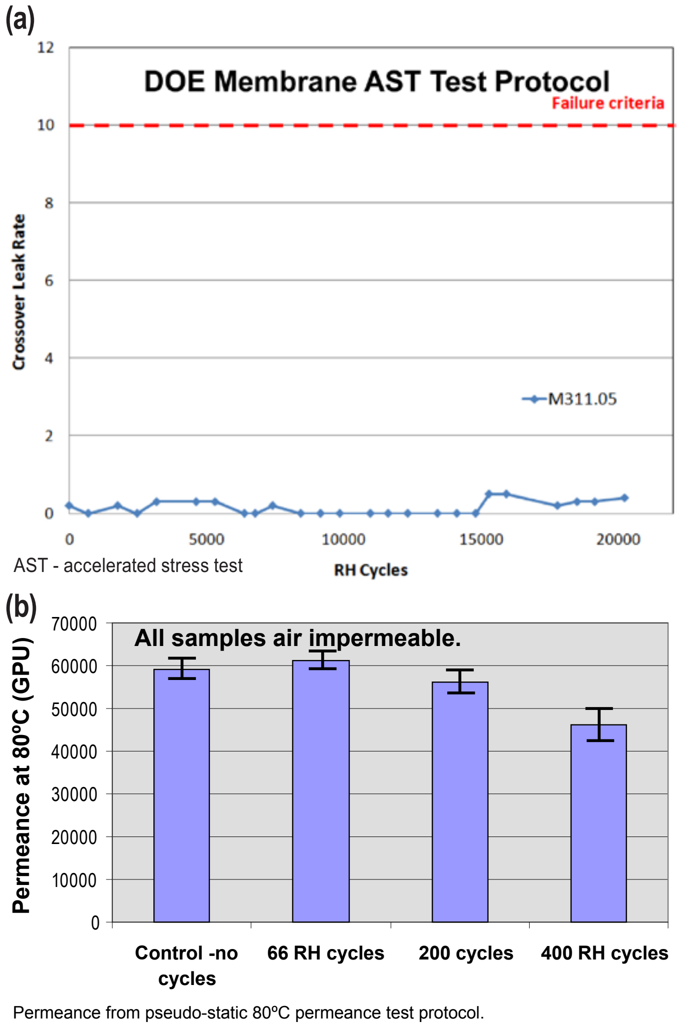

FIGURE 3. (a) RH cycling using a standard DOE test protocol shows the membrane does not leak after 20,000 cycles (data courtesy of General Motors Company). (b). Ex situ RH cycling shows there is no performance loss beyond that expected by holding at the 80°C test temperature. (Ex situ RH cycle is 80°C/88% RH to 20% RH/80°C over 3 hours; samples are restrained during testing.)

Conclusions and Future Directions

- Water transport rates through GORE™ M311 humidification membranes are high.
- Durability testing after extended high temperature soaks, after RH cycling, and after freeze-thaw cycling indicate the M311 membrane has acceptable properties for automotive and stationary application in humidifier modules.
- A high-volume cost model has demonstrated that demonstrates automotive cost targets can be met using the most promising Gore composite membranes.
- Humidifier module modeling and sub-scale module prototypes show that using the high-performance Gore composite humidifier membrane will enable an automotive humidifier module that meets the cost, durability and performance automotive targets.
- In the remaining time in the program, a full-scale humidifier module using the M311 membrane will be assembled and tested.

References

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2. William. B. Johnson, "Materials and Modules for Low-Cost, High Performance Fuel Cell Humidifiers", DOE Annual Review, Crystal City, VA, May 12, 2011, Oral Presentation fc067, available from www.doe.gov.

3. William. B. Johnson, "Materials and Modules for Low-Cost, High Performance Fuel Cell Humidifiers", DOE Annual Review, Crystal City, VA, May 17, 2012, Oral Presentation fc067, available from www.doe.gov.

4. Collette,Floraine M.; Lorentz,Chantal; Gebel,Gerard; Thominette,Francette, "Hygrothermal aging of Nafion", Journal of Membrane Science, 330(1-2), 21-29(2009).

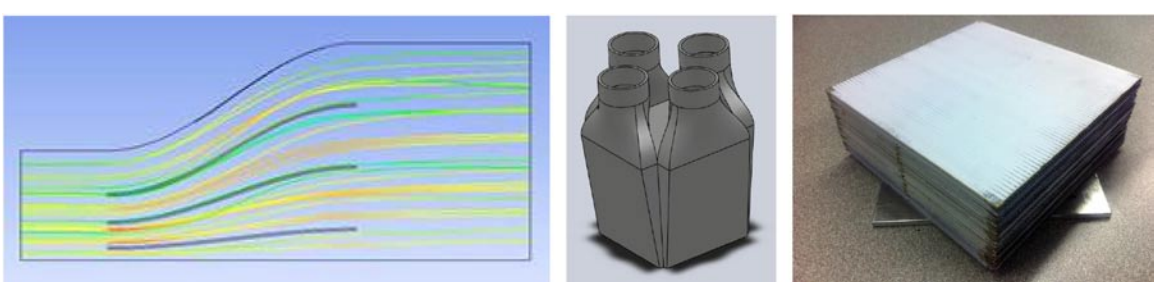

FIGURE 4. Using a finite element model of potential flow field geometries, the velocity contours, (a) have been used to optimize the housing design, (b) several subscale stacks have been built, and the final design leads to a very compact unit, and (c) the initial results from sub-scale modules indicate that the high permeance Gore composite materials will allow modules to be built that have the requisite automotive humidifier size and water transport characteristics

5. Collette,Floraine M.; Thominette,Francette; Escribano,Sylvie; Ravachol,Ang+¿le; Morin,Arnaud; Gebel,G., “Fuel cell rejuvenation of hygrothermally aged Nafion”, Journal of Power Sources, 202, 126-133(2012).

FY 2012 Publications/Presentations

1. Materials and Modules for Low-Cost, High Performance Fuel Cell Humidifiers, DOE Annual Review, May 17, 2012, Oral Presentation fc067.

2. Materials and Modules for Low-Cost, High Performance Fuel Cell Humidifiers, DOE Annual Review, May 12, 2011, Oral Presentation fc067.