

# V.H.1 New High-Performance Water Vapor Membranes To Improve Fuel Cell Balance-of-Plant Efficiency and Lower Costs (SBIR Phase II)

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Collaborators

- Dana Holding Corporation, Maumee, OH
- General Motors Corporation, Detroit, MI
- Membrane Technology and Research Incorporated, Newark, CA

Contract Number: DE-SC0006172

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Project End Date: September 16, 2014

## Overall Objectives

- Develop improved low-cost water vapor membranes for cathode humidification modules in fuel cells.
- Synthesize new polymer molecular architectures, which avoid chemical degradation, increase water vapor transport and exhibit good mechanical durability at lower cost.
- Determine long-term stability of membranes through chemical resistance tests. In parallel, continue the synthesis of higher permeability polymer architectures.
- Down select best candidates for scale up and provide prototypes to collaborators.

## Fiscal Year (FY) 2014 Objectives

- Performance of  $3.32 \text{ g sec}^{-1} \text{ m}^{-2}$  with no chemical degradation over 5,000 hours
- Durability of 5,000 hours with <10% drop in performance
- Crossover leak rate of <5%
- Temperature durability of  $90^\circ\text{C}$  with excursions to  $>100^\circ\text{C}$
- Cost of  $<\$10/\text{m}^2$  at volumes of 500,000 systems per year

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

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

## Technical Targets

- Ionomer membrane performance optimization through improvements in molecular architecture
- Durability improvement
- Scale up of high-performance materials to lower cost

## FY 2014 Accomplishments

- Consistently met the target goal of crossover leak rate less than 5%.
- Passed the 20,000-cycle hour durability test.
- Scaled up the down-selected polymer to 2 kg to verify cost projections.
- Cost target of  $\$20/\text{m}^2$  for the ionomer achieved and  $\$10/\text{m}^2$  is on target.
- $12 \text{ m}^2$  of membrane has been successfully coated through a commercial roll coater.
- Industrial partner testing has expanded to involve significantly higher temperatures than DOE targets.



## INTRODUCTION

Hydrogen fuel cells are one of the more promising alternative energy and propulsion systems with the most promising type of fuel cell for automotive and stationary power applications being the proton exchange membrane (PEM) fuel cell. PEMs have the advantage of high power density at the low operating temperatures required for systems that will see frequent on/off cycling. One of the biggest challenges for PEM systems is the fact that PEMs perform much better with higher water environments to effectively conduct protons from the anode to the cathode of the cell. The design of a membrane humidifier unit as part of the balance of plant has been proposed and has

been emphasized by DOE in the Multi-Year Research, Development, and Demonstration Plan in Table 3.4.9 and Table 3.4.10 to utilize the water produced as a byproduct of the oxygen reduction reaction to humidify the inlet air to the fuel cell [1].

The use of membrane humidifiers for fuel cell applications represents a reasonable value proposition; however, expanding the accessible markets for these membranes to increase volumes and lower manufacturing cost is also beneficial, particularly when the new applications satisfy the overall DOE objectives of saving energy. Dehumidification of feed air to heating, ventilation, and air conditioning systems using these membranes can save as much as 40% of the energy required to condition air [2]. The membranes currently being commercialized do not meeting the desired size, weight and pressure drop requirements for automotive applications. More importantly the durability of current membranes have not been found to maintain performance due to degradation mechanisms of the membrane. In 2012, Gore reported that both their new perfluorinated sulfonic acid (PFSA) and hydrocarbon membranes suffered from detrimental loss in performance with a loss in permeance of up to 60% within 500 hours [3]. This loss in performance was attributed to the potential for anhydride formation and was confirmed using methods developed by Collette for PFSAs [4,5]. Gore also addressed a loss in performance from salt contamination where the membrane lost more than 70% of permeance after being converted to the corresponding sodium salt [3]. These possible means for loss in performance drove us to develop a more robust system, which alleviates these degradation mechanisms.

## APPROACH

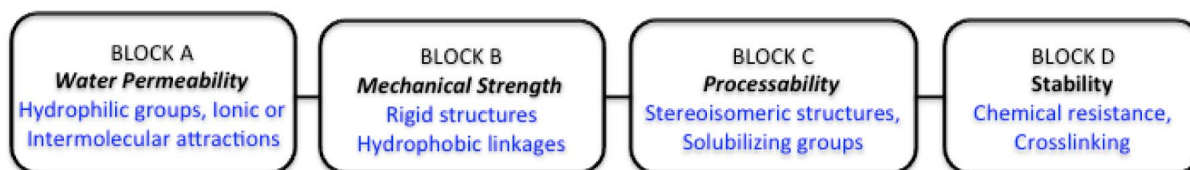
Nafion<sup>®</sup> has been found widely useful as an ion exchange membrane for chloroalkali cells, which has become a very profitable market and has kept the cost of the current PFSAs much higher than what would be needed for membranes within the fuel cell market. The demand for a cheaper membrane material that does not undergo detrimental side processes has been the inspiration for Tetramer's membrane development work. The evolution of Tetramer's basic ionomer technology with polymers designed for hydrogen ion transport in PEM fuel cells has led to a semifluorinated

ionomer that has equaled or exceeded the incumbent PFSA with significant (>50%) cost and processing advantages.

The development of water vapor transfer membranes at Tetramer during this Small Business Innovation Research project has met the target of reproducibly producing a water flux of  $2.58 \text{ g sec}^{-1} \text{ m}^{-2}$  with no chemical degradation. Since thin, unsupported membranes have been found to possess mechanical deficiencies, a supported configuration that increases the mechanical durability of the membrane with minimal detriment to overall flux has been implemented. New membranes with unique polymer design elements that emphasize high water transport while alleviating possible means of performance degradation have been proposed and are the driving force for this contract. The synthesis of these new monomers and polymers has been demonstrated; optimization of polymer architecture is in progress and characterization of long-term water vapor transport by both Tetramer and industry partners is currently being explored.

## RESULTS

The need for a unique polymer design of a water vapor membrane has been addressed by Tetramer through a systematic approach in which four key polymer design elements were explored. These polymer design elements are summarized in Figure 1. The first and most critical parameter was to design a water permeability unit that consists of hydrophilic groups with ionic or intermolecular attractions. The selected polymer structures have potential for water transport without the possible side effects of anhydride formation. The need for mechanical strength has been addressed in our polymer design by incorporating rigid, hydrophobic structures that impart toughness and keep the material from becoming water soluble. The need for processability has received a great deal of attention especially within the membrane world. To make high quality uniform thin films, the need to either melt process or solution cast the polymer can be addressed by the inclusion of stereoisomeric structures to disrupt packing as well as solubilizing groups. The last parameter addressed has been stability in which specific functional groups have been chosen to ensure chemical resistance, as well as chemical groups that allow for crosslinking have been incorporated into the polymer design to impart an additional robustness for the material.



**FIGURE 1.** Water Vapor Membrane Polymer Design Elements

Tetramer membranes have been found to achieve the 2.58 g sec<sup>-1</sup> m<sup>-2</sup> target consistently and currently meet the need for minimal crossover and are being explored for loss in performance over time as well as meeting the highest durability temperature with the lowest cost.

To evaluate membranes for water vapor transport quickly without the need of assembling a full-scale fuel cell system, we have acquired a testing unit from one of our collaborators, MTR and have duplicated the testing conditions that General Motors (GM) used during automotive applications. GM has continued testing our membranes in parallel, which has helped speed up our evaluations. Our current testing has focused on DOE conditions (dry air in: 0.23 SLPM/cm<sup>2</sup> dry gas flow, 183 kPa absolute, 80°C, 0% relative humidity [RH]; wet air in: 0.20 SLPM/cm<sup>2</sup> dry gas flow, 160 kPa absolute, 80°C, 85% RH) which are highlighted in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1]. The progress of membrane performance is shown in Figure 2 in which membranes have improved from a water flux of 1.35 to 3.17 g sec<sup>-1</sup> m<sup>-2</sup>. Membranes from these improvements were then tested for anhydride formation using the methods developed by Collette [4,5] and no anhydride formation was found.

These membranes were recently tested by industrial partners under varying real world commercial conditions and found promising results in comparison to competitor membranes as seen in Figure 3. This testing was shown to expand our current conditions to significantly higher temperatures (>100°C) than the initial DOE conditions. Even at these higher temperatures and more extreme conditions Tetramer’s membranes have been found to perform higher than multiple comparative suppliers.

During the exploration of more extreme conditions, which consisted of higher temperatures, it was found that commonly used casting solvents such as dimethylacetamide have strong interactions with sulfonic acid groups. This interaction then allows for the decomposition of

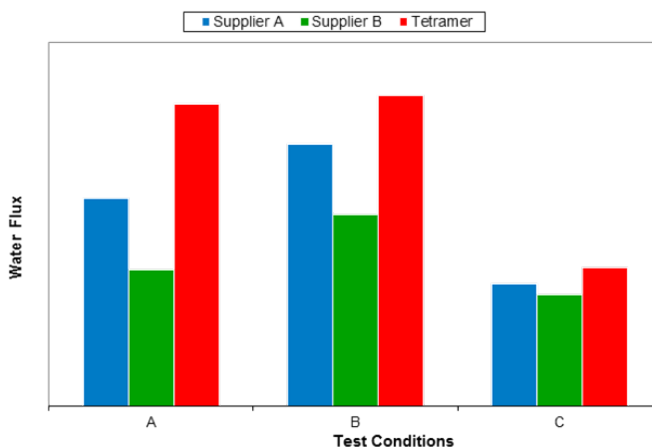


FIGURE 3. Comparison of Tetramer's Membranes vs. Commercial Competition

the dimethylacetamide through acid hydrolysis to form dimethylamine, which is shown in Figure 4a. This dimethylamine can then form ammonium salts with the sulfonic acid groups on the polymer as seen in Figure 4b. To test the effect this amine has on the ionomer a film was treated with an amine and was found to decrease the water flux from 2.61 to 0.94 g sec<sup>-1</sup> m<sup>-2</sup>. The need for a solution to this formation of a detrimental performance loss was initially addressed by a post treatment of the membrane to ensure all the residual solvent was removed. Fourier transform infrared (FTIR) confirmed removal of the residual solvent as seen in Figure 4c.

The development of these membranes is still being pursued and increasing the permeance of the current materials while maintaining these transport properties over long-term durability studies is critical to the success of the project. The down-selected materials from this study will continue to be tested by our industry partners under their conditions to ensure we meet the demands for today’s humidification technology needs.

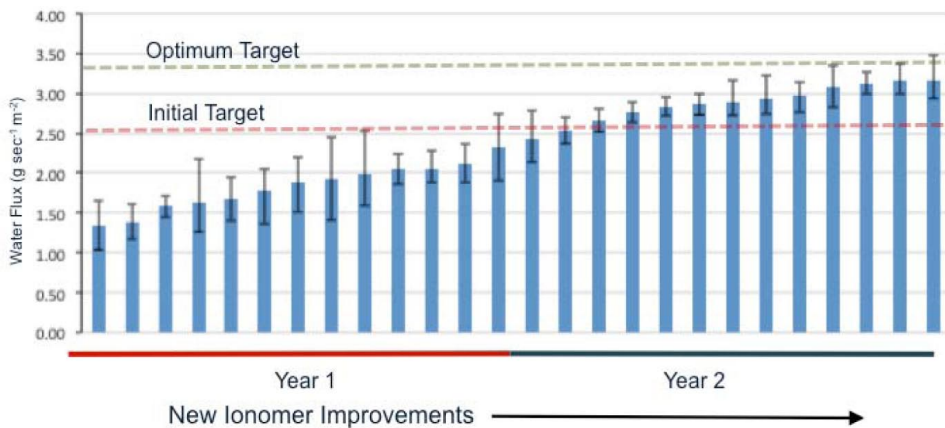
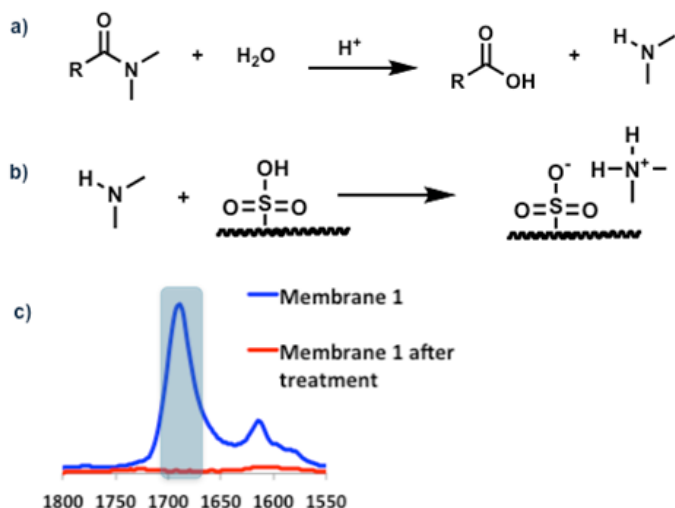


FIGURE 2. New Membrane Initial Performance



**FIGURE 4.** a) Decomposition of amide containing solvent such as dimethylacetamide to the corresponding acid and dimethylamine. b) Reaction of dimethylamine with polymer containing a sulfonic acid group to give the ammonium salt. c) FTIR of sulfonic acid polymer containing dimethylacetamide followed by a 24-hour soaking treatment for the membrane.

## FUTURE DIRECTIONS

- Resolve solvent degradation issue
- Determine optimum support composite matrix
- Long-term testing
- Manufacture 400 m<sup>2</sup> at commercial roll coater
- Construct prototype water vapor transport module

## FY 2014 PUBLICATIONS/PRESENTATIONS

1. Wagener, Earl H.; Morgan, Brad P. “New High Performance Water Vapor Membranes To Improve Fuel Cell Balance of Plant Efficiency and Lower Costs”, DOE Annual Review, Washington DC, June 18, 2014, Oral Presentation FC102, available from [www.hydrogen.energy.gov](http://www.hydrogen.energy.gov).

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1. Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan, Department of Energy Office of Energy Efficiency and Renewable Energy 3.4 – 24 (2012)
2. Zhang, Yinping; Jiang, Yi; Zhang, Li Zhi; Deng, Yuchun; Jin, Zhaofen “Analysis of thermal performance and energy savings of membrane based heat recovery ventilator”, *Energy*, 25, 515-527 (2000).
3. Johnson, William. B. “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.hydrogen.energy.gov](http://www.hydrogen.energy.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).
5. Collette, Floraine M.; ThomINETTE, Francette; Escribano, Sylvie; Ravachol, Angèle; Morin, Arnaud; Gebel, G., “Fuel cell rejuvenation of hygrothermally aged Nafion”, *Journal of Power Sources*, 202, 126-133 (2012).