

V.G.2 New High-Performance Water Vapor Membranes To Improve Fuel Cell Balance-of-Plant Efficiency and Lower Costs (SBIR Phase II)

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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) 2013 Objectives

- Consistently produce membranes with permeance of 18,000 gas permeation units (GPU) at 85°C with no chemical degradation over 2,000 hours
- Durability of 2,000 hours with <20% drop in performance
- Crossover leak rate of <150 GPU
- Temperature durability of 90°C with excursions to 100°C
- Cost of <\$10/m² at volumes of 2,500 kg/yr

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell 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 2013 Accomplishments

- Synthesis of six new monomer and 12 new film forming polymer structures with key design elements.
- Extensive optimization of reaction conditions and purification methods resulting in higher yields and greater purity monomers and polymers.
- Characterization (nuclear magnetic resonance, mass spectrometry, elemental analysis, Fourier transform infrared spectroscopy and gel permeation chromatography) of these materials has been defined.
- New methods to prepare membranes with improved transport performance and durability have been identified.
- Determined that previous polymer structures would not reach the target water vapor permeation or mechanical stability goals.
- Demonstrated the ability to improve structures towards long-term stability through various means.
- Consistently met the target goal of crossover leak rate less than 150 GPU.
- Passed the 20,000-cycle hours durability test.
- Scaled up the down-selected polymer to 100 grams to verify cost projections.



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 cooling 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 has not been found to maintain performance due to degradation mechanisms of the membrane. In 2012, Gore reported that both their new perfluorosulfonic 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 PFSA [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[®] 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 PFSA 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, whose identity will be released after intellectual property is established, 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 project has met the initial target of reproducibly producing 18,000 GPU for water vapor permeance. Since then, 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 are currently being explored.

RESULTS

The design and development of high-performance low-cost water vapor membranes for cathode humidification through unique polymer structures is being explored. The commercially available 25- μm (N111) and 50- μm (N112) Nafion[®] membranes do not meet the 18,000 GPU performance target herein, and neither does a Perma Pure[™] device made with Nafion[®] hollow tube membranes. The water transfer permeance target of 18,000 GPU (gas permeation units, $1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 / (\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$) is a 50% increase over the 25- μm Nafion[®] N111. Tetramer membranes have been found to achieve the 18,000 GPU target consistently and are currently being explored to meet the need for minimal crossover, loss in performance over time, highest durability temperatures and lowest cost.

The need for unique polymer design for water vapor membranes 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. Synthetic chemistry groups such as McGrath's at Virginia Tech have explored this key parameter with critical design elements including the need for block copolymers with hard/soft segments [6]. This concept has inspired some of the current materials being explored, which have shown promise. 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

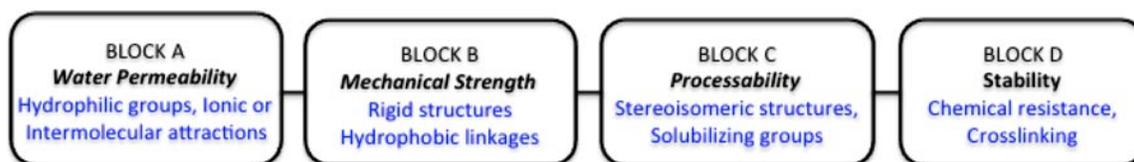


FIGURE 1. Water Vapor Membrane Polymer Design Elements

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 synthons 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.

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 will continue to test our membranes in parallel, which will help speed up our evaluations. GM's testing system is projected to be operational by mid-August. These parameters are summarized in Figure 2 and are currently being explored for all membranes prepared as an initial screening method to evaluate the membranes. For the new structures synthesized to date, five of these new polymer structures have achieved between 17,000 and 20,000 GPU, as seen in Figure 3. The membranes from these were then tested for anhydride formation using the methods developed by Collette [4,5]. These membranes have been exposed to 80°C for 240 hours and 140°C for 4 hours, after which no anhydride formation was observed as seen in Figure 4 [7,8].

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 testing of these polymers for any signs of degradation will be critical followed by an increase in operation temperatures. The down-selected materials from this study will be tested by our industry partners under their conditions to ensure we meet the design demands for today's humidification technology needs.

FUTURE DIRECTIONS

- Continue durability tests at higher temperatures (95°C) and longer times to assure chemical resistance. In parallel, continue synthesis of new polymer architectures to increase water vapor transport from 20,000 GPU to 30,000 GPU.
- Utilize initial results to optimize membrane durability to less than 20% loss in performance after 2,000 hours.

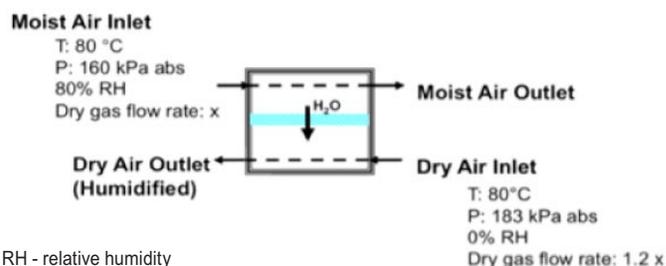


FIGURE 2. Test Conditions for Water Vapor Transport Membranes

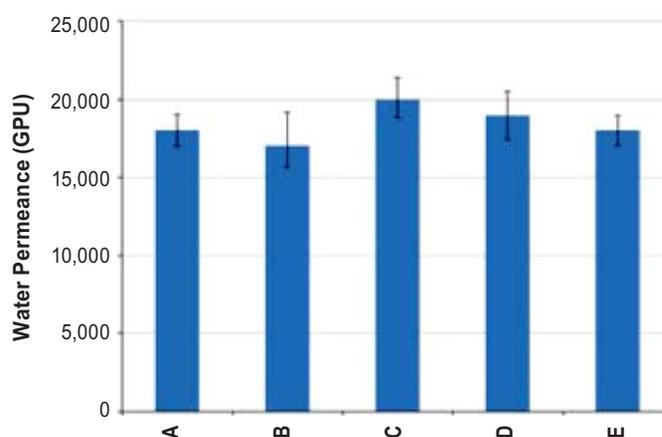


FIGURE 3. New Membranes Initial Performance

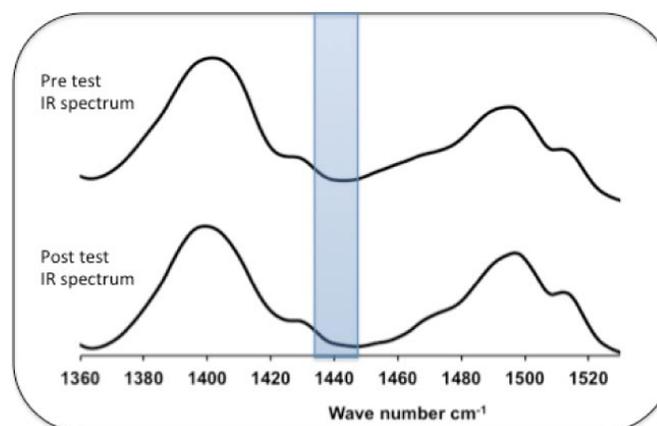


FIGURE 4. Fourier Transform Infrared Spectroscopy of Membrane Pre-Heat Treatment and Post-Heat Treatment at 80°C for 240 Hours

- Use these new molecular architectures to increase temperature durability from 80°C to 90°C with excursions of 100°C.
- Automotive prototype membrane performance testing.
- Down-selected membranes will be tested for non-automotive prototype membrane performance using module prototype production.

FY 2013 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 Merit Review, Crystal City, VA, May 14, 2013, Oral Presentation fc102, available from www.hydrogen.energy.gov.

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8. 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 Merit Review, Crystal City, VA, May 15, 2012, Poster Presentation fc102, available from www.hydrogen.energy.gov.