IV.B.5 Enabling Commercial PEM Fuel Cells with Breakthrough Lifetime Improvements

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Objectives

- This project will result in lifetime improvements of low-temperature proton exchange membranes (PEMs) for fuel cell applications by seeking technologies that will prevent membrane failure.
- This will be accomplished by conducting research that elucidates failure mechanisms and lifetime extension technologies that yield membranes that meet or exceed a lifetime of 40,000 hours operation with <10% degradation in performance.
- As the project progresses, the membranes with increased durability developed under this project will be validated through stack testing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability

Approach

- DuPont and United Technologies Corporation (UTC) have worked together for over three years developing an understanding of mechanisms of fuel cell membrane failure.
- As these mechanisms become understood, various mitigating strategies are identified, developed, and validated through a combination of modeling, *ex situ* peroxide studies, and fuel cell testing (both accelerated and non-accelerated).
- This project is comprised of the optimization and combination of each of the various mitigation strategies.
- Stack testing will be used to validate the improved fuel cell components.

Accomplishments

- Peroxide Mitigation Strategy Development and Optimization
  - Mechanisms of peroxide attack on membranes have been identified, and mechanism-based mitigation strategies have been designed and implemented.
  - Accelerated chemical degradation testing has shown that membranes incorporating these mitigation strategies reduce fluoride emission rate (FER) by a factor of 10 to 100.
  - New structures have been identified that reduce the negative cost and performance effects of these mitigation strategies.
- Chemical Stabilization
  - Non-perfluorinated polymer chain end groups have been demonstrated to be susceptible to chemical attack.
  - Through both process conditions and fabrication techniques, the number of undesirable polymer chain end groups has been reduced to non-detectable quantities. Fenton's test on improved materials show a 90% reduction in FER.
  - Accelerated degradation testing has shown that chemically or mechanically strengthened membranes yield lower FER than control membranes, proving the chemical benefits of membrane stabilization.
- Mechanical Stabilization
  - Significant progress has been made in increasing membrane mechanical properties (*e.g.*, tensile strength, tensile modulus, elongation at break, *etc.*) through both processing conditions and materials selection.
  - Significant progress has been made in achieving isotropy (machine direction *vs.* transverse direction) in these mechanical properties as well as in coefficient of moisture expansion (CME) through both processing conditions and materials selection.
  - Accelerated mechanical degradation testing has shown that membranes with increased mechanical strength do not decay as rapidly, proving the benefits of membrane mechanical stabilization.

Future Directions

- Continue to optimize peroxide mitigation strategies (decrease cost and performance impact).
- Continue to optimize mechanically reinforced membrane.
- Continue to optimize chemically stabilized membrane.
- Investigate other potential chemical degradation mechanisms.
- Implement combined optimized mechanical, chemical, and peroxide mitigation strategies into fuel cell components.
- Correlate accelerated durability testing data with real-time testing results.
- Validate durability improvement through stack testing.

Introduction

This project seeks to improve the operational lifetime of low-temperature PEMs for fuel cell applications by seeking technologies that will prevent membrane failure. This will be accomplished by conducting research that elucidates membrane failure mechanisms and demonstrates lifetime extension technologies that will yield membranes with an operational life span of 40,000 hours operation with <10% performance degradation.

DuPont and UTC have been working together for more than three years developing and validating mechanisms of membrane failure. It is understood that under some conditions in the fuel cell environment, hydrogen and oxygen can combine to form hydrogen peroxide. This peroxide can degrade into radicals that may attack weak spots in the perfluorosulfonic acid (PFSA) polymer. After some degree of chemical degradation, the membrane mechanical properties are negatively affected and the membrane may eventually rupture as it experiences mechanical stresses during fuel cell operation. This project seeks to enhance membrane durability by interrupting each step of this degradation mechanism.

Approach

To mitigate the negative effects of peroxide attack, strategies are being developed and implemented that allow peroxide to decompose benignly before any chemical attack can occur. In addition, modified Nafion® polymers are being developed that demonstrate increased resistance to chemical attack. These two strategies will be optimized and combined in novel composite membrane structures designed to give increased mechanical strength. In parallel, improved edge seal designs will be developed to prevent mechanical stresses from damaging the membrane under or around the edge seal. This project seeks to optimize each of these mitigation strategies and incorporate them, *in toto*, into fuel cell components. The various mitigation strategies will be validated through a combination of modeling, *ex situ* testing, and fuel cell testing (both accelerated and non-accelerated).

Results

Peroxide Mitigation

Our partners at UTC have identified mechanisms of chemical attack of peroxide radicals on the membrane. Using models that describe these physical processes, mitigation strategies that impede these mechanisms have been designed and tested. These improvements have been validated by measuring extent of chemical attack (FER) and degree of membrane degradation (hydrogen crossover current) in the improved products and comparing to baseline products. This has resulted in FER reduction of a factor of 10 to 100 under accelerated testing conditions. Figure 1 illustrates the durability enhancement of this strategy. Since this strategy has proven successful for increasing membrane durability, new structures have been

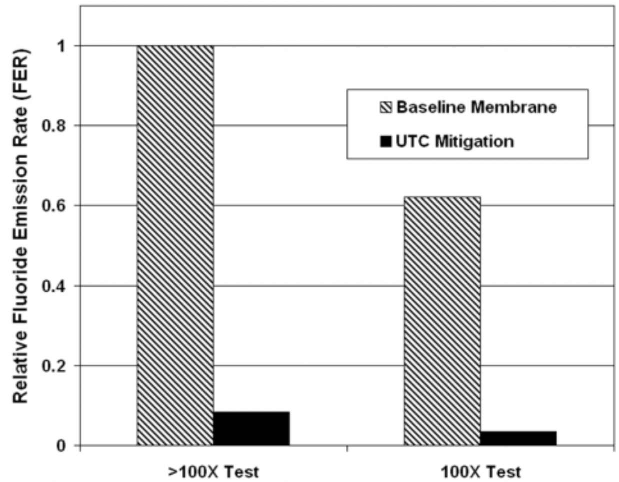

Figure 1. Relative FER for Both Baseline Membrane and Membrane Incorporating Peroxide Mitigation Strategies

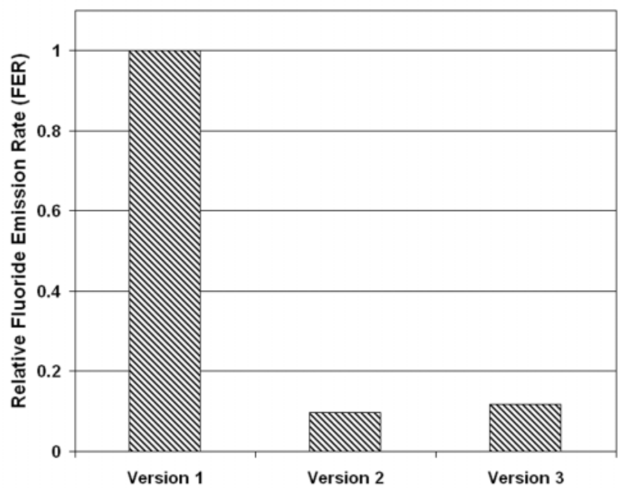

Figure 2. Relative FER for Membranes with Improved Peroxide Mitigation Strategies

identified that reduce the negative cost and performance impacts associated with this technology. Figure 2 shows novel structures that substantially reduce cost and performance impacts while giving even lower FER than the original structures.

Chemical Stabilization

Through both modeling and experimental design, it has been demonstrated that non-perfluorinated polymer end groups are susceptible to chemical attack by peroxide radicals. To interrupt

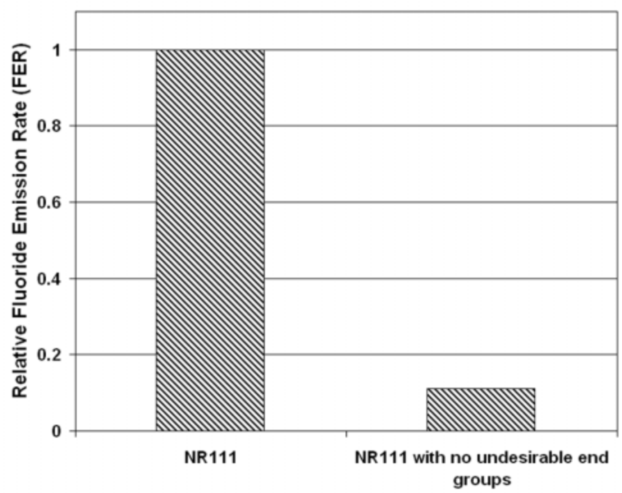

Figure 3. Relative FER for Both Baseline Membrane and Membrane with Reduced Undesirable End Group Count

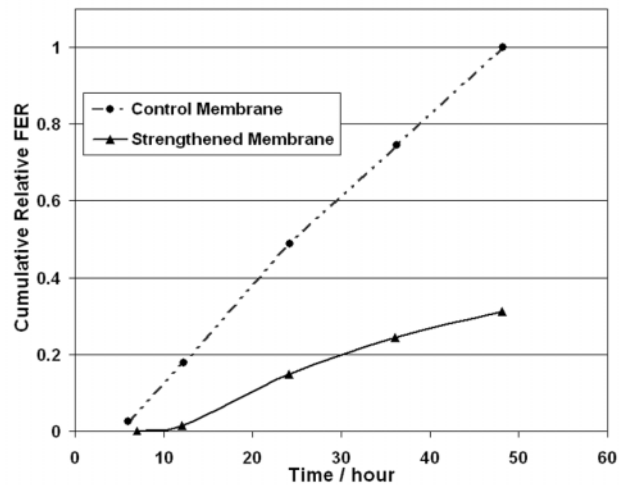

Figure 4. Cumulative FER for Both Control Membrane and Strengthened Membrane Under Accelerated Testing Conditions

this process, the processing capability to reduce the number of undesirable end groups to non-detectable quantities has been developed. This has improved membrane durability, as evidenced by both reduced FER in *ex situ* tests and increased lifetime in fuel cell testing under accelerated conditions. Figure 3 shows a 90% reduction in FER of one such stabilized membrane *vs.* commercial Nafion® NR111 in Fenton testing. Mechanically reinforcing the membrane imparts additional chemical stability, as evidenced in Figure 4. This figure shows reduced FER in a strengthened catalyst-coated membrane (CCM) under accelerated testing conditions.

Mechanical Stabilization

During fuel cell operation, the membrane undergoes substantial mechanical stress (*e.g.*, in sealing area, non-uniform gas diffusion layer compression, shrinking/expansion with changing water content, *etc.*). Therefore, a more durable membrane can be achieved by increasing the physical strength of the membrane. It is also desirable to increase the isotropy of the mechanical properties of the membrane. Both the modification of membrane processing conditions and the selection of membrane materials have substantially increased the mechanical strength (*e.g.*, tensile strength) and, at the same time, have increased the isotropy of various Nafion® membranes. Figure 5 illustrates

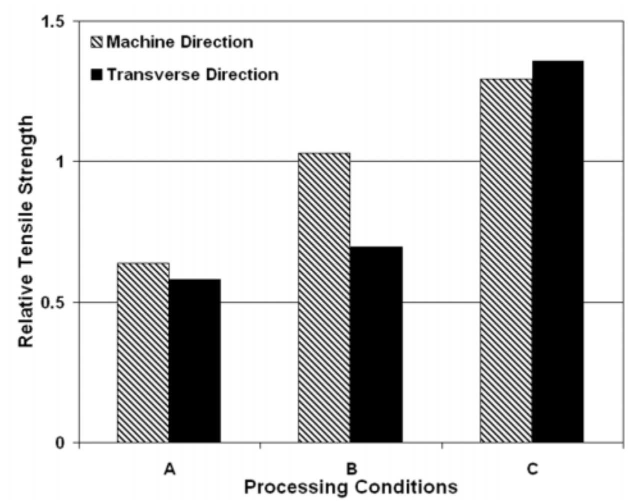

Figure 5. Effect of Processing Conditions on Magnitude and Isotropy of Tensile Strength within a Given Membrane Composition

representative data that demonstrate how the selection of processing conditions has increased both the tensile strength and isotropy of a candidate Nafion® membrane. Figure 6 shows lower mechanical degradation under accelerated testing associated with membranes that have improved mechanical properties.

Conclusions

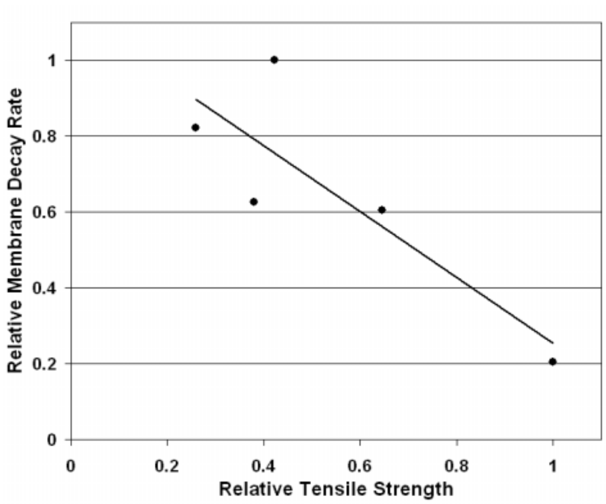

Figure 6. Correlation of Mechanical Membrane Decay Rate with Tensile Strength for a Given Class of Membrane

By impeding the progress at every step of the membrane degradation mechanism, the peroxide mitigation technology, the chemical stabilization of the membrane, and the mechanical stabilization of the membrane have each enhanced the durability of the membrane. It is now possible to consider that the goal of a 40,000-hour fuel cell membrane can be realized once each of these additive improvements is optimized and incorporated into fuel cell components.