V.L.4 Low-Cost Durable Seals for PEMFCs

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- Freudenberg-NOK General Partnership, Plymouth, MI
- Henkel Corporation, Rocky Hill, CT
- Virginia Polytechnic Institute and State University (Virginia Tech), Blacksburg, VA

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Objectives

- Develop a working material specification to guide the development of proton exchange membrane fuel cell (PEMFC) seal materials.
- Synthesize and compound materials that meet the requirements of the materials specification.
- Evaluate candidate materials through accelerated ex situ testing to predict whether the material will meet durability objectives given in Table 1.
- Validate the performance of the best performing material candidate through in-cell testing.

Technical Barriers

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

(A) Durability

Technical Targets

The aim of this project is to develop and evaluate new non-silicone liquid injection moldable (LIM) and dispensable materials to improve durability for both transportation and stationary applications while maintaining or improving on the cost benefits of LIM silicone materials.

TABLE 1. DOE Targets Receiving Focus as Part of this Project

Characteristic	Units	2010 Status	2010 / 2011[a]
Durability	hours	>10,000 hours achieved[b]	5,000/40,000
Sealability at Low Temperature	°C	Meets DOE Targets	-40/-35
Cost[c]	$\$/kW_{net}$	To be evaluated	(2.00–3.77)[d]

[a] DOE Transportation/Stationary targets.
[b] Real-time out-of-cell testing at 90°C.
[c] Based on high volume production (500,000 transportation systems per year/2,000 stationary units per year).
Note: A cost target for seals is not currently carried in the Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan. See footnote (d) below for an explanation of how this target was derived.
[d] Suggested cost target range for transportation applications derived from Reference 1 ($3.77/kW), Reference 2 ($2.10/kW) and conversations with the Fuel Cell Tech Team ($2.00/kW). Based on Reference 1, a reasonable suggested target for stationary applications may be $5.87/kW.

Accomplishments

- Completed more than 10,000 hours of compressive stress relaxation (CSR) testing at 90°C.
- Completed more than 4,500 hours of CSR testing at 120°C.
- Completed more than 10,000 hours of aging in air at 120°C.
- Developed materials that meet all minimum beginning of life (BOL) targets and most desired project goals.
- Developed additional candidate with greater measured BOL tear and tensile strength.
- Developed materials shown to be more stable than one tested silicone and a few tested ethylene propylene diene monomers (EPDMs).
- Accumulated 1,700 hours of in-cell testing.

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Introduction

Seal durability is critical to achieving the 2010 DOE operational life goals for both stationary and transportation PEMFC stacks. The seal material must be chemically and mechanically stable in an environment consisting of aggressive operating temperatures, humidified gases, and acidic membranes.

The seal must also be producible at low cost. Currently used seal materials do not meet all these requirements.

High consistency hydrocarbon rubber compounds (rubbers that are solid or semi-solid prior to curing) that show promise for compatibility with the PEMFC environment are difficult to process in a way that leads to low-cost PEMFC production. Silicone-based LIM rubber compounds which are easy to process in ways leading to low-cost production are highly gas permeable and have been shown to be unstable in PEMFC applications. To produce PEMFC stacks which are both highly durable and low in cost, a seal material with the stability of high consistency hydrocarbon rubber and the processing ease of a LIM silicone is sought.

Approach

To accomplish the objectives of this project, the approach is to develop and evaluate non-silicone LIM seal materials that can meet the specialized mechanical, compatibility, and cost requirements inherent to the design and operation of PEMFCs. To guide material development, a working material specification was developed. Materials developed to this specification by Henkel are evaluated through out-of-cell testing at Virginia Tech, Henkel and UTC Power in simulated environments. Using an appropriate set of accelerated testing techniques, an initial lifetime estimate will be made for the candidate materials. The best candidate or candidates will be selected for in-cell testing to validate the performance of the material in a PEMFC environment. Specimens for out-of-cell testing and full size prototypes for in-cell testing are produced by Freudenberg-NOK General Partnership.

The outcome of the project will benefit the PEMFC industry by providing a seal material specification, a material that satisfies it, and verification that the specification and the material enable a low-cost and durable seal.

Results

The work over the last year has been focused on four tasks:

- Material Development
- The Completion of Out-Of-Cell Testing
- Molding of Prototype Components for In-Cell Testing
- In-Cell Validation Testing

Additional experimental material development was carried out over the last year. The work has yielded FCS3, the final material candidate to be developed as a part of the project. It is a one-part material with the same cure characteristics and thermal stability as FCS2, but with increased strength, modulus, and elongation.

This brings the total of material candidates introduced to four. In Table 2, some key properties of the four are compared to each other and to the materials specification. All four meet the minimum requirements in the material specification with one exception. The viscosity of FCS3 is higher than originally desired. However, initial molding trials indicate that the higher viscosity should be acceptable. While seal components suitable for use in PEMFC applications could be produced from any of the four, the higher strength and elongation of FCS3 broadens the range of design options available.

TABLE 2. Comparison of Key Properties for Candidates Developed To-Date

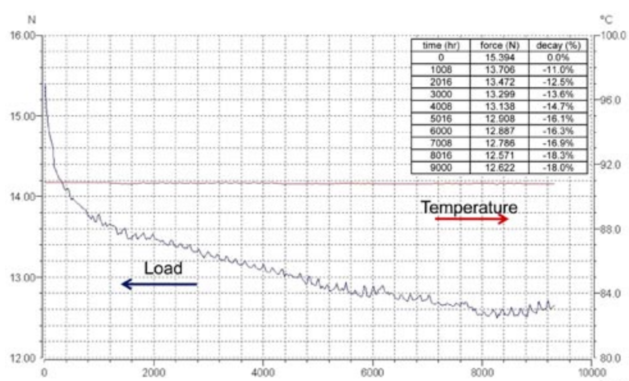
Henkel LIM Hydrocarbon Elastomer Property Table for DOE						
Properties	Project Requirements		FCS0	FCS1	FCS2	FCS3
	Minimum	Ultimate				
Process Properties						
LIM processable	Yes	Yes	Yes	Yes	Yes	Yes
Viscosity @ room temperature (cPs)	<= 700,000	<= 600,000	~ 500,000	~ 543,000	~ 543,000	~ 1,000,000
Mold temperature (°C)	< 135	<= 110	120 to 130	120 to 130	120 to 130	120 to 130
Mold time (second)	<= 400	<= 60	60 to 120*	60 to 120*	60 to 120*	60 to 120*
Mechanical Propreties						
Hardness (Shore A)	15 to 68	30 to 55	31	30	30	49
100% Modulus (Mpa)	0.25 to 3.5	1 to 2.5	0.75	0.68	0.69	1.91
Tensile strength (Mpa)	>= 0.5	>= 0.8	1.3	1.3	1.1	4.86
Elongation (%)	> 125	> 150	163	171	160	222
Tear strength Die C (kN/m)	>= 2.7	>= 5.0	3.7	3.7	3.9	16
Environmental Requirements						
Temperature resistance (°C)	-40 to 85	-40 to 90	-40 to 90	-40 to 90	-40 to 120	-40 to 120
Notes						
*cure schedule: 120 second in the mold @ 120°C and then 1 hour post cure @ 130°C						

Green:	Meets minimum & ultimate goal
Lt Green:	Meets minumum goal
Yellow:	Does not meet project goal, but may be acceptable
Red:	Does not meet project goal

A variety of out-of-cell tests were used in the evaluation of the materials developed for this project such as mass uptake, environmental aging and stress relaxation. The aim was to evaluate the beginning of life properties and to evaluate how those properties changed with time when subjected to combinations of temperatures and chemical environments typical of PEMFC operation.

One of the most important measures for determining the durability of seals is CSR. This is a measure of decay in sealing force with time. During the past year, over 9,000 hours of CSR testing at 90°C in air was completed on FCS2 using a sub-scale molded O-ring seal (SMORS) – a seal over-molded around the perimeter of a porous substrate. The result is summarized in Figure 1. The result agrees with results achieved previously when testing FCS0 CSR plugs in 90°C air, dionized water, and a 50/50 etylene glycol/water solution for 10,000 hours. The key result is that after 9,000 hours, less than 20% load decay was measured. This result is important. Significantly greater values are typically seen in silicones and even some EPDM materials after less than half this time. While these higher values can typically be accounted for in the design of sealing systems, lower values translate directly into increased durability and greater design flexibility.

As mentioned above, CSR testing had previously been conducted on the FCS0 material. This testing used the test specimen configuration specified in ASTM D 6147 Section 7.1.1. Because this geometry is very different than that used to produce a functional fuel cell seal, the CSR testing was repeated with SMORS in all the environments tested previously and also in a 0.1 M H_2SO_4 solution. Testing was completed this year and results are shown in Figure 2. In this case, after more than 4,000 hours, load decay for three aqueous test environments was approximately 20%. It should also be noted that the behavior in the three environments is substantially the same. This indicates, for instance, that the material is resistant to a sulfuric acid solution having a pH of approximately 1.0. This in turn suggests that the material could be directly over-molded onto poly(fluorosulfonic acid) membranes.



time (hr)	force (N)	decay (%)
0	15.394	0.0%
1008	13.706	-11.0%
2016	13.472	-12.5%
3000	13.299	-13.6%
4008	13.138	-14.7%
5016	12.908	-16.1%
6000	12.887	-16.3%
7008	12.786	-16.9%
8016	12.571	-18.3%
9000	12.622	-18.0%

FIGURE 1. Results for CSR testing at 90°C in air. Less than 20% loss in sealing force was observed in 9,000 hours.

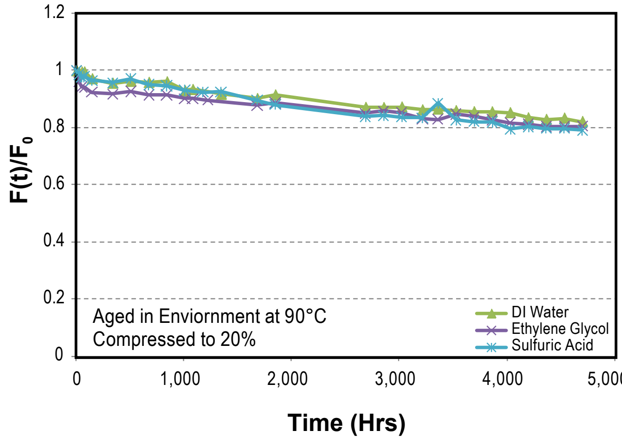


FIGURE 2. Results for CSR testing at 90°C in three aqueous environments of interest to PEMFC. Approximately 20% load loss was observed after more than 4,000 hours.

It is important to recall that the materials developed on this project are hydrocarbon-based elastomers. Given this fact, it is expected that one of the most significant threats to the stability of the candidate materials is oxidation. To evaluate this threat, a comparison of the oxidative stability to some other materials which have been considered for PEMFC applications was carried out. A key result of this work is provided in Figure 3. In this figure, relative change in mass with time is tracked for testing at 120°C. The inlaid figure provides results for 150°C testing completed previously. In this figure, the candidate material is being compared to three EPDM-based materials. Significant changes in the rate of either weight gain or loss can be correlated to significant degradation in mechanical properties. The result indicates that the candidate material has greater oxidative stability than the EPDM-based materials tested.

In addition to out-of-cell testing, two types of prototype seals were molded this year. The first was a seal over-molded onto a plastic sub-gasket. This seal was used for in-cell validation testing, and 1,700 operating hours were accumulated. Post-test evaluation remains to be completed. The second full-size prototype seal produced was of an integrated molded seal configuration. The purpose of this molding activity was to test the effect of different parameters and materials, such as gas diffusion media type, on mold-flow when producing parts with the integrated molded seal configuration. Learning from this activity was used to form the development of a final full-size prototype component.

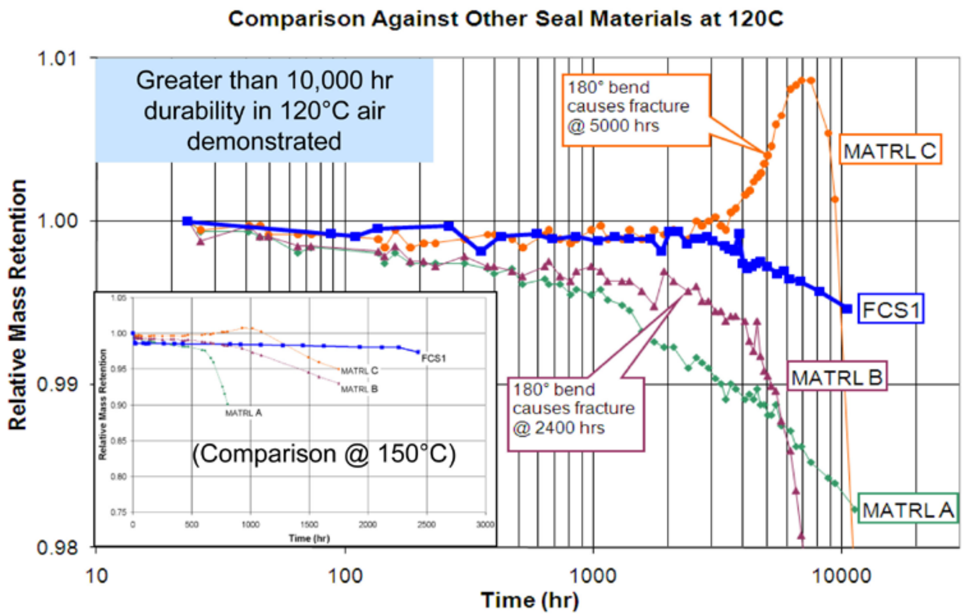


FIGURE 3. Comparison of EPDM and candidate material oxidative stability. The relative change in mass was tracked with time for three EPDM-based materials and FCS1. After more than 10,000 hours, FCS1 exhibits a mass loss of less than 1% based on a 24-hour reference point. The result indicates that FCS1 has higher oxidative stability than any of the EPDM-based materials tested.

Conclusions and Future Directions

Based on the work performed to date for the project, the following can be concluded:

- The material development strategy (synthesis and compounding) is sound.
- Based on all testing completed, the materials developed have a high probability of success for meeting the 2010 DOE goals for use in automotive PEMFC applications and are likely to meet the needs of longer lifetime applications as well.

Activities for the remainder of the project will include the following:

- Evaluation of a high volume capable injection molding technique for over-molding seals around the perimeter of full-size MEAs.
- Additional full-size in-cell testing to further validate out-of-cell test results.
- Complete evaluation of material and processing costs to assess likelihood of meeting suggested cost target at high volume.

References

1. Brian James, Jeffrey Kalinoski, "Mass Production Cost Estimation of Automotive Fuel Cell Systems", DOE Hydrogen Program 2010 Annual Merit Review Proceedings, Washington, D.C., 2010.

2. Jayanti Sinha, Stephen Lasher, Yong Yang, "Direct Hydrogen PEMFC Manufacturing Cost Estimation for Automotive Applications", DOE Hydrogen Program Annual Merit Review Proceedings, Washington, D.C., 2010.