Project title: Low Cost Durable Seals for PEMFCs

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Executive Summary

Seal durability is critical to achieving the 2010 DOE operational life goals for both stationary and transportation PEM fuel cell 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. In this project, the technical team first developed a specification for a seal material, then developed and tested the seal material in comparative bench top testing and, finally, at the single cell level under fuel cell operating conditions. High volume/high throughput mold tooling was made and full scale membrane electrode assemblies (MEAs) were made with the chosen seal material. It is projected that the material(s) developed will achieve DOE cost and durability targets when manufactured in high volumes.

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Project Objectives

- Develop a working material specification to guide the development of PEM fuel cell 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.
- Manufacture MEAs using high throughput manufacturing-type tooling

Technical Barriers Addressed

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:

A. Durability

B. Low Cost

Performance to Technical Targets and Significant Accomplishments

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	End of Project Status	DOE Targets 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}	Expected to meet DOE targets ^e	(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 Hydrogen, Fuel Cells & Infrastructure 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.

^e per Henkel guidance, assumes high volume manufacturing.

Significant 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 EPDM rubbers
- Accumulated 1700 hours of in-cell testing
- Molded parts using LIM hydrocarbon seal materials on UTC Power full-size unitized electrode assembly (UEA) for testing in cell hardware
- Initiated pre-testing analysis for single cell testing of UTC Power full-size UEA using integrated molded seal (IMS) design and LIM hydrocarbon material

Approach

To accomplish the objectives of this project, the approach was to develop and evaluate non-silicone liquid injection moldable (LIM) seal materials that can meet the specialized mechanical, compatibility, and cost requirements inherent to the design and operation of PEM fuel cells. To guide material development, a working material specification was developed. Materials developed to this specification by Henkel were 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 was made for the candidate materials. The best candidate or candidates was selected for in-cell testing to validate the performance of the material in a PEM fuel cell (PEMFC) environment. Specimens for out-of-cell testing and full size prototypes for in-cell testing were produced by Freudenberg-NOK General Partnership.

The outcome of the project will benefit the PEM fuel cell 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.

Project Results

The work over the duration of the project has been focused on the following tasks:

1. Development of a material specification to guide material development
2. Material development
3. Development of out-of-cell test procedures and test fixtures to characterize material candidates
4. Molding of prototype components for in-cell testing
5. In-cell validation testing

Material Specification

A material specification was developed using input from each of the partners in the program to achieve a material that could be produced and molded using conventional techniques and would meet the lifetime requirements for the fuel cell application. See Appendix A for details of the specification that was used to guide material development throughout the program.

Material Development

Four material candidates were developed over the course of the project. 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. FCS3 was chosen for molding onto full-size UEA components.

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 Properties						
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 minimum goal
	Yellow:	Does not meet project goal, but may be acceptable
	Red:	Does not meet project goal

Out-of-Cell Testing and Material Properties Characterization:

Virginia Tech focused their efforts on characterizing several aspects of durability for a hydrocarbon sealant developed for fuel cell sealing applications. Summary results in various areas of testing are listed below:

1. After considering relevant environmental factors, a series of environmental exposure conditions involving air, a 0.1 M sulfuric acid solution, a 50/50 (volume) ethylene glycol/water solution, and de-ionized water were selected for the exposure conditions, along with Fenton's solution for mass uptake studies. Exposure and some testing were performed at elevated temperatures, and in some cases at higher strain values, to accelerate degradation. Because the operating temperatures of fuel cells are so high, however, limited acceleration was possible in aqueous-based solutions.
2. Several standard test methods were employed to characterize the tensile properties, tear resistance, mass uptake, dynamic viscoelastic moduli, thermal properties (by DSC), and surface properties .
3. Several test methods were developed for testing purposes, including:

- a. A simple loading frame that allowed multiple tensile dog bone specimens strained to various levels to be aged in the environments of interest.
 - b. A novel dual chamber stress relaxation fixture that allowed stacks of subscale molded o-ring specimens (SMORS) to be evaluated in air and liquid environments (See Figure 2). The dual chambers allowed for both momentary and relaxed moduli to be obtained, offering opportunities to examine the relative effects of chain cross-linking and scissioning as well as relaxation to be quantified. Both continuous and intermittent stress relaxation tests were possible in two versions of this device.
 - c. A novel method to easily measure pressure leaks in up to 72 cells was developed.
4. Although limited test results with the initial material system (FCS 0) were promising, the VT team reported anomalous and erratic results from the second system (FCS 1), a two-part system. Properties varied from specimen to specimen, with some samples becoming gummy under exposure conditions (including 60oC air). These observations ultimately led to findings that there were mixing, solubility, and curing problems with the two-part system. This resulted in a return to a one-part system for the third system we tested (FCS 2).
5. Both FCS 1 and FCS 2 showed superior performance over a silicone fuel cell sealant in terms of mass gain/loss in liquid and air environments, including Fenton's peroxide solution.
6. Differential scanning calorimetry (DSC) studies suggest that aging in the environment can lower the glass transition temperature of FCS 2 slightly, suggesting possible chemical changes.
7. DMA tests conducted on FCS 2 specimens revealed expected behavior that could be reasonably fit with WLF shift factor relations, which corresponded quite well with thermal shift factors obtained for tear testing.
8. Scanning electron microscopy (SEM) revealed that no cracks appeared to form on the surfaces of specimens aged at elevated temperatures in air when no strain was applied, but did result when specimens were exposed while strained in tension. Similar behavior was also observed for specimens aged in ethylene glycol.

Raised bumps were also observed on the surface of these specimens, perhaps associated with the mass gains seen in this environment. The appearances of the surfaces of samples exposed to de-ionized water were similar to those in air. Specimens exposed to sulfuric acid solution, however, showed much more pronounced degradation features.

9. During an interim period when the Henkel materials were not available, tensile tests were performed on samples of a fuel cell grade silicone sealant that had been mounted in the straining fixtures during aging in the prescribed environments. Significant changes in mechanical properties (modulus, tensile set, and breaking stress) were observed, increasing with the magnitude of the applied strain during aging in all the environments tested.
10. Using the trouser tear configuration on specially prepared, reinforced specimens, clear evidence of the rate dependence of tearing was demonstrated for both FCS 1 and FCS 2. More extensive tear testing of the latter material at several temperatures permitted the construction of tear energy master curves using the time temperature superposition principle (TTSP). The good agreement of the thermal shift factors for tearing (which involved large localized strains) with the shift factors obtained from small strain DMA tests suggested the usefulness of a viscoelastic framework for both constitutive and fracture properties. The tearing energy master curve is believed to offer a promising approach for estimating durability of seals in stressed configurations.
11. The novel stress relaxation fixtures, holding a total of ten SMORS, could be used to intermittently monitor the momentary (of specimens aged in strain-free condition) and relaxed stiffness of the SMORS stacks. The use of these representative geometries rather than bulk elastomer specimens was thought to provide more useful information about how the elastomeric seals might perform in an actual seal configuration in a fuel cell. The use of both momentary and relaxed moduli gave insight into chemical changes in the elastomer as well as relaxation under constant strain conditions. The instruments developed performed reasonably well, although accuracy could have been improved through the use of

even more SMORS in the stacks, as the relatively small displacements imposed resulted in some scatter.

12. Both FCS 1 and FCS 2 specimens showed clear differences in relaxed and momentary moduli, especially in the elevated temperature air environments (90 and 120 C), where oxidative processes and additional cross-linking mechanisms were expected. Much less pronounced differences were seen in the liquid environments, where exposure to oxygen was more limited. Relaxation of sealing force on the order of 15% was seen over times of 4000 hours for most environments.
13. Several of the stress relaxation fixtures were modified to incorporate load cells, permitting continuous readings of the compression force on the stack exposed to stress relaxation. Results proved elusive due to a number of complications associated with testing specimens in immersed environment, resulting in erratic data for some specimens. Nonetheless, relaxation trends were similar to those observed with the intermittent stress relaxation fixtures.

The bench top testing results most applicable to fuel cell MEA mechanical designs were:

1. Compression and stress relaxation experiments and 2. Finite element analysis of a representative molded seal design. Detailed results of these two areas of testing follow.

Compression and Stress Relaxation Experiments

Background

Relaxation of elastomers may involve either physical or chemical relaxation or both.

Physical relaxation of polymers involves the flow of chains past one another as well as the movement of entanglements. For elastomers, in the absence of chemical effects, the physical relaxation phenomenon is reversible upon the removal of the strain [2].

Chemical relaxation may consist of either scissioning of covalent bonds at cross-links or along the backbone of the polymer or additional cross-linking [2; 4]. Chain scissioning of bonds can cause the effective crosslink density of the network and the equilibrium rubber elastic modulus to decrease with time [5]. Additional cross-linking can continue

to occur in rubber materials, as some residual curing agent in the material may exist and can cause further curing in the sample, especially at elevated temperatures. In some cases, additional cross-linking can also occur due to the breaking and reforming of bonds in the material as seen in a dynamic network [1]. In elastomeric components when temperature and/or deformation are large, chain scissioning of cross-links and possibly in-situ cross-linking can result in time dependent softening (relaxation) [6]. For idealized stress relaxation behavior in gaskets, after the initial physical relaxation of the polymer chain, the chemical relaxation process is minimal in comparison to the physical, and provides a steady and constant sealing force in the gasket as a function of aging [7]. It can be seen that measuring the stress of a material at constant temperature and strain in a degrading rubber network provides a measurement of the crosslink density as a function of time. However, this measure of crosslink density is only of the load bearing chains, if the degradation involves additional cross-linking as well as chain scissioning, the new cross-links formed are generally assumed not to be load bearing [8]. Tobolsky recognized this fact and determined that the permanent set in a material, which is a measure of a sample's permanent deformed shape after relaxation, can be correlated to stress relaxation under continuous strain and the momentary stress response [9]. Stress relaxation tests, which hold a sample at a prescribed strain continuously, monitor only the load bearing chains. Any new chains formed contribute little to the stress state; therefore the force relaxation characterized by this test represents a combination of the chains that have undergone scissioning as well as the viscoelastic relaxation at that specific time. A measure of the momentary stress response, which stretches a sample to a prescribed strain then releases it to its initial condition, can provide a measure of the crosslink density of the sum of the original remaining network and the new network formed during degradation at a given time. Momentary loading measurements of the stiffness are conducted by loading a specimen held in the same environment for a brief instant to a set compression length and quickly returning the specimen to its original strain condition. By measuring both momentary stiffness and stress relaxation response, the net rate of scissioning and cross-linking in the sample can be determined [9]. If the degradation involves only chain scissioning and no new networks are formed, both the momentary stiffness and stress relaxation response tests will measure the same crosslink density [8].

By monitoring the rate of relaxation with respect to temperature, lifetime predictions can be made using an Arrhenius approach as this technique assumes that the failure process consists of chemical reactions where the rate of reaction increases with temperature [7]. The Arrhenius model is generally used when thermo-oxidative aging mechanisms are dominant. This approach assumes that the chemical degradation process is controlled by a reaction rate. By plotting the log of the reaction rate versus the inverse of temperature, straight line behavior is expected and allows for simple extrapolations to various temperatures if the Arrhenius approach is valid for the temperature of interest. This method was employed by Ronan for testing stress relaxation in elastomers where he compared the Arrhenius plot obtained from compressive stress relaxation at elevated temperatures in air to the shifts determined from dynamic mechanical analysis and determined them to be in good agreement with each other [1].

In addition to the stress relaxation characterization, uniaxial tension tests can be used to characterize the mechanical behavior of a material. Generally, as polymers age they tend to become more brittle and this could affect any long-term application of the material [10]. Analysis of the mechanical behavior, such as elastic modulus, tensile strength and strain measured at various aging times and conditions, is important to understand for materials that require reliability and or durability in their applications [11]. The aging characteristics of a material can be evaluated as a function of time, environment and strain by prescribing strain on samples subject to various environments and temperatures. Material samples held at different strains in environment could be subjected to additional cross-linking or chain scissioning, which could affect the material properties. Additionally, failure from environment could occur due to chemical interactions affecting the composition of the material and its physical properties as the environment can cause chemical bonds to break and/or reform [12]. Since a material's durability is a function of mechanical behavior, the material's mechanical response will be evaluated in terms of stress relaxation and uniaxial tension to determine the durability of this material.

Experiment

An examination of the durability of fuel cell seals has been conducted to determine the effects of accelerated aging on elastomeric materials designed for fuel cell applications. Two different types of experiments have been carried out to determine the various mechanical properties of these materials specifically stress relaxation and uniaxial tension. Stress relaxation tests have been used to characterize long term durability in accelerated aging conditions. Stress relaxation was chosen because the application for the material tested is sealing and a comprehensive understanding of stress relaxation over time could provide insight into the materials sealing force as a function of aging. Since the geometry tested under these relaxation conditions is complex, the stress will not be directly calculated instead, the relaxation effects will be correlated to force as a function of time. Uniaxial tension tests have been performed to determine the mechanical behavior of these materials in aggressive environments. Uniaxial tension tests carried out under aggressive environments can provide insight into the materials response as a function of aging. Under these types of conditions, material behavior after aging will provide insight into lifetime behavior of these seals.

Materials

The material tested was a hydrocarbon elastomer developed and provided by Henkel Corporation (Rocky Hill, CT). The heat cure material system was cured by heating in a molding tool at 120°C for two to three minutes for sufficient cross-linking to occur for mold removal and then post cured at 130°C for one hour by Freudenberg-NOK (Plymouth, MI). Sheets of 200 mm x 200 mm x 0.5 mm thick samples of pure elastomer were molded for uniaxial tension samples. Sub-scale molded o-rings seals (SMORS), a scaled down version of the full sized part to be used in the membrane electrode assembly, were molded onto 40.5mm diameter disks of 0.356 mm thick gas diffusion layer. In the full size part, the elastomeric gasket will be molded with the membrane electrode assembly in the center of the elastomeric gasket, however for the SMORS tested here; the center of the seal consists of only the gas diffusion layer. These SMORS, seen in Figure

1, are used for stress relaxation tests as they are the geometry that will be used for sealing in the fuel cell and an understanding of the relaxation behavior on the specific geometry used will provide better insight into the actual behavior of these seals in a fuel cell.

Figure 1: Cross-sectional view of a portion of sub-scale molded o-ring (SMORS)

Compressive Stress Relaxation Fixtures

For this experiment, two different fixtures were used to examine the momentary stiffness and relaxation behavior separately. Both fixtures are similar to each other; the only difference is that the continuous fixture has been outfitted with a load cell to measure relaxation at short sampling intervals programmed by the software. The intermittent fixture was designed for testing in a load frame, thus limiting data collection to times when the fixtures were removed from the oven and placed in the test frame for evaluation. The fixtures were made entirely of 316 stainless steel to prevent corrosion in aggressive environments at elevated temperatures.

Figure 2: Intermittent (left) and continuous (right) stress relaxation fixtures [13]

As seen Figure 2, the continuous stress relaxation fixture, used to measure the relaxed state of stress, contains a load cell (Interface WMC-25(Scottsdale, Arizona). This load cell was chosen to provide accurate force measurements for small loads under humid conditions as the samples are immersed in aggressive environments at high temperatures. The load cell is environmentally sealed through the use of the epoxy gasket around the stem of the load cell to insure the environmental and temperature conditions of the test do not affect the recorded load. The load cell is mounted onto the relaxation fixture through the lower plunger; the top stem of the load cell is loaded by a high precision micrometer with a resolution of 0.08 mm. The micrometer is attached to the fixture in the upper bracket and is used to accurately impose a desired compressive displacement on the samples. The intermittent stress relaxation fixture does not contain a measuring device instead the displacement is fixed through use of a 1.5 mm thick washer that imposed the desired compression. This fixture was designed around testing the momentary stiffness as well as stress relaxation simultaneously through the use of two chambers, an upper and a lower. The upper chamber is used to probe the momentary response of a stack of

SMORS that is not loaded during the exposure, but are strained briefly to determine the momentary response and are then returned to their original state. The lower chamber maintains a given compression in the lower samples during environmental exposure by imposing a displacement with the use of a spacer. The lower chamber holds the prescribed strain; by varying the thickness of the spacer different compression levels can be set. This chamber when tested in a load frame measures the relaxation stiffness as a function of time. Both fixtures are placed on a polycarbonate base to allow them to rest on a flat surface. This is needed because the loading rod, which prescribes the desired strain on the lower stack through use of a spacer, protrudes from the base of the fixture. These fixtures are placed in glass containers filled with the liquid environment and then covered with a clamped glass lid to prevent evaporation and contamination.

Stress Relaxation Experiment Preparation

The samples tested in this fixture are a stack of five SMORS arranged between parallel 316 stainless steel washers centered about the loading piston. The stack configuration was utilized to provide a better strain resolution during compression as individual SMORS consist of only 1.5 mm of elastomeric material. By arranging five specimens in series, the strain resolution of the test increases as in order to achieve 20% compression, the stack is compressed 1.5 mm as opposed to 0.3 mm for an individual sample stack. For the continuous fixture, only the lower chamber contains samples as this fixture only measures the force relaxation of the specimen stack. For the intermittent fixture both the upper and lower chambers contain samples as this fixture tests both the momentary stiffness as well as the stress relaxation. The mechanical properties of the SMORS were examined in five different environments: 120°C air, 90°C air, 90°C de-ionized (DI) water, 90°C 50/50 ethylene glycol, and 90°C 0.1 M sulfuric acid solutions. The intermittent stress relaxation fixtures for testing in liquid environment were placed in glass containers, the environment was added, a glass lid was placed on top of the fixture and then the fixtures were placed in a gravity convection oven for environmental exposure. Those tested under air-aging were placed directly in the oven. The continuous stress relaxation fixtures were placed in individual glass containers into which the desired

environment was then added. The chambers were then sealed using a room temperature cure silicone to prevent evaporation and the fixtures were placed in a water bath at 90°C. The continuous stress fixtures were individually sealed due to the height addition from the micrometer and load cell, seen in Figure 2, which prevents the use of a flat lid. The addition of these components caused the overall height of the continuous fixture to be more than the height of the glass container so to minimize evaporation of environment; a room temperature cure silicone was applied between the exterior edges of the continuous fixture and the interior wall of the glass jar. A water bath was used to maintain the desired environmental temperature of the SMORS in the continuous fixture, to prevent direct heating of the load cells as well as the leads connecting the load cell to the data acquisition system. Since the continuous stress relaxation fixtures were heated in a water bath, additional insulation was added to the glass container and the top of the water bath. As illustrated in Figure 3, a PMMA box was added over the water bath to maintain a consistent temperature in the samples and to limit the impact of the laboratory's atmosphere on this sensitive test.

Figure 3: Continuous stress relaxation experimental set-up

All samples were allowed to equilibrate in their environment and temperature for a week under no loading before testing. This extensive equilibrium time is used to insure that the samples relaxation behavior is uniform. Relaxation has been measured for this system for shorter equilibrium times, however the results exhibited erratic behavior uncharacteristic of relaxation. For this reason, a longer equilibrium time was used as results from this equilibrium time show stable behavior.

Uniaxial Tension Experiment Preparation

Uniaxial tension samples were cut out of 0.5 mm sample sheets using an ASTM D412 Die C and a clicker press (Qualitest Inc., Buffalo, New York). The sample ends were reinforced with 20 mm of tape (SA, China) placed on both sides at the top and bottom of the dog bone samples and holes were punched in the sample to hold the sample under prescribed strain conditions in a custom made fixture shown in Figure 4.

Figure 4: Image of dog bone sample

Since these samples are held in strain for long periods of time, the stress concentrations from the pins cause the samples to tear unless the samples are reinforced. The stress concentration from the holes causes the samples to break in air at room temperature after a very short period of time (2-3 days). Since these samples will be held at elevated temperatures for long periods of time, over 2700 hours, the samples were reinforced. The tape is assumed be perfectly bonded for the duration of aging and is assumed to have a constant stiffness as a function of time. The custom built screening fixture was used to hold strain on the samples in environment over long periods of time to provide for accelerated aging. The fixture, seen in Figure 5, was made of 316 stainless steel to

prevent corrosion in aggressive environments. Additionally, holes were drilled into each side at various spacing to allow for different strains to be prescribed on the samples.

Figure 5: Custom built screening fixture used to prescribe held strain on samples

The samples were placed on the screening fixture at three different nominal strain levels (0, 25, and 50 % strain). These strains were presented in a previous student's work where the strain was determined to be 0, 22.14% and 49.18% from a finite element model that considers the taped region to be perfectly bonded [13]. These strains are in good agreement with the strain recorded from the laser extensometer of 0, 22% and 49% and will be reported as 0, 25 and 50% strain as an approximation to the actual strain. For samples tested in a liquid environment, the screening fixture was placed in a glass container, the desired liquid environment was added, a glass lid was added to prevent evaporation, and the loaded fixture was then placed in a gravity convection oven at 90°C to allow the specimens to age. The environments used were de-ionized (DI) water, 50/50 ethylene glycol, and 0.1 M sulfuric acid. For air-aged samples, the screening fixture was placed directly in the oven at 90°C. All samples were aged for four different aging times: 2 weeks, 4 weeks, 8 weeks, and 16 weeks and compared to the as-received material.

Stress Relaxation Test Procedure

The continuous stress relaxation fixture was displaced to 20% compression by using the precision micrometer mounted above the stack. The load was recorded with a 110 Newton Interface WMC-25 load cell connected to a data acquisition system. A custom designed LabView (National Instruments, Austin, TX) code running on a dedicated computer recorded the load measured over the extent of the experiment. The intermittent fixture was removed from the oven to measure the mechanical properties of the samples

periodically and then replaced in the oven to continue the aging process. The intermittent fixture was measured by placing the fixture into an Instron MicroTester 5848 load frame with an auto-calibrated 50 N capacity load cell. The load frame measures the force on the upper and lower stacks and the displacement is recorded from a built-in linear variable differential transformer used to measure the linear displacement of the load frame. By loading the upper and lower pistons separately, the stiffness can be measured over time for the momentary and relaxation states. The upper piston was loaded to a displacement equivalent to 20% compression on the SMORS. Since the lower stack is held in compression, loading the lower piston initially removes contact from the spacer. The point in which the contact from the spacer is completely removed represents loading of the lower stack's SMORS. At the transition point, the slope of the line changes from the loading curve from contact with the spacer to the loading curve of the samples in compression, it is this point which represents the load necessary to hold the material at the prescribed compression and is taken to be the relaxed stiffness. This is calculated by creating linear fits of the two lines and determining their intersection point.

Figure 6 illustrates a comparison of the momentary and relaxed stress loading curves. Measurements were taken at a loading rate of 8 mm/min.

Figure 6: Relaxation Results of 120°C air-aged after one day in the intermittent fixture

Uniaxial Tension Test Procedure

After the samples had reached the desired aging time, they were removed from the screening fixture and cooled to room temperature. Reflective tape markers were placed on the specimen so that a scanning laser extensometer (Fiedler Optoelektronick, GmbH) could be utilized to measure the strain of the specimens without contact. Uniaxial tension tests were performed following the ASTM D412 standard using an Instron 5867 with a 100 N load cell. The samples were gripped using pneumatic compression grips and loaded to failure with a displacement rate of 500 mm/min at room temperature.

Results and Discussion

For each aging environment in the intermittent fixture, load versus strain plots over prolonged times were used to create stress relaxation plots. The decay of the sealing force is represented by $F(t)/F_0$, where $F(t)$ is the force at a given time and F_0 is the initial force at the prescribed compression. The decay of force was plotted against time for both the momentary and relaxed states. For the intermittent fixture, the initial force is taken to be the first time the samples were tested in the load frame. For the continuous fixture, load as a function of time is measured continuously for each environment and then later normalized by F_0 where F_0 is taken a minute after initial loading. The difference in the initial relaxation load between the continuous and momentary fixtures may cause the differences in the results when compared to one another; however this difference is a function of how the fixtures are designed. The continuous fixture is designed to record all values of load for all time. The F_0 for the continuous fixture was recorded after one minute from loading. For relaxation tests that are ramp loaded, t_0 is generally assumed to be five times longer than the loading time. For the continuous fixture, one minute was used for this criterion as it took approximately 10-12 seconds to load the samples manually with the micrometer. The relaxed stack in the intermittent fixture is loaded before testing in the Instron through the use of a spacer. By the time the value is recorded in the load frame, which is approximately 2 minutes after the spacer has been loaded which took approximately 3-5 seconds; the samples had been loaded for longer than five times the loading time so this measurement is taken to be the initial force. The

difference in measuring the initial restoring force could account for difference in the results as a large portion of the relaxation takes place soon after loading. Because of this, the intermittent fixture should measure a smaller decay in force in comparison to the continuous fixture. For each uniaxial tension test, load versus displacement is recorded. Engineering stress is calculated from the original cross-sectional area and strain is calculated from the laser extensometer and crosshead displacement. Ultimate strength and strain are reported as well as the modulus at 100% extension.

Intermediate Fixture Resolution Results

The resolution of this experiment has been determined by testing the same sample multiple times over the course of one day as seen in Figure 7.

Figure 7: Measurement of resolution of the intermittent CSR

It can be seen here that the fixture shows little change for the momentary stiffness over the course of the test. The relaxed stiffness recorded over three different measurement times shows slightly more variation in comparison to the momentary stiffness, however this test is a comparison of just one point so an average of the relaxed stiffness is a better

approximation of the actual value. To do this, tests are conducted in rapid succession and the data presented for the momentary and relaxed states are an average of three runs.

Table 3: Comparison of the results from the intermittent CSR run over one day

Trial #	Momentary	Momentary StDev	Relaxed	Relaxed Stdev
1	26.513	0.072	13.334	0.461
2	26.331	0.072	12.419	0.645
3	25.790	0.087	11.996	0.315

These values have been compared for both the momentary and relaxed stack as well as the standard deviation across one succession of tests seen in Table 3. This figures show that while there is some variation between testing, the differences are small and across a given test there is little deviation. Furthermore, the standard deviation of one test is so small that any error bars shown on the graphs are not visible.

Momentary Stress Response Results

For momentary stress response, the change of load versus time illustrates a measure of the net rate of cross-linking and chain scissioning [9]. If no force decay is seen over time, the rate of cross-linking and chain scissioning is equal to each other or both are non-existent.

Figure 8 illustrates that for SMORS aged in liquid environments, there is little to no change in the normalized load as a function of time.

Figure 8: Momentary stress response in environment from intermittent fixture.

After approximately 1000 hours, the de-ionized water samples show a slight increase in normalized load of approximately 8%. This increase in $F(t)/F_0$ suggests chemical effects of aging in the form of additional cross-links being formed. It can be seen from Figure 8 that the decrease in momentary response for ethylene glycol and sulfuric acid occurs after over 500 hours of aging. This decrease in response denotes chemical effects of aging as significant physical aging effects that contribute significantly to stress relaxation happen on a shorter time scale [1-2; 14]. These cross-links could come from the bonds breaking and reforming in this environment, or additional curing residue being present in these samples. Since these samples are submerged in liquid, an increase in oxygen causing additional cross-linking is unlikely, although this effect can be seen below in the air-aged samples, which exhibit a substantial momentary increase likely associated with an increase of cross-links. One reason for this increase in crosslink density for de-ionized water aged samples could be that these samples undergo less chain scissioning in relation to additional cross-linking in comparison to the other environments which would increase the crosslink density of de-ionized water samples. If this is the case, additional cross-linking could occur from residual curing agents in the samples that are not broken due to the chemical effects of the environment. For both ethylene glycol and sulfuric acid specimens, momentary response show a slight drop in load of approximately 4%,

illustrating that the rate of chain scissioning is slightly higher than that of additional cross-linking, which would explain the drop in sealing force. Some of the decrease in stiffness can be attributed to momentary sample relaxation, where the polymer chains achieve a new equilibrium status in response to periodic strain.

Momentary stress response tests conducted in air illustrate an increase in the stiffness of these materials as a function of time, as seen Figure 9.

Figure 9: Momentary stress response in air from intermittent fixture

This increase in the stiffness suggests a large increase in crosslink density. Also, in general, as polymers age modulus increases and they can become more brittle [15]. Since the increase of the sealing force occurs over a long period of time frame (over 1000 hours), chemical effects are assumed to dominate [1-2].

It can also be seen that the degree of cross-linking is dependent on temperature. In Ronan's work, applying an Arrhenius fit to compressive stress relaxation for elastomeric seals tested showed a good comparison to the shifts determined from dynamic mechanical analysis [1]. For this reason the Arrhenius fit has been determined for the

seals tested in this work, however, since only two temperatures were tested it is unclear if this system follows Arrhenius behavior. The Arrhenius equation assumes that the degradation process is controlled by reaction rate k :

$$k = Ae^{\frac{-E_a}{RT}}$$

where k is the reaction rate, A is the pre-exponential factor, E_a is the Arrhenius activation energy, R is the gas constant (8.314 J/mol-K), and T is the absolute temperature [15]. By computing the slope of the time it takes to reach equilibrium of the chemical reaction for the momentary stress response in air, we can determine the reaction rate for both 90 °C and 120 °C as 1.72×10^{-4} rate of decay/time and 4.47×10^{-4} rate of decay/time respectively. Plotting the natural log of the reaction rate verses the inverse of absolute temperature as seen in Figure 10 we can determine the Arrhenius activation energy.

Figure 10: Plot to determine activation energy.

By taking the natural log of the Arrhenius equation as seen in, we can determine a linear fit to the Arrhenius equation where the slope is equivalent to the Arrhenius activation energy divided by the gas constant.

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right)$$

Since only two different temperature tests were conducted it is not conclusive that this reaction is governed by Arrhenius behavior, however, when carried out for these two temperatures an activation energy of 37.72 kJ/mol was determined. This result is consistent with Gillen where for butyl rubber, higher temperatures reduced the expected activation energy for oxidation processes (from ~80 to 120 kJ/mol to ~38 to 56 kJ/mol) [14]. The low activation energy suggests the presence of diffusion limited oxidation. This effect is present when the rate of oxidation uses up dissolved oxygen faster than it can be replenished by diffusion from the surrounding atmosphere [2; 14].

For the momentary stress response in air, it can be seen that increasing the temperature increases the rate of which the material degrades. For samples tested in air, the momentary stiffness approaches a plateau value of $F(t)/F_0 \approx 1.45$. Furthermore, it can be seen that after approximately 2700 hours, the stress response in 90°C air shows a plateau value very similar to that of 120°C. The fact that the plateau value is reached at a later time for samples aged in air at 90°C when compared to those aged in air at 120 °C is expected as the rate of the chemical reaction is faster at an increased temperature.

Relaxation Results

Relaxation measurements were obtained through two different testing fixtures, intermittent and continuous. Relaxation tests isolate the scissioning reactions in a sample. The decay of load is the direct measure of the physical relaxation of the material coupled with any scissioning of the polymer's molecular chains. Any new network formed (additional cross-linking) in the relaxed state have little impact on the stress state as these networks are in equilibrium in the stretched sample. When the strain is removed from these samples, the new network formed has a direct impact on any compression set

or permanent deformation seen in the sample [9]. The continuous fixture allows for all loads to be recorded as there is the force is recorded while the load is applied. For the intermittent fixture, the compressive displacement is prescribed and then the load is measured separately. The disadvantage of intermittent stress relaxation measurements is the initial loading point where most of the physical relaxation takes place is hard to determine as load is not measured continuously. Figure 11 illustrates the stress relaxation results from the intermittent fixture.

Figure 11: Stress relaxation in environment from intermittent fixture

It can be seen from Figure 11 that stress relaxation has an effect on the samples aged in environment more so than momentary stress relaxation. These samples show an average decay in sealing force of 16% after over 3500 hours. It can also be seen from stress relaxation that after a long period of time the changes in the relaxed stiffness are minimal, indicating that chemical degradation past this point has a minimal effect on the elastomer [7]. The relaxation of liquid samples from the continuous fixture has also been measured in Figure 12.

Figure 12: Stress relaxation in environment from continuous fixture

The continuous fixture has been collecting data for over 4000 hours, and allows a more accurate prediction of the initial sealing force as data is being collected throughout the loading cycle. After 2000 hours, specimens in sulfuric acid and de-ionized seemed to have reached a plateau of 85% and 80% of the restoring force, respectively. Samples aged in ethylene glycol shows unexpected behavior after 3000 hours. The erratic behavior seen in the continuous fixture compared to the intermittent fixture is attributed to the refilling of the container in which the fixture is held in environment; samples aged in both ethylene glycol and de-ionized water are much more sensitive to refilling those samples in sulfuric acid. While these fixtures are sealed as best as possible, they are not air tight as the lower plunger is free to load the samples. This causes some evaporation of the environment and is causes a need for refilling. The containers are refilled with their respective liquid environment; however it is assumed that since these liquids show evaporation the concentration changes as the test continues. The refilled liquid is heated to 90°C, however, for the case of samples aged in ethylene glycol, the percent by volume of EG compared to water is changing as the test is run as the concentration is unknown in the fixture. This does not seem to affect the sulfuric acid environment. One possible reason for this is the ethylene glycol solution is denser than the other solutions and the

density is increasing with an increase in concentration. As the density of the liquid increases, the restoring buoyancy force increases which would result in an increase in the restoring seal force. Stress relaxation on the intermittent fixture has been evaluated for samples aged in air at both 90°C and 120°C as seen in Figure 13.

Figure 13: Stress relaxation in air from intermittent fixture

From Figure 13 it can be seen that the behavior of the stress relaxation in the intermittent fixture has erratic behavior after extended periods of time for 90°C air. For this reason, the 90°C intermittent stress relaxation fixture was restarted using an additional test frame. Currently, we can see in Figure 13 that the restarted data is showing similar trends to the stress relaxation of samples in 120°C air, however, the relaxation is taking place at a slower rate which is to be expected for lower temperatures. Additionally, the 120°C air-aged samples plateau at approximately a 17% force decay after a period of 2500 hours. For 90°C samples the plateau value is not clear as after 3000 hours, an increase in the normalized relaxation force is observed. This increase may be attributed to varying frictional effects in the 90°C stack from loading/unloading cycles.

Uniaxial Tension Results

Tensile strength, ultimate strain and secant modulus at 100% strain were measured and calculated for each tensile test. Comparing these mechanical properties as a function of aging time, environment and strain to those of the as-received material can provide an insight into the durability of the material. Engineering stress is calculated from

$$\sigma = \frac{F}{A_0}$$

where F is the load applied and A_0 is the initial cross-sectional area.

The strains for the samples were recorded directly from the laser extensometer with a resolution of 0.25 microns. Since the laser extensometer has a limited range of extension, and the samples undergo large deformations, the strain obtained from the laser was correlated to the crosshead displacement. This was performed by plotting the strain from the crosshead vs. the laser strain and correcting such that the slope of the line is equal to one as seen in Figure 14.

Figure 14: Correction of strain from laser extensometer to crosshead displacement.

Each property is plotted versus time for each prescribed strain and is compared to the as-received samples. An example of this for samples aged in sulfuric acid can be seen in Figure 15, where tensile strength is plotted versus aging time. Note that for all plots shown the error bars represent $\pm$ one standard deviation.

Figure 15: Tensile strength for sulfuric acid samples versus aging time.

However, it is hard to draw conclusions from each separate environment versus time plot as the results across the samples vary. When looking at the ultimate aging time for each property a comparison can be made. The ultimate strength at failure is plotted for each prescribed strain and environment at the maximum aging time of 2700 hours in Figure 16.

Figure 16: Comparison of tensile strength versus environment

It can be seen that for all liquid environments and prescribed strains, the tensile strength after 2700 hours shows a small decrease. Generally, samples aged in liquid with a prescribed strain show more of a decrease in ultimate strength compared to samples aged free of strain. These samples can undergo chain scissioning and cross-linking, which could the ultimate strength values. Also, a small decrease in tensile strength when compared to the as-received material is observed, which suggests that affect the ultimate strength of liquid-aged samples is not affected by these aging conditions. The tensile strength evaluated at the longest aging time for samples aged in 90°C air shows an increase in the ultimate strength which is contrary to the results seen for samples aged in liquid environments. This is suggestive of an increase in crosslink density for samples aged in air compared to those aged in liquid and was observed earlier from the momentary stiffness results. Figure 17 compares the ultimate strain, to different strain and environments.

Figure 17: Comparison of ultimate strain versus environment

The ultimate strain and tensile strength plots show a similar trend except for air-aged samples. The drop in ultimate strain combined with an increase in ultimate stress for air-aged samples suggests a dramatic increase in the material's modulus, which is clearly seen in Figure 18.

Figure 18: Comparison of secant modulus at 100% strain versus environment.

These results can be explained by chain scissioning and re-cross-linking. Similar to the intermittent stress relaxation, the polymer chains in the strained sample may break and reform and could create a secondary network. Removing the strain in these samples and then testing evaluates the sum of both the remaining original network and the newly formed network. For this case, an increase the materials' behavior in response to loading is indicative of a secondary network being present as the new network can now carry a portion of the load. Additionally, physical aging can be accompanied by increases in stiffness, yield stress, density and viscosity [16-17]. This can be seen for all aging conditions as the secant modulus shows an increase or similar value when compared to the virgin material. A dramatic increase in the secant modulus at 100% for the air-aged samples is observed and follows the results from the momentary stiffness results performed above.

Conclusion

Viscoelastic properties have been evaluated for a hydrocarbon elastomeric molded seal using momentary and relaxed stress response from two different test fixtures. The constitutive properties of these materials have also been compared over varying aging times, strain rates, and environments. For the stress relaxation tests, by comparing the momentary and relaxed states, a comparison can be made between rates of additional cross-linking in the presence of chain scissioning and chain scissioning effects alone. From relaxation tests, it was determined that for momentary stress relaxation, the samples in liquid environment showed little change in restoring force suggesting that the rate of chain scissioning is equivalent to that of additional cross-linking or non-existent. For momentary stress relaxation for air-aged samples, it was seen that the rate of cross-linking was higher than that of chain scissioning as the momentary modulus was increasing. Stress relaxation tests, in liquid environment showed 16% decay in load over time. Additionally, these samples illustrate small changes in relaxation after an extended period of time suggesting, that the chemical degradation process has slowed after 2700 hours. Stress relaxation tests in air showed a similar dependence on temperature,

compared to the momentary tests where the rate of degradation was higher for 120°C samples compared to 90°C. From the uniaxial tension tests, small decreases in the ultimate properties of the material occur after 2700 hours in strain and aged conditions. However, due to additional cross-linking in the strained states, the secant modulus at 100% strain of the material experiences an increase for all cases.

Finite Element Characterization of Seal Design

Critical to the application of seal materials to commercial fuel cell stacks is the mechanical design of the seal. To that end, the compression properties of the seal in configuration must be understood. Finite element analysis (FEA) was used to model a particular seal design that may be viable for commercial fuel cell stacks.

Finite element analysis is widely used to obtain approximate numerical solutions to boundary value problems. Finite element analysis tools, such as ABAQUS, can be used to predict the response of a system when subjected to external loading conditions.

Elastomeric seals are used for a variety of applications where they are subjected to compressive loads, static or dynamic in nature, in the presence of environments. The stress-strain and the contact pressure distribution resulting from the seal compression are good indicators of a seal's performance, as well as of its sealing characteristics[18].

During compression of an elastomeric seal, tensile stress in the interior region and on the outside surface of the seal may cause a failure by propagating a pre-existing flaw or crack due to the opening nature of these tensile stresses[19]. A thorough understanding of the local stress state within generic seal profiles may be useful for optimization of the seal design so as to minimize stresses that may lead to seal failure. Results obtained from finite element analysis can be compared with experimental data to check the accuracy of the solution obtained.

Seal Stress Analysis

To simulate seal compression between two bipolar plates in a fuel cell assembly, a two-dimensional, non-linear, axisymmetric analysis was performed using ABAQUS[20], a commercially available finite element software package. Two seal cross-sections, an O-ring and the SMORS configuration, were considered in the analysis. The seal was meshed with four-node reduced-integration axisymmetric quadrilateral elements, CAX4R, with hybrid formulation. A master-slave relationship was established between the compression platen and seal, respectively to prevent the rigid platen from passing through the seal as it progressively compresses the seal during each computational iteration. Interaction between the compression platens and the seal was established to allow for direct surface-to-surface contact. In order to investigate the effect of interfacial friction between seal and compression platens on the stress/strain profile, the friction coefficient between compression platen and seal material was assumed to be $\mu = 0$ (frictionless) and 0.3 (rough). Fixed boundary conditions were used at the lower compression platen while a displacement ramp was given to the top compression platen such that the top platen moves down by a fixed distance in the axial direction, compressing the seal against the bottom platen to achieve the desired strain. Furthermore, a parallel-face boundary condition was established between top and bottom compression platens to prevent any rotation during simulation. A schematic of the applied boundary conditions is also illustrated for O-ring in Figure 19.

Figure 19: Illustration of the O-ring under compression shown with original and deformed configurations in ABAQUS.

The final deformed shape along with the spatial displacement, stress, strain, contact stress, and contact width distribution, was generated. Table 4 outlines the plan for the finite element analysis for various R/r ratios, where R represents the distance of the center of the seal from axis and r is the diameter of seal cross-section, as illustrated for O-ring in Figure 6.1. When a seal bead is laid out on MEA or any substrate, it may follow a path where the bead has varying curvature represented by the ratio R/r . The lower R/r , the higher is the curvature of the seal at a given location which may result in lower value of contact stress where leakage may occur.

Table 4: Test matrix developed to analyze the seal cross sections using ABAQUS

Seal Bead cross-section	Nominal Compression	Distance from Centerline	Coefficient of Friction (μ)	Parameters of Interest
O-Ring	$10\% \leq \frac{\delta}{2r} \leq 40\%$	$\frac{R}{r} = 1, 10 \text{ \& } 100$	$\mu = 0.1$	Stress distribution: σ_{11} , σ_{22} , σ_{33} Strain distribution: ϵ_{11} , ϵ_{22} , ϵ_{33}
Custom (SMORS)	$10\% \leq \frac{\delta}{2r} \leq 40\%$	$\frac{R}{r} = 20$	$\mu = 0 \text{ \& } 0.3$	Contact stress distribution, σ_c Contact width, b

In order to characterize seal material response and to satisfy the input requirements of hyperelastic material models in ABAQUS®, stress-strain data from uniaxial tension tests of a hydrocarbon-based fuel cell seal material were used in this study and provided as material input into ABAQUS. Various hyperelastic material models were evaluated in ABAQUS by fitting the material models with the experimental data from uniaxial tensile tests. A least-square fitting procedure was used to determine the coefficients for the selected model. Improper fit between the model and test data indicates an unsuitable material model. Figure 20 shows a plot of experimental data and predicted uniaxial behavior and Figure 21 provides information on stability of material models and constants generated from ABAQUS evaluation. It was observed that the two-parameter Ogden model and neo-Hookean models correlate very closely with the uniaxial test data and may also be used for analyzing uniaxial compression up to 50% strain. A two-parameter Ogden model was used in this study to further analyze seal compression between two rigid plates and also to calculate properties such as initial modulus.

Figure 20: Plot of experimental data and predicted uniaxial behavior in tension and compression using various material models.

Material: FCS1			
Job Name: FCS1_12			
Polynomial, N = 1 (Mooney-Rivlin)	HYPERELASTICITY - MOONEY-RIVLIN STRAIN ENERGY		
Ogden, N = 1	D1	C10	C01
Reduced Polynomial, N = 1 (Neo Hooke)	2.327557830E-02	0.361766764	-0.275782468
Reduced Polynomial, N = 3 (Yeoh)	STABILITY LIMIT INFORMATION		
Van Der Waals	WARNING: UNSTABLE HYPERELASTIC MATERIAL		
	UNIAXIAL TENSION:	UNSTABLE AT A NOMINAL STRAIN LARGER THAN	0.1500
	UNIAXIAL COMPRESSION:	UNSTABLE AT A NOMINAL STRAIN LESS THAN	-0.1427
	BIAXIAL TENSION:	UNSTABLE AT A NOMINAL STRAIN LARGER THAN	0.0800
	BIAXIAL COMPRESSION:	UNSTABLE AT A NOMINAL STRAIN LESS THAN	-0.0675
	PLANAR TENSION:	UNSTABLE AT A NOMINAL STRAIN LARGER THAN	0.1300
	PLANAR COMPRESSION:	UNSTABLE AT A NOMINAL STRAIN LESS THAN	-0.1150
	VOLUMETRIC TENSION:	STABLE FOR ALL VOLUME RATIOS	
	VOLUMETRIC COMPRESSION:	STABLE FOR ALL VOLUME RATIOS	

(a)

Material: FCS1
Job Name: FCS1_12

Polynomial, N = 1 (Mooney-Rivlin)	HYPERELASTICITY - OGDEN STRAIN ENERGY FUNCTION WITH N = 1 <table border="1"> <thead> <tr> <th>I</th> <th>MU_I</th> <th>ALPHA_I</th> <th>D_I</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>0.363497748</td> <td>2.56608450</td> <td>1.101153575E-02</td> </tr> </tbody> </table> STABILITY LIMIT INFORMATION UNIAXIAL TENSION: STABLE FOR ALL STRAINS UNIAXIAL COMPRESSION: STABLE FOR ALL STRAINS BIAXIAL TENSION: STABLE FOR ALL STRAINS BIAXIAL COMPRESSION: STABLE FOR ALL STRAINS PLANAR TENSION: STABLE FOR ALL STRAINS PLANAR COMPRESSION: STABLE FOR ALL STRAINS VOLUMETRIC TENSION: STABLE FOR ALL VOLUME RATIOS VOLUMETRIC COMPRESSION: STABLE FOR ALL VOLUME RATIOS	I	MU_I	ALPHA_I	D_I	1	0.363497748	2.56608450	1.101153575E-02
I		MU_I	ALPHA_I	D_I					
1		0.363497748	2.56608450	1.101153575E-02					
Ogden, N = 1									
Reduced Polynomial, N = 1 (Neo Hooke)									
Reduced Polynomial, N = 3 (Yeoh)									
Van Der Waals									

(b)

Material: FCS1
Job Name: FCS1_12

Polynomial, N = 1 (Mooney-Rivlin)	HYPERELASTICITY - NEO-HOOKEAN STRAIN ENERGY <table border="1"> <thead> <tr> <th>D1</th> <th>C10</th> <th>C01</th> </tr> </thead> <tbody> <tr> <td>8.618016485E-03</td> <td>0.232226781</td> <td>0.00000000</td> </tr> </tbody> </table> STABILITY LIMIT INFORMATION UNIAXIAL TENSION: STABLE FOR ALL STRAINS UNIAXIAL COMPRESSION: STABLE FOR ALL STRAINS BIAXIAL TENSION: STABLE FOR ALL STRAINS BIAXIAL COMPRESSION: STABLE FOR ALL STRAINS PLANAR TENSION: STABLE FOR ALL STRAINS PLANAR COMPRESSION: STABLE FOR ALL STRAINS VOLUMETRIC TENSION: STABLE FOR ALL VOLUME RATIOS VOLUMETRIC COMPRESSION: STABLE FOR ALL VOLUME RATIOS	D1	C10	C01	8.618016485E-03	0.232226781	0.00000000
D1		C10	C01				
8.618016485E-03		0.232226781	0.00000000				
Ogden, N = 1							
Reduced Polynomial, N = 1 (Neo Hooke)							
Reduced Polynomial, N = 3 (Yeoh)							
Van Der Waals							

(c)

Material: FCS1					
Job Name: FCS1_12					
Polynomial, N = 1 (Mooney-Rivlin)	HYPERELASTICITY - POLYNOMIAL STRAIN ENERGY FUNCTION WITH N = 3				
Ogden, N = 1	D1	C10	C01	C02	
Reduced Polynomial, N = 1 (Neo Hooke)	D2	C20	C11	C12	
Reduced Polynomial, N = 3 (Yeoh)	D3	C30	C21	C12	
Van Der Waals	9.703500736E-03	0.206248680	0.000000000		
	0.000000000	-4.456420773E-03	0.000000000	0.000000000	
	0.000000000	1.236736764E-03	0.000000000	0.000000000	0.0
STABILITY LIMIT INFORMATION					
UNIAXIAL TENSION: STABLE FOR ALL STRAINS					
UNIAXIAL COMPRESSION: STABLE FOR ALL STRAINS					
BIAXIAL TENSION: STABLE FOR ALL STRAINS					
BIAXIAL COMPRESSION: STABLE FOR ALL STRAINS					
PLANAR TENSION: STABLE FOR ALL STRAINS					
PLANAR COMPRESSION: STABLE FOR ALL STRAINS					
VOLUMETRIC TENSION: STABLE FOR ALL VOLUME RATIOS					
VOLUMETRIC COMPRESSION: STABLE FOR ALL VOLUME RATIOS					

(d)

Material: FCS1					
Job Name: FCS1_12					
Polynomial, N = 1 (Mooney-Rivlin)	HYPERELASTICITY - VAN DER WAALS STRAIN ENERGY FUNCTION				
Ogden, N = 1	MU	LAMBDA_M	A	BETA	
Reduced Polynomial, N = 1 (Neo Hooke)	0.449232109	4.63078651	0.604826135	0.000000000	8.64
Reduced Polynomial, N = 3 (Yeoh)	STABILITY LIMIT INFORMATION				
Van Der Waals	UNIAXIAL TENSION: UNSTABLE AT A NOMINAL STRAIN LARGER THAN 3.5900				
	UNIAXIAL COMPRESSION: UNSTABLE AT A NOMINAL STRAIN LESS THAN -0.9070				
	BIAXIAL TENSION: UNSTABLE AT A NOMINAL STRAIN LARGER THAN 2.2800				
	BIAXIAL COMPRESSION: UNSTABLE AT A NOMINAL STRAIN LESS THAN -0.5332				
	PLANAR TENSION: UNSTABLE AT A NOMINAL STRAIN LARGER THAN 3.5200				
	PLANAR COMPRESSION: UNSTABLE AT A NOMINAL STRAIN LESS THAN -0.7788				
	VOLUMETRIC TENSION: STABLE FOR ALL VOLUME RATIOS				
	VOLUMETRIC COMPRESSION: STABLE FOR ALL VOLUME RATIOS				

(e)

Figure 21: Material parameters and stability limit information on (a) Mooney Rivlin, (b) two-parameter Ogden, (c) Neo-Hookean, (d) Yeoh, and (e) Van der Waals hyperelastic material models.

O-ring Analysis

Figure 22, Figure 23, and Figure 24 show ABAQUS-generated stress (σ_{11} , σ_{22} , σ_{33}) and strain (ϵ_{11} , ϵ_{22} , ϵ_{33}) profiles from simulation of an O-ring with $\mu = 0.1$ under 25% compression for $R/r = 1$, 10 & 100 respectively. The distribution of the strain, ϵ_{22} , shown in Figures 6.4 (b), 6.5 (b) & 6.6 (b), is compressive where the plates are touching the O-ring in the deformed state (the region of contact width). Beyond the contact width, b , the strain is tensile in nature. Also interesting to note is the tensile nature of stresses in the 1 and 3 direction, as shown for σ_{11} and σ_{33} . The presence of tensile stresses (or strains) on the outside surface may be detrimental in the presence of temperature and aggressive environments. Stress increases the rate of diffusion in a material, which can lead to a reduction in material strength over a period of time. The presence of tensile stresses may make the situation worse because any minor flaw or crack in the material could propagate under these opening stresses [19]. Also, the stress/strain distribution is more symmetric as expected as R/r increases.

Figure 22: FEA simulation of seals subjected to 25% compression for $R/r = 1$. The interfacial friction is given by $\mu = 0.1$. Note the asymmetric nature (with respect to 2-direction) of (a) stresses and (b) strains in 1-2-3 directions for O-ring cross-section.

Figure 23: FEA simulation of seals subjected to 25% compression for $R/r = 10$.

The interfacial friction is given by $\mu = 0.1$. The stresses (a) and strains (b) are more symmetrically distributed in 1-2-3 directions for O-ring cross-section.

Figure 24: FEA simulation of seals subjected to 25% compression for $R/r = 100$.

The interfacial friction is given by $\mu = 0.1$. The symmetry in stresses (a) and strains (b) is more pronounced in 1-2-3 directions for O-ring cross-section.

The sealing capability of an elastomeric O-ring seal depends on the contact stresses that develop between the O-ring and the surfaces with which it comes into contact. An illustration of contact stress (σ_c) and contact width (b) is shown in Figure 25. It has been

suggested in the literature [21] that leakage onset occurs when the peak contact stress, $\sigma_{c,max}$, reduces to a value lower than the pressure differential across the seal, p , (i.e., $\sigma_{c,max} \leq p$). Contact stress profiles (σ_c) were generated for the O-ring for rough surface conditions ($\mu = 0.1$), and nominal compression ranging from 5 to 40%. Contact stress profiles were plotted as the nodal stress component versus the x-coordinates (defined as the horizontal distance from the center of the O-ring cross-section to a node along the perimeter), as shown in Figure 26. The information on contact width (b), which is the length of the O-ring that touches the retaining surfaces when viewed from the cross-section (the distance between two points on each profile where the contact stress curve intersects the zero stress line) and peak contact stress ($\sigma_{c,max}$) versus R/r , was extracted from the contact pressure profiles in Figure 26, and results are summarized in Figure 27. Results in Figure 27 indicate that the values of contact width and peak contact stress do not change significantly as the ratio of R/r increases, i.e. as the cross-section of the O-ring gets farther away from the central axis. This is an important observation and may prove to be helpful when seal bead is laid out in a fuel cell stack, such as shown in Figure [22].

Figure 25: Illustration of concept for contact stress and width for O-ring seal.

Figure 26: Contact pressure profile for O-ring for (a) $R/r = 1$, (b) $R/r = 10$ & (c) $R/r = 100$ with rough ($\mu = 0.1$) interfacial condition. The symmetry of pressure is more evident as the ratio of R/r increases.

(a)

(b)

Figure 27: Contact width and peak contact stress profiles for O-ring under compression for different R/r ratios.

SMORS Analysis

It was observed in that increasing the R/r greater than 10 does not lead to significant change in contact stresses and contact width, SMORS compression analysis was also carried out for $R/r = 20$ (also realistic to actual SMORS tested in experiments), according to the plan in Table 4, to generate stress, strain, contacts stress, and contact width profiles versus compression strain. In order to simplify the analysis and save computational time, only half a model of the SMORS was analyzed, where the bottom compression platen was removed and a plane of symmetry at the mid-plane of GDL was used. Fixed boundary conditions were used at the lower edge of the GDL such that no movement was allowed in the 2-direction but permitted in 1-and-3 direction under the applied displacement conditions. Also, top compression platen was replaced by an analytically rigid line which eliminated the need to model both platens in the analysis. Furthermore, a parallel-face boundary condition was established between the analytically rigid line and GDL in order to prevent any rotation during simulation. A schematic of the applied boundary conditions is illustrated for SMORS in Figure 28.

Figure 28: Illustration of the SMORS under compression showing (a) full cross-section with original and deformed shape, and (b) half section used for analysis in ABAQUS.

A typical stress/strain distribution is shown in Figure 29 for 25% nominal compression of the seal; the presence of tensile stresses is evident on the outside surface of the seal, similar to what was observed for the O-ring geometry. Again, the presence of these tensile stresses may be detrimental to a seal, especially if surface flaws are present. Due to hygrothermal fatigue (due to temperature cycling in the presence of moist environment in fuel cell unit), the seal material may degrade over time, resulting in reduced tensile strength/tear strength and eventually leading to surface crack propagation [23]. Any leakage due to seal failure may impede the function of a fuel cell stack. It is therefore critical to design seals so as to minimize the level of tensile stresses on the outside surface. Contact stress profiles were also generated for smooth ($\mu = 0$) and rough surfaces ($\mu = 0.3$) for $R/r = 20$, as shown in Figure 30, and information on contact width and stresses were extracted. As shown in Figure 6.13, the contact width, b , and peak value of peak contact stress, $\sigma_{c,max}$ are not significantly different for frictionless and rough surfaces, indicating that friction does not play a significant role in the distribution of contact stresses and width when a SMORS is compressed.

Figure 29: FEA simulation of SMORS subjected to 25% compression for $R/r = 20$. The interfacial friction is given by $\mu = 0$. The stresses (a) and strains (b) are symmetrically distributed in 1-2-3 directions for O-ring cross-section.

Figure 30: Contact stress profile for frictionless and rough conditions from 10 to 40% compression of SMORS. Note the higher peak contact stress for the case where friction is present between seal and compression platen.

(a)

(b)

Figure 31: Effect of interfacial friction (frictionless $\mu = 0$ and Rough $\mu = 0.3$) between compression platens and seal on (a) peak contact pressure and (b) contact width.

Contact Mechanics of Elastomeric Seals

When an elastomeric seal is installed and compressed, the contact configuration is generally regarded as Hertzian contact[24]. In this case, the contact pressure profile along the horizontal direction of a seal's cross-section becomes a parabola, which is the well-known Hertz pressure distribution. By adopting Hertzian contact, Lindley [4; 8] derived an empirical relationship between a compressive force and fractional compression for a bonded rubber block of circular cross-section:

$$F = 2\pi R \cdot 2r \cdot E_c (1.25C^{1.5} + 50C^6)$$

where F is the total compressive load, $2R$ and $2r$ are the mean and cross-section diameters, respectively, C ($= x/d$ where x is the diametric compression) is the fractional compression, and E_c is the effective compression modulus. The elastic modulus of the compression platen material was regarded to be infinite when compared with that of the seal. The material of the seal was also regarded as incompressible (i.e., Poisson ratio, $\nu = 0.5$). Using Hertz theory [24], the contact width, b and the peak contact stress (the highest value of the Hertz pressure profile), $\sigma_{c \max}$ can be obtained by:

$$b = d \sqrt{\frac{6}{\pi} g(c)}$$

$$\sigma_{c \max} = E_c \left[\frac{16}{6\pi} g(c) \right]^{\frac{1}{2}}$$

where $g(c) = 1.25C^{1.5} + 50C^6$. Dragoni and Strozzi [26] analyzed the problem of O-ring compression using finite element analysis method and proposed a modified relationship given as:

$$b = \frac{3}{2} d C^{\frac{2}{3}}$$

$$\sigma_{c \max} = E_c \left[\frac{10}{3\pi} \right]^{\frac{1}{2}} C^{\frac{3}{4}}$$

For use with equations 6.3 and 6.5, the effective compression modulus, E_c , is given as [27]:

$$E_c = E \cdot (1 + 2K \cdot S^2)$$

where $E = \frac{3}{2}(\mu_1 \times \alpha_1)$ is the small-strain tensile modulus calculated from Ogden material coefficients μ_1 and α_1 provided in Figure 21 (b), K is the numerical factor depending on the hardness of the seal material and goes from 0.9 for 30 Shore A to 0.5 for 75 Shore A, and S is the shape factor given as:

$$S = \text{loaded Area} / \text{force-free Area}$$

and may be defined for the O-ring by an approximate relationship given as:

$$S = \frac{2\pi \cdot R \cdot b}{2 \times \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} 2\pi(R + r \cdot \cos\theta) \cdot d\theta}$$

where b is the contact width and R is the mean radius of the seal cross-section, as illustrated in Figure 32 for various common geometries and O-ring. The seal material used here has a Shore A hardness value of 30 (provided by Henkel Corporation). Therefore a value of $K = 0.9$ was used in Equation 4.2 to calculate E_c .

$$S = \frac{\text{loaded}}{\text{force} - \text{free}} = \frac{\pi \cdot d^2 / 4}{\pi \cdot d h_o} = \frac{d}{4 h_o}$$

(a)

$$S = \frac{\text{loaded}}{\text{force} - \text{free}} = \frac{b \cdot l}{2 h_o (b + l)}$$

(b)

$$S = \frac{2\pi \cdot R \cdot b}{2 \times \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} 2\pi (R + r \cdot \cos \theta) \cdot d\theta}$$

(c)

Figure 32: Shape factor for some common geometries.

Hertz theory is valid if the contacting bodies are assumed to be semi-infinite when compared with the contact dimensions; the strains in the contact region must be infinitesimal to apply the theory of linear elasticity; and the contact surface is frictionless. None of these is valid for the O-ring's contact problem. This has previously been discussed[28], but the results showed that the Hertz theory was applicable until fractional compression of up to 25% [21] or 30% [29]. The contact stress and contact width results obtained from FEA analysis on the O-ring were compared with results obtained by using Lindley's and Dragoni's equations. Figure 33 shows the comparison results (also summarized in Table 5 along with shape factor and compression modulus values) and a good agreement was found between FEA and analytical approaches proposed by Lindley and Dragoni.

(a)

(b)

Figure 33: Contact width and contact pressure data on O-ring compression from FEA analysis and Lindley and Dragoni equations

Table 5: Contact width and contact pressure data on O-ring obtained from FEA analysis and Lindley and Dragoni approach.

Seal Compression (%)	FEA		Shape Factor, S	Compression modulus (MPa)	Lindley		Dragoni	
	b (mm)	CPRESS (MPa)			b (mm)	CPRESS (MPa)	b (mm)	CPRESS (MPa)
5	0.45	0.15	0.08	1.42	0.33	0.15	0.41	0.15
10	0.6	0.24	0.13	1.44	0.55	0.26	0.65	0.26
15	0.81	0.32	0.18	1.48	0.75	0.37	0.85	0.37
20	1.08	0.42	0.22	1.53	0.94	0.48	1.03	0.47
25	1.32	0.54	0.27	1.58	1.13	0.6	1.19	0.58
30	1.57	0.68	0.32	1.66	1.36	0.75	1.34	0.69
35	1.74	0.87	0.39	1.78	1.64	0.97	1.49	0.84
40	2.05	1.14	0.48	1.97	1.99	1.31	1.63	1.02

Theoretical & Experimental Validation of Finite Element Results for SMORS

From experimental testing of SMORS, load versus displacement profiles were obtained, as shown and discussed in chapter 3. Load versus displacement profiles were also generated using Lindley's formula (Equation 6.1) and the FEA method so comparison could be made with experimental data for validation. The total force for a given compression of the seal was calculated from contact width and peak contact pressure profile obtained from FEA, according to the following equation:

$$F_{FEA} = \int_{-\frac{b}{2}}^{\frac{b}{2}} 2\pi(R+x) \cdot \sigma_c(x) \cdot dx$$

where is $\sigma(x)$ the parabolic pressure distribution at the contact width given as:

$$\sigma_c(x) = \sigma_{cmax} \left(1 - \frac{4}{b^2} x^2 \right)$$

and illustrated in Figure 34.

Figure 34: Calculation of total load from contact width and contact pressure profile obtained from FEA of SMORS under compression.

Load values thus obtained from the FEA analysis, the Lindley approach, and the experimental results were plotted against % compression of the seal. Results provided in Figure 6.17 show a very good agreement between Lindley's approach and the experimental data up to 25% compression, whereas the FEA method shows reasonable agreement with experimental data up to 10% compression of the seal. For more than 10% compression of the seal, the FEA results overestimate the load values. This may be attributed to a number of reasons related to assumptions made during axisymmetric modeling of SMORS in ABAQUS. In order to explain the FEA results in light of the comparison shown in Figure 35, it is important to discuss SMORS in detail so that the differences in experimental testing of real geometry and the simplified model analyzed in ABAQUS can be outlined.

Figure 35: Comparison of load versus % compression behavior obtained from finite element analysis in ABAQUS, theoretical approach based on Lindley's empirical relationship and experimental data from SMORS.

As discussed earlier, SMORS stands for sub-scale molded o-ring seal where seal material is molded onto two porous gas diffusion layers (GDL) made of graphite fibers (fiber volume fraction approximately 0.3). During molding process, the seal material was required to impregnate the GDL all along the perimeter (area under seal web) so that

mechanical interlocking could be established to prevent relative slipping between GDL and seal web. Such an assembly was desired so that conditions for a fuel cell application could be mimicked. In a PEM FC stack, two outer GDL layers would sandwich a cathode-membrane-anode assembly (on which a seal material is molded), an illustration of which is shown in Figure 36.

Figure 36: Cross-section of SMORS to illustrate various components of a unitized electrode assembly (UEA) (membrane electrode assembly (MEA) consisting of cathode-membrane-anode assembly + two GDL layers).

In absence of a cathode-membrane-anode assembly, two GDL layers with seal molded outside, illustrated in Figure 37(a), was tested in compression to obtain load versus displacement data. Several simplifying assumptions were made to model the SMORS in ABAQUS is shown in to provide stability during analysis.

(a)

(b)

Figure 37: (a) Simplified SMORS tested in compression stress relaxation tests, and (b) delamination at seal/GDL interface due to poor impregnation of seal material into fibers (Courtesy of Henkel Corporation)

No-slippage between seal and GDL

In the ABAQUS modeling, no slippage was assumed at the seal/GDL interface. However, it was found during post-analysis of seals failed during CSR testing that adequate impregnation of GDL layers was not achieved during molding, as shown in Figure 37(b), which may lead to de-lamination. Such de-laminations at the seal/GDL interface would reduce the load at a given compression during testing. If slippage is allowed at the seal/GDL interface in ABAQUS, significant sliding and lifting of the seal web was observed, as shown in Figure 38 resulting in instability in the model and questionable values of contact pressure and width.

Figure 38: Sliding at seal/GDL interface and lifting of seal web observed in ABAQUS.

Single GDL with Fixed Boundary Conditions

In ABAQUS modeling, only one GDL layer was assumed as opposed to the two GDL layers present in each SMORS with a very fine gap in between where seal material tends to flow during the molding process. The presence of two GDL layers instead of one, adds one more interface at which sliding may occur, leading to reduced load values measured during experimental testing. Also, fixed boundary conditions were applied to the GDL preventing its movement and rotation in all direction. However, compression of SMORS

during the experiment may result in bending, rotation, and crushing of the GDL, as shown in Figure 39, which may possibly result in additional sliding at interfaces in a SMORS. Such assumptions in ABAQUS modeling may lead to higher load values than obtained during the experiment.

Figure 39: Bending & rotation of GDL on compression of SMORS.

Development of Peak Contact Pressure Profile

Due to stress relaxation in the seal compressed between platens, the initial peak contact pressure should decay with time. As illustrated in Figure 6.22, maintaining the peak contact pressure greater than the pressure differential across the seal is important to prevent gas leakage. To develop a long-term peak contact pressure profile and to estimate its value at a given time, time dependent properties, such as modulus decay with time typically obtained from stress relaxation tests, may be used as an input into ABAQUS modeling. When complex seal cross-sections are involved, such as the one studied here, and building a robust finite element model is difficult, an alternative theoretical approach may be used provided the approach correlates well with experimental results. Based on the results discussed above, it is evident that Lindley's analytical approach showed good correlation with experimental results, and if used in conjunction with compression stress relaxation (CSR) data, may be helpful in developing the long-term pressure profile to predict the decay in peak contact pressure with time. If decay in the modulus of the seal material with time, $E(t)$ versus t , can be obtained from CSR tests in a given environment, decay in peak contact stress with time may be estimated by using Lindley's approach such that:

$$\sigma_{\text{cmax}}(t) = E(t) \left[\frac{16}{6\pi} g(c) \right]^{\frac{1}{2}}$$

where modulus E_c in equation 6.3 is replaced by the time-dependent modulus, $E(t)$.

$$\sigma_{cmax}(t \rightarrow t_{lifetime}) \geq P_0 - P_{atm}$$

Figure 40: Illustration of Lindley's approach used to develop peak contact stress profile to predict seal leakage.

Conclusions

For the purpose of understanding the deformation behavior of an elastomeric seal and its sealing performance, finite element characterization of representative seal cross-sections was carried out. Uniaxial test data obtained from experiments was used as material property in ABAQUS and several known hyperelastic material models were evaluated. It was found that the two-parameter Ogden or Neo-Hookean models correlated well with experimental results and also exhibited stability in other modes of seal deformation, such as uniaxial compression, shear etc. For simplicity and robustness, the two-parameter Ogden model was selected to carry out seal analysis under compression. The O-ring cross-section was first studied to understand the stress-strain distribution and to develop

the contact stress and contact width profiles for a range of compression and how they are affected by the seal's radius of curvature. Symmetric stress/strain distribution and insignificant change in values of contact width and peak contact stress were observed as the curvature of the seal increases ($R/r \geq 10$). This observation may be helpful when the seal bead is laid out on a substrate for certain application. A simple analysis conducted on an O-ring configuration proved to be helpful prior to analyzing a complex assembly such as SMORS, where several interfaces and boundary conditions are involved. In order to simplify the modeling process for SMORS, a ratio of $R/r \geq 20$ was selected (corresponds to SMORS tested in CSR experiments) and axisymmetric analysis was conducted on simplified SMORS model. Stress/strain profiles were generated to visualize their distributions within the seal cross-section. Frictionless and rough interfacial conditions between seal material and platens were assumed, but their effect on contact width and peak contact pressure was insignificant. Therefore, further analysis was carried out assuming frictionless conditions at the seal/platen interface.

The finite element model developed for seal analysis was validated through comparison with a contact mechanics approach and experimental data. Load versus displacement (or % compression) results from ABAQUS, Lindley's approach, and experiments were compared and it was found that Lindley's equation correlates well with experimental data whereas ABAQUS overestimates the load values at a given compression. Lindley's approach may also be used to develop contact pressure profiles that may help estimate peak contact pressures at a given time so leaking can be avoided. Assumptions made in ABAQUS to provide stability and simplifying the modeling of the complex SMORS assembly resulted in overestimating the load values and better estimates may be obtained if improved samples could be developed where slipping at the seal/GDL interfaces in SMORS could be avoided by achieving uniform impregnation of seal material into the GDL. This can be achieved by using a multi-point injection mold rather than single point injection one, which is currently used. Good impregnation of GDL layers may also eliminate GDL crushing during compression of the seal. If seal material relaxation behavior is of primary concern, the GDL in SMORS assembly may be replaced by a single rigid substrate that would not crush, bend or rotate and is bonded to the seal under

the web. This will not only provide a rigid support to the seal but also prevent slipping at the seal/GDL interface. Modification of SMORS based on suggestions provided above may provide improved correlation between finite element analysis and experimental data so that future seal designs can be reliably analyzed using robust FEA models prior to manufacturing.

Molding Trials and Test Sample Development

Molding trials and parts manufacture was a critical portion of this development project, since these tasks are necessary to assess and ensure viability of materials for low cost, high volume manufacturing. Seals with various designs were molded onto various materials that are in current use in the fuel cell industry in order to facilitate both benchtop and in-cell testing. A staged approach to the production of prototype seal components was introduced. The first stage was to mold seals suitable for use in benchtop testing. These were the SMORS samples, which used similar seal dimensions and aspect ratios to typical fuel cell seals and were the subject of finite element analysis described in section 3. The second stage was to over-mold prototype seals onto polyethylene naphthalate (PEN) film using hot-runner injection-molding technology typically used for relatively low-volume production. An image of a representative part is shown in Figure 41. These parts were constructed into production-like fuel cell hardware and tested in a single cell stack at fuel cell operating conditions. The third stage involved over-molding full-size seal-on-MEA components using high-volume cold-runner injection-molding technology. These parts were used for testing in a prototype, next-generation cell design.

Figure 41: Examples of prototype MEAs using LIM seals.

Prototype seals molded onto PEN film were used for in-cell validation testing. This seal is shown in Figure 41. The second full-size prototype seal produced was of an integrated molded seal (IMS) configuration UEA and was used for bench top testing in full-size cell hardware (Figure 41). Critical to this molding activity was to test the effect of different parameters such as gas diffusion media (GDM) type/characteristics on mold-flow when producing this type of component. Prototype IMS parts showed defects in the seal areas, such as excessive encroachment of seal material into the active area of the part (aka "flash"). Further molding trials are necessary to optimize molding conditions and materials used to make suitable prototype UEAs for validation testing.

Full-size Component Testing

Fuel cell stack testing was performed on the prototype cell made with FCS2-type LIM seal material. Two single cell stacks were run using an accelerated stress test to validate the durability of the material in a hydrogen/air fuel cell environment. In this test, the cell

is cycled between near open-circuit voltage (OCV) and high current (low voltage). Operating temperature is held constant at above 80°C. Both voltage cycling and high temperature operation are accelerants in this test. The cell stacks lasted approximately 1000h and 1700h, respectively, under the accelerated conditions. These results compare favorably with cells run using baseline seal materials: silicone and EPDM. Figure 42 shows voltage decay over time at various current densities for each cell tested.

- Over 1700 hours accumulated before WEL 57 removed due to a test stand issue
- Accelerated cyclic test designed to stress all cell components
- At BOL, FCS2 cells have similar performance to baseline EPDM and silicone cells
- A review of the weekly diagnostics indicates performance decay is not attributable to seals

Figure 42: Single cell stack testing results for LIM hydrocarbon seals compared to baseline seals.

Pressure film analysis was completed on a single cell constructed using the prototype IMS part. The pressure film image is shown in Figure 41b. The image shows the result of flash material encroaching into the active area of the part, creating a thick, high-load portion of the active area. In the cell, this area is highly loaded relative to the molded seal features around the perimeter of the part. Further molding trials are needed to reduce the

amount of flash and produce a part that will exhibit more even mechanical loading constructed into the cell hardware before validation testing can be completed. In addition, it will be critical to ensure that high quality parts can be manufactured in high volumes using this material, the cold-runner injection molding technology and a suitable seal design.

Products/Publications Developed Under This Project

A material was developed by Henkel that can be scaled to commercial volumes
No patents were developed under this program

Publications

Jason Parsons, “Low Cost, Durable Seals for PEM Fuel Cells”, DOE Hydrogen Program 2008 Annual Merit Review Proceedings, Washington, DC, 2008

Jason Parsons, “Low Cost, Durable Seals for PEM Fuel Cells”, DOE Hydrogen Program 2009 Annual Merit Review Proceedings, Washington, DC, 2009

Jason Parsons, “Low Cost, Durable Seals for PEM Fuel Cells”, DOE Hydrogen Program 2010 Annual Merit Review Proceedings, Washington, DC, 2010

Conclusions

Based on the work performed during this 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

Future Work

UTC Power is interested in continuing to develop and validate the IMS-type full-size components. Potential applications include current and future cell stack designs for transit bus or stationary backup power applications.

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Note: Portions of this Final Report are also found in the report available from Virginia Tech: Klein, J. E.; Divoux, G.M.; Singh, H. K.; Case, S.W.; Dillard, J.G.; Moore, R.B.; Dillard, D.A.; Characterizing Durability of Fuel Cells. September 10, 2010.

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Acronyms

BOL	Beginning of life
LIM	Liquid Injection (Molding or Moldable)
MEA	Membrane electrode assembly; may include gas diffusion media
PEM	Proton Exchange Membrane
PEMFC	PEM Fuel Cell
CSR	Compressive Stress Relaxation
CS	Compression Set
DI	Deionized
EG	Ethylene Glycol
EPDM	Ethylene Propylene Diene Monomer
GDM	Gas-diffusion media
PFSA	Poly(fluorosulfonic acid)
SMORS	Sub-scale molded o-ring seal

Appendix A – LIM Hydrocarbon Seal Material Specification

Requirement	Level 1 - Acceptable Range	Desired	Test Method
BOL Mechanical Properties			
Hardness (Shore A)	15 to 68	30-55	ASTM D2240
100% Modulus (MPa)	0.25 -- 3.5	1 -- 2.5	ASTM D412
Compressibility	>= 25%	>= 33%	ASTM F36/ ASTM D6147
Viscosity @ room temperature (cps)	<= 700,000	<= 600,000	
Cure temperature (°C)	< 135	<= 110	
Cure time (seconds)	<= 400	<= 60	
Tensile (MPa)	>= 0.5	>=0.8	ASTM D412
Elongation (%)	> 125	> 150	ASTM D412
Tear Strength (kN/m) Die C	>= 2.7	>= 5.0	ASTM D624
Environmental Requirements			
Temperature Resistance (°C)	-40 to +85	-40 to +90	
Shelf Life (months / temperature in °C)	6 / -20	6 / >= 5	
Chemical Resistance (all with previously stated temperature requirements)	DI Water	DI Water	Post Testing based on ASTM D471
	Ethylene Glycol	Ethylene Glycol	
	--	Propylene Glycol	
		Hydrofluoric Acid (1.8ppm)	
		Sulfuric Acid (12ppm)	
	Air (0 to100% RH)	Air (0 to100% RH)	
	H2 (0 to 100% RH)	H2 (0 to 100% RH)	

Lifetime (Operating Hours / Total Life)	$\geq 5,000$ hrs / 5 years	$\geq 40,000$ hrs / 10 years	
Extractables (Leachates)	Low level of extractable hydrophobic leachates	Low level of extractable hydrophobic leachates	Proprietary Test Methods
	Low level of ionic leachates	< 20 ppm	ICP
Electrical Properties			
Electrical Resistivity, Bulk and Surface (Ohm-cm)	$\geq 10^{10}$	$\geq 10^{12}$	
Dielectric Strength	> 10 V/mm Field Strength	≥ 100 V/mm Field Strength	
EOL Mechanical Properties			
Compression set (assumes 25% initial compression)	$\leq 70\%$	$\leq 25\%$	ASTM D395
Elongation (%)	$< 100\%$	$< 125\%$	ASTM D412