IV.A.18 Reliable Seals for Solid Oxide Fuel Cells

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Objectives

- Develop reliable, cost-effective sealing techniques for solid oxide fuel cells (SOFCs).
- Determine performance-limiting features of sealing methods.
- Optimize seal properties.
- Determine seal degradation mechanisms and predict useful seal lifetimes.

Approach

- We are making composite seals comprising a glass matrix and powder filler that exhibit a wide range of chemical and mechanical properties.
- The composite approach allows glass and filler properties to be optimized independently.
- Seal thermal and mechanical strains are reduced by selecting glass compositions with glass transition temperatures (Tg) below the SOFC operating temperature.
- Viscosity, coefficient of thermal expansion (CTE), and other seal characteristics can be tailored by adding unreactive powder.
- The volume fraction of the glass phase can be reduced to a minimum for the seal, which reduces reactivity with fuel cell materials.

Accomplishments

- We selected two glasses with properties suitable for further seal development and testing after making extensive measurements on over 30 different custom glass compositions.
- We used the high temperature optical dimension measuring instrument (TOMMI), which allows *in situ* video recording of specimens at elevated temperatures (T<1,700°C), to determine the additive powder composition, particle size, and aspect ratio that optimize composite seal flow and adhesion for the selected glasses.
- A completed series of 2,000-hour tests in air at 750°C of two composite seal compositions on ferritic stainless steal (SS) alloys and yttria-stabilized zirconia (YSZ) electrolyte showed the seal materials are unreactive.
- We measured weight losses with time at 750°C of the pure and powder filled glasses in simulated steam for 2,000 hours and found the extrapolated 40,000-hour weight losses to be less than 5% for both linear and parabolic weight loss mechanisms.
- We developed an apparatus for testing seal adherence and bond strengths at room temperature under 2 atm of internal gas pressure. The best seals survived nine thermal cycles from room temperature to 750°C and back. Those that leaked could be resealed by heating them above 850°C.

Future Directions

- Continue long-term tests of stability of seals and seal materials under realistic environmental conditions. Model weight loss data to predict 40,000-hour performance.
- Modify the pressure test apparatus to allow seal strength measurements at 750°C.
- Use a combination of X-ray photoelectron spectroscopy (XPS), Auger spectroscopy, time of flight secondary ion mass spectrometry (SIMS), and wet chemical analysis to identify the species responsible for the observed (small) weight loss from the sealing glasses when they are heated at 750°C.
- Begin tests of operating button cells sealed with these composite sealing glasses.

Introduction

Seals for SOFC stacks face the most challenging set of performance requirements in the entire field of ceramic joining. The industry teams in the Solid State Energy Conversion Alliance (SECA) program have consistently identified seal development as one of their highest priorities.

Approach

As we have written in previous annual reports, we are using Department of Energy (DOE) support to develop techniques for sealing SOFCs that can be

tailored to the specific requirements of the vertical teams in the DOE/SECA program. The approach is based on our many years of seal development for other applications as applied to the special requirements for SOFC seals. It is evident to us that relief of thermal expansion mismatch stresses will require SOFC seals to incorporate either a ductile metal or a high-viscosity glass that can relieve stresses through viscous creep. Accommodating mismatch stresses, as well as other SOFC design and operational constraints that frequently are in conflict, severely restrict the options for seal materials. Based on our prior experience in ceramic joining and on results obtained on this project, we believe we have the greatest design flexibility using ceramic-filled glasses and metal-filled glass composites. We have demonstrated control of properties such as glass transition temperature and thermal expansion coefficient by varying the compositions, amounts, and microstructures of the different phases. The choices are guided by thermochemical and composite microstructural models that allow us to target specific seal properties for a given design. Our seals are showing great promise in functional and 2,000-hour lifetime tests with results that extrapolate very favorably to 40,000-hour operation.

Results

In this past year we concentrated our efforts on making seals using the two best glass compositions and determining properties necessary to control processing and to demonstrate functionality.

Seal material properties: We have made many measurements of composite viscosities using the parallel plate method in our TOMMI apparatus (thermooptical mechanical measuring instrument, Fraunhofer Gesellschaft, Wurtsburg, Germany). Data on variation of viscosity as a function of composition, relative volume fraction of glass and filler, and temperature allow us to assess the performance of different composites and to choose the best combination of joining material for the specific use conditions. Viscosity controls the flow of seal materials at temperature. If the viscosity is too high the sealant will not flow enough to make the seal and it also will not be able to dissipate thermal expansion mismatch stresses. If the viscosity is too low, the sealant will not stay in the joint and the seal may leak and be too weak. We also measure spreading rates and contact angles of composite sealants on different SOFC materials at temperature in the TOMMI. These properties depend on both viscosities and surface energies of the seal constituents and the data are complementary to the viscosity measurements. Contact angles and spreading rates are needed to specify heating schedules for seal formation and to determine adhesion and compatibility of the seal materials with different substrates.

Seal strengths: It is difficult to measure the absolute strengths of joints in brittle materials such as ceramics. One common technique is to make butt seals in test bars (typically 3x4x40 mm with the seal in the 3x4 mm plane at the 20 mm point) that are then loaded in four point flexure. The load at failure is recorded and the fracture surface is analyzed to determine the fracture origin and to assess whether the failure should be counted as a good data point. Because brittle fracture is stochastic, data on 30 specimens of each condition are typically necessary to evaluate the statistics. Using the measured flexure strength to predict failure in some other geometry requires computational modeling such as the finite element method. The technique can give reliable results but it is labor intensive and it is not a very efficient method for screening a lot of different process variables.

The other approach to determining seal strengths is proof tests either of samples of the actual device or simplified versions that are deemed to embody the essential features. The data are not absolute materials properties in any sense, but they provide relative levels of performance. We have followed this latter method in designing a strength test apparatus in which an annular seal creates a volume that can be pressurized with air. Discs and washers of the desired materials are sealed with different composite sealants to create a small interior volume as shown in Figure 1. The assembly is immersed in water and the pressure is slowly increased until either the seal leaks and air bubbles are detected or 2 atm pressure is reached. Two atmospheres of over pressure is much greater than any pressure differential that has ever been suggested for SOFC operation. Leakers are resealed at the normal process temperature

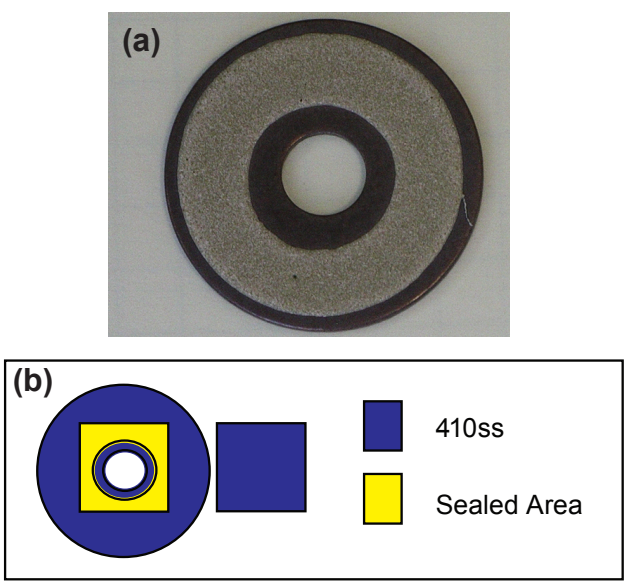

FIGURE 1. (a) Result of a Wetting Experiment for a 14a Glass Composite Sealed to a 410 SS Substrate and (b) the Test Geometry for Measuring Seal Strength/Leak Properties

and retested. Seals that do not leak are heated to 750-850°C, typical of SOFC operating temperature, cooled to room temperature, and retested in the pressure apparatus. We record the number of cycles to seal failure as a function of materials variables and process conditions and determine if the leakers can be resealed. Note that testing strengths at room temperature is not a drawback since any leaks at high temperature will likely be worse at room temperature.

For the strength tests we used a 14a glass-Ag composite sealing composition that was formulated as a matched CTE seal to 410 SS. The rule of mixtures was used to calculate the volume fraction of Ag needed in the glass to adjust its CTE to that of the 410 SS. Composite preforms were made using conventional tape casting techniques. Wetting studies on 410 SS showed the optimum sealing temperature to be 900°C. Seal strengths were determined using a 410 SS to 410 SS sandwich geometry as shown in Figure 1. The crosshatched area in the figure is the actual sealed area tested.

Strength and leak tests were performed at room temperature. As stated above, we assumed that flaws at higher temperatures will likely persist at room temperature and therefore should be detected in our tests. Strength data from the first round of tests are presented in Table 1.

We examined the effects of differences in the tape cast performs on seal strengths. For example, we found that tapes made with finer powders gave higher seal strengths. For the initial experiments we made and tested 15 seals, of which four failed under pressure, giving an average fracture strength of 5.58 N/mm^2. Those fractured specimens were then resealed, retested and gave similar strengths. Other sealed specimens did not fail after as many as nine resealing and testing cycles. Table 2 shows the strength results for seal specimens that never failed. We believe that variations in the seal strengths listed in Table 1 are likely due to defects in the tape. The results in Table 2 show that tapes made with finer powders may give slightly stronger seals, although the strength distributions overlap.

TABLE 1. Seal Strength Values for Specimens that Failed after Pressure Testing

Specimens [#/total]	Seal Material	Initial Fracture Strength [N/mm^2] *10^{-2}	Strength after *n*th Sealing Cycle [N/mm^2] *10^{-2}
2/5 failed	14A Š Ag (coarse powder)	10.16 ± 9.34	8.35 ± 5.53 (3rd)
4/15 failed	14A Š Ag (fine powder)	5.68 ± 2.34	6.84 ± 1.93 (1st)

TABLE 2. Seal Strength Values for Specimens that Never Failed in Pressure Testing

Specimens [#/total]	Seal Material	Minimum Fracture Strength [N/mm^2] *10^{-2}	Strength after *n*th Thermal Cycle [N/mm^2] *10^{-2}
3/5 did not fail	14A Š Ag (coarse powder)	9.68 ± 1.78	>9.68 ± 1.78 (7th)
9/15 did not fail	14A Š Ag (fine powder)	9.83 ± 1.65	>9.83 ± 1.65 (9th)

Long-term tests: We have set up a number of furnaces to test seal stability for extended times at temperature. We have investigated both the pure seal materials and seal materials in combination with different substrates. The test rigs comprise airtight ceramic muffle tubes inside resistance-heated tube furnaces. The ceramic tubes are sealed with end caps that allow gas to be passed through them at temperature. For the steam tests Ar-3%H_2 is bubbled through a 62°C water bath to create a 30% simulated steam atmosphere. Weighed samples are heated in the center of the hot zone under flowing wet hydrogen or air, depending on the specific test. Standard tests last 2,000 hours with the specimens cooled to room temperature at intervals and then weighed. For tests of stability of the seal materials by themselves, specimens are supported on alumina wafers that contribute no weight change since they are inert to the test conditions. For tests of stability of sealants on component materials, which are just getting underway, the seals are placed on coupons of the specific material, e.g. 410 stainless steel or YSZ, and then tested as described. The measured weight changes are plotted as a function of time at temperature.

Concern about vaporization of glass constituents in long-term use of glass sealants has been voiced at various SECA reviews and workshops. Possible preferential loss of boron from borate glasses in different SOFC atmospheres has been a particular issue. The SECA design lifetime is 40,000 hours, which is too long an interval to test in an iterative materials development program. Therefore we have calculated upper and lower bounds to weight loss for both linear and parabolic loss mechanisms assuming a weight loss of 5% at 40,000 hours as a conservative, tolerable level. We made most of our long-term weight loss measurements on two glass compositions, one of which contains almost twice the boron of the other. Comparison of our measured weight losses for times up to 2,000 hours with the predictions of the two weight loss models shows the sealing glass weight losses track the lower parabolic limit pretty well, which strongly suggests that loss of boron or other glass constituents is not an issue for borate glass seals in typical SOFC operating environments. Thus, the weight loss data so far are showing that our borate-based glasses

are stable over long times at the representative SOFC operating temperature of 750°C in both simulated steam and air.

The seal stability experiments have concentrated on Glass 14a and Glass 17, whose as-cast compositions contain 40 mol% B_2O_3 and 25 mol% B_2O_3, respectively. Bulk sections of glass cast from the melt were cut to pieces large enough to give measurable weight losses in our experiments. Both the 14a and 17 glasses were tested with and without a pre-crystallization heat treatment. Pre-crystallized specimens were heated up to 900°C, which is well above the glass T_g (T_g of Glass 14a = 576°C, T_g of Glass 17 = 632°C) and the targeted SOFC operating temperature of 750°C.

Figure 2 shows the 2,000-hour weight loss measurements for Glasses 14a and 17 in air at 750°C. The glass with less boron gave a lower weight loss. The observed weight loss in air for both glass compositions was not affected by the pre-crystallization heat treatment. The maximum weight loss for Glass 14a was found near the end of the 2,000-hour experiment to be about 0.2 wt%. Glass 17 was even more stable with less than 0.05% weight loss over the entire 2,000-hour heating period. After a higher rate of loss for an initial 200 hours at 750°C, Glass 14a settled down to a long period of linear weight loss with time. The weight loss for Glass 17 also increased for the first 200 hours and then maintained a constant weight loss for the rest of the 2,000 hours. However, all the weight losses were very low, so these differences in rates are small.

Figure 3 shows the data from our first measurements of long-term weight loss for Glasses 14a and 17 in a wet-H_2, simulated steam environment. Unlike the results for heating in air, the data for simulated steam did not give smooth weight loss curves for heat treatments longer than 500 hours. We are not sure if the data are accurate or whether there may have been some error in the measurements, so we currently repeating this experiment. Figure 4 is a plot of the data in Figure 3 for only the first 500 hours of heating where the data appear well behaved. During this initial 500-hour period both glasses exhibit a constant weight loss over time, independent of glass composition or pre-crystallization treatment. The pre-crystallized glasses appear to be more stable than the as-cast glass specimens once they have been heated for 300 hours.

Our experiments show that there is higher weight loss in air than in simulated steam initially, as shown in Figure 5. If long-term results in simulated steam are confirmed in our current experiments, then we can conclude that our borate sealing glasses will experience only negligible weight loss in typical SOFC operating conditions. Because we want to know what is evaporating from the sealing glasses we presently are implementing a furnace setup that allows us to capture the evolved species for analysis using atomic absorption-inductively coupled plasma spectroscopic techniques.

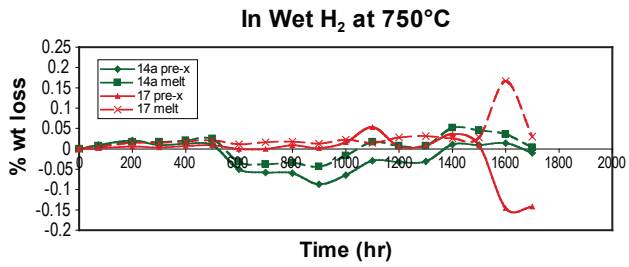

FIGURE 3. Weight Loss for 1,800 Hours for Glasses 14a and 17 in Wet-H_2, Simulated Steam at 750°C

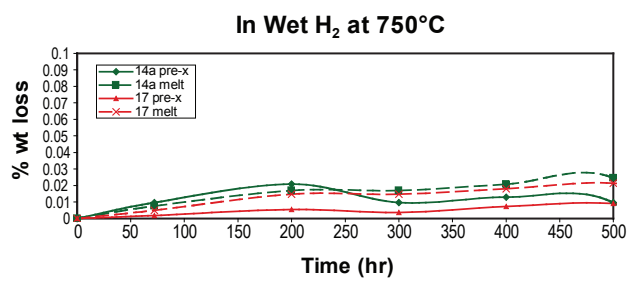

FIGURE 4. Weight Loss Over 500 Hours for Glasses 14a and 17 in Wet-H_2, Simulated Steam at 750°C

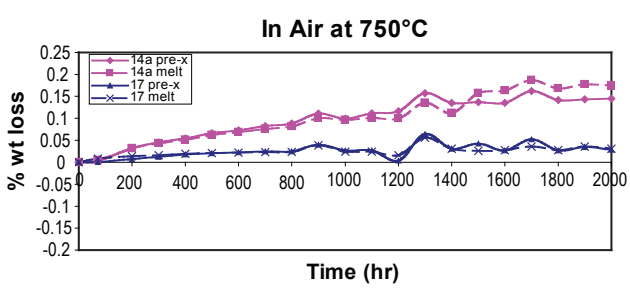

FIGURE 2. Long-Term Weight Loss for Glasses 14a and 17 in Air at 750°C

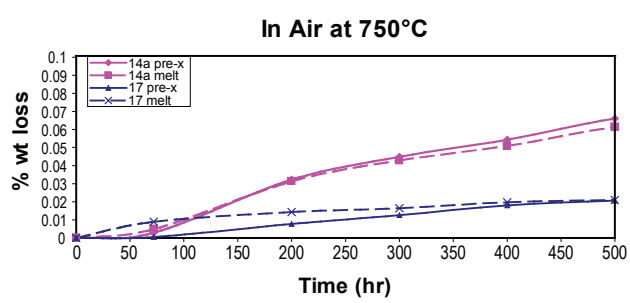

FIGURE 5. Early Stage Weight Losses in Air of Glasses 14a and 17 Show that Glass 17 is More Stable than Glass 14a in Air at 750°C

Summary of Specific Accomplishments:

1. We measured viscosities of glass composites with different types and volume fractions of filler powders and as a function of temperature up to 850°C and selected two compositions with the best properties for further SOFC seal development.
2. We developed a test rig for measuring strengths of seals cycled between room temperature and typical SOFC operating temperatures. Our measurements showed many of the 410 SS to 410 SS seals were hermetic at 2 atm of pressure. Seals that leaked could be resealed by briefly heating them to 900°C.
3. Long-term testing of glass compositions in air and simulated steam, coupled with weight loss projections according to two models, lead us to predict that none of our glass composite sealing compositions would experience more than 5% mass loss in 40,000 hours of operation in typical SOFCs.

Conclusions and Future Directions

Our results to date show that the borate glasses are stable in air and simulated steam for long times at 750°C. The largest weight loss in all the experiments was only 0.2 wt%, observed in air towards the end of a 750°C, 2,000-hour test. The highest weight loss measured in simulated steam was 0.03 wt%. The replication of experiments that is underway should allow us to confirm these low weight losses. The identity of the evaporating species will be revealed by analysis of the captured condensates. We also are planning to analyze surfaces of composite seal materials that have been heated under different test conditions using XPS or SIMS to determine depletion or buildup of constituents in the first few atomic layers. Although these results will not give information on bulk compositional changes, they should show changes in surface compositions with heating.

We have demonstrated that our glasses can be made into composite seals with a wide range of CTEs. Pressure tests to 2 atm of composite seals with CTEs matched to 410 SS showed high strengths after multiple pressure cycles. Seals that did leak could be resealed. The long-term stability, reliability and strength of the glass composite seals demonstrate the versatility of the glass composite seals.

FY 2007 Publications/Presentations

Presentations

1. E. Corral, B. Gauntt and R. Loehman, "Sealing SOFCs with Glass Matrix Composites," SECA Glass Sealing Workshop, National Energy Technology Laboratory, Morgantown, WV, September 20–21, 2006.

2. E. Corral, B. Gauntt and R. Loehman, "Glass Composites for Sealing Solid Oxide Fuel Cells: A Science Based Engineering Approach," Rio Grande Symposium on Advanced Materials, October 10, 2006, Embassy Suites Hotel, Albuquerque, NM.

3. E. Corral, A. Ayala, B. Gauntt, and R. Loehman, "Long-Term Evaluation of Engineered Glass-Ceramic Composites for Solid Oxide Fuel Cell Applications," Materials Science & Technology 2006 Conference and Exhibition (MS&T 06), October 15–19, 2006, Cincinnati, OH.

4. E. Corral, A. Ayala, B. Gauntt, and R. Loehman, "Properties of Engineering Glass Composites for Sealing Solid Oxide Fuel Cells," Materials Science & Technology 2006 Conference and Exhibition (MS&T 06), October 15–19, 2006, Cincinnati, OH.

5. E. Corral, B. Gauntt, R. Loehman, "Glass Composites as Sealing Materials for Solid Oxide Fuel Cells", The American Ceramic Society's 2007 Glass & Optical Materials Division Meeting & 18th University Conference on Glass, May 20–23, 2007, Rochester, New York (invited).

Papers

1. E. Corral, B. Gauntt, R. Loehman, "Controlling Seal Material Properties for Reliable Seal Performance Using Glass-Ceramic Composites," 30th International Conference on Advanced Ceramics and Composites, Daytona Beach, FL, January 21-26, 2007 (invited).