DEVELOPMENT OF A SOLID OXIDE FUEL CELL STACK BY DELPHI AND BATTELLE

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ABSTRACT

Delphi and Battelle are developing a solid oxide fuel cell (SOFC) stack for transportation and stationary applications. This team is part of the Solid State Energy Conversion Alliance (SECA) initiative. This paper describes the status of development of the Generation 2 stack and key progress made in addressing some of the challenges in this technology.

INTRODUCTION

Delphi and Battelle are developing solid oxide fuel cell (SOFC) technology for application in the transportation and stationary markets. Delphi is developing this technology for the transportation market primarily as an on-board auxiliary power unit (APU). This technology being developed for the transportation market is also applicable to the stationary market.

Figure 1. Generation 2 SOFC APU system under development.

After a development period of less than two years, Delphi demonstrated the first gasoline-powered SOFC-APU (1-3) in February 2001. The Proof-of-Concept APU

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system was the first step in implementing and demonstrating the usefulness of SOFC technology as applied to an auxiliary power unit for automotive applications. It demonstrated the functional capabilities of the sub-systems and allowed us to clearly understand and identify the challenges that must be overcome to meet the automotive product requirements. Based on this assessment, Delphi is currently focused on developing a 5 kW Generation 2 solid oxide fuel cell APU (Figure 1) that meets the requirements of the automotive market. Key to the development of the Generation 2 system is the research and development involved in the area of the SOFC stack. Delphi and Battelle are working closely for the development of this critical sub-system. In this paper, we will discuss the ongoing development of the Generation 2 stack and the progress made in addressing the key challenges for this sub-system.

STACK DESIGN

The second-generation stack has been designed with anode supported cells, metallic interconnects and optimized manifolding, aimed at meeting the stringent targets of the transportation industry (1 L/kW, < 4 kg/kW). One of the key features of this design is a robust cassette configuration as the repeating unit of the stack (Figure 2). The cassette includes the cell and the metal frame parts, which are sealed before the assembly of the repeating units into a stack. Currently, extensive testing of stack components and stacks is in progress to optimize the design. Two 30-cell stack modules constitute the stack subsystem in the APU operating at 42 V (nominal).

![Figure 2. Anode supported cell in a metallic cassette.](image)

### Table 1. Stack targets for automotive SOFC APU.

| Stack       | Targets                                      |
|-------------|----------------------------------------------|
| Power       | 6 kW                                         |
| Fuel        | Gasoline based Partial Oxidation reformate   |
| Durability  | 5000 - 10000 hrs                             |
| (continuous)|                                              |
| Durability  | > 5000                                       |
| (thermal cycles)|                                      |
| Fuel utilization | > 60%                                   |
| Start up time | < 20 minutes                                |
| Weight      | < 4 kg/kW                                    |
| Volume      | 1 L/kW                                       |
CELL DEVELOPMENT

The cells used in the Generation 2 stacks are anode-supported, with a 550 μm Ni-zirconia anode supporting a 7 μm yttria stabilized zirconia (YSZ) electrolyte and a 50 μm lanthanum strontium ferrite cathode. Development of these cells is discussed elsewhere (4). In brief, the anode is composed of several tape cast layers, which are laminated together with the electrolyte tape prior to co-sintering. The cathode is then screen printed and fired. A full-scale cell, approximately 12 cm x 12 cm, is shown sealed into a metal frame in Figure 2.

One of the concerns engendered by the need for rapid start-up heating of the stack is that the cells will be subjected to severe stresses caused by temperature gradients. Thermal and structural modeling indicates that, for reasonably rapid heating of the stack, the cells will need to withstand flexural stresses on the order of 100 MPa. Room temperature cell strength is characterized using a “ball-on-ring” biaxial flexure test (ASTM F 394-78) that is applied to the co-sintered bi-layers (anode and electrolyte). These tests have been performed on both as-sintered bi-layers, in which the nickel is present in the oxide form, and on reduced bi-layers, in which the nickel is in the metallic form. For the APU system, the stacks are fabricated and assembled with the cells in the oxidized state, and the anodes are reduced in situ prior to first operation. Figure 3 shows room temperature flexural strength data for several developmental bi-layer types. So far, anode formulation #1 has been tested in both the oxidized and the reduced state. Increasing the sintering temperature from 1375°C to 1410°C has the effect of increasing the flexural strength of both oxidized and reduced bi-layers, presumably by decreasing the residual porosity and increasing particle-to-particle neck size. The main constituents in the anode formulation are NiO and YSZ. Anode formulation #2 contains a different YSZ powder than formulation #1, which results in a 50-60 MPa increase in flexural strength at both sintering temperatures.

![Figure 3](image_url)  
**Figure 3.** Room temperature flexural test data for several anode types.

Additive “A”, which is being tested to adjust the thermal expansion coefficient of the composite, was added to anode formulation #1 in place of some of the YSZ, and the samples were sintered at 1375°C. Comparing to anode #1 sintered at 1375°C, it is
interesting to note that 15% of the additive has little effect, whereas 10% increases the flexural strength by about 50 MPa and 5% increases strength by almost 100 MPa.

Another test is under development to characterize the strength of bi-layers at elevated temperatures. This test is derived from work reported by Knoblauch et al (5). The test is conducted in a glove box under inert atmosphere so that the test pieces can be maintained in the reduced state during heating. A 54 mm reduced bi-layer disk is uniformly heated from above using a quartz halogen lamp. As the disk reaches some pre-determined uniform temperature, another quartz halogen lamp is focused from below on a 6 mm diameter spot in the center of the sample. This causes a central hot spot with circular thermal profiles radiating away from the center. An infrared video camera continuously records the temperature distribution on the sample. The thermal profile is determined just before the sample fractures. The fracture stress can then be calculated from the final thermal profile. The technique has been validated using commercial alumina substrate disks. Figure 4 shows a typical thermal profile with the corresponding stress profile. The histogram of fracture stresses for 28 of the alumina disks is also shown.

Figure 4. (left) Thermal profile of alumina disk just prior to fracture; (center) Calculated stress profile on the same disk just prior to fracture; (right) Histogram of fracture stresses for 28 alumina disks.

SEAL DEVELOPMENT

In the Generation 2 stack design, there are two types of seals as shown in Figure 2; cell-to-frame seals and cassette-to-cassette seals. Our team is developing two types of sealing materials, glass and braze, which may be used alone or in combination in the Generation 2 design. A rupture strength test was developed to facilitate quantitative comparison of seal joint strengths. Figure 5 shows a photo of the test specimen and a schematic of the pressurizing fixture. The metal washer is clamped into the fixture and air pressure is increased until the seal breaks and the ceramic bi-layer disk pops off. Figure 6 shows several rupture strength results. The average rupture pressure for the bare ferritic stainless steel type “A” glass sealed to bi-layer disks was 10 psi. Several factors affect the seal rupture strength. Choice of metal alloy (A, B, C or D) can result in up to a factor of four differences in rupture pressure when the seal is made directly to the bare metal surface. Pre-oxidation of metal B resulted in a slight increase in seal strength. Two braze compositions have been tested using the seal rupture strength method. As shown in Figure C4, braze #1 gave average rupture strengths of 46 and 52 psi, on coated metal A and on metal B, respectively. Braze #2 on coated metal A gave an average rupture pressure of 91 psi.
Figure 5. (far left) Components of rupture strength test specimen; from bottom, metal washer, glass sealing ring, bi-layer disk; (middle) Assembled test specimen. (right) Rupture strength test schematic.

Figure 6. Rupture pressure data for the test shown in Figure 5. Mean rupture pressure and ± one sigma is shown for each sample set.

A test was devised to measure the effectiveness of seals during thermal cycling. A single, intermediate-scale cassette (with 7 cm x 7 cm cell) was glass sealed, under load, at 850°C, between two metal manifold plates, which were in contact with ceramic plates containing electrical resistance heater windings. The device was then cooled to 750°C and the cell reduced using 2.75% H2 in He on the anode side. A gas chromatograph was connected to the cathode air outlet so that any leakage of helium from the anode side onto the cathode side could be monitored during thermal cycling. The percentage of the fuel stream that leaked into the cathode side was calculated from the relative cathode and anode flow rates and the concentration of He detected. Figure 7 shows the results for 14 thermal cycles, in each of which the cassette was heated from near-ambient to 750°C in 22 minutes, then allowed to cool for ~24 hours. The leak, measured each cycle after cooling to room temperature, was near 0.5% of the fuel stream in the first cycle and increased only slightly to just over 0.6% of the fuel stream during the 14 thermal cycles.
Figure 7. Leak rates measured at room temperature for glass sealed intermediate cell during 14 thermal cycles. Leak rates were determined by detecting He in the cathode stream using gas chromatography.

STACK TESTING

Stack Testing with Intermediate Sized Cells

Much of the development of the Generation 2 design has been accomplished by testing of intermediate sized stacks (with 7 cm x 7 cm cell). These stacks have similar design and have an active area about 1/3 that of the full scale cells. Most developmental milestones have been accomplished on intermediate scale stacks prior to being accomplished at full scale. This includes 1000 hours of continuous operation, thermal cycling with minimal power deterioration, and achievement of high power density.

An intermediate sized three-cell stack was operated continuously for 1000 hours. The stack ran at 750°C on 48.5% H₂, 48.5% N₂, 3% H₂O at 2 liters per minute on the anodes and 4 lpm air on the cathodes. Figure 8 shows the stack current plotted versus time. Stack voltage was controlled to 2.1 V, except for periodic sweeps of I-V response, from open circuit to 0.5 V. These periodic sweeps cause the many vertical lines in the stack current data. After burn-in, during the second 24 hours, the average stack current at 2.1 V was 12.91 Amps. During the final 24 hours of the run, the average stack current was 11.88 Amps, or 92% of the baseline average from the second day. Fuel utilization began at 28% and declined to 26%. Note that steady state stack current often increased by about 6% after an I-V sweep, then slowly decreased. The reason for this behavior is unknown, but it seems unlikely to be related to local heating because of the long current decay periods, sometimes lasting for days.

An intermediate sized one-cell stack was thermally cycled five times over 480 hours. Total active area was 33.6 cm². The stack was operated at 750°C on 48.5% H₂, 48.5%
N₂, 3% H₂O at 2 liters per minute on the anode and 3 lpm air on the cathode. During each cycle, the stack was cooled to ambient overnight, and then heated back to operating temperature. Figure 9 is a plot showing the open circuit voltage and power density at 0.7 V for the operating phase of each thermal cycle. The power density decreased from about 4.5 W/cm² and stabilized near 3.9 W/cm². The open circuit voltage remained high, at 1.09 V, indicating good stack sealing at the operating temperature. Figure 10 is a plot of voltage and power density for an intermediate sized one-cell stack, in which performance comparable to one-inch diameter button cells (6) was achieved. The 33.6 cm² stack was operated at on 48.5% H₂, 48.5% N₂, 3% H₂O at 2 liters per minute on the anode and 5 lpm air on the cathode. Power density at 750°C peaked near 0.84 W/cm², while at 800°C the power density peaked over 1.00 W/cm².

Figure 8. Stack current versus time for 1004 hour test run.

Figure 9. Open circuit voltage and power density for stack, measured at 750°C during five thermal cycles.
Figure 10. Power and I-V curves for intermediate-scale stack operating on 48.5% H₂.

Stack Testing with Full Sized Cells

Evaluation of performance with full sized 1-cell stacks to 30-cell stacks (with ~12 cm x 12 cm cells) is ongoing to validate the design and understand the performance characteristics.

The different reformates used for stack evaluation are hydrogen, simulated POx (partial oxidation) reformate containing 20% hydrogen, 23% CO, remainder N₂ and a simulated "recycled" reformate containing 35% H₂, 40% CO, remainder N₂. The flow rates of the reformates in each case is 2 litres/minute. All reformates were humidified with ~3% of water. As expected, the highest power density (350 mW/cm²) was obtained from testing

Figure 11: (left) I-V curve from a 1-cell stack test at 750°C with different simulated reformates. (right) I-V curve from a 26-cell stack test at 750°C with hydrogen.

with hydrogen, followed by simulated "recycled" reformate, followed by 50% hydrogen and then simulated POx reformate (Figure 11). These reformate compositions mimic the hydrogen and carbon monoxide compositions expected from the gasoline and diesel based systems.
Larger stacks are also being assembled and tested as a step towards building the whole stack sub-system for integration into the APU. Figure 11 (right) is an example of data from a 26-cell stack module that was built and tested with hydrogen as fuel. The stack produced power density of ~350 mW/cm² @ 15 V with hydrogen as fuel. Multiple stack modules from short 3-cell stacks to 30-cell stacks are being built and tested. The stack sub-system for the APU consists of two stack modules. Figure 12 shows the complete stack sub-system with two stack modules assembled in electrical series with parallel manifolding. This unit includes the load frame and the current collectors. The stack sub-system as shown in the figure can be integrated directly into the APU system. Testing of these modules by itself and integrated in the APU is in progress.

![Picture of the stack sub-system ready for integration into the APU with two stack modules.](image)

**Figure 12. Picture of the stack sub-system ready for integration into the APU with two stack modules.**

**SUMMARY AND CONCLUSIONS**

This paper summarizes the development by Delphi and Battelle in demonstrating the Generation 2 stack technology. The key points addressed in this paper are:

- Generation 2 stack design with metallic cassettes as the repeating unit
- Cathode development to obtain high cell power densities
- Fabrication of large cells of 12 cm x 12 cm dimensions within acceptable tolerances and good flexural strength for assembly into cassettes
- Development of glass and braze seals for hermetic sealing of the stack and results from seal strength tests
- Thermal cycling tests on stack components and stacks
- Stack test results from 1-26 cell stacks under different conditions including 1000 hour durability test
- Successful fabrication of the complete stack sub-system (two stack modules in series electrically) for integration into the APU system.
Clear progress has been made in taking this technology forward toward meeting the technical targets stated earlier. However, key challenges remain in some areas. They include reducing cost, increasing power density, faster start-up time and increasing durability (steady state and thermal cycling).

Delphi and Battelle are continuing to work on a fundamental level as well as on a system level to address and solve these challenges. The development and the results discussed in this paper are a clear step towards reaching these goals and bringing this novel technology to market.

ACKNOWLEDGEMENTS

This work was partially funded by the Solid State Energy Conversion Alliance, U. S. Department of Energy, National Energy Technology Laboratory. The authors would like to acknowledge the SOFC team for their contributions.

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