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Abstract

The following report documents the technical approach and conclusions made by Acumentrics Corporation during latest budget period toward the development of a low cost 10kW tubular SOFC power system. The present program, guided under direction from the National Energy Technology Laboratory of the US DOE, is a nine-year cost shared Cooperative Agreement totaling close to \$74M funded both by the US DOE as well as Acumentrics Corporation and its partners.

The latest budget period ran from July of 2004 through January 2004. Work was focused on cell technology enhancements as well as BOP and power electronics improvements and overall system design. Significant progress was made in increasing cell power enhancements as well as decreasing material cost in a drive to meet the SECA cost targets.

The following report documents these accomplishments in detail as well as the lay out plans for further progress in next budget period.

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Subtask 2.4- Cell Testing (Continued)

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Subtask 2.4- Cell Testing (Continued)

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Figure 3.4.D	Cell Brazed with 3%H ₂
Figure 3.4.E:	Inside of Figure #1
Figure 3.4.F	Cell Brazed with 5% H ₂
Figure 3.4.G:	Inside of Figure #3
Figure 3.4.H	Deep drawn outlet cups
Figure 3.4.K	The crack observed is the construction of the pseudo-deep-drawn cup and the interface of the two parts to make the cup.
Figure 3.4.L	MIM cap
Figure 3.4.M	Nickel Metal Injection Molded Manifold
Figure 3.4.N	Cell end caps
Figure 3.4.P	Deep drawn end caps
Figure 3.4.Q.	Graph of leakage rate of C-section seal over time.
Figure 3.4.R (a)	Graph of leakage rate of silver paint seal over time.

Subtask 3.4 – Manifold and Cap Development (Continued)

Figure 3.4.R (b)	Graph of straight thread-mica gasket configuration.
Figure 3.4.S	(a), (b) & (c). Photograph of the aluminized manifolds made from 1018, Type
Figure 3.4.T	(a), (b) & (c). Defects present in the aluminized 1018 manifold.
Figures 3.4.U	(a), (b) & (c). Photographs showing the defect areas on the Type 304 manifold.
Figure 3.4.V	(a), (b) & (c). Post-test photographs of manifolds (1018, Type 304, Ni/Type 309).
Figure 3.4.W	(a), (b) & (c). Photographs showing the various colors present and also the spalled coating.
Figure 3.4.X	(a) & (b). Photographs of the known defects present on the 1018 manifold.
Figure 3.4.Y	(a), (b) & (c). Photographs of the known defects present on the Type 304 manifold.
Figures 3.4.Z	(a) & (b). Condition of the aluminized 1018 manifold after 630 hours
Figures 3.4.AA	(a) & (b). Nickel-plated Type 304 manifold after 2010 hours of thermal cycling to 815°C.
Figure 3.4.AB	(a) & (b). Chromium plated and aluminized Type 304 manifold after 2010 hours of thermal cycling to 815°C.
Figure 3.4.AC.	Weight gain of samples over entire 2000 hours of testing.
Figure 3.4.AD	Pack aluminized samples before and after testing (type 304 are on the left of each photograph and the 1018 samples are on the right).
Figure 3.4.AE.	Graph of weight change of Sermatech [®] pack aluminized samples after 2028 hours.
Figure 3.4.AF.	Graph of weight change of VaporKote [®] pack aluminized samples after 1308 hours.
Figure 3.4.AG.	Stabilizing weight of the Type 304 and Type 309
Figure 3.4.AH.	Weight of Allegheny Ludlum alloys with thermal cycling every 24 hours to 838°C in air.
Figure 3.4.AJ	End of the injector tubes with the orifice plugs pressed into the tubes
Figure 3.4.AK	Pressure drop versus flow for the orifice operating under CPOX conditions
Figure 3.4.AL	The manifold voltage for natural gas at 1.7 slpm and 800C
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Figure 3.4.AS	Cathode-to-Manifold Resistance at 80 A, 50% FU and 800 Deg.C

Subtask 3.4 – Manifold and Cap Development (Continued)

Figure 3.4.AT	Cathode-to-Manifold Resistance at 115 A, 70% FU and 800 Deg.C
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Figure 3.4.AY	key process variables during the test operation
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Figure 3.4.BA	Methane conversion at the beginning of a test and 24 hours later
Figure 3.4.BB	methane conversion results
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Figure 3.4.BD	v-j curve for each of the stacks
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Figure 3.4.BE	shows an example of the erratic manifold voltage recorded for Stack #3 on cool down.
Figure 3.4.BF	(a). Electrically isolating braze cap. (b). Braze caps in the manifold.
Figure 3.4.BG	Deep drawn cap for pressing into the manifold.
Figure 3.4.BH	(a). Cell with screw attachment. (b). Cell attached to manifold.
Figure 3.4.BJ	typical test configuration before and after thermal cycling.
Figure 3.4.BK	Current design of the cell-to-manifold connection
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Figure 3.4.BM	Cell-to-manifold Connection Parts
Figure 3.4.BN	Cell to manifold leakage during thermal cycling
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Table 3.4.C	Bisque-Fired AS Tube Dimensions and Shrinkage Values
Figure 3.4.BS	Bisque-fired AS tubes.
Table 3.4.D	Sintered AS Tube Dimensions and Shrinkage Values
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Subtask 4.1 – Tube Drying

Figure 4.1.A	Microwave unit licensed by BTU to conduct microwave-debinding trials.
Figure 4.1.B	Alumina insulation container used to process and transport the tubes during debinding and bisque firing.
Figure 4.1.C:	Alumina insulation container used to process and transport the tubes during debinding and bisque firing
Figure 4.1.D	Temperature measurement of the tube surface using an optical pyrometer.
Figure 4.1.F	Temperature profile versus time for the bisque firing of the anode tubes in a continuous belt furnace at BTU.
Figure 4.1.G	Bisque fired tubes fired at BTU on a belt furnace.

Subtask 4.3 – Electrolyte Deposition

Table 4.3.A	Results from firing the different electrolyte coated tubes
Table 4.3.B	Further bisque fired tubes and then sintered at the lower temperature of 1400°C for six hours
Figure 4.3.A	Change in IR over the lifetime of the test.
Figure 4.3.B	Tosoh curves have indeed shifted to the right with respect to production cells as expected.
Table 4.3.D	Typical electrolyte thicknesses for infiltration of Tosoh electrolyte on Acumentrics' anode support tubes.
Figure 4.3.C	A430286 – 1500°C for 2.5hrs
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Table 4.3.F	NexTech Electrolyte Sintered Tube Dimensions and Leak Rates
Figure 4.3.E	Left: Section reduced from the fuel side; Right: Evidence of the electrolyte flaking off
Figure 4.3.F	Both images 50x with 10xobj Left: Oxidized part showing variable electrolyte thickness and some crazing; Right: Reduced section showing variable electrolyte thickness and electrolyte breaking off. (Sample, B170073)
Figure 4.3.G	Both images 20x 10xobj Left: Oxidized part showing break in electrolyte coverage and variable electrolyte thickness; Right: Reduced part also showing break in electrolyte coverage and variable electrolyte thickness. (Sample, B170073)
Figure 4.3.H	150x 10xobj Left: Oxidized section showing extreme coverage variability; Right: Reduced section showing coverage variability with scale. (Sample, B170073)
Figure 4.3.J	5x 10xobj, Reduced sample showing area of zero EL coverage. This was repeated in other spots on the sample. (Sample, B170073)
Figure 4.3.K	Reduced section showing a large area of the electrolyte flaking off. (Sample, B170133)
Figure 4.3.L	Sample B170090, B390125 and B390129 after reduction. .

Subtask 4.3 – Electrolyte Deposition (Continued)

Figure 4.3.M	NexTech coated sections that were reduced in a full hydrogen atmosphere.
Table 4.3.G	Measurements Taken From Sample B170105 Reduced in Full Hydrogen

Subtask 5.1 – Reforming Technology-Light Hydrocarbons

Figure 5.1.A	Fuel Flow
Figure 5.1.B	Methane Conversion vs. Time for Cermet POX Reactor
Figure 5.1.C	POX Reactor Cermet Tubes
Figure 5.1.D	Closeup of POX Cermet Tubes
Figure 5.1.E	Methane conversion data agreed very closely with the earlier test.
Table 5.1.A	Reforming modes over JM Rh catalyst:
Table 5.1.B	CPOX over JM Rh catalyst: 190 hours of continuous operation
Table 5.1.D	Carbon fouling of catalysts
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Figure 5.1.F	Catalysts from 16 hour composite bed experiment
Table 5.1.F	LPG partial oxidation over Pt and Rh catalyst:
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Table 5.1.H	Comparison of reactor effluent with equilibrium calculation using measured outlet temperature, and inlet compositions *O/C=1.09,T =832°C, ** O/C=1.14,T=879°C
Table 5.1.J	Reactor effluent during attempted extinction
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Figure 5.1.M	LPG conversion over -Rh (reactor temperature 370°C, SV 9700 hr ⁻¹)
Figure 5.1.N	LPG conversion over -Rh (reactor temperature 550°C, SV 3500 hr ⁻¹)
Table 5.1.Q	Comparison of -Rh data with equilibrium
Figure 5.1.P	LPG conversion over BASF Pt-Ce (reactor temperature 370°C, SV 10725 hr ⁻¹)
Figure 5.1.Q	Transition from CPOX to steam reforming over -Rh
Table 5.1.R	Reforming modes over -Rh catalyst:

Subtask 5.1 – Reforming Technology-Light Hydrocarbons (Continued)

Table 5.1.S	CPOX with -Rh- Ni catalyst composite bed; initial conditions
Figure 5.1.S	Catalysts from 16 hour composite bed experiment
Table 5.1.T	Gas Analysis from Generator 503 off-gas manifolds
Figure 5.1.T	Chromatograms of the off-gas from the four stacks
Figure 5.1.U	Chromatograms of the R stack fuel air inlet and the RR CPOX exhaust
Figure 5.1.V	Propane CPOX Reactor
Figure 5.1.W	Propane CPOX experiment setup
Figure 5.1.X	Carbon monoxide and hydrogen selectivities
Figure 5.1.Y	Carbon dioxide and water selectivities
Figure 5.1.Z	Temperature at top of catalyst bed and pressure drop across reactor
Table 5.1.U	Comparison of reactor effluent with equilibrium calculation
Figure 5.1.AA	Comparison of measured temperature increase vs predicted adiabatic temperature increase
Figure 5.1.AB	Comparison of measured pressure drop increase vs predicted 305 pressure drop increase
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Subtask 5.2 – Light fuel desulphurization

Table 5.2.A	S concentrations in the LPG feed
Table 5.2.B	Listing all potential desulfurization candidates for generators.

INTRODUCTION

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The overall goals of Phase I of the program, which represents three years of development, include:

1. Design of a common low cost generator to meet all chosen markets.
2. Development of an anode supported micro-tubular cell capable of twice the power density presently achieved.
3. Prototype testing of a natural gas or propane fueled unit meeting and exceeding SECA goals.

The research and development to achieve the above goals can be listed in five major sub-tasks:

1. **System development and integration** – In this task work is focused on the functionality and cost reduction of major BOP components. Thermal-hydraulic components are being developed and tested as well as the necessary control strategies. Power electronics and control hardware is being refined and cost reduced to meet the goals of the program. Work is also concentrating on thermal recovery and burner designs for stationary and mobile applications.
2. **Cell Technology Development** – In this task work is focusing on improvements in cell power density through material changes and refinements. Composition and morphology of the anode, electrolyte, and cathode are all being addressed to increase cell power.
3. **Stack Technology Development** – In this task work is focused on generator design and assembly to reduce cost and improve reliability. Connections to the anode and cathode for current collection are being optimized. Casting of insulation to net shape or near net shape is also a focal point for cost reduction.
4. **Fabrication and Processing Technology Development** – Work is concentrating around cell manufacturing processes and the interaction between processes. Assurance of the reliability of each major process without the compromise of cell power is critical in this task.
5. **Fuel Processing Technology Development** – Work is focused on the desulfurization of gaseous fuels and integration of this task in the generator design for optimum size and cost. Specification of systems utilizing liquid

fuels for military and APU applications and the critical integration issues are being addressed in this section.

During the latest six-month period, a number of accomplishments were made toward the direction of Phase I goals. Those goals are listed below in the four major categories of cell, generator, BOP, and power electronics. Further details on each subtask in the original statement of work including goals, approach, and conclusions are elaborated in the body of this report.

Cell

- 1. Resolve power density vs. length curve:** The impact of increasing tube length on overall cell power density was further refined. Cells of 36, 70, 140, 210, and 280mm in length were fabricated and electrically tested. The results of these tests showed a fairly linear decrease in power density with length with a peak near 320mW/cm² for a theoretically “zero” length cell. With this information, design improvements on the number of current collection points and the position of those points can be designed.
- 2. 66% power gain with double end connections:** At the end of budget period 1, the power gain from two end take-offs versus one was 33%. During the last six month period, that gain was raised to 66% through improved braze connections and cell to cell electrical connections on the second end. Further advances with three take-off points improved the gain to 86%. The 66% gain was utilized in the phase I cost estimate.
- 3. Reduce electrolyte firing temperature from 1500C down to 1400C:** During the previous reporting period, the electrolyte firing was shown to reduce from 1500C to 1425C while still providing a gas tight electrolyte. During this reporting period, that temperature was further reduced to 1400C while maintaining a gas tight layer.
- 4. Preliminary Demonstration of Isopressed Anode Tubes:** During the latest period, the program to isopress anode tubes rather than utilize extrusion was initiated. The advantage of this process is to reduce the tube manufacturing process cost. At the same time, the addition of a closed one end (COE) tube removes one braze and allows for faster electrolyte deposition. As this process advances, the capability to grade the anode and better engineer its functionality will be realized.
- 5. Electrical Testing of ScSZ electrolytes:** During this reporting period, a number of ScSZ cells were electrically tested at 800C and down to 700C. Through these tests, though it was found that the resistance contribution from the electrolyte reduced, the overall performance did not improve due to interfacial losses at lower temperatures. To realize the gains this material may deliver, development of the cathode and potentially the anode interface must be completed.

6. **Completion of a >10,000 hour Electrical Test:** During this period, the cells which completed over 10,000 hours were removed from test and microanalyzed. It was found that the IR loss represented approximately 2/3rd of the total loss with the balance being polarization. Through microanalysis, it was determined that the silver evaporation was little to non-existent at 800C. Overall, the two cells on test degraded at 2.2 and 4.2%/1000 hours, respectively.
7. **Development of a Microwave Drying/De-Binding Process:** During the period, further advancements on drying and de-binding were made by moving from a convective system to a microwave system. A microwave unit has been shown to dry tubes in less than 2 minutes. Adding microwave de-binding has reduced the overall firing from 44 hours to less than 10 for complete tube bisque firing.
8. **Application of a Lanthanum Chromite Interconnection:** Based upon the gains in power from multiple axial connections, work was started into plasma spray application of a LaCrO₃ layer to provide connection between the anode and cathode layers. Previous work into sintering had been unsuccessful forcing the change to plasma spray. Early tests with this new process were also unsuccessful due to surface quality and the ability of the sprayed particles to stick to the tube. Advances were made in surface preparation and spray parameters which allowed for successful application during the period. Electrical tests have commenced and will be reported in the next budget period.

Generator

1. **Demonstration of a Ceramic Recuperator:** During the period, the first ceramic recuperator was received from Blasch Precision Ceramics. This unit is a fully cast module made from a net shape casting process for alumina. Preliminary testing showed its effectiveness at around 70% which is lower than the 80% achieved from a metallic unit. Further work is ongoing to improve the effectiveness through dimensional changes as well as possible material changes.
2. **Development of a Counter Flow Recuperator:** A counter flow recuperator was developed during the period to improve the overall effectiveness of the recuperator and therefore the system efficiency. The prototype unit was shown to achieve close to 90% effectiveness as opposed to the cross flow unit, which is in the 82% range. This unit is also smaller and therefore lower cost helping meet the SECA cost target.
3. **Determination of air recirculation feasibility:** Based upon analysis, the concept of direct mixing of electrochemically utilized air and new air to the fuel cell stack was shown to not be feasible. The amount of new air which could be introduced was shown to be close to 1-1.5 times

stoichiometry to keep the desired inlet temperature. This resulted in a partial pressure of oxygen on the cathode of 3-5% which was deemed to low to allow maximum power and stability of the cathode material.

4. **Demonstrate MIM Manifolds:** During the reporting period, the first MIM manifolds were received for inspection. A number of out of specification dimensions were encountered which were conveyed to the manufacturer. Changes in the process to form the green body have been made and further samples are under manufacture. Early indications are that these changes will solve the tolerance problems and produce acceptable parts. This change would reduce the manifold cost from near \$150/manifold to less than \$45/manifold in small quantities.
5. **Implementation of Stamped Braze Caps:** The tube end near the fuel injector exit, at this point, has the simple task of being a gas seal. Therefore, a stamped cap was developed and implemented which replaces the expensive machined part and provides the same function. This results in a cost reduction from \$5.20/tube to <\$0.75/tube to achieve the same goal.
6. **MIM Threaded Caps Implementation:** During the reporting period, the MIM threaded braze caps were brought into specification and implemented into the design. These caps reduce the cost per cell from \$12.97 to \$3.22 with further reductions possible.
7. **Cell Modeling:** During the reporting period, single cell models were developed using FEMLAB to characterize cell performance as well as current per unit length. This model was validated with single cell test data and shown to provide excellent agreement. Further work is now ongoing to optimize the number of axial take-off points to maximize both efficiency and cell power. This tool will reduce the number of empirical tests and should accelerate technology advancements.
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BOP

- 1. Long Term Testing of Components:** Work continued during the period on long term testing of BOP components. It was found that the existing Ametek blowers for cooling and POX air delivery are not suitable for the life expectancy of the generator. Also found were problems with valve “stiction” on the fuel delivery train which also could damage the fuel cell stack. Replacements for these components is ongoing and testing has commenced.
- 2. Develop and validate controller firmware and software:** During the last period, work was performed on implementation of a CANBUS architecture reducing the wiring needs dramatically. This work is further being refined at present.

Power Electronics

- 1. Develop a 1W inverter:** Based upon the success of demonstrating a brass board inverter capable of 95% efficiency, a prototype 1W inverter was built to allow for software development. This work is ongoing and allowing for a more careful specification to be written which will minimize overall design time and reduce the number of printed circuit board revisions required.
- 2. Further Testing of a DC-DC regulator:** During the period, further testing has been performed with our DC-DC regulator to demonstrate its robustness in fuel cell applications. To date we have seen no failures with this hardware, which is important since it constitutes the front-end of the inverter under development.

Based upon the results listed above, a number of advancements have been made in the micro-tubular design with a number of new paths forward being defined. The balance of this report will elaborate on the listed accomplishments.

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BOP

- 3. Long Term Testing of Components:** Work continued during the period on long term testing of BOP components. It was found that the existing Ametek blowers for cooling and POX air delivery are not suitable for the life expectancy of the generator. Also found were problems with valve “stiction” on the fuel delivery train which also could damage the fuel cell stack. Replacements for these components is ongoing and testing has commenced.
- 4. Develop and validate controller firmware and software:** During the last period, work was performed on implementation of a CANBUS architecture reducing the wiring needs dramatically. This work is further being refined at present.

Power Electronics

- 3. Develop a 1W inverter:** Based upon the success of demonstrating a brass board inverter capable of 95% efficiency, a prototype 1W inverter was built to allow for software development. This work is ongoing and allowing for a more careful specification to be written which will minimize overall design time and reduce the number of printed circuit board revisions required.
- 4. Further Testing of a DC-DC regulator:** During the period, further testing has been performed with our DC-DC regulator to demonstrate its robustness in fuel cell applications. To date we have seen no failures with this hardware, which is important since it constitutes the front-end of the inverter under development.

Based upon the results listed above, a number of advancements have been made in the micro-tubular design with a number of new paths forward being defined. The balance of this report will elaborate on the listed accomplishments.

Subtask 1.1 – Prototype Stationary System Design

A second stack tester (126 cells) has been completed. Electronic circuit assemblies have been designed and built to simulate analog I/O elements such as thermocouples and flow sensors that exist in the full generator but not the stack tester. This stack tester has special features that allow it to function as a 5kW generator simulator for design development such as firmware verification. The power conversion path may be configured in several ways as shown in **Figure 1.1.A**. For development tasks that might put a fuel cell stack at risk (e.g., a new temperature control loop) the stack may be replaced by an external DC power supply and source impedance model. The simulator control electronics are similar to those used in the actual 5kW generator but contain additional hardware models of thermocouples, stack voltages, and gas handling devices such as flow meters and valves that are not present in the basic stack tester.

The photos below (**Figure 1.1.B** and **Figure 1.1.B**) show the completed stack tester / generator simulator.

Figure 1.1.B Stack Tester / Simulator Right Side View

Figure 1.1.C Stack Tester / Simulator Left Side View

A specialized backup power system has been implemented to allow fuel cell simulator tests, bundle tests, stack tests, and generator tests to be run simultaneously and continuously while unattended. A three-phase input/single-phase output UPS was built using three 2kW DC-AC converter assemblies of the types used in 2kW Acumentrics fuel cell power plants. This is shown in **Figure 1.1.D** and **Figure 1.1.E**. This UPS powers the test area exhaust fan that captures fuel cell exhaust (**Figure 1.1.F**) and a secondary UPS that powers data acquisition and control computers (**Figure 1.1.G**). Normal short term power outages are handled by the three-phase UPS. If the outage is long enough to exhaust the three-phase UPS batteries, then the secondary UPS provides power to safely shut down all the running fuel cells and backup test data.

Figure 1.1.D 2kW Inverters

Figure 1.1.E Pb-Acid Batteries

Figure 1.1.F Test area exhaust fan that captures fuel cell exhaust

Figure 1.1.G Secondary UPS that powers data acquisition and control computers

Work continued on creating a 3D CAD model of the generator system. Additional work was carried out on the insulation and interconnecting piping details for the six stack, interleaved configuration. In addition to the water recovery/steam reformation configuration, a partial oxidation generator configuration is being detailed. A version of the stack model incorporating a partial oxidation reactor at the base of the stack has been created. Interconnect tubing and fittings were added to the 5 kW POX module. The Fuel Cell Module and Gas Utility Module have been integrated into the baseline enclosure model.

Detailed models of the electrical side components have been made and incorporation of these components into the enclosure model is underway. Enclosure manufacturers have been contacted and discussions held regarding alternate enclosure designs and construction techniques.

A detailed Bill of Material (BOM) was prepared for the baseline POX generator. This BOM includes all part and drawing numbers, quantities, pricing and vendor information. It will be updated as the design evolves. Work continued on the refinement and updating of the 3D CAD model of the generator system.

The baseline POX generator was modified to include internal flow baffles between the stacks. These baffles eliminate the need for insulation board in the area between the cells of adjacent stacks. This insulation was difficult to support and it was also difficult to maintain proper clearances at the cells. The stack thermocouple pass-through location was also changed from the rear insulation board to the manifolds. This location provides a more stable location for the thermocouples and brings the thermocouple wiring to the same side of the generator as most of the other plumbing and wiring connections. The BOM was modified to reflect these changes.

The baseline POX generator was modified to include the three pass flexible fin core recuperator. The stack supports were also modified from the pin design to the new “leaf spring” design. The BOM was modified to reflect these changes.

Subtask 1.3 - Control Strategy Development

The software simulator under development will be a combination of software and hardware designed to emulate the entire SOFC system for control system optimization and firmware verification. The simulator will be programmed to run a predetermined set of test scripts to functionally exercise the SOFC control system firmware and hardware. With the simulator, control strategies can be evaluated and feedback loops optimized without utilizing an actual fuel cell system. There will also be hardware-in-the-loop capability where the actual hardware can be used in the place of the model during simulation. An overall block diagram of the simulator is shown in **Figure 1.3.A**.

Figure 1.3.A Software/Hardware Simulator Blocks

On the right hand side of the diagram the SOFC distributed control system boards are shown and they will be running the actual system firmware. The thermocouple input board, FCTC, the balance of plant I/O board, FCIO, the system master controller and communication board, FCCOM and test system are communicating via the CANbus. The control boards are receiving and acting upon stimulus generated by the xPC Target computer and system hardware. The FCCOM board also communicates through an Ethernet connection to the HMI that resides on a third computer.

The xPC target computer is the connection between the Mathwork's simulation software in which various aspects of the SOFC are modeled and the SOFC control system hardware. The xPC system I/O as currently configured for the simulator will require 26 analog outputs, 11 analog inputs, 3 digital outputs, 13 digital inputs and a CANbus interface for monitoring the inter-board serial communication. This can be accomplished with three PCI boards. A PowerDAQ II PCI Analog-Output board from United Electronics Industries, UEI, will perform the analog and digital outputs. A PowerDAQ II PCI Multifunction board also from UEI will handle the analog and digital inputs. The total I/O driver latency time with the UEI boards is approximately 50uS that is 200 times less than the 10mS SOFC control system sampling rate so real time operation can be easily achieved. The CAN interface will be a Softing CAN-AC2-PCI board. The interface circuitry will consist of custom circuitry to condition signals to the appropriate levels for the SOFC control system and xPC PCI boards.

In addition to the computer generated signals from the xPC there will also be system hardware shown in more detail in the block diagram **Figure 1.3.B** below:

Figure 1.3.B Hardware Simulator Blocks

The SOFC stack simulator is modulated from an analog output from the xPC to simulate the fuel cell output voltage, V_{Sim} , and impedance. Electronic circuitry will then generate the individual internal manifold voltages that are monitored by the FCIO control boards. Two digital outputs from the xPC will inject manifold low voltage fault conditions while exercising the system firmware as part of the test conditions. The stack simulator also feeds the Fuel Cell Interface Converter, FCIC, which controls the SOFC

stack output current and was developed during the Phase 1 SECA contract. The FCIC is controlled via the CANbus. The output of the FC-IC is connected to an electronic dynamic load that is modulated by the simulation software to generate system load transients. The shunt provides an output proportional to the fuel cell current and is measured by the FCCOM board. The measured current is compared to a reference to maintain the loading conditions on the fuel cell. The ON/OFF switch, CLEAR and emergency stop button are inputs to the FCCOM control board. The RUN and FAULT LED indications are generated by the control system and monitored by the simulator. The final detailed design of the simulator will not be completed until the final details of the distributed control system are fully worked out.

Work was performed to characterize the balance of plant components and subsystems along with optimizing the various feedback loops.

We have started to migrate the 2407 microcode (used on the centralized controllers) to the 2810 series, which is used in the distributed control boards.

Three new control software code modules have been implemented and tested. The modular state-machine, task sequencer, and analog input over-sampling modules have been tested on a 21 manifold stack tester and a full 5kW fuel cell generator.

An improved control element wiring scheme has been designed that more consistently maps processor I/O ports to dedicated control elements. This consistency aids in the construction and debugging of different fuel cell models (e.g., propane vs. methane).

Two silicone conformal coatings for printed circuit electronics were evaluated : Dow Corning 3-1965 and 3-1765. It is expected that these coatings will help in the move to a distributed control architecture where electronic assemblies may be in close proximity to stack and BOP components. All printed circuit assemblies in the latest 5kW fuel cell generator have been brush coated with the 3-1765 formulation.

A facility to run on either natural gas or customer supplied diesel reformat has been designed and implemented in the latest 5kW generator. New control elements include a manual valve, valve position sensor, proportional valve, gas flow sensor, and gas composition sensor.

A design review meeting was held for the new distributed state machine control strategy. No major design flaws or issues arose at his meeting. The distributed state machine approach of having multiple simple state machines (temperature control machine, fuel control machine, etc.) orchestrated by a simple system state machine has worked out well and will be continued in the future.

We have moved all control electronics to the electronics area of the fuel cell cabinet. Previously, one of the three controller assemblies was located on the stack sheet metal to provide convenient thermocouple access. Now, however, a mass-termination/ bulkhead pass-through scheme for thermocouples and cell voltage sensing is implemented that obviates the advantage of a stack mounted controller.

We are planning to implement a redundant safety feature that will allow self-checking between controller assemblies and safe shutdown if certain controller failures occur.

Documentation has been generated in support of the control software including descriptions of design and operation.

An improved thermocouple cold-junction compensation scheme has been implemented. To save cost, a thermocouple mass-termination/ bulkhead pass-through design was recently implemented. This design forces the thermocouple “cold” junction – where thermocouple metals meet copper - onto the pass-through connector from the fuel cell section to the electronics section. A single thermocouple is routed from the fuel cell side of the pass-through connector through a sealed hole in the bulkhead back to a thermistor location on the fuel cell control circuit board. The fuel cell controller compares the direct thermistor temperature reading to the thermistor-as-read-by-the-thermocouple reading and thereby determines the cold junction compensation needed for all thermocouples in the pass-through connector.

Difficulty in continuously adjusting anode fuel flow has recently been observed in both bundle testers and generators. The software control algorithms that drive this valve have been investigated and are functioning as intended. It now appears that proportional fuel valves are sticking. It’s not clear what is causing this problem. However, suspect valves show signs of excessive wear in the solenoid plunger mechanism.

A vacuum DC contactor is now used to disconnect the fuel cell electrical output from the first stage electronic power converter (FCIC). The control strategy opens this contact during unloaded fuel cell operation or if a system fault occurs. The contactor protects the FCIC from high-voltage stress during unloaded purge gas operation and protects the fuel cell stack in the event of an FCIC short circuit failure.

Subtask 1.4 - Heat Recovery

3 Pass, Cross Flow Metallic Recuperators

Tests were made on a metallic recuperator having a brazed flat tube/fin core geometry for the first pass. In this configuration, flattened tubes with internal fins are utilized. On the exhaust side, corrugated fin material is sandwiched and brazed to the outer surface of the flattened tubes. The test setup was identical to the last test configuration except for changes made to support and insulate the taller fin core unit. This unit is approximately 51 mm taller than the previous bent tube units and therefore structural support spacers were added between the structural frame and the recuperator angle iron supports. Insulation was also added so that the portion of the recuperator extending beyond the frame/insulation package was insulated with at a minimum 1” of ceramic blanket and 2 inches of mineral wool board. The **figure 1.4.A below** shows a top view of the unit along with a close up of the fin/tube assembly.

Figure 1.4.A top view of the recuperator along with a close up of the fin/tube assembly

The **table 1.4.A** below gives the test results. There was a significant improvement over the original and modified bent tube designs. For the three flow rates tested the overall effectiveness of the unit was approximately 80%. The unit was run with and without tiles at the outlet and the tiles were found to have no impact on performance. The pressure drop of the unit was slightly higher than the modified bent tube unit. At operating temperature, the plenum pressure was 625 Pa at 1017 lpm whereas the plenum pressure for the Acumentrics, straight tube, welded unit was 250 Pa at 1060 lpm.

Manufacture and testing of two flat tube/fin core geometries was conducted by Toyo Radiator to characterize the performance of 37 and 46 tube per row configurations. Based on these results the design of a recuperator utilizing the brazed flat tube/fin core geometry for each of the three passes has been completed.

A design review meeting was held with Toyo Radiator to discuss their progress on the design of recuperators using their Flexible Flat Tube heat exchanger (FFTex) core. The assembly of the first three pass, cross flow unit using the FFTex core has been completed and performance testing is expected to take place next month. In addition to the baseline, three pass, cross flow design, a counterflow configuration has been designed. It is projected that this unit will reduce the price of the recuperator by 20%. Detailed design drawings are being prepared and methods of incorporating this configuration into the generator design will be evaluated.

Manufacturer testing of the three pass flexible fin core (FFTex) recuperator (see figure below) was conducted. The initial results were varied; at design conditions the effectiveness of the unit was 81% and at approximately twice the design air flow 84%. Airside pressure drop was higher than projected. Additional testing and a design change to reduce the pressure drop will be made prior to shipment to Acumentrics.

Figure 1.4.B Flexible Fin Core Heat Exchanger Configuration

A three pass, flexible fin core, recuperator was also tested to validate the performance of the unit. The **Figure 1.4.C** below show the unit. Overall effectiveness of 80 to 82% were measured.

Figure 1.4.C A three pass, flexible fin core, recuperator

Figure 1.4.D recuperator effectiveness

Counterflow Metallic Recuperator

A counter flow, FFTex recuperator was received from Toyo and photos of the unit are shown in **Figure 1.4.E** below. This unit achieved an effectiveness of 89% during testing at Toyo Radiator. It has a volume of 0.73 cubic feet compared to a volume of 2.23 cubic feet.

Figure 1.4.E Counter flow, FFTex recuperator

Catacel Recuperator

Design discussions have been initiated with Catacel Corporation regarding a recuperator using their thin foil, reactor technology. Manufacture of a prototype, subscale heat exchanger is underway and this unit will be made available to Acumentrics for heat exchanger performance testing.

A subscale prototype recuperator was received from Catacel and preliminary flow and leakage testing was conducted. The unit is a three pass, rectangular tube, fin core geometry. Leakage testing revealed that there was excessive leakage from the air to exhaust side of the unit and the unit was returned to the manufacture for inspection and repair.

Catacel performed an inspection on their three pass, rectangular tube, fin core recuperator test section and found that there was buckling of the tubes close to the tube sheets. Catacel is investigating ways to effect repairs and to eliminate this problem in future builds.

Ceramic Recuperator

The first ceramic monolith heat exchanger core was successfully fired (**see Figure 1.4.F below**). The core is dimensionally accurate and voids or pores were not visually evident. A pressure check of the passage integrity was made and there was found to be some leakage from the exhaust to the airside of the unit, approximately 1.5 scfm at 1 psi. At the system operating pressure of several inches water column, the leakage should be minimal and have a negligible effect on performance.

Figure 1.4.F Ceramic monolith heat exchanger core

The **Figure 1.4.G** show the unit with the inlet and outlet covers attached. A close-up of the cover clamping arrangement and the recuperator support structure is also shown. A single thickness of 1/8" Fiberfrax felt was used to seal the cover to the ceramic face.

Figure 1.4.G Recuperator Inlet, outlet covers and support structure

A photograph of the recuperator installed in the test stand is provided in **Figure 1.4.H** below. Unlike the metallic recuperator tested where the cathode blower was mounted directly to the inlet cover, in this setup the cathode blower was separately supported and a flexible hose used to deliver the air to the inlet. This was done to avoid putting excessive load on the monolith cover mounting flange.

Figure 1.4.H Recuperator installed in the test stand

Preliminary testing was conducted to determine the effectiveness of the unit and evaluate the structural integrity of the monolith with thermal cycling and operating temperature gradients. The **Figure 1.4.J** below shows the inlet and outlet temperatures for a typical test along with the calculated effectiveness. The unit achieved an effectiveness of 67% with an inlet exhaust temperature of 800 C.

Figure 1.4.J Inlet and outlet temperatures for a typical test along with the calculated effectiveness.

After three thermal cycles the recuperator was removed from the test stand to evaluate the structural and pressure integrity of the unit. There were no signs of cracks but the leakage rate from the unit was rather high which may be the primary reason for the below design performance. The **Figure 1.4.K** below shows the leakage with the covers on and the outlet flange blanked off. This leakage was considerably higher than the leakage reported by Blasch so additional leakage testing of the ceramic core was conducted.

Figure 1.4.K Leakage rate from the unit

The measured leakage of the ceramic core as shown below was also considerably greater than measured at Blasch. This leakage data is with the plenum covers removed and the ends of the air passages blocked, separately and also with the passages combined. Inspection of the Blasch experimental leakage test setup revealed that the pressure reported in their results was primarily the backpressure associated with the flowmeter. It was therefore not possible to determine the before and after testing core leakage change so it is unclear if the leakage is a result of porosity and voids in the casting walls (perhaps due to the thawing of the casting during mold extraction) or due to cracks developed in the casting during thermal cycling.

Figure 1.4.L Additional leakage testing

Offgas Recirculator Heat Exchangers

Offgas recirculation heat exchangers were manufactured to permit cooling and reheating of the offgas in an offgas recirculation/steam reformation configuration. The units are a conventional counterflow, shell and tube design (see **Figure 1.4.M below**), one unit was made using Inconel 600 for the shell and tubes and the second was made with 304 stainless.

Figure 1.4.M Conventional counterflow, shell and tube design

The offgas recirculation heat exchanger was installed on a stack tester as shown in **Figure 1.4.N** below. Final piping and insulation work is being completed and initial testing will be conducted. A reheat loop will be installed in the stack tester furnace cavity to simulate the stack for the initial testing.

Figure 1.4.N Recirculator Integrated Test Setup

Subtask 1.5 – Burner Design

Generator Start-up Burners

Several startup burners have continued to accumulate operating hours as part of stack and bundle tester operation without any problems with fouling.

Propane POX Reactor Start-up Burner

A burner capable of serving as a startup burner for a propane partial oxidation reactor was designed and tested. The burner was designed to operate either as a premixed burner or nozzle mix burner. Preliminary testing was conducted using both natural gas and propane fuels.

Figure 1.5.A Propane POX Catalyst Warm-up Burner

Additional testing was conducted with the startup burner for the propane partial oxidation reactor. Flame pull back into the inlet tube was experienced under certain operating conditions while operating on propane. Burner design changes will be evaluated to eliminate this condition. Since the burner is only needed for a short period of time to preheat the catalyst, reactor operation was still possible and the test results can be found in Section 5.1.

Subtask 1.6-Gas Utilities

Water System Components

Testing of Tuthill pumps (**Figure 1.6.A**) continued through August. Tuthill had identified the cause of the earlier pump failures to be inadequate lubrication between the stainless steel shaft and the driven magnet (embedded in a Teflon rotor). Tuthill modified a pump by drilling a hole in the rotor to increase lubrication. The pump was factory tested for 5 days and shipped to Acumentrics for further testing. The flow rate was 30 mL/min on day one, decreasing steadily to below 10 mL/min by day two. This was the sixth pump test, and exhibited similar failure characteristics to the other five pump tests. All pumps have been returned to Tuthill. No further testing will be conducted until Tuthill have completed a factory test exceeding 720 hours.

Figure 1.6.A Testing of Tuthill pumps

A centrifugal pump was set up and operated for 170 hours at 20 volts supply, delivering 20 mL/min at 4 PSI (**Figure 1.6.B** below). Preliminary testing indicated the pump would deliver over a range from 5-30 mL/min (at 5 PSI). A McMillian 101-3E flow sensor was installed so that the pump could be better characterised. The integration of the McMillian flow sensor represented the last revised layout for 5kW generators, which operate with water recycle. The cost for the centrifugal pump is \$175. The cost for the custom control board is anticipated to be below \$30. An early estimate for the centrifugal pump, variable power supply and flow sensor is less than \$250 per system in modest quantities (100).

Figure 1.6.B March Centrifugal pump model 893 (a) and pump test set up (b)

Fuel Control Valves

Over the past year, a number of proportional valves have been performing poorly with time. The main problem experienced is the valve fails to make small adjustments in fuel flow, especially if the valve is operating at set flow conditions for extended periods. This characteristic is commonly called valve stiction, which creates problems with maintaining varying low fuel flow rates. Unstable generator or test stand operation typically results. Initial inspection of valves were undertaken, with the focus being the valve plunger, in particular the slip ring and characteristic wear marks on the plunger. A new valve, used, and used failing valve were compared and discussions with the manufacturer has taken place.

Figure 1.6.C Inspection of valves

Component Life Testing

The first hard failure of an Ametek blower occurred at approximately 4343 hours at an ambient temperature of 45°C in the environmental chamber. The **Figure 1.6.D** below shows the output flow cycling up and down as part of the test regimen and then suddenly decreasing while the blower temperature increases.

Figure 1.6.D output flow cycling up and down as part of the test regimen

An autopsy was conducted on the Ametek blower that failed while on thermal test. The failure mode is determined to be similar to the first Ametek blower to fail under a preliminary thermal test.

It is possible the temperature distorted the impeller such that the impeller contacted the ribbing on the inside of the blower housing. The clearance between the impeller and the ribs are approximately 0.125-0.18". This condition would have generated additional heat (friction heating) softening the impeller material resulting in further warping of the impeller, eventually overloading the bearing, and further accelerating the destruction of the impeller. An alternative explanation is the impeller creped over time due to the increased temperature and mechanical loading of operation.

Figure 1.6.E Damaged impeller from failed Ametek blower

A second and third Ametek blower has failed during the life test at 45°C. The first blower failed at 4343 hours, the second at 5233 hours and the third at 5391 hours. The test limits were refined after the first and second blower failures such that the failure mechanism could be clearly identified. The Figure 1.6.F below supports the hypothesis that the impeller warped, following by fracturing of the impeller leading to contact between the impeller and housing. The blower becomes inoperative within less than an hour.

Figure 1.6.F Stages of impeller failure (a) and initial failure (b)

Ametek was informed of the blower failures and offered to replace the plastic impeller with an aluminium impeller, while maintaining the cost of the current blower.

Acumentrics has received the modified blower and preliminary testing indicates the performance has been maintained. However, the cost of the Ametek blowers has always been prohibitive to their inclusion in the lower cost generators planned. The Ametek blower will be replaced on the Primary air and Cooling air applications with EBM blowers. This can be done because the system backpressures for these utilities are suitable.

The BOP life test software has been changed to ramp Ametek blower speed between set points. The previous program made constant step changes in blower speed. The new program more accurately reflects fuel cell usage and reduces stress on the blower impellers. The 45 °C BOP life test has now run for 6238 hours.

The BOP life test software has been changed to increase the environmental chamber air temperature from 45°C to 60°C. This change will verify performance for new layout approaches where control electronics will be closer to the stack. After taking data for about 1 month the life test will continue at 45°C.

Blowers (Primary and Cooling Air Manifold System)

Preliminary layout options for replacing Ametek blowers, used to supply “Primary air” and “Cooling air” are evolving (see Figure 1.6.G below). The Ametek blowers will be replaced by EBM blowers which to date have performed better in life tests and are less expensive. The layout work is focussed on ensuring the larger blower can be integrated into the GUM with provision for the customized blower-reducer interface fitting. The Primary Air Manifold will also be redesigned to accommodate the new layout and further reduce cost.

Figure 1.6.G Preliminary layout options for replacing Ametek blowers

A layout for reducing the number of blowers used to supply “primary burner air” and “stack cooling air” was finalized. The final configuration uses one EBM blower and a Neptronics rotary actuated valve. CAD models of the configuration and photos of the test set-up are shown below. The configuration was tested and suitable flow restrictors were determined for the primary air-lines which feed the igniter and burner. Flow-pressure curves simulating increasing line backpressures were developed (see **Figure 1.6.H** below). The valve supplies the required 0-200+ Lpm of cooling air, while the blower can be adjusted between 70-90% to ensure the primary air requirements are met.

Figure 1.6.H Primary and Cooling Air Manifold (PCAM)

The Primary and Cooling Air Manifold (PCAM) configuration reduces the cost of the current components by 60% (**Table 1.6.A** below), and reduces power consumption by 50% (30W) when the generator is under load.

Figure 1.6.J Flow Characterization Setup

Figure 1.6.K Igniter line flow versus simulated back pressure

Figure 1.6.L Burner Line flow versus simulated back pressure, manifold pressure at 8.1\" and Blower at 31 Watts

Figure 1.6.L Manifold pressure versus Cooling line flow rate with valve position

Gas Utility Module Layout/Design

The Gas Utility Module layout (Generator 502 GUM, **Figure 1.6.M** below) was updated such that the water components are assembled as a standalone sub assembly. The gas side of the module will become generic between platforms simplifying development.

Figure 1.6.M Gas Utility Module layout

The layout for a CPOX (Catalytic Partial Oxidation) GUM with optional reformate line was designed, assembled and integrated into Generator 503 (**Figure 1.6.N** below).

Figure 1.6.N CPOX (Catalytic Partial Oxidation) GUM

The Generator 504 GUM was assembled utilizing the Primary and Cooling Air Manifold (PCAM), which was designed, built and tested over a two-month period. This GUM was successfully integrated with a FC module, which is currently operating in the field.

Figure 1.6.P GUM was assembled utilizing the Primary and Cooling Air Manifold (PCAM),

The concept of mounting the control hardware on the GUM frame was explored to further reduce cost and assembly time. Mounting the control hardware on the FC Module side of the Generator Enclosure has the potential to reduce the number of bulkhead connectors, cable lengths and subsequent labor. Two layout options were considered; mounting the hardware on the right side of the GUM and at the base of the GUM frame. No further work has proceeded on these two concepts.

GUM Test Equipment

The Gas Utility Modules undergo testing to ensure components are wired correctly (connector pin to part check) and gas lines are leak free. To improve quality control (QC) of the GUM sub assemblies a test fixture (see **Figure 1.6.Q** below (a)) has been built to facilitate the testing process by speeding up gas leak testing and verification of component operation. The GUM QC Tester was built to the specifications listed in **Table 1.6.B**, which contain the control elements used in a generic 5kW system and displayed on a generator P&ID. The test equipment over time will be used for component calibration and tuning where required (valves, anode and fuel flow meters). Test procedures will be developed to standardise the performance of the GUM sub-assembly.

Figure 1.6.Q Test fixture to facilitate the testing process

Flow Sensors

An alternative to costly mass flow sensors is the use of an orifice plate and a low cost pressure transmitter. Miniture pressure sensors were obtained for evaluation in this configuration. This pressure sensor has a 0-4" w.c. range, which will not provide the resolution required at the lower flow rates for measurement of anode air and fuel especially if the pressure drop across the orifice plate is to be minimized (~ 1 " w.c.). Pressure sensors with a range of 0-1" w.c. are being investigated, along with the allowable fuel:air ratio that the generator could operate, i.e., the minimum accuracy that the system will allow.

Differential pressure flow sensors using office plates were fabricated for $\frac{1}{2}$ " and $\frac{3}{4}$ " pipelines (**Figure 1.6.R** below). A range of orifice sizes ($\frac{5}{16}$ ", $\frac{3}{8}$ ", $\frac{1}{2}$ ") will be tested and data compared to theoretical calculations. The practical limits of these flow sensors will be defined.

Figure 1.6.R Differential pressure flow sensors using office plates fabricated for $\frac{1}{2}$ " and $\frac{3}{4}$ " pipelines

Testing was undertaken using a flow meter to measure the air flowing through the orifice flow meter. An Agilent Digital multimeter was used to record the pressure sensor feedback to a resolution of 1 micro-volt. The differential pressure versus flow rate was recorded for each orifice in a $\frac{1}{2}$ " and $\frac{3}{4}$ " pipe fitting arrangement. A photograph of the test setup is shown **Figure 1.6.S** below.

Figure 1.6.S 1/2" and 3/4" Pipeline Test Fixtures

There is a large discrepancy in the data and the predicted DP versus flow as determined using standard orifice discharge coefficients (see **Figure 1.6.T** below). A reasonable curve fit can be obtained by using a polynomial fit or by adjusting the discharge coefficient accordingly. Examination of the raw data shows that the pressure sensor can measure to a resolution of 0.01" w.c., and exhibits good feedback at lower pressures (0.02-0.5" w.c.), at higher pressure the feedback error increases, due to increased turbulence.

Figure 1.6.T Experimental and calculated data for flow rate versus differential pressure across 5/6", 3/8" and 1/2" orifice sizes through the 3/4" pipe test fixture

Figure 1.6.U Pressure sensor (CPCL04DFC) test data for ¾” Pipe with ½” orifice

DP MV	Error MV	%	DP "w.c.
0.293	0.001	0.34	0.017
0.297	0.001	0.34	0.018
0.327	0.001	0.31	0.023
0.401	0.001	0.25	0.036
0.52	0.001	0.19	0.055
0.68	0.005	0.74	0.082
0.89	0.01	1.12	0.117
1.14	0.01	0.88	0.159
1.77	0.03	1.69	0.265
2.6	0.05	1.92	0.404
3.6	0.1	2.78	0.572
4.8	0.1	2.08	0.773
6.1	0.2	3.28	0.991
10	0.2	2.00	1.644
14.2	0.3	2.11	2.348

Oxygen Sensor

A new oxygen sensor and differential pressure sensor signal conditioning circuit has been designed. It is hoped that these sensors will eliminate some expensive proportional valves and flow sensors. The layout of the new circuit board is shown in **Figure 1.6.V** below.

Figure 1.6.V New circuit board layout.

An oxygen sensor (Teledyne R22A) was integrated into the generator. A fixture was assembled to house the sensor, and mounted so that the fuel-air mix could be monitored. Sample ports located before and after the CPOX reactors are used to feed sample to the sensor. A manual valve is used to proportionate the sample flow, and used sample is exhausted into the cathode air stream at the cathode air blower inlet. The addition of this sensor will provide a check on the fuel-air ratio and may offer cost reduction in fuel-air metering in the future.

A ½" bore orifice plate was installed into the cooling air manifold as an means to measure the cooling injector air flow. Calibration and testing of the orifice plate arrangement will be conducted.

Figure 1.6.W a) Oxygen sensor, b) installed oxygen sensor and cooling air manifold orifice plate

Manifold Voltage Sensing

A new voltage sense system was designed and tested. The layout provides the controller with 28 voltages, and manual measurement of each manifold voltage can be taken. The manifold voltages are measured by connecting high temperature wire to voltage taps, which are located on each manifold. Four 22-position screw gate connectors receive 22 high temperature wires from each stack. Seven of the 22 wires from each stack, via the 22-position connector are routed to the voltage sense fuse board (see **Figure 1.6.X** below), which are then taken to the bulkhead using a ribbon cable and connector. The design and implementation of future voltage sense systems will continue to be refined.

Figure 1.6.X Wires from each stack routed to the voltage sense fuse board.

Figure 1.6.Y Voltage sense wire board (16 wires per board)

Thermocouples

A number of thermocouples have failed during generator testing and an autopsy was performed to determine the problem.

One thermocouple (T-26) failed due to a poor or no junction weld. Another thermocouple (T-23) was too short for the location, and three thermocouples (T-7, T-41 and T-45) were affected by an electrical short to the fuel cell stacks. A physical explanation for this occurring could not be determined through inspection or simple experiments conducted at room temperature.

K-type thermocouples are specified for operating in oxidizing or inert atmospheres, and when subjected to reducing environments form green rot (chromic oxides). The electromotive force of the thermocouple (temperature measurement) is reduced, and the presence of the chromic oxide may provide a grounding path. Therefore, the problem with the thermocouples may be a fabrication issue, with the presence of carbon inside the insulating sheath (from thermocouple insulation burnout) creating a reducing environment over an unknown period. Alternatively, the shorting phenomenon could be an interaction between the ceramic pastes used in thermocouple fabrication and burned off carbon, loose braids of silver, deposits from the cell electrodes during thermocouple placement, etc.

It is suspected these problems will not persist with the new “through the manifold design” which ensures the thermocouples does not rest directly on electrically conducting components. The longest thermocouple will be 11.2” versus 14.5. This will reduce the time it takes for the carbon to be burnt out from the thermocouple insulators. The outer insulation sleeve on the thermocouple wires will also be removed to facilitate carbon burn off.

A Life test has been set up to quantify the thermocouple instabilities at steady state conditions (**Figure 1.6.Z** below (a)) and under thermal cycling (below (b)). This testing will determine if further changes to thermocouple assembly are required. The life test was started 27th December.

Figure 1.6.Z Life test set up to quantify the thermocouple instabilities at steady state conditions (a) and under thermal cycling (b).

Subtask 1.7-DC/AC Inversion

An initial draft of the fuel cell inverter preliminary electrical specification was written for 5kW systems. The AC output will be able to power stand alones in addition to being able to interconnect safely with the power grid. Battery interfacing provides for black start-ups and also provides transient power for fast load changes. The specification calls for 50,000hr changes of fans to increase reliability. This specification will be updated as requirements or performance changes dictate.

Work is progressing on a 2810 DSP based control board for SOFC power conditioner firmware development. This board will simultaneously control two FC-IC inverters in our target configuration. A block diagram is shown in **Figure 1.7.A**.

Figure 1.7.A Power Conditioner DSP Controller

A coding template has been created to help migrate from the TMS320LF2407A (16-bit 40MIPS) to the TMS320F2810 (32-bit 150MIPS) digital signal processor. The new processor is necessary to handle the increased computational complexity of multi-phase and grid-tied SOFC power conditioners using digital control.

A 1Watt SOFC power conditioner hardware simulator has been designed as shown in **Figure 1.7.B**. This is a 1:5000 functional scale model of critical power conversion portions of the final 5-10kW product. When built, it will be combined with a Spectrum Digital eZdsp '2810 development board for algorithm development.

The 1Watt SOFC power conditioner hardware simulator was built and connected to a Spectrum Digital eZdsp '2810 development board. The combination is shown in **Figure 1.7.C**.

Figure 1.7.C 1W Simulator Test Bench

A diagram of a new DC/AC power conversion control strategy has been created as shown in **Figure 1.7.D**. The top half of this diagram shows the battery DC bus inverter and the bottom half shows the fuel cell DC bus inverter. The two inverter AC outputs are combined in a 50/60Hz transformer included in each Power Stage block. This strategy is applicable to split-phase (120V/240V) stand-alone systems though single-phase and grid-connect variations are also being worked on.

A schematic diagram of a printed circuit controller for SOFC power conditioner firmware development has been completed. A peer design review meeting for this assembly was held. When completed, this controller will be combined with full scale 5kW power electronics.

Initial software has been written to generate an open-loop sinusoidal voltage that drives a step-up transformer to generate either single-phase 120 Vac or split-phase 240 Vac. Voltage and current waveforms produced by the simulator are shown in **Figure 1.7.E**. Note that the waveforms shown were measured prior to the transformer. A 130 Ω resistive load is being used.

Figure 1.7.E Inverter Output Voltage (M) and Current (Ch3)

Having achieved open-loop operation, control system design has begun. A model to implement the control is shown in **Figure 1.7.F**. A nested loop topology will be implemented, with a PID compensator for the inner current loop and a P + Resonant compensator for the outer voltage regulation loop (a third outer loop for voltage magnitude regulation may be added as the design evolves).

Figure 1.7.F Control design model

$L_f = 3000\mu\text{H}$ $C_f = 150\text{nF}$ $R_f = 3.36\Omega$ (values implemented in the inverter simulator)

$K_{PR} = 1$ $K_{IR} = 20$ $\omega_{res} = 377 \text{ rad/sec}$ $\omega_{cut} = 10 \text{ rad/sec}$
 $K_{PC} = 10$ $K_{IC} = 0$ $K_{DC} = 0.5$ $\omega_{roll} = 15080 \text{ rad/sec (2400 Hz)}$

As can be seen in Figure 1.7.G, the output will provide good tracking to the reference at the desired output frequency but provides no attenuation at higher frequencies. There is also good rejection of any load component at the fundamental, but no rejection of load harmonics. A possible solution to reject load harmonics would be to include additional resonant compensators dedicated to the major harmonics (primarily 3rd, 5th, and 7th).

The results shown in Figure 1.7.G represent a starting point, and are subject to further optimization. One observation that has been made is that as the filter resonant frequency (currently 7500 Hz) decreases the Q for the closed loop system decreases as well. **Figure 1.7.H** shows the Bode magnitude plot with a filter frequency of 2900 Hz and $K_{DC} = 0$. Note the high frequency roll-off of both the reference and load transfer functions, as well as the simpler inner loop compensator (a simple proportional compensator can be implemented). While this may improve performance and load rejection, the filter will increase in both size and cost.

Figure 1.7.G: 7500 Hz Filter Frequency

Figure 1.7.H 2900 Hz Filter Frequency

The fuel cell interface converter (FCIC) firmware was modified in support of the 5kW simulator / stack tester (see subtask 1.1). Since the stack voltage is lower than a full generator, the FCIC was changed to boost the stack voltage enough to charge the 48V battery bus. This involved re-tuning the boost control loop, expanding the PWM duty cycle range, and scaling the overload threshold levels.

In order to fully test grid-tie functions, the generator test area electric power service must be upgraded. Presently only 3-phase 208V or 1-phase 120V power exists. This upgrade is being done in conjunction with obtaining the necessary grid-tie approval of NSTAR, our electric power provider.

Packaging, interconnection, and cooling design issues are being considered prior to commencing with the detail design of our new 5kW power conditioning module (PCM). Also, the amount and type of ripple-current impressed on the fuel cell by the PCM is being considered in terms of cost and fuel cell performance. An experiment has been designed for Acumentrics fuel cell test stands that will allow short and long term studies of actual ripple-current loading.

Task 2.0-Cell Technology Development

Subtask 2.1 - Anode Tube Composition Optimization

Evaluation of American Elements 45/55 Ni/YSZ and 55/45 Ni/YSZ Anode Materials

As part of the anode tube composition optimization work, American Elements (AE) prepared two different cermet compositions for evaluation by Acumentrics. The first composition, 4014-2, had a composition of 45/55 Ni/YSZ with a standard particle size distribution. The second, 4014-3, had a composition of 55/45 Ni/YSZ with a standard particle size distribution.

The purpose of these tests was to alter the chemical composition of the anode material for comparison with standard AE material in terms of powder properties, anode tube characteristics, and finished cell performance.

Powder Characterization

Initial work with the powders focused on powder characterization. Particle size distribution results, as well as a comparison standard AE distribution, are provided in **Figure 2.1.A** below.

Figure 2.1.A. Particle size distributions for AE experimental powders and a standard AE production powder.

Analysis of the data shows that both experimental powders are within close approximation of the standard particle size distribution, which was intended. **Table 2.1.A** provides the numerical values for powder as measured at Acumentrics.

Table 2.1.A. Particle Size Distribution Data for AE Experimental Powders and Standard AE Production Powder

	4014-2	4014-3	AE Standard
d(10)	0.746	0.727	0.624
d(50)	2.220	2.151	1.200
d(90)	5.985	6.097	3.234

Measurement of the apparent density and tap densities for all three types of powder followed particle size analysis. Results of the measurements, as well as summary statistics, are provided in **Table 2.1.B**.

Table 2.1.B. Apparent and Tap Density Data for AE Experimental Powders and Standard AE Production Powder

	<i>4014-2</i>	<i>4014-3</i>	<i>AE Standard</i>
Avg. App. Density (g/cc)	1.18	1.14	1.23
App. Density Std. Dev. (g/cc)	0.11	0.09	0.02
App. Density C _v (%)	9.34	8.11	1.68
Avg. Tap Density (g/cc)	1.69	1.66	1.84
Tap Density Std. Dev. (g/cc)	0.10	0.60	0.04
Tap Density C _v (%)	5.83	3.54	1.99

Lastly, measurement of powder moisture content was performed prior to each extrusion paste mix. **Table 2.1.C** shows the as-received moisture content for both powder batches, as well as the moisture content of the standard production powder mixed on the same day.

Table 2.1.C. As-Received Moisture Content for AE Experimental Powders and Standard AE Production Powder

	<i>As-Received Moisture (weight %)</i>
4014-2	0.90
4014-3	0.96
AE Standard	1.05

Mixing and Extrusion

In order to begin evaluation of the material properties, several mixes were prepared and extruded from both AE powders. Initial mixes were prepared using the standard production extrusion paste formulation, provided in **Table 2.1.D** below.

Table 2.1.D. Standard Cermet Extrusion Paste Formulation

Cermet Powder	2.00 kg
Methocel	0.10 kg
Binder	
Distilled Water	0.43 kg

For each paste mix, the moisture content of the powder was measured prior to batching. Using the resulting moisture content value, the amount of water in the powder was calculated and subtracted from the water required in Table 2.1.D. Therefore, the actual liquid water added to each batch is slightly different. Initial batches of both 4014-2 and 4014-3 were unsuccessful using the standard paste formulation detailed above due to the fact that they were too dry to mix into a paste.

4014-2 Mixing and Extrusion

Two subsequent batches of 4014-2 cermet were therefore prepared with an additional 25.0g of water with respect to the standard paste formulation. **Table 2.1.E** provides the batch compositions for both mixes.

Table 2.1.E. Extrusion Paste Compositions for AE Experimental Anode Powder 4014-2

	<i>Mix 2</i>	<i>Mix 3</i>
Cermet Powder (kg)	2.00	2.00
Methocel Binder (kg)	0.10	0.10
Distilled Water (kg)	0.433	0.433

Mixing was conducted according to standard operating procedures. Once complete, both mixes were extruded according to standard operating procedure. The material extruded well with no observed problems. Extrusion data is presented in **Table 2.1.F**.

Table 2.1.F. Extrusion Data for AE Experimental Anode Powder 4014-2

	<i>Mix 2</i>	<i>Mix 3</i>
Extrusion Pressure Setpoint	3.00	3.00
Extrusion Velocity Setpoint	1.30	1.30
Extrusion Pressure (psig)	975	996
Tubes Extruded	6	10

Drying shrinkage data for the two batches are provided in **Table 2.1.G** below.

Table 2.1.G. Drying Shrinkage Data for AE Experimental Anode Powder 4014-2

<i>Sample Number</i>	<i>Mix 2 Drying Shrinkage (%)</i>	<i>Mix 3 Drying Shrinkage (%)</i>
1	3.81	3.81
2	3.54	3.62
3	3.83	3.63
4	3.63	3.80
5	3.63	3.46
Avg.	3.69	3.66
Std. Dev.	0.13	0.15
Cv	3.42%	3.97%

Drying shrinkage for both batches was in good agreement, but was less than that typically found in standard production material at 4-5%.

4014-3 Mixing and Extrusion

Four subsequent batches of 4014-3 cermet were prepared with increased additions of added water with respect to the standard paste formulation. **Table 2.1.H** provides the batch compositions for both mixes.

Table 2.1.H. Extrusion Paste Formulations for AE Experimental Anode 4014-3

	<i>Mix 2</i>	<i>Mix 3</i>	<i>Mix 4</i>	<i>Mix 5</i>
Cermet Powder (kg)	2.00	2.00	2.00	2.00
Methocel Binder (kg)	0.10	0.10	0.10	0.10
Distilled Water (kg)	0.455	0.470	0.470	0.70

Mixing was conducted according to standard operating procedures. Once complete, all four mixes were extruded according to standard operating procedure. The material extruded well with no observed problems. Extrusion data is presented in **Table 2.1.J**.

Table 2.1.J Extrusion Data for AE Experimental Anode 4014-3

	<i>Mix 2</i>	<i>Mix 3</i>	<i>Mix 4</i>	<i>Mix 5</i>
Extrusion Pressure Setpoint	3.00	3.00	3.00	3.00
Extrusion Velocity Setpoint	1.30	1.30	1.30	1.30
Extrusion Pressure (psig)	960	949	862	916
Tubes Extruded	8	6	10	9

Drying shrinkage data for these four batches are provided in **Table 2.1.K** below.

Table 2.1.K. Drying Shrinkage Data for AE Experimental Anode 4014-3

<i>Sample Number</i>	<i>Mix 2 Drying Shrinkage (%)</i>	<i>Mix 3 Drying Shrinkage (%)</i>	<i>Mix 4 Drying Shrinkage (%)</i>	<i>Mix 5 Drying Shrinkage (%)</i>
1	3.65	3.43	4.94	4.31
2	3.60	3.87	5.72	4.34
3	3.66	3.76	4.93	4.18
4	3.34	3.88	5.15	4.42
5	3.55	3.92	4.83	4.19
Avg.	3.56	3.77	5.11	4.29
Std. Dev.	0.13	0.20	0.36	0.10
Cv	3.67%	5.31%	7.00%	2.39%

After drying, all tubes from all batches were cut and scribed with a unique identification and processed into finished cells.

Bisque Firing

Dry tubes from both experimental cermet batches were selected and fired in Acumentrics standard production furnace along with standard production tubes. After bisque firing, both sets of tubes remained intact.

As a relative measure of the extent of densification of the tubes, shrinkage was measured for each sample set. Summary statistics for the results of these measurements are provided in **Table 2.1.L** below.

Table 2.1.L. Bisque Firing Shrinkage Data for AE Experimental Anode Tubes

	<i>Control</i>	<i>4014-2</i>	<i>4014-3</i>
Avg. Bisque Fire Shrinkage (%)	3.91	4.03	4.27
Bisque Fire Shrinkage Std. Dev. (%)	0.17	0.21	0.60
C _v (%)	4.45%	5.29%	13.96%

Both of the experimental sample sets had measured bisque fire shrinkages within the specification range for standard production material, 3.8-5.0%, which is expected due to the particle size distributions being identical to standard production material and nickel contents still very close to standard production material.

Cell Processing

Once bisque firing had been completed, tubes were coated with standard yttria-stabilized zirconia electrolyte following standard operating procedures. After dipping, the tubes were sintered at a soak temperature of 1510°C with a soak time of three hours. Measurement of sintering shrinkage was performed to provide a relative measure of anode and electrolyte density. Summary statistics for the results of these measurements are provided in **Table 2.1.M** below.

Table 2.1.M. Electrolyte Sintering Shrinkage for AE Experimental Anode Material

	<i>Control</i>	<i>4014-2</i>	<i>4014-3</i>
Avg. Sintering Shrinkage (%)	18.65	18.85	18.78
Sintering Shrinkage Std. Dev. (%)	0.42	0.15	0.22
C _v (%)	2.27%	0.78%	1.19%

Measured shrinkages, for all three samples, are within the specification range of 17.6-18.8% for standard production tubes.

After electrolyte sintering, tubes were cathode coated, sintered, reduced, and wound with silver wire according to standard operating procedures. Once these processing steps were complete, samples were submitted for cell testing.

Anode Characterization

In order to fully characterize the AE cermet material, several measurements were performed on the prepared tube samples. These measurements included anode resistance; modulus of rupture (M.O.R.) measurements for bisque fired tubes; M.O.R. measurements for electrolyte coated and reduced samples; measurement of the volume percent nickel in the anode material; resistivity and permeability measurements of uncoated, sintered, and reduced tube sections; uncoated and sintered oxide density and porosity measurements; and, uncoated sintered reduced density and porosity measurements.

Resistance measurements were performed for tube samples for both experimental materials as well as a control sample for comparative purposes. Summary statistics for the results are provided in **Table 2.1.N** below.

Table 2.1.N. Measured Anode Resistance Values for AE Experimental Anode Materials

	<i>Control</i>	<i>4014-2</i>	<i>4014-3</i>
Avg. Anode Resistance (m Ω /mm)	2.87	3.14	2.32
Anode Resistance Std. Dev. (m Ω /mm)	0.11	0.16	0.11
C _v (%)	3.97%	5.19%	4.64%

Results show that the material having a smaller volume percent nickel (4014-2) relative to the standard, had a higher measured anode resistance while the higher volume percent nickel material (4014-3) had a lower measured resistance value. These results are in good agreement with theoretical expectations.

MOR measurements were performed using bisque fired tube samples. For the test, a three point bending configuration was used with a span of 100 mm. Sample preparation involved cutting full-length tubes in half and testing each half. Results of the measurements are provided in **Table 2.1.P**.

Table 2.1.P. MOR Data for Bisque Fired AE Experimental Anode Materials

	<i>Control</i>	<i>4014-2</i>	<i>4014-3</i>
Avg. MOR (MPa)	4.12	2.50	2.20
MOR Std. Dev. (MPa)	0.18	0.46	0.15
C _v (%)	4.37%	18.44%	7.00%

Also measured for both powder types was the MOR after electrolyte coating, sintering, and reduction. This measurement provides an indication as to the strength of a finished cell. Results for the two lots, along with a standard, are provided in **Table 2.1.Q** below.

Table 2.1.Q. MOR Data for Electrolyte Coated and Reduced AE Experimental Anode Materials

	<i>Control</i>	<i>4014-2</i>	<i>4014-3</i>
Avg. MOR (MPa)	203.60	205.60	203.27
MOR Std. Dev. (MPa)	9.00	5.64	13.08
C _v (%)	4.42%	2.74%	6.44%

Tube samples for both experimental powders were sintered uncoated and reduced so that the volume percent nickel in the material could be calculated. Results of the reduction, based on weight loss, show that when fully reduced, the 4014-2 material had a nickel content of 47.0% and the 4014-3 material had a nickel content of 54.6%.

Cell Testing - 45/55 Ni/YSZ

Three 45vol% Ni cells were submitted to cell testing for performance evaluation. Before testing, the three cells were evaluated using Acumentrics semi automated QC checker. **Table 2.1.R** below shows the results from these tests, note the high measured anode resistance with respect to the control for all three lower Ni content samples.

Table 2.1.R. QC Data for the 45/55 Ni/YSZ Cells

Cell Number	Cathode Resistance Ω	Anode Resistance m Ω	Leak mmHg/min	End Pressure torr
B270035	903	3.15	8.4	2.6
B270040	825	3.45	28.4	9.3
B270048	3236	3.07	5.5	1.7
B280009 Control	871	2.90	10.32	3.6

All of the cells were brazed at the inlet and cell tested under standard conditions. The 45/55 cermet cells were tested twice, each time in a different cell test stand (CTS). The first cell test was performed in CTS 14. **Figure 2.1.B** below displays the results from this test.

Figure 2.1.B Cell Potential for the 4014-2 AE Cermet Versus Time on Test in CTS

During the first 32 hours under test, the observed cell potential for each 45/55 cell decreased significantly while under load. After this initial observed dip, the cells then began to steadily rise in potential. The observed dip in the early stages of the test has not been witnessed previously when testing standard cells. The cause of the initial drop in potential is not understood at this stage.

At the 144-hour mark, the cells were cooled to room temperature and then put back on test the following day. Upon reloading the cells, the observed potential for each was significantly below the values observed prior to the thermal cycle. During the next several hours, the cells continually climbed in potential until the test was stopped at the 580 hour mark.

Two IR measurements were taken towards the end of the cell test. **Figure 2.1.C** below shows the IR values for the cells at 800°C.

Figure 2.1.C IR Versus Time at 800°C for the 4014-2 AE Cermet Cells

As expected, the IR values for the 45/55 cells shown in the figure above are significantly higher than the standard 50/50 Ni/YSZ cermet which has a value generally between 0.8 and 1.0 ohm-cm². This is not surprising since there is less Ni present in the anode tube material, thus lowering electrical conductivity. Figure 2.1.C also shows that the IR is decreasing during the cell test, at least for elapsed times greater than 420 hours. This decrease in IR helps to explain why the cells' potential increased slowly throughout the cell test although it is unknown due to lack of data what the IR value was at the beginning of the test.

A summary for the first cell test of the 45/55 cells is provided in **Table 2.1.S** below.

Table 2.1.S. Cell Test Summary for the 4014-2 AE Cermet for the First Duration on Test

<u>Tube Num.</u>	<u>Peak Voltage (mV)</u>	<u>End Voltage (mV)</u>	<u>IR (mΩ)</u>	<u>OCP (V)</u>	<u>Time Under Load (hr)</u>	<u>Thermal Cycles</u>	<u>Fuel Utiliz.</u>	<u>Degradation per 1000 hrs</u>
B270035	0.558	0.558	1.694	1.088	552.8	2	75%	Still rising
B270040	0.538	0.538	1.857	1.086	553.5	2	75%	Still rising
B270048	0.534	0.534	1.782	1.091	553.3	2	75%	Still rising

The same cells, detailed above, were put back on test 10 days later in CTS 10. **Figure 2.1.D** below shows the results from this test.

Figure 2.1.D Cell Potential for the 4014-2 AE Cermet Versus Time on Test in CTS 10

When cell B270040 was loaded at the beginning of the second test, output issues were observed. The load was therefore removed from this cell and it was subsequently held at open circuit for the remainder of the test.

Cells B270035 and B270048 saw a drop in potential of between 50 to 60 mV from being taken off test in CTS 14 to being placed back on test in CTS 10. These cells again steadily climbed during the lifetime of the test, but never achieved the same potential obtained in the first cell test although their potential was still rising when the test was terminated. At the 390 hour mark, both loaded cells showed an irregular pattern in the potential curve. This sudden drop and spike in potential was due to the temperature dropping unexpectedly in one of the heating zones. The second cell test was ended after

a further 432 hours of testing due to the poor potential observed for the cells. Peak cell potential for all of the 45/55 cells tested was over 100mV lower than would be expected for Acumentrics standard 50/50 cells.

A summary for the second cell test is provided in **Table 2.1.T** below.

Table 2.1.T Cell Test Summary for the 4014-2 AE Cermet for the Second Duration on Test

<u>Tube Num.</u>	<u>Peak Voltage (mV)</u>	<u>End Voltage (mV)</u>	<u>IR (mΩ)</u>	<u>OCP (V)</u>	<u>Time Under Load (hr)</u>	<u>Thermal Cycles</u>	<u>Fuel Utiliz.</u>	<u>Degradation per 1000 hrs</u>
B270035	0.549	0.549	--	1.088	978	3	75%	NA
B270048	0.518	0.518	--	1.089	978	3	75%	NA
B270040	0.448	--	--	1.089	555.5	3	75%	NA

Cell Testing - 55/45 Ni/YSZ

Three 55vol% Ni cells were submitted to cell testing for performance evaluation. Before testing, the three cells were evaluated using Acumentrics semi automated QC checker. **Table 2.1.U** below shows the results from these tests.

Table 2.1.U QC Data for the 55/45 Ni/YSZ Cells

Cell Number	Cathode Resistance Ω	Anode Resistance mΩ	Leak mmHg/min	End Pressure torr
B270024	786	2.27	6.4	2.1
B270007	N/A	2.23	15.9	5.2
B270026	849	2.46	52.3	17.2
B280009 Control	871	2.90	10.32	3.6

All of the cells were brazed at the inlet and cell tested at standard conditions. Cells for the 55/45 cermet were tested exclusively in CTS 12. **Figure 2.1.E** below displays the life chart recorded from this test.

Figure 2.1.E Cell Potential for the 4014-3 AE Cermet Versus Time on Test in CTS
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As was observed with the 45/55 cells outlined above, all three 55/45 cells started to dip rapidly in potential during the first 48 hours while under load. It is not understood why this initial downward trend in potential was witnessed for both experimental cermets discussed in this report. Each cermet type was tested in a different cell test stand and as such a CTS system error is not believed to be responsible for the observed phenomenon.

After the initial observed dip in potential, all three cells then began to steadily rise in potential in the same manner as the previously tested 45vol% Ni cells. Each 55/45 cell took 1300 hours to reach its maximum potential under standard cell test conditions. Acumentrics standard cells typically take about 48 hours to reach peak voltage. Furthermore, the peak voltage wasn't noticeably higher than standard cells despite having additional nickel present in the cermet.

IR measurements were taken throughout the cell test. **Figure 2.1.F** below shows the IR values recorded for the cells at 800°C.

Figure 2.1.F IR Versus Time at 800°C for the 4014-3 AE Cermet Cells

The IR for each cell decreased throughout the test, explaining a large proportion of the rise in potential observed during the lifetime of the test.

A cell test summary for the 55/45 cells is provided in **Table 2.1.V** below.

Table 2.1.V Cell Test Summary for the 4014-3 AE Cermet for the Second Duration on Test

<u>Tube Num.</u>	<u>Peak Voltage (mV)</u>	<u>End Voltage (mV)</u>	<u>IR (mΩ)</u>	<u>OCP (V)</u>	<u>Time Under Load (hr)</u>	<u>Thermal Cycles</u>	<u>Fuel Utiliz.</u>	<u>Degradation per 1000 hrs</u>
B270024	0.636	0.627	1.268	1.091	1672	1	75%	-2.5%
B270007	0.622	0.616	1.369	1.090	1672	1	75%	-2.6%
B270026	0.604	0.601	1.380	1.079	1672	1	75%	-1.7

In Summary

- Both experimental 45 and 55vol% Ni cermets behaved in a similar fashion while under test. The performance similarities include:
 - An initial dip in performance was observed for both types of cermet in the first 48 hours.
 - After the initial dip, both Ni loadings showed a steady increase in potential for several hundred hours.
 - This steady increase in potential was mirrored, not unexpectedly, by a steady decrease in the recorded IR.

- The different behavior of cells fabricated from both these cermets with respect to cells fabricated from Acumentrics standard material cannot, at this stage, be explained although it is apparent that some region of the cell is becoming less resistive throughout the duration of both tests.
- The observed peak potential under standard operating conditions for both experimental cermets was below that which would be expected for Acumentrics standard cells. It was expected that the 45 and 55vol% Ni cermet samples would straddle the performance of the standard 50vol% Ni cermet.
- The tests carried out upon the cermet powder and tubes/cells during fabrication offer no clue as to the observed differences in cell performance of the two experimental cermets with respect to Acumentrics standard material. Powder particle size, anode tube resistance and Ni content all have tested values in the expected region.
- Further testing of bare cermet tube permeability and conductivity over time at temperature is ongoing to try to deduce the origin of the differences in the cell test data.

Evaluation of Sumitomo Metal Mining Cermet Powders SNZ-363 and SNZ-367

As part of the anode tube composition optimization work, Sumitomo Metal Mining (SMM) prepared two different cermet compositions for evaluation by Acumentrics. Both compositions had a nickel content of 50 vol%. The first composition, SNZ-363, was prepared to have a similar microstructure to standard production material. The second material, SNZ-367, was prepared to have similar thermal characteristics to standard production material. Both the microstructure and thermal characteristics were elucidated at SMM through fabrication of discs from the candidate materials. The purpose of the tests outlined below was to compare both materials with standard production cermet in terms of powder properties, anode tube characteristics, and finished cell performance.

Powder Characterization

Initial work with the powders focused on powder characterization. Particle size distribution results, as well as a comparison standard AE distribution, are provided in **Figure 2.1.G** below.

Figure 2.1.G Particle size distributions for SNZ-363, SNZ-367, and a standard production powder, AE03-21.

Table 2.1.W Particle Size Data for SNZ-363, SNZ-367, and AE03-21

	<i>SNZ-363</i>	<i>SNZ-367</i>	<i>AE03-21</i>
d_{10} (μm)	1.00	0.57	0.77
d_{50} (μm)	2.02	1.31	2.17
d_{90} (μm)	3.81	2.98	5.39

Particle size distribution data showed that the SNZ-363 powder was comparable to standard production powder through most of the distribution, but had a slightly narrower distribution overall. SNZ-367, meanwhile, proved to be finer than both the SNZ-363 and the AE03-21 and slightly narrower.

Table 2.1.X Tap Density Data for SNZ-363, SNZ-367, and AE03-21.

	<i>SNZ-363</i>	<i>SNZ-367</i>	<i>AE03-21</i>
Avg. Tap Density (g/cc)	1.54	1.06	1.70
Tap Density Std. Dev. (g/cc)	0.05	0.02	0.03
C_v (%)	3.42	1.78	1.55

Tap density measurements reinforced this data, with SNZ-367 having a low tap density while the SNZ-363 was an intermediate.

Table 2.1.Y As-Received Moisture Content for SNZ-363, SNZ-367, and AE03-21.

<i>Powder</i>	<i>As-Received Moisture Content (%)</i>
SNZ-363	0.95
SNZ-367	0.71
AE03-21	0.99

As-received moisture contents were comparable, though the low reported specific surface area for the SNZ-367 may be the reason for its lower moisture content.

Mixing and Extrusion

After completion of the powder characterization, several mixes were prepared and extruded for both SMM powders. Because it was received first, the SNZ-363 material was mixed and extruded first. The four initial compositions used are presented in **Table 2.1.Z** below. Water contents are after adjusting for powder moisture content.

Table 2.1.Z Initial Batch Compositions for SNZ-363.

<i>Component</i>	<i>Mix 1</i>	<i>Mix 2</i>	<i>Mix 3</i>	<i>Mix 4</i>
Cermet Powder (g)	2000.0	2000.0	2000.0	2000.0
Methocel Binder (g)	100.0	100.0	100.0	100.0
Distilled Water (g)	411.0	411.0	311.2	356.2

After mixing according to standard operating procedure, mixes 1 and 2 were very soft and could not be extruded. Therefore, the water content was reduced on subsequent batches. Mix 3 proved dry and mix 4 was softer but still much stiffer than mixes 1 and 2. Once mixing had been completed, tubes were extruded from mixes 3 and 4 according to standard operating procedure. Extrusion data are provided in **Table 2.1.AA** below. Tubes were measured for post-extrusion length, dried, and re-measured for post-drying length. Shrinkage upon drying is also included in **Table 2.1.AA**.

Table 2.1.AA Extrusion Data for SNZ-363 Mixes 3 and 4

	<i>Mix 3</i>	<i>Mix 4</i>
Extrusion Pressure Setpoint	3.00	3.00
Extrusion Velocity Setpoint	1.30	1.30
Actual Extrusion Pressure (psig)	685	940
Tubes Extruded	3	6
Avg. Drying Shrinkage (%)	N/A	6.53

No drying shrinkage data is available for mix 3 because all three of the tubes extruded cracked during drying. Drying shrinkage for mix 4 is higher than seen for standard material at approximately 4%.

In order to provide a sufficient number of tubes for further testing an additional two batches were mixed and extruded, both following the same formulation as mix 4 in Table 52.1.AA above. Extrusion results for these batches are presented in **Table 2.1.AB**

Table 2.1.AB Extrusion Data for SNZ-363 Mixes 5 and 6.

Extrusion Pressure Setpoint	3.00
Extrusion Velocity Setpoint	1.30
Actual Extrusion Pressure (psig)	933
Tubes Extruded	14
Avg. Drying Shrinkage (%)	6.31

Mixes were then prepared and extruded for SNZ-367. The two initial mixes prepared were based on the fact that the reported specific surface area for this material was lower than that for SNZ-363. Therefore, it was felt that the water content for this material should be lower, and was adjusted accordingly. Compositions for the initial two mixes are provided in **Table 2.1.AC** below.

Table 2.1.AC Initial Batch Compositions for SNZ-367.

<i>Component</i>	<i>Mix 1</i>	<i>Mix 2</i>
Cermet Powder (g)	2000.0	2000.0
Methocel Binder (g)	100.0	100.0
Distilled Water (g)	314.2	314.2

Both mixes were prepared following standard operating procedure and mixed well. After mixing, both mixes were extruded following standard operating procedure. Again, length was measured after extrusion as well as after drying. Extrusion and drying shrinkage data for both SNZ-367 mixes are presented in **Table 2.1.AD**.

Table 2.1.AD Extrusion Data for SNZ-367 Mixes 1 and 2

	<i>Mix 1</i>	<i>Mix 2</i>
Extrusion Pressure Setpoint	3.00	3.00
Extrusion Velocity Setpoint	1.30	1.30
Actual Extrusion Pressure (psig)	728	697
Tubes Extruded	6	6
Avg. Drying Shrinkage (%)	8.19	8.42

Both mixes extruded well, but drying shrinkage was found to be approximately double what is typically seen with standard production material. In order to provide a sufficient number of tubes for further testing an additional two batches were mixed and extruded, both following the same formulation as mixes 1 and 2 in Table 2.1.DD above. Extrusion results for these batches are presented in **Table 2.1.AE**.

Table 2.1.AE Extrusion Data for SNZ-367 Mixes 3 and 4.

Extrusion Pressure Setpoint	3.00
Extrusion Velocity Setpoint	1.30
Actual Extrusion Pressure (psig)	713
Tubes Extruded	10
Avg. Drying Shrinkage (%)	9.01

Bisque Firing

Once dried, tubes from each cermet lot were cut to 436mm then bisque fired one at a time in a Carbolite lab furnace to determine an appropriate bisque firing schedule. Each tube was bisque fired on monoclinic YSZ with a heat shield placed over the tube during the firing. Standard production cermet, after bisque firing, has an end length of approximately 419 mm and shrinks about 4.0%.

Five separate attempts were made to bisque fire SNZ-367 cermet at five temperatures. Upon inspection of the tubes after firing, they were all found to be cracked along the length. **Table 2.1.AF** below summarizes the bisque firing attempts and the results for the SNZ-367 green tubes.

Table 2.1.AF Bisque Firing Data for Cermet SNZ-367

<i>Tube Number</i>	<i>Bisque Fire Temp. / Hold Time</i>	<i>Bisque Length (mm)</i>	<i>Bisque Shrinkage (%)</i>	<i>Results</i>
B450174	1080°C / 2 hr	424	2.53	Cracked
B450175	1000°C / 2 hr	429.5	1.26	Cracked
B450176	1000°C / 2 hr	429.5	1.26	Cracked
B450177	950°C / 2 hr	430.5	1.03	Cracked
B450178	900°C / 2 hr	431.5	0.80	Cracked

No further bisque firings were attempted with the SNZ-367 cermet because the tubes all cracked despite using an extremely slow burnout schedule. In addition, the tubes also appeared to be too dense to achieve a dense electrolyte coating, indicated by their physical appearance.

Six SNZ-363 tubes were bisque fired to different soak temperatures that ranged from 1080°C to 620°C. All the bisque firings had a soak time of 2 hours. **Table 2.1.AG** summarizes the bisque firing attempts and the results for the SNZ-363 green tubes.

Table 2.1.AG Bisque Firing Trials for SNZ-363

<i>Tube Number</i>	<i>Bisque Fire Temp. / Hold Time</i>	<i>Bisque Length (mm)</i>	<i>Bisque Shrinkage (%)</i>	<i>Results</i>
B450001	1080°C / 2hr	NA	NA	Intact tube
B450002	1060°C / 2hr	NA	NA	Intact tube
B450003	930°C / 2hr	430.5	1.0	Intact tube
B450004	820°C / 2hr	431	0.91	Intact tube
B450006	750°C / 2hr	432.5	0.57	Intact tube
B450005	620°C / 2hr	433.5	0.34	Intact tube

Sumitomo SNZ-363 cermet also appeared to be too dense after bisque firing to allow vacuum infiltration of the electrolyte even when fired at lower soak temperatures.

To determine if the bisque fired tube was too dense to be electrolyte coated, each tube was individually pumped down on the vacuum infiltration device to see what vacuum pressure was achieved. A porous tube will display a lower vacuum pressure. A standard production tube achieves a vacuum pressure of. This reading indicates that the tube is porous enough to achieve a dense uniform electrolyte during the dip coating process.

The Sumitomo bisque fired tubes outlined in Table 2.1.AG above achieved vacuum pressures between. To confirm that the Sumitomo bisque fired tubes were indeed too dense to allow effective vacuum infiltration of electrolyte, two of the bisque fired tubes (B450001 and B450002) were electrolyte coated using vacuum assistance.

Electrolyte Sintering and Leak Testing

After the tubes were electrolyte coated and sintered to 1500°C for 3 hours, the tubes were then reduced to determine their leak rates on Acumentrics leak-testing device. Tube, B450001, had a leak rate of mmHg/min, while tube, B450002, had a leak rate of mmHg/min. These leak rates are extremely high when compared to an average production tube having a leak rate less than mmHg/min.

Resistance

Resistance measurements for tubes fabricated from the two experimental Sumitomo cermets were taken along the length of the tube using a four-point probe methodology. Both SNZ363 and 367 cermets showed a resistance of 0.007 mΩ/mm for a reduced tube length of 360mm, comparable to Acumentrics standard cermet.

In Summary:

- Both Sumitomo cermets required the addition of significantly less water to the formulation during mixing than standard production cermet indicating that they have lower surface areas and/or the cermet particles pack more efficiently during processing. Even with this reduced water addition, both 363 and 367 shrank significantly more than standard production cermet during drying, again suggesting more efficient packing of the cermet particles.
- All bisque firings of SMM 367 were unsuccessful in that the tubes cracked during firing. Shrinkage of the tubes was lower than expected and they appeared dense upon handling.
- The bisque firing trial for SMM 363 tubes was more successful in that the tubes survived the firing process intact. The tubes again appeared dense upon handling which was confirmed by the unsuccessful application of an electrolyte layer by vacuum infiltration.
- The particles in both 363 and 367 cermet formulations appear to pack extremely well during processing into a tube resulting in reduced porosity at the bisque fired stage which in turn results in a tube which is too dense to effectively vacuum infiltrate with electrolyte. Bisque firing at lower temperatures did not alleviate this problem.

Future Work:

- Test the density/porosity of the bisque fired tubes.
- Microscopy of the electrolyte layer.
- Request reformulated cermets from Sumitomo.

Evaluation of Praxair Cermet Powder - Black and Green NiO

Two additional cermet samples have also been received from Praxair to further investigate improving anode bus conductivity and the causes of degradation in the anode structure. The two cermet powders are:

1. 55% Ni and 45% YSZ– a small PSD, low SSA green NiO material, lot number **02-P4946SG**
2. 55% Ni and 45% YSZ– large PSD, high SSA black Ni_2O_3 , lot number **02-P4947SG**

Differences in powder properties, anode tube characteristics, and finished cell performance have been investigated and are detailed below.

Powder Characterization

Initial work focused upon characterization of the supplied cermet material. Particle size distribution results for both powders along with a comparison standard American Elements (AE) distribution, are provided in **Figure 2.1.H** below.

Figure 2.1.H. Particle size distributions for Praxair materials and standard production material.

Analysis of the data shows that 02-P4947SG cermet has a slightly larger particle size with respect to Acumentrics standard cermet material. The 02-P4946SG material however has a much larger particle size distribution than Acumentrics standard cermet material. **Table 2.1.AH** provides the numerical values for powder as measured at Acumentrics.

Table 2.1.AH Particle Size Distribution Data for Praxair and Standard AE Production Cermet

	<i>02-P4946SG</i>	<i>02-P4947SG</i>	<i>AE Standard</i>
d ₁₀ (μm)	9.68	1.53	0.624
d ₅₀ (μm)	19.92	3.50	1.200
d ₉₀ (μm)	32.37	7.15	3.234

Measurement of the apparent density and tap densities for all three types of powder followed particle size analysis. Summary statistics of the results are provided in **Table 2.1.AJ**.

Table 2.1.AJ Apparent and Tap Density Data for Praxair Experimental Powders and Standard AE Production Powder

	<i>02-P4946SG</i>	<i>02-P4947SG</i>	<i>AE Standard</i>
Avg. App. Density (g/cc)	1.16	1.12	1.17
App. Density Std. Dev. (g/cc)	0.01	0.04	0.052
App. Density C _v (%)	1.06%	3.66%	4.48%
Avg. Tap Density (g/cc)	1.40	1.47	1.47
Tap Density Std. Dev. (g/cc)	0.02	0.02	0.059
Tap Density C _v (%)	1.58%	1.63%	4.01%

Lastly, measurement of powder moisture content was performed prior to each extrusion paste mix. **Table 2.1.AK** shows the as-received moisture content for both powder batches, as well as the moisture content of the standard production powder mixed on the same day.

Table 2.1.AK As-Received Moisture Content for Praxair Experimental Powders and Standard AE Production Powder

	<i>As-Received Moisture (weight %)</i>
02-P4946SG	0.64
02-P4947SG	2.20
AE Standard	1.05

Mixing and Extrusion

In order to begin evaluation of the material properties, several mixes were prepared and extruded from both Praxair powders. Two initial mixes were prepared for each powder lot using the extrusion paste formulations, provided in **Table 2.1.AL** below.

Table 2.1.AL Standard Cermet Extrusion Paste Formulation

Cermet Powder	2.00 kg
Methocel Binder	0.10 kg
Distilled Water	0.43 kg

For each paste mix, the moisture content of the powder was measured prior to batching, as described above. Using the measured moisture content, the amount of water in the powder was calculated and subtracted from the water required in Table 2.1.AL. The actual liquid water added to each batch is therefore slightly different. The actual batch compositions for both of the first batches are provided in **Table 2.1.AM** below.

Table 2.1.AM Mix Compositions for Praxair Experimental Powder 02-P4946SG Green NiO.

	<i>Green NiO</i>		<i>Black NiO</i>	
	Mix 1	Mix 2	Mix 1	Mix 2
Anode Powder (g)	2000.0	2000.0	2000.0	2000.0
Methocel Binder (g)	100.0	100.0	100.0	100.0
Distilled Water (g)	417.6	417.6	463.0	513.0

Table 2.1.AN Extrusion Data for Praxair Experimental Powders 02-P4946SG and 02-P4947SG

	<i>Green NiO</i>	<i>Black Ni₂O₃</i>
Extrusion Pressure Setpoint	3.00	3.00
Extrusion Velocity Setpoint	1.30	1.30
Actual Extrusion Pressure (psig)	860	776
Tubes Extruded	17	20

The tubes extruded well with no problems experienced. The wet to dry shrinkage is recorded in **Table 2.1.AP** below. P4947SG, the black NiO, having a similar particle size distribution to Acumentrics standard cermet, also had a similar wet to dry shrinkage, in the region of 4-5%. Conversely the larger particle size P4946SG had a much reduced wet to dry shrinkage at just over 2%.

Table 2.1.AP Drying Shrinkage Data for Praxair Experimental Powders 02-P4946SG and 02-P4947SG.

<i>Sample</i>	<i>Green NiO</i>	<i>Black Ni₂O₃</i>
1	2.28	3.95
2	2.29	3.98
3	2.40	4.17
4	2.46	4.14
5	2.49	3.94
Average (%)	2.38	4.04
Std. Dev. (%)	0.096	0.110
C _v (%)	4.03%	2.73%

Bisque firing of tubes fabricated from Praxair cermet proved to be problematic. Tubes extruded from the green NiO cermet lot, 02-P4946SG, were too dense to vacuum dip coat with electrolyte after bisque firing under standard conditions. Conversely, the black NiO

cermet lot, 02-P4947SG, was too weak to allow vacuum infiltration after bisque firing under standard conditions.

Several trial bisque fire runs for both materials were therefore completed in small Carbolite lab furnaces to determine the bisque fire temperature that will produce a tube that is strong enough to handle yet porous enough to infiltrate with electrolyte.

The basic bisque firing schedule used for each Praxair cermet is outlined in **Table 2.1.AQ** below. The only difference between the firings for the two different cermets was the high soak temperature utilized.

Table 2.1.AQ Bisque firing schedule used for each Praxair cermet

Segment	Heating Rate (°C/min)	Target Temperature (°C)	Dwell (hr)
1	Step	130	3
2	0.5	145	4
3	0.5	155	4
4	1.5	High Temp.	2
5	-6	100	End

Table 2.1.AR and 2.1.AS below provides a summary of results for Praxair cermet tubes bisque fired in Acumentrics laboratory furnaces.

Table 2.1.AR Bisque Firing Summary of Tubes from Praxair Cermet (P4047SG-Black)

Tube #	NiO Type	Furnace #	Shrinkage (%)	High Temp. (°C)	Comments
B400132	Black	6	7.6	1090	Cracked
B400133	Black	7	12.6	1259	Too dense to electr. coat
B400142	Black	7	12.2	1259	Too dense to electr. coat
B400149	Black	7	6.0	1084	Coated with electrolyte
B400148	Black	7	6.0	1084	Coated with electrolyte
B400147	Black	7	6.0	1084	Coated with electrolyte
B400146	Black	7	6.0	1084	Broken during elect. coating
B400145	Black	7	6.0	1084	Broken during elect. coating

Table 2.1.AS Bisque Firing Summary of Tubes from Praxair Cermet (P4046SG-Green)

Tube #	NiO Type	Furnace #	Shrinkage (%)	High Temp. (°C)	Comments
B400129	Green	7	9.4	1169	Too dense to electr. coat
B400128	Green	8	3.2	1025	Coated with electrolyte
B400127	Green	8	2.8	1010	Coated with electrolyte
B400126	Green	8	NA	1010	Broken during handling
B400125	Green	8	3.0	1010	Coated with electrolyte
B400124	Green	8	3.0	1010	Coated with electrolyte
B400123	Green	8	2.9	1010	Coated with electrolyte

After several iterations, the optimal firing temperature utilized for Praxair green nickel oxide tubes was found to be 1010°C with a 2-hour soak, while the optimal firing temperature utilized for the Praxair black nickel oxide cermet was 1085°C with a 2-hour soak. A number of tubes from each cermet batch were then fired using the different bisque firing regimes before being coated with electrolyte. Both batches of Praxair tubes then went through the electrolyte sintering process at the same time to 1510°C with a 3.5-hour dwell. **Tables 2.1.AT and 2.1.AU** summarize the dimensions of the Praxair tubes after being electrolyte sintered.

Table 2.1.AT Sintered Summary of Tubes from Praxair Cermet (P4046SG-Green)

Tube #	Shrinkage (%)	Min OD (mm)	Max OD (mm)	Comments
B400128	21.6	14.16	14.41	Made into a cell
B400127	21.9	14.29	14.63	Made into a cell
B400125	21.8	14.24	14.39	Made into a cell
B400124	21.6	14.24	14.46	Made into a cell
B400123	21.7	14.16	14.41	Made into a cell

Table 2.1.AU Sintered Summary of Tubes from Praxair Cermet (P4047SG-Black)

Tube #	Shrinkage (%)	Min OD (mm)	Max OD (mm)	Comments
B400149	19.3	13.88	14.18	Made into a cell
B400148	19.3	13.90	14.21	Made into a cell
B400147	NA	13.79	14.12	Broke after coating but made into a cell

Both Praxair cermets shrink to a greater extent with respect to Acumentrics standard material, which shows a nominal 18% shrinkage at this stage. All cells listed in these two tables have been made into cells and are currently being evaluated for performance, details from which will be reported at a later date and compared to cell test results obtained for the comparable 55 vol% Ni obtained from American Elements.

To verify the Ni content of the Praxair tubes, they were first reduced and measured for actual Ni content through evaluation of weight loss. Results for the two batches and summary statistics are provided below.

Praxair 55 vol% Ni Experimental Anode Powder Measured Ni Content

	<i>02-P4946SG</i>	<i>02-P4947SG</i>
Sample 1	54.55	54.46
Sample 2	54.55	54.49
Sample 3	54.53	54.54
Avg. Ni Content (%)	54.54	54.50
Ni Content Std. Dev. (%)	0.01	0.04
C _v (%)	0.02%	0.07%

Clearly both Praxair tube samples nominally have the correct Ni loading in the sample at 54.5%

Isostatic Pressing of Tubes

A collaboration with Praxair is in the initial stages of being set up to produce a number of closed-one-end (COE) tubes by isostatic pressing. These tubes will then be fabricated into cells and evaluated for performance. A number of advantages will be realized by moving to a COE tube, these include;

- Decreased number of seals per active area of ceramic. This is expected to increase reliability of the cell.
- Decreased number of overall seals therefore reducing the total cost of the system.
- Efficiencies in time will be realized at the front end of the tube production process.
- Efficiencies in time and yield improvements will be realized during vacuum deposition of the electrolyte.
- It will be possible to fabricate a graded anode structure through utilization of isostatic pressing and consequently the interplay between material conductivity and wall thickness may be optimized.

An initial proof of concept isostatic pressing trial using NiO/YSZ cermet has been completed at Praxair. **Figure 2.1.J** below shows a cermet tube from this trial with an electrolyte coating that was applied by dipping.

Figure 2.1.J Cermet tube with an electrolyte coating that was applied by dipping.

Presently three different cermet powders are being fabricated at Praxair for initial pressing trials using Acumentrics specified cermet and moulds that have been fabricated to Acumentrics specification.

Subtask 2.2-Electrolyte Composition

Scandia Stabilized Zirconia (ScSZ) Investigation

Preliminary investigations into scandia stabilized zirconia (ScSZ) for use as an electrolyte have begun. This electrolyte will potentially lead to improved cell performance due to its higher ionic conductivity with respect to YSZ and also provide the potential to lower the temperature of operation for Acumentrics fuel cells. The ScSZ under investigation was provided by Daiichi and had the following properties.

Formula: $(\text{Sc}_2\text{O}_3)_{0.1}(\text{CeO}_2)_{0.01}(\text{ZrO}_2)_{0.89}$ (10Sc1CeSZ)

Lot No: I1413

D50: 0.55μ

Surface Area: $11.2 \text{ m}^2/\text{g}$

A slurry containing ScSZ powder was first formulated according to standard procedures. The slurry was then milled for 24hrs before application on to bisque fired tubes through vacuum infiltration in a vertical dip station. All processed tubes were then fired at 1510°C for 2 hours.

Particle size distribution of the ScSZ slurry was then measured, the results from which were compared to YSZ production slurry, see the graph below **Figure 2.2.A**.

Figure 2.2.A Particle size distribution of the ScSZ slurry

	D10	D50	D90
ScSZ	0.56 microns	0.82 microns	1.27 microns
Production YSZ	0.60±0.02 microns	0.97±0.04 microns	1.68±0.08 microns

As can be seen the particle size and distribution of the ScSZ powder was similar to that of production YSZ.

The electrolyte dip coated tubes were then fired and fully fabricated into cells, data from which can be found in the **Table 2.2.A** below. Note that both Sumitomo SNZ300 and standard American Elements cermet were investigated as the anode support material.

	SNZ300-7	SNZ300-9	AE-9	AE-323	AE-328
Batch Number	0219-02-SNZ	0219-02-SNZ	0218-01-0319	0323-02-0319	0323-02-0319
Cut Length (mm)	436	436	436	436	436
Bisque Length (mm)	421	420	415	419	420
Shrinkage %	3.4	3.7	4.8	3.9	3.7
Elec Fired Length (mm)	344	344	336	341	342
Shrinkage %	18.2	18.1	19.0	18.6	18.6
Cathode Length (mm)	278	278	279	277	277
Cathode Resistance (kOhms)	1.981	1.833	2.050	1.950	2.055
Cathode Wt.(g)	1.6217	1.5654	1.5547	1.5505	1.4257
Silver Wt. On Tube (g)	18.7363	19.0939	18.5336	18.7706	18.6245
Leak mmHg/min	O/L	O/L	29	3	14

Table 2.2.A Electrolyte dip coated tubes, fired and fully fabricated into cells

As can be seen from the table above, the two Sumitomo tubes that were coated with ScSZ could not be fabricated into leak tight cells. It is not known why this is the case but from previous empirical evidence, the lower shrinkage observed for both Sumitomo cells at the electrolyte firing stage is not conducive to densification of the electrolyte.

Both cells were tested under standard operating conditions of 150mA/cm², 75% fuel utilization and at a temperature of 800°C. After approximately 100 hours under test, cells AE9 and AE323 had reached their maximum potential of 649 and 655 mV respectively. These maximum potential values are on a par with standard production cells with a single braze (SB) in terms of performance, see the V/J curves in the graph below. It should be

noted however that the data set for standard SB cells is small, consisting of just two cells as does the ScSZ data set.

Cell performance evaluation at 700°C was also carried out for the ScSZ dipped cells. The graph below shows that these cells again performed broadly in line with standard SB production cells. This was unexpected since it had been considered that the higher conductivity of the ScSZ at lower temperatures would result in a significant performance improvement at this temperature, see **Figure 2.2.B** below.

Figure 2.2.B Cell performance evaluation at 700°C for the ScSZ dipped cells

The **Figure 2.2.C** below shows the IR values over time for the two different ScSZ cells under test at both 700 and 800°C. The observed IR values are broadly in line with standard production cells.

Figure 2.2.C IR values over time for the two different ScSZ cells at both 700 and 800°C.

Microscopy

A number of ScSZ coated tubes were also submitted for micro analysis to evaluate electrolyte thickness and visually evaluate porosity.

The **Figure 2.2.D** shows a ScSZ electrolyte coated cell after sintering, but before reduction. This image was taken at a magnification of 1000x.

Figure 2.2.D ScSZ electrolyte coated cell after sintering

The **Figure 2.2.E** below shows an ScSZ electrolyte coated cell following reduction. This image was taken at a magnification of 1000x.

Figure 2.2.E ScSZ electrolyte coated cell following reduction.

The **Figure 2.2.F** below shows a production YSZ electrolyte coated cell following reduction. This image was taken at a magnification of 1000x.

Figure 2.2.F Production YSZ electrolyte coated cell following reduction

The preceding images indicate visually that the ScSZ is comparable in thickness and density to the standard production YSZ electrolyte coating. Both YSZ and ScSZ coated cells were dipped for 12 seconds each in the electrolyte slurry.

In Summary:

- Microscopy suggests that the applied ScSZ electrolyte is of uniform thickness around the circumference of the tube with a nominal thickness of 26 microns.
- The ScSZ electrolyte also appeared to be adequately dense with a certain amount of closed porosity distributed evenly around the tube circumference. This is similar in appearance to production YSZ electrolyte.

- The cells that were cell tested did not show improved performance over standard production cells at standard operating conditions. Even at the reduced temperature of 700°C, their performance was only on a par with standard production cells.

Future Work:

- The ionic conductivity of the ScSZ utilized should be verified through fabrication of a bar test piece to make sure that there are no issues with the conductivity of the material itself.
- If the conductivity of the bar test piece is as expected then further cells should be fabricated at a later date and a more in depth analysis carried out.

Subtask 2.3-Cathode Composition

American Elements (AE) provided Acumentrics with a sample of LSM containing higher strontium levels than currently used for standard production cells. The lot number for the powder is T2065. The chemical formula for the sample is $\text{La}_{0.8}\text{Sr}_{0.2}(\text{MnO}_3)$.

A comparison of the performance provided by this experimental LSM with respect to the current production material has been detailed in this report. In addition to a potential performance enhancement, this material is more than 5 times cheaper than the current LSM purchased from Praxair.

C1 and C2 slurries were first formulated from the AE (80/20) LSM cathode material and YSZ (-1 μ) from Unitec. The formulations for the C1 and C2 slurries are shown in **Table 2.3.A** below.

Table 2.3.A: AE Experimental LSM Slurry Formulation

Cathode Slurry	Material Percentages by Weight			
	LSM	YSZ	Terpineol	Iso-Propanol
C1 Slurry	16%	16%	13%	58%
C2 Slurry	40%	NA	13%	47%

The material testing data collected, for both AE cathode slurries, is compared to standard production cathode slurries, in **Table 2.3.B** below.

Table 2.3.B: Comparison of the Slurry Properties for the AE and the Production Cathode

Slurry ID	D₅₀ for YSZ (μm)	Final D₁₀ (μm)	Final D₅₀ (μm)	Final D₉₀ (μm)	Viscosity @ 160 rpm (cP)
AE C1	0.432	0.352	0.635	1.332	9.31
Production C1	0.596	0.322	0.596	1.756	8.30
AE C2	NA	1.038	1.610	2.486	9.85
Production C2	NA	0.897	1.838	4.015	8.66

Tubes were then coated with the AE experimental slurries and sintered at two different high temperatures for 2 hours. The two different temperatures were:

Acumentrics standard cathode coating has a cathode end-to-end resistance 2-3 times higher than the values recorded in the table above even though the weight of applied cathode is typically 300-500 mg greater with the standard formulation.

Two of the 1250°C fired cells, B180374 and B180358 were then cell tested at standard conditions of 150mA/cm², 75% fuel utilization at 800°C. The cells were on test for 498 hours before being removed from the cell test stand to make way for other tests. Both cells displayed peak voltage values comparable to the highest performing cells fabricated from Acumentrics current production LSM material. **Table 2.3.D** below displays a summary of the cell test results produced.

Table 2.3.D: Summary of the Cell Test Results for the Initial Cell Test of the AE Cathode

<u>Tube Num.</u>	<u>Peak Voltage (mV)</u>	<u>End Voltage (mV)</u>	<u>IR (mΩ)</u>	<u>OCP (V)</u>	<u>Time on Test (hr)</u>	<u>Thermal Cycles</u>	<u>Fuel Utiliz.</u>	<u>Degradation per 1000 hrs</u>
B180374	677	667	1.049	1.094	493	2	75%	-7.2%
B180358	682	669	1.014	1.091	493	2	75%	-9.8%

The **Figure 2.3.A** below shows the potential output versus the time the cells were initially on test.

Figure 2.3.A Potential output versus the time the cells were initially on test.

This initial cell test showed that these cells had a significant increase in potential (48mV and 53mV) when compared with the cell that was sintered to. This increase could be attributed to the simple fact that the cathode was sintered to a higher temperature allowing for a lower cathode resistance and thus better connectivity among the cathode particles. In agreement, the IR values observed for both cells fired to are lower than the cell.

The IR versus time in **Figure 2.3.B** below shows that the IR is decreasing during the first 380 hours of testing.

Figure 2.3.B IR is decreasing during the first 380 hours of testing.

The 1250°C cells were then put back on test in a different cell test stand (CTS 10) from the initial one utilized. **Table 2.3.E** below displays a summary of the cell test results produced for the second time the cells were placed on test.

Table 2.3.E: **Summary of the Cell Test Results for the Continued Cell Test of the AE Cathode**

<u>Tube Num.</u>	<u>Peak Voltage (mV)</u>	<u>End Voltage (mV)</u>	<u>IR (mΩ)</u>	<u>OCP (V)</u>	<u>Time on Test (hr)</u>	<u>Thermal Cycles</u>	<u>Fuel Utiliz.</u>	<u>Degradation per 1000 hrs</u>
B180374	631	487	1.114	0.973	1494	6	75%	-22.82%
B180358	633	525	1.199	1.092	1494	6	75%	-17.06%

Figure 2.3.C below shows the potential output versus time on test for the second cell test of the original AE cathode cells tested in Figure 2.3.A.

The results laid out in table 2.3.E above are interesting in that when the cells were put back on test, both had experienced a 34mV drop from the end of one test in CTS12 to the beginning of the second test in CTS 10. Both cells also experienced a nominal drop of 26mV after a 15°C adjustment down in temperature of the cell test stand, 17.3 hrs into the second test run.

Figure 2.3.D below shows that IR increases with time for both cells under test. The IR for cell B180358 continued to increase during the duration of the cell test while the IR for cell B180374 did not change significantly during the last 400 hours on test. This increase in IR, for both cells contributed to the continual decline in the cells' potential during the lifetime of the test although a significant proportion of the perceived degradation can be

attributed to temperature readjustments in the cell test unit outlined in the preceding paragraph.

Figure 2.3.D IR increases with time for both cells under test

In Summary:

- Acumentrics standard cathode coating has a cathode end-to-end resistance 2-3 times higher than the values recorded for the AE LSM even though the weight of applied cathode is typically 300-500 mg greater with the standard formulation.
- Both tested cells displayed peak voltage values comparable to the highest performing cells fabricated from Acumentrics current production LSM material.
- The observed cell potential and hence degradation values are much worse for both cells when transferred to a different cell test stand, CTS10, after 493 hours of operation.
- In addition, the 34mV drop in cell potential from the end of the first test to the start of the second is difficult to reconcile as simply due to the thermal cycle between the two tests. This is stated since during the second cell test, the cells were thermal cycled 6 times and their potential came back up to or within a couple of mV of the potential observed pre cool down. This rebounding trend does not support the 34mV decrease in the potential observed for both cells between the two cell tests.

- Further analysis and cell testing needs to be completed before a confident determination of the material's merit, with respect to the standard LSM, can be concluded.

Subtask 2.4- Cell Testing

For the period:

68,062 cell-hours accumulated in cell testing
89.8% stand capacity

Highlights of testing include:

- The LSM cells powder from American Elements represents a large cost savings in the cathode production.
- The older qualification cells continue to operate at close to 6000hr.
- Five new qualification cells have been placed on test with ½"NPT fittings (Inlet braze cup) and deep-drawn outlet cups. These cells are being tested for braze integrity, and represent significant cost savings per cell going forward.
- Three new stands were brought up in November/December, and all were operational over the Christmas period. Capacity has increased now to six stands (total) with 30 cell positions. All stands have been utilized completely.

The Ni-foam insert into cells in cell testing appears to be a significant step for power enhancement, and are still undergoing testing with degradation rates on the order of 2-5%/1000hr.

Analysis of the 10,000+ hr testing of Acumentrics fuel cells

Four cells were run in cell testing for around 10,200hrs. Two cells had current applied to them throughout the test, and two were run only at the beginning and end of the test.

The four cells used were first run in a qualification of 7mm tests in early 2003 in CTS 5 or CTS6. These four cells, which passed qualification, were then charged to the long-term tester (LTT), which was built specifically for the purpose of running continuously. The long term tester was also charged with four Ni-wire wound cells, which are not considered here. All cells were placed in a single gas manifold, and current was applied to all but two cells (LTT1 and LTT2).

Figure 2.4.A: Long term tester showing the cells in order from the bottom going up (LTT1, LTT2, LTT3, LTT4, Ni-wound cells), with the common manifold to the right, and a vent opening to the left. This picture is taken at approximately 10,175hrs.

Current was applied to a common ground on the manifold and to each cell through the single cathode braid. Current to an individual cell was not externally calibrated or verified in the later three-quarters of this test, but was read by the tester. Gas was passed to the manifold, which had a built-in baffle, and from there was distributed to the 0.035" orifice in the braze cup of each cell. Gas flow could not be verified to an individual cell.

The furnace consisted of two zones run through one transformer. The temperature controller controlled both zones based on a thermocouple placed approximately 6" into the furnace (on the ruler in Figure 1) just below the cells. Another thermocouple was placed near the control thermocouple toward the cell outlet. This reading was recorded in the data compilations. No air was blown into the furnace, and the post-test Ni-wound cells were cracked and broken, suggesting the $P(O_2)$ may have been <0.21 atm.

LTT1 and LTT2 were allowed to flare the fuel completely for the duration of the 2nd run, while LTT3 and LTT4 were run at approximately 40%FU in this tester. As the Ni-wound cells failed, they were also allowed to flare for the duration of the test so as to not disturb the apparatus.

H_2 was flowed through a room-temperature bubbler which was >1 " water column prior to entering the manifold. The line was preheated by running through the furnace. 3% H_2/N_2 could also be introduced to the cells by switching lines at a gas control box prior to the MFC. There was installed a safety ESTOP (to remove applied current, shut off H_2 , and

flow H₂/N₂ to purge) system which worked initially, but failed later in the test causing an oxidation and thermal cycle to occur. A UPS was used to keep the controls operational in case of power outage.

The overall run data file, including cell numbers and individual accumulated hours are listed in the **Table 2.4.A** below.

Cell	LTT1	LTT2	LTT3	LTT4
#	121202-02L	121702-01L	120202-01P3	121902-012L
<i>1st Run</i>	011603 CTS5 Qual	011003 quali CTS5	010703 quali	011003 qual CTS61
<i>2nd Run</i>	032603 LTT	032603 LTT	032603 LTT	032603 LTT
<i>3rd Run</i>	061504 CTS10	061504 CTS10	061504 CTS10	061504 CTS10
Total hours in furnace	10268.5	10272.4	10229.0	10273.1
Total hours on test	86.1	88.7	10202.8	10250.5
Thermal cycles	18	18	18	18
Oxidation cycles	2	2	2	2

Table 2.4.A overall run data file

Below is a **Table 2.4.B** comparing the operating data initially (1st Run) to the final data (3rd Run) for all four cells. It should be noted that degradation rates are based on test or run time. Current was not actually applied to LTT1 and LTT2 for most of the period in the furnace, so their degradations are exacerbated by this fact. If LTT1 and LTT2 are considered to have run for 10,200hr, their degradation rates would be -3.1%/1000hr and -2.1%/1000hr.

		LTT1	LTT2	LTT3	LTT4
1st Run	<i>run time, hr</i>	64.6	68.6	25.7	47.5
	<i>Potential, V</i>	0.707	0.695	0.685	0.661
	<i>Current, A</i>	6.962	6.958	6.986	~7A*
	<i>FU, %</i>	50.7%	42.2%	48.6%	~50%*
	<i>Temp, °C</i>	800	800	800	~800*
* estimate, not available data					
3rd Run	<i>run time, hr</i>	83.9	86.5	10200.6	10248.3
	<i>Potential, V</i>	0.483	0.543	0.393	0.516
	<i>Current, A</i>	6.712	6.711	6.711	6.712
	<i>FU, %</i>	40.0%	40.0%	40.0%	40.0%
	<i>Temp, °C</i>	800	800	800	800
Degradation	<i>%/1000hr</i>	- 1642%/1000hr	- 1222%/1000hr	- 4.2%/1000hr	- 2.2%/1000hr

Table 2.4.B comparing the operating data initially (1st Run) to the final data (3rd Run)

The overall graph for the 1st Run for all four cells is shown in the **Figure 2.4.B** below:

Figure 2.4.B 1st Run for all four cells

Not all data is available for the entire run. However, the end values are correct as a log file was used to show all hand-recorded values. A summary of all the available data from the qualification runs for each cell is shown in the **Table 2.4.C** below

1st Run	Cell→	LTT1	LTT2	LTT3	LTT4
<i>Test time, hr</i>		64.6	68.6	25.7	47.5
<i>Potential, V</i>	150mA/cm ² , 50%FU, 800°C	0.707	0.695	0.685	0.661
<i>Ohmic Resistance, Ω-cm²</i>	800°C	0.895	0.857	1.100	0.947
<i>Open Circuit, V</i>	800°C, 100sccmH ₂ /3%H ₂ O	1.096	1.082	0.097	1.103
<i>Anode shift, mV</i>	100mA/cm ² , 50%FU, 800°C	N/A	N/A	N/A	N/A
<i>Cathode shift, mV</i>	100mA/cm ² , 50%FU, 800°C	N/A	N/A	N/A	N/A
<i>A-C, Ω (@run hours, hr)</i>	25°C	18000000 (69.0)	12000 (71.6)	590000(1076)	650000 (1125)
<i>Area, cm²</i>		44.8	44.8	44.8	44.8

Table 2.4.C Qualification runs.

These cells passed QC and made it to qualification, but there is no readily available record of their starting QC values.

2nd Run

The second run was the main run of the test. To emphasize a few main points:

1. The cells went through two cycles where there was oxidation. One was a loss of H₂ with current applied, and the second was a loss of temperature with current applied. After each cycle, the cells were reduced for 24hrs under H₂ atmospheres at 800°C before reloading.
2. All four cells saw the same gas and temperature cycles. The run time differed due to the application of current only.
3. Due to the long-term tester configuration, gases were not calibrated through the test, and standard tests normally performed, such as iR, anode/cathode shifts, etc., could not be done.

2nd Run Post-Test

When the furnace was opened after >10,000hrs in the 2nd Run, the cells were carefully examined. Of significance, the Ag force wire (braid and backbone) appeared to be relatively pliable and withstood repeated bending.

In general, the cells appeared to be in excellent shape except for LTT3 which was oxidized and broken. The QC readings, except for leak, were taken and are recorded in the **Table 2.4.D** below:

	LTT1	LTT2	LTT3	LTT4
A-A, $m\Omega$	9.27	8.09	11.58	9.32
A-C, Ω	3785	664	8.2	600
C-C, $m\Omega$	4.06	3.45	2.89	3.57

Table 2.4.D QC readings, except for leak

The cells were then loaded into CTS10 to run them under fully controlled conditions in our latest stand type.

3rd Run

Figure 2.4.C 6.7 A(150mA/cm²) and 40%FU at 800°C for the approximately 17 hours shown

The cells were run at 6.7 A(150mA/cm²) and 40%FU at 800°C for the approximately 17 hours shown in the above graph **Figure 2.4.C**. Highlights include:

1. LTT3 showed a very low OCP of 0.896V, proving the cell was in fact broken and leaking. In addition, the cell could not hold 40%FU at these currents and was run at 27%FU instead. Despite that, it was the only cell with degrading performance.
2. LTT4 went right to its potential and stood there without movement over the course of the test. Clearly the cell is stable in the 24-hr time frame.
3. Both LTT1 and LTT2 were climbing throughout the test. Normally, cells when first run will climb to about 92% of their final voltage in the first 24 hours of testing. Even though these cells have been tested for ~80 hours and in a furnace for about 10,200hrs, they have not stabilized. Current is clearly a factor, especially when compared to LTT4.

	LTT1	LTT2	LTT3	LTT4
OCP, V	1.088	1.090	0.896	1.092
iR, $\Omega\text{-cm}^2$	1.882	1.655	1.566	1.092

On shutdown, the cell QC data was

	LTT1	LTT2	LTT3	LTT4
$A-A, m\Omega$	9.35	8.10	12.47	9.41
$A-C, \Omega$	600	29440	0.632	420
$C-C, m\Omega$	2.88	2.93	2.80	2.81

The overall testing of the cells is shown in the graph below:

Degradation analysis

The cause of degradation appears to not be completely resistance related (although the difference in measurement techniques and stands may be an unknown factor).

	LTT1	LTT2	LTT3	LTT4
<i>Change in potential (1^{st} to 3^{rd} run), V</i>	-0.224	-0.152	-0.292	-0.145
ΔiR (1^{st} to 3^{rd} run) at $150mA/cm^2$, V	-0.148	-0.120	-0.070	-0.022
%iR of total voltage change	66%	79%	24%	15%

Of interest is the change in cells run for only a short time versus the cells run the entire 10,000 hours. It appears that iR plays a large role in initial changes, but significantly less over long periods of time. It appears to be a strong function of current rather than time at temperature. Determination of the reason for this non- iR degradation will need to be explained by microanalysis.

Microanalysis

Analysis of the cell-drop phenomenon in brazing based on different tests.

- 1 Lack of intimate contact between the cell and the braze material due to inadequate melting of the braze material seems to be one of the major reasons for the poor performance of the explored cells.
- 2 Monitoring the cell drop is the only step we presently have to ascertain whether the washers have melted so as to make adequate contact with the bottom of the cell.
- 3 It must be ensured that those cells, which do not register a drop while being brazed, are rejected.
- 4 Also, it may be worthwhile to try and quantify the magnitude of cell drop that would be considered adequate for intimate contact.

Outlet Braze Cup Integrity:

The outlet braze cup of cells were thermal cycled under air/NHMix dual atmospheres to test quality of the connection by visually determining Oxide growth. Cells were thermal cycled 0, 1, 10, 25, and 50 times for comparison. In general, it was seen that the Oxide growth was substantial. The follow-up test is the same set of thermal cycles in a higher H₂ brazing gas atmosphere.

Figure 2.4.D Cell B120259 (1 thermal cycle):

Figure 2.4.E Cell B1400051 (1 thermal cycle):

Figure 2.4.F Cell B120501 (10 Thermal Cycles)

Figure 2.4.G Cell B060109 (25 Thermal Cycles): Oxidation present between the Anode and braze joint.

Figure 2.4.H Cell B120502 (50 Thermal Cycles): Oxidation present between the Anode and braze joint.

Data from the long-term test cells was collected for thickness measurements along the length of the cells. No significant differences were noted between cells.

Long term Tester Cell #1:

	Fuel IN	MID	Fuel Out
	Average	Average	Average
Anode	800.48	816.03	784.43
Cathode	22.91	20.36	15.94
Electrolyte	24.24	26.81	20.27

Long term Tester Cell #2:

	Fuel IN	MID	Fuel Out
	Average	Average	Average
Anode	814.13	836.33	798.13
Cathode	27.64	25.36	23.13
Electrolyte	18.66	19.38	17.86

Long term Tester Cell #3

	Fuel IN	MID	Fuel Out
	Average	Average	Average
Anode	797.18	837.70	792.93
Cathode	26.27	21.43	15.06
Electrolyte	37.28	39.38	34.16

Long term Tester Cell #4

	Fuel IN	MID	Fuel Out
	Average	Average	Average
Anode	821.70	838.68	815.08
Cathode	32.33	18.70	19.53
Electrolyte	21.30	21.97	19.69

The analysis of the silver to this point has been cursory, but it has been observed that silver migration varied throughout the different locations of the same cell (i.e., silver

migration was present in varying degrees in the Fuel inlet, Mid-Length, & Fuel Outlet of the same Anode, Cathode and Electrolyte layers). More analysis should be available in upcoming months.

Injector Tubes After 400 hrs Operation

The purpose of this test was to observe the oxide layer visible on sections of this injector tube. The injector was subjected to reformed propane.

Fourteen samples were mounted in epoxy. It should be noted that not all samples were exactly perpendicular to the base. The inner and outer walls of each sample were photographed in an attempt to determine the thickness of the oxide layer at that point. In general, no clear definition of the oxide layer could be determined. There were cracks noted to a depth of about 10 μm , with oxide layers observed on the scale of 2-5 μm . The cracks may indicate oxide growth or high stress levels in that region. However, in places, the surface was rough ($\pm 3\mu\text{m}$) in comparison to the measurement, and oxide was not visible in other places. Quantitative analysis is difficult if not impossible. In general, more time is probably required for quantitative results.

Figure 2.4.J (yellow bar in the epoxy represents 10 μm - it was placed at the wrong point)

Braze caps from Braze resistance experiment

This section covers the four braze joints used on the two cells in the braze joint test experiment which has been discussed in degradation meetings and SECA reports to date. The purpose of this test was to attempt to quantify the increase in braze joint resistance over time at temperature and with current flowing through the joints. This report will only report on the physical appearance of the braze joints tested, not the overall test or results.

To seal the joints for dual atmosphere testing, two tubes with densified EL coatings were reduced and brazed with inlet cups at both ends. Gas flowed in one end of the 1st tube, and the outlet from that tube flowed into the inlet of the 2nd tube. In this way, a dual atmosphere was maintained.

Anode tube No	braze order	electrons flow	gas flow	Anode tube resistance/ m$\square$	braze resistance / m$\square$
B060333	1	away	away	1.42	0.30
B060333	2	toward	toward	1.42	0.15
B060120	3	toward	toward	1.36	0.20
B060120	4	away	away	1.36	0.27

The flow tube that connected the tube also connected the tubes and joints electrically. Current was applied from the inlet of the 1st tube, and taken from the outlet of the second tube. Current flow was through the inlet braze joint on the 1st tube, through the anode of the 1st tube, to the outlet braze joint of the 1st tube. The current went through the gas flow connection to the inlet of the 2nd tube, through the 2nd tube, to the outlet of the 2nd tube, and back to the external circuit. Taps were placed on all four braze joints and current was held constant. Resistance measurements could be taken between the taps, and adjusted for previously measured tube resistance changes based on actual tube resistance readings. The sum of the resistances of the braze joints of a single tube could be isolated.

	Anode tube No	A-A resist at 20°C/ m$\square$	time at 800°C/ hrs	Leak rate cm³/min.”H₂O
INITIAL	B060333	1.42	6	0.52
	B060120	1.34	6	0.42
FINAL	B060333	1.92	1184	0.23
	B060120	1.88	1184	0.16

This was the second attempt at this experiment.

“Good” Braze Joints

These two joints on cell B060120, labeled “3” and “4” in reference to both the gas flow and current flow in and out respectively, appeared to be stable in testing. When each was cut, it was divided into the two sides, “A” and “B.” Four samples (3A, 3B, 4A, 4B) were created from one tube with two brazes. Braze resistance for the combination of the two joints at 800°C increased from 0 $\square$ to 0.55 m $\square$ after 1184 hours of testing.

Figure 2.4.K: 20x (10x obj) Sample #3A showing a view of oxidation at EL surface

Figure 2.4.L: 20x (10xobj) picture of the bottom joint of #3A showing the good contact at the bottom interface, good contact between the braze material and EL, and no sign of oxidation. The EL appears to have significant porosity.

Figure 2.4.M: 5x (10xobj) view showing #3A with bubbles noted along the interface. No oxidation of the braze material is apparent.

The formation of the gap at the interface on the inside of the tube is apparent. This is conceivably formed by the difference in volume between molten and solidified braze material, and the resulting stresses. The gap size corresponds reasonably well to the calculated difference. A high stress region can be observed in the inside corner of the AN as well, showing high stress levels present at that corner.

Figure 2.4.N: 5x (10xobj) picture of #3A showing the gap forming along the inner surface.

The other side of sample 3 showed the same sort of pattern, with intimate bonds at the interface (except where bubbles were observed), intimate contact at the bottom of the tube, and a gap on the inside of the AN. Stresses appeared to be identical to the other side of the sample.

Figure 2.4.P: 5x (10xobj) for #3B showing the same pattern as the other side; a gap at the interface and stress buildup at that corner.

Figure 2.4.Q: 5x (10xobj) Sample #4A showing good intimate contact with a small gap forming on the inside of the anode.

Two flaws in the EL were spotted, however. These flaws may have occurred during the brazing process, but it is difficult to determine. In both cases, the EL layer was missing, there was a gap in the braze coverage, and neither the braze nor the anode appeared to be oxidized.

Figure 2.4.R: Both pictures 20x (10xobj) of sample #4A, showing the lack of EL layer, gap in the braze coverage, and no apparent oxidation of the braze or anode layers at that point.

Figure 2.4.S: 5x (10xobj) Sample #4B showing the gap on the inside of the anode, and good contact at the interface.

In general, the contact at the bottom of the two braze joints on this cell appeared to be excellent. Very little to no gap could be observed at the bottom, unlike cells observed in the past. The EL appeared to have a large amount of porosity in it, but that did not seem to affect overall performance. There were sections in the braze joint where there was no electrolyte.

“Bad” braze joints

Tube B060333 has joints “1” and “2,” which were cut into 1A, 1B, 2A, and 2B. At least one of these braze joints as suspect (possibly both since they could not be separated in the experimental measurements) as resistance at 800°C from 0 Ω to 4.2 m Ω after 1184 hours.

The difficult part of the analysis is the two braze joints had a slightly better appearance than the “Good” braze joints. No anomalies were found in comparison to the other two braze joints, and the contact between the braze and anode appeared to be at least equivalent to that found in the other joints. The pictures are included below for documentation, but no glaring difference for the 5x difference in final resistances could be determined.

Figure 2.4.T 5x (10xobj) Sample 1A showing good intimate contact between the braze and anode at the bottom and at the interface.

Figure 2.4.U: 20x (10xobj) Sample 2A showing good contact, and a slight gap between the anode and braze at the bottom of the cell.

Figure 2.4.V: 5x (10xobj) Sample 2B showing the ending of the braze on the inside of the anode, and good contact at the interface.

Both braze joints appeared to be equivalent. The “Good” braze joint exhibited more flaws than the “Bad,” which could not be explained in these pictures. Coverage and contact in these joints appeared, in general, as good or better than has been observed in the past. No conclusion on performance could be drawn from this analysis.

Pack Aluminized 1018 and 304

Four samples were received. Two were mounted and polished, photographed, etched, and photographed again to show the aluminizing layers. One SS304 and one SS1018 sample have been held untouched. The results clearly show a layer, although the integrity of the layer could potentially be questioned. It is unknown what processing was done to the sample prior to submission. The SS1018 etched easily, but the SS304 sample did not etch well after 30min, and was photographed “as etched” at that point.

Because the phenomena observed could not be easily explained, it would be suggest that significant-time testing occur with multiple atmospheres, thermal cycles, and with and without scratching the coating.

SS1018 Sample

There was a clear delineation of the sprayed/coated area as observed in the pictures shown below.

Figure 2.4.W: 5x (10x obj) picture of corner showing the 437Φm layer on the surface. Left is unetched, right is etched.

All along the interface between the coating and the bulk materials, holes could be seen. It could not be determined if these holes were present due to processing, reaction, or contamination. All around the sample, the coating appeared to adhere well to the surface.

Throughout the surface of the sample, a second phase or contamination phase was observed. This phase or contamination appeared to be adhered, but, again, no guess could be made as to its composition or origin. It could potentially be the initial growth of an oxide layer. The exact nature of the coating is unknown.

Figure 2.4.X: etched sample showing layer and observed surface contamination noted throughout the sample.

Finally, strata were noted just below the coating layer. They appeared to be inherent to the sample (not due to the cutting) as they were perpendicular to the surface when observed. (Saw cuts would be expected to be unidirectional throughout the sample, and not necessarily perpendicular.) They are difficult to see in the photograph, but could be seen with direct observation.

Figure 2.4.Y: 20x (10x obj) showing strata observed just below the surface of the coating

SS304 Sample

Figure 2.4.Z: 5x (10x obj) pictures of the SS304 sample showing the coating layer. Left is unetched and right picture is etched.

This sample also exhibited a clear coating on the surface. The coating appeared to be uniform (~437mm thick) throughout, although this may be the effect of the pitting (explained below). It was unclear if the coating was part of the pitted surface or if it was separate. For the sake of this report, it was assumed to be part of the coating. The sample did not etch after 30 minutes in Nital. The etched photograph is the result that was observed after that 30 minutes.

The surface of the coating appeared to have large pits or material losses, evidenced by the rough edges observed in **Figure 2.4.Z**. On closer observation, it appears to actually possess three layers: 1. bulk sample; 2. a pitted layer that ended at a definite point below the coating; and 3. a surface coating which appears dense except where portions are missing. See Figure below.

Figure 2.4.AA: 50x (10x obj) showing what appears to be three distinct layers in this sample: a bulk material, a pitted layer, and a coating.

The holes in the pitted layer appear rounded, suggesting reaction or contamination. It does not appear to be a polishing defect. The surface appears to have a new phase occurring as well in places, and loss of material in other places. It is not clear if this is the onset of oxidation, and material is being lost, or if the coating was non-uniform from the start, or if the coating has been subjected to mechanical stress and broken off (where material is lost).

1. Both samples appear to have a relatively well-adhered coating. Both coating, though, appear to exhibit formation of a new unknown phase at the surface, and the SS304 coating appears to have lost material in places.
2. The SS1018 sample shows strata below the coating surface.
3. The SS304 sample shows pitting either within the coating, or just below the coating surface.

Before use of this technique, it would be useful to thoroughly test the samples for significant time periods in multiple atmospheres, with and without scratching the surface. From these samples, it was unclear what was occurring in the samples. Long-term testing would be suggested to attempt to clarify these phenomena.

CPOX Anode Support tubes

The end of one of the cells was cut length-wise to observe the edge, and to determine if there was a length effect associated with the cells.

There exist three distinct layers in this system:

1. What appears to be a zirconia-only layer on the outside, especially at the inlet end and inside of the tube, but also located to a lesser degree on the outside of the tube. This layer is gray and tends to blend in with the epoxy.
2. A layer of dense Ni encapsulating zirconia within. The zirconia appears to be of the same size as the bulk when view at high magnification, suggesting it remained in place and intact throughout the process. When viewed under backscatter light, this region appeared very flat and uniform after polishing.
3. The bulk tube, inside these other two layers. This appears to be a normal anode cermet, with pores mixed with Ni and zirconia. This section appeared unaffected.

Figure 2.4.AB: two separate sections of the inlet of a tube, (5x 10xobj) showing dense layers at the end and on the inside. Due to color-blending with the epoxy, the zirconia skeleton on the outside is not visible.

Figure2.4.AC: 20x 10xobj picture of a corner of the tube.

Ni transport appears to have occurred one of two ways: by nickel hydroxide formation and transport, or by massive sintering. Both are reasonable given the atmosphere at the inlet to the tube and the heat. Each of these four cells dealt with 31.5x the flow of an individual cell. With the exothermic CPOX reaction components at highest concentration at the inlet to the cell and the number of reactions the greatest, the heat would also be high. This could easily lead to the sintering of the Ni back into the tube.

NiO could form in this system, especially at the inlet, where the mixed O_2 in the air has not yet reacted with the methane. Some water is probably present in the system (humidity of air and small amounts potentially formed by reaction prior to the bed). If the high heats are present, NiO can combine directly with H_2O to form $Ni(OH)_2$ which is volatile. Traveling into the anode structure and depositing in the presence of fuel could aid in either the sintering of the Ni (placement of very small sinterable particles within the structure) or the filling of the void by the same deposition. It is not clear which would be better.

POX on Ni is a strong surface reaction. If the surface area of the Ni is reduced, as is seen in this case, it is not unlikely that the overall reaction rate would be reduced for a given superficial area. The Ni used in the anode tube is relatively large to start with in comparison to normally accepted catalytic Ni, and a surface reduction could be very critical to overall performance. The reaction may effectively work its way down the tube, reducing the surface area due to sintering (rather than a more standard oxidation deactivation mechanism), slowly forcing the reaction to take place in the individual tube.

If this happens, the reaction in the tube, although less, may go through the same phenomena over longer periods of time (at least 31x the time it takes for deactivation in the POX reactor). This is even more detrimental there, however, as the dense layer will close gas transport paths on the anode side. The second phenomena is a loss of transport volume, due to the lack of methane reaction. This will reduce distribution effectiveness, which is currently a concern.

Two possible solutions for this both rely on the removal of heat from the system. The first is the addition of larger Ni particles into the tubes, making them a packed bed. Although they would have low catalytic activity, they could transfer heat from the surface, slowing any heat effects. The second is the use of a small pre-POX bed that would be designed to reduce the amount of reaction required at the tube inlet. A combination of the two might be the use of catalyst packed into the tube. Pressure drops should be carefully controlled in that case.

Tosoh cells at fired at 1500°C, 1450°C, and 1400°C

Three cells were fired at different temperature with Tosoh powder to check for the ability to fire at lower temperatures. The overall results are in the **table 2.4.E** below:

<i>Cell</i>	Firing Temp, °C	Firing Time, hr	Average El thickness $\pm$ Std. Deviation (mean), μm	Comments
<i>A430286</i>	1500	2.5	26.0 $\pm$ 1.1 (26.3)	consistent layer
<i>A430299</i>	1450	2.5	26.1 $\pm$ 1.0 (25.9)	consistent layer
<i>A430291</i>	1400	6	27.0 $\pm$ 1.3 (27.0)	consistent layer

Table 2.4.E Three cells were fired at different temperature with Tosoh powder

All showed some porosity in the electrolyte. It should be noted that the cells were not fully reduced and showed green spots. The firing time and temperature appeared to have little to no effect on the thickness of the electrolyte. The electrolytes observed were extremely consistent in thickness all the way around the cell. No major flaws (lack of electrolyte or large bulges of electrolyte) were observed in any of the samples. Only three sections, one for each cell (taken from what appeared to be an un-oxidized section) were analyzed.

Overall, this is a positive result in the drive for lower firing temperatures.

Plasma Sprayed LaCrO₃

In the oxidized form, tube B180312, coated with a band of lanthanum chromite interlayer was handed to Microanalysis. This interlayer (IL) had been plasma sprayed onto the tube, and the tube reduced. The LaCrO₃ spalled during the heatup.

The cutting and mounting of the sample resulted in additional spalling of the layer due to the stresses involved. Parts that fell off were saved for analysis and a section where it appeared tube oxidation began was also saved, although nothing substantive was found in the oxidized section. A small section was saved with the IL still adhered.

Figure2.4.AD: Left and right sides of the IL section saved. Only about 5mm in length. 5x 10xobj

In the above figure, the oxidation of the tube can be observed in the line in the anode (AN) section, where there is a change in porosity and morphology. The outside (near the interlayer) is oxidized and the inner part reduced. The thickness varied substantially, but was measured in more uniform parts to be about 54 μ m.

When zooming in on the sample, poor adhesion between the IL and AN was readily apparent.

Figure2.4.AE Crack between the IL and AN along the length of the interface- very poor adhesion. 20x 10xobj.

It is unclear whether this poor contact is the result of spraying or the oxidation/reduction process and associated volume changes. In the IL itself, individual splats can be observed, with a significant amount of porosity between them.

Figure2.4.AF 100x 10x obj Individual splats can be easily seen in this picture, showing a porosity between the splats and swirl patterns at various points in the coating.

Figure2.4.AG 150x 10xobj Porosity is more readily apparent in this photograph, with large voids also present in the IL coating.

The porosity and potentially non-uniform coatings may be the result of:

1. *Low tube/powder temperatures on spraying*- if the tube is cooled too much and/or the powder cooled too much, it will be difficult to sinter the IL materials. This may also affect the adhesion to the surface and adhesion between splats.
2. *Directional control*- if there is too much cooling, interfering with the flame, the powder will be angled in a non-uniform way. The gun flame should be laminar in nature for the best results. Cooling may also affect the powder temperature.

3. *Densification*- higher temperatures or longer times may be required for densification. This does not address in any way the effect of the Ni volume change on reduction.

It appears the splats are not sintering well to one another.

A loose sample was observed as well to see if the same effect was observed. Because of potential angle-of-mounting issues, no thickness measurements were taken.

Figure 2.4.AH 100x 10xobj Loose sample showing the same swirl arrangement and porosity found in the sample still attached to the AN.

In air, after falling off or delaminating from the AN, the IL should sinter well. For all samples, there was no instance in which the coverage looked like the theoretical splats built upon each other, similar to bricks.

Tube Sprayed at Nextech and Sintered to 1350°C for 2hr

A tube was sent to Nextech where it was coated with their electrolyte (EL) spraying process, sintered at 1350°C for 2hr, and sent back. At Acumentrics, the tube was placed in the reduction furnace and reduced under CPOX conditions. When the tube came out, only the bottom part of the tube was reduced, the top section remaining oxidized. Two samples were cut from the tube: one from the reduced section and one from the oxidized. Both were examined as seen below.

Both sections of tube showed some crazing of the EL and some small amount of porosity, but overall, a very dense EL layer. The layer thickness, however, was extremely variable as seen in the pictures below:

Figure 2.4.AJ Both pictures 50x with 10xobj Left: Oxidized part showing variable EL thickness and some crazing; Right: Reduced section showing variable EL thickness and EL breaking off.

The outer surface of the EL was very uniform, but the valleys and hills of the anode (AN) penetrating and retreating from that surface varied considerably.

Figure 2.4.AK Both pictures 20x 10xobj Left: Oxidized part showing break in EL coverage and variable EL thickness; Right: Reduced part also showing break in EL coverage and variable EL thickness

Contact between the EL and AN appeared to be intimate at all points. EL thickness varied between $15\mu\text{m}$ and $0\mu\text{m}$, and could vary rapidly as seen in the pictures below. The average was closer to $10\mu\text{m}$ overall in places with relatively uniform coverage. The measurement, however, was extremely difficult.

Figure2.4.AL 150x 10xobj Left: oxidized section showing extreme coverage variability; Right: reduced section showing coverage variability with scale (both pictures are to the same scale).

While some porosity was observed in the EL, the sample showed a very dense and uniform layer overall. There were sections in the reduced sample that were missing, but this might be attributed to the oxidation/reduction cycles undergone. The main issue here appears to be twofold:

1. The thickness of the layer is simply not sufficient to provide a gas tight seal; and
2. The anode surface roughness appears to be able to severely compromise the integrity of the EL layer.

Figure2.4.AM 5x 10xobj Reduced sample showing area of zero EL coverage. This was repeated in other spots on the sample.

The Nextech sample appears to potentially provide a dense layer at a lower sintering temperature and shorter time.

Suggestions for improvement based on observations include:

1. Increasing the thickness of the layer to eliminate the very thin regions
2. Understanding any surface “cleaning” done prior to or during the process
3. Understanding the reason for the high sinterability (additives, particle size, surface area, etc.) to aid in understanding any possible performance effects.

MIM 1/4" NPT Sample Inlet Cup Cut and Polished

The sample MIM 1/4"NPT thread inlet braze cup was received and checked for dimensions. Dimensionally, there are no flaws that would keep the cup from being used in brazing. The cup was cut in half and polished to observe the presence of porosity. This was done to begin to establish a standard for the MIM parts.

Basic observations include the fact that porosity tended to reside at the edges of the part and in the corners. There was some observed in the threads, and the thread edges appeared somewhat non-uniform, although not significantly more than observed on machined cups.

Figure2.4.AN 5x 10xobj View of typical porosity occurring at edge of part. Regions with more apparent porosity tended to be toward the edge of the part or in corners.

Figure2.4.AP 50x 10xobj Porosity at the edge of a thread. Some scrape marks are visible. The edge of the thread is rough in comparison to other, more simply formed, edges on the part.

Figure 2.4.AQ 100x 10xobj Close-up of porosity at one point of the cup, showing a cleaner edge.

Overall, the cup appears to be highly densified, and apparently has no flaws which might be considered fatal.

A more definitive test will be with the brazing and oxidation of the cup. This will subject the cup to additional stresses, and observed oxidation patterns and rates will be a strong indicator of the extent of porosity and any effect it might have.

Cell Modeling

A workshop by Comsol at the University of South Carolina specifically on the use of Femlab 3.1 for fuel cells and batteries was attended. The latest version of the software is well suited for the modeling of the tubular fuel cell. Besides optimized performance, particularly useful modifications are:

- 1) Cavity radiation. A ray tracing method is used to rigorously calculate the matrix of view factors. This is a useful tool for accurate modeling of an SOFC bundle or stack, and CPOX reactors
- 2) Orthogonal elements and extruded meshes. This is especially useful when it is known *a priori* that gradients in the solution will be quite different in orthogonal directions, *e.g.* in thin shell problems. This feature is particularly useful for the modeling of the electrolyte and electrodes
- 3) Independent meshing of different geometries. Femlab allows the coupling of variables obtained in different solution geometries, (*e.g.* coupling of the gas phase concentration in a packed bed to the gas phase concentration at a catalyst particle interface). By allowing the meshing to be independent in different geometries the solution time can be greatly reduced for thin shell problems which occur in the anode supported fuel cell.
- 4) Adaptive meshing. Useful for stiff problems.
- 5) Interface for Solidworks and other programs.

A trial version of Femlab 3.1 was also obtained. Equations and methodology for modeling of the cell, and CPOX reactors were formulated. A working model of a single braze fuel cell at isothermal conditions was developed and tested on the Femlab 3.1 platform (Comsol, Inc.) .

The model assumes radial symmetry. The silver busbar and current collector is approximated as a conducting sheath of the same cross-sectional area of the silver braids currently used as the bus-bar. By appropriately scaling the radial dimension of the YSZ electrolyte and LSM cathode collector by a factor of 100, it is possible to create a mesh for the anode tube, electrolyte and cathode current collectors with a reasonable number of elements. In this first model, the actual anode and cathodes (*i.e.* where the electrochemical reactions occur), are approximated with the application of the Butler-Volmer equation at the inner and outer surfaces of the electrolyte. The parameters used are given in **Table 2.4.F**

Symbol	Description	Value	Unit
σ_E	Electrical conductivity of electrolyte	0.024	S cm ⁻¹
σ_A	Electrical conductivity of anode cermet	3000	S cm ⁻¹
σ_C	Electrical conductivity of LSM	60	S cm ⁻¹
σ_{Ag}	Electrical conductivity of silver	142857	S cm ⁻¹
t_E	Electrolyte thickness	2.5×10^{-3}	cm
t_A	Anode support tube thickness	0.15	cm
t_C	Cathode LSM current collector thickness	3.5×10^{-3}	cm
A_{Ag}	Cross sectional area of silver bus-bar/collector	0.16	cm ²
J_{OC}	Cathode exchange current density	0.1	A cm ⁻²
J_{OA}	Anode exchange current density	2.0	A cm ⁻²
D_{H_2}	Binary diffusivity of H ₂ -H ₂ O	8.6	cm ² s ⁻¹
D_E	Effective H ₂ diffusivity in anode cermet	0.86	cm ² s ⁻¹

Table 2.4.F: Model Parameters

The mesh has a total of 8052 elements and once the initial solution has converged (30-60s), parametric solutions can be calculated in ~15s.

The cathode exchange current density parameter was obtained by fitting the model VJ prediction to the VJ data collected from a 280mm cell after 24 hours (081004 CTS 10, cathode length experiment). The fit is shown in Figure 2. By calculating all the resistive losses in the cell, the ohmic component of the potential loss was calculated as 0.91 Ohm.cm², which compares favorably with the average area specific resistance measured for this kind of cell using current interrupt (0.80-0.95 Ohm.cm²).

Experimentally, measures of the average exchange current density have been derived by fitting the low end VJ by the equation.

$$V = E_N - Rj - \frac{R_G T}{2F} \ln \left[\frac{j}{2j_o} + \frac{1}{2} \sqrt{\left(\frac{j}{j_o} \right)^2 + 4} \right]$$

where R is the experimentally obtained area specific resistance and E_N and j_o are used as fitting parameters. Using the same parameters as in Table 1, a low end VJ (obtained at a constant fuel flow of 208 ccm) was also predicted from the model and fit by the equation above. The experimental value obtained for the 280mm cell in 081004 CTS 10 is 26.9 mA cm^{-2} . The fit from the data generated by the model gave a value of 26.2 mA cm^{-2} .

Figure 2.4.AR: Comparison of a VJ generated with the model (Table 2.4.B), with experimental VJ data (75% FU)

The conductivities of the SOFC components have been measured at Acumentrics or are well documented in the literature. Layer thicknesses have also been set based on measurements using optical microscopy. The only fitting parameters in the model are the exchange current densities, of which the anode parameter was fixed at a high value based on literature reports. Thus, *only* the cathode exchange current density was used to fit the VJ curves (constant fuel utilization and low current density).

Task 3.0 – Stack Technology Development

Subtask 3.1 – Cathode Current Collector Improvements

Silver ink is required to reduce the interfacial resistance between the cathode and silver wire current collection system of Acumentrics current cell design. Previous studies have suggested that the quantity of silver ink applied to this interface affects the rate of cell degradation. In order to evaluate this further, three different orifice size metal caps have been fabricated which essentially meter out different quantities of silver paint on to the silver wire.

The three orifice sizes are shown in the **Table 3.1.A** below along with the measured quantity of silver ink metered out on to the wire per unit length. The 0.02” orifice size is Acumentrics current standard.

Orifice Size Inch	Orifice Size μ	mg Silver Paint Applied/m of silver wire
0.020	508	122
0.018	457	92
0.015	381	54

Table 3.1.A The three orifice sizes

A series of cells have been fabricated using the three different orifice sizes to meter silver paint on to the wire. The appearance of cells wound using each different orifice size are shown in the images below **Figure 3.1.A**. For reference, a further set of cells has been fabricated with the cathode fully painted with silver ink.

Figure 3.1.A Cells wound using each different orifice size

Cells fabricated from each different iteration are presently in the cell testing queue.

Cathode Length Experiments

Significant losses in cell performance are predicted as a result of the relatively low conductance of the anode support tube (anode bus bar) and silver braids (cathode bus bar). The intent of this cell test was to elucidate the effect of length on cell performance.

Five cells with cathode lengths of 36, 70, 140, 210, and 280 mm were tested for ~1150 hours, primarily at 800°C, a fuel utilization of 50% and a nominal current density of 250mA/cm². Current interrupt and V-I data was routinely obtained throughout the test. Some data was also obtained at 700°C and 850°C.

At the primary conditions the cells attained potentials of 0.66, 0.69, 0.66, 0.57 and 0.51V respectively from shortest to longest cathode length, after 150 hours. The poor performance of the shortest cell was most probably due to a lower than intended operating temperature. Thermocouples placed in the cell midsections at hour 886 gave the operating temperatures as 784, 809, 823, 815 and 809°C respectively.

After 910 hours the cathode bus bar of each cell was enhanced with two extra silver braids, doubling the bus bar conductance. Again at the primary conditions, the voltage increases were 0, 5, 7, 26, and 46 mV, respectively. At 150 mA/cm² and 50% FU the voltage increases were -3, 3, 4, 15 and 27 mV, respectively.

Despite the different currents, and predictions of markedly different peak current densities, all cells degraded at similar rates. The polarization resistance increased at ~0.3-0.4 mOhm.cm²/hr. The abrupt onset of degradation for the 210 and 280mm cells was 150 hours, immediately after a simple increase in the fuel flow. This is bewildering as lowering the fuel utilization is typically thought to stress the cell less. From VJ and current interrupt analysis, the degradation was shown to be due to both ohmic and polarizing mechanisms. The onset of degradation for the smaller cells was around 400 hours, apparently solely from a polarizing mechanism. Anode shifts were stable throughout the test. Insufficient cathode shifts were measured to prove that the cathode porosity was constant, but it is highly unlikely given that this is a ceramic component and changes in other cell tests cathode shifts are not seen in general.

Exchange current densities estimated from low end VJ analysis did not change although the polarization resistances increased by 12-40% during the same time period (0-700 hours). The low end VJ analysis also did not support the speculation that the cells were operating at temperatures different from the nominal temperature. This was especially noticeable for the case when the cells were operated at 700°C and any deviations in temperature would likely be expressed in the actual exchange current density. The validity of the low end VJ analysis technique needs to be studied further if it is to be a useful tool for studying cathode development and degradation.

No mechanisms for the cell degradation were inferred from the analysis.

Many of the anomalous results in this test are qualitatively explained, but a complete cell model would be useful for quantitative analysis of the data.

Significant losses in cell performance can be attributed to the relatively low conductance of the anode support tube (anode bus bar $\square A_x=1760 \text{ S cm}^2$) and silver braids (cathode busbar $\sim 2250 \text{ S cm}^2$ for 2x16 strand braids). For instance, for a nominal current density of 150 mA/cm^2 , losses in the cermet were estimated to be bounded as shown in **Figure 3.1.B**. At the standard cathode length of 28 cm the resistive losses in the anode are estimated to be between 55 and 108mV.

Figure 3.1.B : Estimates of the bounds for the anode resistive loss in nominal 15 mm cells of various length

Moreover, because of the bus bars' relatively low conductance it is believed that the current density distribution peaks near the current take-off. Bounds for these profiles have been calculated for the case when a) the cathode bus bar conductance is much greater than that of the anode b) polarization resistances are small c) fuel utilization is very low (**Figure 3.1.B**). In the real cell, resistances in the cathode bus bar will tend to further peak the current distribution at the takeoff, whereas polarization resistances will tend to flatten the distribution.

It is widely believed that current density plays a role in electrode degradation¹ and so aside from the resistive losses, the cell length may play an important role in cell degradation. For the standard Acumentrics cell, estimates show a peak current density of $400\text{-}500 \text{ mA/cm}^2$ to be quite reasonable (**Figure 3.2.C**).

In this experiment an attempt is made to quantify the effects of the cell length by evaluating the performance and degradation of cells of different length at different temperatures.

¹ e.g. Tu, H., Stimming, U., "Advances, aging mechanisms and lifetime in solid oxide fuel cells", *J. Power Sources*, 127,(2004), 284-293

Figure 3.1.C: Theoretical estimate of the effect of length on current density profiles (Cathode lengths – 18,36,70,140,210 and 280mm)

Cell Fabrication

Six electrolyte coated anode support tubes (15 mm OD x 330 mm nominal) were selected from the ceramic processing line for this experiment. Different effective cell lengths were created using scotch tape to interrupt the C1 and C2 dip coatings at different lengths. In this way, cells of 18mm, 36mm, 70mm, 140mm, 210 and 280mm were created (**Figure 3.1.Da**). After drying the cathode, the tape was stripped and the typical firing schedules were followed through reduction, to silver winding. At this point, using standard procedures, silver was only wound onto the cathode section of interest (**Figure 3.1.Db**), before the cells continued through brazing (single end only) to cell testing. The same batches of anode cermet, electrolyte slurry and cathode slurries (C1 and C2) were used for all cells.

Figure 3.1.D: Control of cell length by masking

Cell Testing

The cells were to be tested at 75% fuel utilization, the standard operating point for the current generation of cells, however for the small cells this would lead to low flow rates for which the accuracy of the mass flow controllers (0-1LPM) could not be guaranteed and moreover, where the effect of system leaks would be exacerbated. For this reason most experiments were conducted at 250mA/cm² and 50% fuel utilization and the 18mm cell was not put on trial.

A summary of tests performed during the 1175 hour cell test are:

- VJ curve and ohmic resistance measurements (by current interrupt) were routinely obtained throughout the test at 50% and 75% fuel utilization.
- Low end VJs (0-25mA/cm², 0.8mA/cm² steps) at low fuel utilization (4-10% FU max).
- Testing at temperatures of 700, 800 and 850°C
- Routine anode and cathode shifts
- Doubling the cathode conductance by the addition of two extra braids at 890 hours

Results and Analysis

The 5 cells of 36-280mm length were under load for a total of 1150 hours, mostly at the current density of 250 mA/cm² and 50% fuel utilization (**Figures 3.1.E and 3.1.F**). All cells degraded throughout the test at approximately the same rate when degradation is measured in mV/khr.

Although the degradation of the control cell is similar to the average of cells for the year (-11.4 % for DB cells), the sudden onset of degradation at hour 140, *seemingly for all cells*, is puzzling and it is not clear at this stage what could have precipitated it. Degradation makes it difficult to compare absolute performances with standard cells, however in view of the almost constant decline in the performance of all cells (in mV/khr) it is still meaningful to compare relative performances (**Table 3.1.C**).

The column following the potential enhancement at each temperature, is the % of the voltage change that can be attributed to resistance (measured using the current interrupt method). In general the performance gains for the smaller cells are due to changes in both the polarization and resistance, as might be expected due to the different current distributions. Note that for the 36mm cell at 700°C, the difference in ohmic resistance would have lead us to expect the difference in potential to be 7.8 times higher than what

Figure 3.1.E: Cell life graph 0-600 hrs

Figure 3.1.F: Cell life graph 600-1200 hour

was actually seen. The gain from the resistance change is offset by what must be a massive increase in the polarization. There is evidence to suggest that this may be due to the cell being at a lower temperature than intended (see next section). However an analysis of the low end VJ suggests that at 700°C the exchange current densities of all the cells are the same.

* 800°C ** with Ag braid

Cell length and temperature effects

From **Table 3.1.C**, cell performance is seen to be a strong function of length, the one anomaly being the 36mm cell, which generally operated at lower potentials than the larger 70mm cell. After the first thermal cycle at ~860 hours, thermocouples were added to the cathode midpoint in each cell and, in order from smallest to largest, the temperatures were 784, 809, 823, 815 and 809°C. Thus there was a 30°C difference between the 36 and 70mm cells and a 43°C between the 36mm and 140mm cells. This is most likely a result of the cell location and the proximity to the furnace openings. Noting that $dV/dT \sim 1.8 \text{ mV}/^\circ\text{C}$ for *standard cells* near 800°C², the potentials at 809°C can be estimated, whereafter the incremental increases in performance from smallest to largest would be 122, 104, 60, 30 and 0 mV respectively.

Silver bus bar addition and temperature effects

The effect of the silver bus bar is qualitatively in line with expectation, in that the strongest effects are seen for the longest cells where the bus bar must carry significantly larger currents. It has been previously shown that the conductance of the Ag bus bars (standard configuration) is comparable to the conductance of the anode cermet³, and so if resistive losses on the anode side are significant, it is expected that similar effects must apply to the cathode bus bar. What is strange, however, is the abrupt increase in cell potential between the 140mm cell and the 210mm cell.

This may also be an effect of the variation in the average cell temperatures, in particular the effect of temperature on current distribution. It was shown in CE-04-028 that the current density is controlled by the ratio of resistances in the transverse direction to those in the axial direction - for small values of this ratio the current density is peaked around the cell take-off. Since the resistances in the transverse direction (activation polarization and electrolyte resistance) *decrease exponentially* with temperature, whereas the resistances of the bus bars (Ag braid and Ni cermet) increase only linearly with temperature, the current density distribution for the 140mm cell may be weighted more towards the current take-off compared with the larger cells, *i.e.* because of its higher temperature (823°C) losses in the silver bus bar are lower due to the current path length on the 140mm cell in contrast with the larger cells.

² The data in this report suggests an average of 2.2°C, for both spans of 700-800°C, and 800-850°C

³ 2246 S/cm² for Ag busbar and 1758 S/cm² for the cermet, both at 800°C

Cathode and Anode Shifts

The electrode shifts are given in **Tables 3.1.E and 3.1.F**. Typically cells run at 800°C and 150 mA/cm², have a cathode shift and an anode shift of –34mV and –14mV respectively. In this cell test the current densities are much higher at 250mA/cm², and so the shifts are expected to be larger. A comparison between cells however is interesting. For larger cells (>140mm) the anode shifts are similar, while for the smaller cells the anode shift is significantly and consistently lower throughout the test. This can be qualitatively understood from the current distributions. For all cells when the H₂ concentration is lowered to ~50%, current production is forced nearer the current takeoff leading to higher activation and concentration polarization effects. This effect would be exacerbated in long cells however the size of the effect is not obvious and would be best explored by cell modeling. The experimental length effect on the shift is suspicious in that it only appears for the smallest cells. It is possible then that the deviations in the shifts could be caused by inaccuracy of the flow meters at low flows. However it is also possible that the anomalous length dependence is a result of the temperature variations between the cells.

Elapsed Time / hrs	Temp. /°C	Current density mA/cm ²	Anode Shift /-mV				
			36mm	70mm	140mm	210mm	280mm
336	800	250	17	21	29	30	32
405	700	150	7	10	18	18	22
724	800	250	15	18	28	28	28
889	800	250	11	18	27	27	28
1173	800	250	17	24	28	29	

Table 3.1.E : Anode shifts during experiment (all at 50% fuel utilization)

Elapsed Time / hrs	Temp. /°C	Current density mA/cm ²	Cathode Shift /-mV				
			36mm	70mm	140mm	210mm	280mm
405	700	150	59	53	49	48	40
692	800	250	50	52	51	57	47

Table 3.1.F : Cathode shifts during experiment (both at 50% fuel utilization)

Exchange Current Densities

Low end VJ data fit with the following expression⁴ using least squares regression

$$V = E_N - Rj - \frac{R_G T}{2F} \ln \left[\frac{j}{2j_o} + \frac{1}{2} \sqrt{\left(\frac{j}{j_o} \right)^2 + 4} \right]$$

⁴ The non-linear portion of this equation is a simplification of the Butler-Volmer equation for activation polarization. The use of this expression for describing activation kinetics has not yet been rigorously justified and so the j_o values obtained herein should only be used for comparisons between cells with the same geometry.

The area specific resistance, R , was obtained independently from current interrupt measurements and the outlet Nernst potential E_N was calculated from thermodynamic data. The exchange current densities are shown in **Figure 3.1.G**

Figure 3.1.G: Exchange current density estimates.

At 400 hours when the stand temperature was 700°C, the exchange current densities are all very close $12 \pm 1 \text{ mA/cm}^2$, whereas at the higher temperatures the differences between cells is more pronounced (**Figure 3.1.H**). This *may* be evidence of the flattening of the current distribution with increased polarization and electrolyte ohmic resistance; in the extreme case of an even current distribution, the activation polarization loss is also even across the length of the cell, leading to the same estimate of the exchange current density.

Figure 3.1.H: Exchange current density at 800°C vs cell length

At the higher temperature of 800°C the exchange current densities are quite different from each other. Figure 3.1.G suggests that the apparent exchange current density scales

inversely with length. This could be interpreted to be a result of the higher effective current densities that are experienced by portions of the long cells; in contrast with the data point at 700°C the current distribution is more peaked near the current take off.

Note that the true dependence of apparent current density on length is likely distorted by the variations in temperature. The temperatures measured in the cell from smallest to largest were 784, 809, 823, 815 and 809°C. *This creates a serious contradiction between this analysis and the data in Table 3.1.C.* The thermocouple data and the voltage response of the 36mm cell strongly suggest that it is operating at a lower temperature than the other cells. However the exchange current density is also a strong function of temperature and so we would have expected to see the difference in Figure 3.1.H.

No single piece of data is absolutely conclusive and so it is important that further work be done on proving the usefulness of low end VJ analysis.

Degradation

Except for those obtained at 700°C, the VJ curves can all be very well approximated by lines fit through the outlet Nernst potential⁵. The negative of the gradient of the VJ in these cases can be interpreted as an apparent resistance including both activation polarization and ohmic contributions (**Figure 3.1.J**). The ohmic contribution to the resistance is independently measured using current interrupt methods (**Figure 3.1.K**) and so the polarization resistance can be found by subtraction (**Figure 3.1.L**). Note that the dips in the curves at 900 hrs and 1050 hrs are due to the extra Ag braid and temperature increase to 850°C respectively. Salient features in the graphs are:

**Figure 3.1.J: Total apparent area specific resistance over the cell operating lifetimes.
Data at 700°C is not included**

⁵ An exception is the VJ for the 36mm cell where it has been noted that the temperature was lower than expected, and for which flow rates are too low to achieve accuracy in the fuel utilization. Analyses based on VJ curves do not include the 36mm cell

1) From the life graph (Figure 3.1.E) it appears that degradation started for all cells at ~140 hours. The abrupt change in voltage slope for the 210 and 280mm cells is remarkable bearing in mind that the *only* change was to *increase* the fuel flow to each cell! The data in Figure 3.1.E suggests that the degradation for the shorter cells actually started near 400 hours. Events that occurred before 400 hours are cell operation at 1) high current density ($250\text{mA}/\text{cm}^2$) and high utilization (75%), 2) cell operation at low temperature (700°C).

2) The ohmic resistances of the 210 and 280mm cells are very close over the entire lifetime of the test (Figure 3.1.J), particularly at early times. One might expect both the ohmic and polarization resistances of the cell to increase as the length increases since simultaneously the current density near the take off increases and more current must be produced farther from the current take-off. From Figure 3.1.J it is clear that the total *apparent* resistance of the cell increases with length suggesting that the difference in performance of the two cells is due to polarization resistance. The question arises as to whether this polarization is due to differences in the cell fabrication (perhaps unintended microstructural differences), or due to a manifestation of the interplay between polarization and ohmic resistances and their effect on the current distribution.

3) The 210 and 280mm cells had a strong resistive contribution to the degradation over the majority of the cell test. The average rates at which the ohmic resistances increased were 0.15 and $0.20\text{ Ohm}\cdot\text{cm}^2/\text{KHR}$ respectively for the period before the addition of the silver bus bar. These rates increased to 0.45 and $0.69\text{ Ohm}\cdot\text{cm}^2/\text{KHR}$ after the bus bar addition. Eventually the 280mm cell potential rapidly degraded (~1080 hours), accompanied by a drastic increase in resistance. This degradation signature, moreover the rate at which the resistance increased, was similar to that observed for suspected braze joint failures in previous experiments (e.g. $0.3\text{ Ohm}\cdot\text{cm}^2/\text{KHR}$).

Figure 3.1.K: Area specific resistance over the cell operating lifetimes as measured by current interrupt

4) The area specific polarizations are reasonably similar for the 70, 140 and 210mm cells, but significantly higher ($\sim 0.2 \text{ Ohm.cm}^2$) for the 280mm cell. The polarizations do not correlate with cell length, but this may again partially be a result of temperature; the lowest polarization resistance is for the 140mm cell, which also runs at the highest temperature. Nevertheless, the *rate* at which the polarization resistances increase ($0.3\text{-}0.4 \text{ mOhm.cm}^2/\text{hr}$) are similar for all cells. The expectation from several analyses have shown that for the standard cells the current density is not likely to be uniform. For instance for a nominal current density of 150 mA/cm^2 the current distribution near the cell takeoff of a standard 280mm cathode is probably closer to 400 mA/cm^2 . For short cells the current density is expected to be almost uniform across the cell length (Figure 2). Current density is often claimed to be a strong factor in cell degradation and thus it was expected that if current density was the main cause of degradation, then all cells would degrade at different rates. The larger cells do initially show increases in the cell polarization however a clear trend distinguishing the cell lengths is not apparent.

5) One might expect the current distribution to change if the polarization resistances increase and this would in turn manifest a change in the area specific ohmic resistance. Although ohmic resistance increases were seen for the 210 and 280mm cells, no significant change was seen for the smaller cells. The cell resistance has axial contributions from the bus bars, which generally increase as the current distribution gets flatter. The resistance contribution from the transverse interfacial path generally reacts in the opposite fashion – even current distributions result in lower losses at the interfaces⁶. Thus it is conceivable that for small shifts in the current distribution there may be no significant change in the area specific resistance.

Figure 3.1.L: Area specific polarization resistance over the cell operating lifetimes

⁶ Note that the resistance under discussion is an area specific quantity

Discussion and Conclusion

The purpose of this experiment was to improve our understanding of the effects of cell length on performance and degradation. As expected, at the same nominal current density, there is a clear dependence of the cell potential on cell length. Non-uniform temperatures appear to have obfuscated accurate quantification of length effects.

Nevertheless, **Table 3.1.G** and **Figure 3.1.M** compare the potential loss due to cell ohmic resistance as measured by current interrupt, with predictions from the resistive network model. The resistive network model was derived under restrictive circumstances and in particular does not account for losses in the cathode and cathode bus bar.

Cathode length /mm	Experimental Ohmic loss /mV	Predicted Ohmic Loss/mV			
		Anode +Electrolyte		Anode	
		min	max	min	max
36	65	40	40	7	7
70	79	50	51	16	17
140	137	80	87	42	54
210	216	117	142	68	108
280	222	155	215	93	182

Table 3.1.G: Comparison of network mode prediction and experimental data (250mA/cm²)

* experimental measurement from current interrupt

** predicted from network model; $\rho_E=33.3\text{Ohm.cm}$, $\rho_A=3.1\times 10^{-4}\text{Ohm.cm}$, diameter 1.45cm, wall thickness 1.5mm, electrolyte thickness 40 μm , 2 cm anode bus bar connection to braze cup.

Figure 3.1.M: Comparison of experimental and resistive network predictions for potential loss due to ohmic resistance

In all cases, not surprisingly, the predictions are lower than the experimental measurement, implying the presence of other resistive elements such as the cathode bus bar and cathode current collector (LSM), as well as electrode resistances. It was demonstrated in this experiment, that doubling of the Ag bus bar conductance increased the performance of the 28 cm cell by 27mV and 46mV at 150 and 250 mA/cm²

respectively, and so this correction for the cathode bus bar alone would bring the experiment and prediction into agreement.

Degradation did not have a strong correlation with total current or cell length. It has been surmised in the past that locally high current densities may be effecting changes in the electrodes. However, in this experiment the polarization resistances increased at similar rates in spite of the prediction that the current densities along the cells are markedly different. It is interesting to note that the exchange current densities as found by curve fitting do not change significantly with time, despite changes in the polarization resistance of 12-40% within the same time period. This would imply that the degradation is not due to charge transfer polarization⁷.

Ohmic resistance increases were only apparent for the 210 and 280mm cells. The cell resistances at room temperature are compared at the start of the test and at the end of the test in **Table 3.1.H**.

Cell Length /mm	Anode-Anode resistance at 25°C/ mOhm		Anode-Cathode resistance at 25°C/mOhm	
	initial	final	initial	final
36	2.72	3.6	200000	200000
70	2.72	3.87	200000	75000
140	2.6	3.28	198	44700
210	2.72	4.73	138000	227
280	2.73	5.18	200000	55900

Table 3.1.H: Comparison of cell resistances before and after testing

Apparently no dead shorts occurred, nor was there any evidence from VJ curves or fuel utilization curves of electrical shorts.

The analysis of the cell performances points to the necessity for developing a complete cell model, incorporating transport and electrochemical phenomena. With only a speculative understanding of the current density profiles and how they are affected by fuel flow and current loading, quantitative analysis of cell performances is difficult.

At this time preparations have been made to repeat this cell test and a variant. Precautions will be taken to ensure temperature uniformity. In the length cell repeat, the study will be aimed at repeating the voltage performances, but will also look more critically at which factors precipitate degradation. In the last study, degradation seemed to occur after the fuel utilization of the cells was suddenly *decreased*, and again after prolonged operation at 700°C. A separate experiment will look at the effects of current density. Five cells with 70 mm long cathodes have been prepared and each of these will be run at 800°C at a

⁷ The fitting of low end VJ curve to the Butler Volmer equation has no rigorous basis, and although some sensitivity of the low end Vj to exchange current density was demonstrated in this experiment, it was not able to explain the poor performance of the 36mm cell at 700°C, which must be related to polarization. More experimentation and analysis of this technique is required

single current density current densities in the range of 100-500 mA/cm² at low fuel utilization

Subtask 3.2 – Anode/Cathode Current Collection

Braze resistance experiment

The braze resistance experiment was restarted and finally completed 11184 hours at 800°C with an electrical current of 12 A for the majority of the test life. The resistivity of the brazes was calculated by subtracting the estimated contribution from the sintering anode tube. These results are shown in **Figure 3.2.A**.

Figure 3.2.A: Braze resistances 12A current, 800°C, 100ccm H₂
(each curve represents data for two brazes)

Note that for both curves there is a marked increase in the resistance when the current is dropped to 8A. This could either suggest that the braze resistance is a function of current or that there is calibration issue with the shunt resistance.

A preliminary autopsy of the brazes showed the following results:

	Anode Tube No	A-A resistance @ 20°C/mΩ	Time @ 800°C/hrs.	Leak Rate cm ³ /min."H ₂ O
INITIAL	B060333	1.42	6	0.52
	B060120	1.34	6	0.42
FINAL	B060333	1.92	1184	0.23
	B060120	1.88	1184	0.16

Anode Tube No	Braze Order	Electrons Flow	Gas Flow	Anode Tube Resistance/mΩ	Braze Resistance/mΩ
B060333	1st	away	away	1.42	0.30
B060333	2nd	toward	toward	1.42	0.15
B060120	1st	toward	toward	1.36	0.20
B060120	2nd	away	away	1.36	0.27

Table 3.2.A: Braze autopsy

Figure 3.2.B: Braze condition after 1184 hours at 800°C

At room temperature one cannot distinguish the bad braze(s) from the good braze(s), either by leak rates nor resistance measurements. The brazes will be sectioned for microscopic analysis.

Chromite Layer Connection

In support of a cell configuration where chromite bands are applied directly to the anode support (AS) tube to enable current collection along the length of the cell, work was initiated to determine possible methods of making an electrical connection between the chromite bands and the cathode of the next cell in series. A number of silver bands were painted onto an AS tube over a chromite layer. These were to be the base for the connections. On top of these silver bands were wrapped silver wires and braids. The 1st connection (on the left of the figure) was a silver braid wrapped tightly around the silver band. The 2nd connection was 4-ply silver wire wrapped 4 times around the AS tube. The 3rd and 4th connections were the same as the 1st and 2nd respectively with the addition of silver paint over the braid/wire for increased adhesion.

Figure 3.2.C Various configurations of silver braid and wire were wrapped around the AS tube.

The setup was placed into a furnace and heated to 800°C overnight to sinter the silver and provide a possible electrical connection.

Observations:

1. The silver wire/braid did not adhere to the oxidized AS tube at all,
2. The silver paint adhered to the oxidized AS tube and to the chromite layer
3. The silver wire/braid adhered to the silver paint
4. The samples with the extra silver paint (3 & 4) adhered better to the chromite layer compared to the samples without the extra silver paint.
5. The thermal expansion difference between the silver and the chromite (& AS tube) did not seem to have loosened the silver-to-chromite connections. None of the silver wires/braids was loose around the AS tube.

6. When pulling the wire/braid rings off the AS tube, the silver paint stayed connected to the silver wire/braid. This suggested that the weakest adherence is the silver-to-chromite connection.

Figure 3.3.D Left shows the paint preferentially adhering to the braid. Right shows the chromite layer after the test (most of the silver stayed with the braid).

The next test involved using a number of silver bands ($\frac{1}{4}$ " wide with $\frac{1}{4}$ " spacing between bands) to connect to the chromite layer. Silver paint was used between the bands and the chromite AS tube. Silver braids were wrapped around these connections. One pair of connections were painted with extra silver on top of the braid to enhance the adhesion (2) and also the electrical connection. Another pair of connections used a high temperature spring clip to press the braid into the chromite layer (3).

Figure 3.3.E Sample setup showing the various connection geometries

As shown in the graph below, after 984 hours and 41 thermal cycles, the resistance of sample #3 had stabilized at a value of approximately $3.7 \, \Omega$ at 838°C . This resistance value takes into account the length of the silver braids, the contact resistances and the resistance of the chromite layer. This value does not allow the calculation of the contact resistance of the silver braid-to-chromite layer, but it does verify that a stable connection was possible with the system under test. From the graph of the results of the other two connection geometries, there is not a stable connection formed. This is obvious by observing the connections after the test. The silver paint had spalled off the chromite layer, preferentially adhering to the silver braid. As the sample was thermally cycled, the silver paint became mobile and was separated from the chromite surface, causing the slowly increasing resistance. The photo below shows the test piece after 1000 hours of operation.

Figure 3.3.F Resistance of the various connection geometries

Figure 3.3.G Connection sample after 1000 hours of operation

Connection #1 (right) had minimal contact to the chromite layer and was easily removed from the anode support (AS) tube at the end of the test. It is assumed that due to the large difference in thermal expansion between the silver and the AS tube, that the silver braid opened up under high temperature and then contracted upon cooling, thus causing relative movement between the two parts, resulting in an unsatisfactory electrical connection.

Connection #2 (center) was also easily removed from the AS tube. The silver paint preferentially adhered to the silver braid and thus came off with the braid, leaving a bare chromite surface.

Connection #3 had the Hastelloy X spring clips to compress the silver braid onto the chromite band. This method proved to be successful and even after 41 thermal cycles and 1000 hours of operation, the clips still had a compression force, pushing the braid onto the chromite band. At approximately 500 hours of operation, the connection resistance stabilized as shown on the resistance graph.

The next experiment will involve a connection based upon the Hastelloy X spring clip and a contact fabricated from silver strip. The figure below shows the test sample and geometry of the clips.

Figure 3.3.H Second generation spring clip interconnect test sample

After 768 hours and 32 thermal cycles, the resistance had stabilized at a value of approximately $2.7 \, \Omega$ at 838°C . This resistance value took into account the length of the

silver braids, the contact resistances and the resistance of the chromite layer. This value does not allow the calculation of the contact resistance of the silver braid-to-chromite layer, but it does verify that a stable connection is possible with the system under test.

Figure 3.3.J Resistance of Chromite Sample

Sulzer Metco Collaboration

One of the limiters in terms of cell performance is the conductivity of the anode bus. This issue is presently being addressed in two ways.

1. Higher Ni content and differing particle morphology cermets are presently being evaluated.
2. Work has been initiated to apply lanthanum chromite bands along the length of the cell. This will allow the fabrication of longer length cells with a number of current take off positions or chromite bands along the length.

Initial investigations in to plasma spraying a chromite band took place at Sulzer on 08 24 04. This section deals with a more rigorous evaluation of the whole spraying process with investigation in to the following areas.

1. Sample Preparation

The following sample preparation parameters have been investigated:

- a. Surface roughness after grit blasting with different materials
- b. Part cleaning with compressed air and ethanol

2. Spray parameters

The following spray parameters have been investigated:

- a. Gun power
- b. Feed rate
- c. Cooling air
- d. Heating of the part prior to application

Sample Preparation:

Surface preparation is considered crucial to the successful application of a chromite band onto anode support tubes, particularly since overlap of the electrolyte surface is required to produce a leak tight cell. Adhesion between the electrolyte and the chromite is particularly difficult to achieve due to the fully dense, smooth nature of the electrolyte surface after sintering. To enhance adhesion of the chromite to the electrolyte and indeed the anode, grit blasting of these surfaces with different media, SiC 36 mesh and alumina 24 mesh was investigated.

The **Figure 3.2.K** below shows a tube that was grit blasted with both alumina and SiC, after which an evaluation of surface roughness was performed on each different surface preparation. Visually, both grit blasted surfaces appeared similar.

Figure 3.2.K Tube that was grit blasted with both alumina and SiC.

To estimate surface roughness, a basic mechanical profilometer was used. All surface profile values are quoted as the arithmetical mean deviation and are quoted in micro inches, see **Table 3.2.B** below.

Grit blast medium	Mesh	Nominal particle size (microns)	Average of three readings (micro inches)	Comments
Control	Control	Control	23	Bare tube, no grit blast
SiC	36	500	147	
Alumina	24	710	125	

Table 3.2.B Surface profile values

The table above shows that grit blasting with either SiC or Al_2O_3 significantly roughens the tube surface. The roughest surface profile was however attained with the SiC grit, even though this grit is smaller in particle size than the alumina.

All following surface preparation of tubes utilized SiC grit as this gave the roughest surface after blasting, thus allowing a greater propensity of the sprayed coating to key in to the anode substrate and electrolyte. At this stage, any potential issues with Si contamination of the electrolyte due to the grit blasting medium have been ignored.

The majority of tubes used for evaluation in these coating trials had a band masked off in the electrolyte coating process which after firing resulted in a break in the electrolyte half way along the tube length.

To prepare these tubes for coating, the pieces were first wrapped with tape either side of the intended grit blast region to protect the area of electrolyte which after coating would not be covered with chromite, see **Figure 3.2.L** below.

Figure 3.2.L Anode and electrolyte areas to be grit blasted

The sample was then hand grit blasted using SiC grit for a pre determined time period. **Figure 3.2.M** below shows the roughened surface, note the roughened narrow electrolyte bands either side of the bare anode tube, which provide the chromite/electrolyte overlap area.

Figure 3.2.M Roughened surface which provide the chromite/electrolyte overlap area.

After grit blasting the masking tape was removed, any excess dust was then blown from the tube using compressed cylinder air. The area to be coated then went through a final cleaning process with ethanol before spraying.

Plasma Spraying

In the previous plasma spray trial, masking tape was used to define the spray area, this resulted in a thickness step change between the electrolyte and the chromite. To achieve a gradient at the edges of the spray profile, a masking device was fabricated. This consisted of a steel plate, which had a square orifice cut in to it. The dimensions of the orifice were 30mm in length and 25mm in width. This produced a band on the tube which was nominally 30-31mm in length. Tubes sprayed utilizing this steel masking device had a gradual tailing off of the chromite band towards the edges of the spray profile, creating a much improved coating in terms of visual integrity at the edges of the of the spray path.

The spraying setup utilized is shown in **Figure 3.2.N**. The tube is clamped in the rotational fixture behind the steel masking device. The test piece was then spun at 1700 rpm and the gun traced out the path shown by the white arrows during spraying.

Figure 3.2.N Spraying setup

After setting up the fixturing, a number of samples were then sprayed to test the masking device. It was found that if the test piece was positioned at a distance of 3-5mm behind the masking device, an evenly coated tube resulted with what appeared to be a smooth tail off of sprayed powder at the extremities of the band.

Figure 3.2.P below shows a x-sectional representation of the as sprayed chromite band which overlapped the electrolyte by 5mm on either side.

Figure 3.2.P X-sectional representation of the as sprayed chromite band which overlapped the electrolyte by 5mm on either side.

After setting up the fixturing, a number of tubes were sprayed using different spray parameters in an attempt to optimize the bonding between the chromite and the anode substrate, these parameters include:

- a. Gun power
- b. Feed rate
- c. Cooling air
- d. Heating of the part prior to application

The **Table 3.2.B** below shows different conditions investigated and the spraying regime that each particular tube under test experienced during coating.

Test #	Tube Number	Gun Power (kW)		Feed Rate (g/min)		Cooling Air		Heat Tube (Number of torch passes)	
		22	30	13.5	6.2	On	Off	2	10
8	1.B390064		•		•		•		•
Electrolyte Coated Tube									
10	2.B390065	•			•		•		•
Electrolyte Coated Tube									
9	3.B390135	•			•		•		•
Electrolyte Coated Tube									
6	4.B320001		•	•			•		•
Electrolyte Coated Tube									
3	1.B320002		•	•		•		•	
Electrolyte Coated Tube									
7	2.B320003		•		•	•			•
Electrolyte Coated Tube									
2	1.B320005		•	•		•		•	
Electrolyte Coated Tube									
1	2.B320006		•	•		•		0	0
Electrolyte Coated Tube									
4	1.B320007		•	•			•		•
Electrolyte Coated Tube									
5	1.B320008		•	•			•		•
Electrolyte Coated Tube									
12	B390048		•	•		•		0	0
Bare NiO Tube									
11	B390042		•	•		•		0	0
Bare NiO Tube									

Table 3.2.B Conditions investigated and the spraying regime that each particular tube under test experienced during coating.

During the spraying trials outlined above, a study was also undertaken to determine the temperature that the actual tube was heating up to immediately after the preheating and coating stages with and without cooling air present. All temperatures were measured with an IR probe immediately after the torch had moved away from the piece, see **Table 3.2.C** below.

Tube ID	No. of Preheat Passes	Tube Temp °C	Air on/off in Preheat	No. of Coating Passes	Tube Temp °C	Air on/off in Spraying
B390124	2	52	On	0		
	10	74	On	0		
	10	121	Off	0		
B320007	10	121	Off	20	107	On
B320008	10	121	Off	20	138	Off

Table 3.2.C All temperatures were measured with an IR probe.

The data in the table shows that the largest differences in tube surface temperature occur as a result of the cooling air being on or off. The values in the table should only be used as a relative measure as it is known from empirical evidence that the tube cools very quickly after the torch has passed by and therefore it is likely that actual local temperatures experienced by the tube at its surface will be much higher.

The history of each tube coated under the different spraying regimes outlined in the table above will now be discussed in greater detail.

Resistance measurements at temperature have been carried out on B320008 and B390135. Measurements were taken on the as sprayed tube through heating to 800°C in 100°C increments. After equilibration at each particular temperature had been reached the resistance was measured by the four point probe method, from which the conductivity was calculated, see curves in **Figure 3.2.Q** below.

Figure 3.2.Q Resistance was measured.

Neither B320008 nor B390135 tubes underwent any sintering step to ensure that the applied chromite was dense before resistance measurements were taken. After testing for resistance, tube B320008 was removed from the furnace at 180°C at which point it was noted that the chromite coating was fully intact. After 10 minutes of cooling outside the furnace, the coating delaminated from the tube aggressively, causing flakes of chromite to be ejected from the surface. Tube B390135 was left in the furnace until completely cool after resistance testing, thus negating any thermal shock issues which may have occurred with B320008. On inspection of the tube, the chromite was again delaminated from the anode. Both these tubes underwent different spray conditions for chromite application. Tube B320008 had a utilized a gun power of 30kW and a feed rate of 13.5 gmin⁻¹ whilst tube B390135 utilized a gun power of 22kW and a feed rate of 6.2 gmin⁻¹.

Tube B320001 was also tested for resistance in the same way, showing a conductivity of 19.7 S/cm at 800°C, the chromite coating again delaminated from the tube upon cooling.

Subsequent tubes for conductivity testing were subjected to thermal treatment up to 1400°C for two hours. This was to determine whether the chromite density and also the bond between the chromite and the substrate could be enhanced.

During thermal treatment of tubes B320003 and B320006 to 1400°C for two hours, the chromite layer delaminated from the grit blasted electrolyte surface, see **Figure 3.2.R** below of B320006. The chromite however appears to be well attached to the grit blasted anode surface, inferred by the clear demarcation lines between the two different surfaces.

Figure 3.2.R Chromite layer delaminated from the grit blasted electrolyte surface

It should be noted that tube B320003 had 10 torch passes before spraying while B320006 was processed without preheating the tube before spraying. This is noted since it has been considered that the reducing nature of the plasma could be reducing the surface NiO to Ni upon preheating. Subsequent thermal cycling of the tube in oxidizing conditions would then lead to conversion back to NiO and therefore delamination of the chromite coating due to the commensurate lattice expansion. This does not appear to be the case however since the chromite in contact with the anode on tube B320003 appears intact after thermal treatment in an oxidizing environment.

Post spraying heat treatment at 1400°C for 2 hours, appears to result in a chromite layer which does not delaminate from the anode substrate but does delaminate from any areas where electrolyte is present even though both surfaces have been grit blasted.

To investigate this further, a number of tubes without electrolyte coatings were sprayed with chromite, and as such the chromite contacted only NiO. After plasma spraying, two of these tubes B390042 and 48 were then thermally treated to 1400°C for 2 hours, after which, there was no evidence of delamination on either tube, see **Figure 3.2.S** below of B390042.

Figure 3.2.S No evidence of delamination on either tube

Both cells were then resistance tested using the four point probe method at increasing temperature increments up to 800°C. The following temperature resistivity curves were obtained.

Figure 3.2.T Resistance was measured.

The first point to note is that the initial resistivity data point at room temperature is significantly below that observed for the samples tested as sprayed, tubes 320008 and 390135 described above. This suggests that an appreciable amount of sintering of the chromite layer has taken place upon heat treating the tubes to 1400°C for two hours, resulting in increased conductivity. Indeed the conductivity of both tubes at 800°C also shows a significant increase over the conductivity of the as sprayed tubes B390135 and B320008. There was no evidence of chromite delamination on either tube after resistance testing.

Due to the improved delamination resistance upon thermal treatment described above, tube B390042 has been sectioned for micro both at Sulzer and Acumentrics to verify coating thickness, integrity and porosity. Results from these investigations will be reported at a later date. Tube B390048 is being utilized for silver current collection evaluation over time, results from this trial will also be reported at a later date.

Tubes B390065, B320007 and B320005 were submitted for micro analysis. All three samples were cut in half through the band, one half was then investigated without further processing while the other half was heat treated to 1400°C. Upon heat treatment, the chromite coated on top of the electrolyte again delaminated to some extent but as expected the chromite in contact with the anode remained intact, see **Figure 3.2.U** below.

Figure 3.2.U Tubes B390065, B320007 and B320005 micro analysis.

Tubes B390065 and B320007 were investigated at Acumentrics while tube B320005 has been sent to Sulzer for evaluation. Micro results from Sulzer have not yet been received and as such will be discussed in a subsequent report. Acumentrics micro report detailing findings from the plasma spraying of these two cells has however been completed

This report suggests that the chromite layer is highly porous in the as sprayed condition, with little change in appearance upon heating to 1400°C for two hours. This observation does not appear to be in agreement with resistance data outlined above, which shows a significant improvement in conductivity upon thermal treatment.

Microscopy also suggests poor adhesion/contact between the chromite and electrolyte, this agrees with empirical data already discussed. Further, it has been noted that between the chromite and anode, there appeared to be the presence of a 'trough', providing a clear delineation between the two different layers. This trough may be a high porosity region, but it was evident throughout at the interface, indicating poor contact between the chromite and the anode.

Thermal Expansion Coefficient (TEC)

It has been considered that one reason for the chromite delamination upon thermal treatment is due to a thermal expansion mismatch between the chromite layer and the other cell components which the chromite contacts. Such materials include the anode and the electrolyte which have both previously been evaluated for thermal expansion and have the following TEC values.

Acumentrics cermet (Ox)	$12.1 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
Acumentrics electrolyte	$10.4 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$

To estimate the TEC of the chromite used in the plasma spray trials, the as delivered powder was pressed in to a bar, 1 inch in length, then fired in a dilatometer to 1500°C. The trace below **Figure 3.2.V** shows the shrinkage of the bar upon firing. It should be noted that the sudden dip in the curve at 250°C corresponds to binder burnout from the sample.

Linear Shrinkage of LaCaCrO₃ Bar

Figure 3.2.V shrinkage of the bar upon firing

The sample was then evaluated for TEC in an air atmosphere up to 1000°C, the resulting percent linear change curve is shown **Figure 3.2.W** below.

% Linear Change of LaCaCrO₃ With Temperature

Figure 3.2.W percent linear change curve

From this data the TEC was calculated and found to be in the region of $9.3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, low with respect to the anode substrate. Is desirable to have all ceramic cell components as close as possible with respect to TEC and as a general rule within 20% of each other. This particular chromite formulation exceeds this desirable value. Ideally a chromite would be

utilized with the same TEC as the electrolyte to ensure no mismatch between the two materials upon thermal cycling of the cell.

In Summary:

- The masking device used for all trials was successful in that a smooth taper was observed at the edges of the spray profile.
- No delamination of the chromite band could be determined visually on any tube post spraying.
- Resistance testing at 800°C of the as sprayed chromite layers showed conductivity values in the region of 14 – 19 Scm^{-1} for the tubes that were evaluated.
- Upon cool down from resistance testing, the chromite layer of the as sprayed tubes delaminated from all areas whether in contact with anode or electrolyte, regardless of the spray conditions employed.
- Thermal treatment to 1400°C for two hours after spraying resulted in a chromite band which delaminated from areas in contact with the electrolyte only upon cooling. Any chromite in contact with bare anode remained adhered to the tube regardless of the spray conditions employed.
- Upon thermal treatment to 1400°C for two hours after spraying, the chromite conductivity at 800°C increased significantly to nominally 30 Scm^{-1} , suggesting some densification of the sprayed layer. This conductivity value agrees well with literature values quoted in air.
- The integrity of thermally treated coatings was good even after the thermal cycle experienced during resistance testing.
- The TEC of the chromite material has been estimated to be $9.3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, lower than the electrolyte and therefore not ideal.

Future Work:

Future work will focus upon addressing the delamination of plasma sprayed chromite from the electrolyte overlap region during thermal cycling. To this end, further plasma spray trials are being arranged at Sulzer.

A roughened electrolyte surface in the chromite/electrolyte overlap region is presently being investigated at Acumentrics. It is considered that this roughened surface will allow the chromite to key into the electrolyte more successfully upon spraying.

Full sintering of the tube after thermal spraying will also be investigated. This will be achieved by firing the electrolyte coated tube below the usual 1510°C to retain a small amount of shrinkage in the tube which after spraying with chromite can be utilized to help densification and adherence of the applied layer to the substrate and electrolyte.

A strontium doped lanthanum chromite plasma spray powder will also be procured and evaluated. There are several reasons for evaluating Sr as an A site dopant in addition to Ca, these include:

1. Sr doping has a greater effect on the TEC of LaCrO_3 than Ca doping and as such the resultant TEC should be a closer match to that of the electrolyte.
2. The expected isothermal expansion under reducing atmospheres for Sr doped LaCrO_3 is less than that observed for Ca doped material.
3. Sr doped LaCrO_3 also has improved mechanical strength in reducing environments.

Subtask 3.3 – Generator Design

CPOX System Configuration

Based on the experience and results obtained with water recovery/reinjection systems to obtain fuel steam reformation, a further investigation into the design and performance of a simplified partial oxidation system was initiated. It is believed that in situations where overall efficiency (thermal + electrical) is paramount, the partial oxidation system can meet the goals at a lower installed cost than a water recovery/reinjection system.

An updated energy balance for the POX configuration has been prepared and system statepoints for a range of cell and system operating conditions has been generated. The **Figure 3.3.A** below shows the process schematic along with temperatures at key points in the process for a chosen load condition and cell v-j curve.

Cell Voltage	0.752	Current	9.49	DC Power	3596.5
No of Cells	504	Gen Eff AC	29.07%	Gen Eff DC	34.85%
Fuel Utilization	0.7	O/C	1.2	Heat Loss	13.14%
K Factor	2.8	% Reform in Reactor	100	Flue Loss	29.85%
Heat Loss (w/m^2)	300	Air Stoichs	6	Therm Recov	21.26%
Power	3000	Offgas in DC %	0	Energy Close	99.10%
BOP Power	250	Heat Exchanger Eff	0.839		
Slope	-2			Anode Fuel (lpm)	17.0
En	0.900	Gen Eo	75.6	Cathode Air (lpm)	680
Cell Temp	800	Gen V	63.2	Burner (lpm)	0.3

Figure 3.3.A The process schematic along with temperatures at key points in the process for a chosen load condition and cell v-j curve

An air preheater to preheat the incoming anode air utilizing the exhaust flow leaving the recuperator was designed. As shown in the **Figure 3.3.B** below, the unit uses a single tube, serpentine arrangement and will be located in the exhaust hood directly below the hot water coil. Air preheated to 300 C will then be mixed with natural gas leaving the desulfurizer.

Figure 3.3.B Air preheater to preheat the incoming anode air utilizing the exhaust flow leaving the recuperator

An air/fuel mixing tube and stack manifold system was also designed to deliver the anode air-fuel mixture to the POX reactors at the base of each stack. Ambient temperature pressure drop versus flow measurements (see **Figure 3.3.C** below) were taken for the anode side components for the baseline POX configuration. The component configuration is shown in the **Figure 3.3.D** below. Mixing studies were also conducted to verify that adequate mixing of the anode air and fuel streams is accomplished in the mixing line to ensure a uniform O/C ratio to each of the stacks.

Figure 3.3.C Ambient temperature pressure drop versus flow measurements

Figure 3.3.D component configuration

Fuelcell Module Test

A four stack, integrated FC Module test was conducted to prove out the baseline POX configuration and obtain system performance data. The **Figure 3.3.E** below show the module during the final assembly stages. This module contained the first implementation of anode tube POX reactors at the base of the stacks, an air preheater for the anode air, individual offgas sparge tubes below the recuperator and an ambient temperature desulfurizer. The module was operated continuous for 48 hours. The **Figure 3.3.F** below shows the average and minimum manifold voltages for each stack along with the corresponding current. As can be seen in the graph, there were several times during the test that load was removed. Several of these load removals were a result of system shutdown cause by faulty thermocouple readings. Stack (cathode air) thermocouples which enter the stack area through the cell end wall and essentially rest on the cells have a tendency (although fully ceramic sheathed) to pick up stack voltage and therefore give a faulty temperature reading. A design change was implemented in which all stack thermocouples enter the cathode air chamber through the manifolds. This allows the thermocouples to be fully supported and no longer come in contact with the cells.

Figure 3.3.E FC Module during assembly, 4 stacks, 21 Manifolds per stack

Figure 3.3.F FC Module Manifold Voltages and Current

The **Figure 3.3.G** below shows the load curve during the second half of the test operation after initial start up problems were overcome and stable operation was obtained. Also shown below is the recuperator effectiveness and the status of the startup burner valve. This shows that even at these relatively low powers, thermal balance was achieved. Also shown on this curve is the cell fuel utilization which was maintained at approximately 55%.

Figure 3.3.G FC Module Load Curve

Recuperator Performance

A second, four stack FC module test was conducted to further characterize the performance of the stacks and the integrated system. System operation was stable over the course of the 300 hour test but a flow imbalance to the stacks limited generator power output and resulted in ultimate shutdown of the system due to low manifold voltages in the right hand stack. The **Table 3.3.A** below gives the individual manifold voltages for the four stacks along with the stack averages. Analysis of the stack inlet and outlet anode gases showed that the outboard stacks (left and right) were operating at a higher fuel utilization than the inboard stacks (left/ctr and right ctr). With a fuel utilization of 50% as calculated by the measured stack current and input fuel and air flows, the stack fuel utilization from left to right based on the inlet to outlet gas composition change was 65, 57, 57 and 82%.

Pressure measurements of the anode fuel system further lead to the conclusion that a flow imbalance to the stacks was the cause of the low stack voltages. The **Table 3.3.B** below shows the fuel manifold and stack pressures at both operating temperature and at ambient temperature. It is unclear what caused the flow imbalance; the system will be inspected to evaluate the problem.

Stack Baffles

To date the area between adjacent stacks has been filled with insulation board to prevent cathode air from bypassing the cells. This space between cells is a result of the fact that the cells can not be located to the extreme edges of the manifolds, due to the compression rods and chamber wall thicknesses, and also because run out of the cells due to brazing and machining tolerances requires additional clearance to prevent adjacent cells from contacting. The insulation board has proved troublesome and costly since it must be custom fitted to the gap, has significant organic binder, is very friable if not supported rigidly and is heavy. A baffle design was devised to eliminate the need for the partition walls. As shown in the **Figure 3.3.H** below baffles which overlap with the adjacent stack were added to the cooling manifolds to serve as flow restrictors to the cathode air in this region. The baffles are secured to 3/8" tubing which extends the length of the cells and which in turn is secured to a attachment block welded to the cooling manifold.

Figure 3.3.H Baffles which overlap with the adjacent stack were added to the cooling manifolds to serve as flow restrictors to the cathode air in this region

The stack baffles were installed on a four stack, FC Module and tested. Stack temperatures were acceptable and there were no problems with shorting to the metallic baffles.

Stack Support

Thermal cycling of stacks in the stack tester and as an FC Module has shown that the stack support system currently used has not provided sufficient unrestrained vertical movement of the stacks while allowing too much lateral movement. A simple, leaf spring arrangement has been designed, built and tested which can eliminate the shortcoming of the existing pin design. The pin design, as depicted below **Figure 3.3.J**, was prone to binding due to differential thermal expansion and the side loading placed on the pin by the cantilevered cells. Once binding occurred permanent distortion of the support structure or the stacks themselves was possible resulting in opening of the manifold sealing gasketing and/or damage to cells, plenums or structural insulation.

Figure 3.3.J Pin design

The spring support, in conjunction with locking the base of the stack to the stack supports with a set screw arrangement, assures that the stack is free to expand without permanently distorting the support structure. An added benefit is that the thin nature of the support reduces the heat loss to the support frame.

Figure 3.3.K Spring support, in conjunction with locking the base

A four stack, FC module was equipped with the baffles and stack support design changes and tested. After several thermal cycles and 300 hours of operation the stack supports were functioning well.

Power Lead Connection

Since the output terminals of the stack are non-cooled and operate at approximately 125°C, the degradation of the contact resistances may be significant. Up to this point, tin-coated copper terminals have been used, but this temperature is at the extreme end of the recommended operating temperature for tin terminals. Thus an experiment was set up to pass a current (60 A) through two different connector geometries, at 125°C, and measure the voltage drop across each part of the connectors, over time.

A 3/8" diameter nickel 200 rod was machined with 1" of 3/8"-16 thread on each end. At the base of one end of the thread, a nickel washer (back plate) was welded on. The photo below **Figure 3.3.L** shows the basic geometry of the two connections.

Figure 3.3.L Geometry of the power lead connections

The connection on the left of the figure consists of a brass nut, Belleville[®] washer, brass washer, tin-plated copper terminal, brass washer and brass nut. This connection was torqued to 80 lb-in.

The connection on the right consists of a nickel backing washer, tin-plated copper terminal, stainless steel washer, Belleville[®] washer and a stainless steel nut. This connection was also torqued to 80 lb-in.

Figure 3.3.M Close-up of the two connection geometries

Testing of the power lead connection was carried out throughout the reporting period. The Figure 3.3.N below show the connection resistance with time. After 1560 hours and 18 thermal cycles, the resistances are stable. It seems that the contacts will be stable under these conditions within a fuel cell unit. The lowest resistance connection is the one utilizing the nickel-backing washer. Testing will continue for a total of 2000 hours.

Figure 3.3.N The connection resistance with time

Chromite Interconnect Stack Configuration

Stack/generator layouts which utilize a chromite interconnect layer at various positions along the length of the cell have been investigated. A key component of this current collection arrangement is the fact that it is unnecessary to carry current through the fuel/offgas manifold which can greatly simplify the stack configuration. If the cells are electrically isolated from the manifolds, as discussed in Section 3.4, then a common manifold can be utilized. Alternatively, individual manifolds made from sheet metal or extruded shapes can be utilized.

The **Figure 3.3.P** below depict a stack layout wherein the cells are electrically isolated and individual manifolds are connected to fuel and offgas rails. The cells are positioned in a vertical configuration and the manifolds are spaced to allow cathode air to flow upwards from a plenum below the stack. Not shown in these models is the interconnect that would create the series and parallel electrical connections along the length of the cells

Figure 3.3.P Stack layout wherein the cells are electrically isolated and individual manifolds are connected to fuel and offgas rails.

Steam Generator/Superheater

Failure of a steam superheater on a steam reformed propane generator resulted in shutdown of the generator. The loss of steam prior to steam/fuel mixing lowered the actual O/C ratio which caused carbon formation and eventual plugging of the steam reformation reactors. The **Figure 3.3.Q** below shows the pressure drop versus flow data for the reactors after operation with the incorrect O/C ratio (Original Catalyst) and after the reactors were refilled with new catalyst.

Figure 3.3.Q The pressure drop versus flow data for the reactors after operation with the incorrect O/C ratio

In this generator, each reactor was connected to two 20 manifold, 100 cell stacks and the imbalance in reactor flows resulting from uneven plugging of the catalyst beds caused a shutdown of the generator on low voltage in one of the stack assemblies.

A photograph of the failed steam superheater is shown below **Figure 3.3.R**. As can be seen in the photo, a cracked developed near a weld joint where the tube wall was thinned due to the undercutting of the fill material in the weld heat zone. A thin wall, 0.020" wall, half inch Inconel 600 tube was used for the steam collection header. Not only is this where the failure occurred but there was considerable distortion of the headers due to the thermal stress induced by the welding and during thermal cycling of the generator.

Figure 3.3.R Failed steam superheater

A new superheater was manufactured and a field replacement completed. The new superheater was made with 0.035" wall headers and the heat transfer tubing was changed from 3/8" to 1/4" OD to improve the weld joint between the tubes and headers.

Although field replacement of the cracked steam superheater (and catalyst) was carried out successfully, system performance of the steam reformed propane generator could not be returned to its original condition as a result of a number of factors. The most likely factor is that more cells than originally suspected, and field replaced, were damaged due to operation on inadequately reformed propane or perhaps due to an imbalance in fuel flow to the stacks. Secondly, it is possible that carbon deposits in the cell injector system resulted in uneven fuel flow to the individual cells within a manifold. This imbalance results in fewer cells carrying the load as well as damage to the cells that have a shortage of fuel. Thirdly, the generator experienced an excessive number of starts and stops at times with inadequate cover gas to protect the cells. These thermal cycles along with possibly further degrading the cells, probably resulted in premature degradation of the temperature sensing thermocouples, voltage sense connections and current collection connections.

The Exit Glacier generator is being returned to Acumentrics for rebuild and additional laboratory testing. This will be performed the first quarter of '05 and the unit will be returned to the site in the spring of '05. Although, a thorough inspection must be performed to determine what is required to properly refurbish the unit, it is anticipated that the cells will be replaced, fuel injectors cleaned, catalyst replaced, and thermocouple and voltage sense instrumentation upgraded.

In addition, the control software will be upgraded with our latest version which is much more robust and operator friendly. One of the ongoing difficulties has been the difficulty in implementing changes to the operation of the system due to the inflexibility of the code compounded by the remote site location (no telephony). The new software platform which is under development will address many of these shortcomings.

The water system will also be improved to ensure that the system is operating at the correct steam to propane ratio. A feedback control of the water will be added which was not available when the unit was shipped but has been laboratory tested over the last few months.

Offgas Recirculator

As described in the semi-annual report a regenerative blower was modified to permit elevated temperature operation and sealing between the blower housing and the shaft. This blower was operated for approximately 400 hours to obtain blower performance data and to evaluate the integrity of the shaft seals and bearing system. A cut away schematic of the blower is shown below. There was no obvious degradation of the blower components and a pressure test of the shaft seal showed that the seals were in good shape with approximately 20 mlpm at 10" w.c. (ambient temperature and zero shaft rpm). There was some indication that the primary shaft bearing had rotated relative to the bearing housing but this did not apparently cause misalignment of the shaft.

Figure 3.3.S Regenerative blower

Figure 3.3.T Static leak check

The blower was re-assembled and operated for another 500 hours. As described in Section 1.4, the blower and associated heat exchangers have been installed on a stack tester to permit closed loop, integrated operation of the system. Testing of the system will be carried out during the next reporting period.

Subtask 3.4 – Manifold and Cap Development

Braze Joint Development

An experiment was done with various Cu compositions to determine the effect of dual atmosphere with current on Cu. The goal was the identification of possible alloys for use in brazing, manifolds, injector tubes, or other applications. It is generally well understood that Cu forms an oxide layer that does not remain in intimate contact with the bulk Cu, and scales. Brazing with Cu, however, has been successful for over 2000hr in cell testing at this point, suggesting that even slight improvements to the Cu material through doping might have substantial positive impacts for fuel cell systems. In addition, if a scale could be formed that adhered to the Cu, there might be potential for use as a manifold where a low material loss rate is acceptable.

Figure 3.4.A completed setup for the Copper Alloy Experiment

The above **Figure 3.4.A** represents the completed setup for the Copper Alloy Experiment. The left hand side of the setup has a threaded nipple that will serve as the inlet for gas transportation through the entire set of specimens. The samples are numbered 1-13 from the left going right in this picture. The composition of the samples was as follows:

In the test, the temperature was held at 800°C, 19A were applied along the length, and 97%H₂/3%H₂O was flowed through the inside with air on the outside. After 250hrs testing, the samples were removed from the furnace and appeared as follows:

Figure 3.4.B Samples were removed from the furnace

where the Ni is now on the left. Tremendous amounts of scale were noted to have fallen from the samples. The two samples that appeared to oxidize very slowly are numbers 4 and 10, Be-doped Cu. Both appeared to provide substantial oxidation resistance. All the others clearly were worse, with the pure Cu scaling into a powder that easily fell from the sample.

The parts have been removed from the furnace and cut. They will be measured and weighed to determine roughly the amount of Cu lost to the furnace, and cross-sections polished to see the effect of dual atmosphere.

1/4" NPT cups

Six cells were brazed into 1/4" NPT threaded cups with a large bore opening. The results were mixed. Although the cups appear to be easily brazed, the balance of the gas appears to be blowing the Cu braze material, from the inside, out of the cup. This results in acceptable contact, and sometimes acceptable leak, but little Cu at the joint. Because of this, a new fixture is being designed that will reduce the flow to the inside of the cell to levels previously found in the standard 1/8" NPT cups. That fixture should be completed in the upcoming month.

The question of the brazing atmosphere has come into question with the determination of the outlet braze cup viability. 5%H₂/Ar was used originally to provide a reducing atmosphere for the brazing operation. Due to safety concerns, the mixture was changed to 3%H₂/Ar, at the same flowrate. While not a large change, it is clear that the cups after brazing exhibited more tarnish, suggesting NiO formation, and possibly O₂ penetration into the system.

An experiment has been started to utilize 5%H₂ again to determine its effect on cup integrity. Eight cells were brazed with cups in the 5%H₂ mixture, showing no tarnish. Currently they are being thermal cycled, and results should be available within the next two months.

There appears to be an increase in the amount of water in the cells, leading to high apparent leak rates. The graph below **Figure 3.4.C** is the accumulated data for 42 cells. The "pumpdown" number is a correlated number describing the leak rate, which is done under a vacuum gradient. The cells, just after brazing, were checked for leak, leading to the distribution shown by the squares in the graph. Previously, a pumpdown of 275 was considered the cutoff point for poorly performing cells. After heating overnight at 120°C, the same cells show a very consistent distribution at a much lower overall leak rate. There was no overlap between the two groups.

Figure 3.4.C accumulated data for 42 cells

This phenomena is being explore to determine the best method of processing the cells, and trying to determine any changes that have occurred. Clearly, though, water in the pores of the cells appears to have an effect on the apparent leak rate of the cells after the brazing process.

Cu Be Experiment

In the Cu Be experiment, an individual SOFC was to be mated with an Outlet Braze Cup. (The amount of Be in the Cu Alloy is 2% by weight.) In the first braze attempt the welding gas mix was kept the same as for normal production runs. (This gas composition was 3% H₂ and 97% Ar.) The results were not as promising as expected. During the melting process of the Cu Alloy it was noticed that the materials that make up the Alloy had separated into their individual components. What was Cu melted into the cups and the Be ended up as a dry flaky substance sitting around the Outlet Cup edge. (See Figures below)

Figure 3.4.D: Cell Brazed with 3% H₂

Figure 3.4.E: Inside of Figure #1

In attempt to see if increased rates of H₂ would alleviate this problem the Welding Gas Mix changed to 5% H₂ and 95% Ar. Again the results were similar. The interior of the braze cup was not filled with the brazing material. (See Figures below)

Figure 3.4.F: Cell Brazed with 5% H₂

Figure 3.4.G: Inside of Figure #3

With these results, Be-doped Cu will not be used in brazing.

Inlet Cup Thermal Cycling

Currently the Inlet Cup Thermal Cycling Experiment is almost complete. The Thermal Cycler has completed the final series of tests, both 25 and 50 Cycles on separate Inlet Cups. Several conclusions can be drawn at this point in time: From the Single Thermal Cycle Test to the 50 Thermal Cycle Test the degree of Cu oxide formation has increased. The depth the Cu oxide has traveled down the electrolyte edge has increased, almost reaching the base of the inlet cup. However, the differences between 25 and 50 thermal cycles has yet to be analyzed.

Deep Drawn Cups Brazing Trials

Deep drawn outlet cups will decrease the current expense from \$5.18/Outlet Cup to \$1.22/Outlet Cup. A pseudo-validation process was performed on cups manufactured in house to have the correct wall thicknesses- the major concern with the new cups.

Figure 3.4.H Deep drawn outlet cups

Three experiments were performed:

Experiment #1: A single braze setup to test the feasibility of using the deep drawn outlet cup.

Result #1: A single brazed deep drawn outlet cup was successful on the first attempt. The Cu material wetted the SOFC properly.

Figure 3.4.J Braze Interface at 200 times magnification
(Cell#A220044)

Anode-to-anode resistance was observed to go down with the brazing of the deep drawn cup from 2.81m Ω to 2.79m Ω , probably due to the better contact.

Experiment #2: An eight-cell run was done to test the variability between braze positions.

Result #2: Two eight-cell runs were completed with no problems. The braze joints on these new outlet cups are no different than the braze joints seen on current production outlet cups.

Figure 3.4.K The crack observed is the construction of the pseudo-deep-drawn cup and the interface of the two parts to make the cup.

Experiment #3: Multiple eight-cell runs to test the viability as the system temperature became steady-state.

Result #3: The consecutive-run test also completed with no significant issues.

In conclusion, the pseudo-deep drawn cups appear to be braze-able. With the significant cost savings associated with them, there is no reason to not proceed forward with large-scale trials.

Currently a new leak checker is being created to decrease the time and effort consumed by the QC procedure while increasing its reliability. This device is the same one used by cell manufacturing and should help correlate QC values from the beginning to the end of SOFC creation. All necessary drawings for the device have been updated and the required parts have been placed on order. Most of the fabrication concerning the largest physical parts that make up the QC Device have been made or are in some of their final stages of completion. All that is required to finish the QC Device is to complete the machining of the smaller components that will test the SOFC's A-A and A-C as well as the Leak Checker's Fast Tester internal components. (A few ordered parts are still due to arrive, these parts are also needed to finish the QC Device.)

Quarter Inch NPTF Braze Cap and Deep Drawn Braze Cap holders were completed in the machine shop. Several runs were conducted to test the feasibility of using these new cups. The result ended with the completion of 24 Double Brazed cells containing both the .25" NPTF and Deep Drawn Brazing Caps. The brazing parameters for both these new cups remained constant with previous inlet and outlet brazing cap parameters. However, due to the inability to braze a large number of runs it is believed that some tweaking may be required to help increase the quality of braze joints produced during these tests.

MIM Manifolds and Caps

Tooling was manufactured for the metal-injection-molding of manifolds and caps. Initial trials for the braze caps revealed a difficulty in removing the part from the mold resulting in cracking of the green part. The cap design was changed to include a 0.5 degree draft on both sides of the outer cap wall and the tooling was modified. Another set of trial parts were manufactured using the modified tooling (0.5 degree draft on cap sides). Samples were received from the manufacturer and were determined to be acceptable from a dimensional standpoint. Additional caps will be manufactured to allow for braze trials. The photo below **Figure 3.3.L** shows a MIM cap.

Figure 3.4.L MIM cap

MIM manifolds were also produced and the results were encouraging. The initial quantity produced were made from stainless. An initial sintering trial of pure nickel manifolds was made with less than acceptable results but a good deal was learned regarding how the nickel material behaves especially its shrinkage characteristics. A second sintering trial of nickel manifolds was made and the parts came very close to meeting specification. The waviness of the gasket sealing surface is the primary concern. This is particularly pronounced at the thread wall where the large change in mass, at and between the holes, results in shrinkage differences.

Figure 3.4.M Nickel Metal Injection Molded Manifold

Additional sintering and inspection of MIM manifolds has led to the conclusion that incorporation of the NPTF threads without secondary machining will be nearly impossible. This is a result of the large variation of material thickness surrounding the holes which leads to uneven shrinkage and an oval hole. MIM manifolds will therefore be produced with only pilot holes for the threads and the threads will be post machined into the manifolds.

The MIM manufacturer, Flomet, has identified a machine shop which can perform the secondary machining operations on the MIM manifolds. Additional tooling has been manufactured to produce pilot holes in-lieu of threaded holes in the MIM part. Injection trials have been made and sintering of these parts will be accomplished during the next reporting period.

Further work will be performed on the gasketed cap design, which can provide the necessary sealing without a gas tight thread to thread fit. It is believed that a straight thread having the necessary engagement for a gasketed seal can be molded into the part.

Additionally the tooling will be modified to rectify the “knit line” by increasing the number of gates and gating to fill better and faster.

Deep Drawn End Caps

Cell end caps were manufactured by UTI Corporation using deep drawing technology. A photo of the cap is shown below **Figure 3.4.N**.

Figure 3.4.N Cell end caps

The deep drawn end caps were successfully brazed and the cells were incorporated into manifolds to permit operation of the caps in a five manifold module. The figure below shows the cells as attached to one of the manifolds. The subassembly has been on test for 325 hours without any problems.

Figure 3.4.P Deep drawn end caps

“Straight” Thread Braze Cap

Testing was performed to evaluate the performance of a “straight”, parallel thread on the braze cap instead of the NPTF threads currently utilized. It is believed that the straight threads, similar to spark plug threads, will be simpler to manufacture into the braze caps as well as the manifolds. The experimental setup consisted of a female 14 mm x 1.25 thread formed inside a thick-walled tube with a closed end. At the closed end a gas connection was attached. A plug (and C-section sealing washer) was screwed into the apparatus with a torque of 18 lb-ft and placed into a furnace. The setup was heated to 800°C with thermal cycling to room temperature every 24 hours. The gas (N₂) was flowed into the cavity of the setup and the pressure was monitored. The gas pressure was increased to 10” w.c. and the flow was observed. This was performed once every 24 hours (once per thermal cycle).

From the **Figure 3.4.Q** below it can be seen that the seal was gas tight (@ 10”w.c.) for 408 hours, before the seal was breached.

Figure 3.4.Q. Graph of leakage rate of C-section seal over time.

This experiment was repeated with a slightly different setup. The C-section seal was removed in favor of applying silver paint to the threads. The same experimental conditions were used for this experiment. The graph shows that this sealing arrangement only lasted two thermal cycles (48 hours) before leakage @ 10”w.c. was observed.

Figure 3.4.R(a) Graph of leakage rate of silver paint seal over time.

A third setup, using a mica gasket to provide a face seal is being tested. The experimental apparatus consists of a $\frac{1}{2}$ " threaded bolt with a mica sealing gasket that is screwed into a hollow fixture. Every 24 hours the experiment goes through a thermal cycle to 800°C. After the thermal cycle, a pressure test is performed by pressurizing the inside of the fixture, at room temperature, to determine the integrity of the mica seal. This sealing setup has an additional advantage of providing electrical isolation with simple modifications, if it becomes necessary with future designs.

The straight thread-mica gasket configuration has been on test for the bulk of the reporting period, accumulating 2112 hours of operation and 88 thermal cycles. There is still no leakage at 10" w.c.

Figure 3.4.R(b) Graph of straight thread-mica gasket configuration.

Manifold Material Investigation

In an effort to find a lower cost alternative to nickel manifolds, an investigation of the suitability of lower grade stainless steels with and without protective coating has been initiated. With the planned use of chromite interconnects along the cell, the need for the manifold to serve as an electrical conductor will be eliminated affording some additional manifold design flexibility.

Iron aluminides are well known to have excellent oxidation and sulfidation resistance due to the formation of an external, protective alumina scale¹. Thus, an aluminide coating would be a good candidate for improving the oxidation/corrosion resistance of ferritic and austenitic steels, provided that it can be easily applied, mechanically sound and economical.

The aluminide coating is formed using a CVD process. AlCl_3 is formed inside a reaction chamber and heated to approximately 900-1100°C to vaporize the AlCl_3 and to obtain the appropriate reaction temperature. The vapor then coats the substrate material to form the intermetallic compounds ($\text{FeAl}/\text{Fe}_3\text{Al}$ or $\text{NiAl}/\text{Ni}_3\text{Al}$ for a nickel substrate)

Vapor Phase Aluminizing & Chromium/Nickel Plating

Two manifolds were fabricated from bar-stock. The materials were Type 304 and low carbon steel. These were aluminized using a chemical vapor deposition (CVD) technique at Sermatech[®]. The resulting manifolds were placed into a furnace and heated to 815°C for 65 hours.

Two more Type 304 manifolds were fabricated and plated with a 0.020" thick layer of chromium and the other was plated with nickel. The idea behind these two samples was to determine whether the increased concentration of chromium (or nickel) on the surface would form a sufficient barrier to oxidation at 815°C and thus provide an alternative method to aluminizing.

Figure 3.4.S (a), (b) & (c). Photograph of the aluminized manifolds made from 1018, Type 304 and Ni200/Type 309. (enlarge for clarity)

There were a number of defects present that required observation after the experiment to determine the extent of damage that they might cause. The 1018 manifold had three areas of interest where the aluminizing coating was not consistent.

Figure 3.4.T (a), (b) & (c). Defects present in the aluminized 1018 manifold.

The first photograph shows a shaded/matt area on the corner of the manifold. This was due to the manifold touching the fixture inside the coating furnace. The next photograph shows a definite line across the front face of the manifold, also due to the manifold resting on part of the furnace fixturing device.

There were three defect areas on the Type 304 manifold, again related to fixturing devices. **Figure 3.4.U.** illustrates these defects.

Figures 3.4.U (a), (b) & (c). Photographs showing the defect areas on the Type 304 manifold.

Post 65 hour Test Results

The results suggest that the aluminized manifolds withstood the rigors of oxidation at 800°C for 65 hours. **Figure 3.3.V** shows the manifolds after the test.

Figure 3.4.V (a), (b) & (c). Post-test photographs of manifolds (1018, Type 304, Ni/Type 309).

1018 Manifold

A number of irregularities can be observed. From the complete manifold photograph, various colors can be seen on the surface of the 1018 manifold. It is unsure whether this means varying thickness of coating or varying degrees of oxidation, or both.

Upon close inspection of the 1018 manifold, it can be seen that some of the coating might have spalled. The thickness of the coating at these points must be determined by cross-section examination, at the conclusion of testing.

Figure 3.4.W (a), (b) & (c). Photographs showing the various colors present and also the spalled coating.

The known pre-test defects also showed interesting results. Where the fixture had touched the manifold during the vapor deposition process, the coating was, to some degree, substandard. This conclusion was decided upon due to the oxidation that had taken place. **Figure 3.4.X** shows the action of the oxidative atmosphere after 65 hours at 815°C. The manifold showed a black oxide that formed a raised surface. This oxide is assumed to be iron-based due to the nature of the substrate.

Figure 3.4.X (a) & (b). Photographs of the known defects present on the 1018 manifold.

Type 304 Manifold

Given the overall uniformity of the color of the Type 304 manifold, it could be suggested that the coating thickness was more consistent, or, the coating had superior adhesion to the Type 304, compared to the 1018 material. The known pre-test coating defects showed much less degradation than the 1018 manifold. This was to be expected since Type 304 has a higher oxidation resistance than 1018. **Figure 3.4.Y.** shows the three defect areas.

Figure 3.4.Y (a), (b) & (c). Photographs of the known defects present on the Type 304 manifold.

Only one of the three defects showed any degradation of the substrate material (figure 7(c)). The corner of the manifold was resting on the fixture and produced a mark that faded out across the front face of the manifold. Not surprisingly, the black iron oxide was most obvious where the fixture was touching the manifold.

Post 2000 Hour Test Results

The manifold furnace test was continued to evaluate the long term oxidation resistance of the materials. A number of interesting observations were made over the course of the 2000-hour testing session. What became apparent after a relatively short time (270 hours) was that the

aluminized low carbon steel sample was continuously gaining weight (oxidizing). The oxide layer was getting thicker and eventually, the sample was removed from the test. The manifold had ‘exploded’ with oxidation, and was deemed a failure. The aluminized coating could not protect the sample. This was due to the mobility of the iron, penetrating through the alumina protective coating at 815°C (**Figure 3.4.Z**).

Figures 3.4.Z(a) & (b). Condition of the aluminized 1018 manifold after 630 hours at 815°C with 7 thermal cycle to room temperature.

The next least suitable sample was the nickel-coated Type 304 manifold. The nickel plating spalled off during the first thermal cycle, leaving a thin layer of a mixed oxide of nickel, chromium and iron. Subsequent thermal cycling eventually stabilized the sample weight after approximately 1350 hours. The surface texture of the sample was rough where parts of the original thick nickel plating were still attached (similar to 320 grit sandpaper).

Figures 3.4.AA (a) & (b). Nickel-plated Type 304 manifold after 2010 hours of thermal cycling to 815°C.

The final two samples were chromium-plated Type 304 and aluminized Type 304. Initially, most of the chromium plating spalled off in the first thermal cycle but the weight change

stabilized immediately afterwards. Subsequent thermal cycles did not change the weight much at all (0.14 g lost or 0.02% of initial weight).

The aluminized Type 304 gained 0.2 g (0.03% of initial weight) over the 2000 hours of the test. This is assumed to be the oxidation of the intermetallic aluminide on the manifold surface, producing the protective alumina coating.

Figure 3.4.AB (a) & (b). Chromium plated and aluminized Type 304 manifold after 2010 hours of thermal cycling to 815°C.

These last two samples are deemed to be successful. The chromium-plated manifold must be repeated with a thin (0.005") hard chromium-plating to verify the results.

Figure 3.4.AC. Weight gain of samples over entire 2000 hours of testing.

Pack Aluminizing

A number of Type 304 and 1018 low carbon steel samples were coated using a method called pack aluminizing. This consisted of either:

1. packing the samples into a powder and sintering, or
2. coating the samples with a slurry and sintering.

The samples used were Type 304 and 1018 low carbon steel. They were thermally cycled every 24 hours in air to 816°C. The aluminized Type 304 samples showed no sign of oxidation other than the protective alumina coating. However, the 1018 low carbon steel samples oxidized severely and were removed from the test at 1700 hours.

Figure 3.4. AD Pack aluminized samples before and after testing (type 304 are on the left of each photograph and the 1018 samples are on the right).

Sermatech[®] Samples

After 2028 hrs the first Type 304 sample had gained 0.0030 g and the second sample had gained 0.0015 g. This represents a weight gain of 0.03% and 0.02% respectively. This is considered an insignificant weight gain that can be attributed to the Al_2O_3 formed on the surface of the sample. No signs of oxide spalling were apparent.

After an initial weight gain attributed to the formation of the Al_2O_3 layer on the 1018 samples, the weight remained stable. At approximately 1000 hours into the test, the weight of both the 1018 samples began to rise, indicating the formation of more oxide. It was postulated that after 1000 hours, the iron in the bulk of the sample had penetrated through the aluminizing layer and had oxidized on the surface. This weight increase continued until the samples were removed from the experiment.

After 1668 hrs the first 1018 sample had gained 0.2949 g and the second sample had gained 0.4258 g. This represents a weight gain of 3.27% and 4.53% respectively. The aluminized 1018 was deemed a failure.

Figure 3.4.AE. Graph of weight change of Sermatech[®] pack aluminized samples after 2028 hours.

VaporKote[®] Samples

After 1308 hrs the Type 304 sample had gained 0.0340 g. This represents a weight gain of 0.10%. This is considered an insignificant weight gain that can be attributed to the Al_2O_3 formed on the surface of the sample. No signs of oxide spalling were apparent. The experiment is still active.

The aluminized 1018 sample commenced weight gain from the beginning of the experiment and did not stop until the sample was removed from the experiment after 858 hours. The sample gained 7.5359 g, which represents a weight gain of 19.65%. The aluminized 1018 was deemed a failure.

Figure 3.4.AF. Graph of weight change of VaporKote[®] pack aluminized samples after 1308 hours.

Control Samples

A set of control samples were also being tested. These consist of coupons of Type 304 and Type 309. After 800 hours and 8 thermal cycles, the weights of both samples have stabilized under the oxidizing conditions. **Figure 3.4.AG.** shows the initial high rate of weight gain (oxide layer formation).

Figure 3.4.AG. Stabilizing weight of the Type 304 and Type 309 over time at 838°C, with thermal cycling every 24 hours.

Conclusions

The vapor phase experiments showed that the aluminizing coating certainly improved the oxidation resistance for all the materials tested. The least conclusive was the 1018 low carbon steel, which initially showed signs of oxidation at the coating defects only, and eventually catastrophic failure of the whole sample after approximately 180 hours.

After 2010 hours, the most promising samples were aluminized Type 304 and chromium plated Type 304. Both of these samples withstood the rigors of a stack environment for the full length of the experiment.

In order to fully determine the most economic method between the aluminizing process and the chromium plating, another experiment must be performed with a more conventional chromium plating process and to assess the performance of this technique.

After 1308 hours, the pack aluminized Type 304 samples were still stable with respect to oxidation resistance at 815°C. These results show that the process of pack aluminizing forms a coating onto Type 304 that can withstand stack operating conditions.

The Type 309 (non-aluminized) sample also seems to be stabilizing. The Type 304 sample has shown a loss of weight at approximately 700 hours. This could be an indication of a spalling oxide layer. An extended length of time will determine the practicality of this material.

There is evidence to suggest that a manifold fabricated from Type 309 will withstand the stack operating conditions. However, the actual atmosphere within the stack is different (fuel-rich and also high steam concentration), thus long term stack testing is required for a definitive answer.

Oxidation Resistance of AL 347HP and AL 20-25+Nb at 800°C in Air

Two alternative manifold materials were selected for testing, under stack operating conditions, to determine if their oxidation resistance could withstand the rigors of the fuel cell environment.

A coupon of each material (AL 347HP & AL 20-25+Nb) was placed into a furnace and thermally cycled to 838°C every 24 hours, in air, and the weight change was measured.

After 1560 hours and 65 thermal cycles the AL 347HP had lost 0.0039 g (0.25% of total weight) and the AL 20-25+Nb had gained 0.0032 g (0.15% of total weight).

Figure 3.4.AH. Weight of Allegheny Ludlum alloys with thermal cycling every 24 hours to 838°C in air.

The AL 347HP is slowly losing weight and the AL 20-25+Nb is relatively stable. This experiment will continue for at least 2000 hours. At this stage both materials are stable enough to be used as manifold materials. Experiments using the fuel and exhaust gases from the stack must be implemented to ensure longevity of the materials.

Fuel Injectors

To date, the injector tube has been used to ensure uniform fuel flow to the cells by creating a significant pressure drop across the injector. This has been accomplished by sizing the tube outer diameter and wall thickness to the appropriate dimensions. A problem with this method is that for standard drawn tubing the combination of outer diameter tolerance and wall thickness variation can lead to significant inner diameter variation resulting in significantly different flow characteristics for individual injectors. Although this can be minimized by specifying the inner diameter, the ID is more difficult for the manufacture to hold and can lead to problems with pressing the injectors into the manifolds due to the varying OD. It is very expensive to maintain tight tolerances on both OC and ID.

The use of an orifice either machined into the manifold or built into the injector is a viable alternative to control the flow. In a first pass at testing this alternative configuration, a two manifold bundle was assembled which included orifice plugs at the end of the injector tubes. The orifices were sized at 0.035" diameter with a 0.150" hole depth. A 1/4" tubing with 0.035" wall was used in place of the 1/8" – 0.35" wall baseline injector. The photo (**Figure 3.4.AJ**) below shows the end of the injector tubes with the orifice plugs pressed into the tubes. Pressure measurements were during the bundle test to quantify the pressure drop. The graph (**Figure 3.4.AK**) below shows the pressure drop versus flow for the orifice operating under CPOX conditions. Also plotted is pressure data for 1/8" OD – 0.035" wall injecting tubing. In addition to the better cell to cell afforded by the orifice, the orifice also allow a simpler method to adjust the pressure drop as power levels and therefore cell flow requirements change. The orifice can be simply made larger whereas the injector tubing wall thickness and/or diameter must be changed making it a more difficult change since it can impact the braze cap design and the manifold design.

Figure 3.4.AJ End of the injector tubes with the orifice plugs pressed into the tubes

Figure 3.4.AK Pressure drop versus flow for the orifice operating under CPOX conditions

5 Manifold Assembly Testing

Testing of five manifold subassemblies continued to evaluate cell and stack component performance in a configuration approaching full stack conditions.

Tests were run on bundle 052604-1 (bundle tester 1, bay 3) to observe the oscillation response in the manifold voltage for natural gas at 1.7 slpm and 800C. Only load current was varied. No oscillation was observed up to 20A load. Small oscillations appeared at 30A. Full amplitude oscillations (50mV) occurred at 40A and up.

Figure 3.4.AL The manifold voltage for natural gas at 1.7 slpm and 800C

Tests were also performed to determine if there was a change in the voltage oscillation in response to a change in fuel from natural gas to a 50% H/50% N mixture. Both cases were run with the same bundle and bundle tester under similar conditions of 45% FU, 60A load, 800C. As shown in the plots below, the oscillation was present with both natural gas and hydrogen as the fuel source.

Figure 3.4.AM 60A, 45% FU, 800C

Five manifold subassembly test was initiated to evaluate the performance of a number of stack and cell design changes. The manifolds consisted of cells with 1/4" NPT braze caps and 1/4" injectors with 0.040" orifice plugs. Four of the manifolds had cells with deep drawn end caps. The bundle included a POX reactor and one 309 manifold. The 309 manifold was included in the test to determine whether it was possible to change the manifold material from nickel 200 to Type 309 without increasing resistive losses associated with the silver current collection tab-to-Type 309 manifold connection. If this is successful, a great cost saving can be realized. The bundle has been instrumented with additional voltage taps to evaluate individual component losses and make a better comparison to cell test data. The subassembly has been on test for 325 hours to date and the preliminary results reported in this report. The graphs below **Figure 3.4.AN** summarize the key operating conditions.

BT 12202004-1 Braid/contact losses at constant flow, ~830°C

BT 12202004-1 Cell voltages at 115A ($0.15A \cdot cm^{-2}$), 70% FU, ~800°C

Figure 3.4.AN the key operating conditions

The following diagram **Figure 3.4.AP** illustrates the contacts that were wired to the bundle test in order to procure the testing information. Each combination of connections allows a resistance to be measured and thus a loss to be calculated. Ultimately, every connection or lead will have a resistance and a degradation rate associated with it.

Figure 3.4.AP Schematic of the Bundle Test Setup

The resistance of the silver braid from the cathode to the silver tab was measured, using two of the cells in the top manifold. The voltage tap wires were connected at the silver tab crimp and at the cell-to-cathode junction. Measurements were taken at two different operating points to determine the effect of load on the resistance. The first graph **Figure 3.4.AQ** shows the characteristics of the resistance over approximately one week. At a load of 80 amps the resistance of one of the braids decreased, whereas the other was constant. At a load of 115 A the resistance of both the silver braids was decreasing.

Figure 3.4.AQ characteristics of the resistance over approximately one week

Figure 3.4.AR Cathode-to-Silver Tab Braid Resistance at 115 A, 70% FU and 800 Deg.C

The resistance of the path from the cathode end of the silver braid to the manifold was measured to determine the degradation associated with the Type 309 manifold due to oxide layer formation between the silver tab and the manifold. Path 8-12 was the resistance of the silver braid + Type 309-to-silver tab contact. The other three paths were the resistance of the silver braid + nickel-to-silver tab contact. The graphs show that for the Type 309 connection at 80 A, there is an increase in resistance, but for the case of 115 A load, there is a slight decrease in resistance. The nickel connections seem to behave in a more stable manner with minimal resistance change over the week of testing at 80 A. However, at 115 A, the silver-to-nickel connections show a much larger decrease in resistance over a week.

Figure 3.4.AS Cathode-to-Manifold Resistance at 80 A, 50% FU and 800 Deg.C

Figure 3.4.AT Cathode-to-Manifold Resistance at 115 A, 70% FU and 800 Deg.C

An analysis was performed on the manifold tests conducted in 2004, to determine the average performance curve in these tests. The first table shows a the test and the resulting Vj curve. All tests are five-manifold tests with six cells per manifold. FU was roughly calculated according to:

$$FU = \frac{\text{total current} \bullet 6.97 \frac{\text{sccm}}{\text{A}} \bullet \frac{1}{6} \frac{\text{manifold}}{\text{cells}}}{CH_4 \text{ flow} \bullet 1000 \frac{\text{sccm}}{\text{slpm}} \bullet \frac{1}{30} \frac{1}{\text{cells}} \bullet 2.85 \frac{\text{fuel by POX}}{\text{methane}}} \times 100\%$$

If the O/C ratio is incorrect, or reformation was used, this calculation would be in error. In general, however, so many points were collected that small variations should not effectively matter. Multiple FU ranges were obtained if possible. However, two ranges can show effectively the same data due to the fact the test may have been run on the edge of a range; points would be split mathematically at the same effective operating point.

X:\Manifold Test folder	a	b	FU range	#Manifolds	#cells/man
Test 012604	-2.3503	0.905	40%-50%	5	6
	-2.1509	0.873	50%-60%		
Test 040204	-3.2144	1.012	50%-60%	5	6
	-2.8882	0.971	50%-60%		
Test 040704-1	-0.9042	0.734	60%-70%	5	6
	-1.7814	0.848	50%-60%		
	-1.5549	0.816	40%-50%		
Test 042704-1	-3.361	1.005	30%-40%	5	6
	-2.489	0.920	40%-50%		
	-2.425	0.912	50%-60%		
Test 052604-1	-2.2894	0.838	50%-60%	5	6

1. It is not clear why the Vj curves for test 040704-1 are significantly better than all others. Likely the 60-70% FU data is not real, but the $-1.78\Omega\text{-cm}^2$ and $-1.55\Omega\text{-cm}^2$ slopes are on the order of 330mm 75%FU 800°C in cell testing.
2. The 30%-40% data of Test 042704-1 shows resistance increasing with increase fuel flow. This is not logical in past testing, indicating there is likely some temperature or current phenomena occurring that is not understood at this point.
3. The performance differences between the different FU and times for a single run have to be assumed to be roughly negligible. A second analysis will be needed.

If we average all the tests, we get an average 'a' of $-2.310\Omega\text{-cm}^2$ and a 'b' of 0.894V. If we neglect the unexplainable data of Test 040704-1 and the 30-40% data in Test 042704-1, we get an 'a' of $-2.544\Omega\text{-cm}^2$ and a 'b' of 0.919V. As a worst-case scenario, we use the lowest of the two values:

$$V = -2.544\Omega - \text{cm}^2 j + 0.894V; \quad j = \left[\frac{A}{\text{cm}^2} \right] V = [V]$$

On average, this is right in line with previously published results.

CPOX Testing

A partial oxidation reactor was designed, built and tested to evaluate the performance of a reactor meeting the design goals of rapid start up, low fouling capability, high conversion and low cost. The approach was to use standard anode cermet tubes in a configuration that could be an integral part of the stack geometry. The **Figure 3.4.AU** below shows the configuration of the prototype reactor. The reactor having the same manifold structure and footprint as the main stack assembly consist of four $\frac{3}{4}$ " tubes each containing an anode cermet tube. A $\frac{1}{2}$ " center tube delivers the preheated air/fuel mixture to the inlet plenum. The air/fuel mixture leaving the tubes is connected to chambers which in turn are connected to the stack fuel plenum. Also shown below is a photograph of the plenum end of the reactor. The stubs extending to the left of the plenum enable reuse of the reactor by simply cutting off the tubes ends and welding on new end caps once the reactor tubes are reloaded. The initial prototype was manufactured with 304 SS tubing which shows a good deal of oxidation after 150 hours of operation and several thermal cycles.

Figure 3.4.AU Configuration of the prototype reactor

For initial testing the reactor was installed on a 5 manifold, 30 cell bundle tester. The standard bundle test configuration was modified to permit bleed off of a portion of the reacted fuel from the assembly fuel plenum. In this way a full stacks fuel flow could be passed through the CPOX reactor without creating excessive back pressure which would occur if all the reactant was to pass through the cell injectors. The **Figure 3.4.AV** below show the bypass valve and bundle arrangement.

Figure 3.4.AV The bypass valve and bundle arrangement.

In addition to the normal bundle tester cathode air thermocouples above and below the bundle, additional thermocouples were placed down the center of an anode cermet tube, at the exit of the tubes, in the fuel plenum and in the cathode air directly above the reactor. Sample ports were also installed at the reactor outlet, manifold fuel plenum and the manifold offgas plenum.

After establishing baseline steady state conditions, the CPOX reactor air/fuel flow was varied and inlet and outlet samples taken for each condition for GC analysis. The natural gas conversion data for the test can be found in Section 5.1. After the initial round of sampling it

was established that the O/C ratio as measured by the control system (calculated using the air and fuel flowmeter calibrations) was high and this was corrected for and sampling performed again as the air/fuel flowrates were decreased.

The following figures (Figure 3.4.AW – Y) show some of the key process variables during the test operation. As shown in the graphs, after the initial round of flow setpoints and gas sampling the system was held at constant flow for approximately 100 hours before the flows were again varied and samples taken.

Figure 3.4.AW key process variables during the test operation

Figure 3.4.AX key process variables during the test operation

Figure 3.4.AY key process variables during the test operation

At the conclusion of the test campaign, the ends of the containment tubes were cut off and the anode support (AS) tubes were removed. The inlet ends of the AS tubes had a white color on the inside. The white coating was easily scratched off to reveal the gray cermet tube underneath. The white material extends approx. 2" into the inside of the tube. There is also a black oxide-looking area on the same ends of the tubes. Samples of the materials have been submitted for optical microscopy and SEM analysis.

Figure 3.4.AZ Tubes were cut off and the anode support (AS) tubes were removed.

Additional testing was conducted with the anode cermet POX reactor to verify the O/C ratio and to acquire conversion and selectivity data. This testing was conducted on Stack Tester #1 and prior to the test the air and fuel flow meters were re-calibrated. The **Figure 3.4.BA** below shows the methane conversion at the beginning of a test and 24 hours later. During this time period the o/c ratio was between 1.35 and 1.47 and explains some of the scatter in the data.

Figure 3.4.BA Methane conversion at the beginning of a test and 24 hours later

For each of the stacks described above, a POX reactor was installed at the base of the stack. On three of the stack tests, gas samples were taken at the reactor inlet and outlet to determine the performance of the POX reactors and to quantify the composition of the gas entering the stack fuel manifold. The methane conversion results for these tests are shown below.

Figure 3.4.BB methane conversion results

Additional testing was conducted with the anode cermet POX reactor to determine the long term stability of the reactor. This testing was conducted on Stack Tester #1. The system was run for approximately 400 hours before shutdown to inspect the reactor. The results of the testing is presented in section 5.1. After this long at temperature, it was not possible to unscrew the access caps to remove the anode cermet tubes so the caps had to be drilled out to remove the tubes. Different sealing approaches are being considered to provide a easier method for accessing the tubes.

Stack Testing

Shakedown testing of the stack tester was completed and four 21 manifold, 126 cell stacks were successfully tested. Each stack was brought up to temperature on purge gas, switched to natural gas/steam operation and loaded to approximately 80 amps.

Manifold resistances were recorded before and after each test as well as stack leakage rates.

The stack tester anode supply piping was modified to permit operation of stacks and test components on a POX fuel stream as well as a steam reformed fuel stream. The system was used to debug the generator control software and to evaluate transition behavior when switching from POX startup to steam reformed operation.

A re-test of a stack tested in November was undertaken to determine if there was a change in performance after several thermal cycles and several thousand miles of road travel. Although there was no obvious damage to the stack, it was clear from the state of the insulation package and verified with on an on board vibration monitor that the stack had seen significant vibration in traveling back and forth from Massachusetts to Idaho. The stack was

placed in stack tester #1 and a performance map obtained. The graph below in **Figure 3.4.BC** gives the v-j curve for the initial test of the stack and after the road travel along with approximately 4 additional thermal cycles and 75 hours of operation.

Figure 3.4.BC Curve for the initial test of the stack and after the road travel

Four 21 manifold, 6 cell per manifold stacks were assembled and tested to further characterize cell, manifold and stack performance when operating on a POX gas stream. For each stack, voltage vs current performance data was obtained and manifold resistances were recorded before and after testing. The **Figure 3.4.BD** below gives the v-j curve for each of the stacks. Also shown below is a typical voltage plot for one of the stacks (#1) undergoing step changes in load.

Figure 3.4.BD v-j curve for each of the stacks

On two of the stacks (#1 & #3) low manifold resistances (<1 ohm) indicated that one or more cells on each of these manifolds may have been shorted. These manifolds had voltages well below average and also showed signs of erratic open circuit voltage on cool down while on purge gas. The tables below give the manifold resistances before and after the initial test. Those manifolds marked in red were removed from the stack and the cell causing the low manifold resistance replaced. The stacks were then retested. The figure below shows an example of the erratic manifold voltage recorded for Stack #3 on cool down; V02 corresponds to Manifold 44, V05=M47 and V07=M49.

Stack Manifold Resistances (Red=replaced, Yellow=less than 10 ohms)

Stack 1		
Manifold #	Assembly (ohms)	Post Test (ohms)
21	2.26E+05	1.00E+05
20	3.63E+05	1.00E+06
19	9.32E+03	1.00E+07
18	1.48E+06	4.00E-01
17	1.71E+06	6.35E+03
16	9.12E+05	1.00E+07
15	2.45E+04	4.45E+04
14	1.49E+06	1.00E+07
13	4.41E+05	2.52E+03
12	1.41E+06	1.00E+07
11	5.81E+06	1.18E+04
10	7.84E+05	8.00E+06
9	9.09E+05	2.50E+06
8	3.85E+05	4.26E+06
7	4.80E+06	1.21E+03
6	3.58E+05	9.00E+05
5	1.04E+05	4.60E+06
4	1.85E+05	6.00E+06
3	1.58E+05	1.36E+04
2	3.87E+05	1.00E+07
1	4.50E+03	4.82E+03

Stack 2		
Manifold #	Assembly (ohms)	Post Test (ohms)
22	1.07E+04	1.32E+06
23	6.09E+04	1.87E+05
24	1.51E+05	8.88E+02
25	2.67E+04	3.80E+00
26	6.60E+03	2.60E+02
27	1.88E+04	3.25E+05
28	1.79E+04	7.50E+05
29	5.02E+04	2.25E+05
30	9.74E+04	5.15E+06
31	8.35E+03	1.00E+07
32	1.74E+05	2.66E+02
33	4.65E+05	1.00E+07
34	1.08E+06	1.00E+07
35	1.45E+04	3.62E+05
36	5.87E+05	9.30E+00
37	1.08E+06	1.00E+07
38	3.00E+05	1.00E+07
39	1.38E+04	8.23E+06
40	4.58E+06	7.76E+04
41	1.34E+06	1.00E+07
42	5.47E+04	8.85E+05

Stack 3			Stack 4		
Manifold #	Assembly (ohms)	Post Test (ohms)	Manifold #	Assembly (ohms)	Post Test (ohms)
63	4.70E+05	1.37E+05	64	2.10E+04	2.90E+06
62	7.40E+05	1.00E+07	65	2.06E+05	3.20E+06
61	6.30E+05	1.00E+07	66	1.81E+05	2.70E+06
60	1.20E+05	1.08E+06	67	8.40E+04	1.18E+04
59	1.00E+06	1.00E+07	68	1.49E+05	6.80E+00
58	5.90E+05	1.00E+07	69	2.50E+06	1.57E+03
57	4.00E+05	1.00E+07	70	8.10E+03	7.90E+05
56	2.20E+05	6.15E+06	71	3.90E+04	9.42E+02
55	7.90E+05	1.00E+07	72	1.15E+05	2.20E+06
54	1.15E+05	1.40E+06	73	1.09E+05	2.40E+06
53	1.35E+05	2.05E+04	74	2.28E+05	2.33E+02
52	1.00E+04	1.52E+04	75	7.20E+03	2.00E+00
51	8.00E+05	1.00E+07	76	8.90E+04	2.10E+06
50	2.94E+06	1.00E+07	77	8.50E+04	2.70E+06
49	3.77E+05	7.00E-01	78	1.10E+04	1.80E+06
48	1.77E+06	1.00E+07	79	4.00E+06	1.30E+06
47	7.49E+04	2.42E+01	80	2.51E+05	3.00E+06
46	5.08E+04	9.37E+04	81	2.20E+03	2.24E+02
45	1.78E+05	1.00E+07	82	3.00E+06	1.70E+06
44	2.53E+05	1.07E+06	83	7.50E+05	4.20E+06
43	6.26E+05	6.38E+02	84	3.80E+06	3.40E+06

Table 3.4.A The Manifold resistances before and after the initial test.

Manifold & Cap Configuration with Chromite Interconnect

A cell configuration with current collection taking place along the length of the cell through chromite bands bonded to the cell anode allows for a significantly different and less costly manifold and manifold/cell connection than currently being utilized. Because the manifolds do not need to serve as the anode bus, the manifold can be a common manifold as long as the cells can be electrically isolated from the manifold. A number of ideas were developed to obtain this functionality.

The first method consists of a ceramic insert, which is either cemented or pressed into a deep drawn (wall thickness of 0.020") metal cap. The cell would then be cemented into the ceramic insert, forming a cell-to-manifold connection with electrical isolation. The order of assembly would be to attach the ceramic insert to the metal cap, braze all the cap assemblies to the manifold body and then cement the cells into place during the assembly of the stack.

Figure 3.4.BF (a). Electrically isolating braze cap. (b). Braze caps in the manifold.

An alternative method would be to deep draw a metal cap including a feature for pressing the cap into the manifold. The order of assembly would be to attach the ceramic insert into the metallic shell, cement the cell into place and then interference-fit the cell assemblies into the manifold, during stack assembly.

Figure 3.4.BG Deep drawn cap for pressing into the manifold.

A further method would be to fabricate (metal injection mold or screw machine) a cap that has a screw feature on it for screwing into the manifold (or alternatively using a backing nut). Once again the order of assembly would be to attach the ceramic insert into the metallic shell, cement the cell into place and then screw the cell assembly into the manifold during stack assembly.

Figure 3.4.BH (a). Cell with screw attachment.

(b). Cell attached to manifold.

In order for these cell attachment methods to be successful, a number of parameters must be carefully controlled. The primary concern is the material thermal expansion coefficient (TEC) compatibility. A series of prototypes will be made and experiments conducted to validate the bonding concepts and overall connection integrity.

A test of a number of ceramic cements is underway to determine if a ceramic joint can be made between fuel cells and metallic or ceramic tubes. This needs to be determined due to the fact that there must be an electrically insulating connection between the cell and the manifold for designs in which chromite bands are used to transfer current from anode to cathode.

A number of tubes were selected for joint testing:

0.675" od x 0.120" wall thickness alumina tube	(C1)
0.850" od x 0.085" wall thickness alumina tube	(C2)
0.500" od x 0.063" wall thickness alumina tube	(C3)
0.590" od x 0.060" wall thickness fuel cell	(Cell)
0.500" od x 0.020" wall thickness Inconel 600 tube	(M1)
1" od x 0.049" wall thickness Type 304 tube	(M2)
0.625" od x 0.125" wall thickness alumina bisque	(C4)
Cotronics® 904 zirconia cement	(904)
Silicon carbide cement	(SiC)

The photographs below show a typical test configuration before and after thermal cycling.

Figure 3.4.BJ typical test configuration before and after thermal cycling.

The initial results of the experiments reveal that a thermal expansion coefficient (TEC) difference of $4.1 \mu\text{m m}^{-1} \text{ }^{\circ}\text{C}^{-1}$ is too great to achieve a successful bond over the temperature range of room temperature to 800°C . With a TEC difference of $1.0 \mu\text{m m}^{-1} \text{ }^{\circ}\text{C}^{-1}$ a successful bond could be achieved over this same temperature range.

Several prototype cap assemblies were manufactured for testing trials. The figure below shows the geometry of the connection. The gray part is a deep drawn tube with a flange at one end. The red part is a cap made from an electrically insulating material, as is the yellow part (washer). The blue part is a fuel cell. The whole assembly is connected together with an electrically insulating ceramic cement. A set of tools were developed to allow some of these deep drawn, flanged tube parts to be fabricated in-house for testing purposes.

Figure 3.4.BK Current design of the cell-to-manifold connection

Machined male and a female tool parts were manufactured to permit the flanged part to be made from $\frac{1}{2}$ " x 0.020" wall Inconel 600 tube by a pressing operation. The photo below shows one of the manufactured parts. A number of different length tubes were tried before the correct length was established. If the tube was too short then a small flange was produced. If the tube was too long then the tube buckled before forming the flange. It was found that the largest diameter flange possible, without buckling was $\frac{5}{8}$ ". For a few hours work, a few thousand dollars was saved in prototype tooling costs and approximately 4 weeks waiting for the parts.

Figure 3.4.BL Final in-house flanged tube

A number of companies were contacted and quotes have been obtained for the deep drawn tube, ceramic cap and ceramic washer. With volume production, these parts are projected to costs \$0.12, \$0.09 and \$0.03, respectively. The cost of the ceramic caps is highly dependent on the material utilized. The costs given are for parts made using Steatite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 3\text{MgO}$). Quotes for these parts in alumina are approximately 7 times higher.

Two ceramic caps were designed and fabricated using alumina bisque to fit the standard (15 mm) cells. The difference between the two caps was in the deep drawn part diameter and thus the base hole in the ceramic cap was changed to suit this part. Caps were fabricated with 3/8" and 1/2" diameter base holes. These caps were sintered at 1500°C for 2 hours to densify the material to reduce leakage.

Ceramic washers were also fabricated to fit inside the ceramic caps, to complete the assembly. The cement used to join these parts together was Cotronics® 904. The photograph below shows the individual parts that make up the assembly.

Figure 3.4.BM Cell-to-manifold Connection Parts

The assemblies were tested with thermal cycling to 838°C every 24 hours in air. The gas leakage at room temperature was used as a measure of assembly integrity. After 648 hours and 27 thermal cycles, the leakage was stable at 15 mL min⁻¹ @ 0.5" w.c. and 25 mL min⁻¹ @ 1" w.c. This was a very high leakage rate and was considered a failure for a fuel cell system. The leakage was probably due to the thermal expansion mismatch between the alumina cap and the cell, thus there was too much stress between these two parts to form a gas-tight joint. See **figure 3.4.BN** below.

Figure 3.4.BN Cell to manifold leakage during thermal cycling

Two ceramic caps were also designed and fabricated from magnesia to fit the standard (15 mm) cells as shown in **Figure 3.4.BP**. Caps were fabricated with $\frac{1}{2}$ " diameter base holes. These caps were sintered at 1500°C for 2 hours to densify the material to reduce leakage.

Figure 3.4.BP Ceramic caps designed and fabricated from magnesia

As with the alumina sample, they were tested with thermal cycling to 838°C every 24 hours in air. The gas leakage at room temperature was used as a measure of assembly integrity.

After 672 hours and 28 thermal cycles, the leakage was $<0.84 \text{ mL min}^{-1}$ @ 0.5" w.c. for both samples and approximately 1.3 mL min^{-1} and 2.2 mL min^{-1} @ 1" w.c. This is considered very low leakage and thus this geometry/materials setup is successful. The **Figure 3.4.BQ** below shows the reduction in leakage with increasing number of thermal cycles and time at 838°C.

Figure 3.4.BQ The reduction in leakage with increasing number of thermal cycles and time at 838°C.

Threaded Anode Supported Cell

An alternative approach to the cemented cap design discussed above is to machine threads directly into the anode tube and to use this thread as a means of locking a cell into a ceramic cap. The thread would be a loose fit into the female part, with the thread gap filled with ceramic cement to effect a gas-tight seal (up to approximately 2" w.c. sealing ability).

A number of dried AS tubes (standard 15 mm diameter) were into 3" lengths and an external thread machined into the dried tube. These parts were chucked in a lathe and, using a single point cutting tool, a thread (3/4"-11) was formed by turning 0.002" of material off at each pass, to slowly form a thread. The completed parts were placed into a furnace and heated to 1200°C for bisque firing and then fully sintered at 1500°C for 2 hours. The parts were measured for diameter and length at each stage of the firing regime to determine the shrinkage involved.

The first attempt yielded a very rough thread where parts of the thread had been ripped out by the tool. This thread was cut at a rotational speed of 800 rpm. A section of the threaded tube broke off due to the penetration of the thread into the tube wall, leaving a very thin wall thickness.

The second attempt was performed at a much lower speed of approximately 300 rpm. The thread profile was also modified by rounding the tip of the tool. This was decided upon to reduce the possibility of forming a sharp corner at the root of the thread and thus removing a stress-raising point. The thread formed was much cleaner (less pieces missing). A section of the threaded tube broke off due to the depth of the thread. Approximately 0.020" wall thickness was left when the section broke off.

The third attempt was also performed at a low speed of 300 rpm and the depth of the thread was controlled to be only half of the wall thickness. These samples were successful in that a clean thread was produced and no cracking of the AS tubes was apparent. Due to the limited depth of the thread, a pseudo-Acme thread profile was formed. Instead of the standard pointed profile on a typical $\frac{3}{4}$ "-11 UNC, a truncated profile was formed with a rounded thread root.

The machined samples were measured in order to determine the shrinkage during the sintering stages.

Table 3.4.B Dried AS Tube Dimensions

Pre-fired Dimensions		(inches)			
Sample	1	2	3	4	5
Diameter	0.745	0.744	0.731	0.734	0.734
Thread Length	0.843	0.918	0.619	0.629	0.739

Figure 3.4.BR Dried/Machined AS tubes.

Table 3.4.C Bisque-Fired AS Tube Dimensions and Shrinkage Values

Bisque-Fired Dimensions		(inches)			
Sample	1	2	3	4	5
Diameter	0.703	0.722	0.707	0.718	0.71
Thread Length	0.812	0.886	0.602	0.61	0.718
Tot. Length	0.812	0.886	2.781	2.849	2.826

Shrinkage		(percent)			
Sample	1	2	3	4	5
Diameter	5.6	3.0	3.3	2.2	3.3
Thread Length	3.7	3.5	2.7	3.0	2.8

1

2

3

4

5

Figure 3.4.BS Bisque-fired AS tubes.

Table 3.4.D Sintered AS Tube Dimensions and Shrinkage Values

Sintered Dimensions

Sample	1	2	3	4	5
Diameter	0.568	0.577	0.564	0.573	0.568
Thread Length	0.661	0.716	0.482	0.501	0.577
Tot. Length	0.661	0.716	2.244	2.308	2.296

Shrinkage (percent)

Sample	1	2	3	4	5
Diameter	19.2	20.1	20.2	20.2	20.0
Thread Length	18.6	19.2	19.9	17.9	19.6
Tot. Length	18.6	19.2	19.3	19.0	18.8

Overall Shrinkage

Sample	1	2	3	4	5	Ave.
Diameter	23.8	22.4	22.8	21.9	22.6	22.7
Thread Length	21.6	22.0	22.1	20.3	21.9	21.5

Figure 3.4.BT Sintered AS tubes.

The final thread profile was measured to be approximately 9/16"-14. This is not a typical thread, the closest being 9/16"-12 or 9/16"-18. If the female ceramic cap is also made in-house, then this does not pose a problem, since both parts can be designed to be compatible. The machining of the anode support tubes was successful. This provides an opportunity for an alternative method for connecting cells to ceramic caps.

ⁱ P.Tortorelli, J.DeVan. Behavior of Iron Aluminides in Oxidising/Sulfidizing Environments. *Mat. Sci. Eng.* A153 (1992) 573-7.

Task 4.0 – Fabrication and Processing Technology Development

Subtask 4.1 – Tube Drying

BTU Collaboration

Acumentrics current best firing profile, for bisque firing green tubes, takes on the order of 44 hours from cold to cold. Collaboration with BTU has continued in an effort to utilize microwave-debinding technology followed by bisque firing in a continuous belt furnace to reduce this bisque firing time and therefore increase cell throughput without adversely affecting cell performance.

Microwave debinding followed by bisque firing on a belt furnace has been reported previously. Unfortunately in previous trials, the tubes did not produce electrolyte coatings that were dense. The reason for this was thought to be low shrinkage in the bisque fire, less than 2%, which was not recouped during the electrolyte firing. Indeed, the electrolyte firing shrinkage was actually compromised in that the shrinkage was under 17%, not the expected 18% plus seen for standard production tubes. It is unknown however whether the reduced shrinkage at the electrolyte sintering stage originates from the fact that the tubes were microwave debinded or the fact that the belt furnace bisque fire was slightly less aggressive than Acumentrics standard profile, due to the limitations of the belt furnace being used. This will be investigated further below.

The furniture used for the previous trial was also not ideal in that two different sets were required, one for microwave debinding and one for the belt bisque fire. This was necessary since a single solution could not be found and as such problems arose when the fragile tubes had to be transferred between the two during processing. Possible furniture solutions are also detailed below.

Green anode tubes, from batch TF-220904-01-AE-03-20, were sent to BTU for bisque firing trials, the debinding step of which was completed in the microwave unit shown below in **Figure 4.1.A**. This prototype unit is different from the one utilized in previous trials in that the cavity is much smaller. The unit is still however a variable frequency microwave (VFM)

Figure 4.1.A: Microwave unit licensed by BTU to conduct microwave-debinding trials.

In order to fully utilize microwave technology for debinding, followed by a conventional belt furnace for bisque firing, kiln furniture that is suitable for both processes must be sourced to eliminate direct tube handling. There are however restrictions as to what types of refractories can be placed in the microwave unit during debinding. Refractories with a low dielectric constant are favorable in order to minimize coupling with the kiln furniture material. In addition, the material employed for the debinding has to be able to withstand the bisque firing temperature (1095°C) and not contaminate the tubes.

As a first step to determining what this furniture might comprise, an alumina container was constructed, fabricated from high purity Zircar AA-30 insulation board. This alumina insulation has a low density and a very low dielectric loss, which is required to allow the microwaves to pass through the material with little interaction while heating the tubes. However, alumina is not an ideal material since historical evidence shows that it may contaminate the tubes due to a reaction that takes place between the nickel oxide and the alumina body. The constructed alumina kiln furniture is shown in **Figure 4.1.B** and **4.1.C** below.

Figure 4.1.B

Figure 4.1.C:

Alumina insulation container used to process and transport the tubes during debinding and bisque firing.

The hole in the lid of the alumina container was to allow the surface temperature of the tube to be measured during debinding. An optical pyrometer was used to measure this while inside the microwave unit. The light from the pyrometer can be seen on the tube in **Figure 4.1.D**.

Figure 4.1.D: Temperature measurement of the tube surface using an optical pyrometer.

A number of trials were then completed to determine the optimum debinding profile for tubes in the microwave unit. **Figure 4.1.E** below shows a temperature versus time profile for an actual microwave debinding run for Acumentrics anode support tubes. The current best practice time to debind production tubes in Acumentrics electric batch furnace is 13 hours compared to 3.75 hours with the use of the microwave unit, a significant time saving of 9.25 hours.

Figure 4.1.E: Temperature profile versus time for the debinding of Acumentrics anode support tubes in a microwave unit.

After the tubes were microwave debinded, they were cooled to room temperature and then placed on a belt furnace to be bisque fired in the same alumina insulation container as seen in Figure 4.2.3. The tubes were heated to 1110°C and held for 4 hours before being cooled back to room temperature.

A temperature versus time graph for the bisque firing conducted at BTU is shown in **Figure 4.1.F** below.

Figure 4.1.F: Temperature profile versus time for the bisque firing of the anode tubes in a continuous belt furnace at BTU.

After bisque firing, the tubes were inspected. **Figure 4.1.G** below shows the results from two separate runs, the top three tubes from one run and the bottom three tubes from a second run which included a less aggressive debinding section. One tube from the second run remained intact after firing; the others were cracked predominantly in the center of the tube. This type of cracking is due to the friction between the tube and the furniture, which impedes shrinkage during firing, thus causing cracking in the center.

Figure 4.1.G: Bisque fired tubes fired at BTU on a belt furnace.

Post bisque firing, all tubes showed an alumina residue (white discoloration) left behind where the tube was in contact with the kiln furniture, see image above.

Modifications to the kiln furniture therefore need to be made to eliminate tube cracking and also the alumina contamination issue. Steps to achieve this have already been undertaken and will be reported at a later date.

The microwave debinded tubes shrunk by 3.7% which is at the low end of Acumentrics specification, but still in the acceptable shrinkage range. This is in contrast to the previous microwave debinding trial where the tubes shrunk by less than 2% at this stage.

The tube that remained intact after bisque firing was then processed into a cell. Before coating the tube with electrolyte, the alumina residue was removed. The electrolyte coating was deemed to be good so the tube was sintered along with production tubes in the standard way. The electrolyte sintered tube shrunk 19.1%, which is adequate to achieve a dense electrolyte coating.

This is again in contrast to the previously reported microwave debinded tubes which only shrank by 16.7% at the electrolyte sintering stage, resulting in a non leak tight coating.

The improved shrinkage numbers recorded in this trial therefore suggest that microwave debinding is not the cause for the lower shrinkages observed in the previous trial which resulted in non leak tight coatings.

The reduced shrinkage numbers observed in the last trial must therefore be the result of the lower belt bisque firing schedule, which in turn resulted in a lower electrolyte firing shrinkage. This appears counter intuitive in that it was expected that a lower bisque firing shrinkage should result in a higher electrolyte firing shrinkage but this is not the case.

In Summary:

- Microwave debinding cuts the processing time from 13 hours to 3.75 hours, a time saving of 9.25 hours.
- The total time to microwave debind and belt bisque fire tubes is approximately 10 hours compared to the current 44 hours required when using Acumentrics standard production furnace. This time can be reduced even more if a microwave unit is placed in line with the belt furnace, thus allowing for the bisque firing to commence right after the tube has been debinded.
- Alumina furniture is suitable for use in both the microwave debinding step and the belt bisque firing stage. Unfortunately, it appears that alumina cannot be used as the material that is in direct contact with the tubes during the bisque firing due to contamination left on the tubes after processing.
- The friction between the furniture and the tube needs to be minimized to prevent circumferential cracking.
- Acceptable tube shrinkage values were observed for both the bisque firing and electrolyte sintering stages of processing.
- The reduced shrinkage numbers that were observed in the last trial at the electrolyte sintering stage have been proven to be the result of lower bisque firing temperatures in the belt furnace rather than microwave debinding itself.
- It has been possible to process one cell so far using this greatly reduced bisque firing time.

Subtask 4.3 – Electrolyte Deposition

Tosoh Electrolyte Evaluation

It is desirable to lower the firing temperature that is required to produce a fully dense electrolyte for a number of reasons, some of which include:

1. It is beneficial to the cost and life of furnace linings
2. It is beneficial to the cost and life of kiln furniture
3. Energy costs are reduced
4. Firing times are reduced
5. There is a lower propensity for solid state interactions to take place at lower firing temperatures.

To reduce the electrolyte firing temperature, a more sinter active electrolyte coating must be applied to the anode substrate and preferentially, a cermet material should be utilized in conjunction that shows comparable conductivity to Acumentrics current cermet at the lower temperatures being investigated.

Preliminary investigations into reducing the firing temperature have focused upon Unitec YSZ electrolyte with and without a 0.5% by weight addition of Al_2O_3 (standard production YSZ) and also Tosoh YSZ with and without the same addition of alumina. As yet, no enhancement in cermet shrinkage at lower firing temperatures has been investigated.

Electrolyte slurries for each different YSZ grade under investigation were formulated in the standard way, following the standard procedure but with commensurate adjustments made for samples containing 0.5% alumina.

The different electrolyte slurries were then coated upon bisque fired tubes and initially fired at 1450°C for 2.5 hours. This was to establish a baseline from which to discard formulations that did not appear suited to lower temperature firing.

Table 4.3.A below shows the results from firing the different electrolyte coated tubes to 1450°C for two hours.

1,450°C for 2.5hrs							
Cell #	Slurry	Bisque (mm)	Sintered (mm)	% Shrinkage	Leak MP (torr)	Leak Slope (torr/sec)	Leak (mm Hg/min)
215	Production Unitec	287	239	16.72	113.9	4.953	297
216	Production Unitec	287	240.5	16.20	524.6	23.422	1405
328	Unitec + Al ₂ O ₃	288	240.5	16.49	121.8	5.299	318
82	Unitec + Al ₂ O ₃	289.5	242	16.41	338.9	15.456	927
335	Tosoh + Al ₂ O ₃	289	240.5	16.78	24.85	0.799	48
336	Tosoh + Al ₂ O ₃	289	240.5	16.78	20.11	0.567	34
299	Tosoh	288	241	16.32	17.99	0.470	28
338	Tosoh	288.5	240.5	16.64	18.34	0.486	29

Table 4.3.A results from firing the different electrolyte coated tubes

When firing the electrolyte at the lower temperature of 1450°C for 2.5 hours, the tube shrinks by a nominal 16.5%. This value is low enough to allow an estimation of tube leak rate without reducing the tube prior to evaluation.

The measured leak values in the table above are the leak measured point (MP) or vacuum decay value measured in torr at the end of the test and also the leak slope which is the slope of the decay curve measured in torr/second.

Leak rate data outlined in the table above shows that Acumentrics standard Unitec electrolyte cannot be sintered to the correct degree at this lower temperature without a longer soak time. Conversely Tosoh YSZ electrolytes with and without the addition of alumina showed leak rates that pass Acumentrics current production standard of 50mm Hg/min and will therefore be investigated further.

Tosoh slurries with and without alumina additions were then coated on further bisque fired tubes and then sintered at the lower temperature of 1400°C for six hours. The results from these trials are detailed in the **Table 4.3.B** below.

Cell #	Slurry	Bisque (mm)	Sintered (mm)	% Shrinkage	Leak MP (torr)	Leak Slope (torr/sec)	Leak (mm Hg/min)
290	Tosoh	289	243	15.92	23.74	0.777	47
290	Tosoh	REDUCED			84.05	3.125	189
292	Tosoh+ Al ₂ O ₃	289	243.5	15.74	62.42	2.713	162
289	Tosoh+ Al ₂ O ₃	289	240.5	15.74	96.67	4.159	250

Table 4.3.B Further bisque fired tubes and then sintered at the lower temperature of 1400°C for six hours

The data in the table indicates that Tosoh electrolyte without the addition of alumina is superior in terms of leak tight behavior at this lower temperature. Unfortunately only one data point is available to support this statement at this time. Upon reduction of this test sample, cell 290, the observed leak rate increased from 47 to 189 mm Hg/min, a value that is not acceptable for fabricated production cells.

Two full length cells for performance analysis were however fabricated using Tosoh YSZ electrolyte slurry and fired at 1400°C for six hours. Fabrication data for these two cells is shown in **Table 4.3.C** below.

Cell #	Slurry	Bisque (mm)	Sintered (mm)	% Shrinkage	Cathode (g)	Leak Slope (torr/sec)	Leak (mm Hg/min)
B220120	Tosoh	418.5	351.5	16.01	1.7032	0.5163	31
B220121	Tosoh	418.5	352	15.89	1.7248	0.2159	13

Table 4.3.C Performance analysis for two full-length cells using Tosoh YSZ electrolyte slurry and fired at 1400°C for six hours

The leak data for these two cells in the reduced form passes Acumentrics standard leak values. This was unexpected since the data above for the test sample suggested that the cells would not be adequately leak tight. As noted above however, this was based upon the results from one test sample which may have had undetected floors in the coating. The two cells were then submitted to cell testing for performance analysis which is detailed below.

Cell Performance

Performance results for the cells, B220120 and B220121, show that at standard operating conditions of 150 mA/cm², 75% fuel utilization and 800°C, the cells hit a peak of 633 and 641mV respectively after 40 hours of operation. These values are low with respect to standard production cells. Indeed the peak values obtained for two production cells B170393 and B170372 tested in the same cell test stand at the same time was 667 and 675 mV, respectively. The peak values were again reached after 40 hours of operation.

The OCP for both Tosoh cells is acceptable at 1.091 and 1.097 respectively, measured after 210 hours of operation, suggesting that the electrolyte coating is sufficiently leak tight. The ohmic resistance for both Tosoh cells is however higher than that observed for standard cells at 1.240 and 1.185 Ωcm^2 respectively, measured after 70 hours of operation. The **Figure 4.3.A** below shows the change in IR over the lifetime of the test.

Figure 4.3.A Change in IR over the lifetime of the test.

A step change in ohmic values can be observed between production cells B170393 and B170372 and the Tosoh electrolyte cells. These higher observed ohmic values for both Tosoh cells over their lifetime is likely the result of the lower sintering temperature that these cells experienced during processing. At these lower electrolyte sintering temperatures, it is considered that Ni interconnectivity is diminished in the tube, therefore lowering the conductivity of the tube, resulting in the observed increase in IR values. This appears to be in line with empirical data for B220120 and B220121, which both showed increased anode to anode (A-A) resistance values of 4.11 and 3.93m Ω respectively after reduction. A standard production cell generally has a lower A-A value of between 2.2-3.0m Ω when the whole tube length of the cell is evaluated. The microstructure at the anode electrolyte interface may also be less efficient when lower firing temperatures are employed.

Both cells underwent 6 thermal cycles during testing. The lifetime of the test lasted for 860 hours in total, including 827 hours where the cells were actually loaded. The degradation value over the lifetime of the test were high at 9.39 and 10.50% per 1000 hours for B220120 and B220121 respectively.

It was considered that the lower tube shrinkage of 16% observed for the Tosoh cells with respect to the usual 18% plus observed for production cells would lead to a shift to the right in the resultant fuel utilization curves. This is expected since there is a commensurate increase in tube porosity at this lower firing temperature from approximately 27% for standard production cells to 34% for the Tosoh coated cells.

The Figure 4.3.B below shows that both Tosoh curves have indeed shifted to the right with respect to production cells as expected. The magnitude of the shift is however small, considering the 7% increase in porosity of the tube upon reduction.

Microscopy

Further tubes were coated with Tosoh electrolyte, fired at the different evaluation temperatures and then submitted for micro analysis to determine the electrolyte thickness and to evaluate density.

The **table 4.3.D** below shows the typical electrolyte thicknesses for infiltration of Tosoh electrolyte on Acumentrics' anode support tubes. As can be seen, the thickness for each firing condition is nominally the same.

Cell	Firing Temp, °C	Firing Time, hr	Average El thickness $\pm$ Std. Deviation (mean), μm	Comments
A430286	1500	2.5	26.0 $\pm$ 1.1 (26.3)	consistent layer
A430299	1450	2.5	26.1 $\pm$ 1.0 (25.9)	consistent layer
A430291	1400	6	27.0 $\pm$ 1.3 (27.0)	consistent layer

Table 4.3.D Typical electrolyte thicknesses for infiltration of Tosoh electrolyte on Acumentrics' anode support tubes.

Figures 4.3.C through 4.3.E below show the electrolyte fired at the three different temperatures.

Figure 4.3.C A430286 – 1500°C for 2.5hrs

Figure 4.3.D A430299 – 1450°C for 2.5hrs

Figure 4.3.E Cell A430291 – 1400°C for 6hrs

The figures show that all three electrolyte layers fired at the different temperatures contain porosity. It is however difficult to determine from the images whether the lower fired electrolyte contains more porosity than that fired at 1500°C although it is intuitive to believe that this is the case. The porosity that is visible for each sample appears to be closed.

In Summary

- It is possible to fire Tosoh electrolyte onto standard Acumentrics tubes at 1400°C and still retain an electrolyte that is dense enough for cell operation.
- Performance of cells fired to 1400°C is poor with respect to production cells in terms of the peak power observed. It also appears that cell degradation is worse for the Tosoh coated cells.
- It is evident from resistance data of the reduced cells that Ni interconnectedness is compromised at lower firing temperatures. It is considered that this is at least one

reason for the higher IR value observed for both Tosoh cells and consequently a contributor to their lower performance.

- The FU curves for the Tosoh cells are shifter to the right of the production cell curves as would be expected. The magnitude of the shift however appears small when considering the 7% increase in apparent porosity.
- Microscopy of the electrolyte fired at different temperatures shows that all the coatings are nominally 26 microns thick. Each different electrolyte also contains porosity, which appears closed in nature.

NexTech Collaboration

The goal of this investigation is to provide a path to realize lower sintering temperatures for the electrolyte, without jeopardizing the conductivity of the anode tube and while still achieving a dense leak tight coating. A lower sintering temperature for the electrolyte will also allow for utilization of cheaper furnace refractories and kiln furniture.

Bisque fired tubes processed at Acumentrics were sent to NexTech Materials to be spray coated with their latest electrolyte formulation. Two different coatings were applied to the tubes. First, an active layer, consisting of gallium doped ceria (GDC) and nickel oxide, was spray coated onto the anode tube. Then an electrolyte, consisting of scandia-stabilized zirconia, was spray coated onto the tube. Some tubes received two electrolyte coats to increase the electrolyte thickness and therefore promote a leak tight electrolyte layer. The electrolyte-coated tubes were then sintered in a Carbolite box furnace to 1350°C with either a 2-hour soak or a 4-hour soak. **Table 4.3.E** provides a breakdown of how the tubes were processed at NexTech. It must be noted that Acumentrics received conflicting answers on how the tubes were processed during conversations with NexTech, particularly with respect to firing temperatures and times.

Table 4.3.E Processing Conditions for Tubes Electrolyte Coated and Sintered at NexTech

Shipment Num.	<i>Tube ID</i>	Number of Coats	Sintering Temp. (°C)	Soak Time (hrs)
1	NexTech B170073	1	1350	2
	NexTech B170105	1	1350	2
2	NexTech B170090	1	1350	2
	NexTech B390133	1	1350	2
3	NexTech B390129	2	1350	4
	NexTech B390125	2	1350	4

After electrolyte sintering, the tubes were sent back to Acumentrics for evaluation.

Upon receipt of the tubes from NexTech, the dimensions of each sample was then measured, followed by leak testing and comparison to a standard production tube that was sintered to 1510°C for 3 hours. The order with which the tubes were received from NexTech along with their dimensions and leak rates are provided in the **Table 4.3.F** below. Also note the differences in length and outer diameter of the NexTech coated tubes, which have a spread of up to 12 mm difference in length.

Table 4.3.F NexTech Electrolyte Sintered Tube Dimensions and Leak Rates

<u>Tube Number</u>	<u>Length (mm)</u>	<u>Max OD (mm)</u>	<u>Min OD (mm)</u>	<u>End Measured Pressure (torr)</u>	<u>Leak Rate (mm Hg/min)</u>
NexTech B170073*	366	15.74	15.33	729.0	1422.9
NexTech B170105*	368	15.93	15.47	354	915
NexTech B170090*	364	15.65	15.28	6.3	19.3
NexTech B390133*	362	15.82	15.40	119	329
NexTech B390125*#	356	15.62	15.03	1.4	4
NexTech B390129*#	358	15.43	15.07	6.5	19
Acumen. B170045	342	14.52	14.17	8	15

* These tubes were not reduced when leak checked.

These tubes had two electrolyte coatings applied.

From the table above, it is apparent that three of the tubes coated at NexTech do not meet Acumentrics current QC standard leak rate cut off which is currently set at 50mmHg/min, even though these tubes were tested in the oxidized form. The tubes with poor leak rates had highly translucent coatings, suggesting that the electrolyte was dense in nature but possibly too thin to provide an adequately leak tight cell. The desired thickness for the electrolyte coating established at Acumentrics is considered to be in the range of 25 to 30 μm .

Four different reduction runs were completed to try to reduce the NexTech electrolyte coated samples detailed in table 2 above. An attempt was made to reduce all samples, even those with high leak rates.

The first reduction run was performed on B170073, the tube with the worst leak rate of 1423 mmHg/min. The tube was placed in Acumentrics standard reduction furnace with both sides full with production samples and reduced under standard CPOX conditions.

After reduction, the tube had only reduced 29% of the way along its length from the fuel inlet side while the standard production tubes that were being processed at the same time were reduced along their entire length. The images below in **Figure 4.3.F** were taken after the reduction attempt. Figure 4.3.E

Figure 4.3.E Left: Section reduced from the fuel side; Right: Evidence of the electrolyte flaking off

The NexTech tube sample B170073 was then submitted to microscopy to have the electrolyte coating thickness determined.

Two samples were cut from the tube above: one from the reduced section and one from the oxidized. Both sections of tube showed some crazing of the electrolyte and some small amount of porosity, but overall, a very dense electrolyte layer. The layer thickness, however, was extremely variable as seen in the images below in **Figure 4.3.F**.

Figure 4.3.F Both images 50x with 10xobj Left: Oxidized part showing variable electrolyte thickness and some crazing; Right: Reduced section showing variable electrolyte thickness and electrolyte breaking off. (Sample, B170073)

The outer surface of the electrolyte was very uniform, but the valleys and hills of the anode penetrating and retreating from that surface varied considerably.

Figure 4.3.G: Both images 20x 10xobj Left: Oxidized part showing break in electrolyte coverage and variable electrolyte thickness; Right: Reduced part also showing break in electrolyte coverage and variable electrolyte thickness. (Sample, B170073)

Contact between the electrolyte and anode appeared to be intimate at all points. Electrolyte thickness varied between 15 μm and 0 μm , and could vary rapidly as seen in the pictures below in **Figure 4.3.H**. The average was closer to 10 μm overall in places with relatively uniform coverage. The measurement, however, is extremely difficult.

Figure 4.3.H: 150x 10xobj Left: Oxidized section showing extreme coverage variability; Right: Reduced section showing coverage variability with scale. (Sample, B170073)

While some porosity was observed in the electrolyte, the sample showed a very dense and uniform layer overall. There were sections in the reduced sample that were missing (see **Figure 4.3.J**), but this might be attributed to the oxidation/reduction cycles undertaken in the reduction process.

Figure 4.3.J 5x 10xobj, Reduced sample showing area of zero EL coverage. This was repeated in other spots on the sample. (Sample, B170073)

The second attempt to reduce a NexTech coated tube was conducted on sample B390133, again despite the poor leak rate observed in the oxide state. This sample had a leak rate substantially better than B170073 but is still considered unacceptable at 329mm Hg/min.

The tube was placed in the large reduction furnace and reduced at standard CPOX conditions. After the reduction process, the tube had only reduced 35% along its length from the fuel side with a large portion reoxidizing due to the electrolyte flaking off. The photo below of **Figure 4.3.K** was taken after an attempt was made to reduce sample B170133.

Figure 4.3.K Reduced section showing a large area of the electrolyte flaking off. (Sample, B170133)

It is probable that the electrolyte delaminated from the tube as a result of variable coverage, indicated by the micro results for tube B170073 reported above. During reduction of the tube, the poor electrolyte coverage would allow re-oxidation of the Ni to occur and thus a commensurate local expansion to take place. This then results in the electrolyte delaminating from the tube revealing further Ni, which is then, free to

reoxidize, thus perpetuating the problem. No further analysis was performed on B170133.

A third reduction attempt was performed on the three tubes that had the lowest leak rates in the oxidized state, B170090, B390125 and B390129. Prior to reduction, the tubes were cathode coated and sintered to 1250°C for 2 hours. It was thought that the low leak rates, measured for these tubes, would provide a dense enough electrolyte coating to produce a finished cell for performance evaluation.

The tubes were again reduced in Acumentrics standard reduction furnace and processed at standard CPOX conditions. After the reduction it was noted that the tubes had only reduced partially along their length from the fuel side, see **Figure 4.3.L** below.

Figure 4.3.L: Sample B170090, B390125 and B390129 after reduction. .

Despite the low measured leak rates in the oxidized state, all three tubes show major delamination of the electrolyte and cathode from the anode, suggesting that the electrolyte is again compromised.

To determine the quality and thickness of the electrolyte coating for the above cells, sample B390125 was submitted for microscopy. NexTech reported that this sample along with B390129 had 2 electrolyte coats applied before sintering. The micro report is not yet complete and as such will be added at a later date.

A fourth and final reduction run was completed upon sample B170105. Prior to reduction, this tube was cut in half with one section fired to Acumentrics standard electrolyte firing temperature of 1510°C for three hours, the other section underwent no further processing. This was to determine if the electrolyte was leak tight at higher processing temperatures and also to verify that the electrolyte was delaminating from the tube as a result of a variable electrolyte coating rather than anything to do with the GDC interlayer. Both halves of the tube were then reduced in a 97/3% H/H₂O atmosphere at 825°C for 16 hours in a tube furnace. Other experimental Praxair tubes were also in the chamber during the reduction.

Upon completion of the reduction process, it was noted that both halves of the tube had intact electrolyte suggesting, as expected, that the delamination was indeed due to the applied electrolyte layer that was compromised, rather than anything to do with the GDC interlayer. There was however some cracking of the electrolyte on the section that was sintered to 1510°C. These cracks propagated about a centimeter from where the tube was sectioned in half. No other cracks were observed on the two sections. The photo of **Figure 4.3.M** below shows the two sections after reducing in a hydrogen atmosphere. The longer tube in the photo was sintered to 1510°C.

Figure 4.3.M NexTech coated sections that were reduced in a full hydrogen atmosphere.

The sections were then leak tested, measured for dimensional and weight changes, followed by an evaluation of tube resistance per unit length. **Table 4.3.G** below summarizes the post measurements taken for the two reduced sections.

Table 4.3.G Measurements Taken From Sample B170105 Reduced in Full Hydrogen Atmosphere

Measurement	Sintered to 1510°C	Sintered to 1350°C
Weight	71.2445 g	59.3821 g
Post Weight	61.4400 g	51.1917 g
% Weight Loss	13.76 %	13.79 %
Length	191 mm	167 mm
Post Length	191 mm	167 mm
Leak Rate	754.9 mmHg/min	1124.5 mmHg/min
End Pressure	269 torr	406 torr
Anode Resistance	0.102 mΩ/cm	0.253 mΩ/cm

As can be seen in the table above, both samples reduce to the same degree and as expected the length of each does not change during reduction. The measured leak rate for both tubes is very poor although some improvement was realized upon firing one half of

the tube to Acumentrics current production temperature. The resistance of the anode per unit length for the 1350°C sample is more than double the resistance measured for the other half of the tube, which was fired at 1510°C. It is evident that on moving to lower sintering temperature electrolytes, lower sintering temperature anodes must also be investigated if the performance of the cell is to be maintained.

In Summary;

- The electrolyte applied by NexTech appears to be generally too thin and also variable in nature. Indeed, microscopy has shown that the electrolyte of cell B170073 varied between 0-15 microns on the tube.
- This variable electrolyte thickness is the result of poor processing by NexTech but there is also a contribution from the inherent roughness of the tube surface.
- Micro has also shown that the electrolyte does in fact appear to be dense, even when utilizing the reduced firing temperature of 1350°C.
- The reason for electrolyte delamination from the cell upon reduction in Acumentrics standard reduction furnace is thought to be due to the variable electrolyte thickness, which results in a non leak tight electrolyte coating and therefore allows reoxidation of the Ni.
- B390125 and B390129 were supposedly processed with the application of two electrolyte coatings and as such the integrity of the electrolyte should have improved. Leak testing of these tubes in the oxidized form showed that they passed Acumentrics standard QC test and were indeed more leak tight than previously sent cells. Closer examination of the tubes however showed that they had shrunk more than the previously sent samples, suggesting a more aggressive firing schedule had been used at NexTech. As such the tubes would appear more leak tight in the oxidized form as the tube is more dense and therefore contributes further to the leak value. Upon reduction of these cells, the electrolyte again delaminated, suggesting that the electrolyte was again compromised. Micro of these cells is currently taking place and will be reported in December's report.
- It is apparent from this study that temperatures approaching 1350°C could be achieved for the electrolyte firing with greater control of the electrolyte coating procedure.
- Performance of cells fired at 1350°C may be compromised due to the higher anode resistance resulting from the decreased Ni interconnectivity.

Task 5.0 – Fuel Processing Technology Development

Subtask 5.1 – Reforming Technology-Light Hydrocarbons

Natural Gas Partial Oxidation Processing

As discussed in Section 3.4, an anode cermet POX reactor was operated for approximately 400 hours to determine the long term stability of the reactor. GC samples were taken periodically to determine the inlet and outlet gas compositions. As seen in the conversion chart below there was an initial drop in the methane conversion over the first 96 hours of operation but this was followed by a steady methane conversion rate of approximately 65%. The reactor was operated at a fuel flow rate of 4.8 lpm and on oxygen to carbon ratio 1.2. Since the reactor appeared to reach steady state, the test was terminated after 16 days of operation to inspect the tubes. As shown in the photos below, there was no carbon build up in or on the tubes or in the reactor. There was some loss of nickel at the end of the tubes but this was limited to the first several millimeters. The reactor consisted of five such tubes, with one of the tubes handling all of the gas flow and serving mainly as a preheater section and the other four tubes handling $\frac{1}{4}$ the fuel flow. Only three of the tubes are shown; two of the tubes were fractured in removing the tubes from the reactor. The reactor will be outfitted with five fresh tubes and the test restarted.

Figure 5.1.A Fuel Flow

Figure 5.1.B Methane Conversion vs. Time for Cermet POX Reactor

Figure 5.1.C POX Reactor Cermet Tubes

Figure 5.1.D Closeup of POX Cermet Tubes

A repeat of the above POX reactor test was conducted to further validate the results. New cermet tubes were installed in the reactor prior to the start of the test. GC samples were taken periodically to determine the inlet and outlet gas compositions. As shown below, the methane conversion data agreed very closely with the earlier test. As in the earlier test, over the first 96 hours of operation the methane conversion dropped to 65% but then remained constant. The reactor has been submitted for autopsy which will be performed during the next reporting period.

Figure 5.1.E Methane conversion data agreed very closely with the earlier test.

LPG Reforming

Tests were started on a simple 0.5 wt% Rh impregnated alumina catalyst from Johnson Matthey (JM). In a preliminary screening experiment the catalyst was crushed to 1.4-2mm particles and was operated successfully in each of the reforming modes.

	CPOX	ATR	ATR	ATR	SR
O₂/ccm	70	45	45	45	-
N₂/ccm	250	169	169	169	169
C₃/ccm	39.6	39.6	39.6	39.6	39.6
H₂O/ml hr⁻¹	-	5.2	5.2	5.2	11.2
SV / cc g⁻¹hr⁻¹	9700	9900	9900	9900	12500
O/C	1.2	0.8	0.8	0.8	-
S/C	-	1	1	1	2.2
T preheat/ °C	350	350	400	500	500
T catalyst*/°C	616	522	575	633	452
CH₄	12.3	14.3	16.1	11.7	12.6
H₂	5.9	10.9	16.0	24.9	23.3
H₂O	5.8	24.2	19.4	14.6	27.9
CO	3.3	1.4	1.9	4.8	3.2
CO₂	11.4	12.7	14.2	13.4	8.3
N₂	61.1	35.1	32.4	30.5	24.6
C₃H₈	0.1	1.4	-	-	0.1
C₂H₆	-	-	-	-	-

Table 5.1.A: Reforming modes over JM Rh catalyst:

* Measured temperature at front of catalyst

Rh CPOX long term

The Rh catalyst was tested for CPOX in a separate experiment where 1.8 g of 1/8" pellets were packed into a 1/2" OD inconel reactor. Performance was maintained throughout 190 hours of continuous operation, the effluent concentrations being constant within experimental error. The elemental balance had a discrepancy <1%

	measured	equilibrium 636°C	equilibrium 800°C
O₂/ccm	70	70	70
N₂/ccm	250	250	250
C₃/ccm	39.6	39.6	39.6
SV /cc g⁻¹hr⁻¹	12100	-	-
O/C	1.2	1.2	1.2
S/C	-	-	-
T_{preheat}/°C	370	-	-
T_{catalyst}*/°C	636	636	800
CH₄	9.8%	-	-
H₂	11.7	27.6	29.1
H₂O	6.1	6.6	2.7
CO	7.7	12.1	21.7
CO₂	10.4	6.0	2.1
N₂	53.9	47.7	44.4
C₃H₈	0.3	-	-
C₂H₆	-	-	-

Table 5.1.B: CPOX over JM Rh catalyst: 190 hours of continuous operation

* Measured temperature at front of catalyst

A calculation of equilibrium at 636°C suggests a 29% selectivity for carbon, clearly at odds with the experiment. At 800°C carbon is not (thermodynamically) favored, but in either case it is clear that the actual effluent composition does not reach thermodynamic equilibrium

CPOX/ATR/SR reactor

The main application of an LPG Fuelled SOFC is power generation in rural or isolated areas where ancillary utility streams such as water and natural gas are not available. For robust operation it is envisioned that the reforming mode of the LPG reactor must transit through operating regimes. At start-up, before water is available for steam reforming, the reactor operates in CPOX mode producing a nominal flow of syngas sufficient for maintaining reducing conditions and generating a small amount of power. As water is recycled the air content is gradually reduced and autothermal operation ensues. Ultimately peak efficiencies are obtained with the reactor in steam reforming mode only, producing a pre-reformed stream rich in CH₄, CO and H₂.

A two stage reactor is currently being considered with the first component being an active ATR/CPOX catalyst (*e.g.* Rh/Al₂O₃) followed by a second component of an adiabatic pre-reforming catalyst (*e.g.* Ni based catalyst). Typically precious metal catalysts are active for all reforming modes, and further, have enhanced carbon and sulfur resistance. It is conceivable then that a single bed of the Rh catalyst would suffice if a cost and reliability analysis was favorable.

The main obstacle to reliable operation is carbon formation. In its envisioned operation the two catalyst beds will transit through a variety of operating temperatures, and H/C and O/C ratios. At certain times carbon *will* be favored at equilibrium and so it is important to first choose catalysts exhibiting coke resistance, and second, minimize the time for which the catalysts are exposed to such conditions.

Three types of carbon are generally considered:

	Whisker Carbon	Encapsulating Polymeric Carbon	Pyrolytic Carbon
Formation	Diffusion of C through Ni, nucleation and whisker growth	Slow polymerization of C _n H _m radicals on Ni surface	Thermal cracking of hydrocarbon, Deposition of C precursors on catalysts
Effects	No deactivation, but sudden breakdown of catalyst and increased ΔP	Progressive deactivation	Encapsulation of catalyst Deactivation Increased ΔP
Temperature	>450°C	<500°C	>600°C
Critical parameters	High temperature Low S/C No enhanced H ₂ O adsorption Aromatic feeds	Low Temperature Low S/C Low H/C Aromatic feeds	High Temperature High void fraction Low S/C High pressure Catalyst acidity

Table 5.1.D: Carbon fouling of catalysts

Note whisker carbon is formed by dissolution of C in the Ni lattice with subsequent nucleation at the rear of the catalyst. This process results in extremely long strands or threads of carbon. This mode of deactivation is not expected for Rh catalysts.

Table 5.1.E compares the gas phase compositions sampled from the reactors for the two Ni catalysts

	G1-80	57-7
O₂/ccm	70	70
N₂/ccm	250	250
C₃/ccm	39.6	39.6
Rh cat./g	1.93	1.93
Ni cat./g	2.02	2.23
SV* /cc g⁻¹hr⁻¹	5500	5100
O/C	1.2	1.2
S/C	-	-
T preheat/ °C	370	370
Tcatalyst*/°C	727	757
CH₄	15.8%	13.9%
H₂	4.9	9.3
H₂O	5.2	3.4
CO	1.3	2.8
CO₂	14.9	14.5
N₂	58.0	56.1
C₃H₈	-	-
C₂H₆	-	-

Table 5.1.E: CPOX over JM Rh catalyst: 190 hours of continuous operation

* Measured temperature at front of catalyst

Both experiments were kept running for 16 hours.

Figure 5.1.F: Catalysts from 16 hour composite bed experiment

The catalyst didn't show any signs of significant coke buildup although some carbon may have been on its surface (**Figure 5.1.F**). However the other catalyst coked completely and the catalyst fragments were complete destroyed. In fact the emergency purge valve had to open to vent the reactant gases, which reached a pressure of 10 psi. The Rh catalyst surfaces looked clean -the carbon fragments that appear in Figure 5.1.F have likely resulted from the coking of the other catalyst, or from pyrolysis of propane caused by the bed blockage. Seeing that the transition from CPOX to SR is likely to be completed in a few hours it appears that the catalyst is the ideal catalyst to follow the Rh CPOX catalyst. Its coke resistance is probably due to its high activity and small Ni crystallite size. Being a pre-reforming catalyst is designed to work at low temperatures.

LPG Partial Oxidation -Catalyst screening

Two Pt catalysts were screened for LPG partial oxidation – Pt on CeO₂/ ZrO₂ and Pt on a proprietary Cu spinel support

	C1	C2	Rh/Al ₂ O ₃
O₂/ccm	75	75	70
N₂/ccm	260	260	250
C₃/ccm	41.5	41.5	39.6
Time/hrs	2	208	190
SV / cc g⁻¹hr⁻¹	11000	10700	12100
O/C	1.2	1.2	1.2
T preheat/ °C	350	350	350
T catalyst/°C	750	420*	636
CH₄	0	1.8	9.8
H₂	2.5	22.4	11.7
H₂O	13.6	2.9	6.1
CO	1.6	10.1	7.7
CO₂	11.4	9.6	10.4
N₂	64.7	51.7	53.9
C₃H₈	6.5	1.5	0.3
C₂H₆	-	-	-
C3 conversion	37.3	81.5	96.5

Table 5.1.F: LPG partial oxidation over Pt and Rh catalyst:

* Measured temperature at front of catalyst, possibly bad thermocouple placement

In **Table 5.1.F** the performances of the catalysts are compared with the Johnson-Matthey Rh/Al₂O₃ catalyst. Of the two formulations, only the Pt/CeO₂ formulation (C2) performed satisfactorily. The Pt/Cu spinel had a propensity for total oxidation as seen by the high concentrations of CO₂ and H₂O and low propane conversion. Corroborating evidence is the high temperature seen at the front of the bed. In contrast, the Pt/CeO₂ catalyst had a lower selectivity for total oxidation products. The temperature at the front of the bed is also remarkably low and is consistent with a direct mechanism for partial oxidation. This is typical of Pt catalysts. C2 was kept on line for 208 hours during which the performance was stable. A faint scent of aromatic compounds was noticed in the reactor effluent but was not detected by GC. An autopsy of the reactor contents showed a light coating of carbon on the catalyst but carbon fouling of the inconel reactor walls. This fouling was not seen for the Rh catalyst tested the previous month and may hint at gas phase reactions even though the reactor temperature was quite low. This catalyst will be re examined.

The price of ruthenium is ~\$60/oz compared with ~\$900/oz for Rh and so a Ru catalyst (0.5 wt% Ru on Alumina) was screened for partial oxidation activity. The catalyst was not as active as the Rh catalyst for the partial oxidation of LPG, but was still resistant to coke formation. No carbon was observed even after a 100 hour trial at a reactor temperature of 500°C. From the gas analysis the deactivation, appeared to stabilize, but there are concerns of slow deactivation via the formation of the unstable volatile oxide RuO_4 . In the immediate term the Rh- Al_2O_3 catalyst has been chosen as the best catalyst having very high activity and coke resistance but the Ru catalysts is worthy of further study

Operation of dual mode CPOX/SR reactor

The dual mode configuration of precious metal catalyst/ pre-reformer catalysts was tested for CPOX of LPG (O/C=1.2) at the temperature of 500°C for 16 hours. Whisker carbon is favored at these temperatures and a Rh catalyst combination indeed showed destruction of the catalyst at the catalyst junction. This experiment was repeated with a Ru catalyst/alumina/CATALYST 2 with the same result. Since the dual mod reactor only operates at CPOX conditions at start up, this latter experiment was retried under a simulated start condition for a fuel cell

The CPOX reaction (O/C=1.20, SV ~9500 hr^{-1}) was ignited at 240°C and the reactor temperature increased from 240-500°C over 2 hours. At 500°C steam was added (S/C=1) and the reactor temperature increased to 550°C. This is the average temperature expected in the fuel cell adiabatic pre-reforming reactor. At this time the reactor was operated in steam reforming mode only (S/C=2.3) for 3 hours before the reactor power was turned

off, simulating the cool down. At this time air was admitted to the reactor and the steam flow dropped (O (from air)/ $C = 1.2$, $S/C = 1$). When the reactor temperature was $\sim 250^{\circ}\text{C}$ the steam flow was turned off ($S/C = 0$, $O/C = 1.2$) and the CPOX mode allowed to continue until the temperature at the bed end was $\sim 180^{\circ}\text{C}$. At this time all reactants were stopped. Subsequent analysis of the reactor contents showed no carbon anywhere. This is a very encouraging result for the dual mode reactor.

Propane CPOX Reactor

A subscale propane CPOX reactor was designed, built and preliminary testing initiated. The reactor has a two inch diameter and for the initial testing was filled with 127 gms of 1/8" 0.5 wt% Rh/ Al_2O_3 catalyst pellets, for a bed height of approximately 2.5 inches. A half inch layer of 1/8" alumina was placed above and below the catalyst to serve as heat shields. The sketch below shows the reactor configuration and the photo shows the test setup. The reactor was incorporated into a bundle tester which permits automatic control of the anode air and fuel flows, desulfurization of the propane, data logging and incineration of the CPOX products. Plots of the reactor operating temperature are also presented below. The reactor is preheated by firing a stoichiometric propane/air mixture above the catalyst bed. Once the catalyst has been brought up to temperature the burner is extinguished and the air flow adjusted to achieve the desired oxygen to carbon ratio for CPOX reaction ($O/C = 1.2$). As can be seen in the temperature graphs **Figure 5.1.G**, autothermal operation was achieved and the reactor temperatures remained steady with constant flow rate. GC samples were taken during the test period. There was no propane detected in the outlet samples but exact conversion data is uncertain due to a systematic sampling error. Reactor pressure drop measurements indicated that there was no change in bed pressure drop and therefore no fouling of the bed with carbon. The reactor will be operated over the next several months to investigate the long term stability of the reactor and catalyst and to establish the conversion performance under a range of space velocities.

Figure 5.1.G Autothermal operation was achieved and the reactor temperatures remained steady

Extinction behavior of the Rh/Al₂O₃ catalyst

Experiments were performed to gain some insight into the extinction behavior of the Rh catalyst from Johnson Matthey. Approximately 5g of the catalyst was fixed in a ½” tubular inonel reactor and heated to 260°C under and LPG air feed (O/C=1.2). The reactor temperature was gradually reduced and the reactor effluent sampled using the GC. Catalyst extinction is intimately related to heat transfer to and from the catalyst and thus data obtained at the laboratory scale should be used carefully when surmising the behavior of full scale reactors. This caveat notwithstanding, the Rh catalyst seemed to show autothermal¹ operation.

¹ Not to be confused with autothermal reforming, the autothermal descriptor is used here to indicate that with the gas flows undisturbed the catalyst remained ignited at room temperature.

T_{preheat}/ °C	350°C	240°C	75 °C
T_{catalyst}* /°C	674°C	607°C	516 °C
Species			
CH₄	11.9%	8.6%	4.5%
H₂	6.2%	8.4%	9.6%
H₂O	5.9%	8.1%	8.8%
CO	3.8%	6.0%	6.9%
CO₂	11.7%	11.2%	9.6%
O₂	-	-	-
N₂	60.2%	64.8%	62.2%
C₃H₈	0.1%	1.6%	2.8%
C₂H₆	-	-	-
C3 conversion	99.1%	83.9%	70.8%

Table 5.1.G: Reactor effluent during attempted extinction

* Measured temperature at front of catalyst

There was no evidence of carbon seen on the reactor or catalyst after shut-down. The low ignition temperature (~250°C) the suggestion of an autothermal point at O/C=1.2 implies that the catalyst can provide a reducing gas during start up and shut down

A modification was made to the propane CPOX reactor test stand to allow for parallel operation of propane bottle to permit on-line replacement of bottles. A long term test was then initiated. At the time of this report the reactor had been running continuously for 356 hours. A nominal O/C ratio of 1.2 has been employed throughout the test . An LPG flow rate of 3.6 SLPM was used during the first 126 hours and 4.5 SLPM subsequently . These flows correspond to space velocities of 14600 hr⁻¹ and 18700 hr⁻¹ respectively. In both cases propane conversion was 100%.

Although propane conversion has been 100% throughout the test and the selectivities for H₂ and CO appear constant at ~80% (see **Figure 5.1.H** below), the O/C ratio started an upwards drift from 1.09 to its current value of 1.19 after the propane flow rate was increased at 126 hours. This drift was accompanied by commensurate increases in the selectivities for CO₂ and H₂O. The anomalous datapoint near 110 hours was due to an upset condition caused by changing of the LPG tank

Figure 5.1.H Propane conversion has been 100% throughout the test and the selectivities for H₂ and CO appear constant at ~80%

Figure 5.1.J: Carbon dioxide and water selectivities

The increase in propane flow rate initially resulted in a sharp jump in the reactor temperature of $\sim 20^{\circ}\text{C}$, and in the pressure drop of 1.9" W.C. Since then, both have steadily increased.

It is possible that these rises are in response to the increasing O/C ratio, *i.e.* the extra oxygen must result in higher exothermicity because of the increase in total oxidation products. Generally pressure drop is also an increasing function of temperature due to the increases in viscosity and velocity head. The expected temperature and pressure drop rises accompanying the increasing O/C ratio can be estimated. First it is noted that since the selectivity change for all species for the step increase in reactant flows was minimal suggesting that equilibrium is achieved. This is seen in the comparison of products to the equilibrium spectrum (**Table 5.1.H**).

Species	SV=14600 hr ⁻¹ *		SV=18700 hr ⁻¹ **	
	exp.	equil.	exp.	Equil.
CH ₄	1.63%	0.14%	1.50%	0.03%
H ₂	27.92%	29.23%	26.93%	28.18%
H ₂ O	0.30%	1.17%	0.74%	1.76%
CO	20.60%	22.16%	19.78%	21.41%
CO ₂	1.59%	0.81%	1.87%	1.06%
O ₂	0.63%	0.00%	0.80%	0.00%
N ₂	47.32%	46.49%	48.38%	47.56%

Table 5.1.H: Comparison of reactor effluent with equilibrium calculation using measured outlet temperature, and inlet compositions *O/C=1.09,T =832°C, ** O/C=1.14,T=879°C

An investigation will be made as to the source of the O/C increase. The reactor flowrate was reduced to the initial 3.6 SLPM of propane flow to moderate the bed temperatures and to evaluate the O/C ratio at the lower flowrates.

Selective oxidation of higher hydrocarbons in NG over Rh/Al₂O₃ catalyst

The coke resistant properties, and high activity of the Rh catalyst suggest application in the selective partial oxidation of higher hydrocarbons in natural gas. NG in Japan for instance has higher concentrations of butane, propane and ethane than NG in the US.

The higher hydrocarbons have created problems such as premature gas phase ignition or coking of reactors due to the low decomposition temperatures of these species. A catalyst can conceivably use this aspect of their chemistry in order to selectively convert these higher species without initiating the NG reaction. This is due to the lower bond strength of the C-C bonds relative to the C-H bonds.

An experimental was run where propane was blended with methane to simulate a propane rich natural gas. Such a mixture is sometimes used by natural gas utilities to improve the BTU content of the gas in winter. Depending on the ignition characteristics of methane, the heat released during the oxidation of the higher hydrocarbons can also result in full conversion of the feed gas.

A simulated natural gas with ~12% propane was used in this preliminary experiment. Ignition occurred at about 250°C. Oxygen was fully converted and the effluent has a high concentration of total oxidation products – there is the high potential for heat loss from the reactor leading to inefficiency. The results are shown in **Table 5.1.J**:

	Simulated NG	Effluent
T_{preheat}/ °C	-	280°C
T_{catalyst} */°C	-	614°C
Species		
CH₄	84.67%	12.4%
H₂	-	6.8%
H₂O	-	10.9%
CO	-	2.5%
CO₂	0.69%	8.4%
O₂	-	-
N₂	0.69%	58.3%
C₃H₈	12.32%	0.7%
C₂H₆	1.63%	0.1%
C3 conversion	-	73.4%
C1 Conversion	-	28.6%

Table 5.1.J: Reactor effluent during attempted extinction

- Measured temperature at front of catalyst, SV=13000 cc/g.hr

Although the conversion of propane is much higher than the conversion of methane, the molar quantities of carbon from the two species that are oxidized are actually comparable. A separate experiment showed that the catalytic ignition for industrial grade methane (1.8% ethane, 0.4% propane) occurred at only 270°C. It appears that Rh is similar to Pd in that it can also activate methane ignition at low temperature. Another possibility may be to use a very dilute <0.1wt% Pt or Ru catalyst. Pt is not as good as Pd for methane activation and it is less selective for total oxidation products. The table below list the potential candidates for reforming/CPOX/ATR catalyst. Currently, it is felt that the JM Rh catalyst is an excellent precursor for NG streams as it will knock down any higher hydrocarbons such as propane. It also acts as an excellent catalyst for propane POX reactions. Not all catalysts on this table have been tried to date.

CPOX Screening Experiments

Commercial catalysts and experimental catalysts from BASF (Rh and Pt) were tested (**Table 5.1.K**).

The experimental setup is shown in **Figure 5.1.E**. Although the main emphasis of the investigation was CPOX of propane, autothermal and steam reforming were also briefly examined on some catalysts as these reforming modes allow for higher efficiencies in the fuel cell (**Table 5.1.L**). In anticipation of carbon formation a pressure relief valve (10 psi) was situated before the main reactor with its exhaust plumbed to the vent. The nominal reactant flow rates for CPOX, ATR and SR are given in **Table 5.1.M**

O₂ was metered using a 50 ccm O₂ MFC, N₂ with a 1 LPM N₂ MFC and the LPG with two 50 ccm methane MFCs. Flow rates were calibrated using a bubble flow meter and the calibration checked at regular intervals. Catalysts particles were broken and screened to 1.4-2mm size in most cases, although in some noted experiments the large 1/8” cylinders were used

Figure 5.1.J: Experimental set-up

Dual reforming mode reactor

Essentially the same set-up as shown in **Figure 5.1.J** is used for the bench scale trials of the dual reforming mode reactor. The catalyst bed was made up of two abutting sections; a bed of partial oxidation catalyst followed by a Ni based steam reforming catalyst. Two types of Ni based catalyst were tested (**Table 5.1.L**). Both the JM-Rh and JM-Ru catalysts were used as CPOX catalysts for the dual reforming reactor bench scale trial. The pellets were crushed to between 1.4 mm and 2 mm to make their size comparable with the 1.5mm pellets.

Nickel catalysts are more prone to carbon deposition than precious metal catalysts, especially when an equilibrium potential exists. An initial screening experiment tested the composite bed for stability under partial oxidation ($O/C=1.2$) with the reactor temperature at 370°C . This temperature is considered to be high enough for heterogeneous reactions to take place and is in the temperature range where encapsulating carbon is favoured. It is also likely to be close to the temperatures that would exist in the reforming bed when

partial oxidation occurs on the precious metal catalyst. Testing was also conducted at the reactor temperature of 550°C, *i.e.* in a temperature regime where whisker carbon is promoted. The CPOX reactions were run for 16 hours after which the beds were cooled under nitrogen and visually examined for carbon formation.

Catalyst Autothermal Temperature

The startup sequence for the CPOX reactor depends on the existence of an autothermal point, *i.e.* when the catalytic reactions are still ignited in the limit of no heat input. If this is the case no provision would need to be made for the initial preheating of reactants. The existence of such a point was verified for the Johnson Matthey 0.5 wt% Rh catalyst in a ¾" OD bench-top reactor.

5g of the catalyst was thermally insulated from the inconel reactor walls using ceramic paper, the paper also acting as a radiation shield at the front and rear of the bed. The tubular furnace provided the initial heat for igniting the heterogeneous reactions and the reactants (O₂, N₂ and LPG) were fed to the reactor such that O/C~1.2 at a space velocity of ~4000 hr⁻¹. After ignition, the furnace was shut off and the reactor allowed to cool to ambient, while the catalyst temperatures and reactor effluent was monitored.

CPOX

The results for the CPOX catalyst screening experiments are given in **Table 5.1.P**. From the point of view of propane conversion, the performance of the first catalyst appears superior to all other catalysts.

Note: selectivities do not always add up exactly to 100% because of uncertainties in the flows and concentration measurements

* 2.1g of alumina was ground down to 1.4-2mm particles and mixed with 3g of catalyst in an attempt to remove hot spot formation

** 5g of catalyst was used in a ¾" inconel reactor, ceramic paper was used to insulate catalyst from walls. due to limitations of the controllers, SV could not be increased

In all cases significant carbon buildup as previously seen on Ni catalysts, was *not* seen on the catalysts, although a light dusting of steady state carbon were sometimes seen on the leading edge of the bed and, in a few cases carbon was found to accumulate on metal surfaces down stream of the catalyst beds.

Figure 5.1.K: Degradation of -Rh-Cu

As the conversion of propane fell there was an increase in the selectivities for water and carbon dioxide - in line with the observation that, despite the activity change, oxygen conversion was always 100%. The catalyst appeared to change from a partial oxidation catalyst to a total oxidation catalyst. The product distribution from the Rh-Cu and -Pt-Cu experiments are very similar despite the fact that the metals have quite different catalytic properties. This suggests that there may be an issue with catalyst preparation. In the case of the -Rh-Cu catalyst copper metal was apparent on the quartz reactor suggesting that the support in these cases may not have been stable.

The -Ru catalyst (**Figure 5.1.L**) also changed activity after time online, the conversion slowly dropping from 95% to 80% . At the lower reactor temperature of 370°C the conversion is quite high but when the reactor was shut down and restarted at the higher temperature of 500°C the conversion abruptly drops and continues to decrease. The reasons for the change are not clear. Carbon was not apparent in the reactor anywhere, however the catalyst pellets appeared lighter in color suggesting possibly metal loss.

These results are in stark contrast to the performance of the -Rh catalyst, which maintained its stability over the entirety of a 190 hour test at 370°C and a 160 hour test at 550°C

Figure 5.1.L: LPG conversion over -Ru

Figure 5.1.M: LPG conversion over -Rh (reactor temperature 370°C, SV 9700 hr⁻¹)

Figure 5.1.N: LPG conversion over -Rh (reactor temperature 550°C, SV 3500 hr⁻¹)

Species	% Species in gas phase		
	Equilibrium 550°C, no C	Equilibrium 550°C	Experiment after 20 hrs
CH ₄	8.1%	3.3%	5.3%
H ₂	14.3%	18.1%	19.2%
H ₂ O	4.2%	10.2%	2.7%
CO	8.9%	4.3%	14.1%
CO ₂	9.0%	8.4%	6.2%
O ₂	0.0%	0.0%	0.0%
N ₂	55.5%	55.7%	52.6%

Table 5.1.Q Comparison of -Rh data with equilibrium

In **Table 5.1.Q** the gas phase composition obtained from the -Rh experiment at 550°C is compared with equilibrium expectations. Carbon is favoured at equilibrium, however it is clear from visual observation of the precious metal catalysts that they do not accommodate carbon-forming reactions. The first two columns give the gas phase compositions expected when carbon is not considered and when carbon is considered as an equilibrium species. The effluent from the reactor does not match either, suggesting equilibrium is not attained, despite the every low space velocity in this particular experiment. It also implies that the catalyst was stable during the experiment and that this stability was not due to the catalyst bed being so large that any deactivation couldn't be seen.

The Pt-Ce catalyst was also performed reasonably well at 370°C. Even though the particles are smaller for the catalysts and there is probably less propensity for

Figure 5.1.P LPG conversion over BASF Pt-Ce (reactor temperature 370°C, SV 10725 hr⁻¹)

reactant channeling, the conversion is much less than the -Rh catalyst. However, although the C3 conversion was only 80%, compared to 97% for the -Rh catalyst, it had a much higher selectivity for H₂ and CO. This is in agreement with observations in the literature that partial oxidation over Pt based catalysts tends to follow a direct route. This would result in lower temperatures at the front of the bed and also higher selectivities for H₂ and CO, rather than their oxidized counterparts. After the 200 hour run, carbon deposits were found on the inconel surfaces after the packed bed. This could be the result of disproportionation of C through the Boudouard reaction. Some studies have also suggested that owing to poor steam reforming ability, alkenes are also common products from adiabatic partial oxidation and these have a tendency to polymerize. The GC saw no traces of alkenes however.

Autothermal Reforming and Steam Reforming

The results of autothermal and steam reforming trials on -Rh are shown graphically in **Figure 5.1.Q** and quantitatively in **Table 5.1.R**.

Figure 5.1.Q: Transition from CPOX to steam reforming over -Rh

	Reforming Mode				
	CPOX	ATR	ATR	ATR	SR
Inlet conditions					
SV / cc g ⁻¹ hr ⁻¹	9700	9900	9900	9900	12500
O/C	1.2	0.8	0.8	0.8	-
S/C	-	1	1	1	2.2
T preheat/ °C	350	350	400	500	500
T catalyst*/°C	616	522	575	633	452
Composition %:					
CH ₄	12.3	14.3	16.1	11.7	12.6
H ₂	5.9	10.9	16.0	24.9	23.3
H ₂ O	5.8	24.2	19.4	14.6	27.9
CO	3.3	1.4	1.9	4.8	3.2
CO ₂	11.4	12.7	14.2	13.4	8.3
N ₂	61.1	35.1	32.4	30.5	24.6
C ₃ H ₈	0.1	1.4	-	-	0.1
C ₂ H ₆	-	-	-	-	-

Table 5.1.R: Reforming modes over -Rh catalyst:

* Measured temperature at front of catalyst

In this experiment, 2.3g of -Rh was packed into a ½” inconel reactor and tested over the various reforming modes for ~16 hours. Continuous testing greater than 8 hours could not be performed because of the small volume of the syringe pump. Propane was completely converted over -Rh at 500°C. No carbon was found on the catalyst at shut down.

Steam reforming was also attempted with the -Ru catalyst. Despite S/C=2.3 and a reactor temperature of 550°C, propane conversion was only 50%.

Dual Reforming mode (CPOX/SR) Reactor

The composite beds were tested consecutively; the first, followed by the second. The temperature of the reactor (the pre-heat temperature) was maintained at 370°C, and gas flows were used. It is expected that at these conditions (a) C is thermodynamically favored, and (b) deposition rates should be higher than gasification rates. **Table 5.1.S** compares the gas phase compositions sampled from the reactors for the two Ni catalysts. After 16 hours of testing the -RH/C2 was essentially carbon free. A light dusting of carbon was noticed near the front of the C2 bed. This is in dramatic contrast to the -Rh/C3 bed. Although the effluents from both composite beds were initially very similar, the pressure drop across the C3 bed started to increase. After 16 hours it was noticed that the pressure drop was so great that bypass valve opened.

* Measured temperature at front of -Rh catalyst, ** space velocity for CPOX catalyst only

Figure 5.1.R: Comparison of catalysts from the composite bed experiments

The catalysts are compared in **Figure 5.1.R**. When it is considered that the initial volumes of catalyst were almost the same, the degree to which coking occurred in the C2 bed can be fully appreciated. The C2 particles were completely destroyed suggesting that carbon was formed in the pores, rupturing the catalyst support. The pellets however suffered no damage and no significant carbon build-up was observed.

The Rh catalyst surfaces looked clean -the carbon fragments that appear in **Figure 5.1.S b)** have likely resulted from the coking of the C3, or from pyrolysis of propane caused by the bed blockage. Seeing that the transition from CPOX to SR is likely to be completed in a few hours it appears that the C2 is the ideal catalyst to follow the -Rh catalyst. Its coke resistance is probably due to its high gasification activity and small Ni crystallite size. Being a pre-reforming catalyst it is designed to work at low temperatures, unlike the C3.

The -Rh composite bed was re-tried at the almost the same conditions, but with a reactor temperature of 550°C. After 16 hours the reactor was cooled under N₂ and visually inspected. The C2 pellets immediately abutting the Rh catalyst were damaged. There was evidence of both encapsulating carbon and whisker carbon; some pellets were swollen with carbon and others were encased with carbon.

Catalyst Autothermal Temperature

The existence of such a point was verified for the 0.5 wt% Rh catalyst in a ¾" OD inconel reactor. The tubular furnace provided the initial heat for igniting the heterogeneous reactions and the reactants (O₂, N₂ and LPG) were fed to the reactor such that O/C~1.2 at a space velocity of ~4000 hr⁻¹. As in the past, ignition occurred near a catalyst temperature of 250°C. After ignition the furnace was shut off and the surrounds

allowed to cool. Despite the insulation modifications it was clear that the inconel tube was acting as a heat fin. Although the preheating furnace was off, its control thermocouple still measured a temperature of 65°C even after 46 hours of operation. A thermocouple at the front of the bed measured a temperature of 465°C whereas the adiabatic temperature for a thermally equilibrated effluent is ~800°C.

The reaction appeared very stable with the inlet temperature measuring 465°C, and propane conversion at 75%. After 46 hours of operation no sign of carbon was seen on the catalyst. Since the peak temperature was quite gentle, coke deposition was not expected.

Conclusion

The results of this investigation should be considered as preliminary data for the design of a 5kW pilot scale reactor. Hydrogen production by CPOX is desirable because of the minimal balance of plant. In the ideal case, once the catalytic reactions are ignited, 100% conversion is achieved and selectivities are stable. Perhaps, the minimum requirement to reach this condition would be the preheating of the feed. In this investigation however we see that despite only precious metal catalysts being screened, only the -Rh catalyst approached this ideal activity.

The ignited steady state is achieved by a balance of heat and mass transfer rates. The ignited state remains mass transfer controlled unless heat loss from the system is excessive. Heat generation depends on the gas flow rate, and the catalyst surface area per unit volume, and the boundary layer thickness. Heat loss depends on the thermal conduction and the surface area of the reactor shell. Since area/volume ratios are large in small diameter reactors, there is the possibility that unless heat is actually added to the system the reaction exothermicity is not sufficient to maintain the ignited state and the reactions extinguish, the reactor cools, and conversion falls to almost zero. The presence of the autothermal point for the -Rh catalyst in the 3/4" reactor strongly suggests that, unless a deactivating mechanism is initiated by the high temperatures, an autothermal point will also exist in the larger reactors. In the present study at the autothermal point, propane conversion was only 75%, but since higher temperatures will exist in the pilot scale reactor, 100% propane conversion can be expected. The high temperature, however, can also lead to catalyst deactivation either through solid-state reactions, including sintering, but also through carbon deposition through gas phase pyrolysis. The catalyst temperature can be controlled to some extent by the mixing of alumina pellets with the catalyst pellets².

The dual reforming mode bed concept is viable, but only with the C2 nickel catalyst. However the long term stability of such a system is not known. Even with the G1-80 carbon did form on the catalyst at the higher temperature of 550°C and so it would be safest not to use Ni catalysts at all. The C2 is also known to be pyrophoric due the small Ni crystallites. If it is exposed to air while cooling down there is the risk of deactivation.

² Recupero, V., Pino, L., Di Leonardo, R., Lagana, M., Maggio, G., "Hydrogen generator, via catalytic partial oxidation of methane for fuel cells" *J. Power Sources*, 71, 1998, pgs 208-214

Given these potential problems with the Ni catalysts and since the -Rh catalyst also had good steam reforming activity, the prudent approach for initial fuel cell prototypes would be to use the -Rh catalyst for both CPOX and steam reforming.

The poor activity of the Ru catalyst for steam reforming was surprising. Rh and Ru are usually considered to have superior intrinsic kinetics for steam reforming, even compared to Ni. The current cost of Rh, Ru, Pt and Ni are \$1355, \$80, \$884, and \$0.41, per troy ounce, respectively. At precious metal loadings of 0.5wt% and a Ni loading of 50 wt%, the metal costs per kg of catalyst are \$217.82, \$142.11, \$12.86 and \$6.54 respectively. The key figure is the estimated cost for the Ru metal, almost 17 times less than the price of Rh. In this investigation the Ru catalyst's performance was fair; it showed strong resistance to coking, with relatively high activity. However, given the large price differential, the Ru catalyst metal loading could be easily increased several times to compensate for what appears to be a lower intrinsic activity. There have been a few reports suggesting that the catalytic activity of Ru is similar to Rh³, however despite what appears to be large economic potential, research on Ru catalysis is less extensive.

Despite the resistance of the catalysts to carbon formation at an O/C=1.2, it should be remembered that, below 800°C, the thermodynamic potential for carbon formation still exists. For one of the catalysts, 0.5wt% Pt/CeO₂-ZrO₂, significant carbon was found on the metal surfaces downstream of the catalyst, despite the reactor temperature being as low as 370°C. To avoid carbon formation, the residence time of the synthesis gas in the piping between the reactor and manifolds should be minimized.

Propane partial oxidation and reforming

Commercial LPG is reformed to synthesis gas by CPOX over a 0.5 wt% Rh/alumina catalyst. The final reactor setup is shown in Figures 1 and 2. The catalyst loading is 127g.

Gas samples were taken from Generator 503 on the afternoon of 6/1/05. Viewing down the manifold end of the stacks, the stacks are labeled as LL(left-left), LC (left-center), RC, and RR.

Gas samples were taken from:

1. the fuel/air inlet pipe feeding stacks RR and RC
2. the outlet from the CPOX reactor feeding stack RR
3. each of the off-gas chambers of all 4 stacks (*i.e.* stack effluent)

³ Freni, S., Calogero, G., Cavallaro, S., "Hydrogen production from methane through catalytic partial oxidation reactions"

Choudhary, T.V., Goodman, DW, "Methane activation on ruthenium; the nature of surface intermediates", *Topics in Catalysis*, 20,1-4 (2002), pgs 35-42

For (1) the sample was fed directly into the sampling bag using the system pressure, for (2) the sample was introduced first through the condenser and then into the sampling bag using the system pressure, and for (3) the sample was obtained using the condenser and a gas sampling pump. After the necessary purging of the condenser and sample lines, the sampling bag was filled over the course of 1 minute, during which time the fuel cell current, fuel flow, and air flow were noted.

The O/C ratio was estimated from the sample from the fuel air inlet (1) and this was used for fuel utilization calculations for the stack. Some oxygen was observed in the samples from the off-gas chambers (3), and this must have been introduced from air leaks during sampling, since the off-gas is a reducing gas at high temperature. As such, corrections were applied to the gas measurements to both the oxygen and nitrogen peak areas in these samples. Since water cannot be measured using the GC, it had to be calculated using a minimization of the discrepancy resulting from a comparison of the atomic percentages in the inlet (from gas sample (1) and the current) and outlet (gas sample (3)).

The fuel utilization was calculated using the expression:

$$FU = \left(1 - \frac{\left(\frac{0.79 \times OC}{2 \times 0.21} + 3 \right) (x_{CO} + x_{H_2})}{4 - OC} \right) \times 100\%$$

where OC is the O/C ratio. The expression assumes that the fuel gas is methane and that there are no gas leaks in the off-gas manifolds or cells. Note that the current does not appear in this expression although it does have a slight effect on the inference of the hydrogen and carbon monoxide concentrations.

If no uncertainty is assumed in the current (including no leakage current from internal shorts) an estimate of the fuel and air to each stack (and subsequently the total flows) can be estimated, again through minimization of the atomic discrepancy with the off-gas water content and fuel flow as the minimizing variables, and with the O/C ratio constrained to the value measured in (1)

Results and Analysis

The results are summarized in **Table 5.1.T** with a visual summary of the measured off-gas compositions in **Figure 5.1.T**.

	Fuel Cell Stack			
	RR	RC	LC	LL
Stack current /A	35.5	34.3	34.5	33.6
Atom discrepancy RMS	2.1%	2.9%	2.5%	3.4%
CH₄ per stack /SLPM	2.5	3.4	3.3	2.9
Air per stack /SLPM	9.0	12.3	12.1	10.4
FU%	82%	56%	58%	65%
Off-gas Composition				
H₂	5.3%	12.9%	12.2%	10.2%
H₂O	28.8%	21.4%	22.0%	24.2%
CO	2.4%	5.8%	5.6%	4.5%
CO₂	15.4%	12.2%	12.3%	13.7%
N₂	48.0%	47.7%	47.8%	47.4%

Table 5.1.T: Gas Analysis from Generator 503 off-gas manifolds

Note that the analysis uses 1) the O/C ratio from sample (1), 2) the noted stack current at the time of measurement (3), and 3) the compositions as measured in sample (3). The total fuel flow to each stack is thus found independently using the atomic discrepancy minimization. The total fuel and air flow to the generator are subsequently calculated as the sum of the individual flows (corrected to the same current of 35.5A) as 12.5 SLPM and 45.1 SLPM respectively (O/C=1.52). These numbers are to be compared against the generator flow meter values of 14.6 SLPM and 42 SLPM respectively.

From **Table 5.1.T** the fuel utilization is clearly higher in the RR and LL stacks, and this is also seen from the quantitative calculation in Table 5.1.T. The higher fuel utilization can be interpreted to be the result of poor fuel distribution and fuel leaks (as is assumed in the calculations of Table 5.1.T) – or as the result of short circuit currents or air leaks into the off-gas manifold. If flow distribution is assumed to be equitable, and the fuel flow fixed at 14.6 SLPM, the estimated effective currents would be 51.8, 36.6, 37.7 and 42.8A for stacks RR, RC, LC, LL respectively. In both cases the utilizations are minimally effected by this change in viewpoint and are essentially the same as given in Table 5.1.T.

Figure 5.1.T: Chromatograms of the off-gas from the four stacks

Note: oxygen peak in outlet manifold is likely due to air leakage during sampling and has been accounted for in calculations

Figure 5.1.U: Chromatograms of the R stack fuel air inlet and the RR CPOX exhaust

Note: the presence of small amounts of hydrocarbons in the NG. These have been ignored in the aforementioned calculations

Analysis of the CPOX outlet of stack RR is also consistent with the O/C ratio from sample (1) of 1.52. Methane conversion was estimated as 82%, with CO and H₂ selectivities both approximately 81%.

Long-term propane testing

Rapid catalyst light-off was consistently achieved using the pre-heating burner without issue. The burner only needed to operate for seconds in order for the catalyst light-off temperature of ~250°C to be achieved. Steady state reactor temperatures and pressures were within 10% of their final values within 10 minutes. The following results were obtained from a long term CPOX test started on 12/22/04. At the time of this report the reactor had been running continuously for 356 hours. A nominal O/C ratio of 1.2 has been employed throughout the test. An LPG flow rate of 3.6 SLPM was used during the first 126 hours and 4.5 SLPM subsequently. These flows correspond to space velocities⁴ of 14600 hr⁻¹ and 18700 hr⁻¹ respectively. In both cases **propane conversion was 100%**. Higher space velocities cannot be achieved in the current configuration owing to limitations of the air blower.

Although propane conversion has been 100% throughout the test and the selectivities for H₂ and CO appear constant at ~80% (**Figure 5.1.V**), the O/C ratio started an upwards drift from 1.09 to its current value of 1.19 after the propane flow rate was increased at 126 hours. This drift was accompanied by commensurate increases in the selectivities for CO₂ and H₂O (**Figure 5.1.W**). The anomalous datapoint near 110 hours was due to an upset condition caused by changing of the LPG tank

⁴ Space velocity is defined in this report as the number of reactor volumes of gas (at 25°C, 1atm) processed per unit time.

Figure 5.1.V: Propane CPOX Reactor

Figure 5.1.W: Propane CPOX experiment setup

Figure 5.1.X Carbon monoxide and hydrogen selectivities

Figure 5.1.Y: Carbon dioxide and water selectivities

The increase in propane flow rate initially resulted in a sharp jump in the reactor temperature of ~20°C, and in the pressure drop of 1.9" W.C. Since then, both have steadily increased (**Figure 5.1.Z**)

Figure 5.1.Z: Temperature at top of catalyst bed and pressure drop across reactor

It is possible that these rises are in response to the increasing O/C ratio, *i.e.* the extra oxygen must result in higher exothermicity because of the increase in total oxidation products. Generally pressure drop is also an increasing function of temperature due to the increases in viscosity and velocity head. The expected temperature and pressure drop rises accompanying the increasing O/C ratio can be estimated. First it is noted that since the selectivity change for all species for the step increase in reactant flows was minimal suggesting that equilibrium is achieved. This is seen in the comparison of products to the equilibrium spectrum (**Table 5.1.U**).

Species	SV=14600 hr ^{-1*}		SV=18700 hr ^{-1**}	
	exp.	equil.	exp.	equil.
CH ₄	1.63%	0.14%	1.50%	0.03%
H ₂	27.92%	29.23%	26.93%	28.18%
H ₂ O	0.30%	1.17%	0.74%	1.76%
CO	20.60%	22.16%	19.78%	21.41%
CO ₂	1.59%	0.81%	1.87%	1.06%
O ₂	0.63%	0.00%	0.80%	0.00%
N ₂	47.32%	46.49%	48.38%	47.56%

Table 5.1.U: Comparison of reactor effluent with equilibrium calculation using measured outlet temperature, and inlet compositions *O/C=1.09,T =832°C, ** O/C=1.14,T=879°C

For an ideal adiabatic reactor then, it is possible to calculate the maximum temperature rise at equilibrium and use this temperature, to estimate the expected increase in the pressure drop using Ergun's equation for flow in packed beds. The results of such an analysis are presented in **Figures 5.1.AA and 5.1.AB**. Note that the data is presented in the form of incremental differences from the initial pressure drop and temperature.

Figure 5.1.AA: Comparison of measured temperature increase vs predicted adiabatic temperature increase

The predictions are generally in reasonable agreement, matching the trend with time, but more importantly there is an obvious correlation in both figures of the measured and theoretical variables with the experimental increase in O/C ratio.

Having noted the agreement in the incremental changes, some discrepancies in the *absolute* theoretical and predicted quantities should be noted. Considering the pressure drop first, at 0 hours, the predicted pressure drop is 6.25" W.C. compared with an experimental value of 5.5" W.C. This agreement is actually quite good considering the assumptions used in applying the Ergun equation, *i.e* constant temperature, velocity, and constant composition. In particular, the temperature has been assumed to be the experimental measurement averaged over the bed at 0 hours, plus the *predicted* adiabatic temperature change at longer times. The composition is assumed to be the equilibrium reformat composition as calculated at 800°C, but this is obviously also the highest possible flow rate in the bed.

Figure 5.1.AB: Comparison of measured pressure drop increase vs predicted pressure drop increase

The entrance temperature was measured to be ~100°C throughout the test, leading to a calculation of the adiabatic temperature (at 0 hours, O/C=1.09) of only 766°C. The lowest temperature measured in the bed, however was 833°C. Since the reactor is not perfectly adiabatic, we would expect the temperature to be even lower than 766°C. The high temperature could be due to a poor temperature measurement at the entrance, *i.e.* the

reactant flow is much higher than 100°C, but is most likely due to the local hot spots in the catalyst bed. The temperature measured at the outlet sampling point⁵ is ~700°C – in line with expectations.

The measured *bed* temperatures are shown in **Figures 5.1.Y** and the maximum temperature at the front of the bed is currently in excess of 1000°C. It is clear then, that the path to equilibrium over this catalyst, must utilize the total oxidation and steam reforming steps. High surface area catalysts are difficult to stabilize at high temperature. The alumina support used in the current catalyst is based on γ -alumina, an unstable form, which will revert to the low surface area α -alumina when exposed to temperatures greater than 800°C⁶. Thus while propane partial oxidation currently appears successful, one can expect the catalyst to deactivate with time, and steps should be taken to reduce the temperature. This may require diluting the catalyst with inert alumina pellets, or the use of a different catalyst system, possibly incorporating platinum. Many research groups are optimizing bimetallic precious formulations for these types of reactions.

Figures 5.1.AC: Catalyst bed temperatures

A final note is with regard to the desulphurization. LPG usually contains a cocktail of sulfur species comprised of thioxanes, mercaptans and carbonyl sulfide, incorporated though processing and odorizing. From CE-04-046, the 9L adsorbent bed should last for ~1000 hours, but since the setup used in this test utilizes only the Puraspec adsorbent, which has questionable efficacy for carbonyl sulfide, it is possible for sulfur to still enter

⁵ This sample point is after a 6" long mixing length containing alumina spheres

⁶ From discussion with Dr Lee Chi at Johnson Matthey, NJ

the reactor. However, although the air-fuel entering the reactor does have a strong malodorous scent, mercaptan and COS chemical detector tubes show no sign of sulfur in either the inlet or outlet reactor gas streams. The same mercaptan tubes, however, also did not detect sulfur in the natural gas (to generator 503), which should contain at least 4ppmV of mercaptans. This calls into question the reliability of the chemical detector tubes in general and since the nose can typically detect sulfur to ppb levels the actual extent of desulfurization is unclear at this time.

Conclusion

The propane CPOX reactor has met expectations of rapid start-up and moderate term stability. At the time of this intermediate report the reactor was 356 hours into a 500 hour test, and at a space velocity of $\sim 18,700 \text{ hr}^{-1}$ ($\sim 27 \text{ SLPM H}_2$ equivalent), propane conversion remained at 100% with hydrogen and carbon monoxide selectivities of at least 80%, giving a fuel gas of $\sim 47\%$ syngas. Temperatures and pressures have crept up during the test, but this can mostly be attributed to the drift in the O/C ratio from 1.09 to 1.18.

There has been no significant outward sign of catalyst deactivation, but the high temperatures measured at the axis of the bed suggest that the alumina support will probably lose surface area.

The extent of desulfurization is unclear, but if sulfur is entering the reactor it is having no noticeable effect on activity.

Subtask 5.2 – Light fuel desulphurization

To support the development of an all-purpose room temperature de-sulfurizer an investigation into common odorant blends was undertaken.

Oxychem, one of the main odorant suppliers, makes odorant blends from the following S containing species.

- i-propyl mercaptan (IPM)
- t-butyl mercaptan (TBM)
- n-propyl mercaptan (NPM)
- dimethyl sulfide (DMS)
- tetrahydrothiophene (thiophane, THT)
- secondary butyl mercaptan (SBM)
- diethyl sulphide (DES)
- methyl ethyl sulphide (MES)

Of these species DMS is considered the most difficult to adsorb. BASF is skeptical that the DESULF-2 will have sufficient activity to remove the DMS at room temperature and have thus started higher temperature trials on our advice.

DMS is less likely to be used as an odorant in the US but can form during the hydrolysis of other species. At least two Japanese NG utilities use a 50:50 molar TBM/DMS blend known as RP Captan 60/40. Typical concentrations are 8ppmW S total.

Based on bed sizes of 9L of Puraspec 2085 (Johnson-Matthey) and 10L of DESULF-1 (BASF), the useful bed lifetimes have been estimated for different S concentrations in the LPG feed in **Table 5.2.A**:

Average S conc. in feed /ppmW	180	125	60
Time online*/ hr	2800	4031	8398
DC. Energy/ kW.hrs	28000	40310	83980
COS/ ppmW S**	<116	<100	<32
THT/ S-S /ppmW S**	<75	<52	<25

Table 5.2.A S concentrations in the LPG feed

* at maximum flow-rate of 18 SLPM – 10kW DC output

** limits for the given kW.hrs

In the worst case, the beds should be sufficient for 2800 hours with propane flowing at 18 SLPM, or more generally 28000 kW.hrs DC. For a continuous 5kW DC output, for example, the beds should last for ~5600 hours.

List of Acronyms and Abbreviations:

AC	Alternating Current
ANSI	American National Standards Institute
ASCII	American Standard Code for Information Interchange
BOM	Bill of Material
BOP	Balance Of Plant
CAD	Computer Aided Design
CAN	Controller Area Network
CM	Common Mode
CPOX	Catalytic Partial Oxidation
DC	Direct Current
DSP	Digital Signal Processor
DTA	Differential Thermal Analysis
EEPROM	Electrically Erasable Programmable Read-Only Memory
EMC	ElectroMagnetic Compatibility
ESTOP	Emergency Stop
FCIC	Fuel Cell Interface Converter
FCS	Fuel Cell Stack
FCUPS	Fuel Cell Uninterruptible Power Supply interface
FET	Field Effect Transistor
FU	Fuel Utilization
GUM	Gas Utility Module
HMI	Human-Machine Interface
IC	Investment Casting
I/O	Input / Output
IR	InfraRed
LED	Light Emitting Diode
lpm	Liters per minute
MIM	Metal Injection Molding
mlpm	Milliliters per minute
MOR	Modulus of Rupture
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
NPT	National Pipe Thread
NYSERDA	New York State Energy Research and Development Authority
PC	Personal Computer
PCB	Printed Circuit Board
P&ID	Piping and Instrumentation Diagram
PID	Proportional Integral Differential
POX	Partial Oxidation
PLC	Programmable Logic Controller
PWM	Pulse Width Modulation
ROM	Read Only Memory
RPM	Revolutions Per Minute
RPTS	Rapid Prototype Test Station
SEM	Scanning Electron Microscope

SiC	Silicon Carbide
SOFC	Solid Oxide Fuel Cell
SPI	Serial Peripheral Interface
TEC	Thermal Expansion Coefficient
TGA	Thermal Gravimetric Analysis
UPS	Uninterruptible Power Supply
TI	Texas Instrument
w.c.	Inches water column
YSZ	Yttria Stabilized Zirconia