AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 2

**Monolithic Solid Oxide Fuel Cell Technology
Advancement for Coal-Based Power Generation**

**Annual Report
October 1991 - September 1992**

May 1993

Work Performed Under Contract No.: DE-AC21-89MC26006

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
Allied Signal Aerospace Systems and Equipment
Torrance, California**

MASTER

rb
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

CONTENTS

<u>Section</u>		<u>Page</u>
1.	INTRODUCTION	1-1
2.	BACKGROUND ON MONOLITHIC SOLID OXIDE FUEL CELLS	2-1
	2.1 DESIGN CONCEPT	2-1
	2.2 DESIGN FEATURES	2-2
3.	MATERIALS RESEARCH AND DEVELOPMENT	3-1
	3.1 STUDY OF INTERCONNECT INTERACTION (TASK 2)	3-1
	3.1.1 Objective	3-1
	3.1.2 Two-Material MSOFC	3-1
	3.1.3 Four-Material MSOFC	3-8
	3.1.4 Study of (La,Ca)CrO ₃	3-13
	3.1.5 Liquid Phase Sintering of (La,Ca)CrO ₃	3-25
	3.2 LONG-TERM CATHODE STABILITY	3-34
	3.2.1 Objective	3-34
	3.2.2 Discussion	3-34
	3.3 REFERENCES	3-42
4.	FABRICATION	4-1
	4.1 FABRICATION DEMONSTRATION	4-1
	4.1.1 Objective	4-1
	4.1.2 Fabrication of Cells and Stacks	4-1
	4.2 DEFECT ANALYSIS	4-45
	4.2.1 Objective	4-45
	4.2.2 Analysis	4-45
	4.2.3 References	4-46
5.	TESTING ON COAL GAS	5-1
	5.1 PERFORMANCE TESTING	5-1
	5.1.1 Objective	5-1
	5.1.2 Single-Cell Testing	5-1
	5.1.3 Stack Testing	5-6
	5.1.4 Posttest Analysis	5-16

CONTENTS

<u>Section</u>		<u>Page</u>
6.	QUALITY DEVELOPMENT	6-1
6.1	EVALUATION OF NONDESTRUCTIVE EVALUATION (NDE)	
	METHODS	6-1
6.1.1	Objectives	6-1
6.1.2	Results	6-1
6.2	STRESS ANALYSIS OF STACKS	6-3
6.2.1	Objective	6-3
6.2.2	Discussion	6-3
6.3	QUALITY CONTROL OF SOURCE MATERIALS	6-3
6.3.1	Objective	6-3
6.3.2	Evaluation of Lanthanum Chromite	6-3

1. INTRODUCTION

This report describes the work performed under Contract DE-AC21-89MC26006, for the U.S. Department of Energy (DOE)/Morgantown Energy Technology Center (METC) program. The report covers the period October 15, 1991 through September 30, 1992.

The program is being conducted by a team consisting of AlliedSignal Aerospace Systems & Equipment (ASE) (formerly AiResearch Los Angeles Division) and Argonne National Laboratory (ANL). The objective of the program is to advance materials and fabrication methodologies to develop a monolithic solid oxide fuel cell (MSOFC) system capable of meeting performance, life, and cost goals for coal-based power generation. The program focuses on materials research and development, fabrication process development, cell/stack performance testing and characterization, cost and system analysis, and quality development.

2. BACKGROUND ON MONOLITHIC SOLID OXIDE FUEL CELLS

The monolithic solid oxide fuel cell (MSOFC) is a recent design concept in fuel cell technology. The MSOFC is made up of all solid components, permitting fabrication into unique shapes unachievable in fuel cell systems having liquid electrolytes. The MSOFC design places the thin ceramic components of the fuel cell in a lightweight, compact structure of very small cells. The monolithic design eliminates inactive structural support, increases active surface area, and lowers voltage losses caused by internal resistance. This results in a MSOFC with high efficiency, excellent performance, and power per unit mass or volume unequaled in any other solid oxide fuel cell configuration.

2.1 DESIGN CONCEPT

In a MSOFC, fuel and oxidant produce a dc current by combining electrochemically across the solid oxide electrolyte at an operating temperature of 1000°C. Oxygen in the oxidant fed to the cathode accepts electrons from the external circuit to form oxide ions that are then conducted through the dense electrolyte to the anode. At the anode, oxide ions combine with hydrogen in the fuel to form water, liberating electrons as shown in Figure 2-1. Cells of the MSOFC are connected by an interconnect to build voltage. The interconnect carries electrons from the anode of one cell to the cathode of the next in electrical series.

Figure 2-1. Solid Oxide Fuel Cell Chemistry

There are two versions of the MSOFC, coflow and crossflow. In the coflow version, the monolithic fuel cell consists of a honeycomb-like array of adjacent fuel and oxidant channels that resemble corrugated paperboard (Figure 2-2). Oxidant channels are lined with a porous cathode, and fuel channels are lined with a porous anode. A gastight layer of electrolyte is located between the anode and cathode. An interconnect, which is also gastight, connects the cells in electrical series.

Figure 2-2. Coflow Monolithic Solid Oxide Fuel Cell

The typical thickness of the layers is 25 to 100 μm , and the distance from cell to cell is 1 to 2 mm. As shown in Figure 2-2, the MSOFC is made of two types of laminated structures, each composed of three ceramics—anode/electrolyte/cathode and anode/interconnect/cathode. The laminated structure containing the electrolyte is appropriately corrugated. The corrugations form the gas seals at the edges of the monolithic structure (which is extremely important because the gas seal has been a stumbling block in solid oxide fuel cell planar design).

In the crossflow version, the fuel and oxidant channels are formed by corrugated anode and cathode layers and are oriented at right angles to each other (Figure 2-3). The anode/electrolyte/cathode and anode/interconnect/cathode composites are flat and stacked alternately between the corrugated anode and cathode layers. The crossflow version results in the power density being reduced by a factor of about 2, compared with that of the coflow version; however, the crossflow version offers a simpler means of ducting gases in and out of the monolithic fuel cell.

2.2 DESIGN FEATURES

Small cells of lightweight self-supporting ceramics are the key to the MSOFC potential. The small size of individual cells in the monolithic structure increases the active surface area. For example, a coflow MSOFC with channels about 1 mm in diameter has a ratio of active surface area to volume of about $9.4 \text{ cm}^2/\text{cm}^3$ (Figure 2-4). This is about seven times the ratio for tubular solid oxide fuel cells of 1 cm in diameter.

More importantly, the small cell size in the MSOFC reduces voltage losses due to internal electrical resistance. Because current is carried in-plane by the electrodes in both conventional and monolithic designs, a decrease in the cell size decreases the

Figure 2-3. Crossflow Monolithic Solid Oxide Fuel Cell

Figure 2-4. Monolithic Configuration, Providing a Maximum Active Surface Area per Unit of Volume

internal electrical resistance. In MSOFC's, the major source of internal voltage loss is the resistance that electrons encounter in the cell ceramic components. Inside the operating fuel cell, an oxidation reaction (the electrochemical reaction of hydrogen fuel) releases electrons on the anode side of the barrier that separates oxygen channels from fuel channels. Flowing along the anode, electrons travel around the fuel-channel wall and across the interconnection to the cathode of the adjoining oxygen channel (Figure 2-2).

The electrons then flow along the cathode around the oxygen channel to the cathode/electrolyte interface, where they are consumed in a reaction (with oxygen) that produces an oxide ion. The oxide ion is transported through the plane of the electrolyte, reacts with hydrogen on the fuel side of the electrolyte to produce electrons, and the process continues. In this way, the electron current traverses the multicell monolithic structure. Because individual cells in the monolithic fuel cell are small, electron/ion paths are short and resistive losses are low. The lower resistance of the monolithic fuel cell improves cell efficiency by about 10 percent. As a result of lower internal resistance, the MSOFC's can be operated at higher current densities than conventional fuel cells while achieving the same output voltage.

The power density for the MSOFC is higher than that of conventional solid oxide fuel cells and other electrical power-generating technologies. The high power density results from the higher surface area, higher current density, and lower weight. The lower weight in the monolithic design is primarily the result of eliminating inert supports, which is possible because the thin ceramic layers are self-supporting. Because of the shorter current paths involved in the monolithic design, electrodes can be thinner, which reduces weight further.

Because the monolithic design employs thin electrodes, diffusion losses are minimized. The cell voltage is determined by the pressures of the reactants and products at the electrode/electrolyte interface. Thus, any reduction in the pressure at the reaction site represents a loss in voltage, and therefore efficiency. A loss in voltage due to reduced pressure is given by

$$[RT/nf] \ln (P_{\text{eff}}/P_{\text{gas}})$$

where P_{eff} is the pressure at the interface

P_{gas} is the pressure of the bulk gas stream

P_{eff} is dependent on the diffusion of reactants and products through the electrodes. In tubular designs, the thick support tube (30 percent porosity) and thick electrodes represent large diffusional barriers. The monolithic design minimizes diffusion losses by eliminating the thick support tube and employing thin electrodes.

In addition to gas diffusion limitations, a potential barrier exists to charge transport across phase boundaries between the electrodes and the electrolyte. This is associated with the electrode reactions. The voltage loss due to this barrier is the activation potential. At the operating temperature of the MSOFC, reaction rates are very

rapid, so it is not necessary to provide a very thick electrode to ensure sufficient active surface area.

Practical cell operation is always strongly exothermic. Cooling is required in order to maintain a desired cell operating temperature. The MSOFC can be cooled by providing excess oxidant beyond that required by the cell reaction. The temperature rise of this stream will carry off heat. The MSOFC can also be cooled by heat-absorbing reactions within the cell. If the fuel is a relatively complex molecule, it can be broken down or reformed in the cell. These reactions are endothermic and can contribute substantially to cell cooling. Examples are the steam reforming of methane and other hydrocarbons such as those found in natural gas, coal gas, and those produced in the decomposition of methanol.

Fabrication of the MSOFC requires incorporation of four thin cell components into the monolithic structure. The MSOFC is fabricated by forming thin ceramic components as green (unfired) layers, incorporating them into the monolithic structure, and cofiring the structure at elevated temperatures to form the required sintered body. Since the fabrication of the fuel cell requires only a single high-temperature processing step, the MSOFC has potential for low-cost manufacturing.

Table 2-1 summarizes the key features and the benefits offered by the MSOFC design.

TABLE 2-1	
FEATURES AND BENEFITS OF MONOLITHIC DESIGN	
Feature	Benefit
Small cell size	<ul style="list-style-type: none">● Increased active surface area● Low internal resistance● Improved efficiency
Corrugated structure	<ul style="list-style-type: none">● No high-temperature seals● Robust structure
Self-supporting structure	<ul style="list-style-type: none">● Lightweight● Compactness● High power and energy densities
Single high-temperature processing step	<ul style="list-style-type: none">● Potential low-cost manufacturing

3. MATERIALS RESEARCH AND DEVELOPMENT

3.1 STUDY OF INTERCONNECT INTERACTION (TASK 2)

3.1.1 Objective

Densification of the interconnect under relatively moderate firing conditions (1350°C in air) remains the main challenge in fabricating the MSOFC. While the interconnect ($\text{La}_{0.8}\text{Ca}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$) densifies to high density (90 to 95 percent) when fired alone, it does not densify when fired in contact with electrodes; interaction with the electrodes apparently inhibits its densification. Two approaches are being explored for obtaining a dense interconnect. One approach is to fabricate a two-material cell comprised of only electrolyte and interconnect materials. Because such a cell contains no LaMnO_3 , more severe conditions (higher temperature or more reducing gas atmosphere) can be used to densify the interconnect. The second approach is to manage the interaction better between interconnect and electrodes to obtain high density in the usual four-material cell.

3.1.2 Two-Material MSOFC

In the two-material MSOFC, the cathode and anode of cathode-electrolyte-anode composites are made from interconnect material; these layers must remain porous during firing. At the same time, the interconnect and electrolyte layers must densify nearly completely. In addition, strong bonds must be formed between the electrolyte and electrodes and between the interconnect and electrodes. The electrolyte composites made using interconnect material ($\text{La}_{0.8}\text{Ca}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$) as the electrodes had both dense electrolyte and porous electrodes. However, the bonding between the electrolyte and electrodes was very weak, as seen by the fact that the electrodes detached from the electrolyte in several cases.

To improve bonding between the electrodes and electrolyte, electrolyte composites were tape cast with electrodes that consisted of 10-, 20-, or 30-wt% partially stabilized zirconia (6 mol% Y_2O_3) mixed with the interconnect material. All composites were fired for 1/2 hr at 1400°C in air. Bonding in the 10- and 20-percent composites was weak, and the electrodes detached from the electrolyte when samples were broken for microscopic examination. Bonding was stronger in the 30-percent composite, and the electrodes did not detach. Figure 3-1 focuses on one of the electrolyte/electrode boundaries in the 30-percent composite, and shows that the electrolyte is dense while the electrode is porous, as desired. However, the boundary between electrolyte and electrode is sharp, suggesting that the bonding might be weak and that it could be improved further. To improve bonding, more zirconia was added to the electrodes, in the amount of 35- and 40-wt% partially stabilized zirconia. Figure 3-2 shows that distinct boundaries still exist between the electrolyte and electrodes of the 40-percent composite, suggesting that more zirconia might be necessary. However, addition of too much zirconia might degrade the electrochemical performance of the composites, so more zirconia will be added to the electrodes only if the electrochemical performance of the 30-, 35-, and 40-percent composites proves to be satisfactory.

Figure 3-1. Interface of the 30-Percent Composite Showing Dense Electrolyte and Porous Electrode

Figure 3-2. 40-Percent Composite with Dense Electrolyte and Porous Electrode

F-66168

There must also be a strong bond between the electrodes and the interconnect. To test the bonding between interconnect and electrodes, five-layer composites (LC/EI/Zy/EI/LC) were tape cast, where LC is 100 percent $\text{La}_{0.8}\text{Ca}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$, E is 65-wt% $\text{La}_{0.8}\text{Ca}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ /35-wt% TZ-3Y, and Zy is 70-wt% TZ-8Y/30-wt% TZ-3Y. These composites were fired at 1400°C in air for 1/2 hr. All composites were intact after firing, suggesting that bonding is sufficiently strong for fabrication of a two-cell stack.

Bonding in electrolyte composites was improved by using a five-layer graded structure, rather than the three-layer structure. Two different five-layer composites were made by co-casting, with the only difference being in the inner bond layers; the other layers were the same. In composite 1, the bond layers contain 80% ZrO_2 /20%LC whereas the bond layers of composite 2 contain 65% ZrO_2 /35%LC. The makeups of these composites are given below:

<u>Composite 1</u>	<u>Composite 2</u>
35% ZrO_2 /65%LC	35% ZrO_2 /65%LC
80% ZrO_2 /20%LC	65% ZrO_2 /35%LC
100% ZrO_2	100% ZrO_2
80% ZrO_2 /20%LC	65% ZrO_2 /35%LC
35% ZrO_2 /65%LC	35% ZrO_2 /65%LC

Composites 1 and 2 were fired at temperatures of 1400°, 1500°, and 1600°C for 1/2 hr in air; then the bonding was evaluated by scanning electron microscopy on polished cross-sections. For comparison, the following three-layer composites were fired at the same temperatures:

<u>Composite 3</u>	<u>Composite 4</u>
30% ZrO_2 /70%LC	40% ZrO_2 /60%LC
100% ZrO_2	100% ZrO_2
30% ZrO_2 /70%LC	40% ZrO_2 /60%LC

Figure 3-3 shows micrographs of composite 1 fired at 1400°C. Figure 3-3a shows the overall view of the composite, and Figures 3-3b and 3-3c show magnified views of the interfaces between the various layers. The large cracks seen in Figure 3-3a are results of the specimen mounting procedure. Such cracks disappeared when the mounting procedure was changed. The large vertical crack on the left side of the composite suggests that the bonding between layers is good, because the crack runs through the outer layer rather than along the interface. This indicates that the bond is stronger than the material of the outer layer. Figure 3-4 shows similar views of composite 1 fired at 1500°C. Bonding appears to be good, and, because the polishing procedure was changed, no cracks are evident.

Figure 4-3 shows composite fired at 1400°, 1500°, and 1600°C. Composite 4 is expected to have the best bonding of the three-layer composites, because it contains the most ZrO_2 in the electrode layer, but a sharp boundary is evident between the

A. Overall Composite

B. Interface Between Electrolyte (left) and Bond Layer Containing 80% ZrO_2 (right)

C. Interface Between Layer Containing 80% ZrO_2 (left) and Electrode with 35% ZrO_2 (right).

F-66169

Figure 3-3. Micrographs of Composite 1 Fired at 1400°C Showing Improved Bonding Between Electrolyte and Electrodes.

A. Overall Composite

B. Interfaces Between Electrolyte (left layer), Bond Layer with 80% ZrO_2 (middle layer), and Electrode with 35% ZrO_2 (right layer).

Figure 3-4. Micrographs of Composite 1 fired at 1500°C

F-66170

A. Fired at 1400°C

B. Fired at 1500°C

C. Fired at 1600°C, Showing a Sharp Boundary Between Electrolyte and Electrodes

Figure 3-5. Micrographs of Composite 4 (40% ZrO_2 in Electrodes)

F-66171

electrode and electrolyte layers, even when the composite is fired at 1600°C. This suggests that the bonding remains weak in three-layer composites even when they are fired at high temperature.

Ac impedance was used to test the electrochemical performance of the LC electrode/YSZ/LC electrode (IEI) composites in reducing (H_2/H_2O) and oxidizing (air) atmospheres. The results are summarized in Table 3-1. Past results from tests performed on IEI cells without the intermediate doped $LaCrO_3$ /YSZ layer and without YSZ in the electrode are shown for comparison.⁽¹⁾

TABLE 3-1							
AREA-SPECIFIC RESISTANCE (OHM-CM ²) OF IEI COMPOSITES AT 1000°C							
Sample	Air Atmosphere		H_2/H_2O Atmosphere		Air and H_2/H_2O		Total
	Interfacial	Bulk	Interfacial	Bulk	Interfacial	Bulk	
IEI	0.184	0.484	2.91	1.10	3.58	0.801	4.38
IEI-8	0.109	1.17	1.40	2.79	1.63	2.11	3.74
IEI-15	0.124	0.475	0.790	1.16	1.01	0.905	1.91
IEI-16	0.148	0.356	1.48	1.58	1.62	1.17	2.51
IEI-18	0.149	0.415	1.04	1.32	1.35	0.940	2.29
IEI-19	0.100	0.915	0.678	1.18	(0.780)	(1.05)	(1.83)
() = Calculated from single atmosphere results. Compositions: IEI: doped $LaCrO_3$, YSZ, doped $LaCrO_3$. IEI-8: 35 wt% YSZ/65 wt% doped $LaCrO_3$, YSZ, 35 wt% YSZ/65 wt% doped $LaCrO_3$. IEI-15,18,19: 35 wt% YSZ/65 wt% doped $LaCrO_3$, 80 wt% YSZ/20 wt% doped $LaCrO_3$, YSZ, 80 wt% YSZ/20 wt% doped $LaCrO_3$, 35 wt% YSZ/65 wt% doped $LaCrO_3$. IEI-16: 35 wt% YSZ/65 wt% doped $LaCrO_3$, 65 wt% YSZ/35 wt% $LaCrO_3$, YSZ, 65 wt% YSZ/35 wt% $LaCrO_3$, 35 wt% YSZ/65 wt% doped $LaCrO_3$.							

Microscopic examination of the interfacial regions in the composites indicates that the addition of YSZ to the electrode improves the electrode/electrolyte bonding. This improved bonding is reflected in the drop in interfacial impedance between IEI and IEI-8. However, this decrease in interfacial impedance is partially offset by an increase in bulk impedance resulting from the relatively poor conductivity of the doped $LaCrO_3$ /YSZ mixture compared to pure doped $LaCrO_3$ ($0.89 \text{ ohm}^{-1}\text{cm}^{-1}$ vs $31.1 \text{ ohm}^{-1}\text{cm}^{-1}$).⁽¹⁾

The addition of an intermediate 80-wt% (IEI-15) or 65-wt% (IEI-16) YSZ layer decreases the total cell resistance by 49 and 33 percent, respectively. As shown in Table 3-1, the drop in total cell impedance can be attributed mainly to a decrease in the bulk impedance rather than in the interfacial component. A significant difference between IEI-15 and IEI-8 lies in the thickness of the YSZ electrolyte layer. The electrolyte

layer thickness in IEI-15 is 74 μm vs 103 μm for IEI-8. However, the addition of the 80-wt% YSZ intermediate layers to IEI-15 increases the total thickness of layers between the electrodes (162 μm) to more than that of IEI-8. Since the electrode thicknesses are identical in the two cells, the lower bulk impedance of IEI-15 indicates that 80-wt% YSZ/20-wt% doped LaCrO_3 is more conductive than pure YSZ. The same conclusion can be reached about the conductivity of 65-wt% YSZ/35-wt% doped LaCrO_3 by comparing IEI-16 and IEI-8.

By comparing the data presented for IEI-15, 16, and 18 to the data for IEI-8, it is evident that the benefit of the intermediate bonding layers in reducing the interfacial impedance is marginal compared to their contribution to the bulk impedance. In terms of a two-material fuel cell, the best compromise between decreasing the interfacial impedance and minimizing an addition to the bulk impedance is a three-layer cell with YSZ/doped LaCrO_3 electrodes and as thin an electrolyte layer as possible.

The total cell impedance has been further reduced by decreasing the thicknesses of all five layers. The thicknesses of the YSZ, 80-wt% YSZ, and 35-wt% YSZ layers have been reduced by 34, 37, and 43 percent, respectively, in IEI-18 and IEI-19, as compared to IEI-15. The best total cell impedance obtained to date is 1.83 ohm-cm^2 .

The single atmosphere results presented in Table 3-1 consistently show the impedances in reducing atmospheres to be higher than those in oxidizing atmospheres. This supports the conclusion that the doped LaCrO_3 /YSZ mixture is a satisfactory cathode material but an unsatisfactory anode material.

3.1.3 Four-Material MSOFC

The LaCrO_3 interconnect does not completely densify in the usual four-material MSOFC because the liquid that aids sintering migrates into the electrodes before densification is complete. To improve densification, an attempt is being made to increase the amount of liquid phase present during sintering, so that migration of some liquid does not significantly affect densification. In the past, attempts to increase the amount of liquid phase included the addition of CaCrO_4 , which melts at $\sim 1200^\circ\text{C}$ according to the phase diagram. It has been reported that CaCrO_4 is not useful for this purpose, however, because it forms Cr_2O_3 , which coats the grain boundaries and inhibits densification. It has also been reported that compositions closer to the 1022°C eutectic would be more useful for this purpose. To prevent migration of the liquid phase before sintering can proceed, the liquid phase should not form until the sintering temperature has been reached ($\sim 1200^\circ\text{C}$). According to the phase diagram, the "941" composition exhibits a local maximum in melting point (1288°C in oxygen), and may be ideal. For this reason, the "941" composition was prepared for use as a sintering aid.

"941" was tested as a sintering aid for Ca/Co-doped LaCrO_3 . In this work, "941" was added to Ca/Co-doped LaCrO_3 deficient in calcium, so that a final composition of $\text{La}_{0.70}\text{Ca}_{0.30}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$ was obtained after sintering/reaction. Formation of LaCrO_3 containing excess calcium or lanthanum was intentionally avoided, because such material is expected to be unstable and susceptible to hydrolysis reactions. The amounts of "941" added and the initial Ca/Co-doped LaCrO_3 compositions are given below:

x	y	a	b	c
0.94	0.025	0.74	0.24	0.11
0.89	0.050	0.79	0.17	0.11
0.83	0.075	0.84	0.09	0.12
0.78	0.100	0.90	0.00	0.13

Precursors of the various LaCrO_3 compositions and "941" were made by the liquid-mix method. The "941" precursor was calcined for 24 hr at 975°C in air, whereas the LaCrO_3 precursors were calcined for 24 hr at 750°C in air. The appropriate amounts of $\text{LaCrO}_3(\text{X})$ and "941" (Y) were mixed with mortar and pestle. Then pellets were pressed and fired according to the schedules given below. To determine the effectiveness of "941" as a sintering aid, each LaCrO_3 composition was also fired without any "941" added. To this point, "941" has been tested with two Ca-deficient compositions: $\text{La}_{0.79}\text{Ca}_{0.17}\text{Cr}_{0.90}\text{Co}_{0.11}\text{O}_3$ and $\text{La}_{0.90}\text{Ca}_{0.00}\text{Cr}_{0.90}\text{Co}_{0.13}\text{O}_3$. It has also been tested with $\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$, the composition with a slight Ca excess that has been shown to densify alone but not in composite tapes. The results of this study are given in Table 3-2.

Comparing the densities of Ca-deficient compositions with no "941" added, to the same compositions with "941" added shows that "941" aids densification to a certain degree, but the final densities are still too low for the MSOFC. For example, the density of $\text{La}_{0.79}\text{Ca}_{0.17}\text{Cr}_{0.90}\text{Co}_{0.11}\text{O}_3$ increases substantially from 2.65 to 3.97 g/cm^3 , but this density is still very low for the interconnect. Comparing the density of $\text{La}_{0.79}\text{Ca}_{0.17}\text{Cr}_{0.90}\text{Co}_{0.11}\text{O}_3$ to that of $\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$ shows that a very slight decrease in the Ca content causes a drastic decrease in density from ≈ 6.1 to 2.65 g/cm^3 . This is consistent with the idea that it is a Ca-rich liquid which aids densification in $\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$. When $\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$ is fired in composite tapes, migration of the Ca-rich liquid leaves a Ca-deficient material that densifies poorly. On the other hand, addition of "941" to $\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$ causes a decrease in its density, suggesting that the stoichiometry must be tightly controlled to obtain highly dense material. If the density is in fact strongly dependent on the Ca content, then addition of "941" to $\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$ in composite tapes might be a method for replacing calcium that is lost by migration of the liquid phase.

Another approach was attempted in order to limit migration of the transient liquid phase from the interconnect in the standard four-material cell. The method for limiting migration is to delay liquid formation until after the onset of densification for the electrodes ($\approx 1050^\circ\text{C}$), because the migration paths are reduced when these layers are relatively dense. By replacing calcium with strontium to give an interconnect composition of $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$, the liquid formation temperature is expected to increase from $\approx 1020^\circ\text{C}$ to $\approx 1250^\circ\text{C}$.

TABLE 3-2				
RESULTS OF STUDY EXPLORING THE POSSIBLE USE OF "941" AS SINTERING AID FOR Ca/Co-DOPED LaCrO ₃				
LaCrO ₃ Composition	Heat Treatment	Moles LaCrO ₃	Moles "941"	Density, g/cm ³
La _{0.79} Ca _{0.17} Cr _{0.90} Co _{0.11} O ₃	1400°C/1 hr	0.89	0.00	2.65
"	"	0.89	0.05	3.97
"	1020°C/2 hr 1400°C/1 hr	0.89	0.00	2.69
"	"	0.89	0.05	3.88
"	1500°C/1 hr	0.89	0.00	2.85
"	"	0.89	0.05	4.11
"				
La _{0.90} Ca _{0.00} Cr _{0.90} Co _{0.13} O ₃	1400°C/1 hr	0.78	0.00	3.21
"	"	0.78	0.10	3.98
"	1500°C/1 hr	0.78	0.00	3.24
"	"	0.78	0.10	4.25
"				
La _{0.80} Ca _{0.22} Cr _{0.90} Co _{0.10} O ₃	1400°C/1 hr	1.00	0.00	6.1-6.2
"	"	0.95	0.05	5.21
"	"	0.90	0.10	4.57

Two trilayer tapes (AIA and CIC) were made to test the densification of La_{0.8}Sr_{0.22}Cr_{0.9}Co_{0.1}O₃ in composite tapes. In these and all subsequent representations of composite tapes, A represents the anode, I the interconnect, and C the cathode. Symmetric trilayers were made, rather than an AIC, to avoid problems with a shrinkage mismatch. The trilayers were fired in air at 1500°C for 1 hr. After firing, fracture surfaces of the trilayers were examined by SEM. Figures 3-6a and 3-6b show that the interconnect densified well in the AIA. Figure 3-7a shows that a dense layer also formed in the CIC, but the dense layer was thin, and interaction between the interconnect and cathode was still evident. Figure 3-7b shows a second CIC in which the interconnect was not completely dense, but its density was higher than in the trilayers made with La_{0.8}Sr_{0.22}Cr_{0.9}Co_{0.1}O₃. These figures show that La_{0.8}Sr_{0.22}Cr_{0.9}Co_{0.1}O₃ shows promise as an interconnect material, but interactions, primarily with the cathode, still hinder its complete densification in trilayers.

To test new cell assemblies in which cathode/interconnect interactions might be reduced, Al's were fired with the interconnect layer contacting a corrugation made from

(a)

(b)

Figure 3-6. SEM Micrographs of AIA Fired at 1500°C in Air for 1 hr at Magnifications of (3-6a) ~ 350 X and (3-6b) ~ 2000 X

F-88172

(a)

(b)

Figure 3-7. SEM Micrographs of Two CIC's Fired at 1500°C in Air for 1 hr

F-66173

either $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ or $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$. A cathode flat layer was laid on the other side of the corrugation in both cases to simulate the arrangement in an actual cell. Al's were also fired by themselves as a comparison. In all cases, the interconnect layer was $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$, and the assemblies were fired in air for 1 hr at 1500°C .

Figures 3-8a and 3-8b show the interconnect layer of an Al fired by itself. Although densification was not complete, the density was high, and testing showed the composite to be impervious to water, an indication that the porosity was not connected. Of the Al's fired in contact with corrugations, the interconnect densified best when in contact with the $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ corrugation. This might be expected, because the interconnect composite did not contact the cathode at all in this arrangement. Figure 3-9 shows the interconnect layer of an Al fired in contact with a $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ corrugation. The density of the interconnect in Figure 3-9 appears comparable to that in Figure 3-8, suggesting that densification of the interconnect is not significantly hindered in such a cell assembly. It further suggests that only slightly improved densification of the interconnect is necessary in such a cell assembly.

3.1.4 Study of $(\text{La},\text{Ca})\text{CrO}_3$

The densification of perovskite lanthanum chromites has been extensively studied. Recently, Mori⁽²⁾ and others have fully densified calcium-doped lanthanum chromites at relatively low temperatures (1200° to 1400°C) by adding excess calcium. Their powder processing involved calcining above 1000°C , followed by grinding and reheating to obtain a single-phase solid solution of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ with $0.2 \leq x \leq 0.4$.

This study was focused on lower-temperature powder preparation (800°C) and sintering (1050° to 1300°C) of $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_3$. (The powders intentionally were slightly chromium-rich to avoid the possible appearance of excess lanthanum compounds which would cause the mechanical integrity of the sintered component to degrade; this was also found to affect sinterability.) At calcining temperatures of 800°C or less, CaCrO_4 was found to coexist with $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_3$ for $x \geq 0.2$. However, CaCrO_4 is soluble at higher temperatures and dissolves into the matrix when sintered above its solubility limit. Since CaCrO_4 melts incongruently, its use as a liquid-phase sintering aid is restricted. However, the Ca-Cr-O system includes other compositions that may react and melt with the CaCrO_4 . In particular, the eutectic composition, $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ and a calcium-rich ternary compound, $\text{Ca}_3(\text{CrO}_4)_2$ were investigated. Attempts were made to use these compositions to densify calcium-doped lanthanum chromites.

3.1.4.1 Experimental Procedures

3.1.4.1.1 Powder Processing

All powders were prepared using a modified Pechini method. Metal nitrates or carbonates were dissolved into water and nitric acid and then mixed with an ethylene glycol/citric acid mixture having a mole ratio of 1:1:1. The solution was boiled to drive off water and nitrates and allowed to gel. The gel was then put in a drying oven at $\sim 120^\circ\text{C}$. As the gel dried, it foamed and charred. The char was milled and reheated to

(a)

(b)

Figure 3-8. SEM Micrographs of Al Fired by Itself at 1500°C for 1 Hr in Air at Magnifications of (3-8a) ≈ 350 X and (3-8b) ≈ 1500 X

F-66174

F-66175

Figure 3-9. SEM Micrograph of Al Fired in Contact With $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ Corrugation

about 400°C to remove residual carbon. The resulting powders were then milled and calcined to various temperatures as needed.

3.1.4.2 Quench Study

$\text{La}_{0.59}\text{Ca}_{0.4}\text{CrO}_4$ powder prepared at 400°C and containing CaCrO_4 was isostatically pressed into 1.2-cm pellets at 210 MPa. Green densities approached 50 percent of the calculated theoretical density. The pellets were heated at a rate of 8°C/min and quenched in water from the temperatures: 490°, 1075°, 1175°, 1230°, 1275°, 1350°, and 1400°C. One pellet was held at 1400°C for 2 hr and then furnace-cooled, and another was held at 1400°C for 3 min and then air-quenched.

Microanalysis and energy dispersive analysis were performed on fractured surfaces using a JEOL scanning electron microscope (SEM).

3.1.4.3 Thermal Analysis

Thermogravimetric and differential thermal analyses (TG/DTA) were performed on $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_4$ $0.1 \leq x \leq 0.4$, CaCrO_4 and $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4-8}$ powders using a Netzsch TGA/DTA system. The furnace heating rate for each run was 10°C/min and peak

temperatures were 1200° and 1600°C. Both alumina and platinum-type crucibles were used.

3.1.4.4 X-Ray Diffraction Study

Calcined powders were analyzed for phases present using X-ray diffraction on either a Sintag or a General Electric diffractometer.

X-ray densities were calculated from d-spacing measurements on the Sintag. The Sintag was calibrated in the relevant d-spacing range using a silicon wafer.

The solubility of CaCrO_4 in $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_3$ was also studied by X-ray diffraction using the Sintag. Disk specimens for $x = 0.1, 0.2$, and 0.3 were sintered for 2 hr at temperatures of 1100°, 1200°, 1300°, 1400°, and 1500°C. More work is being done to determine the solubility limits. In addition, solubility data for compositions ranging from $x = 0.35$ to 0.60 are presently being accumulated.

An additional experiment was performed on powder and disk specimens of $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_3$, $x = 0.3$ and 0.4 to see if CaCrO_4 would segregate at temperatures at which the solubility limit of Ca in LaCrO_3 was exceeded. The disks and powders were heated to 970°C for 4 hr and analyzed by X-ray diffraction to ensure the presence of CaCrO_4 . Powder and pellets were then heated to 1500°C for 2 hr to dissolve the CaCrO_4 into the matrix and again analyzed for the phases present. Finally, the specimens were annealed at 850°C for 100 hr and analyzed for phases present.

3.1.4.5 Depth Profiles on $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$

Auger electron spectroscopy (AES) depth analysis was conducted on compacted powders and sintered pellets of $\text{La}_{0.99}\text{Ca}_{0.1}\text{CrO}_3$. The powders were uniaxially pressed to 70 MPa after calcination at 800°C for 8 hr. The sintered pellets were prepared by isostatically pressing the powders to 210 MPa after calcination at 400°C. Sintering was carried out at 1500°C for 2 hr.

The AES instrument had a sputtering area of about 10 mm² and electron beam area of about 3 mm². Sensitivities for each element were back-calculated from bulk measurements. As a consequence of analyzing rough surfaces, only a qualitative estimate of the sputter depths could be obtained. This was acceptable as a first approximation, however, a microprobe technique that is able to analyze a smaller area must be used in future experiments to clearly define the depth profile of an individual particle.

3.1.4.6 $\text{La}_{0.69}\text{Cr}_{0.3}\text{O}_3$ / Ca-Cr-O Reaction Study

Powders of the compositions CaCrO_4 , $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$, $\text{Ca}_3\text{Cr}_2\text{O}_8$ and CaCO_3 were prepared as above. The calcination temperatures varied between 400° and 800°C to avoid melting. As a result, the $\text{Ca}_3\text{Cr}_2\text{O}_8$ composition consisted of a CaO-CaCrO_4 mixture rather than the pure $\text{Ca}_3(\text{CrO}_4)_2$ phase. Hence, the notation $\text{Ca}_3\text{Cr}_2\text{O}_8$ is used. The effect of using this as opposed to single-phase $\text{Ca}_3(\text{CrO}_4)_2$ will be shown later.

To observe the melting characteristics of the four Ca-Cr-O compositions, 1.2-cm-dia disks were pressed from each composition and placed on 2.5-cm-dia disks of $\text{La}_{.69}\text{Ca}_3\text{CrO}_3$ and $\text{La}_{.675}\text{Ca}_3\text{CrO}_3$. The reaction couples were then heated to 1100°C and in a separate run to 1230°C, held for 2 hr and furnace-cooled. Later, 1.2-cm disks of $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ and $\text{Ca}_3\text{Cr}_2\text{O}_8$ were placed on 2.5-cm disks of CaCO_3 , heated to 1230°C and furnace-cooled.

3.1.4.7 Nonstoichiometric Mixtures

A nonstoichiometric compound, $\text{La}_{.675}\text{Ca}_3\text{CrO}_3$, was prepared using the modified Pechini technique described above. It was calcined at 800°C for 8 hr and mixed with each of the powders: CaCO_3 , $\text{Ca}_3\text{Cr}_2\text{O}_8$ and $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ in reagent grade methyl alcohol. After milling, the powders were dried, and isostatically pressed into 1.2-cm disks at 210 MPa. Two disks of each composition were then sintered at 1020°C for 2 hr and at 1400°C for 1 hr. The following reactions were used to estimate the stoichiometry of the final products:

3.1.4.8 Discussion

3.1.4.8.1 Phase Relations

Two phases appear when lanthanum chromite powders ($x > 20$ percent Ca) made from the Pechini method are calcined at 800°C for 8 hr. Calcium chromate (CaCrO_4) and a lanthanum calcium chromate solid solution ($\text{La}_{.99-x}\text{Ca}_x\text{CrO}_4$) first appear at the burnout of carbon and crystallization of the char above 400°C. Thermal analysis shows the transformation of lanthanum chromate to lanthanum chromite between 700° and 800°C is apparent from the large endothermic peak shown in Figure 3-10. This peak shifts to lower temperatures as the Ca content increases. The DTA also shows that a liquid phase forms in all the $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$ composition at approximately 1030° to 1080°C.

By comparing Figure 3-10 and the $\text{CaO-Cr}_2\text{O}_3$ phase diagram,⁽²⁾ shown in Figure 3-11, it became evident that the liquid phase formed at ~1030°C in the $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3/\text{CaCrO}_4$ mixture was actually the eutectic associated with the CaCrO_4 phase. However, CaCrO_4 melts incongruently forming a eutectic liquid, $\text{Ca}_{1.09}\text{Cr}_{.91}\text{O}_{4.8}$ and a higher melting point solid, CaCr_2O_4 . This indicated that CaCrO_4 is ineffective as a sintering aid for $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$.

3.1.4.8.2 Reaction Mechanism

Using this information, and the results from Auger spectroscopy, X-ray diffraction, and from SEM analysis, a reaction mechanism is proposed which explains the sintering

Figure 3-10. DTA Runs of $\text{La}_{.79}\text{Ca}_{.2}\text{CrO}_3$ (LCC-20), $\text{La}_{.69}\text{Ca}_{.3}\text{CrO}_3$ (LCC-30) and $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_3$ (LCC-40) in Pt. Heating Ramp Rate $10^\circ\text{C}/\text{min}$

behavior up to and including the solubility temperature of CaCrO_4 in these powders. Figure 3-12 illustrates the mechanism.

When the powders are calcined below the solubility limit, CaCrO_4 appears in X-ray patterns of $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$. However, at this stage, SEM micrographs do not seem to show the presence of distinct CaCrO_4 crystallites. This might be further studied with back-scatter techniques in subsequent SEM analyses.

The Auger results suggest the formation of a calcium-rich layer upon initial sputtering of the powders (Figure 3-13 and 3-14). This gives evidence of the CaCrO_4 coating proposed in the first step of the mechanism. At $\sim 1030^\circ\text{C}$, incongruent melting occurs. The liquid formed is very reactive towards the excess chromium in the $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$ as is later discussed in the reaction studies section. It is tentatively believed that calcium in the liquid at the coating/particle interface is absorbed, leaving behind a composition which acts as a barrier to lanthanum transport.

Particle rearrangement also takes place in this temperature range which suggests that there is liquid present at particle contact points.

Although not shown in the model, it becomes apparent that the Ca-Cr-O phase also begins to segregate from the $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$ (into large masses), as shown in the SEM photomicrograph of Figure 3-15, for a quenched $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_3$ specimen. The specimen was heated at 1400°C for 3 min and was air-quenched. It appears that the dendritic CaCrO_4 structure has segregated from the $\text{La}_{.59+\delta}\text{Ca}_{.4-\delta}\text{CrO}_3$ matrix.

B-27016

Figure 3-11. Equilibrium Phase Diagram for the CaO-Cr₂O₃ System.
After Ford and White⁽²⁾

Particles after calcining at 800°C are coated with CaCrO_4 .

B-27017

Figure 3-12. Proposed Sintering Mechanism for The $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_3$ System

Figure 3-13. Auger Analysis of Pressed Pellet of $\text{La}_{0.69}\text{Ca}_{0.30}\text{CrO}_3$

Figure 3-14. Auger Analysis of Sintered Surface of $\text{La}_{0.69}\text{Ca}_{0.30}\text{CrO}_3$

F-64417-A

Figure 3-15. A SEM Micrograph of $\text{La}_{0.59}\text{Ca}_{0.4}\text{CrO}_3$ Air-Quenched from 1400°C

Elemental analysis using EDS shows no measurable amount of lanthanum within the CaCrO_4 . Mixtures of CaCrO_4 and lanthanum carbonate are presently being made to further study the solubility of lanthanum in CaCrO_4 .

At higher temperatures (now being determined for each composition) the CaCrO_4 completely dissolves into the matrix. This became evident when all the compositions containing CaCrO_4 second phase (up to 40-percent calcium) were X-rayed after sintering at 1500°C . In addition, the CaCrO_4 was observed to reappear after the pellets had been annealed at 800°C for 100 hr, suggesting that these reactions are reversible.

3.1.4.8.3 Reaction Studies

The reaction studies, although providing only qualitative results, give more insight to the reactions of the Ca-Cr-O compositions with $\text{La}_x\text{Ca}_y\text{CrO}_3$ or other substrates. It was observed that when a CaCrO_4 disk was heated on either alumina or platinum substrates, to temperatures as high as 1500°C , a liquid exsolved out and spread over the substrate leaving a porous skeleton of the disk. However, at 1030°C , $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ melted completely in a platinum TG/DTA crucible but not in alumina. Interactions between Ca-Cr-O compositions and various substrates were then studied.

The first experiment consisted of 1.2-cm disks of CaCrO_4 , $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$, $\text{Ca}_3\text{Cr}_2\text{O}_8$ and CaCO_3 , on 2.5-cm disks of $\text{La}_{0.69}\text{Ca}_{0.3}\text{CrO}_3$. After heating at 1100°C for 2 hr, the CaCrO_4 retained its size and shape, but had lost liquid into the $\text{La}_{0.69}\text{Ca}_{0.3}\text{CrO}_3$ and had the characteristic porous, skeletal appearance. The $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ had

contracted, deformed, and liquified at the interface with the substrate. The $\text{Ca}_3\text{Cr}_2\text{O}_8$ remained unchanged in size and shape but changed from a bright yellow ($\text{CaO} + \text{CaCrO}_4$) to a dark green color (perhaps formation of $\text{Ca}_3(\text{CrO}_4)_2$.) No evidence of melting could be seen, however the CaCO_3 pellet transformed into unsintered CaO .

The main contrast between the 1100°C and the 1230°C run is that at 1230°C , the $\text{Ca}_{1.09}\text{Cr}_{.91}\text{O}_{4.8}$ had completely melted into the substrate and the $\text{Ca}_3\text{Cr}_2\text{O}_8$ had clearly melted, contracted, and densified areas of the $\text{La}_{.69}\text{Ca}_{.3}\text{CrO}_3$ substrate beneath it.

When the same Ca-Cr-O pellets were set on $\text{La}_{.675}\text{Ca}_{.3}\text{CrO}_3$ substrates and heated to 1230°C for 2 hr, the $\text{Ca}_{1.09}\text{Cr}_{.91}\text{O}_{4.8}$ and the $\text{Ca}_3\text{Cr}_2\text{O}_8$ experienced poor melting. Although this experiment needs to be repeated, it seems to indicate that the Ca-Cr-O compositions have a greater difficulty melting in the presence of excess chromium. As in the case of the alumina setters, the calcium in the system may be leached out preferentially, leaving an unreacted solid.

To prove this, $\text{Ca}_{1.09}\text{Cr}_{.91}\text{O}_{4.8}$ and $\text{Ca}_3\text{Cr}_2\text{O}_8$ pellets were set on CaCO_3 disks and heated them to 1230°C . At about 1030°C , the $\text{Ca}_{1.09}\text{Cr}_{.91}\text{O}_{4.8}$ began to melt and spread over the surface of the substrate forming a clear sessile drop. The $\text{Ca}_3\text{Cr}_2\text{O}_8$ also began to melt near 1230°C . It soaked into the CaO substrate and the pellet on top quit melting only after the liquid had soaked the zirconia setter beneath the CaO . Apparently, the liquid phase is very reactive to solids which will readily dissolve calcium ions such as, alumina, zirconia, and chromium excess lanthanum chromite.

3.1.4.9 Nonstoichiometric Mixtures

ASE believed that mixing a calcium-rich, congruent melting powder of Ca-Cr-O with chromium excess $\text{La}_u\text{Ca}_v\text{CrO}_3$ ($u + v < 1$) would cause reaction liquid phase sintering to occur. The composition of the mixture would be such that it ultimately formed a stoichiometric product.

Compositions based on the three chemical equations (1), (2), and (3) were prepared. The eutectic composition $\text{Ca}_{1.09}\text{Cr}_{.91}\text{O}_{4.8}$ and $\text{Ca}_3(\text{CrO}_4)_2$ qualified as congruent melting liquid phases. Calcium carbonate served as a control end member. Disks of the mixtures from equations (1) and (2) were first heated to 1020°C for 2 hr and then heated to 1400°C and annealed for 1 hr. An identical heating schedule was used later for mixtures of equation (3).

The mixture from equation (2) sintered to 90 percent of full density whereas the other compositions showed little improvement over the conventional compositions. SEM micrographs of the fractured specimen are shown in Figures 3-16 and 3-17. Figure 3-16 shows well-sintered grains that have grown as large as 5 microns. Figure 3-17 is a back-scatter photo that shows the chemical homogeneity. Although the calculated reaction results in a lanthanum-rich product, the ceramic appears to be chemically homogeneous. Presently, the chemical stability is being studied by heating the pellet in a humid environment. To date, the pellet has shown no evidence of degradation. X-ray diffraction will be performed on the specimen following the humidity tests.

Figure 3-16. SEM Micrograph of Sintered $\text{La}_{0.618}\text{Ca}_{0.4}\text{CrO}_3$ (Calculated Composition). Heated at $1020^\circ\text{C}/2\text{ Hr}$ and $1400^\circ\text{C}/\text{Hr}$

F-64416

Figure 3-17. Sintered $\text{La}_{0.618}\text{Ca}_{0.4}\text{CrO}_3$. SEM Elemental Back-Scatter Image

3.1.4.10 Conclusions

According to German³, the solubility of the liquid phase in the solid must be low and the solubility of the solid in the liquid must be high for optimum liquid phase sintering. Many of our results show just the opposite. This may be a result of exceeding the optimum heating ranges. Continuing work will center on determining the solubility limits of CaCrO_4 in LaCrO_3 and La in CaCrO_4 . From this work, optimum densification of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ may be identified by determining the temperature region of low liquid and high solid solubility for a given composition.

3.1.5 Liquid Phase Sintering of $(\text{La,Ca})\text{CrO}_3$

Recent work has focused on improving processing techniques to gain uniform green microstructures, in addition to compiling results on the low temperature reactions (400° to 1300°C) in the calcium doped lanthanum chromium oxide system.

The liquid mix technique used to prepare previous compositions resulted in powders composed of irregular shaped aggregates as large as $50\text{ }\mu\text{m}$ and a non-uniform size distribution. Green compacts fabricated by uniaxial and isostatic pressing showed poorly packed microstructures. Such a green state was previously ignored since liquid phase sintering is typically accompanied by particle rearrangement which improves the packing density. In our system, this mechanism was observed as large agglomerates composed of $0.1\text{ }\mu\text{m}$ crystallites rearranged into a compact with greater packing efficiency. However, this process was not as efficient as hoped and large pores were preserved in the microstructure at the completion of sintering.

The intention was to improve the powder processing and consolidation steps and obtain a better green microstructure, to gain a better perspective on the mechanism of sintering. A milling study on char particles was performed since these particles were thought to break down easier than the aggregates obtained after calcination. A low temperature calcination in neutral atmosphere was used to control carbon burn-out as well as to obtain the lanthanum chromate (LaCrO_4) intermediate phase. A consolidation technique using colloidal dispersions is presently being employed to acquire a uniformly packed green state.

In addition to improvements on the powder processing and consolidation stages, results on the study of reactions occurring within the $400\text{-}1300^\circ\text{C}$ temperature range are presently being concluded.

The LaCrO_4 intermediate phase was studied because of the high solubility of calcium in its crystal structure. The consolidation of powders using colloidal dispersions is achieved easier when only a single phase material is dispersed. In addition, the formation CaCrO_4 upon the transformation of LaCrO_4 to LaCrO_3 , will more likely be evenly distributed in a compact than if it were allowed to precipitate and grow during powder calcination.

The liquid phase formation in calcium doped lanthanum chromite is found to be a result of the incongruent melting of CaCrO_4 . The properties of the liquid are related to the $\text{CaO-Cr}_2\text{O}_3$ phase system.

A solubility diagram has been constructed to illustrate the solubility of CaCrO_4 in LaCrO_3 versus temperature. This diagram is helpful in determining optimum calcium additions and sintering temperatures.

Binary mixtures of powders are presently being prepared and studied to increase the volume percent of liquid phase. Previous work involved milling fully calcined (800°C for 8 hr) non-stoichiometric compositions together to ultimately obtain stoichiometric products. Equation (4) is an example of one of the mechanical mixtures prepared.

The emphasis on the present work with binary powder mixtures is to obtain better a green microstructure using the colloidal dispersion technique.

3.1.5.1 Experimental Procedure

3.1.5.1.1 Powder Processing

Powders were prepared based on the modified resin process proposed by Tai *et al.*⁽⁵⁾ Metal nitrates or carbonates were dissolved into water and nitric acid and the solution was combined with an ethylene glycol/citric acid mixture having a mole ratio of 1:1:1. The solution was heated to drive off water and nitrates, and allowed to form a gel. The gel was then poured into large, shallow, ceramic dishes in a pre-heated drying oven at approximately 120°C . The gel boiled rapidly in the pan and charred. Unlike the previous method of charring in tall beakers, this technique obtained better combustion of the polymer, producing a fluffy, gray colored ash.

3.1.5.1.2 Milling Study

A milling study was performed to determine the advantage of milling the char before calcination. Char, having the final composition $\text{La}_{.89}\text{Ca}_{.1}\text{CrO}_3$, was milled in reagent grade ethyl alcohol using a Sweco vibratory mill for 2, 4, 6 and 8 hours. Micro-analysis of the milled char particles was performed on a scanning electron microscope and particle size was determined using a sedigraph-type particle size analyzer.

3.1.5.1.3 Lanthanum Chromate

The formation of the monoclinic LaCrO_4 phase was accomplished by slowly heating milled char under a flowing argon atmosphere to 550°C and held for 8 hr. The char was also spread in a thin layer along a large MgO tube to ensure uniform heating.

3.1.5.1.4 Powder Classification and Consolidation

A powder classification and consolidation technique for lanthanum chromite was previously developed by Jang.⁽⁶⁾ His general procedure is as follows. Single-phase calcium doped lanthanum chromate powder is heated to 400°C for 2 hr to drive off surface water. The powder is then removed from the hot furnace and cooled in a desiccator. Methyl ethyl ketone is mixed with an optimum percentage of Menhaden fish oil in a beaker. The cooled powder is then mixed in this solution using an ultrasonic probe.

The dispersion is allowed to sit for a predetermined time to allow the settling of large aggregates. The dispersion is then poured off into a tube and centrifuged, to form a compact of the dispersed powders. The clear solution is then poured off and saved for future use for similar powders. The resulting compact is then dried to a green state.

Binary mixtures of lanthanum chromite and liquid phase powders will be prepared in a similar manner as described above with the exception that single phase powders will be dispersed and classified in separate containers and then mixed together before forming the green compact in the centrifuge.

3.1.5.1.5 Liquid Phase Characteristics

The formation of the liquid phase within calcium doped lanthanum chromite was analyzed by using SEM and energy dispersive analysis (EDS) on quenched specimens. Melting and freezing points were determined using differential thermal analysis (DTA). X-ray diffraction studies were also performed to analyze lanthanum solubility within CaCrO_4 . Characteristics of the liquid were studied by placing pellets of composition $\text{Ca}_3\text{Cr}_2\text{O}_8$, $\text{Ca}_{1.2}\text{CrO}_4$ and CaCrO_4 on various substrates and heating beyond their melting points and observing the melting behavior.

3.1.5.1.6 Solubility of CaCrO_4 in LaCrO_3

To determine the solubility of CaCrO_4 in LaCrO_3 , uniaxially compacted pellets of calcined $(\text{La,Ca})\text{CrO}_3$ containing exsolved CaCrO_4 , $20\% \leq \text{Ca} \leq 65\%$ were heated in air between 900°C and 1450°C for 12 hours and air quenched. The specimens were then polished to remove surface effects. Phase analysis was performed using X-ray diffraction.

3.1.5.2 Discussion

3.1.5.2.1 Powder Processing

Powders made by the liquid mix (Pechini) process and calcined above 800°C have crystallite sizes of about $0.1\ \mu\text{m}$ which are typically fused together into aggregates as large as $50\ \mu\text{m}$. Microanalysis shows that the final aggregate size and shape is dictated by size and shape of the char particles. Char particles are amorphous according to X-ray diffraction and in the SEM have the appearance of an organic residue. Since the char particles are relatively soft, it was believed to be advantageous to mill the powders before calcination.

Micrographs (Figures 3-18 and 3-19) of the milled char indicate a particle size reduction from as large as $50\ \mu\text{m}$ for "as is" powder to less than $2\ \mu\text{m}$ after milling for eight hours. Figure 3-20 illustrates the particle size distribution of powders milled for eight hours and calcined at 550°C in Argon.

3.1.5.2.2 LaCrO_4 Phase

Lanthanum chromate (LaCrO_4), is a low temperature phase which is stable below 650°C . This compound has two polymorphs, tetragonal $14_1/\text{amd}$ (141) and

Figure 3-18. LaCrO_x Char Particles

Figure 3-19. LaCrO_x Char Particles, Milled 8 Hours

Figure 3-20. Particle Size Distribution of $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_4$,
Calcined $550^\circ\text{C}/8\text{Hr}/\text{Argon}$

monoclinic, $\text{P2}_1\text{n}$ (14). Monoclinic LaCrO_4 is formed in powders upon the burn-out of organics. X-ray diffraction of the above calcined powder indicates that lanthanum chromate forms a solid solution with calcium chromate, allowing substitutions as high as 40 percent.

Thermal analysis indicates the chromate phase loses oxygen and transforms to orthorhombic lanthanum chromite above 650°C . It is shown in Table 3-3 that this transition temperature is dependent on the amount of calcium within the system. Although this effect is not completely understood, it gives further evidence that calcium is incorporated within the LaCrO_4 lattice, forming a solid solution.

TABLE 3-3	
THE EFFECT OF CALCIUM ADDITIONS ON THE $\text{LaCrO}_4 \rightarrow \text{LaCrO}_3$ TRANSITION TEMPERATURE	
Composition	Transition Temperature
$\text{La}_{.89}\text{Ca}_{.1}\text{CrO}_4$	$\sim 770^\circ\text{C}$
$\text{La}_{.79}\text{Ca}_{.2}\text{CrO}_4$	710°C
$\text{La}_{.69}\text{Ca}_{.3}\text{CrO}_4$	705°C
$\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_4$	655°C

There has previously been difficulty in forming the pure LaCrO_4 phase. Since residual organics were retained within the char, the burn-out process was difficult to control as a result of combustion heating. Hence, the temperature often increased above the lanthanum chromate to lanthanum chromite transition within the interior of the mound of powder. This resulted in a partial, and sometimes a complete transition to the lanthanum chromite phase.

The carbon burn-out reaction was prolonged by slowly heating the char under an argon atmosphere to 550°C and holding for 8 hours. Thermogravimetric analysis under the same heating rate, temperature and hold time shows a gradual weight loss which eventually stabilizes, an indication that most of the organic material was burned off.

3.1.5.2.3 Liquid Phase Characterization

The liquid phase formed in the $(\text{La,Ca})\text{CrO}_3$ system, was found to be the result of the incongruent melting of CaCrO_4 . This phase exsolves at the transition of LaCrO_4 to LaCrO_3 when calcium substitutions exceed 10 percent and calcination temperatures range from 800°C to 1200°C . Figure 3-21 is a comparison of the melting and freezing peaks of $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_3$ (LCC-40) with that of the Ca-Cr-O eutectic composition ($\text{Ca}_{1.2}\text{CrO}_4$). The sharpness of the melting peak of $\text{Ca}_{1.2}\text{CrO}_4$ is an indication of a congruently melting liquid. Conversely, the wide shallow melting peak of LCC-40 indicates an incongruently melting liquid. In addition, the matching onset temperatures of the melting and freezing peaks in $\text{Ca}_{1.2}\text{CrO}_4$ are an indication of a single melting point.

The eutectic liquid is highly mobile and unstable. It spreads and wets adjoining porous solids (such as setter plates), especially those with a high calcium solubility. Calcium then diffuses from the liquid into the solid leaving a solid residue. Figures 3-22 and 3-23 show the results of the reaction studies of various Ca-Cr-O compounds set on porous $\text{La}_{.5}\text{Ca}_{.5}\text{CrO}_3$ pellets.

The CaCrO_4 pellets in each case formed a small amount of liquid which was drawn into the porous substrate, leaving behind a skeleton of unreactive solid. Evidence of densification in the $\text{La}_{.5}\text{Ca}_{.5}\text{CrO}_3$ showed immediately below the CaCrO_4 pellet.

The eutectic, $\text{Ca}_{1.2}\text{CrO}_4$ as well as the calcium rich specimens, $\text{Ca}_3(\text{CrO}_4)_2$ are seen to dissolve less readily into the substrates which have a greater chromium excess. The shape of the top pellets also indicate that less efficient melting occurred on these substrates. This is an indication of reactivity of the calcium within the liquid phase. Calcium diffuses out of the eutectic liquid when in contact with a solid having a high solubility for calcium, leaving behind an unreactive solid. Other reaction studies with $\text{Ca}_{1.2}\text{CrO}_4$ and $\text{Ca}_3(\text{CrO}_4)_2$ on Pt and CaCO_3 showed complete melting. In these cases, the calcium remained within the liquid, allowing it to melt completely.

The eutectic liquid also appears to have a low solubility for other metal cations. Qualitative EDS analysis of the liquid phase in $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_3$ contained no measurable amount of lanthanum. In addition, a solubility experiment was performed in which 2 and 5% La_2O_3 was mixed and reacted with CaCrO_4 . X-ray diffraction analysis indicated

Figure 3-21. DTA Melting and Freezing Peaks of Ca_{1.2}CrO₄ and La_{0.59}Ca_{0.4}CrO₃ Liquid-Phase

the formation of LaCrO₃. Further work needs to be done to better understand this portion of the LaCrO₃-CaCrO₄ solubility diagram.

3.1.5.2.4 Solubility Diagram

The Ca-Cr-O eutectic liquid reabsorbs into the perovskite lattice at temperatures dependent on the calcium composition. Figure 3-24 is a solubility diagram showing progress on this study. Solubility temperatures will ultimately be determined by following lattice parameter changes as a function of temperature. One difficulty in obtaining this diagram is the recent discovery that the orthorhombic-rhombohedral transition in LaCrO₃ has an effect on the solubility of CaCrO₄. Apparently, the high temperature rhombohedral structure has a lower solubility than does room temperature orthorhombic.

1230°C 2hr

CaCrO_4 on $\text{La}_{0.675}\text{Ca}_3\text{CrO}_3$

$\text{Ca}_{12}\text{CrO}_4$ on $\text{La}_{0.675}\text{Ca}_3\text{CrO}_3$

$\text{Ca}_3(\text{CrO}_4)_2$ on $\text{La}_{0.675}\text{Ca}_3\text{CrO}_3$

Figure 3-22. Reaction Couples, $\text{La}_{0.675}\text{Ca}_3\text{CrO}_3$ Substrate

1230°C 2hr

CaCrO_4 on $\text{La}_{0.69}\text{Ca}_3\text{CrO}_3$

$\text{Ca}_{12}\text{CrO}_4$ on $\text{La}_{0.69}\text{Ca}_3\text{CrO}_3$

$\text{Ca}_3(\text{CrO}_4)_2$ on $\text{La}_{0.69}\text{Ca}_3\text{CrO}_3$

F-66164

Figure 3-23. Reaction Couples, $\text{La}_{0.69}\text{Ca}_3\text{CrO}_3$ Substrate

Figure 3-24. The Solubility of CaCrO_4 in LaCrO_3 vs Temperature

3.1.5.2.5 Binary Powder Mixtures

Binary powder mixtures of $\text{La}_x\text{Ca}_y\text{CrO}_3$ and $\text{Ca}_n\text{Cr}_m\text{O}_4$ have shown promise in obtaining dense lanthanum chromite. The composition prepared according to equation (4-1) obtained 90 percent theoretical density. The current goal is obtaining uniform green microstructures of the mixed powders using the above mentioned dispersion techniques.

3.2 LONG-TERM CATHODE STABILITY

3.2.1 Objective

The objectives of this subtask are to determine the effect of long-term operation of the MSOFC on the cathode performance and to develop a unified theory of interfacial and bulk phenomena in the fuel cell. Densification, manganese migration, and other physical and chemical changes of the cathode may be a problem in long-term fuel cell operation. Determining and understanding the mechanisms of interfacial reactions and degradations will allow the cathode to be modified to improve its overall performance.

3.2.2 Discussion

Efforts in this area were expended in several areas. The performance of two CE/E/CE composites was examined to determine their electrochemical characteristics and to obtain data useful for the modeling effort. The conductivity of three Ca and Co doped LaCrO_3 samples was determined. Three doped $\text{LaCrO}_3/\text{Y}_2\text{O}_3$ -stabilized ZnO_2 (YSZ)/doped LaCrO_3 symmetric composites (referred to as I/E/I) were studied to evaluate the possibility of making a two-material MSOFC.

The interfacial resistance, determined by ac impedance, of four CE/E/CE composites at 1000°C as a function of oxygen partial pressure is shown in Figure 3-25. The results from the ED033 composites were included in the previous report and are given here for comparison. In general, the two 1:5:1 composites performed much better than the 1:1:1 composites. Assuming all composites were fabricated similarly with the only significant difference being in the relative thickness of the layers, then the 1:1:1 composites with the thicker cathode layers should have performed better. Since the reverse is true, one could conclude that the electrochemical properties of the cathode layers are quite different. An indication of this was seen when one of the cathodes in each of the two 1:1:1 composites delaminated during dc polarization studies on the composites.

The interfacial resistance of the CE/E/CE composites can be compared to that of composite 11930 which was fabricated earlier than the ED composites. The interfacial resistance as a function of oxygen partial pressure of 11930 and two other 1193 composites studied previously is given in Figure 3-26. All three composites performed similarly and much better than the ED composites studied above.

In a continuing effort to obtain data useful to the electrochemical modeling effort, dc polarization studies were conducted on the CE/E/CE with the results given in Figure 3-27. The oxygen and air curves clearly show two reaction mechanisms that were postulated and discussed in a previous report. One of these mechanisms is

B-27023

Figure 3-25. Interfacial Resistance of CE/E/CE Composites at 1000°C as a Function of Oxygen Partial Pressure (Circles are 1:5:1 Composites and Squares are 1:1:1 Composites)

B-27024

Figure 3-26. Interfacial Resistance of CE/E/CE Composites at 1000°C as a Function of Oxygen Partial Pressure

Figure 3-27. Polarization Curves of CE/E/CE Composite 11930 at 1000°C and the Indicated Oxygen Partial Pressure in Atm

dominant at low-current densities and the other at high-current densities. Also, the transition region between the two mechanisms is dependent on the partial pressure of oxygen. It is interesting to note that the air curve and the lowest oxygen partial pressure curve show the onset of a limiting current.

The work completed at Argonne on the electrochemical model of the solid-oxide fuel cell was transferred to the University of Oklahoma. The model has been developed to the point of requiring a considerable amount of parametric studies and reaction mechanism variation. It was felt that the program would be better served by transferring the modeling work because of the type of effort involved in these tasks and amount of time required to perform these tasks. Argonne is continuing to work with Professor Lobban and his graduate student to complete the development of the model.

The conductivity of three Ca and Co doped LaCrO_3 samples was measured. A comparison of their conductivity in oxidizing (air) and reducing ($\text{H}_2/\text{H}_2\text{O}$) environments at 1000°C is given in Table 3-4. It can be seen that their conductivity is more than adequate for the MSOFC. The temperature dependence of the conductivity of the three samples in air is given in Figure 3-28. The stability of these samples in reducing environments was only partially examined: One of the samples (04291-1) was left in a reducing environment for 24 hr without any significant loss of conductivity. It should be noted that its conductivity in air changed from 43.9 to 37.8 $\Omega^{-1}\text{cm}^{-1}$ after the reducing cycle.

Figure 3-28. Conductivity of Ca- and Co-doped LaCrO_3 Interconnect Samples in Air as a Function of Temperature

TABLE 3-4		
CONDUCTIVITY OF Ca- AND Co-DOPED LaCrO_3 INTERCONNECT SAMPLES AT 1000°C		
Sample	Air Atmosphere Conductivity in $\text{ohm}^{-1}\text{cm}^{-1}$	$\text{H}_2/\text{H}_2\text{O}$ Atmosphere
04291-1	37.8	2.65
03121-1	57.7	0.476
09171-1	46.8	2.33

Ac impedance was used to examine the electrochemical performance of three I/E/I composites in reducing ($\text{H}_2/\text{H}_2\text{O}$) and oxidizing (air) environments. The results of these studies are given in Table 3-5. The first two samples tested were fabricated similarly with no YSZ in the electrode layers. The performance of these composites with air on both sides was somewhat on the high side, but in general acceptable. In contrast, the composite's performance in a reducing environment was very poor. Since the conductivity of the LaCrO_3 drops off precipitously in reducing environments, a small increase in the bulk resistance was to be expected, but the dramatic increase in both the bulk and interfacial resistances in reducing environments was surprising.

TABLE 3-5						
BULK AND INTERFACIAL AREA SPECIFIC RESISTANCE OF I/E/I COMPOSITES AT 1000°C (CALCULATED VALUES GIVEN IN PARENTHESES)						
Sample	Air Atmosphere		$\text{H}_2/\text{H}_2\text{O}$ Atmosphere (all values in $\text{ohm}\cdot\text{cm}^2$)		Air and $\text{H}_2/\text{H}_2\text{O}$	
	Interfacial	Bulk	Interfacial	Bulk	Interfacial	Bulk
1st I/E/I (no ZrO_2)	0.256	0.274	3.10	0.875	3.49 (3.36)	0.515 (0.575)
2nd I/E/I (no ZrO_2)	0.184	0.484	2.91	1.10	3.58 (3.09)	0.801 (0.792)
IEI-8 (35 wt% ZrO_2)	0.109	1.17	1.40	2.79	1.63 (1.51)	2.11 (1.98)

The electrochemical performance of the I/E/I composites with an oxidant on one side and a fuel on the other can be predicted from the single atmosphere results. This is shown in the last two columns of Table 3-5 with the calculated values given in parentheses below the measured values. Note that the interfacial values are shown as the

total (sum of cathode and anode interfacial effects) values for the oxygen partial pressure gradient work and are individual electrode values for the single atmosphere work.

I/E/I composites were fabricated with considerable amounts of YSZ in the electrode layers in an effort to improve their electrochemical performance and bonding of electrode layers to the electrolyte layer. Besides improving the physical bond between the electrode and electrolyte layers, YSZ was added to spread out the three-phase area and increase the effective electrochemically active area. A composite with 35 wt% YSZ in the electrodes (IEI-8) was tested and the results are given in Table 3-5. As expected, there was a dramatic decrease in interfacial resistance of the composite in both reducing and oxidizing environments. Unfortunately, there was also a significant increase in the bulk resistance of the composite. Some increase in the bulk resistance was expected, but the size of the increase was much higher than it should have been.

Ac impedance was used to examine the electrochemical performance of three I/E/I composites (IEI-9, IEI-11, and IEI-14) in reducing (H_2/H_2O) and oxidizing (air) environments. The results of these studies are given in Table 3-6. Also given in Table 3-6 are the previous results on other I/E/I composites. By comparing the results from the first two I/E/I composites with the results from IEI-8 and IEI-9, the addition of YSZ to the electrode clearly improves the overall performance of the composites with the 40 wt% YSZ composite being better than the 35 wt%. A similar trend in the results for both IEI-9 and IEI-8 was observed.

Posttest examination of IEI-8 revealed that while the electrode/electrolyte bond had improved, it was still relatively weak with mostly point contacts. Diffraction studies of the IEI-8 electrode material revealed that no $La_2Zr_2O_7$ was present in measurable quantities (approximately 5%). This indicates that there is less interaction between the YSZ and the $LaCrO_3$, than was observed for YSZ and $LaMnO_3$. It should be noted that the presence of a very thin interfacial reaction layer of $La_2Zr_2O_7$ probably would not have been detected by the diffractions studies.

A significant improvement in bonding was observed by increasing the firing temperature $100^\circ C$. While caution must be used in making direct comparisons between composites IEI-8 and IEI-11, because IEI-11 was a five-layer composite with extra doped- $LaCrO_3$ layers (no YSZ) on the outside. The bulk area specific resistances for IEI-11 were much lower than that of IEI-8. In fact, the overall performance of IEI-11 was the best of all cells tested.

The addition of a bonding-layer of 80 wt% YSZ (balance doped- $LaCrO_3$) further improved the bonding, but the composite (IEI-14) exhibited a significant decrease in electrochemical performance with IEI-14 having the worst overall performance of all the I/E/I cells tested. Both the interfacial and bulk components of IEI-14 showed marked increases in area specific resistance.

TABLE 3-6

BULK AND INTERFACIAL AREA SPECIFIC RESISTANCE OF I/E/I COMPOSITES
AT 1000°C (CALCULATED VALUES GIVEN IN PARENTHESES)

Sample	Air Atmosphere		H ₂ /H ₂ O Atmosphere		Air & H ₂ /H ₂ O		Total Cell
	Interfacial	Bulk	Interfacial	Bulk	Interfacial	Bulk	
1st I/E/I	0.256	0.274	3.10	0.875	3.49	0.515	4.00
{no ZrO ₂ }					(3.36)	(0.575)	(3.94)
2nd I/E/I	0.184	0.484	2.91	1.10	3.58	0.801	4.38
{no ZrO ₂ }					(3.09)	(0.792)	(3.88)
IEI-8	0.109	1.17	1.40	2.79	1.63	2.11	3.74
{35 Wt%; Fired @ 1400°C}					(1.51)	(1.98)	(3.94)
IEI-9	0.164	0.526	1.34	2.37	1.09	1.71	2.80
{40 Wt%; Fired @ 1400°C}					(1.50)	(1.45)	(2.95)
IEI-11	0.172	0.242	(1.22)	(1.30)	1.39	0.892	2.28
{35 Wt% & 0 Wt%; Fired @ 1500°C}							
IEI-14	0.339	0.650	3.06	2.56	4.88	2.00	6.88
{80 Wt% & 35 Wt%; Fired @ 1500°C}					(3.40)	(1.60)	(5.00)
(All values in ohm-cm ²)							

The addition of 20 wt% doped-LaCrO₃ to the electrolyte was expected to decrease the conductivity of the electrolyte slightly, but not have a major impact on the electrochemical performance of the composite. In order to examine the effect of small additions of doped-LaCrO₃ to the electrolyte's conductivity, a pellet of 10 wt% doped-LaCrO₃ (balance YSZ) was fabricated. Its conductivity at 1000°C was 0.0458 $\Omega^{-1}\text{cm}^{-1}$ as compared to 0.12 $\Omega^{-1}\text{cm}^{-1}$ for YSZ. This significant decrease in conductivity suggests that the 80 wt% YSZ layers added just to improve bonding, significantly hurt performance of the composite by increasing the bulk resistance of the sample.

The conductivity of two doped LaCrO₃ samples were measured in oxidizing (air) and reducing (H₂/H₂O = 97/3) environments. One of the samples contained no YSZ (LC-361) and the other had 35 wt% YSZ (LC-359). At 1000°C the conductivity of LC-361 was 31.1 $\Omega^{-1}\text{cm}^{-1}$ in air and 2.28 $\Omega^{-1}\text{cm}^{-1}$ in a reducing environment. Considering that this was a porous sample, its conductivity agrees well with previous measurements on similarly doped LaCrO₃ samples. In contrast, the conductivity of LC-359 was much lower than expected. At 1000°C its conductivity was 0.890 $\Omega^{-1}\text{cm}^{-1}$ in air and 0.0717 $\Omega^{-1}\text{cm}^{-1}$ in a reducing environment. The change in conductivity of more than an order of magnitude is much higher than would be expected from classical theories on mixed conductors, indicating that possibly not all the LaCrO₃ particles are in contact with each other.

As pointed out above, the addition of YSZ to the electrode material improves the electrode-layer bonding and should decrease the interfacial resistance of the SOFC by spreading out the three-phase electrochemically active area. However, it does increase the bulk resistance of the electrode layer. The significant drop in electrolyte conductivity with the addition of only 10 wt% LaCrO_3 suggests that the actual increase in electrochemically active area may be small. The measured conductivity values of the 35 wt% LaCrO_3 indicate that the addition of YSZ to the electrode material does prohibit its use as a corrugation in the stack, and the I/E/I's in the stack may require an additional pure LaCrO_3 layer on the outside, such as in IEI-11, to spread out the current from the corrugation contacts.

While more work needs to be done to confirm the experimental results attained thus far and to improve the ionic and electronic conductivity of the electrode material, one fact is clear in all these I/E/I electrochemical studies. LaCrO_3 is a much better cathode material than anode material. The performance of the material as a cathode is similar to that of LaMnO_3 and the performance as an anode has consistently been an order of magnitude worse. This makes one consider that possibly a three-material fuel cell would be the best compromise between performance and fabrication.

3.3 REFERENCES

- (1) *Monolithic Solid-Oxide Fuel Cell Technology Advancement for Coal-Based Power Generation, Quarterly Technical Progress Report for January-March 1992*, prepared by Argonne National Laboratory for AlliedSignal Aerospace Systems & Equipment
- (2) M. Mori, N. Sakai, T. Kawada, H. Yokokawa, M. Dokiya, "Low-Temperature Air-Sinterable Lanthanum Calcium Chromite with Chromium Deficit for SOFC Separator," *Denki Kagaku*, 58 (1990) 528.
- (3) W. Ford, J. White, *Trans. Bri. Cer. Soc.*, 48, 417, (1949).
- (4) R. German, *Liquid Phase Sintering*, Plenum Press, N. Y., p. 182, (1985).
- (5) L. Tai, P. Lessing, "Modified Resin-Intermediate Processing of Perovskite Powders - Parts I and II...", *J. Mater. Res.*, 7 [2] 502-519 (1992).
- (6) F. C. Jang, "Dispersion Behavior of Aluminum Oxide, Lanthanum Manganite, and Lanthanum Chromite Powders in Liquids," Ph.D. Dissertation, University of Missouri-Rolla, Rolla, MO (1991).

4. FABRICATION

4.1 FABRICATION DEMONSTRATION

4.1.1 Objective

The objective of this task is to fabricate MSOFC cells and stacks of increasing power output to demonstrate the viability of the fabrication process.

4.1.2 Fabrication of Cells and Stacks

MSOFC cells and stacks are being made using a fabrication sequence based on the tape-calendering technique. Primary activities included batch preparation and characterization, fabrication of single cells and multicell stacks, bonding studies, inter-connect development, and shrinkage matching .

4.1.2.1 Batch Preparation and Characterization

Batch preparation efforts were concentrated in two areas: providing a tape supply for cell and stack fabrication, and investigating formulation modifications to improve the structural performance of the baseline materials. Several batches were prepared last quarter using the established procedures. The prepared batches were characterized in terms of weight-loss during firing, sintered density, and total firing shrinkage (diametral).

Baseline anode (A) and cathode/electrolyte intermediate (CE) batches were made to replenish the tape supply. The average properties of these batches are summarized in Table 4-1. Figures 4-1 and 4-2 show the properties of these anode batches along with those prepared since May 1991. The properties of these batches fall within the ranges expected for baseline materials.

TABLE 4-1				
AVERAGE SINTERED PROPERTIES OF MSOFC BATCHES				
Baseline Batch	Diametral Shrinkage, Percent	Weight Loss, percent	Density, g/cc	Theoretical Density, percent
A11191-1	17.7 ± 0.9	23.1 ± 0.1	4.38 ± 0.18	71.5 ± 3.0
A11201-1	17.6 ± 1.0	22.9 ± 0.1	4.48 ± 0.09	73.1 ± 1.5
A11201-2	19.6 ± 0.5	22.6 ± 0.2	4.33 ± 0.13	70.7 ± 1.9
A11211-1	19.3 ± 1.3	22.9 ± 0.2	4.43 ± 0.11	72.2 ± 1.8
CE03122-1	21.2 ± 0.5	23.7 ± 0.2	5.00 ± 0.10	79.7 ± 1.6
CE03132-1	22.0 ± 0.3	24.0 ± 0.2	4.88 ± 0.15	77.7 ± 2.4
CE03132-2	21.2 ± 0.6	23.5 ± 0.1	4.86 ± 0.17	77.4 ± 2.7

Figure 4-1. Properties of Baseline Anode Batches Made Since May 1991

Figure 4-2. Sintered Properties of Baseline CE Batches Made Since May 1991

Two high solid loading anode batches were prepared. High solid loading anodes were used to fabricate the flat plate in single cell stacks and anode-covered modules. An anode batch (A01072-1) of high solid loading was first prepared using the torque rheometer. Based on the favorable results of the torque rheometer batch, a larger batch (A01172-1) was then prepared using the Banbury mixer. The average sintered properties of the two new anode batches are given in Table 4-2. Figure 4-3 compares the properties of these batches with batch A07030-1 (high solids loading) and other baseline batches.

TABLE 4-2				
AVERAGE PROPERTIES OF HIGH SOLIDS LOADING ANODE BATCHES				
Batch	Diametral Shrinkage, %	Weight Loss, %	Density, g/cc	Theoretical Density, %
A01072-1	17.2 ± 0.4	21.8 ± 0.0	4.64 ± 0.08	75.6 ± 1.3
A01172-1	16.9 ± 0.4	21.6 ± 0.1	4.48 ± 0.13	73.1 ± 2.1

Figure 4-3. Sintered Properties of High Solids Loading Anodes (50 vol % Solids) vs Baseline Andoes (47 vol % Solids)

Other batches were made in an effort to improve the structural performance of the baseline batches. The primary objective was to decrease the magnitude and frequency of defects in modules and stacks. The approach was to toughen the baseline

materials. Toughening was made by replacing portions of the zirconia components with alumina in each of the anode (A), electrolyte (E), and cathode-electrolyte intermediate (CE) formulations. The addition of alumina has been shown to increase the strength and toughness of stabilized zirconia in previous work.^(1,2)

Modified anode (A10241-1), electrolyte (E10241-1) and intermediate (CE11071-1 and CE11071-2) batches were prepared based on this toughening approach. Table 4-3 shows the average sintered properties for these batches.

TABLE 4-3				
AVERAGE PROPERTIES OF MODIFIED BATCHES				
Modified MSOFC Batch	Diametral Shrinkage, Percent	Weight Loss, percent	Density, g/cc	Theoretical Density, percent
A10241-1	16.5 $\pm$ 0.5	23.5 $\pm$ 0.1	4.15 $\pm$ 0.06	69.9 $\pm$ 1.1
E10241-1	13.2 $\pm$ 0.1	17.8 $\pm$ 0.1	5.43 $\pm$ 0.05	99.9 $\pm$ 0.9
CE11071-1	22.4 $\pm$ 0.8	24.6 $\pm$ 0.1	5.14 $\pm$ 0.18	85.5 $\pm$ 3.0
CE11071-2	22.2 $\pm$ 0.4	24.8 $\pm$ 0.1	5.05 $\pm$ 0.17	83.9 $\pm$ 2.8
A01282-1	15.6 $\pm$ 0.4	18.7 $\pm$ 0.0	4.69 $\pm$ 0.11	79.4 $\pm$ 1.8
CE01212-1	21.7 $\pm$ 0.3	24.4 $\pm$ 2.8	5.21 $\pm$ 0.07	8.6 $\pm$ 1.2

An anode batch (A01282-1) was prepared with the addition of alumina and with no pore former for the interconnect work in an effort to control the pore volume and firing shrinkage of the anode and wicking in the interconnect. The sintered properties of this batch are shown in Table 4-3. In addition, a Banbury batch of alumina-modified CE (CE01212-1) was made. The properties of the modified CE batch are also presented in Table 4-3.

Using X-ray diffraction, the phase compositions of the modified materials were evaluated and compared to the baseline materials. Table 4-4 shows the phase compositions of the baseline and modified batches. In the anode layer, all of the alumina (in both the baseline and the modified material) reacts with nickelous oxide to form a nickel aluminate phase; the zirconia remains as a separate phase in the anode. In the electrolyte layer, the zirconia and alumina remain as separate phases. In the intermediate layer, the lanthanum zirconate phase, which is seen in the baseline, is suppressed by the formation of a manganese aluminate phase in the modified material.

TABLE 4-4		
PHASES PRESENT IN BASELINE AND MODIFIED MSOFC BATCHES		
	Baseline	Modified
Anode (A)	NiO ZrO ₂ NiAl ₂ O ₄	NiO ZrO ₂ NiAl ₂ O ₄
Electrolyte (E)	ZrO ₂	ZrO ₂
Cathode/electrolyte (CE)	ZrO ₂ LaMnO ₃ La ₂ Zr ₂ O ₇	ZrO ₂ LaMnO ₃ Mn ₂ AlO ₄

4.1.2.2 Cell and Stack Fabrication

Fabrication of flat single cell modules and stacks with minimum observable defects for subsequent second-step bond was this effort's primary objective. More than 200 single-cell modules and stacks were made to support second-step bond development and multicell stack building. In addition, efforts were initiated to evaluate single cells, modules, and stacks containing thin-film electrolytes.

The fabrication of single-cell modules concentrated on the 2.5-in. and 1.3-in. green footprint single-cell modules. The emphasis of the work was to minimize the degree of bowing in fabricated samples while maintaining gas-channel shape retention and structural integrity. Flatness could only result from high constraint weight; however, the higher weight caused corrugation collapsing as the tapes softened during binder extraction. Firing runs with different constraint weights were carried out and the results were used to select a tradeoff constraint weight for each module size.

Several modifications were made in the processing of single-cell modules. Significant progress was made in the fabrication of modules with electrode cover and in the use of a creep-sintering process. Single-cell modules of a 1.3-in. footprint area were fabricated with either an A or CE cover layer bonded on in the green state. Several anode and CE batches with different solids loading levels were used as cover layers to determine the most suitable combination. Evaluation of initial results indicated that the high shrinkage of the anode layer caused significant bowing of fabricated samples. Therefore, a higher solids loading anode (A07030-1) was used for the anode corrugation as well as anode cover. This construction resulted in flat anode-covered modules with minimal observable defects. Using A07030-1 as the anode corrugation in CE-covered modules produced similar results. The ability to fabricate electrode-covered modules improves the two-step stack-building process by lessening the number of second-step bonds.

To obtain flat stacks with well-defined gas channels, varying the constraint weight during processing was attempted; low weight was used for low-temperature binder extraction and high weight was used for the sintering temperature regime. This

variation can be performed by splitting the processing run into two steps. In the first step, the green sample is constrained with a low weight and fired to a temperature lower than sintering temperature but higher than binder burnout temperatures. The sample can then support more weight. In the second step, the sample is then fired to the sintering temperature with a higher constraint weight. This higher load assists in flattening the sample during sintering, a type of creep-assisted sintering. Two maximum temperatures were investigated for the first step. The first, 600°C, is just above the binder burnout temperature, while the other, 1300°C, is just below the sintering temperature. Going up to 1300°C in the first step proved better because the resulting stacks had fewer defects. The constraint weight used in the second step is double that used in the first step. This creep-sintering process has yielded flat modules and electrode-covered modules with minimal observable defects.

The single-cell stack fabrication effort also involved the evaluation of the effect of altered electrode cover layer thicknesses and the impact of Al₂O₃-toughened components on single-cell stacks.

A series of single-cell stacks, consisting of varied electrode cover layer thicknesses, were fabricated and processed. The objective of this effort was to evaluate cover thicknesses for stack flatness improvement. The standard single-cell stack cover layer green thickness is 13 mils. Table 4-5 shows the combinations of anode and cathode cover layer thicknesses evaluated.

TABLE 4-5		
SINGLE-CELL STACKS WITH VARIOUS COVER THICKNESSES		
Stack ID	Anode Thickness, mils	Cathode Thickness, mils
EB037-1	13	13
EB037-2	13	26
EB037-3	26	13
EB037-4	26	26

Visual and optical microscopic examination of the sintered samples indicated that fabricating single-cell stacks with 13-mil electrode cover layers gave the best results. All stacks that were fabricated with either a 26-mil anode or cathode cover layer possessed severe defects and delaminations. Although the cathode covers layers remained extremely flat in stacks constructed with 26-mil cathode covers, the anode layers within these stacks sintered to a concave shape, causing delamination and severe defects within the stacks.

An effort was made to reduce the magnitude and frequency of the defects (particularly the hairline V-cracks commonly seen in CE corrugations) found in single-cell stacks. The approach taken to reduce these defects was to incorporate toughened

components in single-cell stacks. Experiments were carried out to find the best combination of toughened layers and baseline layers when structural integrity and electrochemical performance were considered in single cells and single-cell stacks.

To find the best structural combination, matrices of single-cell discs (green dia = 1.25 in.) and single-cell stacks (green dimensions = 1.3 in. x 1.3 in.) were fabricated. Table 4-6 shows the matrixes and the yields for each combination of cell and stack.

TABLE 4-6				
RESULTS OF CELLS AND STACKS FABRICATED WITH BASELINE AND MODIFIED COMPONENTS				
Component			Results	
A	E	CE	Single-Cell Disk (Yield)	Single-Cell Stack (Observation)
Baseline	Baseline	Baseline	8/10	Defect Type II
Baseline	Modified	Baseline	0/4	Defect Type IV
Modified	Baseline	Baseline	4/4	Warped
Modified	Modified	Baseline	4/4	Warped
Baseline	Baseline	Modified	4/4	No observable defects
Baseline	Modified	Modified	4/4	Defect Type III
Modified	Baseline	Modified	4/4	Warped
Modified	Modified	Modified	3/4	Warped, slumped
Defect Type II: Defect (hairline crack) barely identifiable at 70X and not found within electrolyte layer				
Defect Type III: Defect (hairline crack) easily identifiable at 70X and not found within electrolyte layer				
Defect Type IV: Defect (hairline crack) found in or through electrolyte layer				

From these results, it was concluded that a combination of baseline A, baseline E, and modified CE was structurally the best combination considered. Several 1.3-in. (green footprint area) single-cell stacks have been successfully processed and subsequently fabricated into multicell stacks using the second-step bonding technique.

A number of baseline single-cell stacks were also processed using the creep-sintering technique. Optical microscopic examination of baseline single-cell stacks after processing showed the presence of a few common defects. However, the degree of bowing was dramatically reduced compared to single-cell stacks processed by the conventional sintering method. In addition, single-cell stacks constructed with baseline anode, baseline electrolyte and Al_2O_3 -toughened CE were fabricated and processed using the creep-sintering technique. Visual and optical examination of the stacks after

processing showed the presence of very few defects and the absence of bowing. Several of these stacks were selected for multicell bonding and testing.

Based on the results obtained and discussed above, it was decided to carry out a study to define the most suitable building block for the two-step bonding process. Several matrix experiments were designed and performed to determine stack geometry and processing parameters for a given batch combination to produce building blocks with minimal defect count. The experiments covered several batch combination and stack geometry variables. The variables on batch combination included standard and high solid loading A and standard and alumina-modified CE. The variables on stack geometry were single cell module, electrode-covered module, and single cell stack. Samples were processed via standard firing process or the creep-sintering process. Sintered samples were judged on defect type and frequency, flatness, and process throughput.

The results of the experiments indicated that single cell stacks possessed the highest defect frequency while the single cell modules had the lowest. The defect type and frequency of the electrode-covered modules depended on batch combinations. In general, single cell modules composed of baseline anode, electrolyte, and cathode/electrolyte intermediate were superior in all categories. These samples possessed a type I yield over 90 percent and a gap of approximately 4 mils as measured on the optical comparator. This measured gap also represents a 33 percent decrease in degree of bowing compared to modules fabricated earlier. Furthermore, the throughput was highest for single cell modules. This high throughput could be obtained for modules by the standard firing process rather than the more complex creep-sintering process necessary for electrode-covered modules and single cell stacks. Based on these results, single cell modules are the present choice for multicell stack building blocks.

In addition to the matrix experiments described above, a number of multicell stacks were fabricated by the two-step cofiring process. The stacks were fabricated to test the feasibility of bonding formulations and procedures and to provide samples for performance testing. The details of the stacks fabricated are given in Table 4-7. Except when noted, the stacks were bonded using the 50/50 (50 vol percent A or CE and 50 vol percent I) bonding tapes. In general, the stacks showed excellent bond integrity. Several two-cell stacks were sectioned and showed good bonding contact within the stacks. Figure 4-4 is an example of the cross section of a two-cell stack cut perpendicular to the anode corrugations.

F-66155

Figure 4-4. Cross Section of a Two-Cell Stack Cut Perpendicular to Anode Corrugation

TABLE 4-7			
FABRICATED MULTICELL STACKS			
ID No.	No. of Cells	Building Block Type*	Remark
EH12-1	2	B	No delamination. Good bonding contact as observed at edges under 70X
EH13-1	2	C	As above
EH14-1	2	B	Confirmed EH12-1
EH15-1	2	B	Used for testing
EH15-2	2	C	Used for testing
EH16-1	3	A, B	No delamination. Good bonding contact as observed at edges under 70X
EJ17-1	5	A, B	As above
EH18-1	2	B	As above, 75A/25I and 25CE/75I mixes for bonding
EH19-1	2	B	For thermal cycling
EH19-2	2	B	For thermal cycling
EH20-1	2	A	No delamination. Anode tape for bonding A cover to A corrugation
*A = single-cell module B = electrode-covered single-cell module C = single-cell stack			

Efforts were initiated in the area of single-cell, module, and stack fabrication containing thin-film electrolytes. Multilayer tapes were made to a thickness ratio specified from the stress analysis. Single-cell discs were sintered to 1350°C for 0.5 hr. Initial results of the single cells were poor because most discs fractured after being fired. More samples will be fabricated to confirm this result. Figure 4-5 shows microstructures of two single-cell discs, one containing baseline electrolyte made of tailored yttria-stabilized zirconia (YSZ) powders and the other electrolyte made of as-received YSZ. Both electrolytes are fully dense and approximately 10 micron thick. The electrode/electrolyte interfaces display good bonding.

4.1.2.3 Bonding Studies

A number of multicell stacks were fabricated by the two-step cofiring process. The stacks were made from single-cell modules or single-cell stacks of a 1-in. and 2-in. footprint area (sintered area). After firing, all the stacks showed bonding without delamination.

A. Baseline YSZ Electrolyte (ED 099-2)

F-65876

B. As-Received YSZ Electrolyte (ED 099-8)

Figure 4-5. SEM Micrographs of Single Cells Containing Thin-Film Electrolytes

Extensive evaluation and characterization were performed on bonded samples. The key results are summarized below:

- (a) The bonding step did not cause any damage or cracking to the interconnect or the bonded single-cell modules or stacks.
- (b) Bonded stacks showed excellent strength. Several samples were sectioned without delaminating.
- (c) The anode/anode and anode/interconnect had excellent bonding contact, whereas the cathode/interconnect needed improvement.
- (d) Bonded stacks were thermally cycled (3 cycles to 900° to 1000°C) and remained bonded.

Modifications of bonding materials and procedures have resulted in improved bonding contact. Examples of improved bonding are shown in Figure 4-6.

Early development of a bonding formulation focused on materials for the cathode-electrolyte intermediate (CE) to interconnect (I) bond. Since the poor contact of the CE-I bond appeared to be due to the high shrinkage and low toughness of the bonding tape, evaluation of CE bond formulations concentrated on solids loading, powder reactivity, and use of a toughening agent. Four batches were prepared according to the matrix shown in Table 4-8. Each formulation was used in a CE-I bond with both corrugation/flat plate and flat plate/flat plate bond geometries. Figure 4-7 shows a typical area of the flat plate/flat plate bonds.

TABLE 4-8			
CE BOND FORMULATIONS			
Formulation No.	Solids Loading	Reactivity	Toughening
1	Low	High	No
2	Low	High	Yes
3	High	Low	No
4	High	Low	Yes

All formulations yielded good bonds as shown in the photographs. The low solids loading formulations (Nos. 1 and 2) have better bonding tape homogeneity, making them preferable.

Further bonding development efforts concentrated on the investigation of bonding formulation and procedures that reduce firing shrinkage and minimize cracking and delamination of bonding materials during second-step firing. Based on the results presented above, the current approach was to add interconnect material to the A and CE

(a) Anode Corrugation/Interconnect

F-64418

(b) Intermediate Corrugation/Interconnect

Figure 4-6. Micrographs of Bonding Between Interconnect and Electrode Corrugations (80X Magnification)

(a) Bond Formulation 1

(b) Bond Formulation .

(c) Bond Formulation 3

(d) Bond Formulation 4

Figure 4-7. Cross-Section of Bonding Between Flat Cathode/Electrolyte Intermediate (CE) (Top) and Interconnect (I) (Bottom) (Magnification = 64X)

bond formulations. The addition of interconnect was expected to reduce shrinkage of bonding tapes, resulting in less cracking and improved bonding contact.

Initial bonding experiments were performed using electrode and interconnect plates and 50 percent electrode material + 50 percent interconnect tape as bonding material. Visual and optical examination of bonded samples after firing indicated minimal cracking of bonding materials and excellent bonding contact. As an example, a micrograph of a polished cross section of a bonded CE/I sample is given in Figure 4-8. The sample shows excellent contact between the bonding material and CE and I plates.

Figure 4-8. Polished Cross-Section of CE/I Bond Using 50CE/50I Bonding Material

Based on the initial results, electrode/interconnect tapes of different compositions were investigated for bonding various flat plates and electrode corrugations. Preliminary results (for firing to 1250°C for 1 hour) are shown in Table 4-9. The results show that the mixture tape was inferior to the pure, high solids loading anode tape for the A cover/A corrugation bond. Conversely, mixture tapes were better than pure CE tape for the CE cover/CE corrugation bond. Also, mixture tapes appeared to be excellent for I plate/electrode corrugation bonds. Figure 4-9 shows optical micrographs of the bonds between A cover and anode corrugation using A bonding tape and 50A/50I bonding tape and between CE corrugation and I plate using 50CE/50I bonding tape.

*A. Good Bonding of A Cover - A Corrugation
Using Pure Anode Tape*

*B. Delamination of A Cover - A Corrugation
Using A/I 50/50 Composite Tape*

*C. Good Bonding of CE Cover - CE Cover Us-
ing CE/I 50/50 Tape. Magnification 80x*

F-66157

Figure 4-9. Micrographs of Polished Cross-Sections

TABLE 4-9		
BONDING RESULTS		
Bond	Formulation	Result
A cover - A corrugation	A/I 100/0	Good bonding
	A/I 75/25	Good bonding
	A/I 50/50	Delamination
I cover - A corrugation	A/I 50/05	Good bonding
	A/I 75/25	Good bonding
CE cover - CE corrugation	CE/I 100/0	Delamination
	CE/I 50/50	Good bonding
	CE/I 25/75	Delamination
I cover - CE corrugation	CE/I 50/50	Good bonding
	CE/I 25/75	Good bonding

X-ray diffraction patterns of the different bonding tapes fired at 1250°C for 1 hour are shown in Figure 4-10. The 50/50 CE/I material displays splitting of the LaCrO_3 / LaMnO_3 peaks; splitting is absent in the 25/75 material. The lanthanum chromite (of the I) and lanthanum manganite (of the CE) patterns overlap to a high degree, therefore splitting indicates that both phases coexist in the 50/50 material while one phase, probably lanthanum chromite, constitutes the majority of the 25/75 material. No lanthanum zirconate phases were found in either formulation. For the A/I materials, the 50/50 formulation showed trace amounts of nickel chromite and calcium zirconate reaction products whereas the 75/25 formulation displayed only peaks associated with the constituents.

The effect of thermal cycling on bond integrity has been evaluated by firing bonded single cell stacks from room temperature to 1000C three times followed by examination of polished cross-sections. Cycled stacks remained handleable and the outer edges appeared unaffected upon microscopic examination at 70x magnification. No new defects were introduced within the trilayer and any defects present before thermal cycling did not propagate. Examination of polished cross-sections indicated that the bonding integrity did not appear to be affected by thermal cycling.

The bonding development effort then proceeded with two objectives: (1) to identify bonding formulations and techniques that would give good electrochemical performance and (2) to supplement understanding of the bond process through characterization of bond formulations and bonded layers. These efforts culminated in bonded single-cell and two-cell stacks demonstrating the best electrochemical performance to date.

To determine the mechanical integrity of second-step anode bonds under testing conditions, several anode-anode (A/A) and anode-interconnect (A/I) coupons were

Figure 4-10. X-Ray Diffraction Patterns of Bonding Materials

bonded with pure A and A/I composite tapes and then exposed to reducing environments. All bond formulations and configurations held after hydrogen reduction of the NiO to Ni metal. Therefore, it is concluded that anode-anode and anode-interconnect bonds have the ability to withstand testing environments.

Several types of single-cell stacks were constructed, differing in the layer used for cover plates and/or the bonding formulations. The purpose of this effort was to identify bond formulations for building multicell stacks and assessing the effect the different cover plates and bond formulations would have on performance. Table 4-10 summarizes the results obtained on stacks constructed for this effort.

As seen from Table 4-10, stacks with an interconnect plate substituting for an anode cover had poor CE bonds and a tendency to delaminate during application of the current collector. This indicates a weak bond and poor thermal cyclability. From these results and performance test results, no further work on the use of the interconnect as a cover plate along with the CE cover plate was pursued.

TABLE 4-10			
EFFECTS OF DIFFERENT COVER PLATES AND BOND FORMULATIONS			
Stack Construction	Anode Bond Formulation	CE Bond Formulation	Result
A-sc mod-CE	A/I (100/0)	CE/I (50/50)	Good bonds; tested
	A/I (75/25)	CE/I (25/75)	Poor bonding
	A/I (50/50)	CE/I (50/50)	Good bonding
A-sc mod-I	A/I (100/0)	CE/I (50/50)	Good bonds; tested
I-sc mod-CE	A/I (100/0)	CE/I (50/50)	Good bonds: CE plate delaminated during test preparation.
I-sc mod-I	A/I (100/0)	CE/I (50/50)	Poor CE/I bond; CE plate delaminated during test preparation.
	A/I (75/25)	CE/I (25/75)	Poor CE/I bond
	A/I (50/50)	CE/I (25/75)	Poor CE/I bond; CE plate delaminated during test preparation.
Note: sc mod means single-cell module			

In general, single-cell modules show slight bowing after processing. Modules containing baseline A, E, and CE tend to bow along the anode corrugation length. Bowing along the CE corrugation length is minimal. To compensate for the module bowing in bonding, combinations of thick and thin bonding tapes were used. This approach showed improved bonding contact in bonded stacks. Another attempt to circumvent module bowing was to polish the high points of the corrugations, thus

removing the bowing. Polishing the corrugations resulted in increased contact when the polished module was bonded with the cover plates. Several flattened stacks were bonded to flat plates and processed. A cross section of a bonded single-cell stack (EE337-01) made by this technique is shown in Figure 4-11. In general, a significant improvement in the bond contact area was observed with this technique. However, the polishing technique caused hairline trilayer cracking when the sample was examined under a microscope at 70X. The effects of hairline cracks in electrolytes on stack performance are not known at present.

Based on the performance of EE332-01 type stacks (see Section 5), several two- and three-cell stacks were fabricated. A set of two- and three-cell stacks were made to compare the effect of single and multiple interconnect layers and bonds against single-cell stacks. Table 4-11 lists the contents of this set of stacks. Figure 4-12 shows the polished cross section of a two-cell stack EE344-01, a sister stack to EE344-03.

TABLE 4-11				
CONTENTS OF TWO- AND THREE-CELL STACKS				
Stack No.	No. of Cells	A/A Bond Formulation	A/I Bond Formulation	CE/I and CE/CE Bond Formulations
EE344-03	2	A/I(100/0)	A/I(50/50)	CE/I(50/50)
EE344-02	3	A/I(100/0)	A/I(50/50)	CE/I(50/50)
EE355-04	2	A/I(100/0)	A/I(100/0)	CE/I(50/50)
EE346-01	3	A/I(100/0)	A/I(100/0)	CE/I(50/50)

One of the two-cell stacks, EE344-03, was tested. It performed close to a single-cell stack (see Section 5). The other two-cell stack, EE355-04, had better contact at the anode-interconnect interface based on the sister stack examination. The pure anode bond material appears to be better than an A/I formulation for anode corrugation-interconnect plate bonds. The fabricated three-cell stacks were examined. Microscopic inspection of the three-cell stack outer edges and cross sections showed a bond quality and character similar to the two-cell stacks.

Bond formulations were characterized by diametrical shrinkage, density, thermal contraction coefficient, and thermal expansion coefficient measurements. Figure 4-13 shows diametrical shrinkage and density values for the five bonding formulations used so far. Measurements were made after processing at 1250°C for 1 hr and 1350°C for 0.5 hr. The lower temperature was used for second-step bonding. Figure 4-13 shows that both shrinkage and density decreased as the interconnect was added to the anode. Conversely, for the CE-interconnect composite tapes, shrinkage and density increased with the interconnect additions. Table 4-12 lists the thermal contraction and expansion data for the bonding formulations.

Thermal contraction measurements were taken upon cooling after processing the tapes at 1250°C for 1 hr, as used for second-step bonding. Expansion was measured

F-65082

Figure 4-11. Polished Cross Section of a Single-Cell Stack Made by Bonding Polished Module with Flat Cover Plates (EE 337-01)

Figure 4-12. Polished Cross Section of Bonded Two-Cell Stack (EE344-01)

ANODE-INTERCONNECT COMPOSITES

INTERMEDIATE-INTERCONNECT COMPOSITES

Figure 4-13. Firing Shrinkage and Density of Bonding Formulations

upon reheating to approximately 1100°C. There are minor differences in contraction and expansion between the formulations.

TABLE 4-12		
THERMAL CONTRACTION AND EXPANSION COEFFICIENTS FOR BONDING FORMULATIONS		
Formulation	Contraction, $\times 10^{-6}/^{\circ}\text{C}$	Expansion, $\times 10^{-6}/^{\circ}\text{C}$
A/I (100/0)	12.6	13.2
A/I (75/25)	13.4	13.8
A/I (50/50)	13.5	14.2
CE/I (50/50)	12.5	13.1
CE/I (25/75)	12.4	13.1
Note: Range for thermal contraction coefficient: 1086°C to 100°C. Range for thermal expansion coefficient: 100°C to 1082°C. Measurement error approximately 3.5 percent.		

4.1.2.4 Interconnect Studies

This effort focused mainly on the cofiring of the interconnect laminated with the other cell components. Emphasis was placed on the effect of the lamination on interconnect densification. In addition, effects of interconnect powder characteristics were investigated. Tapes were prepared with lanthanum chromite powders treated in a variety of ways. The tapes were evaluated to determine any processing or powder preparation conditions that could influence densification.

Tapes were initially prepared using the as-received powder (surface area = 2.91 m²/g) and powder that was ball-milled and calcined (surface area = 1 to 2 m²/g). The measured surface area is average surface area for spherical agglomerates of the lanthanum chromite. In most cases, the as-received powder when mixed with the binder and plasticizer could not be rolled into a tape. Tapes made of lanthanum chromite, which was milled and calcined, could easily be made into tapes; however, only a maximum density of 94-percent theoretical density was achieved by sintering at 1400°C for 1 hr. The as-sintered and fractured surfaces of this material, shown in Figure 4-14, indicate that there is a lot of enclosed porosity residing at the grain boundaries.

The tape composed of the as-received powder that would not roll was heated to remove the binder so that the powder could be used in subsequent batches. The powder had a surface area of 18.5 m²/gm after it was debindered. The high surface area indicated that the soft agglomerates were broken down during shear mixing when the plastic mass was being formed. This powder was calcined at temperatures above 1000°C for 5 hr and then made into tapes. Sintering of this tape resulted in densities of

As-Sintered

Fracture

F-64414

Figure 4-14 As-Sintered and Fracture Surfaces of Lanthanum Chromite Sintered 1400°C for 1 hr. Powder from Lot 0260, Ball-Milled and Calcined

94-percent theoretical density, similar to those of the previously prepared material (ball-milled and calcined). The as-sintered surface of this material, shown in Figure 4-15, is more uniform and shows very little porosity in the microstructure. The fracture surface shows a similar distribution in the amount of porosity in the microstructure as compared to the sample shown in Figure 4-14; however, the size of the porosity is much larger in the sample in Figure 4-15.

This result indicates that the as-sintered microstructure can be improved by breaking down the agglomerates in the as-received powder into their individual particles. There is no change, however, in the sintered density of the material.

The interconnect work centered on fabricating and processing A/I, C/I, CE/I, and A/I/CE tapes, bonding them to anode and intermediate corrugations, and evaluating sintering and densification of the bonded structures. The interconnect material used in this work had the composition $\text{La}_{0.84}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$. The anode, cathode, and intermediate tapes used were standard baseline batches. All bilayers and trilayers used in this study were fabricated such that the thickness of the anode and cathode were no greater than 12 μ .

Initially, A/I bilayers were bonded to anode corrugations and C/I and CE/I bilayers were bonded to CE corrugations. Figure 4-16A shows a SEM micrograph of the fracture surface of an A/I bilayer bonded to an anode corrugation. Good bonding was observed between the bilayer and the corrugation. Figure 4-16B shows a lower magnification of the sample shown in Figure 4-16A. In Figure 4-16B, two areas are identified A and B, and high magnification micrographs of these areas are shown in Figures 4-17 and 4-18. In Figure 4-17, the A series of micrographs shows the interconnect at position A of Figure 4-16B. It can be seen from these photographs that both the grain size and density of the material increased as the distance increased from the bond site. Figure 4-18 shows the same progression at area B of Figure 4-16B. In this series of micrographs, the density does not appear to change; however, the grain size increases dramatically as distance increases from the anode. Additional studies by EDS have indicated that the inhibition of grain growth near the anode is due to ZrO_2 diffusing out of the anode and into the interconnect.

A similar study was carried out for CE/I and C/I bilayers bonded to CE corrugations. Figure 4-19 shows the SEM micrographs of the fracture surface of a C/I bilayer bonded to a CE corrugation. The bonding of the C/I to the CE corrugation looks very good. Figures 4-20 and 4-21 show the change in microstructure at the points indicated A and B in Figure 4-19B. Figure 4-20 shows the fracture surfaces of the interconnect at increasing distances below the bond site. This series of micrographs shows a dramatic change in grain size and density as the distance from the bond increases. Figure 4-21 shows the fracture surfaces of the interconnect at various distances from the cathode layer, at position B. In this series of micrographs there was little or no change observed in the microstructure or density of the interconnect.

Polished cross sections of the bonded materials were evaluated to determine porosity levels in the interconnect. Figure 4-22 shows an optical micrograph of a polished cross section of an A/I bilayer bonded to an A corrugation. The interconnect in

As-Sintered

Fracture

F-64415

Figure 4-15 As-Sintered and Fracture Surfaces of Lanthanum Chromite Sintered 1400°C for 1 hr. Powder from Lot 0260, Previously Made into Tape in As-Received State

F-65875

Figure 4-16. SEM Micrographs Showing Fracture Surface of A/I Bilayer Bonded to A Corrugation

F-65884

Figure 4-17. SEM Micrographs of Interconnect at Increasing Distance from A/I:A Bond

F-65887

Figure 4-18. SEM Micrographs of Interconnect at Increasing Distance from Anode

F-65877

Figure 4-19. SEM Micrographs Showing Fracture Surface of C/E Bilayer Bonded to CE Corrugation

F-65886

Figure 4-20. SEM Micrographs of Fracture Surfaces Showing Changes in the Interconnect at Various Distance from the C/I:CE Bond

F-45585

**Figure 4-21. SEM Micrographs of Fracture Surfaces Showing Interconnect
Microstructure at Various Distances from Cathode**

F-65878 -A

Figure 4-22. Optical Micrograph of a Polished Cross Section of A/I Bonded to an Anode Corrugation Showing Porosity (Gray Area) by Bond Region

the local area of the bond site is porous and very dense in areas not bonded to the anode corrugation. The incomplete densification of the interconnect is due to the liquid chromate phases being drawn out of the interconnect by the porous anode. Figure 4-23 shows high magnification optical micrographs of C/I and CE/I bilayers bonded to CE corrugations. In Figure 4-23A, CE/I bonded to CE, the interconnect has a layer of porosity adjacent to the CE layer. Also, the porosity in the interconnect appears to be uniform across the thickness of the interconnect. In Figure 4-23B, C/I bonded to CE, there is a larger amount of porosity adjacent to the bond site which decreases rapidly, corresponding to the micrographs shown in Figure 4-20. From the SEM and optical micrographs, it appears that the interconnect densifies better when it is adjacent to unmodified cathode material. The cracks observed in the samples resulted from the mounting and polishing steps.

F-65880

Figure 4-23. Optical Micrographs of Polished Cross Sections of (A) CE/I on CE and (B) C/E on CE Showing Porosity in Interconnect

The work with the C/I and CE/I bilayers was extended to trilayers. Two types of trilayer were fabricated, one being A/I/CE and the other an A/I/C. Both tapes were bonded to CE corrugations and sintered. The optical micrographs of the polished cross sections, shown in Figure 4-24, verify that the trilayer fabricated with an unmodified cathode layer (C) densifies much better than one with the modified cathode (CE). Again, the cracks observed in the polished samples resulted from the mounting and polishing of the sample.

Sintering studies were carried out to determine if the bilayer and trilayer could be bonded to single-cell modules and sintered successfully. Modules prepared with baseline materials were obtained and bonded to A/I, C/I, or A/I/C tapes on one side of the module. Samples were sintered at 1400° and 1350°C for 1 hr. In most cases when modules bonded with an A/I flat plate were sintered, they came out flat and crack-free. However, when modules were sintered with C/I flat plates, the modules fractured across the CE corrugation. In the case of an A/I/C trilayer flat plate bonded to the anode side of the module, the module showed warping towards the CE corrugation. When the trilayer was bonded to the CE corrugation, the sintered module fractured across the CE corrugation.

The work thus far was carried out using interconnect tapes with a solids loading of 50-vol percent. Interconnects with a lower solids loading were investigated in an attempt to reduce the observed warping and fracture when the bilayer and trilayers were bonded to the modules. Thus, the above mentioned studies were repeated using an interconnect tape fabricated with a 47-vol% solids loading. The results, however, showed no improvement.

In other experiments the main variable evaluated was the thickness ratio of the anode or cathode and interconnect layers. Bilayers were fabricated with decreasing electrode-to-interconnect thickness ratio, i.e., the electrode thickness decreased (interconnect thickness increased) while the overall thickness of the tape remained constant (about 10 to 11 mils or 255 to 280 μ). Figure 4-25 shows the progression of decreasing anode thickness and its effect on the densification of the interconnect in the A/I bilayer. It was observed that when the anode thickness was less than 15 μ both the anode and interconnect became fully dense when sintered at 1400°C for 1 hour. Figure 4-26 shows the same progression for CE/I bilayers. Again, both the CE and interconnect became fully dense when the CE thickness was less than 15 μ .

It appears that in these thin anode and cathode layers, the electrode pore volume fills with chromate liquid phases from the interconnect during firing and densifies, thus allowing the interconnect to also fully densify. In the thicker electrode layers, however, the pore volume greatly exceeds the volume of liquid generated and acts as a sink for the liquid, preventing both layers from densifying.

Trilayers were fabricated with thin anode and cathode layers. The A/I/CE trilayers were sintered at 1400°C for 1 hour. Figure 4-27 shows a fracture surface of such a trilayer. Several distinct features were observed for the sintered trilayers: (1) the interconnect is fully dense, (2) the anode cannot be visually distinguished from the interconnect, and (3) the CE/I interface is slightly porous and has a finer grain size.

F-65879

Figure 4-24. Micrographs of A/I/CE and A/I/C Bonded to CE Corrugations

F-66166

Figure 4-25. SEM Photographs of Anode/Interconnect Bilayers Showing Influence of Layer Thickness on Interconnect Densification

F-66167

Figure 4-26. SEM Photographs of Cathode/Interconnect Bilayer Showing Influence of Layer Thickness on Interconnect Densification

Elemental line scans (40 equidistant points) were carried out on polished cross sections of the A/I/CE trilayer to determine the diffusion profiles of the various elements. A typical scan of Ca, Co, La, and Cr is shown in Figure 4-28. From this analysis, cobalt was observed to be uniformly distributed across all three layers as was chromium in the anode and interconnect. There was a higher concentration of calcium in the cathode than anywhere else. X-ray diffraction was used to identify compounds present in the anode layer. Figure 4-29 shows the diffraction pattern taken from the anode surface. This figure shows that the phases present are LaCrO_3 and CaZrO_3 and trace amounts of NiO and ZrO_2 .

4.1.2.5 Shrinkage and Thermal Expansion Studies

The main thrust of this effort was to measure the shrinkage profile of toughened electrode compositions. The objective was to determine the effect of the toughening additive (alumina) on sintering shrinkage profiles of the anode and intermediate layers.

Figures 4-30 and 4-31 compare the sintering shrinkages of toughened anode (Figure 4-30) and CE (Figure 4-31) with their baseline counterparts. As can be seen from Figures 4-30 and 4-31, the addition of alumina causes some differences in anode sintering behavior, whereas little change in total shrinkage occurs in the modified intermediate. Since the effect of alumina addition on shrinkage is minimal in the CE, the incorporation of the toughened intermediate into single-cell and stack fabrication is expected to have an insignificant effect on stack structural integrity. This has been shown to be the case, as shown earlier.

Thermal contraction and expansion coefficient (TCC and TEC) measurements were carried out on bonding formulations and interconnect materials. Measurement procedures and data for the bonding formulations are presented in Table 4-12. The TCC of two interconnect batches (I04242-1 and I05222-1) was measured. Measurement procedures for TCC involved heating tape samples to 1400°C in the dilatometer and measuring contraction upon cooling to 100°C . TEC was measured on these samples by reheating to approximately 1300°C . A previously sintered, thin plate sample of I10101-1 was also measured for TEC. Table 4-13 contains the TCC and TEC data for the interconnect batches. Currently, multicell stack fabrication uses I10101-1 for the interconnect layer; however, the TEC data show that I04242-1 and I05222-1 could replace I10101-1 without affecting stack thermal expansion characteristics.

20320-1

B-27001

Figure 4-28. Concentration Profile of Ca, Co, La, and Cr Across A/I/CE Trilayer

Figure 4-29. XRD Pattern of Anode in A/I/CE Trilayer

B-27002

AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

2 of 2

Figure 4-30. Sintering Shrinkage Profiles of Baseline and Toughened Anodes (A)

Figure 4-31. Sintering Shrinkage Profiles of Baseline and Toughened Cathode/Electrolyte Intermediates (CE)

TABLE 4-13		
THERMAL CONTRACTION AND EXPANSION COEFFICIENTS FOR INTERCONNECT BATCHES		
Batch Number	Contraction, $\times 10^{-6}/^{\circ}\text{C}$	Expansion, $\times 10^{-6}/^{\circ}\text{C}$
I10101-1	NA	14.3
I04242-1	14.2	14.3
I05222-1	13.8	14.1
Note: Range for thermal contraction coefficient: 1290°C to 94°C. Range for thermal expansion coefficient: 95°C to 1288°C. Measurement error approximately 3.5 percent.		

4.2 DEFECT ANALYSIS

4.2.1 Objective

The objective of this task is to analyze defects in MSOFC cells and stacks and correlate identified defects to material and fabrication parameters. Correlation can be used to suggest fabrication modifications to minimize defects.

4.2.2 Analysis

Defect analysis during this reporting period was focused on single-cell module characterization using the simplified defect classification system and on characterization of module flatness. Based on the frequency of observed defects, a simplified classification system has been developed and is shown in Table 4-14.

TABLE 4-14	
SIMPLIFIED DEFECT CATEGORIES FOR SINGLE-CELL MODULES	
Category	Description
I	No defect found
II	Defect (hairline crack) barely identifiable at 70X and not found within electrolyte layer
III	Defect (hairline crack) easily identifiable at 70X and not found within electrolyte layer
IV	Defect (hairline crack) found in and through electrolyte layer
V	Macroscopic crack or fracture

Defect examination of 100 1-in. modules showed the following distribution:

<u>Defect Type</u>	<u>Number of Modules</u>
Type I	57
Type II	7
Type III	17
Type IV	8
Type V	11
Total	100

Flatness characterization was performed on fabricated modules. A number of module samples containing different CE baseline batches were examined. Optical comparator measurement results, summarized in Table 9-15 (made on 1-in. footprint single-cell modules using either CE08291-1 or CE03122-1 baseline CE layers), revealed no difference in sample flatness.

TABLE 4-15		
COMPARATOR MEASUREMENTS ON SINGLE-CELL MODULES USING DIFFERENT CE LAYERS		
CE Layer Contained	Average Gap, in.	Standard Deviation, in.
CE08291-1	0.0037	0.0026
CE03122-1	0.0032	0.0023

An effort was also initiated to correlate the observed defect frequency to the baseline batch combinations used in single-cell modules.

A preliminary analysis has shown that the batch combinations might affect the resulting defect frequency. Figure 9-32 exemplifies this for 2.5-in. green footprint modules. (The letters along the bottom of the figure denote the particular batch used for that layer within the module.) Figure 9-32 shows how changing module composition by one batch can affect the frequency of the type of defect observed. The reasons for this effect are not known at this time because of complications caused by other factors such as processing parameters. Further compilation and analysis are expected to lead to a better understanding of this observation on defect frequency.

4.2.3 References

1. AlliedSignal, unpublished results.
2. O. Yamamoto, *et al.* "Electrical and Mechanical Properties of Zirconia-Alumina Composite Electrolyte," in *Proceedings of the Second International Symposium on Solid Oxide Fuel Cells*, Commission of the European Communities, 1991, pp. 437-444.

GREEN PLAN AREA: 2.5" x 2.5"
THRU ST1768/EE228

B-27004

Figure 4-32. Defect Frequency for Single-Cell Modules Fabricated with Different Batches

5. TESTING ON COAL GAS

5.1 PERFORMANCE TESTING

5.1.1 Objective

The objective of this task is to assess the electrochemical performance characteristics of MSOFC cells and stacks under conditions of pressure, temperature, gas composition, gas flow rate, and current density. Test results will be used to provide inputs to support materials, fabrication, and quality improvements.

5.1.2 Single-Cell Testing

The testing of single cells concentrated on three efforts: (1) assessing the electrochemical performance and life of single cells fabricated with different thickness ratios and batch compositions, (2) evaluating better methods to apply current collectors to single-cells, and (3) evaluating a removable seal for single cell testing.

During this reporting period, performance testing of a number of single cells was carried out. The tested cells were fabricated with different layer thickness ratios and batch compositions. The testing mainly included determination of open-circuit voltage (OCV) and area-specific resistance (ASR), controlled current polarization experiments, and life tests. Performance data were typically obtained with humidified hydrogen as fuel and air as oxidant. The schematic diagram of the single-cell test setup is shown in Figure 5-1.

- Cell ED065-8—Single-cell ED065-8 was fabricated with baseline anode and electrolyte layers and an Al_2O_3 -toughened cathode-electrolyte layer, using a 2:1:1 (A:E:CE thickness ratio) construction. The initial performance curve for ED065-8 is shown in Figure 5-2. The OCV was stable at 1.01 v. The initial ASR was 1.2 ohm-cm². This ASR is slightly higher than the typical value of 0.7 to 1.0 ohm-cm² obtained for strictly baseline 2:1:1 single cells.
- Cell ED065-7—This cell contained baseline A, baseline E, and alumina-modified CE. The cell construction was a 2:1:1 layer thickness ratio. The cell polarization curve is shown in Figure 5-3. The observed open circuit voltage (OCV) under those conditions was 1.046 v, close to the theoretical value of 1.055 v. The area specific resistance (ASR) of the cell calculated from the slope of the polarization curve was about 1 ohm-cm². Based on this result, it appears that the electrochemical performance of alumina-modified CE is comparable to that of baseline CE.

The cell was operated under 250 ma/cm² load for about 170 hours. The operation was inadvertently terminated due to brief power loss in the laboratory test area. The initial cell voltage under the load was 0.69 v and the final cell voltage was 0.53 v. During the load operation period, the OCV decreased about 60 mv. After testing, visual examination of the cell showed debonding or dewetting of the seal material on the cathode surface. This might allow

Figure 5-1. MSOFC Single-cell Test Apparatus

Figure 5-2. Polarization Curve of Cell ED065-06,
Temperature = 1000°C, Fuel = 97% H₂/3% H₂O, Oxidant = Air

Figure 5-3. Polarization Curve of Cell ED065-07
Temperature = 1000°C, Fuel = 97% H₂/3% H₂O, Oxidant = Air

small gas cross leakage in the cell, causing performance degradation during the life test.

- Cell ED076-12—This cell was a baseline single cell of 2:1:1 construction. The initial OCV was 1.02 v and the ASR of the cell was 0.9 ohm-cm² at 1000°C. This ASR value was consistent with the performance expected for baseline cells. The cell was then operated under 250 ma/cm² load. The cell voltage under those load conditions was 0.78 v. The voltage degraded slowly over time. After 88 hr of operation, the cell voltage under load was 0.57 v and the OCV was 0.85 v. Increasing the hydrogen flow rate significantly reduced the voltage, indicating a possible gas cross-leakage. The test was terminated after 90 hr of operation. A post-test analysis confirmed there was cross-leakage through the sealing cement.
- Cell ED040-08—This cell was also a baseline cell of 2:1:1 construction. The initial OCV was 1.05 v and the ASR of the cell (obtained from the cell polarization curve) was 0.8 ohm-cm². A long-term load test (250 ma/cm²) was performed on the cell. The results are summarized below.

<u>Time, hr</u>	<u>Cell Voltage, v</u>	<u>Open Circuit Voltage, v</u>
0	0.85	1.05
64	0.79	0.99
138	0.76	0.97
165	0.75	0.96
264	0.68	0.95
310	0.66	0.94

This long-term test was terminated after 310 hr. The post-test analysis indicated there was a small leak in the seal material. This explained the slow degradation of the OCV and cell voltage with time.

Since the present platinum paste method is unreliable and time-consuming, two alternate methods to attach current collectors were evaluated. Both methods involved applying current collectors to single cells using the same materials utilized in multicell stack bonding. The first method involved dissolving anode and cathode bonding tapes in alcohol to form a slurry. The slurry of each electrode material was then used to apply current collectors to the appropriate electrode surfaces of single cells. Single cells ED045-26, ED040-45 and ED040-36 were prepared in the manner discussed above and performance tests were conducted on each cell. Each of the cells was fabricated from baseline materials and constructed with an A:E:CE layer thickness ratio of 2:1:1. The cells were heated to 1000°C under helium before testing commenced. Performance tests were conducted at 1000°C with 97 percent H₂/3 percent H₂O as fuel, and air as oxidant. The test results are summarized below:

- ED045-26—During initial performance testing, severe voltage instabilities occurred at a current of 500 ma. The sample was allowed to stabilize for 48 hr, and a performance test was performed without voltage instabilities. The performance curve for ED045-26 is presented in Figure 5-4. The ASR obtained was 0.96 ohm-cm². The OCV was stable at 1.05 v.
- ED040-45—During performance testing, severe voltage instabilities were experienced at a current of 50 ma. The polarity was reversed at 400 ma for 20 sec in an attempt to improve performance. However, voltage instabilities were encountered at 100 ma. The OCV was stable at 1.02 v.
- ED040-36—Voltage instabilities occurred at 50 ma during performance testing. The voltage instability was overcome by performing an electrolysis at 800 ma for approximately 5 min. Figure 5-5 shows the polarization curve generated after reverse polarization. The resulting ASR was 1.4 ohm-cm². The OCV was stable at 0.98 v.

An additional method was evaluated to attach current collectors to cells which involved adding platinum powder to the slurry mixtures of each of the electrode materials. The slurry/Pt powder was mixed until a homogeneous mixture resulted. Current

Figure 5-4. Performance Curve of Cell ED045-26
 T = 1000°C, Fuel = 98% H₂/3% H₂O, Oxidant = Air

Figure 5-5. Performance Curve of Cell ED040-36 After Electrolysis at 0.8 amp for 5 min: T = 1000°C, Fuel = 97% H₂/3% H₂O, Oxidant = Air

collectors were attached to the electrode surfaces of the single-cell ED040-35 using the slurry/Pt mixture. Single-cell ED040-35 was prepared using this method and a performance test was conducted. Performance testing was performed with the conditions mentioned earlier. The results are presented below.

- ED040-35—Voltage instabilities were encountered at 400 ma during performance testing. The sample was allowed to stabilize overnight under H₂; however, voltage instabilities still persisted at 400 ma. The OCV was stable at 1.015 v.

One possible reason for the voltage instabilities observed during performance testing appears to be a poor contact between the platinum screen current collector and the electrode surface. Therefore, the present current collector application method continues to be used for single-cell testing.

Platinum screen current collectors are applied to single-cell samples using the standard platinum paste method. However, it was determined that increasing the metallizing temperature (from 800° to 900°C) minimizes the problems of current collector detachment encountered in the past.

FiberFrax LDS moldable insulation caulk was evaluated as a candidate to provide a removable (noncement) material for sealing single-cell discs for performance testing.

- ED040-4—This single cell was prepared for testing and applied to the test rig using LDS moldable caulk as a sealant. The initial OCV obtained for FD040-4 (with 97 percent H₂/3 percent H₂O as fuel, and air as oxidant) was 0.85 v. This OCV is lower than the typical value of 1.05 to 1.07 v obtained for single cells. A performance test was not performed due to a slow degradation of the OCV over time, indicating the presence of a significant leak. Upon observation of FD040-4 after cooling to room temperature, large gaps between the LDS moldable material and the single cell were observed.

5.1.3 Stack Testing

During this reporting period, a number of single-cell and multicell stacks were tested. The manifold and stack test setups are schematically shown in Figures 5-6 and 5-7. Results for each stack are discussed below.

- EB023-02—Single-cell stack EB023-02 was performance tested and then held under an endurance test for nearly 200 hr. Open-circuit voltage and area-specific resistance were checked on a regular basis. Performance for the stack is shown in Figure 5-8. As can be seen, OCV's were relatively stable, while ASR gradually increased (higher resistances) over a period of days ranging from 1.7 to 2.4 ohm-cm², with the exception of the first day under test. It is not fully understood why the initial curve for day 1 is lower than the following days. It is speculated that the nickel in the anode was still being reduced, but this would be difficult to verify at operating conditions. The curves generated for Figure 5-8 were all taken with 20 percent H₂/80 percent He (humidified), and air at 1000°C. Stack EB023-02 was tested with a

A-97897

Figure 5-6. Gas Manifolding of MSOFC Stacks

Figure 5-7. Illustration of Stack Preparation

Figure 5-8. Performance of Single-Cell Stack EB023-02

variety of fuel concentrations and humidities, to determine their effect on performance. By running the stack without humidity, and 20 percent H₂ /80 percent He, an OCV of 0.965 was obtained.

- EG196-04—Two-cell stack EG196-04 performed much more poorly than expected due to a manifold leak, which was confirmed by a post-test analysis.
- EG259-02—In an attempt to eliminate external variables during performance testing, an alternate manifolding procedure was utilized for the testing of two-cell stack EG259-02. The alterations involved prefiring a majority of the manifold components using Aremco 516 zirconia-based cement before the stack was inserted into the manifold. The stack was then inserted into the manifold and sealed using Aremco 571 magnesia-based cement. The 516 cement was not used to seal the stack in the manifold since it was determined that it may induce cracks in the stack as a result of expansion during curing. The stack's OCV was 1.527 v, and the ASR was 15.94 ohm-cm² (7.97 ohm-cm² per stack).
- EH15-1—The performance of this two-cell stack was tested with humidified hydrogen and air. The stack showed an OCV of 1.93 v. The stack ASR was extremely poor.
- EH15-2—EH15-2 was a two-cell stack. The stack performed poorly and showed an OCV of 1.80 v, compared with the theoretical value of 2.11 v.
- EE309-02—EE309-02 was a single-cell stack. Under the conditions of hydrogen fuel and air oxidant at 1000°C, an excellent OCV of 1.01 v was achieved, but the ASR was poor.
- EE355-4—Two-cell stack EE355-4 had an initial OCV of 1.74 v and an area-specific resistance (ASR) of 1.0 ohm-cm² per cell. The polarization curve for stack EE355-4 is shown in Figure 5-9.
- EE382-02—The performance of this two-cell stack was tested with hydrogen and air at 1000°C. The initial OCV was 1.75 v and the ASR was 1.4 ohm-cm² per cell. The polarization curve for two-cell stack EE382-02 is presented in Figure 5-10.
- EE377-1—EE377-1 was a four-cell stack which had an initial OCV of 3.61 v and an ASR of 2.7 ohm-cm² per cell. Figure 5-11 shows the polarization curve for EE377-1.
- EE343-02—A single-cell stack, EE343-02, was manifolded and tested using the new glass sealant material. The stack showed a maximum OCV of 0.99 v with an ASR of 2.5 ohm-cm². Figure 5-12 shows the polarization curve for stack EE343-02.
- EE332-01—EE332-01, a duplicate of stack EE343-02, was manifolded for testing with Aremco 516 cement in an effort to ascertain the effectiveness of

Figure 5-9. Polarization Curve for Stack EE355-4

Figure 5-10. Polarization Curve for Stack EE382-02

Figure 5-11. Polarization Curve for Stack EE377-1

Figure 5-12. Polarization Curve for Stack EE343-02

the glass sealant. The polarization curve of EE332-01 is shown in Figure 5-13. The observed OCV was 0.99 v. The ASR of the stack was 3.0 ohm-cm². These results indicate that the glass sealant material possibly overcame stress-induced fracturing of the second-step bonds, leading to more robust, less resistive electron paths.

Figure 5-13. Polarization Curve for Stack EE332-01

- EE344-03**—The polarization curve for two-cell stack EE344-03 is shown in Figure 5-14. The observed maximum OCV was 1.80 v. The stack showed an ASR of 2.5 ohm-cm² per cell. Four additional electrochemical performance curves were generated for EE344-03 at 800°, 900°, 1000°, and 1050°C. The results are shown in Figure 5-15. As expected, the OCV degraded slightly with increasing temperature and the ASR decreased with increasing temperature. Stack EE344-03 was cooled to room temperature and heated back to 1000°C to evaluate its response to thermal cycling. The OCV recovered successfully, however the ASR degraded to 3.4 ohm-cm² per cell, as shown in Figure 5-16. A life test was performed on the stack. Stack EE344-03 was tested with an applied load of 200 ma for approximately 600 hr. The initial stack voltage at a 200-ma load was 1.28 v. The stack voltage showed an improvement to 1.43 v over time. The polarization curve after 600 hr of life testing is shown in Figure 5-17. The ASR of the stack initially was 2.5 ohm-cm². After 600 hr of operation, the ASR of stack EE344-03 improved to 2.15 ohm-cm².

Figure 5-14. Polarization Curve for Two-cell Stack EE344-03

Figure 5-15. Polarization Curves for Stack EE344-03 as a Function of Temperature

Figure 5-16. Performance of EE344-03 After One Thermal Cycle

Figure 5-17. Performance of EE344-03 After 600 Hr

5.1.4 Posttest Analysis

Posttest analysis was performed on tested stacks. The analysis mainly included visual inspection and optical microscopic examination of cross sections of manifolded stacks.

- Stack EG259-02: This stack was a two-cell stack fabricated by bonding two electrode-covered modules to an interconnect. The stack had some minor cracks in the anode and cathode layers. Most of these cracks may have resulted from the mounting and sectioning process. The CE/I bonds appear good, with a large number of contact points between the corrugations and the interconnect layer. The A/I bonds show cracking and separation away from both the anode corrugations and the interconnect flat plate. However, this may just be in the areas observed since this stack showed reasonable performance.

The major defect observed in the stack is that the well through which the current collector exits the manifold was not sealed on the anode side of the stack. In fact, two thirds of the length of the stack were exposed to air, which allowed the fuel to leak from the stack during testing. It is believed that the major part of the performance losses of this stack during testing is due to the incomplete seal around the current collector on the anode side of the stack.

- Stack EH15-1: This was a two-cell stack fabricated by bonding two single-cell stacks together with an interconnect. The anode of the stack was observed to be partially oxidized during cooling. This allowed cracks in the anode prior to sectioning to be discriminated from those resulting from manifolding or processing. There were several cracks observed in the anode corrugates. Cracks were also observed in the A/E/CE trilayer. These cracks could be caused by mounting or cutting the stack.

The stack was sectioned perpendicular to the anode and cathode corrugates and at 45° to the corrugates. In all cross sections, the bond materials did not make complete contact to provide a pathway for current flow. The poor performance of this two-cell stack appeared to be due to the poor bonding of the individual stack to the interconnect. The exact cause for this poor bonding cannot be determined from this post-test analysis. Possible causes include cycling of the stack during current collector application and manifolding.

- Stack EE316-01—The stack was a two-cell stack made by bonding two single-cell modules. The stack was manifolded with Alfi'ax (Carborundum Co.), an alumina based cement, instead of the zirconia based Aremco 516 currently in use. The objective of this post-test analysis was to determine possible causes for the poor performance of this stack.

No cracks could be seen on the external surfaces of the manifold or in the cement. Upon sectioning the manifolded stack, some air bubbles (pockets) were observed in the cement. The number of air pockets was much less than normally observed when the Aremco 516 is used. The cement appeared to bond well to the stack and seal off the current collectors from the air.

The stack was sectioned perpendicular to the anode and cathode cover plates and at 45 deg to the corrugates. In all sections, the bond between the intermediate corrugates and the cover plate made good contact. The anode bond, however, only made contact between the anode corrugates and the cover plate at about 30 to 40 percent of the bond sites observed. The bonds toward the edge of the cell did not appear to make any contact between the cover plate and the corrugations. The delamination or fracture of the anode bond material occurred near the anode cover plate. The anode corrugates also showed distortion from their sinusoidal shape to a square wave shape. This distortion can be related to the processing of the tape and the constraint weight used during sintering.

From this posttest analysis, the reasons for the poor performance of this stack cannot be determined.

- Stack EE309-02—The stack was a single-cell stack made by bonding a single-cell module with anode and cathode cover plates. The stack was manifolded with the Aremco 516 cement.

The stack was sectioned perpendicular to the anode and cathode cover plates at 45 deg to the corrugates. In all sections observed the bond between the intermediate corrugates and the cover plate made good contact.

The anode bond made contact between the anode corrugates and the cover plate in about 30 to 40 percent of the bond sites. The bond material at the bond site was relatively thick and contained some very large cracks. The delamination or fracture occurred near the anode cover plate. There were some cracks observed in the anode and cathode corrugation and cover plates and in the trilayer, but not severe enough to prevent the stack from operating.

The analysis did not identify any cracking or delamination that could explain the poor performance of this stack. The reasons for the observed performance of the stack cannot be determined from this post-test analysis.

- Stack EE305-01—Stack EE305-01 was a single-cell stack made by bonding a single-cell module with anode and cathode cover plates. Aremco 516 cement was used in manifold sealing.

The anode corrugates showed good bonding to the anode cover plate. As noted in the previous post-test analysis, the anode bond was relatively thick

and had some air pockets and cracks in it. There were some cracks in the anode corrugates and cover plate.

The A/E/CE trilayer showed several significant cracks in the trilayer region. Larger cracks filled with epoxy were observed in all cross sections, indicating that the cracks existed before the stack was mounted.

The CE corrugation bonded with the interconnect cover plate except near the edges of the cell. The last three to four corrugates near the edge did not bond with the cover plate. The bond material appeared to be pulled away from the corrugation. There were some cracks observed in both the interconnect flat plate and the cathode corrugations.

It appears that the poor performance of this stack was due to the cracks in the A/E/CE trilayer. The number and degree of these cracks were more severe than in the last several stack tests.

- Stack EE332-01—This stack was a single-cell stack made by bonding a single-cell module with anode and cathode cover plates. This stack was manifolded with Aremco 516 cement.

The stack was sectioned perpendicular to the anode and cathode cover plates at 45 deg to the corrugates. The bond between the intermediate corrugates and the cover plate appeared to make good contact and was intact in all sections observed.

The anode bond made good contact between the anode corrugates and the anode cover plate. Only one or two of the bonds were fractured, a significant improvement over previous stacks analyzed. The anode bond was thinner than those used in previous stacks. The delamination or fracture occurred near the anode cover plate.

There were some cracks observed in the anode and cathode corrugation and the A/E/CE trilayer; however, they were not severe.

From this analysis, the improved performance of this stack is believed to be due to the improvement of the anode bonds. The improvement of the bonds may be related to technique and the use of less (e.g., thinner tapes) material to bond the corrugations to the flat plates.

- Stack EE303-02—The stack was a single-cell stack made by bonding a single-cell module with anode and cathode cover plates. The manifold of this stack was sealed using Corning glass.

When the manifold was placed under vacuum to infiltrate the fuel cell with polymer, air was observed to leak from the manifold from the sidebars. The largest leak was observed around the fuel inlet.

The stack was sectioned perpendicular to the anode and cathode cover plates at 45 deg to the corrugates. In all sections, the bonds appeared to make good contact between the corrugates and the cover plates. Only one or two of the anode bonds were separated from the anode cover plate.

There was little damage to the stack from the new glass sealant. Some reactions between the glass and the electrodes were observed on the edge of the stack. In the case of the anode where the glass was in contact with the stack, the anode did not reduce. Portions of the top cover plate, several hundred microns in length, around the edges of the stack did not reduce during the testing of this stack.

There were some cracks observed in the anode and cathode corrugation and the A/E/CE trilayer. There were several severe cracks in the A/E/CE trilayer. However, they may have occurred on cooling, resulting from the new sealing material. The new glass sealing material did not seal the manifold completely. This may be overcome by applying more glass to the manifold. The glass appeared to be relatively inert, having little effect on the fuel cell and did not appear to lead to any unusual damage upon cooling.

6. QUALITY DEVELOPMENT

6.1 EVALUATION OF NONDESTRUCTIVE EVALUATION (NDE) METHODS

6.1.1 Objectives

The objectives of this subtask are to: (1) evaluate promising NDE methods that can be used to improve the yield of reliable ceramics for MSOFC's during processing and in final fabricated parts, and (2) recommend NDE methods best suited to ensure the quality of commercial-scale fabricated MSOFC's.

6.1.2 Results

This subtask is complete. A topical report entitled *Nondestructive Characterization Methods for Monolithic Solid Oxide Fuel Cells* will be issued. An abstract of the report and the recommendations are given below.

6.1.2.1 Abstract

Monolithic solid oxide fuel cells (MSOFC's) represent a potential breakthrough in fuel cell technology, provided that reliable fabrication methods can be developed. Fabrication difficulties arise in several steps of the processing: first, the fabrication of uniform, thin (305 μm), single-layer and trilayer green tapes (The trilayer tapes of anode/electrolyte/cathode and anode/interconnect/cathode must have similar coefficients of thermal expansion to sinter uniformly and to have the necessary electrochemical properties.); second, the development of fuel and oxidant channels in which residual stresses are likely to develop in the tapes; third, the fabrication of a "complete" cell for which the bond quality between layers and the quality of the trilayers must be established; and last, attachment of fuel and oxidant manifolds and verification of seal integrity.

The purpose of this report is to assess nondestructive characterization methods that could be developed for application to laboratory, prototype, and full-scale MSOFC's.

6.1.2.2 Recommendations

NDE recommendations are summarized in Table 6-1, along with a priority ranking. The highest priority recommended is the development of NDE methods for as-calendered tapes, specifically the trilayer tapes. A high priority should also be given to development of acoustic emission tests to detect onset of cracking during sintering and to determine maximum outgassing of organics during debinding. Further, a high priority should be given to development of NDE methods for as-calendered single-layer tapes and Sr-doped LaMnO_3 and LaCrO_3 powders. Development of NMR and FTIR spectroscopy should be undertaken as NDE methods for as-blended material. This may require a higher priority should recyclable material be combined with new material. There is also a concern about the impact of thermal histories and the molecular structure of the polymers.

TABLE 6-1

SUMMARY OF POSSIBLE NDE METHODS

Process Step (for Material)	Starting Materials (powders) Sr-doped LaMnO_3 LaCrO_3	Blended Materials	Flat As-cast Green Tapes		Corrugated Green Tapes (Formed Channels)	Debinding	Sintering	Nonmanifolded Sintered Stack	Manifolded Sintered Stack
			Single Layer	Trilayer					
Defect types Material character	Powder characteristics	Uniformity of blend, surface chemistry	Thickness, density	Density, thickness, cracks	Residual stresses		Onset of cracking	Cracks in electrolyte or interconnect delaminations	Gas leakage
NDE methods suggested		^1H NMR spectroscopy	Acoustic microscopy (two-sided) Low-kv through-transmission X-ray Infrared imaging		FTIR, raman spectroscopy		Acoustic emission	Acoustic resonance, optical holography, optical borescopes	Gas pressure by H_2 leak detection
Priority	High	Medium	Medium	Medium	Medium	High	Highest	Medium	Low

Although not specifically noted here, if a bond material is used to bond single cells to interconnects, some form of NDE will be necessary to qualify these bonds. Sonic resonance methods have recently been developed for similar applications, and this should be pursued because of the relative inaccessibility of the surfaces for inspection.

6.2 STRESS ANALYSIS OF STACKS

6.2.1 Objective

The objective of this effort is to perform stress analysis on the MSOFC, to predict its behavior under different conditions (firing, operating, and off-normal conditions). From the stress calculations, critical stress areas will be defined. Model solutions will be used to reduce stresses in critical areas.

6.2.2 Discussion

A thin-electrolyte approach was evaluated via the cooldown stress model. Table 6-2 compares the stresses for various thin-electrolyte approaches vs the current baseline (2:1:1) and 1:5:1 A/E/CE geometries. A/E/CE anode and cathode stresses are greatly reduced in such an approach. The highest stresses were incurred in the corrugated cathode.

The current MSOFC finite-element stress model is being expanded to include the "heat up" portion of the firing cycle and multicell stack thermal processing. The heat-up modeling will include the effects of constraint weights, frictional effects, and heat-up temperature profile. The effect of mechanical "creep" in maintaining stack shape and relieving stress will be evaluated. The model will include the entire thermal processing cycle for a two-cell stack. Recommendations for improved designs, processes, and material properties will be provided.

Plans also call for modeling the effect of manifolding on stack integrity, as it is suspected that the stacks may be damaged as the result of the manifolding materials or processes.

6.3 QUALITY CONTROL OF SOURCE MATERIALS

6.3.1 Objective

The objective of this task is to evaluate the characteristics and quality of source materials for use in the fabrication of the MSOFC. Variations in material characteristics and their effect on MSOFC fabrication will be quantified, and the acceptable quality (material requirements) of source materials will be specified.

6.3.2 Evaluation of Lanthanum Chromite

SSC, Inc., a supplier of LaCrO_3 powders, has been carrying out an analysis to determine the stoichiometry of Ca, Co-doped lanthanum chromite (lot 147) supplied to AlliedSignal. Their analysis indicated that the powder had a 10 percent excess of lanthanum, which displaced calcium and led to the formation of excess calcium chromate

TABLE 6-2						
STRESS ANALYSIS RESULTS						
Factor	Thin Electrolytes				2:1:1	1:5:1
Trapezoid side ratio	0.2	0.2	0.2	0.2	0.2	0.2
Anode thickness	0.005	0.005	0.007	0.007	0.005	0.0014
Electrolyte thickness	0.0005	0.0002	0.0005	0.0002	0.0025	0.0072
Cathode thickness	0.005	0.005	0.003	0.005	0.0025	0.0014
Corrugation thickness	0.010	0.010	0.010	0.010	0.010	0.010
Corrugation height	0.050	0.050	0.050	0.050	0.050	0.050
Flat anode thickness	0.010	0.010	0.010	0.010	0.010	0.010
Flat cathode thickness	0.010	0.010	0.010	0.010	0.010	0.010
Location	Stress					
	Ksi	Ksi	Ksi	Ksi	Ksi	Ksi
Anode	15.6	15.3	12.9	12.8	18.1	24.8
Electrolyte	-25.1	-25.6	-29.9	-27.1	-25.0	-21.2
Cathode	9.2(-13.9)	9.1(-14.6)	7.5(-16.4)	8.0(-14.5)	13.3	12.5
Corrugated cathode	11.3	11.3	12.6	13.2	11.4	11.7
Corrugated anode	6.9(-12.2)	6.7(-11.7)	6.1(-10.5)	6.1(-12.4)	8.0(-14.5)	19.4(-20.7)

during sintering. Based on this analysis, a second lot of powder with 4 percent excess calcium was prepared.

Chromite powder with a composition of $\text{La}_{0.84}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ (A-site rich with 4 percent excess calcium) was received from SSC and fabricated into a tape. Samples were sintered at 1400°C and 1350°C for 1 hr. The samples sintered at 1400°C densified to 97.9 percent theoretical density (ThD), while those sintered at 1350°C densified to 97.7 percent ThD. Figure 6-1 shows SEM micrographs of two Ca,Co-doped lanthanum chromite compositions (stoichiometric and A-site rich) sintered at 1400°C for 1 hour. The composition of the material shown in Figure 6-1A is stoichiometric (A-site:B-site = 1) and the material has a density of 94 percent theoretical. Figure 6-1B is the SEM micrograph of a sample prepared with A-site rich material (A:B = 1.04) and sintered to 98.0 percent ThD. The A-site rich composition appeared to have more liquid phase during firing, resulting in higher densification.

Based on these results, a more detailed evaluation of Ca,Co-doped LaCrO_3 powders of various compositions was performed. The evaluation concentrated on the effects of varying Cr:Co and La:Ca ratios on the densification (and microstructure) of the double-doped material. The compositions evaluated were $\text{La}_{0.84}\text{Ca}_{0.2}\text{Cr}_{0.9\pm x}\text{Co}_{0.1}\text{O}_3$ (for varying Cr:Co ratios) and $\text{La}_{0.84\pm x}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ (for varying La:Ca ratios).

The effect of the Cr:Co ratio was evaluated in samples made with Ca,Co-doped LaCrO_3 powders (supplied by SSC, Inc.) of Cr:Co ratio varying from 9.2 (1.02) to 8.6 (1.08); the A:B (La:Cr) ratio is shown in parenthesis. As-received powders were batched, rolled into tapes, and sintered at 1300°C, 1350°C, and 1400°C for 1 hr in air. Sintered samples were then characterized for density and microstructure. The density was measured using the buoyancy in water technique. The microstructure was examined by scanning electron microscopy. The results of the density measurements are listed in Table 6-3.

TABLE 6-3				
DENSITY OF LANTHANUM CHROMITE SAMPLES FOR VARYING CR:CO RATIO				
Cr:Co Ratio	A:B Ratio	Sintering Temperature, °C		
		1300	1350	1400
8.6	1.08	*	*	*
8.8	1.06	*	92.0	92.8
9.0	1.04	*	93.7	97.9
9.2	1.02	*	92.9	96.8
*Unable to accurately measure density due to $\text{La}(\text{OH})_3$ formation on surface of lanthanum chromite during density measurement.

(a) $A/B = 1$

(b) $A/B = 1.04$

F-66162

Figure 6-1. Fracture Surfaces of Ca, Co-doped LaCrO_3 Sintered at 1400°C for 1 Hr

Figure 6-2 shows SEM micrographs of fracture surfaces of the sintered samples. As seen from the micrographs (Figure 6-2 A, D, G, and J), poor densification occurred in the samples sintered at 1300°C for 1 hr. The samples with a Cr:Co ratio of 8.6 (Figure 6-2 B and C) showed improved densification at higher sintering temperatures. On the other hand, when sintered at 1350° and 1400°C, the samples with a Cr:Co ratio of 9.0 and 9.2 (Figure 6-2 H, I, K, and L) showed nearly complete densification. From the above results, it appears that a sintering temperature greater than 1300°C is required to densify Ca,Co-doped LaCrO₃, and higher Cr:Co ratio improves the sinterability of the material. Higher Cr:Co ratio probably produces more chromium-containing liquid phases in the material during sintering, resulting in improved densification.

The effect of the La:Ca ratio was evaluated in samples made with powders of La:Ca ratio varying from 3.8 (0.96) to 4.2 (1.04); the A:B ratio is shown in parenthesis. Samples were sintered at 1350° and 1400°C for 1 hr in air and the density and microstructure of the sintered samples were evaluated. The density of the samples is listed in Table 6-4.

TABLE 6-4			
DENSITY OF LANTHANUM CHROMITE SAMPLES FOR VARYING LA:CA RATIO			
La:Ca Ratio	A:B Ratio	Sintering Temperature, °C	
		1350	1400
3.8	0.96	92.0	92.6
4.0	1.00	91.5	93.2
4.1	1.02	*	*
4.2	1.04	93.7	97.9
*The accuracy of the density values obtained for the samples was suspected; measurements are being redone.			

Figure 6-3 shows SEM micrographs of fracture surfaces of samples with an La:Ca ratio of 3.8, 4.0, and 4.1, sintered at 1350°C and 1400°C. The micrographs of the samples with a La:Ca ratio of 4.2 are shown in Figure 6-2, H and I. Figure 6-3 A to F show relatively no inherent differences in the microstructure of the samples, thus no changes in densification with these compositions. A comparison of Figure 6-3 A to F with Figure 6-2 H and I shows a dramatic increase in grain size of the samples having the La:Ca ratio of 4.2 and higher density. It appears that increasing the La:Ca ratio to 4.2 increases the density and grain size significantly. The reason for these increases may be due to a larger amount of transient liquid phases formed at that composition, resulting in grain growth and improved densification.

Figure 6-2. Micrographs of Fracture Surfaces of $\text{La}_{0.84}\text{Ca}_{0.2}\text{Cr}_x\text{Co}_{1-x}\text{O}_3$ for Different Cr:Co Ratios at 1300°C, 1350°C, and 1400°C for 1 Hr ((A-C) Cr:Co = 8.6, (D-F) Cr:Co = 8.8, (G-I) Cr:Co = 9.0, and (J-L) Cr:Co = 9.2)

1300°C

1350°C

1400°C

F-45000

Figure 6-2. (Continued)

Figure 6-3. SEM Micrographs of $\text{La}_x\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ Sintered at 1350°C and 1400°C with (A-B) $x = 0.76$, (C-D) $x 0.80$, and (E-F) $x 0.82$

DATE

FILMED

10/21/94

END