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**MONOLITHIC SOLID OXIDE FUEL CELL
TECHNOLOGY ADVANCEMENT FOR
COAL-BASED POWER GENERATION**

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SECTION 1

INTRODUCTION

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 January through March 1992.

The program is conducted by a team consisting of AiResearch Los Angeles Division of Allied-Signal Aerospace Company 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

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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 steam

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

SECTION 3
PROGRAM OVERVIEW

3. PROGRAM OVERVIEW

Figure 3-1 is a work breakdown structure (WBS) for the program, showing six major tasks and 25 subtasks. Solid line boxes indicate tasks in which significant results have been achieved. Dashed line boxes indicate tasks that have been started, but for which no reportable results are available. Unboxed tasks are those that have not yet been started.

The following paragraphs summarize the progress made on various tasks during this quarter.

3.1 STUDY OF INTERCONNECT/CATHODE INTERACTION (TASK 2.2)

TBD

3.2 STUDY OF LONG-TERM CATHODE STABILITY (TASK 2.3)

TBD

3.3 FABRICATION DEMONSTRATION (TASK 3.1)

Primary activities of the MSOFC fabrication effort this quarter focused on batch preparation and characterization, fabrication of single cells and multicell stacks, bonding studies, interconnect development, and shrinkage matching.

Two new batches of high solid loading anode batches were prepared, as well as a batch of alumina-modified CE, baseline batches of CE, and an alumina-rich anode batch. These batches were characterized in terms of diametrical shrinkage, weight loss, density, and theoretical density. Also prepared this quarter were two interconnect batches with as-received powder from two different suppliers and a CE batch made without pore former in a effort to control the pore volume of the cathode.

A study was initiated to define the most suitable building block for the two-step bonding process. The results of the experiments indicated that single cell stacks possessed the highest defect frequency while the single cell modules had the lowest.

Bonding development efforts concentrated on investigation of bonding formulation and procedures that reduce firing shrinkage and minimize cracking and delamination of bonding materials during second-stage firing.

Interconnect work this quarter centered on fabricating and processing A/I, CE/I and A/I/CE tapes. The main variable evaluated in this work was the thickness ratio of the layers. It was tentatively found that thinner anode and cathode layers allow the interconnect to achieve better densification.

3.4 DEFECT ANALYSIS (TASK 3.3)

Defect analysis efforts this quarter centered on characterization of the flatness of single cell modules and optical examination of cross sections of modules and optical examination of cross sections of modules and bonded single cell stacks. It was

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Figure 3-1. Work Breakdown Structure for MSOFC Technology Advancement for Coal-Based Power Generation Program

concluded that recent improvements in processing techniques have led to a 50 percent improvement in flatness of single cell modules.

3.5 TESTING ON COAL GAS (TASK 4)

One single (tri-layer) cell was tested this quarter, made of the alumina-modified CE. The cell showed very good performance, indicating that the electrochemical performance of the alumina-modified CE is comparable to that of the baseline CE. Two two-cell stacks and one single-cell stack were tested this quarter for electrochemical performance. Efforts have also been concentrated on improving materials and procedures for stack manifolding.

3.6 STACK PERFORMANCE MODELING (TASK 5.1)

The mathematical model of the fuel cell is complete. The model simulates the electrochemical, electrical, thermodynamic, and chemical equilibrium processes occurring in the cell.

3.7 EVALUATION OF NDE METHODS (TASK 6.1)

This subtask is essentially complete. A draft copy of the final topical report is currently being reviewed.

3.8 STRESS ANALYSIS OF STACKS (TASK 6.2)

The computer stress model of MSOFC stacks is currently being expanded to include the "heat-up" portion of the firing cycle.

3.9 QUALITY CONTROL OF SOURCE MATERIALS (TASK 6.3)

SSC, Inc. and Rhone Poulenc have been carrying out an analysis of lanthanum chromite powders to determine the effect of stoichiometry on densification.

SECTION 4

MATERIALS RESEARCH AND DEVELOPMENT (TASK 2)

4. MATERIALS RESEARCH AND DEVELOPMENT (TASK 2)

4.1 STUDY OF CATHODE/INTERCONNECT INTERACTION – TRI-LAYERS (TASK 2.2)

4.1.1 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. For this approach to be successful, the electrode layers (made from $\text{La}_{0.8}\text{Ca}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$) must remain porous during firing whereas the electrolyte must densify nearly completely, and the bonding between electrolyte and electrodes must be strong. To this point, electrolyte composites have been fabricated with dense electrolyte and porous electrodes, but bonding between the electrolyte and electrodes has been weak. During the past quarter, the bonding in electrolyte composites has been improved. The second approach is based on the idea that the interconnect does not densify in the four-material cell because the liquid that aids sintering migrates into the neighboring electrode layers before the onset of densification. It is thought that better densification would result if the sintering aid did not melt until after the onset of densification, because migration of the liquid phase into neighboring layers would thereby be limited. During the past quarter, the so-called “941” composition ($\text{Ca}_3\text{Cr}_2\text{O}_8$) has been tested as a sintering aid, because its melting point is near the onset of densification.

4.1.2 Results

4.1.2.1 Two-Material MSOFC

Bonding in electrolyte composites was improved by using a five-layer graded structure, rather than the three-layer structure used previously. Two different five-layer composites were made by co-casting, with the only difference being in the inner bond layers; the other layers are the same. In Composite No. 1, the bond layers contain 80% ZrO_2 /20%LC whereas the bond layers of Composite No. 2 contain 65% ZrO_2 /35%LC. The makeups of these composites are given below:

<u>Composite No. 1</u>	<u>Composite No. 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 No. 1 and No. 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 No. 3</u>	<u>Composite No. 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 4-1 shows micrographs of Composite No. 1 fired at 1400°C. Figure 4-1a shows the overall view of the composite, and Figures 4-1b and 4-1c show magnified views of the interfaces between the various layers. The large cracks seen in Figure 4-1a are thought to result from 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 4-2 shows similar views of Composite No. 1 fired at 1500°C. Bonding appears to be good, and because the polishing procedure was changed, no cracks are evident. Measurement of the electrochemical performance of these composites is in progress.

Figure 4-3 shows Composite No. 4 fired at 1400, 1500, and 1600°C. Composite No. 4 is expected to have the best bonding of the three-layer composites, because it contains the most ZrO₂ in the electrode layer, but a sharp boundary is evident between the 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.

4.1.2.2 Four-Material MSOFC

In the past quarter, "941" was tested as a sintering aid for Ca/Co-doped LaCrO₃. In this work, "941" was added to Ca/Co-doped LaCrO₃ deficient in calcium, so that a final composition of La_{0.70}Ca_{0.30}Cr_{0.90}Co_{0.10}O₃ was obtained after sintering/reaction. Formation of LaCrO₃ 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 LaCrO₃ 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

Figure 4-1a

Figure 4-1b

Figure 4-1c

Figure 4-1. Micrographs of Composite No. 1 fired at 1400°C showing improved bonding between electrolyte and electrodes. Figure 4-1a shows the overall composite, Figure 4-1b shows the interface between the electrolyte (left) and the bond layer containing 80% ZrO_2 (right), and Figure 4-1c shows the interface between the layer containing 80% ZrO_2 (left) and the electrode with 35% ZrO_2 (right).

Figure 4-2a

Figure 4-2b

Figure 4-2. Micrographs of Composite No. 1 fired at 1500°C. Figure 4-2a shows the overall composite, Figure 4-2b shows the interfaces between the electrolyte (left layer), bond layer with 80% ZrO_2 (middle layer), and electrode with 35% ZrO_2 (right layer).

Figure 4-3a

Figure 4-3b

Figure 4-3c

Figure 4-3. Micrographs of Composite No. 4 (40% ZrO_2 in electrodes) fired at 1400°C (Figure 4-3a), 1500°C (Figure 4-3b), and 1600°C (Figure 4-3c) showing a sharp boundary between electrolyte and electrodes.

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 slight Ca-excess that has been shown to densify alone but not in composite tapes. The results of this study are given in Table 4-1.

TABLE 4-1				
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)
$\text{La}_{0.79}\text{Ca}_{0.17}\text{Cr}_{0.90}\text{Co}_{0.11}\text{O}_3$	$1400^\circ\text{C}/1 \text{ hr.}$	0.89	0.00	2.65
"	"	0.89	0.05	3.97
"	$1020^\circ\text{C}/2 \text{ hr.}$ $1400^\circ\text{C}/1 \text{ hr.}$	0.89	0.00	2.69
"	"	0.89	0.05	3.88
"	$1500^\circ\text{C}/1 \text{ hr.}$	0.89	0.00	2.85
"	"	0.89	0.05	4.11
"				
$\text{La}_{0.90}\text{Ca}_{0.00}\text{Cr}_{0.90}\text{Co}_{0.13}\text{O}_3$	$1400^\circ\text{C}/1 \text{ hr.}$	0.78	0.00	3.21
"	"	0.78	0.10	3.98
"	$1500^\circ\text{C}/1 \text{ hr.}$	0.78	0.00	3.24
"	"	0.78	0.10	4.25
"				
$\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$	$1400^\circ\text{C}/1 \text{ hr.}$	1.00	0.00	6.1-6.2
"	"	0.95	0.05	5.21
"	"	0.90	0.10	4.57

Comparing the densities of Ca-deficient compositions with no "941" added, to the same compositions with "941" added, we see 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 $\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$ 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.

4.1.2.3 Future Work

Work in the two-material cell depends on the performance of the five-layer composites. If their performance is satisfactory, fabrication of small two-cell stacks will proceed. If performance is poor, consideration will be given to how the performance might be improved.

For the four-material cell, various amounts of "941" will be added to $\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$ in composite tapes. The tapes will be fired and examined to see if densification has improved.

4.2 LIQUID PHASE SINTERING OF $(\text{La,Ca})\text{CrO}_3$

4.2.1 Introduction

Recent work has focused on improving processing techniques to gain uniform green microstructures, in addition to compiling results on the low temperature reactions ($400^\circ\text{C} - 1300^\circ\text{C}$) 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 $50 \mu\text{m}$ 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 $0.1 \mu\text{m}$ 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.

It was sought 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 400-1300°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 (4-1) 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.

4.2.2 Experimental Procedure

4.2.2.1 Powder Processing

Powders were prepared based on the modified resin process proposed by Tai et al. [1]. 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.

4.2.2.2 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. Microanalysis of the milled char particles was performed on a scanning electron microscope and particle size was determined using a sedigraph-type particle size analyzer.

4.2.2.3 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.

4.2.2.4 Powder Classification and Consolidation

A powder classification and consolidation technique for lanthanum chromite was previously developed by Jang [2]. 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.

4.2.2.5 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.

4.2.2.6 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 , $20\% \leq \text{Ca} \leq 65\%$ where 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.

4.2.3 Results and Discussion

4.2.3.1 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 4-4 and 4-5) of the milled char indicate a particle size reduction from as large as 50 μm for "as is" powder to less than 2 μm after milling for eight hours. Figure 4-6 illustrates the particle size distribution of powders milled for eight hours and calcined at 550°C in Argon.

Figure 4-4. LaCrO_x Char Particles

4.2.3.2 LaCrO₄ Phase

Lanthanum chromate (LaCrO₄), is a low temperature phase which is stable below 650°C. This compound has two polymorphs, tetragonal 14₁/amd (141) and monoclinic, P2₁n (14). Monoclinic LaCrO₄ 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 4-2 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 LaCrO₄ lattice, forming a solid solution.

Figure 4-5. LaCrO_x Char Particles, Milled 8 Hours

Figure 4-6. Particle Size Distribution of $\text{La}_{0.59}\text{Ca}_{0.4}\text{CrO}_4$, Calcined $550^\circ\text{C}/8\text{Hr}/\text{Argon}$

TABLE 4-2	
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.

4.2.3.3 Powder Classification and Consolidation

Current efforts focus on optimizing the properties of the colloidal dispersion and the settling time for powder classification.

4.2.3.4 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 4-7 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 4-8 and 4-9 show the results of the reaction studies of various Ca-Cr-O compounds set on porous $\text{La}_u\text{Ca}_v\text{CrO}_3$ pellets.

Figure 4-7. DTA Melting and Freezing Peaks of $\text{Ca}_{1.2}\text{CrO}_4$ and $\text{La}_{0.59}\text{Ca}_{0.4}\text{CrO}_3$ Liquid-Phase

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 $\text{La}_u\text{Ca}_v\text{CrO}_3$ 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.

1230°C 2hr

CaCrO₄ on La_{0.675}Ca₃CrO₃

Ca_{1.2}CrO₄ on La_{0.675}Ca₃CrO₃

Ca₃(CrO₄)₂ on La_{0.675}Ca₃CrO₃

Figure 4-8. Reaction Couples, La_{0.675}Ca₃CrO₃ Substrate

1230°C 2hr

CaCrO₄ on La_{0.69}Ca₃CrO₃

Ca_{1.2}CrO₄ on La_{0.69}Ca₃CrO₃

Ca₃(CrO₄)₂ on La_{0.69}Ca₃CrO₃

Figure 4-9. Reaction Couples, La_{0.69}Ca₃CrO₃ Substrate

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 the formation of LaCrO_3 . Further work needs to be done to better understand this portion of the LaCrO_3 - CaCrO_4 solubility diagram.

4.2.3.5 Solubility Diagram

The Ca-Cr-O eutectic liquid reabsorbs into the perovskite lattice at temperatures dependent on the calcium composition. Figure 4-10 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 LaCrO_3 has an effect on the solubility of CaCrO_4 . Apparently, the high temperature rhombohedral structure has a lower solubility than does room temperature orthorhombic. Dilatometric studies are presently being run to help determine the transition temperatures between the two crystal structures so that the solubility study may be continued.

4.2.3.6 Binary Powder Mixtures

Binary powder mixtures of $\text{La}_u\text{Ca}_v\text{CrO}_3$ 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.

4.3 LONG-TERM CATHODE STABILITY

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.

Work this quarter has concentrated on examining the performance of the doped- LaCrO_3 (YSZ)/YSZ/doped- LaCrO_3 (YSZ) symmetric composites (referred to as an I/E/I), as well as determining the conductivity of the electrode materials used in the I/E/I composites. These studies are being conducted to evaluate the possibility of developing a two-material MSOFC.

As pointed out in the previous quarterly, experience with these SOFC electrodes indicates that good bonding between the electrode and electrolyte layers is essential for good electrochemical performance. Therefore, efforts were concentrated on improving the bonding between the electrolyte and electrode layers. While discussed in more detail in another section, two basic approaches were utilized. As discussed in the

Figure 4-10. The Solubility of CaCrO_4 in LaCrO_3 vs. Temperature

previous quarterly report, the first was to use mixtures of doped-LaCrO₃ in YSZ in the electrode layers. The other approach was to increase the firing temperature.

AC impedance was used to examine the electrochemical performance of three I/E/I composites (IEI-9, IEI-11, and IEI-14) in reducing (H₂/H₂O) and oxidizing (air) environments. The results of these studies are given in Table 4-3. Also given in Table 4-3 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%. As discussed in the previous quarterly, a similar trend in the results for both IEI-9 and IEI-8 was observed.

TABLE 4-3							
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)							

Post-test 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 La₂Zr₂O₇ was present in measurable quantities (approximately 5%). This indicates that there is less interaction between the YSZ and the LaCrO₃, than was observed for YSZ and LaMnO₃. It should be noted that the presence of a very thin interfacial reaction layer of La₂Zr₂O₇ probably would not have been detected by the diffractions studies.

A significant improvement in bonding was observed by increasing the firing temperature 100°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-LaCrO₃ 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-LaCrO₃) 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.

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 Ω⁻¹cm⁻¹ as compared to 0.12 Ω⁻¹cm⁻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 Ω⁻¹cm⁻¹ in air and 2.28 Ω⁻¹cm⁻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 Ω⁻¹cm⁻¹ in air and 0.0717 Ω⁻¹cm⁻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 and in previous reports, 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% LaCrO₃ suggests that the actual increase in electrochemically active area may be small. The measured conductivity values of the 35 wt% LaCrO₃ 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 LaCrO₃ 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. LaCrO₃ is a much better cathode material than anode material. The performance of the material as a cathode is similar to that of LaMnO₃ 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.

4.4 REFERENCES

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- [2] 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).

SECTION 5
FABRICATION (TASK 3)

5. FABRICATION (TASK 3)

5.1 FABRICATION DEMONSTRATION (TASK 3.1)

5.1.1 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.

5.1.2 Fabrication of Cells and Stacks

MSOFC cells and stacks are being made using a fabrication sequence based on the tape calendaring technique. This technique is explained in the October-December 1989 Quarterly Report, AiResearch Document 89-63136(3), pages 3-1 through 3-3. Primary activities during the last quarter included batch preparation and characterization, fabrication of single cells and multicell stacks, bonding studies, interconnect development, and shrinkage matching.

5.1.2.1 Batch Preparation and Characterization

Batch preparation efforts during this quarter focused on batch preparation and characterization to support stack fabrication and interconnect studies. All of the batches were made according to the MSOFC fabrication method described in previous reports. The batches were characterized by density, weight loss, and shrinkage measurements.

During this reporting period, two high solid loading anode batches were prepared to replace batch A07030-1. 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 5-1. Figure 5-1 compares the properties of these batches with batch A07030-1, and to the baseline batches prepared in November 1991.

A Banbury batch of alumina-modified CE (CE01212-1) was made based on the results of the torque rheometer batches prepared last quarter. The average sintered properties of the modified CE are also presented in Table 5-1. Figure 5-2 compares the properties of this batch to those of earlier alumina-modified CE batches and to the baseline CE batches prepared in August, 1991.

During this reporting period, it was also necessary to prepare additional baseline CE batches to replace the depleted supply. Three baseline CE batches (CE03122-1, CE03132-1, and CE03132-2) were prepared in the Banbury mixer and the average properties of these batches are shown in Table 5-2. For comparison, Figure 5-3 shows the batch properties of the CE batches prepared since May, 1991.

TABLE 5-1				
AVERAGE SINTERED PROPERTIES OF MSOFC BATCHES PREPARED DURING THE FIRST QUARTER, 1992				
Batch	Diametrical Shrinkage (%)	Weight Loss (%)	Density (g/cc)	Theoretical Density (%)
A01072-1	17.2 $\pm$ 0.4	21.8 $\pm$ 0.0	4.64 $\pm$ 0.08	75.6 $\pm$ 1.3
A01172-1	16.9 $\pm$ 0.4	21.6 $\pm$ 0.1	4.48 $\pm$ 0.13	73.1 $\pm$ 2.1
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
CE02252-1	TO BE MEASURED			
I02132-1				
I02132-2				

To support the interconnect studies, four batches were prepared: two torque rheometer interconnect batches, a torque rheometer CE batch with no pore former, and a torque rheometer anode with addition of alumina with no pore former.

The interconnect batches were made with as-received powder from SSC (I02132-1) and Rhone Poulenc (I02132-2). These batches were used to evaluate the use of electrode:interconnect thickness ratio to control liquid phase wicking during interconnect densification.

A CE batch (CE02252-1) was made without pore former in an effort to control the pore volume of the cathode and, thus, the level of wicking in the interconnect during cofiring. The sintered properties of this batch are presently being compiled and will be presented at a later date.

An anode batch (A01282-1) was prepared with 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 5-1.

5.1.2.2 Cell and Stack Fabrication

During this reporting period, this effort was concentrated on two areas: determination of the most suitable building block for multicell stack fabrication based on current batch combinations and processing parameters, and fabrication of multicell stacks using the two-step cofiring process.

Figure 5-1. The Sintered Properties of the High Solid Loading Anodes (50% Vol% Solids) vs. the Baseline Anodes (47 Vol% Solids)

Figure 5-2. The Sintered Properties of the Alumina-Modified CE Batches vs. the Baseline CE Batches

TABLE 5-2				
AVERAGE SINTERED PROPERTIES OF BASELINE MSOFC BATCHES PREPARED DURING THE FIRST QUARTER, 1992				
Baseline Batch	Diametrical Shrinkage (%)	Weight Loss (%)	Density (g/cc)	Theoretical Density (%)
CE03122-1	21.2 $\pm$ 0.5	23.7 $\pm$ 0.2	5.00 $\pm$ 0.10	79.7 $\pm$ 1.6
CE03132-1	22.0 $\pm$ 0.3	24.0 $\pm$ 0.2	4.88 $\pm$ 0.15	77.7 $\pm$ 2.4
CE03132-2	21.2 $\pm$ 0.6	23.5 $\pm$ 0.1	4.86 $\pm$ 0.17	77.4 $\pm$ 2.7

Based on the results obtained in the last quarter, 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 during the two previous quarters. 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 during this quarter. 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 5-3. 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

Figure 5-3. The Sintered Properties of the Baseline CE Batches Made Since 5/91

TABLE 5-3			
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
3H20-1	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			

bonding contact within the stacks. Figure 5-4 is an example of the cross section of a two-cell stack cut perpendicular to the anode corrugations.

5.1.2.3 Bonding Studies

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. The current approach was to add interconnect material to the A and CE 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

Figure 5-4. Cross Section of a Two-Cell Stack Cut Perpendicular to Anode Corrugation

micrograph of a polished cross section of a bonded CE/I sample is given in Figure 5-5. The sample shows excellent contact between the bonding material and CE and I plates.

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 5-4. 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 5-6 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.

X-ray diffraction patterns of the different bonding tapes fired at 1250°C for 1 hour are shown in Figure 5-7. 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. Measurements are currently being carried out on the conductivity of the bonding materials.

The effect of thermal cycling on bond integrity has been evaluated by firing bonded single cell stacks from room temperature to 1000°C 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. Thermal cycling and examination of more bonded samples are being carried out to confirm this result.

Several single cell stacks have been fabricated from single cell module building blocks based on the efforts described above. These stacks have shown reproducibility in terms of bond integrity and microstructure. In addition, the new bonding formulations and procedures were used to successfully bond a 2 in. single cell module with anode and CE covers.

5.1.2.4 Interconnect Studies

The interconnect work this quarter centered on fabricating and processing A/I, CE/I and A/I/CE tapes. The interconnect tapes used in this work were fabricated using powders obtained from SSC ($\text{La}_{0.84}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$) and Rhone-Poulenc ($\text{La}_{0.78}\text{Ca}_{0.2}\text{Cr}_{0.88}\text{Co}_{0.1}\text{O}_3$). The anode and cathode tapes used were baseline A

Figure 5-5. Polished Cross-Section of CE/I Bond Using 50CE/50I Bonding Material

TABLE 5-4		
BONDING RESULTS		
Bond	Formulation	Result
A cover – A corr	A/I 100/0	good bonding
	A/I 75/25	good bonding
	A/I 50/50	delamination
I cover – A corr	A/I 50/05	good bonding
	A/I 75/25	good bonding
CE cover – CE corr	CE/I 100/0	delamination
	CE/I 50/50	good bonding
	CE/I 25/75	delamination
I cover – CE corr	CE/I 50/50	good bonding
	CE/I 25/75	good bonding

and CE batches. Sintered A/I, CE/I, and A/I/CE samples were evaluated for interconnect densification and elemental interaction.

The main variable evaluated in this work 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 10-11 mils or 255-280 microns). Figure 5-8 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 microns both the anode and interconnect became fully dense when sintered at 1400°C for 1 hour. Figure 5-9 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 microns.

It is believed 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 5-10 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.

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 5-11. From this analysis, cobalt

b)

c)

Figure 5-6. Micrographs of Polished Cross-Sections Showing Examples of:
a) Good Bonding of A Cover – A Corr. Using Pure Anode Tape,
b) Delamination of A Cover – A Corr. Using A/I 50/50 Composite Tape,
c) Good Bonding of CE Cover – CE Corr. Using CE/I 50/50 Tape.
Magnification 80x

Figure 5-7. X-Ray Diffraction Patterns of Bonding Materials

Figure 5-8. SEM Photographs of Anode/Interconnect Bilayers Showing Influence of Layer Thickness on Interconnect Densification

Figure 5-9. SEM Photographs of Cathode/Interconnect Bilayer Showing Influence of Layer Thickness on Interconnect Densification

Figure 5-10. Fracture Surface of A/I/CE Trilayer Showing Densification of Anode, Interconnect, and Cathode Layers (1400 °C For 1 Hr.)

A/I/CE TRILAYER

Figure 5-11. Concentration Profile of Ca, Co, La, and Cr Across A/I/CE Trilayer

20320-1

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 5-12 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 . During the next quarter, large A/I/CE tapes will be fabricated and characterized and co-sintering of A/I/CE in contact with electrode corrugations will be pursued.

5.1.2.5 Shrinkage Studies

Shrinkage measurements were delayed due to the installation of improved operational software and scheduled equipment maintenance. These alterations are expected to reduce measurement error and increase confidence in generated data. Determination of the new system baseline and quantification of measurement error are now underway. After calibration, dilatometry measurements on bonding formulations, interconnect materials, and new CE batches will commence. Old batches will be reanalyzed to ensure proper comparison.

5.2 DEFECT ANALYSIS (TASK 3.3)

5.2.1 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.

5.2.2 Analysis

During this quarter, defect analysis centered on characterization of the flatness of 1 in. footprint single cell modules and optical examination of cross sections of modules and bonded single cell stacks.

The flatness of single cell modules was determined by an optical comparator. Optical comparator measurements of sintered modules processed this quarter showed significant improvements in module flatness. The measured average gap was approximately 4.0 mils with an average standard deviation from flatness of 2.0 mils. Single cell modules processed during the previous two quarters possessed an average gap of approximately 6.0 mils and average standard deviation of 4.0 mils. These improvements are mainly due to better processing techniques.

Sintered modules and bonded single cell stacks were mounted in epoxy, cross-sectioned, and polished for optical microscopic examination. The objective was to identify defects within the module structure (especially cracks in the electrolyte and at the electrode corrugation/trilayer interface) that could not be seen at the edges. Examination of polished cross-sections from sintered modules (Type I, III, and IV) and bonded single cell stacks showed that many defects seen in the micrographs are the result of sample preparation. Improved preparation procedures are being implemented to obtain better representation of "real" defects within the structure.

Figure 5-12. XRD Pattern of Anode in A/I/CE Trilayer

SECTION 6
TESTING ON COAL GAS (TASK 4)

6. TESTING ON COAL GAS (TASK 4)

6.1 PERFORMANCE TESTING (TASK 4.1)

6.1.1 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.

6.1.2 Single Cell Testing

A single cell (ED065-7) was tested during this reporting period. This cell contained baseline A, baseline E, and alumina-modified CE. The test was carried at 1000°C with 97 percent H₂/3 percent H₂O fuel and air. The cell polarization curve is shown in Figure 6-1. 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 small gas cross leakage in the cell, causing performance degradation during the life test.

6.1.3 Stack Testing

Efforts this quarter have concentrated on improving the manifolding materials and procedures. Sample manifolds (containing no fuel cell) have been fabricated, fired, and tested for leakage under operating conditions. Decay-type leak tests were performed using N₂, He, and H₂. Several new techniques, including vacuum-impregnation of the base structural material and the use of non-porous (gas-tight) base material, have been tried. A wide variety of currently available sealants have been studied, but all show leakage at operating temperatures, especially with He and H₂. One possible solution to this problem, a relaxing glass seal, is now under investigation.

Two two-cell stacks, EH15-2 and EH15-1, were tested this month, at ANL. Their geometry is described below. EH15-2 showed an OCV of 1.80 V, compared to a theoretical value of 2.11 V. EH15-1 showed an OCV of 1.93 V. The ASR, however, was extremely poor for both stacks; the reasons for this are discussed in the next section.

One single-cell stack was also tested this month, EE309-02. An excellent OCV of 1.01 V was achieved, but the ASR was poor. Post-test analysis is now underway to determine the cause.

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Figure 6-1. Polarization Curve of Cell ED065-07
Temperature = 1000°C
Fuel = 97% H₂/3% H₂O
Oxidant = Air

6.1.4 Post-Test Analysis

Post-test analysis was completed on two stacks, EG259-02, tested in December 1991, and EH15-1, tested in March 1992. EG259-02 was fabricated by bonding two electrode-covered modules to an interconnect, while EH15-1 was fabricated by bonding two single cell stacks together with an interconnect to form a two-cell stack.

Stack EG259-02: 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: The anode of the stack was 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.

SECTION 7

QUALITY DEVELOPMENT (TASK 5)

PERFORMANCE AND COST ANALYSIS

7. PERFORMANCE AND COST ANALYSIS, TASK 5

7.1 STACK PERFORMANCE MODELING, TASK 5.1

7.1.1 Objective

The objective of this task is to develop a mathematical model of a crossflow MSOFC to obtain a better understanding of the interactions among the various design and operating variables, and their effects on the overall performance of the stack.

7.1.2 Results

A mathematical model of the MSOFC called FCELL is complete. The model simulates the electrochemical, electrical, thermodynamic, and chemical equilibrium processes occurring in the cell. A single cell within the MSOFC stack is modeled. This cell is assumed to be sufficiently deep within the stack so that end effects may be neglected. The horizontal plane of the cell is divided into a two-dimensional grid of rectangular areas or elements. Each element has a single, centrally located node. The elements are sufficiently small that the nodal values of temperature, pressure, concentration, etc. can be used over the entire element for the calculation of local current densities and heat fluxes. The mass balance, energy balance, and expressions for the electrochemical and electrical phenomena are set up and solved for each element.

The inputs to the program include the geometry of the fuel cell, the cell operating voltage, and the inlet fuel and oxidant temperatures, pressures, flow rates, and compositions. The model can operate with any fuel that contains any or all of the following constituents: hydrogen, water, simulated diesel fuel ($C_{16}H_{34}$), carbon monoxide, carbon dioxide, methane, oxygen, or nitrogen. Air or pure oxygen can be used as the oxidant. If desired, the program can operate in a mode in which the user specifies the cell current, fuel utilization, or maximum desired cell temperature in place of the cell voltage or one of the inlet flow rates. In this mode of operation the program uses an additional iteration loop to determine the cell performance based on the input values. The program outputs include the temperature, composition, Nernst potential, and current at each node. Also, a number of performance parameters are calculated such as the fuel and oxidant utilization, total cell power, fuel efficiency, and average temperatures.

SECTION 8
QUALITY DEVELOPMENT (TASK 6)

8. QUALITY DEVELOPMENT, TASK 6

8.1 EVALUATION OF NONDESTRUCTIVE EVALUATION (NDE) METHODS (TASK 6.1)

8.1.1 Objectives

The objectives of this subtask are to: (1) evaluate, develop, and implement 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) select and develop NDE methods best suited to ensure the quality of commercial-scale fabricated MSOFC's.

8.1.2 Results

This subtask is complete. A draft copy of the final report entitled, *Nondestructive Characterization Methods for Monolithic Solid Oxide Fuel Cells* is currently being reviewed.

8.2 STRESS ANALYSIS OF STACKS (TASK 6.2)

The current MSOFC finite-element stress model is being expanded to include the "heat up" portion of the firing cycle and multi-cell 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.

It is planned to also model 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.

8.3 QUALITY CONTROL OF SOURCE MATERIALS (TASK 6.3)

8.3.1 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.

8.3.2 Evaluation of Lanthanum Chromite

During the past two quarters, SSC, Inc. has been carrying out an analysis to determine the stoichiometry of Lot 147 Ca, Co-doped lanthanum chromite. 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 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 only densified to 97.7 percent ThD. The electrical conductivity of these materials is currently being evaluated and will be reported in the next quarterly. Figure 8-1 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 8-1A is stoichiometric (A-site:B-site = 1) and the material has a density of 94 percent theoretical. Figure 8-1B 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.

Also during this quarter, lanthanum chromite obtained from Rhone-Poulenc was evaluated for use in the MSOFC. The composition of this material as determined from wet chemical analysis was $\text{La}_{0.78}\text{Ca}_{0.2}\text{Cr}_{0.88}\text{Co}_{0.1}\text{O}_3$. This material was fabricated into a tape and sintered at 1400°C and 1350°C for 1 hour. The resultant densities were 97.7 and 94.7 percent of theoretical, respectively. This material was the first lot of powder produced by Rhone-Poulenc for Allied-Signal. Further lots are being investigated to determine if Rhone-Poulenc can consistently reproduce the powder.

Figure 8-1. Fracture Surfaces of Ca, Co-Doped LaCrO_3 Sintered at 1400°C For 1 Hr.
 A) $A/B = 1$ B) $A/B = 1.04$

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