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Supporting Research for MSOFC Development

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CONTRACT INFORMATION

Contract Number	DE-AC-21-89MC26006
Contractor	Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439
Contractor Project Manager	Kevin M. Myles
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METC Project Manager	Richard Gibson (Allied Signal)
Period of Performance	Sept. 1989 to Sept. 1992

OBJECTIVE

Argonne National Laboratory is providing support to Allied Signal Aerospace Company in the development of the monolithic solid oxide fuel cell (MSOFC).

PROJECT DESCRIPTION

During the current reporting period, ANL's effort was concentrated on exploring the co-sintering of anode/interconnect/cathode trilayers, investigating the interfacial electrochemistry, and performing stress analysis.

Co-sintering of the anode/interconnect/cathode trilayer is an important step in the manufacturing of multicell MSOFC structures. The interconnect, separates fuel and oxidant streams of adjacent cells and must therefore be dense. It also connects the individual cells mechanically and electrically, requiring strong bonding between adjacent anodes and cathodes, and also requiring low electrical resistances.

The difficulty in co-sintering anode/interconnect/cathode trilayers is matching the sintering characteristics of the three layers. The interconnect material, strontium-doped lanthanum chromite, is typically sintered to high density at temperatures exceeding 1600°C and low oxygen partial pressures.[1] Under these conditions the lanthanum manganite air electrode decomposes. To make trilayers, conditions must be found for obtaining dense lanthanum chromite in the 1300-1400°C range. Earlier attempts to use sintering aids in the lanthanum chromite were unsuccessful. During this reporting period, several dopants were explored.

RESULTS

Co-sintering of anode/interconnect/cathode trilayers

The initial approach to lowering the sintering temperature of lanthanum chromite was to explore double doping with calcium on the lanthanum site and cobalt on the chromium site. Powders were made by the Pechini method and were calcined at 700°C. After optimizing the doping levels, we were able to make dense interconnect tapes at 1400°C in air, as shown in Fig.1.

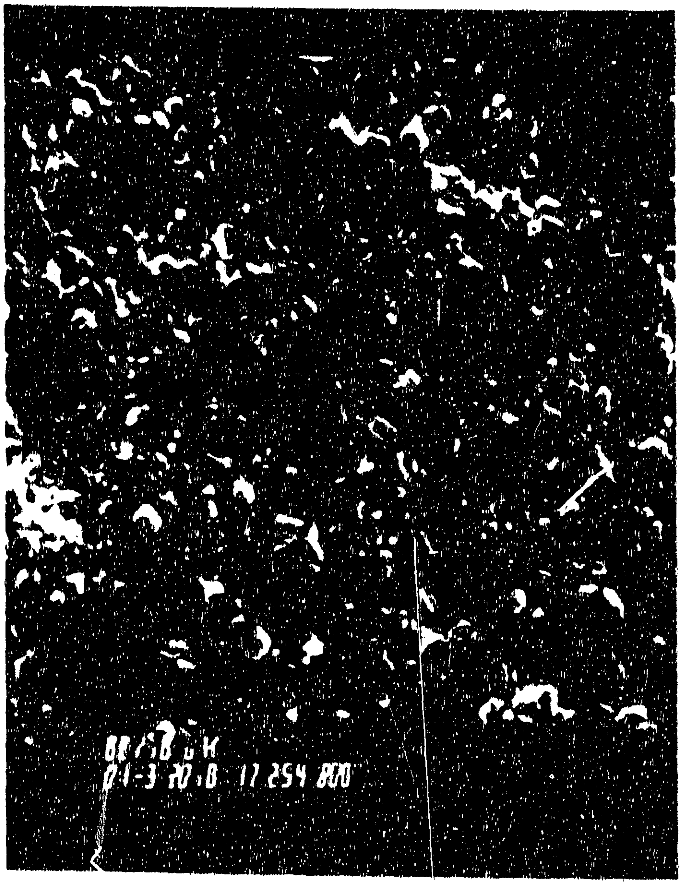


Figure 1. Lanthanum Chromite Sintered at 1400°C

Figure 2. Tri-layer Sintered at 1400°C.

However, when the same material was used for making anode/interconnect/cathode trilayers, the interconnect was found to be too porous, as shown in Fig. 2. Since calcium and chromium were detected in the cathode, it appeared that a liquid phase was forming in the interconnect and was wicking out into the adjacent cathode layer.

Shrinkage and differential thermal analysis (DTA) data, as shown in Figs. 3 and 4, indicate that the liquid may be forming in the temperature range of 1000-1050°C. Interestingly, the CaO-Cr_2O_3 phase diagram shown in Fig. 5 has a eutectic at 1022°C. It appears that a calcium chromate liquid phase is forming when calcium-doped $LaCrO_3$ is heated up. The liquid is wicked into the anode and cathode structure, resulting in a loss of material that leads to porosity in the interconnect layer. By using new dopants for the lanthanum chromite, we have been able to fabricate trilayers with dense interconnects.

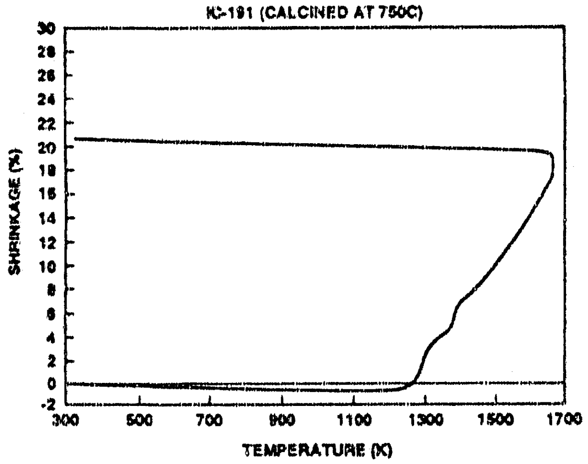


Figure 3. Shrinkage of $La_{0.8}Ca_{0.22}Cr_{0.9}Co_{0.1}O_{3-x}$

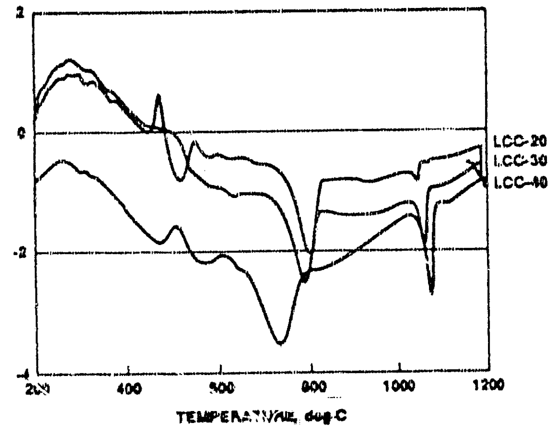


Figure 4. Differential Thermal Analysis of $La_{0.79}Ca_{.2}CrO_3$, $La_{0.69}La_{0.3}CrO_3$, and $La_{0.59}Ca_{2.4}CrO_3$

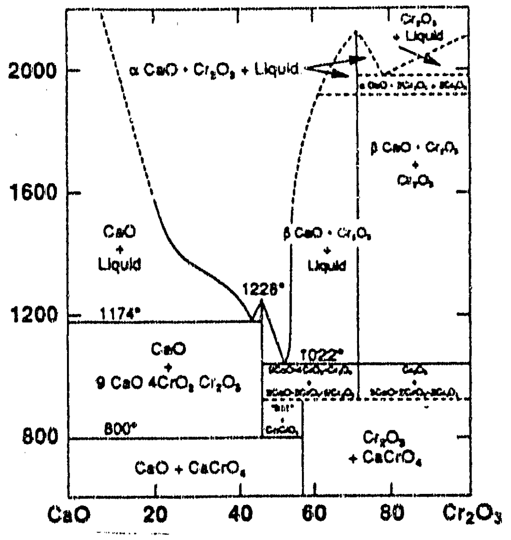


Figure 5. $CaO \cdot Cr_2O_3$ Phase Diagram

An alternative route to overcoming the wicking problem was to explore whether the conventional anode and cathode materials could be replaced by porous lanthanum chromite. Trilayers consisting of $LaCrO_3/ZrO_2/LaCrO_3$ were made and tested electrochemically. Figure 6 shows the interfacial resistances of several such two-material fuel cells. The early versions had a relatively high interfacial resistance on the fuel electrode, indicating that lanthanum chromite is not a very good hydrogen electrode. However, reformulating the two electrodes, we have made steady progress toward reaching the goal.

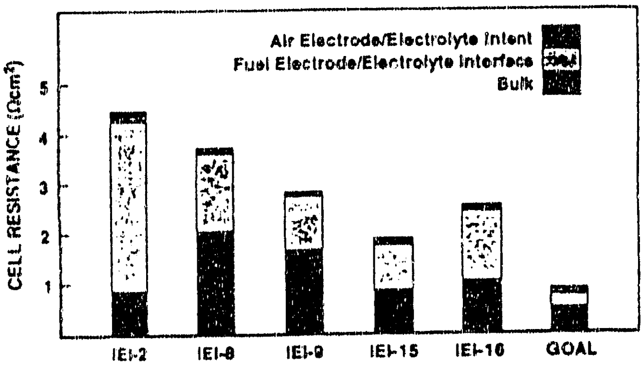


Figure 6. Resistance of $LaCrO_3/ZrO_2/LaCrO_3$ Fuel Cell

Interfacial Electrochemistry

During the testing of single cells, we noticed that the concentration of oxygen in the oxidant had a pronounced effect on the polarization curves. Fig. 7 shows polarization curves at oxygen concentrations of 3.5, 20.9, and 100%. At first glance, one would attribute the potential differences to diffusion overpotentials in the air electrode. However, such diffusion overpotentials at 1000°C, given the dimensions of the electrode pores, were calculated to account for only a few millivolts.

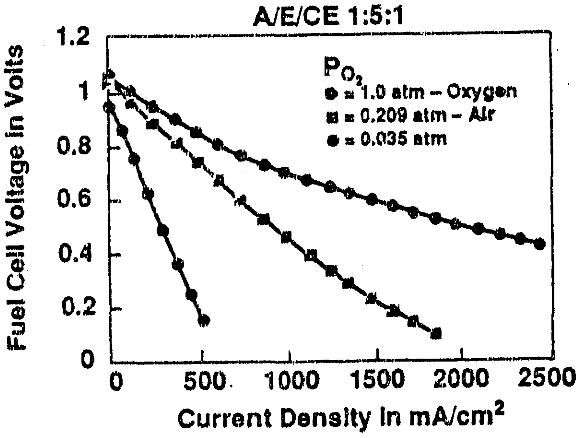


Figure 7. Polarization Curves of $Ni/ZrO_2/ZrO_2/LaMnO_3$ Tri-layers at Different Oxygen Partial Pressures

To better understand the reasons for the effect, we measured interfacial resistances of cathode/electrolyte/cathode trilayers over a range of oxygen partial pressures. These results are given in Fig. 8. It is evident that the interfacial resistance changes by about an order of magnitude over the 3.5-100% oxygen range.

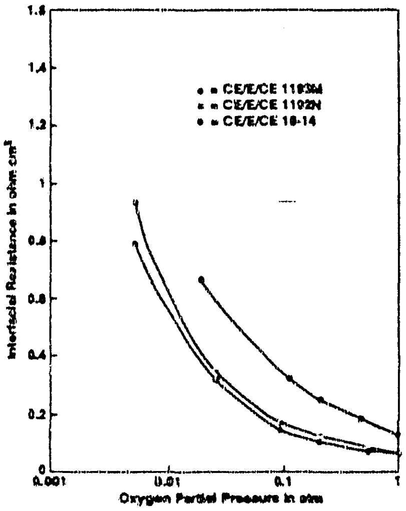


Figure 8. Interfacial Resistance of $LaMnO_3/ZrO_2/LaMnO_3$ Tri-layers

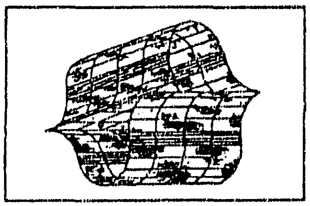
We interpret these results to indicate that the concentration of electrochemically active species is changing dramatically. Conversely, the composition of the interface will also affect the concentration of these species, as is evident by the difference between the three curves.

Stress Analyses

A model of the monolithic structure was developed of calculate stresses during cool-down. The model consists of a flat anode/electrolyte/ cathode corrugations on the outside faces. An illustration is shown in Fig. 9. Using the measured physical property values given in Fig. 9, fracture maps were calculated. The results, shown in Figs. 10 and 11, indicate that fairly thin electrolytes and anode/electrolyte/cathode thickness rations of 2:1:1 are optimal.

REFERENCES

[1] Groupp and Anderson, J. Am. Ce. Soc., 59, 449



Nodal Model

	Anode	Electrolyte	Cathode
Young's Modulus (MPa)	1.38×10^{5}	1.80×10^{5}	1.23×10^{5}
Poisson's Ratio	0.3	0.3	0.3
Fracture Strength (MPa)	100	185	95
Thermal Expansion Coeff. (/°C)	11.38×10^{6}	10.53×10^{6}	10.89×10^{6}

Mechanical Property Values

Figure 9. Stress Analysis of the Monolithic Structure

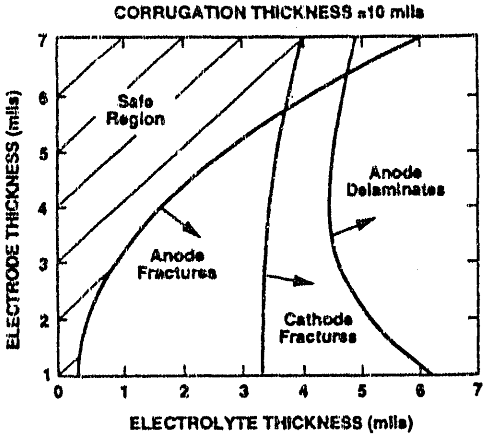


Figure 10. Fracture Map of a Single Cell due to Thermal Stresses during Cooldown after Sintering

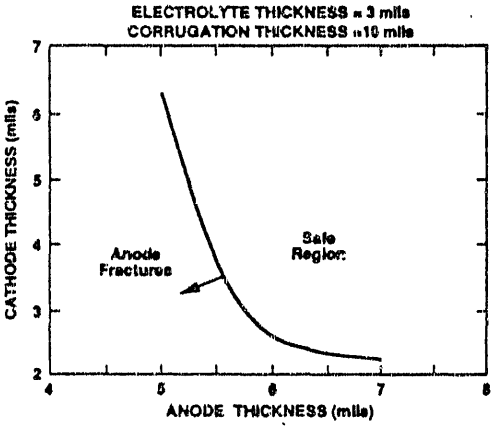


Figure 11. Fracture Map of a Single Cell with Fixed Electrolyte and Corrugation Thicknesses due to Thermal Stresses during Cooldown after Sintering

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