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Alternative Materials for Solid Oxide Fuel Cells:
Processing and Interactions of Materials

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Authors:

J.L. Bates
T.R. Armstrong
L.A. Chick

Contractor:

Pacific Northwest Laboratory
Battelle Memorial Institute
P.O. Box 999
Richland, WA 99352

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Alternative Materials for Solid Oxide Fuel Cells: Processing and Interactions of Materials

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Pacific Northwest Laboratory
Operated for the
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Battelle Memorial Institute
under contract DE-AC06-76RLO 1830
P.O. Box 999
Richland, Washington 99352
(509) 375-3938

Dr. J. Lambert Bates
Dr. Timothy R. Armstrong

Dr. Larry A. Chick
Dr. Timothy R. Armstrong
Dr. J. Lambert Bates

Diane Hooie

April 1, 1993 to June 30, 1993

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OBJECTIVES

The purpose of this research is to develop alternative materials for solid oxide fuel cell (SOFC) interconnections and electrodes with improved electrical, thermal, and electrochemical properties. Another objective is to develop synthesis and fabrication methods for these materials whereby they can be processed in air into SOFCs. The approach is to (1) develop modifications of the current, state-of-the-art materials used in SOFCs, (2) minimize the number of cations used in the SOFC materials to reduce potential deleterious interactions, (3) improve thermal, electrical, and electrochemical properties, (4) develop methods to synthesize both state-of-the-art and alternative materials for the simultaneous fabrication and consolidation in air of the interconnections and electrodes with the solid electrolyte, and (5) understand electrochemical reactions at materials interfaces and the effects of component composition and processing on those reactions.

BACKGROUND INFORMATION

Solid oxide fuel cells (SOFCs) continue to develop as promising, clean, and efficient technology for the direct conversion of hydrogen and fossil fuels to electrical energy. Standard materials we use in state-of-the-art designs are: the air electrodes, $\text{La}(\text{Sr})\text{MnO}_3$; the fuel electrode, $\text{ZrO}_2 \cdot \text{Ni}$ cermet, the interconnection, $\text{La}(\text{Mg})\text{CrO}_3$ or $\text{La}(\text{Sr})\text{CrO}_3$, and the electrolyte, Y_2O_3 -stabilized ZrO_2 . The use of these different material combinations of manganite, chromite, zirconia, and nickel in state-of-the-art SOFCs pose several materials fabrication and performance related problems.

New alternative materials with improved properties that can be more easily fabricated into fuel cells are needed for the further development of cost efficient and improved performance SOFCs. An important key is the development of a SOFC interconnection material that can be sintered in air to a high density at temperatures less than 1500°C . It should have a good thermal expansion match with and intimately bond to both the air and the fuel electrodes, without forming

deleterious interactions at the interfaces. At present time this has not been attained with the state-of-the-art $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ interconnections.

PROJECT DESCRIPTION

The overall approach for this research and development is to:

- Minimize the number of cations in the electrode, electrolyte, and interconnection by developing yttrium compounds, such as $\text{Y}(\text{Ca})\text{CrO}_3$ as the interconnection, and $\text{Y}(\text{M}')\text{MnO}_3$ as the air electrode.
- Develop advanced synthesis and fabrication processes for air sintering, below 1500°C , of chromite interconnections through (1) the use of sintering aids; and (2) the synthesis of sub-micrometer powders.
- Establish methods for the simultaneous processing and consolidation of air-sinterable powders.
- Electrochemically evaluate interface reactions (in reproducible and controlled laboratory tests) for both the alternate and state-of-the-art materials and cell components developed under this program.
- Evaluate the chemical reactivity and interdiffusion effects that take place between the various fuel cell components: electrolyte/cathode, interconnect/cathode, and interconnect/anode.

This paper describes a comprehensive study that assessed the processing of air-sinterable chromites, the sintering mechanism of chromites, and the chemical reactivity and interdiffusional effects between the interconnect, air, and fuel electrodes. Materials evaluated were $\text{La}_{0.7}\text{Ca}_{0.31}\text{CrO}_3$ (LCC31), $\text{La}_{0.7}\text{Ca}_{0.29}\text{CrO}_3$ (LCC29), $(\text{Y}_{0.6}\text{Ca}_{0.4})_{1.05}\text{Cr}_{0.95}\text{O}_3$ (YCC105), $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM), $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCM), $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ (YCM), and $\text{Y}_{1-x}\text{Sr}_x\text{MnO}_3$ (YSM).

RESULTS

Experimental Procedure

The required compositions were prepared by the glycine-nitrate process using a stoichiometric molar ratio of glycine-to-nitrate^{1,2}. The powder was calcined at 650°C for 0.5 hr. Reaction couples were formed to study the migration of cations and anions between the SOFC materials and to determine if any secondary phases developed at the interface. The two materials for each interaction couple were fabricated into a bilayer configuration using a two-step process. First, one powder was placed into a die and lightly compacted by uniaxial pressing. The second powder was added to the die and the two were consolidated (no binder) by uniaxial pressing at 35 MPa. This step was followed by isostatically pressing the disks, 21 mm diameter by 2 mm thick, at 140 MPa. The pellets were sintered in an electric resistance furnace by heating 5°C/min to 1300°, 1400°, and 1500°C and soaking for 1 hour in air. These temperatures were chosen because they cover a broad range over which SOFCs may be thermally processed. A cross-section of each sample was mounted, polished, and examined by scanning electron microscopy. Energy dispersive spectroscopy (EDS) was used to measure the cation diffusion distances.

Phase formation during co-sintering was investigated by thoroughly mixing the as-synthesized powders (1:1 ratio) and uniaxially pressing the powder into disks. The samples were heated following the same schedule used for sintering, except they were quenched after soaking for 1 hr at temperature. The disks were ground in a mortar and pestle and analyzed by x-ray diffraction (XRD) to determine the reaction products.

Tape Casting of Glycine-Nitrate Powders

Tape casting studies included evaluations of dispersants, binders, and plasticizers. The powders used in this study were $\text{La}_{0.7}\text{Ca}_{0.31}\text{CrO}_3$ and $(\text{Y}_{0.6}\text{Ca}_{0.4})_{0.99}\text{Cr}_{1.01}\text{O}_3$ prepared by the glycine-nitrate process. The solvent used was an azeotropic mixture of 66% methyl ethyl ketone and 34% ethanol. Acrylic binders were chosen for the study due to their wide commercial

acceptance, and for most of the study phosphate esters were used as the dispersant.

Figure 1 shows the viscosity versus concentration of dispersant curves for suspensions containing 45 wt% solids of as-synthesized LCC31. The minimum viscosity was achieved with a 1 wt% PS-21A (aliphatic phosphate ester) and 3.5 wt% for the CS-1361 (aromatic phosphate ester) addition. These results are similar to those reported by Chartier³ in which he concluded that the aromatic ester adsorbs more slowly, possibly because of its large size with respect to that of the aliphatic ester. No distinct minima was observed in the viscosity when Menhaden fish oil was used. When a shear stress was applied to the slip they showed pseudo-plastic behavior at all dispersant concentrations except at the minimum for PS-21A, where the slip displayed Newtonian behavior. The other dispersants showed only pseudo-plastic behavior at all dispersant levels.

The average particle size of the as-synthesized powder was ≈ 60 nm and the average agglomerate size was 30 μm . The powders were coarsened by heat treating at 800°C and 1000°C for 2 hours. The average particle sizes after treatment at 800°C and 1000°C were ≈ 150 nm and 800 nm, respectively. The agglomerate size of the heat treated powders decreased to 17 μm and 15 μm . These powders were ball milled to determine the amount of milling necessary to break up the agglomerates without destabilizing the suspension. The studies carried out showed that no more than 5 hours of milling was needed to break up the agglomerates. The average agglomerate size, after milling, decreased to 1 μm and 3.5 μm for powders coarsened at 1000°C and 800°C. The LCC31 coarsened at 650°C had a bimodal distribution after milling with one maxima at 3 μm and the second at 0.8 μm .

Figure 2 shows the viscosity versus concentration dispersant curve for a suspension with 65 wt% (20 vol%) LCC31, dispersed with PS-21A, and ball milled for 5 hours. The three curves show the effect that particle size and agglomerate size have on the slip viscosity. LCC31 heat-treated at 650°C requires nearly 8 times more dispersant than the same powder heat-treated at 1000°C, that had a larger particle size and smaller agglomerate size.

Figure 3 shows the viscosity versus concentration dispersant curve for suspensions composed of LCC31 coarsened at 1000°C, dispersed with PS-21A, and ball milled for 5 hours. The curves displayed in Figure 3 show that as the solids loading increases from 65 wt% (20 vol%) to 80 wt% (35 vol%) the viscosity increased from 10 centipoise to 400 centipoise and the amount of dispersant needed to disperse the powder increased from 0.25 wt% to 0.75 wt%.

The best results for dispersing LCC31 and YCC99 were achieved using aliphatic phosphate esters. Suspensions with 85 wt% solids loading have been tape cast using ≈ 1.0 wt% dispersant. Acrylic binders with low glass transition temperatures have been used as binders with polyglycol and benzyl butyl phthalate as plasticizers.

Chromite Sintering

The SOFC interconnect must be sintered to high density so that it will provide a gas-tight seal between the electrodes. Furthermore, decreasing the cost of SOFC manufacturing to the point that the technology is economically competitive may require that the ceramic components are sintered together in one step. In order to prevent decomposition of the manganite cathode, such co-sintering would have to be performed in air at temperatures near or below 1400°C, conditions that are not favorable to chromite densification. For these reasons, a substantial effort has been devoted to developing air-sinterable chromites. Recently, it has been shown that chromite densification can be substantially improved by slightly enriching the overall concentration of A-site relative to B-site⁴⁻¹⁶. We have focused our recent investigations on the reasons for the substantially improved densification of LCC31 relative to that of LCC29.

As discussed previously¹⁷, the sintering shrinkage curves for LCC29 and LCC31 heated at 2°C/min, both exhibit periods of rapid shrinkage. However, there are two characteristic differences between the curves; the first rapid-shrinkage event starts almost 100°C lower in LCC31 than in LCC29 (about 950°C versus about 1040°C). Also, LCC31 exhibits a second rapid-shrinkage event, starting near 1150°C, that takes the sample

Figure 1. Viscosity versus dispersant concentration for different dispersants. Suspension contained 45 wt% LCC31.

Figure 2. Viscosity versus dispersant concentration for LCC31 coarsened at 650°, 800°, and 1000°C. Suspension contained 65 wt% LCC31, dispersant was PS-21A.

Figure 3. Viscosity versus dispersant concentration for different solids loadings of LCC31. Dispersant was PS-21A, phosphate ester.

to near full density by 1300°C. The same characteristic differences are exhibited between chromium-enriched and chromium-depleted compositions in the Y(Ca)CrO₃ system.

In order to investigate the phase changes associated with the rapid-shrinkage events, a series of quenched samples was prepared. These samples were heated at 2°C/min, then air quenched from various peak temperatures. Results of XRD analyses on the quenched pellets are listed in Tables 1 and 2. The fraction of Ca in the perovskite phase was estimated from the perovskite orthorhombic unit cell volume, which was determined from XRD. In addition to the perovskite phase, samples quenched from temperatures up to 1126°C were found to contain CaCrO₄. The concentration of CaCrO₄ in each sample was estimated based on comparison of major peak intensities. The LCC29 sample that was quenched from 1067°C also contained approximately 0.5 wt% of β -CaCr₂O₄. No additional crystalline phases were detected in any of the other samples, however, the presence and quantity of x-ray amorphous material was inferred by performing a material balance to account for the total amounts of cations introduced during synthesis. This x-ray amorphous material, which was present in all samples up through 1126°C, may consist of poorly crystallized phases or the glassy remnants of liquid phases. The material balance calculations indicated that the X-ray amorphous material in LCC31 samples had slightly more Ca than Cr, with the atom ratio, Ca/Cr = 0.53/0.47. The corresponding ratio for the LCC29 samples was Ca/Cr = 0.48/0.52.

These XRD results clearly establish that over half of the Ca resides in non-perovskite phases at the onset of sintering (926°C). Although the glycine-nitrate synthesized chromites are composed of a single perovskite phase after combustion, much of the Ca is exsolved from the perovskite during calcination, forming the CaCrO₄ and other minor phases. This exsolved Ca, along with the associated Cr, dissolves back into the perovskite phase during sintering. In Figure 4, the Ca concentrations determined for the perovskite phase are plotted along with the dilatometer shrinkage curves. This plot shows that, for both samples, dissolution of the Ca into the perovskite proceeds at roughly constant rates

up to 1126°C, then more rapidly proceeds to completion at 1207°C. The more rapid dissolution is concurrent with the second rapid-shrinkage event in LCC31. Both materials experience rapid dissolution of Ca in this temperature interval, however, only LCC31 exhibits rapid densification.

The binary phase diagram between Ca and Cr oxides in air is relevant to the transitory conditions involved in chromite densification because the non-perovskite material is mainly composed of these two components. The most recent version of this diagram is published by Adendorff et al.¹⁸ from de Villiers et al.¹⁹. This diagram shows a eutectic on the Ca-rich side of CaCrO₄ (Ca/Cr = 0.55/0.45, atom basis) at 1061°C. As discussed above, the X-ray amorphous portion of LCC31 probably has a Ca/Cr ratio near that of the eutectic and thus could be expected to melt almost completely by 1150°C. Therefore, it seems plausible that the second densification event in LCC31, near 1150°C, is due to liquid-phase sintering. In contrast, the X-ray amorphous portion of LCC29 probably has a Ca/Cr ratio that places it in the " β -CaCr₂O₄ + liquid" phase region at 1150°C, as indicated by the detection of β -CaCr₂O₄ along with CaCrO₄ at 1067°C. Therefore, the non-perovskite material in LCC29 might be expected to melt incongruently, retaining substantial solid phase at 1150°C. Nevertheless, *both* materials could be expected to form some liquid phase near 1061°C.

It is well known that A-site enriched chromites contain liquid-phase remnants after sintering, but evidence of liquid formation has not been reported in A-site depleted samples, although these have been found to contain isolated Cr-rich deposits^{8,10,14}. However, an LCC29 sample quenched from 1400°C contained isolated Cr-rich inclusions which, upon examination by SEM in polished cross section, were found to consist of rounded perovskite-like grains embedded in a matrix of essentially pure Cr oxide. This matrix phase may be a liquid-phase remnant that was progressively isolated and enriched in Cr as most of the original liquid was dissolved into the perovskite.

This leaves the problem of explaining why the LCC29 material does not densify even though a

Table 1. Results of XRD analyses of $\text{La}_{0.7}\text{Ca}_{0.29}\text{CrO}_3$ samples heated at $2^\circ\text{C}/\text{min}$ in air to peak temperature, then quenched.

Peak Temp. $^\circ\text{C}$	Ca Concentration in Perovskite Phase (x)	Mole Fraction $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ Phase	Mole Fraction CaCrO_4 Phase	Mole Fraction X-Ray Amorphous Phase
800	0.07	0.75	0.13	0.12
926	0.12	0.79	0.11	0.10
1015	0.15	0.83	0.09	0.09
1067	0.17	0.85	0.04	0.11
1126	0.17	0.86	0.03	0.12*
1207	0.30	1.00	---	trace
1296	0.30	1.00	---	trace
1530	0.30	1.00	---	trace

* Includes ≈ 0.5 wt% of $\beta\text{-CaCr}_2\text{O}_4$ (JCPDS-ICDD #9-146).

Table 2. Results of XRD analyses of $\text{La}_{0.7}\text{Ca}_{0.31}\text{CrO}_3$ samples heated at $2^\circ\text{C}/\text{min}$ in air to peak temperature, then quenched.

Peak Temp. $^\circ\text{C}$	Ca Concentration in Perovskite Phase (x)	Mole Fraction $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ Phase	Mole Fraction CaCrO_4 Phase	Mole Fraction X-Ray Amorphous Phase
800	0.08	0.75	0.13	0.12
926	0.13	0.79	0.11	0.10
1015	0.17	0.84	0.08	0.09
1067	0.18	0.85	0.05	0.09
1126	0.20	0.87	0.04	0.09
1207	0.31	1.00	---	trace
1296	0.31	1.00	---	trace
1530	0.31	1.00	---	trace

liquid phase is formed. In the case of LCC31, Figure 4 indicates that densification may not result directly from liquid formation, but rather from the subsequent dissolution of the liquid into the perovskite. This might indicate that the liquid does not adequately wet the solid perovskite in LCC31 until dissolution begins²⁰. However, substantial Ca dissolution also takes place in the LCC29 material within the same temperature range; why does this not also lead to densification? The simple answer might be that liquid does not form in the LCC29 material, even though the present XRD analysis and the binary phase diagram indicate that it should.

It has been proposed that vapor-phase transport plays a role in preventing densification of the A-site depleted materials, such as LCC29^{4,8}. Yokokawa et al.² argue that the presence of minor quantities of Cr_2O_3 will substantially increase the vapor pressure of CrO_3 , causing vapor-phase transport and formation of Cr_2O_3 at intergranular necks, thus preventing further densification. This theory is supported by the work of Meadowcroft and Wimmer²¹, whose data indicate that pure Cr_2O_3 vaporizes at a much higher rate than does LaCrO_3 .

A key experiment was completed that clarifies the role of vapor-phase transport in chromite

sintering. The experiment is shown schematically in Figure 5. Pellets of LCC31 were placed in the furnace either in the open (air) atmosphere or contained within a double crucible arrangement in which the solid powder controlled the atmosphere surrounding the sample. As seen in, Figure 6, the sample in air and those surrounded by Al_2O_3 or La_2O_3 powders reached high density. However, when Cr_2O_3 powder controlled the atmosphere, the sample did not sinter well. This implies that the presence of substantial CrO_3 vapor in the atmosphere destroys the effectiveness of the liquid phase, perhaps by affecting the wetting angle of the liquid.

Material Interactions

Interconnect/Cathode Interactions

X-ray diffraction analysis of mixtures of LCC31 and LSM10 indicated that a solid solution formed between the two materials at all temperatures studied. The resulting crystal structure of the solid solution was determined to be orthorhombic. The only evidence of complete solid solution formation in the YCC/YCM system occurred when YCC105 and YCM60 were heat treated at 1500°C . The crystal structure and lattice parameters of the solid solution indicated orthorhombic symmetry similar to that of yttrium chromites. X-ray diffraction data collected from the solid solutions corresponds well with earlier work reported by Koc et. al.²².

Figure 7 shows a YCC105/LSM10 reaction couple sintered at 1400°C for 1 hour. The interface in these samples is characterized by a dense reaction zone approximately $90\text{ }\mu\text{m}$, the majority of which resides on the interconnect side. This dense interfacial region is enriched with calcium and chromium and its thickness was found to be invariant with temperature. Aside from the interface the remainder of the interconnect and cathode are porous. Calcium and chromium migration into the cathode was observed approximately $100\text{ }\mu\text{m}$ and $80\text{ }\mu\text{m}$ beyond the dense interfacial region.

Figure 8 shows a YCC105/LCM20 reaction couple sintered at 1400°C for 1 hour. The interfacial region in these samples is similar to

Figure 4. Sintering shrinkage curves for LCC31 and LCC29. Triangular symbols are estimated levels of Ca in the perovskite phase.

Figure 5. Schematic of solids controlled atmosphere setup.

Figure 6. Effect of solid phase-controlled atmosphere on sintering of LCC31 at 1300°C / 1 hr.

those observed between YCC and LSM, shown in Figure 7. The samples sintered at 1400° and 1500°C had a dense reaction zone at the interface approximately 80 μm thick. This region is again enriched in calcium and chromium with chromium migrating 70 μm past the dense region into the cathode at the temperatures observed. Again, as in the YCC/LSM reaction couples the interconnect only densified near the interface. EDS analysis of the interface indicated some distinct differences in microchemistry. Areas of the interface on the interconnect side were found to have a higher concentration of calcium and chromium than other areas within the dense region, indicating possible melting and migration of CaCrO_4 . On the cathode side of the interface, the material was enriched in calcium and depleted in chromium. The composition of the interface is similar to the composition of the dispersed phase within the reaction zone. These calcium rich regions were not found in samples sintered at lower temperatures.

Figure 9 shows a LCC31/LSM10 reaction couple sintered at 1400°C. In these interaction couples there is no distinct interface. An interfacial zone can be approximated in the region where there is formation of a second phase between LCC31 and LSM, indicated by arrows in the micrograph. EDS of the dispersed phase indicates that it is a calcium rich $(\text{La,Ca})(\text{Cr,Mn})\text{O}_3$ phase, while the surrounding material is $(\text{La,Ca})(\text{Cr,Mn})\text{O}_3$ solid solution. $(\text{La,Ca})(\text{Cr,Mn})\text{O}_3$ solid solutions are reported to have a lower electrical conductivity than LSM^{22} , but this should not lead to an increase in the interfacial resistance between these two materials because the relative amount of the calcium rich second phase is minimal and does not form a continuous barrier.

Sintering at 1500°C does not result in an increase of second phase material observed at the interface. The only change observed in the microstructure with increased sintering temperature is further densification of the LSM. The characteristics of these couples are nearly ideal, the LCC is dense, the LSM is porous, and the interfaces are relatively free of low conducting second phases. In the LSM/LCC31 couples no manganese diffusion into LCC31 is observed at

Figure 7. YCC105/LSM10 reaction couple sintered at 1400°C/1 hr.

Figure 8. YCC105/LCM20 reaction couple sintered at 1400°C/1 hr.

Figure 9. LCC31/LSM10 reaction couple sintered at 1400°C/1 hr.

the temperatures studied, however, the distance both calcium and chromium diffused into the LSM increased with increasing sintering temperature.

Figure 10 is a reaction couple composed of LCC31 and LCM20 sintered at 1400°C for 1 hour. These interfaces are clean with the only noticeable feature being a porous region at the interface. Otherwise the interconnect is dense and the cathode porous. Sintering at higher temperatures results in increased densification of both the interconnect and cathode. Chromium migration into the cathode is limited to approximately 65 μm .

In this study six different combinations of interconnect/cathode were evaluated. The results for the samples in which YCC105 was used as the interconnect material were not encouraging. Large interfacial regions rich in calcium and chromium formed in the sample. When YCC was adjacent to YCM60 the interface was porous, in contrast to the dense interfacial region that formed when adjacent to LSM or LCM. However, the formation of these wide interfacial regions indicates that a liquid phase is forming and migrating during the sintering process. The extensive migration of chromium into the cathode in these samples is a result of both liquid and vapor phase transport. The majority of the liquid collects at the interface forming wide continuous interfacial layers. However, it has yet to be determined if these layers and reactions lead to increased interfacial resistance.

Similar reaction couples were prepared with LCC31 as the interconnect. Nearly ideal interfaces resulted adjacent to LCM or LSM. When the LCC was next to YCM, CaMnO_3 formed noncontinuous dense regions. Continuous interfacial layers formed when samples were sintered at 1500°C. No other dense interfacial region was observed in any of these samples. The interconnect was dense in all the samples, indicating that migration of the liquid phase is limited. The data suggests that the presence of yttrium in the calcium and chromium rich liquid phases may change their wetting characteristics, resulting in the formation of dense interfacial layers. The presence of yttrium in the liquid phase is supported by evidence that yttrium

Figure 10. LCC31/LCM20 reaction couple sintered at 1400°C/1 hr.

migrated from the YCM cathode into the LCC interconnect.

Interconnect/Anode Interactions

A phase equilibria study was carried on the $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3/\text{NiO} \cdot \text{ZrO}_2$ system to determine the compositional and temperature ranges over which phases form between the two components. Figure 11 shows the resulting phase diagram. No reaction phases were formed when the Ca content was less than 13 mole percent. Between 13 and 33 mole percent Ca, NiCr_2O_4 forms, and above 33 mole percent Ca, both NiCr_2O_4 and CaZrO_3 form. At low Ca concentrations (10 mole percent) NiCr_2O_4 forms at temperatures as low as 975°C. The formation temperatures decrease to 925°C as the Ca concentration increases to 30 mole percent.

These studies indicate that both the lanthanum and yttrium chromites react with the anode to form dense interfacial layers when sintered at temperatures greater than 1400°C. However, when temperatures less than 1400°C are used, the interfacial reaction area is no longer dense, but neither is the interconnect. It appears that the liquid phase needed to densify the interconnect wets the anode well.

Conclusions

These studies indicate that interfacial reactions occur between SOFC materials when either

Figure 11. $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3/\text{NiO-ZrO}_2$ phase diagram.

yttrium chromite is used as the interconnect or yttrium manganite is used as the air electrode material. The exact reason why yttrium chromite or manganite leads to more extensive reactions upon sintering is unknown. However, it may be due to modification of the wetting characteristics of the liquid phase by yttrium.

More severe reactions occur between the interconnect and the anode than anticipated. It appears from these preliminary studies that the liquid phase generated by the interconnect wets the anode well, leading to enhanced densification of the anode and decreased densification of the interconnect.

It was established that A-site enriched chromites sinter to high density below 1300°C in two rapid shrinkage stages, whereas their A-site depleted counterparts only exhibit the first of these rapid shrinkage events and do not reach high density. Phase changes are similar between A-site depleted and A-site enriched materials; over half of the Ca has been exsolved into non-perovskite phases by the onset of sintering, and this Ca, along with associated Cr, dissolves back into the perovskite phase during sintering.

FUTURE WORK

The emphasis of this project over the next several years will be co-sintering and interactions between SOFC materials, including both state-of-the-art and alternative compositions. Issues involved in co-sintering and interactions between couples of these materials and with the YSZ electrolyte will be investigated. Emphasis on thermal expansion and sintering shrinkage tolerances for the sintering of thin-layer composites. These composites will be fabricated by conventional low cost processing techniques, diffusion of additive cations, and wicking of transient liquid phases into adjacent components, formation of deleterious crystalline interaction phases between components, and effects of interlayers to prevent limit or prevent diffusion of cations.

In addition to the interactions between components that occur during fabrication and sintering, this program will address mechanisms and effects of interactions that occur during SOFC operation. One of the goals of this work will be to develop valid accelerated testing techniques to predict the long-term performance of SOFC components.

The fabrication and processing of SOFC materials will be further emphasized. These efforts will be integrated with the activities of other DOE and GRI SOFC contractors.

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