FABRICATION OF INTEGRAL FLOW-FIELD / INTERCONNECTS FOR PLANAR SOFC STACKS

Christopher Milliken and Ashok Khandkar
Ceramatec, Inc.
2425 South 900 West
Salt Lake City, Utah 84119

Abstract

Acceptor doped LaCrO₃ materials have been used for interconnects in SOFCs for about 20 years owing to their high conductivity and thermodynamic stability. These materials present fabrication challenges especially related to sinterability. This paper reports on investigations of the effect of processing conditions on the microstructure and properties of doped LaCrO₃ ceramics. LaCrO₃ was green formed by tape casting as well as by uniaxial die pressing. Samples were densified by pressureless sintering in air. Liquid formers were added as sintering aids. Samples were also hot pressed in inert atmosphere in graphite dies. Microstructural examination of the sintered ceramics revealed that in reducing conditions the material reacts with graphite forming complex carbide phases. Such decompositions were found to affect the mechanical stability by propagating microcracks in order to relieve stresses arising from volume changes associated with phase reconstitution. The electrical conductivity of sintered compacts is reported. Conditions for obtaining high densities and thermal and mechanical stability against both structural and chemical phase changes are discussed.
Introduction

Development of planar geometry SOFC stack technology hinges critically on the ability to stack single cells connected electrically in series, with a ribbed bipolar separator serving as the interconnect. The interconnect, with integral flow-fields must channel the anodic and cathodic reactant gases to the electrode/electrolyte interfaces, prevent the direct chemical oxidation of the fuel gas and provide adequate electrical conductance from one cell to the adjacent cell. In a planar bipolar SOFC stack operating at 1273K, the interconnect is exposed to fuel gases which have low oxygen activity ranging between $10^{-20}$ to $10^{-15}$ on the anode side and oxidant gases with high oxygen activities ranging from $10^{-4}$ to $10^{-1}$ on the cathode side. In addition, there may be temperature variations present from the inlet to the outlet side leading to fairly large gradients in current density across the planar interconnect. Thus, the interconnect is typically subjected to extreme environmental conditions of high temperatures, chemical environments and thermal stresses arising from current density variations.

Doped LaCrO$_3$, currently the interconnect material of choice, presents special difficulties in meeting the simultaneous functional requirements of high density, controlled stoichiometry and phase stability during fabrication and fuel cell operating conditions. The primary difficulty in air sintering of LaCrO$_3$ based materials arises from the volatility of Cr from the structure at temperatures in excess of 1400°C, causing porosity to develop. This is minimized by sintering in reducing atmospheres, with oxygen activities of $10^{-12}$ to $10^{-10}$ at 1500-1700°C, as reported by Groupp and Anderson (1). Meadowcroft (2) used SrCO$_3$ and Flandermeyer et al. (3) used low melting oxide eutectics as well as La, Y and Mg fluorides upto 8-10 % by weight to increase density of sintered compacts. In an alternate approach, Balkevich et al. (4) have doped Ca (0.05 atom fraction per LaCrO$_3$ and Anderson (5) have incorporated various dopants, on both A and B sites of the perovskite structure, to enhance the sinterability in air. These dopants presumed to give a hitherto unidentified transient liquid phase, which help sinterability, in air at temperatures below 1500°C. In the fabrication of thin planar LaCrO$_3$ ceramics these sinterability problems pose rather severe challenges in reducing porosity to
acceptable levels. Incorporation of liquid phase sintering aids can lead to variations in sintered density of thin structures as well as to deleterious surface reactions with other materials in direct contact during the sintering process.

A detailed fabrication study on doped LaCrO$_3$ was carried out with a view to determine the effect of processing conditions on microstructure and properties. Methods to obtain high density including variations in fabrication processes, and transient liquid sintering aids were examined. The resulting microstructure and measured properties were correlated with processing conditions. On the basis of the experimental results, the influence of specific processing conditions on the fabrication of the thin planar interconnects and evolution of the microstructure were examined. General conclusions on fabrication and long term stability of LaCrO$_3$ are made. This paper reports on the influence of various fabrication process conditions on the microstructure, properties and phase composition of interconnects.

**Experimental**

Strontium doped LaCrO$_3$, La$_{1-x}$Sr$_x$CrO$_3$ with $x=0.1$ and $0.2$, was made by the liquid mix method (6). Briefly, this process involves dissolving soluble salts of the cations in a citric acid solution (1.14 % by weight), adding ethylene glycol and heating the solution carefully to dryness. The resulting polymer char is calcined at temperatures of between 800-1000$^o$C to burn off all traces of organic residue and form the crystalline powder structure. The composition was characterized to be single phase using XRD. Typically these powders had a surface area of between 14-18 m$^2$/g when calcined at temperatures of between 700-850$^o$C. Densification studies were carried out on pressureless sintered powder compacts, tape cast substrates as well as on compacts sintered under controlled heating rates and temperature, pressure and atmosphere. The starting powders were milled in ethanol or acetone with the binders (1 - 2 % by weight poly-vinyl butyrol, B-78, Monsanto). The powders were dry screened -80 mesh after evaporation of the solvents. Powder compacts were made by uniaxial and/or isostatic pressing at 35 and 200 MPa, respectively,
to the desired shape. Specimens were sintered in air and controlled atmospheres at temperatures between 1400-1650°C. The heating rate was kept constant at 2°/min and 10°/min. Samples were held at temperature for two hours. A ZrO₂ crucible was used to cover the specimens. (This was essentially to "contain" the Cr vapors). Sintering studies were also conducted on doped LaCrO₃ samples obtained from Anderson (Dept. of Mat. Science, University of Missouri, Rolla). Alternatively, hot pressing was performed at temperatures between 1200-1600°C in an Ar environment, using graphite dies loaded uniaxially under a pressure of 28-30 MPa. Densities were measured by the Archimedean method and correlated with porosity measurements on polished cross-sections observed by optical microscopy and scanning electron microscopy. The effect of sintering aids and process conditions was determined from examination of the microstructures using scanning electron microscopy (SEM) complemented with measurement of electrical conductivity (2- and 4-probe AC and DC methods), determination of phase assemblage by X-ray diffraction (XRD), analytical microscopy such as scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA) and thermal expansion characteristics.

Results and Discussion

Liquid Phase Sintering

Sr-doped LaCrO₃ compacts made by uniaxial compaction at 35 MPa gave typical green densities of about 42 - 45% of theoretical. Specimens pressed uniaxially followed by iso-static pressing at 200 MPa gave somewhat higher green densities of about 45 - 48% of theoretical. Sintered densities at temperatures between 1500 and 1650°C yielded densities of 58-80% of theoretical, consistent with the literature. Microstructural examination of polished cross-sections revealed a gradation in porosity with increased porosity at the surface. A greater amount of porosity was observed at the higher sintering temperatures. This is to be expected owing to the greater volatility of Cr at the higher sintering temperatures. Specimens compacted using iso-static pressing sintered to greater densities (upto 80% of theoretical) compared to those compacted by uniaxial pressing alone. No significant effect of heating rate was
observed. The La$_2$O$_3$-Cr$_2$O$_3$ phase diagram (7) suggests that transient liquid phase sintering may not occur below about 1900°C and hence no major effect of heating rate is to be expected. SEM examination of the calcined powders showed that they were porous agglomerates (15-20 μm mean size) with rather well formed necks between sub-micron sized primary particles. Figure 1(a) shows the morphology of La$_{0.9}$Sr$_{0.1}$CrO$_3$ calcined at 850°C and milled for 6 hours in ethanol using ZrO$_2$ media. Figures 1(b) and (c) show particle morphology after milling for 8 and 24 hrs. While the mean particle diameter has reduced there appears to be a substantial fraction of hard agglomerated particles. Sinterability studies on these milled powders are incomplete, however preliminary results show that green powder compacts have densities similar to those of powders milled for 8 hrs. Addition of lubricants such as polyethylene glycol helped to increase both green density and sintered density. These results are tabulated in Table 1.0

Several sintering aids were selected, from among transition metal and alkaline earth halides, on the basis of melting point, valence and ion size. The sintering aid ideally would assist in mass transport aiding the sintering process and would then completely

### Table 1.0

| Compaction                  | Density (% Theoretical) | Comments       |
|-----------------------------|-------------------------|----------------|
|                             | Green                  | Sintered       |
| Uniaxial                    | 40                      | 58             | 1% PVB       |
| Uniaxial + Iso-static       | 47                      | 66             | 1% PVB       |
| Uniaxial                    | 47                      | 72             | 1% PVB + PEG |
| Uniaxial + Iso-static       | 53                      | 80             | 1% PVB + PEG |
| Uniaxial + Iso-static       | 55                      | 90             | 1% PVB; powder milled for 24 hrs. |
volatalize off without contaminating the grain boundaries (with a deleterious effect on the conductivity). With regard to the possible chemical effects, formation of insulating phases at the grain boundaries may not be entirely ruled out. Since the thermodynamic properties of many possible phases are not known, selection was made on the assumptions that any slight solubility of cations from the sintering aid should not be deleterious from the standpoint of conductivity. From prior literature as well as on the basis of initial trials, about 2% (atom fraction) of the sintering aid was milled into the LaCrO$_3$ powders as described above. Densification was clearly aided by the use of the fugitive sintering aids. Figure 2 shows the fired density for the selected sintering aids and Figure 3 shows the density variation as a function of the melting temperature and ionic size. Among the different sintering aids evaluated, MgF$_2$ was shown to be the best sintering aid. In order to determine an optimal MgF$_2$ content, various amounts of MgF$_2$ were added and sinterability was investigated. Figure 4 shows that about 2% (atom fraction) of MgF$_2$ is adequate in densifying LaCrO$_3$. EPMA results on polished cross-sections of such specimens revealed clean grain boundaries with no Mg concentration at internal surfaces. Measured conductivities, plotted in Figure 5, on cylindrical specimens using standard 2-probe ac impedance methods and on bar specimens using 4-probe dc techniques were in agreement with previously reported literature values (8,9) indicating no effect of the sintering aid on the electronic conduction properties. The bulk thermal expansion coefficient measured using a dilatometer was also in agreement with the literature.

**Sintering of Thin Planar Interconnects**

Sintering of thin (100-150 μm thick) tape cast LaCrO$_3$ interconnects resulted in a graded porosity microstructure similar to that described earlier. The sintered ceramic interconnects were fragile and exhibited systematic differences in surface conductivity which could be correlated with changes in stoichiometry of the surface layers compared to the bulk. Figure 6 shows the profile of normalized elemental Cr, Sr and La map across a 120 μm thick interconnect. The top surface shows Cr depletion and an associated La enrichment. The Sr content is uniform across the specimen. The
arrows point to a Cr enriched area (with a corresponding La depleted area) along the profile. This is due to the presence of a large pore in the thin planar structure where Cr enrichment occurs most probably by the predominant evaporation-condensation mass transport mechanism operative at the sintering temperatures. Previous studies on volatilization of Cr$_2$O$_3$ (10) suggest that Cr volatilizes off by forming CrO$_3$ vapor. Assuming a similar volatility mechanism to be operative, the defect reaction can be written as:

$$3\text{Cr}^x + \frac{3}{2} \text{O}_2 \rightarrow \text{V}_{\text{Cr}} + \text{CrO}_3 + 3\text{h}^+$$ \[1\]

Electronic conductivity in LaCrO$_3$ materials is p-type arising from charge compensation of Cr$^{3+}$ to Cr$^{4+}$ (electron holes) upon divalent ion substitution on the La$^{3+}$ sites. The proposed conductivity mechanism is due a small polaron hopping on the Cr sites. This hole carrier density is sensitively affected by non-stoichiometry arising from Cr volatility. Associated with the Cr loss and the resulting Cr vacancies $\text{V}_{\text{Cr}}$, additional p-type defects may be formed in the lattice. This causes an increase in conductivity at the surface as was determined using the van-der Pauw technique. The above reaction assumes some non-stoichiometry being permitted on the Cr sub-lattice in the perovskite structure. The phase diagram shows that LaCrO$_3$ is a line compound and therefore Cr loss must be accompanied by precipitation of La$_2$O$_3$. Although the exact surface concentrations could not be estimated and while no La$_2$O$_3$ or La(OH)$_3$ was detected in XRD examination, clear evidence of non-stoichiometry in the Cr sub-lattice was seen from the EPMA results.

The above results suggest that in tape cast structures where the surface is a greater fraction of the ceramic compared to powder compacts, vapor transport and surface diffusion effects dominate the initial sintering process. This is because these processes generally tend to have lower activation energies and greater values than other mass transport processes. During the temperature regime where the sintering aid is molten, some particle rearrangement is expected. At higher temperatures, once the liquid evaporates from the ceramic, the dominant mechanism that will contribute to densification will be bulk diffusion. The build up of the CrO$_x$ rich phase in inter-particle necks with concomitant loss in grain surface area must greatly reduce the driving force for
sintering. This can be inhibited by two factors: the diffusion distances are greater because of neck growth (possibly resulting in pore isolation also) as well as increased Cr volatility at the higher temperatures. The implications for sintering of thin planar interconnects, with or without integral flow-fields, are that a minimum amount of sintering aid must be used so as to minimize porosity caused by decomposition and volatility of the sintering aid. Further, in case of liquid phase assisted sintering, the sintering aid must be uniformly dispersed not only between agglomerates but also within each agglomerate. This will ensure uniform wetting of individual crystallites thus greatly aiding in densification. Alternative fabrication methods which give more uniform and high density green bodies with smaller interstices between agglomerates may alleviate densification problems. Ideally, appropriate dopants in LaCrO₃ which have a transient eutectic liquid phase at temperatures below 1500°C, would be the best choice. Development in the latter direction is being carried out by Anderson (5) as well as by the authors.

*Hot Pressed LaCrO₃*

Extensive work was performed to establish optimal hot pressing temperatures and time schedules required for densifying LaCrO₃. Some hot pressing was also done with dies machined with flow-field grooves. Typical densification curves are shown in Figure 7. The powders were pressed for a minimum of 40 min. after reaching the desired highest temperature. Hot pressing could be accomplished at a minimum temperature of 1450°C at pressures of about 28 MPa. Generally, densification stopped after about 40 minutes at temperature. Typical densities obtained were in excess of 98% of theoretical in the bulk of the specimens. This is attributed to particle sliding and rearrangement upon application of pressure. Further, the reducing conditions suppress the volatility of Cr thus enabling the densification process. Figure 8 shows the strain rate as function of temperature. The curve shows two densification regimes at about 1200 and at 1500°C. XRD of the surface of the as hot pressed specimens revealed the presence of additional phases such as La₂O₃, and the complex carbide Cr₂₃C₆. XRD of the bulk of the hot pressed specimens did showed peaks attributable to LaCrO₃ alone suggesting that the LaCrO₃ may have
reacted with graphite at the surface only. Examination of the microstructure for phase composition using EPMA revealed some La enrichment associated with pores both in the bulk as well as at the surface. Long term exposure of such hot pressed specimens to ambient air at room temperature caused the surface to form a powdery film which was identified by XRD as La(OH)$_3$. Eventually, these specimens disintegrated. These latter observations support the XRD results.

The phase assemblage in hot pressed specimens can be understood by considering the thermodynamic stability of LaCrO$_3$ during the hot pressing process. The oxygen activity in the hot-press is controlled by C/CO equilibrium given by the reaction:

$$2C + O_2 \rightarrow 2CO$$ .................................................. [2]

The equilibrium oxygen partial pressures for reaction [2] are plotted in Figure 9. Also plotted are the oxygen partial pressures for reaction [3] as below:

$$\frac{4}{3}Cr + O_2 \rightarrow \frac{2}{3}Cr_2O_3$$ .................................................. [3]

Although thermodynamic data for Sr-doped LaCrO$_3$ are not known, reaction of LaCrO$_3$ to form the complex Cr carbide phase appears to be favored under the experimental condition used. The reaction pathway is difficult to predict in the absence of available thermodynamic data. Based on the present results it appears likely to proceed directly by the carbothermal decomposition of LaCrO$_3$ to form the carbide phase at the surface. Figure 10(a) shows the microstructure of a hot-pressed specimen exhibiting high density in the bulk and surface porosity at the graphite/ceramic interface. In Figure 10(b), the light contrast specks seen in the micrograph confirm the presence of Cr rich inclusions in the bulk. From the EPMA results the normalized Cr/C molar ratio can be calculated to be 1.7:1. This could result from a mixture of Cr and Cr-carbides or a mixture of Cr carbides of differing stoichiometry ranging from 1.5:1 to 3.83:1. A La/Cr molar ratio about 2:1 was detected in association with these Cr rich areas, suggesting that La$_2$O$_3$ lies in the vicinity of the Cr-rich inclusions. The possibility that LaCrO$_3$ could dissociate to form La$_2$O$_3$ and Cr$_2$O$_3$ with a simultaneous reaction to
form Cr$_2$C$_6$ may not be discounted. In iso-structural compounds such as Sr-doped LaMnO$_3$ as well as spinels such as MgCr$_2$O$_4$ such dissociations are well documented.

Conductivities of the as hot pressed surface, measured at room temperature by the Van-der Pauw method, indicated that the conductivity was about two orders of magnitude below that of specimens sintered in air. This degradation is due to the surface reactions of LaCrO$_3$ with the graphite die hardware. On grinding off this surface layer, the conductivity was measured to be lower compared to specimens sintered in air. This is readily understood by considering that in low activities of oxygen, the defect structure of p-type LaCrO$_3$ will be dominated by oxygen vacancies with charge compensation given by:

\[
\begin{align*}
O^x_0 & \rightarrow \frac{1}{2} V^{\cdot\cdot}O + \frac{1}{2}O_2 + 2e^- \quad \text{[4]} \\
\text{and} \quad Cr^x_{Cr} + e^- & \rightarrow Cr^x_{Cr} \quad \text{[5]}
\end{align*}
\]

On annealing these hot pressed specimens at 1000°C in air for about 8 hours, the conductivity recovered to values similar to that of specimens sintered in air. This is consistent with the microstructural observations. However, after annealing, the specimens warped presumably due to volume expansion of the lattice caused by oxygen uptake. This caused micro-cracking in the ceramic especially in ribbed interconnects with integral flow-fields. This is not surprising since differential stresses caused by volume expansion will be greater at regions where the cross-section of the ceramic changes.

These results suggest that the defect structure of hot pressed specimens is dominated by effects of oxygen non-stoichiometry in the LaCrO$_3$ lattice. Even if the interconnect material is "reduced" during hot pressing, the amount of La$_2$O$_3$ and Cr$_2$O$_3$ phases present in the microstructure are below detectable limits of XRD and, in any case, do not affect conductivity. The effects on long term stability are currently unknown and are being assessed by in-cell tests.
Conclusions

Powder compacts of Sr doped LaCrO₃ can be sintered to high densities with closed porosities by incorporating liquid formers such as MgF₂. The benefit of such liquid formers is difficult to realize for thin tape cast bodies, where a porosity gradient is formed with the surface layers having greater porosity. The volatility of Cr appears to be the main factor inhibiting densification of such structures.

Hot pressing was used primarily as a method of obtaining fine grained well sintered specimens of near theoretical density and as a tool to study sinterability of LaCrO₃ ceramics. While the technique is cumbersome and most likely not commercially viable for fabrication of SOFC interconnects, sinterability was shown to be greatly enhanced by the combined use of reducing atmospheres and pressure. The reaction products with graphite are localized at the surface of the ceramic and the graphite die interface and do not affect the conductivity after removal of the surface layers by grinding and annealing in air. The phase assemblage in the bulk of hot pressed LaCrO₃ ceramics can be controlled to give oxygen deficient LaCrO₃. The conductivity can be as high as air sintered specimens after annealing in air. However, stresses arising from differential expansion can cause microcracking of interconnects, especially those with integral flow fields.

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FIGURE 1(a) - TYPICAL MORPHOLOGY OF \( \text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3 \) CALCINED AT 800°C AND MILLED IN ETHANOL FOR 6 HRS.

FIGURE 1(b) - POWDER MORPHOLOGY OF \( \text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3 \) CALCINED AT 800°C AND MILLED IN ETHANOL FOR 8 HRS.

FIGURE 1(c) - POWDER MORPHOLOGY OF \( \text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3 \) CALCINED AT 800°C AND MILLED IN ETHANOL FOR 24 HRS.
FIGURE 10(a) - MICROGRAPH OF HOT PRESSED LSC SHOWING DENSITY GRADIENTS AND SURFACE REACTION LAYER (133X)

FIGURE 10(b) - MICROGRAPH OF HOT PRESSED LSC SHOWING Cr RICH INCLUSIONS (LIGHT CONTRAST SPECKS, 1330X)