INSTABILITIES IN DOPED LANTHANUM CHROMITE IN REDUCING ENVIRONMENTS

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ABSTRACT

Lattice expansion, phase stability, and dimensional stability of interconnect materials, particularly acceptor doped lanthanum chromites, have been examined over a wide range of temperatures and oxygen partial pressures. Reduction of doped lanthanum chromite caused a substantial increase in the unit cell volume. Expansion of the chromites was found to be rapid and reversible showing expansion at temperatures as low as 700°C. The critical oxygen partial pressure at which expansion was observed was found to decrease with decreasing acceptor dopant concentration and with decreasing operation temperature.

INTRODUCTION

One of the most critical technical challenges hindering development of solid oxide fuel cells (SOFC) is the development of an air sinterable interconnect material that is stable at high-temperatures in a variety of environments. The role of the interconnect is two-fold; it acts as an electrical connection linking individual cells in series and as a gas separation barrier preventing mixing of the fuel and air. The chosen material must have high electronic conductivity, a thermal expansion match to the other cell components, high mechanical strength, high thermal conductivity, and be chemically and physically stable in reducing and oxidizing environments at 1000°C. The only known materials that meet these requirements at high temperature are alkaline earth doped lanthanum chromite ((La, Sr, Ca)CrO3) and yttrium chromite ((Y, Ca)CrO3).

The interconnect in an SOFC is subjected to a dual atmosphere (air on one side and fuel on the other). The oxygen partial pressure, P(O2), of the incoming fuel may be as low as 10^{-18} atmospheres, and may rise to 10^{-8} atmospheres after depletion of the hydrogen from the fuel stream. On the oxidant side of the interconnect the P(O2) will exceed 10^{-6} atmospheres. The result is an extreme oxygen partial pressure gradient across the interconnect that may result in gradients in the electrical conductivity, thermal expansion, and mechanical strength.
In recent years, work on lanthanum chromite has centered on developing materials that will sinter at temperatures less than 1400°C. Very little work has focused on evaluating the stability of chromites in reducing environments (1-4). Two independent studies have shown that lanthanum chromites expand on reduction (1,2), with the expansion being greatest at oxygen partial pressures well within the effective operating range of an SOFC. Further, it has been reported that linear expansion of doped chromites increases with both decreasing P(O2) and increasing dopant concentration (Ca or Sr) (2). Other studies of lanthanum chromite in reducing environments have shown immediate and drastic decreases in mechanical strength and electrical conductivity, as well as phase segregation in the microstructure (3-5). The purpose of this study was to fully evaluate the affects of reducing environments on stability, crystal structure, phase homogeneity of alkaline-earth doped lanthanum and yttrium chromite.

**EXPERIMENTAL PROCEDURE**

(La1-xSrx)CrO3 and (La1-xCax)CrO3 powders, where x was varied from 0.1 to 0.4, were synthesized using the glycine-nitrate process (6). All powders synthesized for this study had an A/B ratio equal to unity. The powders were precalcined at 650°C for 0.5 hour to decompose any residual organic material and then calcined at 1000°C for 1 hour. The powders were uniaxially pressed into bars (46mm x 16mm x 3mm) at 55 MPa followed by isostatic pressing at 138 MPa for dilatometric studies. Samples were sintered in air at 1500° to 1650°C for 5 hours. The density of (La1-xSrx)CrO3 and (La1-xCax)CrO3 samples when x was greater than 0.2 were greater than 90% of theoretical density for samples sintered in air at 1650°C (5 hrs). When x was less than 0.2 the sintered density was ~80% of theoretical. All (Y1-xCax)CrO3 had sintered densities greater than 95% ThD when sintered at 1600°C for 5 hours.

Dilatometry and thermogravimetric analysis measurements (TGA) were used to study the dependence of the physical properties of sintered lanthanum chromites on ambient P(O2) and temperature. Dilatometry experiments were carried out on sintered bars (10 mm x 3mm x 3mm) with densities similar to those reported earlier. Dilatometry experiments as a function of the P(O2) were carried out using a buffered CO2/Ar-4%H2 gas system, enabling expansion measurements to be made over an oxygen partial pressure range from 10^-5 to 10^-18 atmosphere at 800, 900, and 1000°C. To ensure complete mixing of the gases, flow rates of 300 sccm were used. Drag forces from the gas flow in the dilatometer were evaluated and corrected for by carrying out similar experiments using an invariant standard (Al2O3, 99.9% dense). Calibration curves generated as a function of temperature and P(O2) were used to normalize the expansion measurements on the chromite specimens. Samples were initially heated at 2°C/min to the soak temperature (700 to 1000°C) in air and allowed to equilibrate for approximately 1 hour. After equilibration the oxygen partial pressure was changed, and measurements were taken until sample expansion was no longer noticeable. This process was repeated until data over the complete P(O2) range was collected. TGA measurements were carried in an Ar-4%H2 gas system at temperatures between 700°C and 1000°C. X-ray diffraction analysis was carried out on all samples sintered in air to determine the lattice parameters and phase homogeneity. All samples in this study were single phase perovskite after synthesis. Samples reduced at 10^-18 atmospheres were cooled under reducing conditions to room
temperature and evaluated using x-ray diffraction to evaluate changes in the lattice parameters as a result of reduction.

RESULTS AND DISCUSSION

Figure 1 is a plot of the isothermal linear expansion relative to the dimension in air at 700, 800, and 900°C for La$_{0.76}$Sr$_{0.24}$CrO$_3$ (denoted LSC-24) as a function of time. The specimens were equilibrated in air, reduced in Ar-4% H$_2$, and then re-oxidized in air. It was observed that the expansion in reducing environments was rapid at 800°C and 900°C (approaching equilibrium in one to two hours) and reversible. When air was introduced the samples contracted very rapidly to within ~0.05% of their initial length. This figure indicates that LSC expands significantly at temperatures as low as 700°C and that the kinetics of the reaction increase with temperature due to an increasing oxygen exchange rate (7).

Figure 2 shows the effect of decreasing P(O$_2$) on the linear expansion of LSC-24 as a function of temperature. This sample showed no effect of reducing environment from ambient pressure to 10$^{-8}$ atmosphere at 1000°C. As the P(O$_2$) was lowered further, the sample steadily expanded, reaching a maximum expansion of ~0.23% at 10$^{-18}$ atmospheres. Figure 2 also clearly shows that the onset (critical oxygen partial pressure) of expansion moved towards lower oxygen partial pressures with decreasing temperature. Both figures 1 and 2 indicate that the magnitude of expansion decreases with decreasing temperature.

Figure 3 is a plot of isothermal expansion at 1000°C as a function of P(O$_2$) for La$_{1-x}$Sr$_x$CrO$_3$ where x was varied from 0.16 to 0.30. This data indicates that the expansion of these materials increased not only with decreasing P(O$_2$) but also with increasing Sr content on the A-site. The critical oxygen partial pressure at which expansion was first observed was higher for samples having Sr concentrations greater than 20 mole percent.

Figure 4 shows a comparison between LSC-20 data of Srilomsak et al. (1) and the present measurements for LSC-20 and LSC-24. There are significant differences between the two sets of data. The onset of expansion reported by Srilomsak et al. occurred at 10$^{-10}$ atmospheres, two orders of magnitude higher than equivalent samples examined by the authors. A second notable difference is in the magnitude of the expansions. This 40% difference may be due to the presence of strontium chromate, SrCrO$_4$, as a secondary phase in the sample measured by Srilomsak et al. (1). Observations of single phase Sr and Ca chromate indicate that they expand rapidly on reduction and decomposition. The critical partial pressure increases with increasing temperature. Significant amounts of secondary chromate phase may enhance the expansion upon reduction. Another plausible explanation is that the composition of the sample may be closer to LSC-24 than LSC-20 as indicated by the similarity of data in Figure 4.

Specimens with either Sr or Ca show similar expansion behavior in reducing environments. Figure 5 shows a plot of the isothermal linear expansion at 700, 800, and 900°C for La$_{0.7}$Ca$_{0.3}$CrO$_3$ (denoted LCC-30) as a function of time in an atmosphere of
As observed previously in LSC-24 the expansion is reversible and the degree of expansion increases with temperature. However, in LCC-30 the amount of expansion the sample undergoes at 700°C is considerably less than that for comparable Sr materials. Figure 6 shows the linear expansion of La_{0.7}Ca_{0.3}CrO_3 as a function of temperature and oxygen partial pressure. At 800°C the critical oxygen partial pressure is 10^{-14} atmospheres and increases to 10^{-10} at 1000°C. The maximum expansion at 10^{-18} atmospheres was 0.24% at 800°C and 0.37% at 1000°C.

Acceptor doping of lanthanum chromite (substitution of Sr or Ca for La) can be charge compensated either electronically (through the conversion of Cr^{3+} to Cr^{4+}) or ionically (through the creation of oxygen vacancies), as shown by the electroneutrality relation in Equation 1 (Kroger-Vink notation; brackets denote concentration).

\[ [\text{Sr}_{\text{La}}] = [\text{Cr}_{\text{Cr}}^+] + 2[\text{V}_o^-] \]  \hspace{1cm} [1]

At high oxygen partial pressures, this compensation is electronic, as verified experimentally in a study by Pederson and Dake using XPS (8) in which the Cr^{4+} concentration was found to be equivalent to the A-site acceptor concentration. At low oxygen partial pressures, charge compensation is dominated by the formation of oxygen vacancies, as shown in Equation 2.

\[ \text{La}^{3+}_x \text{M}^{2+}_x \text{Cr}^{3+}_x \rightarrow \text{La}^{3+}_x \text{M}^{2+}_x \text{Cr}^{4+}_x + 2\text{O}_2 \]  \hspace{1cm} [2]

TGA analysis on these samples by the authors has verified an appreciable decrease in mass due to oxygen evolution during reduction (9). The weight loss (vacancy formation) and gain due to oxygen removal and uptake from the lattice correspond well with the observed reversible linear expansion as well as with electrical conductivity measurements carried out by others (10,11). Based on this information, it would be expected that increasing the acceptor concentration in lanthanum chromites would result in increased expansion upon reduction as the higher initial concentration of Cr^{4+} is reduced to Cr^{3+}, resulting in an increased concentration of oxygen vacancies in the lattice.

The removal of oxygen from the perovskite lattice results in an increase in lattice cell dimensions, and, therefore, an increase in specimen volume as indicated by Srilomsak et al. (1) and Armstrong et al. (9). The observed expansion may result from the increase in cation size accompanying the reduction of Cr^{4+} to Cr^{3+} and/or an electrostatic repulsive forces between adjacent Cr cations separated by oxygen vacancies. The changes in cell volume, as determined by XRD analysis, are shown in Table I. Samples were reduced at 800 to 1000°C and cooled under reducing conditions to prevent re-oxidation of the sample.

Comparison of the LSC-30, LCC-30 and LSC-20 and LCC-20 expansion data is shown in Figure 7. In both cases the Ca doped lanthanum chromite expands more than the Sr doped lanthanum chromite. Studies are in progress to determine the cause of this
difference in behavior. It is possible that, in the same reducing atmosphere, LSCs are more stable toward oxygen loss than the LCCs. Alternatively, the oxygen loss in a given atmosphere may be the same for both materials, but the LSC lattice may expand less than the LCC lattice.

Figure 8 shows data for linear expansion as a function of dopant content from this study and from Schafer and Schmidberger (2) in 10^{-15} atm P(O_2) at 1000°C. In both studies, it is apparent that the relationship between expansion and dopant content was approximately linear over a wide range of composition. The relationship between sample expansion and dopant concentration (denoted by the slope) is 0.013% expansion/mole % dopant for LSC and 0.015% expansion/mole % dopant for LCC materials. It is clear, however, (from the fact that the linear fits shown in Figure 8 have negative y-intercepts) that this linearity cannot hold for very low dopant levels. The data presented in Figure 8 show very good agreement over the entire composition range for the LSC materials. However, there is a large disparity between the expansion measurements for the two sets of LCC data presented in this figure. The data presented by the authors are similar to that of LSC. The data by Schafer and Schmidberger (2) show a significant deviation. While still linear, their data shows nearly a 1:1 correlation between the expansion and the Ca concentration. The data of Schafer more closely match the expansion data at 10^{-18} atmospheres obtained in the present investigation.

Table I. Change in Unit Cell Volume After Reduction in a P(O_2) of 10^{-18} atm

| Composition | Temp. (°C) | Oxidized Volume (Å³) | Reduced Volume (Å³) | Change in Volume (%) |
|-------------|------------|----------------------|---------------------|---------------------|
| LCC-15      | 1000       | 231.7                | 233.0               | 0.56                |
| LCC-20      | 1000       | 230.8                | 231.8               | 0.40                |
| LCC-25      | 1000       | 230.1                | 231.7               | 0.70                |
| LCC-30      | 1000       | 228.2                | 231.3               | 1.34                |
| LCC-30      | 900        | 228.2                | 231.2               | 1.25                |
| LCC-30      | 800        | 228.2                | 229.4               | 0.52                |

LCC-15 = La_{0.85}Ca_{0.15}CrO_3

CONCLUSIONS

Alkaline-earth doped lanthanum chromites expand readily when reduced in oxygen partial pressures less than 10^{-8} atmospheres. The expansion is rapid and reversible. The onset of expansion, critical P(O_2), shifts to lower oxygen partial pressures with decreasing temperature and decreasing alkaline earth content in the interconnect. Furthermore, the degree of expansion observed in the samples at any P(O_2) was dependent on the dopant concentration and the temperature; sample expansion increased with increasing temperature and dopant concentration. The relationship between sample expansion and dopant concentration was linear for A-site dopant levels exceeding 0.15 mole percent. Similarly, the relationship between sample expansion and temperature was linear except at 10^{-18} atmospheres. Observations indicate that the expansion may be a result of two processes: 1) the increase in size of the Cr ion resulting from reduction from
the +4 to +3 oxidation state, and 2) from changes in the electrostatic nature of the unit cell due to oxygen vacancy formation that accompanies the change in chrome oxidation state (see Equation 2).

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Figure 1. Linear Expansion of LSC-24 in Ar-4%H₂ at 700°, 800° and 900°C.

Figure 2. Linear Expansion of LSC-24 as a Function of Temperature and Oxygen Partial Pressure.

Figure 3. Linear Expansion of La₁₋ₓSrₓCrO₃ as a Function of Oxygen Partial Pressure at 1000°C.

Figure 4. Comparison of LSC-20 Linear Expansion Data.
Figure 5. Linear Expansion of LCC-30 in Ar-4%H₂ at 700°, 800° and 900°C.

Figure 6. Linear Expansion of LCC-30 as a Function of Temperature and Oxygen Partial Pressure.

Figure 7. Comparison of Linear Expansion Data of 20 and 30 Mole Percent Doped LSC and LCC at 1000°C.

Figure 8. Maximum Linear Expansion at 10⁻¹⁵ atm (1000°C) for LSC and LCC compared to Similar Data From Ref. (2)