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INTRODUCTION

One of the most critical technical concerns in high-temperature SOFCs is the physical, chemical, and electrical stability of the interconnect (typically a doped lanthanum chromite) in the dual (oxidizing and reducing atmosphere) SOFC environment. The reducing or fuel side may experience oxygen partial pressures ($P(O_2)$) from 10^{-18} to 10^{-6} atmospheres, while the oxidizing side may have $P(O_2)$ from 10^{-6} to greater than 1 atm. These conditions limit the possible candidate materials to lanthanum or yttrium chromites. In the past decade, much work has centered on development of air-sinterable chromites and understanding their physical properties; little work, however, has focused on the stability of these chromites in dual environments.¹⁻³

Anderson^{4,5} has shown that oxygen vacancies form in doped lanthanum or yttrium chromites in oxygen partial pressures below 10^{-10} atmospheres at 1000°C. Schafer and Schmidberger¹ have reported that linear expansion of doped chromites increases with both decreasing $P(O_2)$ and increasing dopant concentration (Ca or Sr). Milliken et al.³ observed immediate and drastic decreases in the mechanical strength of the interconnect upon exposure to a reducing environment. Sakai et al.² found that both Ca or Sr modified lanthanum chromite showed phase segregation upon prolonged exposure to dual environments.

EXPERIMENTAL

Chromite powders were synthesized using the glycine-nitrate process. The powders were calcined at 1000°C for 1 hour and then uniaxially pressed into bars (46mm x 16mm x 3mm) at 55 MPa and isostatically pressed at 138 MPa. Samples were sintered in air. The dependence of the physical properties of sintered lanthanum chromites upon ambient $P(O_2)$ and temperature (using dilatometry, thermogravimetric analysis, and oxygen permeation measurements) were studied. $La_{1-x}A_xCrO_3$ and $Y_{1-x}Ca_xCrO_3$, where A is Ca or Sr and x was varied from 0.1 to 0.4 were evaluated in this study. The $P(O_2)$ was varied using a buffered CO_2/Ar -4% H_2 gas system, enabling expansion measurements to be made over a partial pressure range from 10^{-5} to 10^{-18} atmosphere at 800, 900, and 1000°C.

RESULTS AND DISCUSSION

Figure 1 shows a plot of the isothermal linear expansion at 800, 900, and 1000°C for $La_{0.7}Ca_{0.3}CrO_3$ (denoted LCC-30) as a function of $P(O_2)$. This sample shows no effect of reducing environment from ambient pressure to 10^{-9} atmosphere at 1000°C. At lower oxygen partial pressures the sample steadily expands, reaching a maximum expansion of $\approx 0.35\%$ at 10^{-18} atmospheres. Figure 1 also clearly shows that the onset of expansion moves towards lower oxygen partial pressures with decreasing temperature, indicating an increase in activation energy necessary for the expansion to occur. After the critical $P(O_2)$ has been reached the expansion process occurs rapidly and reaches equilibrium within one to two hours, as indicated in Figure 2. Figure 2 is a plot of the isothermal linear expansion of $La_{0.7}Ca_{0.3}CrO_3$ as a function of temperature and time in Ar-4% H_2 . It was observed that the expansion behavior at 1000°C (not shown) was very similar to the expansion at 900°C. This figure indicates that the expansion

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is rapid and reversible and the kinetics of the reaction increase with temperature, but change little above 900°C.

Figure 3 shows a plot of isothermal expansion at 1000°C as a function of $P(O_2)$ for LCC-30, LSC-30 and YCC-30. The maximum expansion at 10^{-18} atm for LCC-30 is 0.37%, LSC-30 is 0.33% and YCC-30 is 0.20%. This data indicates, that for doped lanthanum chromite, the expansion increases the size of the A-site dopant decreases. Further, the data indicates that yttrium chromite expands significantly less than lanthanum chromite for the same concentration of calcium.

The expansion observed in these samples can be directly related to the formation of oxygen vacancies as reported by Anderson^{4,5} and the reduction of Cr^{4+} to Cr^{3+} as shown in equation 1:

The removal of oxygen anions from the perovskite lattice eliminates the electrostatic attraction between those anions and the surrounding cations, causing increased electrostatic repulsion between those unshielded cations. The net result is an increase in lattice cell dimensions, and, therefore, an increase in specimen volume. While the reduction of Cr^{4+} to Cr^{3+} may also contribute to the expansion of the unit cell, it is believed that the reduction in shielding potential is the dominant mechanism of expansion in these materials.

It is well known that A-site enriched chromites undergo liquid phase sintering due to the formation of transient liquids at elevated temperatures. These liquids are a result of calcium chromate, which exsolves from the perovskite lattice at ≈ 700 to $1000^\circ C$ and then melts at $1050^\circ C$. At $1200^\circ C$, the calcium chromate appears to redissolve into the perovskite lattice. After sintering, these chromites contain liquid-phase remnants. Evidence of liquid formation has not been reported in A-site depleted samples, although these have been found to contain isolated Cr-rich deposits. It has not been reported in the literature whether this phenomena of chromate exsolution is reversible when the samples are thermally cycled or how the remnant liquid phase in the microstructure reacts when exposed to reducing environments.

The microstructure of $La_{1-x}Ca_xCrO_3$ samples was examined after exposure to reducing environments, oxidizing environments (control), and/or sequential exposure to reducing and oxidizing conditions. Control samples examined after sintering or after heating in air at $1000^\circ C$ showed no discernible phase segregation or impurity phases at the grain boundaries. Similarly, samples exposed to severe reducing conditions (10^{-18} atm at $1000^\circ C$) showed no phase segregation. However, $La_{1-x}Ca_xCrO_3$, particularly where x was 0.3 or greater, showed a change in the fracture mechanism after exposure to a reducing environment. Prior to reduction, $La_{0.7}Ca_{0.3}CrO_3$ showed intergranular fracture. After reduction, however, the fracture mechanism changed to intragranular fracture. This indicates that grains became weakened as a result of the large lattice expansion that the sample experienced.

Samples undergoing sequential exposure showed other microstructural features. After sequential exposure to a reducing and oxidizing environment, a Ca- and Cr-rich secondary phase was apparent in the microstructure. This phase was most likely calcium chromate and an amorphous phase similar in composition. The fracture mechanism changed following reduction. After re-oxidation, however, the fracture mechanism was intragranular. Intergranular fracture occurred in the sequentially exposed samples due to the presence of a weak grain boundary phase, either calcium chromate or an amorphous phase.

The presence of calcium chromate can be supported by thermogravimetric analysis (TGA) of the $La_{1-x}Ca_xCrO_3$ samples during the oxidation-reduction process. Because oxygen is being removed

from the lattice it can be directly monitored by weight loss measurement. Figure 4 shows a typical TGA plot of $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ during reduction and reoxidation. The weight loss due to oxygen removal from the lattice corresponds with the sample's linear expansion. Further, upon reoxidation there is a net gain in mass of oxygen. This may be direct evidence of the formation of calcium chromate in the microstructure, since the formation of this phase is accompanied by a net gain in oxygen. Repeated reduction and re-oxidation led to greatly enhanced rates of weight loss and gain, indicating a permanent change in microstructure.

The chromite interconnect in an SOFC should be gas-tight because, in multi-stack planar designs, it directly connects the fuel electrode of one cell with the air electrode of another. If the interconnect is not gas-tight, part of the fuel will be consumed without producing any electricity. Partial reduction of the interconnect at the fuel electrode can create oxygen vacancies and support ionic transport of oxygen from the air to the fuel side. Estimations of the likely oxygen flux in these materials vary by more than two orders of magnitude.^{6,7}

Oxygen flux through sintered LCC pellets were determined using mass spectrometry. Flowing air or oxygen was present on one side, while Ar-4% H_2 was introduced on the other. The seals were determined to be helium leak-tight. Rates of permeation were calculated both from the quantity of water that was produced on the hydrogen side and from the quantity of hydrogen that was consumed. Permeation rates were 0.035 sccm/ cm^2 at 825°C increasing to 0.045 sccm/ cm^2 at 925°C. Permeation rates are in reasonably good agreement with the findings of Yokokawa et al.⁷, but considerably smaller than those given by Yasuda and Hikita.⁶ It is noted that a small oxygen permeation may be beneficial, allowing the effective oxygen activity within the interconnect to remain high enough that lattice expansion is avoided.

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Figure 1. Isothermal linear expansion for LCC-30 as a function of oxygen partial pressure and temperature.

Figure 2. Isothermal linear expansion for LCC-30 as a function of time. Reduction in 4% hydrogen in argon followed by re-oxidation in air.

Figure 3. Isothermal linear expansion for the indicated compositions as a function of oxygen partial pressure at 1000°C.

Figure 4. TGA results for LCC-30 in air and in 4% hydrogen in argon.