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MIXED OXYGEN ION/ELECTRON-CONDUCTING CERAMICS FOR OXYGEN SEPARATION

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ABSTRACT

Solid mixed-conducting electrolytes in the series $La_{1-x}A_xCo_{1-y}Fe_yO_{3-\delta}$ (A=Sr,Ca,Ba) are potentially useful as passive membranes to separate high purity oxygen from air and as cathodes in fuel cells. All of the compositions studied exhibited very high electrical conductivities. At lower temperatures, conductivities increased with increasing temperature, characterized by activation energies of 0.05 to 0.16 eV that are consistent with a small polaron (localized electronic carrier) conduction mechanism. At higher temperatures, electronic conductivities tended to decrease with increasing temperature, which is attributed to decreased electronic carrier populations associated with lattice oxygen loss. Oxygen ion conductivities were higher than that of yttria stabilized zirconia and increased with the cobalt content and also increased with the extent of divalent A-site substitution. Thermogravimetric studies were conducted to establish the extent of oxygen vacancy formation as a function of temperature, oxygen partial pressure, and composition. These vacancy populations strongly depend on the extent of A-site substitution. Passive oxygen permeation rates were established for each of the compositions as a function of temperature and oxygen partial pressure gradient. For 2.5 mm thick membranes in an oxygen vs nitrogen partial pressure gradient, oxygen fluxes at 900°C ranged from approximately 0.3 sccm/cm^2 for compositions high in iron and with low amounts of strontium A-site substitution to approximately 0.8 sccm/cm^2 for compositions high in cobalt and strontium. A-site substitution with calcium instead of strontium resulted in substantially lower fluxes.

INTRODUCTION

Perovskite compositions in the $(La,Sr)(Co,Fe)O_{3-\delta}$ system have been studied as candidate materials for applications such as solid oxide fuel cell cathodes, oxygen separation membranes, and membrane reactors.[1-10] At elevated temperatures, these compositions exhibit substantial mixed (anionic and electronic) conductivity. The oxygen

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anion conductivity in these materials can be quite large relative to other oxygen conductors, such as yttria-stabilized zirconia (YSZ). The mixed conducting behavior results in a spontaneous flux of oxygen through dense sintered materials in an oxygen partial pressure ($P(O_2)$) gradient. Under these conditions, gaseous oxygen on the high $P(O_2)$ side of the material is reduced to anionic oxygen at the surface, transported ionically through the material to the low $P(O_2)$ side, and re-oxidized to O_2. The ionic current due to the flux of oxygen ions is offset internally by an electronic current, eliminating the need for electrodes and external circuitry.

Teraoka et al[1-3] investigated several $(La,Sr)(Co,Fe)O_{3-\delta}$ compositions using oxygen permeation and four-probe dc techniques. At 800°C, ionic conductivities were on the order of 0.01-1 S/cm, while electronic conductivities exceeded 100 S/cm. The ionic conductivity increased sharply with increasing Sr content and decreased slightly with increasing Fe content. The increasing ionic conductivity with increasing Sr content was attributed to an increase in the oxygen vacancy concentration as trivalent La cations were replaced by divalent (acceptor) Sr cations. While compositions highest in Sr and Co tend to offer the highest oxygen fluxes, other factors must also be considered. For example, $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ provides very high oxygen permeability but exhibits very limited chemical and structural stability in reduced $P(O_2)$ environments.[4] Kruidhof et al[7] observed that, at lower temperatures (e.g., 750°C), the oxygen flux through several compositions high in Sr and/or Co (e.g., $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$) decreased substantially with time. This degradation in behavior was attributed to an order-disorder transition which caused the oxygen vacancies to become immobile below a composition-dependent transition temperature. The purpose of the present study is to increase the understanding of the synthesis and electrochemical properties of materials within the $La_{1-x}(Sr,Ca,Ba)_xCo_{1-y}Fe_yO_{3-\delta}$ system, in order to assist their successful utilization in electrode and oxygen membrane applications.

DISCUSSION OF CURRENT ACTIVITIES

A simple code is used to refer to the compositions under study. Compositions in the system $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ are designated by LSCF followed by numerals indicating the relative proportions of each cation. For example, $La_{0.6}Sr_{0.4}Co_{.2}Fe_{0.8}O_{3-\delta}$

is designated LSCF-6428, $La_{0.2}Sr_{0.8}Co_{.8}Fe_{0.2}O_{3-\delta}$ is designated LSCF-2882. $La_{1-x}Ba_xCo_{1-y}Fe_yO_{3-\delta}$ compositions and $La_{1-x}Ca_xCo_{1-y}Fe_yO_{3-\delta}$ compositions are designated by LBCF and LCCF, respectively. The required compositions were prepared using the glycine-nitrate combustion synthesis technique.[11] The LSCF compositions were essentially single phase perovskites after calcination at 850°C, while the LCCF and LBCF compositions tended to require higher temperature treatment before yielding a high proportion (>95 wt.%) of the desired perovskite phase.

Thermogravimetric analysis was performed on calcined powder specimens using a heating rate of 5°C/min and a cooling rate of 2°C/min. The TGA measurements were performed in several different atmospheres (air; 10,000 ppm O_2 in Ar; 1,000 ppm O_2 in Ar; 100 ppm O_2 in Ar). TGA results for the LSCF compositions when heated and cooled in air are shown in Figure 1. Substantial reversible weight loss was observed at elevated temperatures. This weight loss was due to a partial loss of lattice oxygen, so that the oxygen deficiency, δ, increased with increasing temperature. The temperature at which oxygen loss began to occur decreased as the Sr content increased. The magnitude of the oxygen loss increased with increasing Sr content. This behavior is consistent with previously reported results for two of these compositions (LSCF-6428,4628).[5] The effect of ambient $P(O_2)$ on weight loss behavior was examined by performing TGA measurements in various atmospheres. The magnitude of the oxygen loss upon heating increased only slightly as the ambient $P(O_2)$ was reduced. In 10,000 ppm O_2, full re-oxidation was observed in high Co materials upon cooling (as in air), but re-oxidation did not occur in atmospheres of 1,000 and 100 ppm O_2 (Figure 2). Compositions containing less cobalt did not experience full re-oxidation in the 10,000 ppm O_2 environment. For a given Sr content (e.g., $x = 0.6, 0.8$), the degree of re-oxidation during cooling in the 10,000 ppm O_2 atmosphere decreased with increasing substitution of Fe for Co.

The ionic transport number in these compositions is less than 1%, so that bulk electrical conductivities obtained by 4-probe pulsed dc measurements on sintered specimens provided a measure of the electronic conductivities of the materials. Typical sintering temperatures were 1150-1250°C with dwell times of 2-4 hours. Plots of log σT vs. 1000/T (σ is conductivity (in S/cm) and T is absolute temperature) for the LSCF compositions are shown in Figure 3. At lower temperatures, conductivities increased linearly with increasing temperature, with activation energies on the order of 0.05-0.16 eV. This behavior is consistent with a small polaron conduction mechanism (i.e., localized electronic carriers with a thermally activated mobility).[12] At higher temperatures, conductivity was observed to decrease substantially with increasing temperature. This exaggerated decrease at high temperatures is attributed to a decreasing concentration of electronic charge carriers (electron holes, $h^\bullet$) as the oxygen content of the material decreases. This process can be represented (Kroger-Vink notation)[13] as:

$$2h^{\bullet} + O_O^x \Rightarrow V_O^{\bullet\bullet} + \tfrac{1}{2}O_2 \qquad [1]$$

Thus, two electron holes are eliminated for each oxygen ion leaving the lattice. While this decrease in oxygen stoichiometry with increasing temperature reduces the electronic carrier concentration, it simultaneously increases the concentration of the ionic charge carriers (oxygen vacancies). Plots of σT vs. 1000/T for the LCCF compositions tended to remain relatively linear at temperatures where the LSCF composition exhibited the pronounced decline in conductivity, suggesting that the electronic carrier concentrations in these materials remain essentially constant over a wider temperature range than is the case for the LSCF materials.

Passive oxygen permeation was measured using sintered disc specimens sealed in an alumina test cell with gold gaskets. Air and oxygen were used as source gases with nitrogen as the carrier gas. Oxygen flux was measured as a function of temperature using heating and cooling rates of 0.65°C/min and gas flow rates of 25-30 sccm. Temperature-dependent oxygen permeation rates (in oxygen vs. nitrogen) through sintered specimens of several LSCF, LBCF and LCCF compositions (2.3 - 3.1 mm thick) are shown in Figure 4. For the LSCF compositions, increased Sr content resulted in a substantial increase in flux. This was consistent with the TGA results which showed that the degree of oxygen deficiency increased with increasing Sr content. The increase in oxygen flux with increasing temperature can thus be attributed to two factors: increasing mobility of the lattice oxygen ions, and increasing concentration of lattice oxygen vacancies. Fluxes for the LCCF compositions were significantly lower than for the LSCF compositions.

Ionic conductivities were calculated from the flux rates using the relation:[14]

$$\sigma_i = \frac{4\,F\,J\,t}{R\,T\,\ln\left[P(O_2^{I})/P(O_2^{II})\right]} \qquad [2]$$

where F is Faraday's constant, J is flux (in A/cm2), t is specimen thickness, R is the gas constant, T is absolute temperature, and $P(O_2^{I})$ and $P(O_2^{II})$ are the oxygen partial pressures on each side of the specimen. The calculated ionic conductivities at 900°C are shown in Table I. The LSCF compositions exhibited significantly higher conductivities than YSZ (also shown in Table I). These values are similar to conductivities obtained with a 4-probe dc technique by Teraoka et al.[2] Ionic transport numbers were calculated by dividing the ionic conductivity by the total conductivity.

Table I. Ionic and Electronic Conductivities at 900°C

Composition	Ionic Conductivity (S/cm)	Electronic Conductivity (S/cm)	Ionic Transport Number
LSCF-6428	0.23	252	9.1×10^{-4}
LSCF-4628	0.40	219	1.8×10^{-3}
LSCF-2828	0.62	120	5.2×10^{-3}
LSCF-2882	0.87	310	2.8×10^{-3}
LCCF-4628	0.03	52	5.8×10^{-4}
LCCF-4682	0.01	296	3.4×10^{-5}
YSZ	0.10	--	1

Aging effects on oxygen flux behavior are being studied through long term permeation measurements. Kruidhof et al[7] reported that, for some compositions in the LSCF system, substantial degradation of flux occurred at temperatures below a composition-dependent order-disorder transition temperature as the oxygen vacancies within the structure became ordered and, therefore, immobile. Figure 5 shows their data for $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ at 750°C. In the present study, flux through a different LSCF composition (LSCF-2882) was measured at 775°C (Figure 5). Only a slight decrease (approx. 4%) in flux was observed after operation for 340 hours. This behavior indicates that LSCF compositions remain viable candidate materials for oxygen permeation applications at intermediate temperatures (e.g., 750-800°C).

The removal of lattice oxygen from the perovskite structure results in a volumetric expansion in the material. This phenonenon is being investigated using controlled atmosphere dilatometry on sintered bars to measure linear expansion as a function of ambient $P(O_2)$. Results for LSCF-6428 at three temperatures are shown in Figure 6. It is apparent that even mildly reducing conditions altered the oxygen stoichiometry sufficiently to cause significant linear expansion. The magnitude of the expansion was similar to that observed in lanthanum chromite materials, but the expansion occurred in much higher oxygen partial pressures due to the lower enthalpy of oxygen vacancy formation in cobaltite-ferrite perovskites.

Ease of fabrication is an important factor in the successful utilization of these materials; a tubular geometry is desirable for oxygen separation applications. Open end tubes have been fabricated from LSCF-6428 powders using rubber bag tooling and 22 ksi cold isostatic pressure. Sintered densities (after heat treatment at 1250°C for 4 hours in air) were 95% of theoretical. Final inner and outer diameters were approximately 0.28 and 0.40", respectively.

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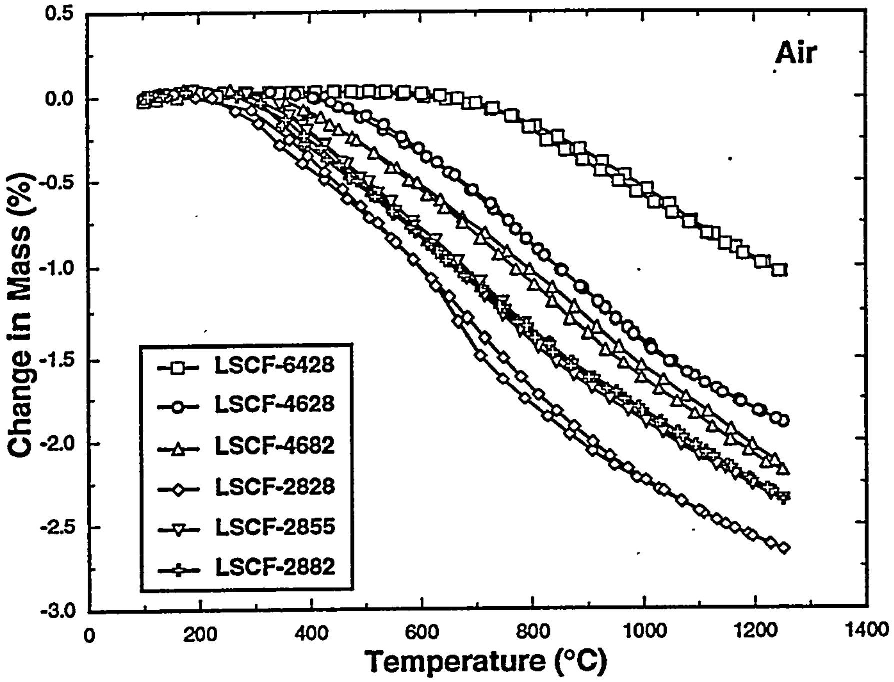

Fig. 1. Thermogravimetric measurements on LSCF compositions in air.

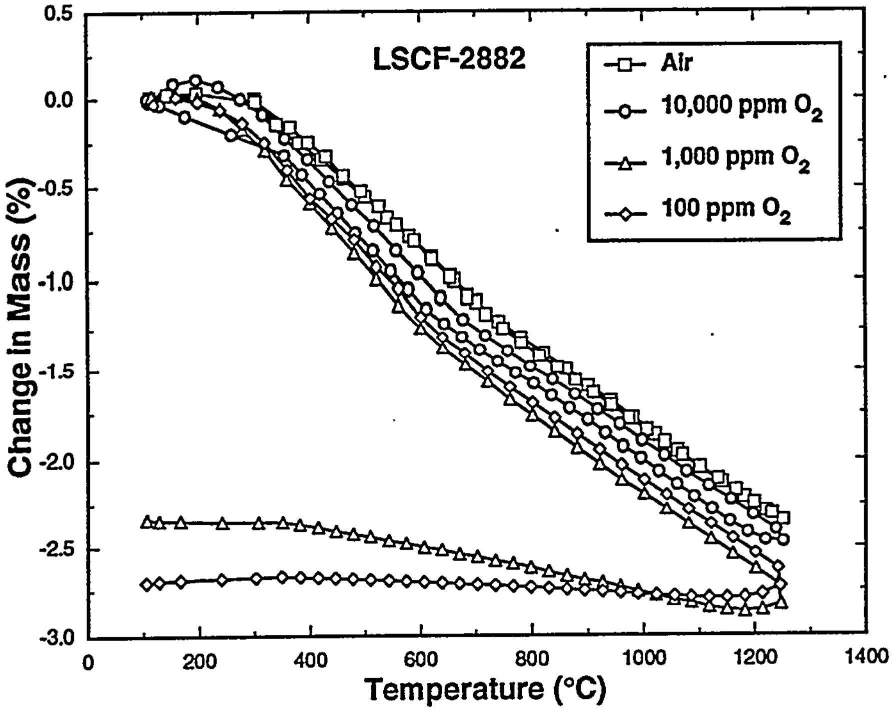

Fig. 2. Thermogravimetric measurements on LSCF-2882 in various atmospheres.

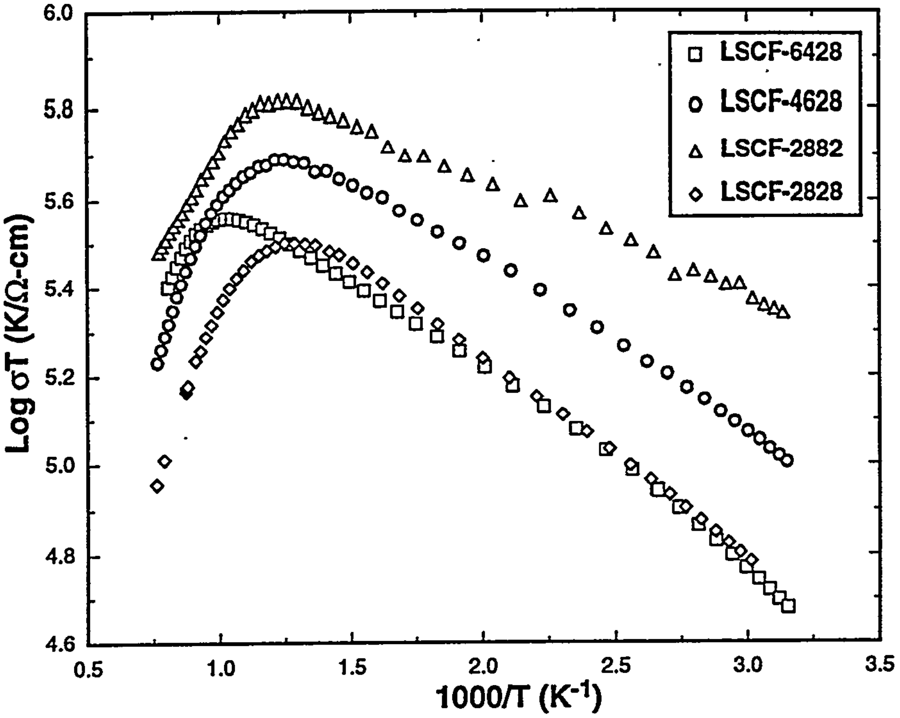

Fig. 3. 4-probe dc conductivity data for the indicated LSCF compositions.

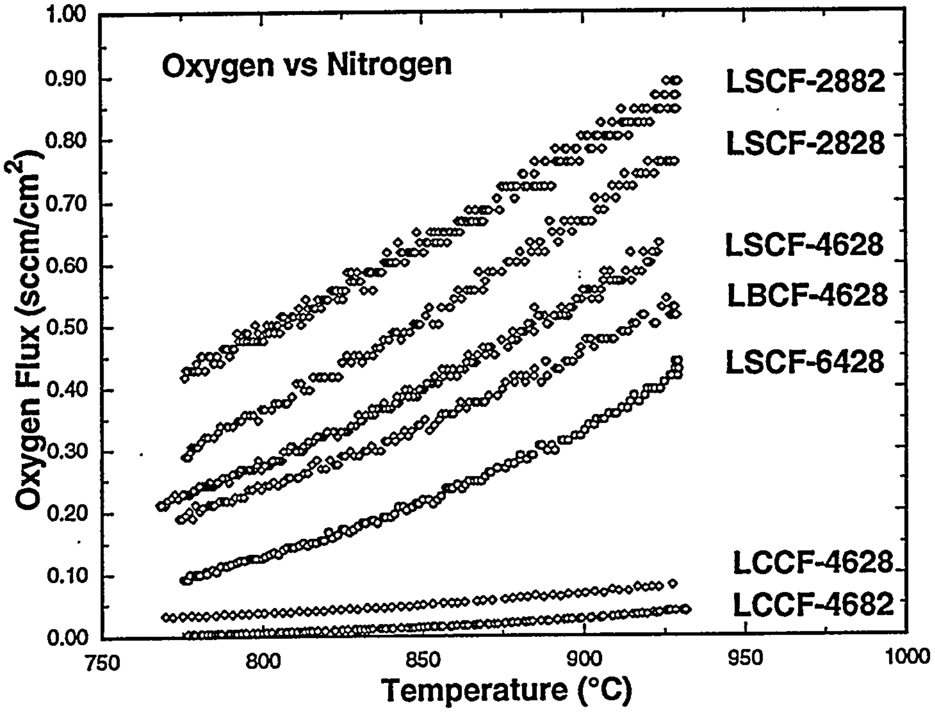

Fig. 4. Oxygen permeation as a function of temperature for the indicated compositions.

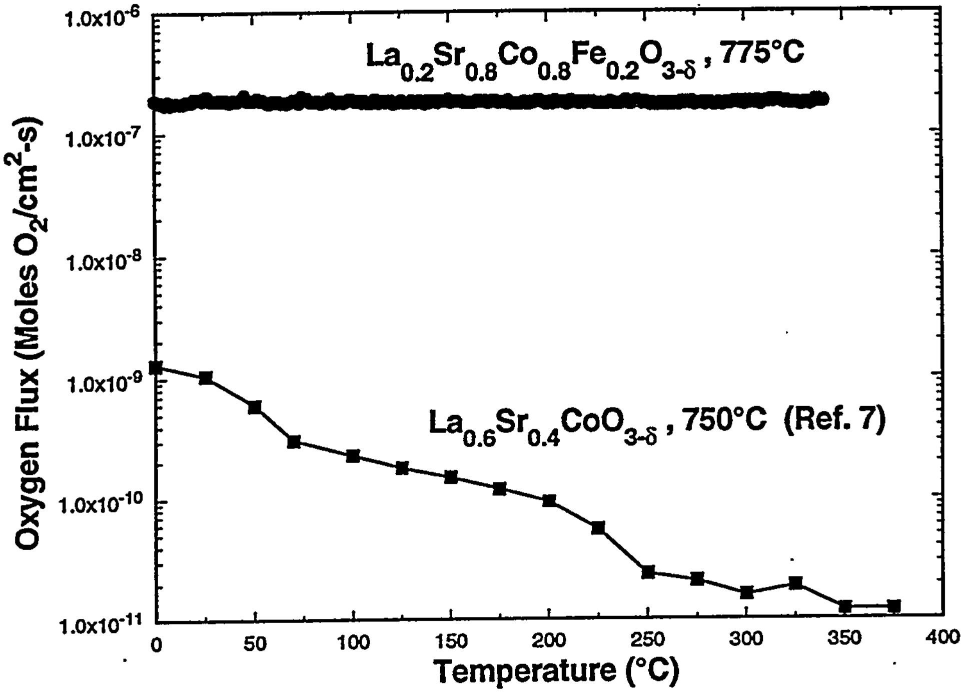

Fig. 5. Oxygen permeation as a function of time for the indicated compositions.

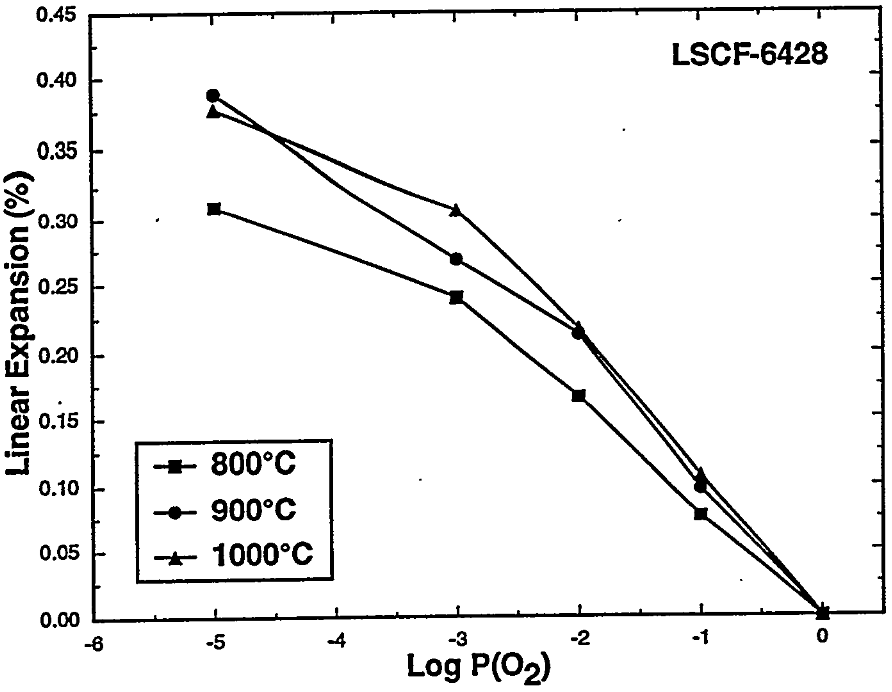

Fig. 6. Linear expansion of LSCF-6428 as a function of ambient $P(O_2)$.