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ELECTROCHEMICAL PROPERTIES OF MIXED
CONDUCTING $\text{La}_{1-x}\text{M}_{1-y}\text{Fe}_y\text{O}_{3-8}$ (M=Sr, Ca, Ba)

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Electrochemical Properties of
Mixed Conducting
 $\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$
($\text{M} = \text{Sr}, \text{Ca}, \text{Ba}$) Perovskites

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At elevated temperatures, some ABO_3 perovskite-type oxides having Co and Fe as B site cations exhibit substantial mixed (anionic and electronic) conductivity. Because of this behavior, they are candidate materials for applications such as solid oxide fuel cell cathodes and oxygen separation membranes.¹⁻⁶ The purpose of the present study is to increase the understanding of the effects of composition, temperature, and environment on the electrochemical properties of selected materials within the $\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($\text{M} = \text{Sr}, \text{Ca}, \text{Ba}$) system in order to evaluate their applicability for the above-mentioned applications. Characterization techniques include XRD, SEM, TGA, dc conductivity, dilatometry, oxygen permeation measurements, and iodometric titration.

TGA results showed that, upon heating in air, $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) compositions exhibited a substantial weight loss at elevated temperatures; this weight loss was reversible upon cooling. This weight loss upon heating resulted from a partial loss of lattice oxygen. The temperature at which oxygen loss began to occur was highly dependent on the composition; oxygen loss occurred at lower temperatures as the Sr content increased. The magnitude of the oxygen loss at high temperatures increased with increasing Sr content. TGA measurements were also performed in various atmospheres to study the effect of ambient oxygen partial pressure, $P(\text{O}_2)$, on weight loss. The magnitude of the oxygen loss upon heating increased only slightly as the ambient $P(\text{O}_2)$ was reduced. In 10,000 ppm O_2 , full re-oxidation was observed in high Co compositions upon cooling (as it was in air), but re-oxidation did not occur in atmospheres of 1,000 and 100 ppm O_2 . Compositions with less cobalt did not experience full re-oxidation in the 10,000 ppm O_2 environment.

Iodometric titration was used to determine the oxygen content ($3-\delta$) of LSCF compositions at room temperature. This reference point, in combination with the weight loss information from the TGA measurements, was used to determine the oxygen stoichiometry as a function of temperature. At low temperatures, the oxygen content was near 3.00, except in compositions with a high Sr and Co content, which were substantially oxygen deficient. At high temperatures (as expected from the TGA results) the oxygen deficiency for all compositions was substantial, especially for the high Sr materials.

Electronic conductivities were measured by 4-probe dc measurements. At lower temperatures, conductivities increased with increasing temperature, consistent with a small polaron conduction mechanism. At higher temperatures, conductivities of

LSCF compositions tended to decrease substantially with increasing temperature. This decrease at high temperatures can be attributed to a decreasing concentration of electronic charge carriers (electron holes) as the oxygen content of the material decreases. Unlike the LSCF compositions, the $\text{La}_{1-x}\text{Ca}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LCCF) compositions did not exhibit the pronounced decline in conductivity at elevated temperatures. The plots of $\log \sigma T$ vs. $1000/T$ are relatively linear over the entire temperature range, indicating that the carrier concentrations in these materials remain nearly constant. This behavior implies that the oxygen stoichiometry in these materials is essentially independent of temperature.

Oxygen permeation rates (in an oxygen vs. nitrogen gradient) through sintered specimens of LSCF, LCCF, and LBCF compositions were measured as a function of temperature (See Figure 1). In the LSCF compositions, increased Sr content resulted in a substantial increase in flux. This was consistent with the experimentally observed increased loss of lattice oxygen with increasing Sr content at high temperatures. The increase in oxygen flux with increasing temperature can be attributed to two factors: increasing mobility of lattice oxygen vacancies, and increasing concentration of lattice oxygen vacancies. Fluxes measured using air rather than oxygen as the source gas tended to be substantially lower than those measured in oxygen vs. nitrogen due to the reduced $P(\text{O}_2)$ gradient. Fluxes for the LCCF compositions were significantly lower than for the LSCF compositions. Ionic conductivities were calculated from the flux rates. The calculated values of ionic conductivity for the LSCF compositions at 900°C were higher than the conductivity of YSZ at that temperature (approx. 0.1 S/cm).

Dilatometric linear expansion measurements were performed as a function of atmosphere and temperature in order to evaluate the dimensional stability of these materials. Substantial expansions (on the order of 0.4% for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$) were observed as the ambient $P(\text{O}_2)$ was reduced from 1 atm to approx. 10^{-5} atm (Figure 2).

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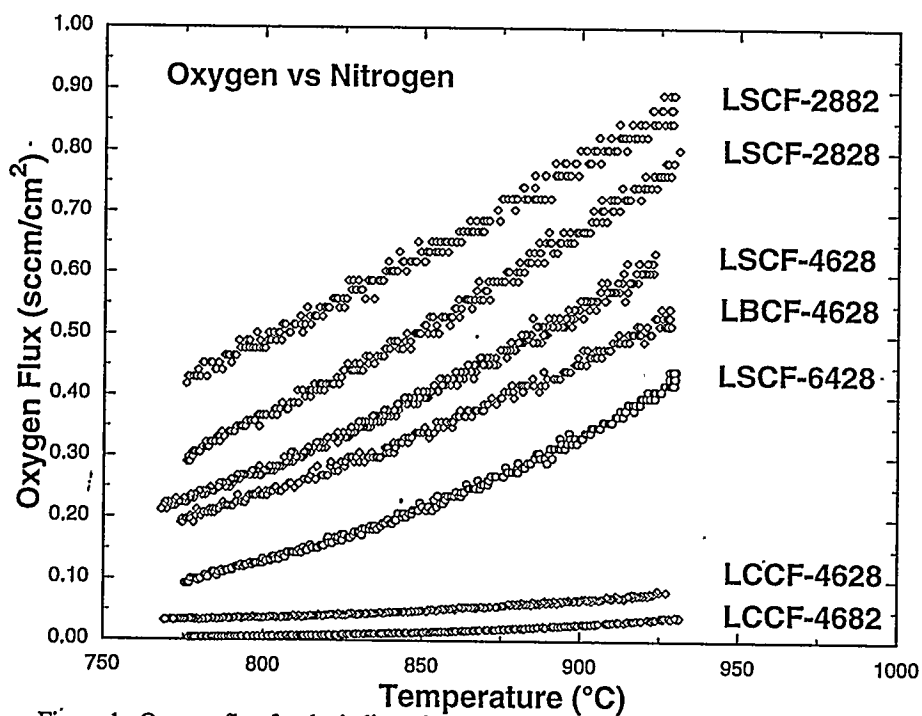


Figure 1. Oxygen flux for the indicated compositions as a function of temperature.

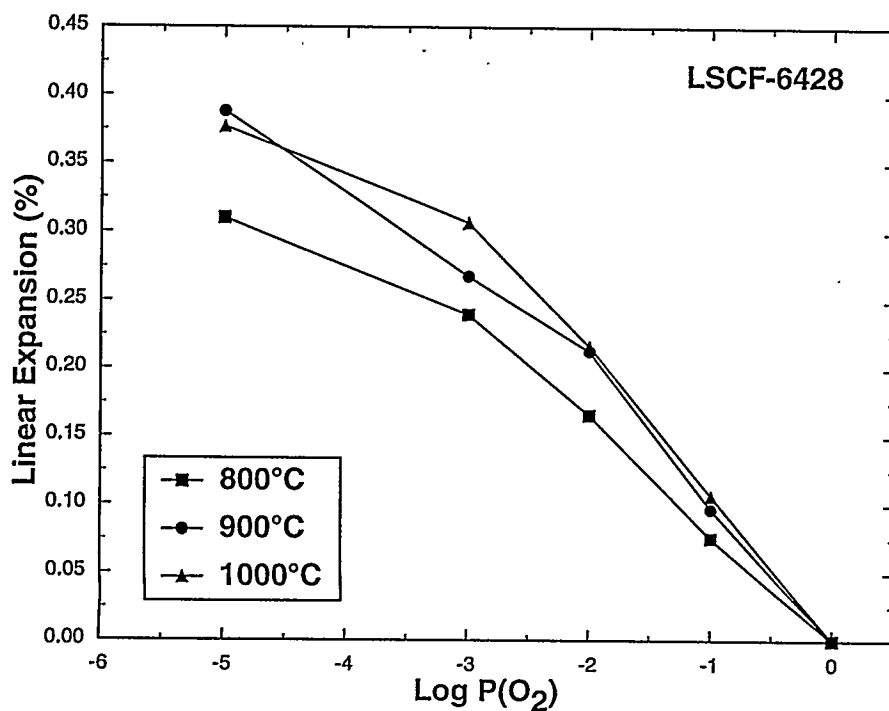


Figure 2. Linear expansion of LSCF-6428 as a function of ambient oxygen partial pressure.