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Review Of P-type Doped Perovskite Materials For SOFC And Other Applications

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Review of p-type doped perovskite materials for SOFC and other applications

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p-type perovskite-type oxides are candidates for use as components of high temperature fuel cells and as oxygen separation membranes. The particular properties that these applications require are reviewed. The characteristics that these oxides have which allow them to satisfy many of these requirements are discussed and a defect model presented. The status of the utilization of these oxides and of the areas which need to be addressed such as thermal expansion and sintering characteristics are reviewed.

1. Introduction

p-type oxides which are of the perovskite crystal structure are being utilized in a number of high temperature electrochemical processes such as solid oxide fuel cells (SOFC), electrolysis, reduction of oxygen, oxygen sensors and oxygen separation membranes. The reason that this class of oxides has so many applications is that they either possess many of the properties required by these applications or can have properties tailored to meet a given application by substitutions of a wide range of cations onto the lattice.

Each application has its own set of unique property requirements on the oxide, however, all of them tend to fall into the following:

(i) Thermodynamic stability over the applicable temperature and oxygen activity range. e.g. for SOFC applications, the interconnect must be stable over the oxygen activity range of 10^{-18} to 1 atm at 1000°C.

(ii) Sufficient electrical conductivity over the range of operation. e.g. for SOFC, the interconnect must have electrical conductivity > 1 S cm^{-1} and the cathode > 50 S cm^{-1} at 1000°C.

(iii) Sufficient chemical stability in contact with other components.

(iv) Mechanical stability with other components. i.e., sufficient strength and thermal expansion match.

(v) Mixed electronic and ionic conductivity. This is important for the SOFC cathode, catalysis and oxygen separation membranes.

It is the intent of this review to discuss the characteristics that these oxides possess which allow them to have such a wide and variable range of properties. For example, the tendencies of acceptor doped p-type oxides to form oxygen vacancies upon reduction leads to mixed electrical conductivity.

It will be shown that an understanding of the defect structure and defect chemistry makes it possible to "tailor" properties to the needs of a given application. It will also be suggested that this understanding leads us to predictability of properties which opens avenues to new utilization of these oxides.

Specific examples of LaMnO$_3$, and LaCrO$_3$ being used as SOFC cathodes and interconnects respectively will be given.

2. Defect chemistry

Perovskite-type oxides, of the ABO$_3$ structure, with trivalent transition metal ions in the B and a trivalent rare earth in the A position, are *p*-type conductors. As a result, their native (majority) nonstoichiometric defects are cation vacancies (oxygen excess) and electron holes, with oxygen vacancies being the minority. Since most of the studies have been with lanthanum on the A site, most of the discussion will center on LaBO$_3$ compounds.

Our thermogravimetric investigations on LaCrO$_3$ [1] and LaMnO$_3$ [2], as well as those of others [3] on the LaBO$_3$ perovskites, show that the oxygen vacancy content in these oxides is small, even at sufficiently low oxygen activity, that dissociation occurs. This is because oxygen vacancies *are not* the native (or majority) nonstoichiometry defects in these oxides. Since in this structure the mobility of oxygen vacancies is much greater than that of cation vacancies, if we wish to enhance the ionic conductivity, we must increase the oxygen vacancy concentration beyond that due to the nonstoichiometry.

Our results and others [1–5] indicate that high concentrations of oxygen vacancies can be induced into the structure by the substitution of acceptors onto either the A or B sites. What is observed is illustrated schematically in fig. 1 which is a plot of the oxygen content of A$_{1-x}$A$'_x$BO$_{3\pm\delta}$ as a function of oxygen activity at a constant temperature that is sufficiently high that equilibrium may be attained.

In region I, excess oxygen exists and the native nonstoichiometric reaction

$$\tfrac{3}{2}O_2 \rightleftharpoons 3O_O + V'''_A + V'''_B + 6h^\cdot$$
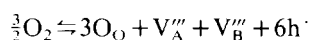
prevails and the electroneutrality condition is

$$p = 3[V'''_A] + 3[V'''_B] .$$

In this region the oxygen vacancy content is extremely small. In all of the examples we could find the oxygen vacancy content is <0.02 even at the oxygen activity, where dissociation occurs [2].

As the oxygen activity decreases, the excess oxygen content decreases until the concentration of acceptor dopants is sufficient to become the majority defects. In this region (II) the electroneutrality becomes

$$p = [A']$$

and oxygen stoichiometry prevails. The region is essentially void of both oxygen and cation vacancies.

Due to the acceptors no oxygen activity dependence on either the electrical conductivity or weight loss is observed since the carriers are constant and no weight loss can be measured. As the oxygen activity decreases, oxygen deficiency starts to appear (region III) and the electrical conductivity begins to decrease and weight loss is observed. The loss of weight is due to the reversible formation of oxygen
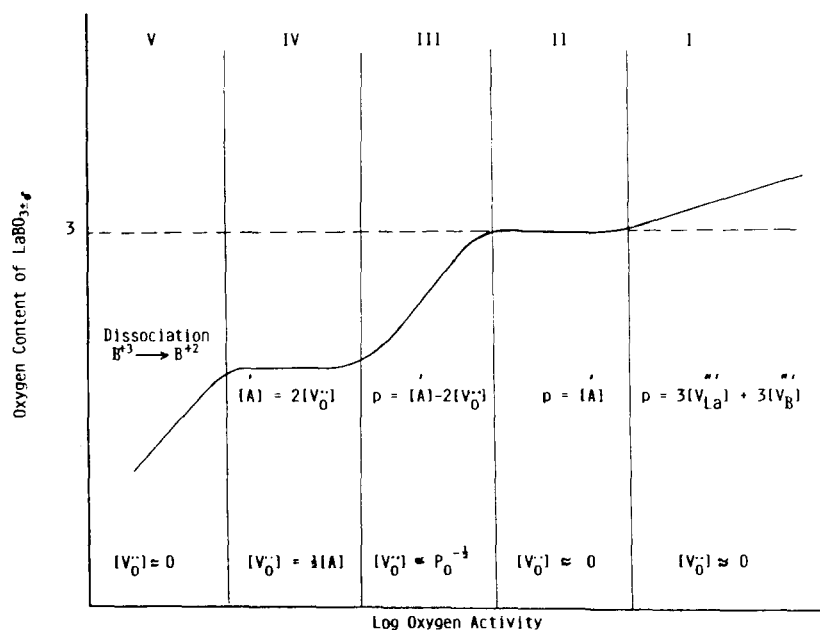

Fig. 1. Oxygen content, $(3 \pm \delta)$ in acceptor doped LaBO$_{3\pm\delta}$ as function of oxygen activity at constant temperature. The B site is occupied by a transition metal ion.

vacancies which tend to compensate the acceptor dopants. This decreases the carrier concentration according to the expression

$$p = [\text{acceptor}] - 2[\text{oxygen vacancies}] .$$

Based upon this general behavior we and Mizusaki et al. [4–6] have been able to formulate a model which describes the redox characteristics. The essentials of the model are illustrated in our reports on LaCrO$_3$ [1] and LaMnO$_3$ [2]. For the case of Sr doped LaMnO$_3$ one expects ionic compensation at low oxygen activity, due to formation of oxygen vacancies (V$_O^{\cdot\cdot}$), and electronic compensation at high oxygen activities due to Mn^{3+} → Mn^{4+} transitions, which according to Kröger–Vink [7] notation is given by,

$$La_{1-x}Sr_x'Mn_{1-y}Mn_y^{\cdot}O_3$$

$$\rightleftharpoons La_{1-x}Sr_x'Mn_{1-y+2x}Mn_{y-2x}^{\cdot}O_{3-x} + x/2O_2 .$$
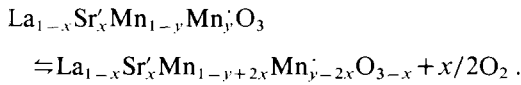
The electroneutrality condition for this region (III) becomes

$$p = [Sr'] - 2[V_O^{\cdot\cdot}] .$$

It is expected that when the total conductivity starts to decrease, the partial oxygen ion conductivity should increase due to the increase in oxygen va-

cancy concentration and the conductivity should move from electronic to mixed ionic/electronic to ionic as the oxygen activity is decreased. The measurements confirm these predictions with regards to the overall trends, as shown in figs. 2 and 3. However, at the present time we are unable to identify the range of partial conductivities, so the detailed behavior and its effect on properties has not been confirmed.

As the oxygen activity decreases, eventually the oxygen vacancy concentration will be given by

$$[Sr'] = 2[V_O^{\cdot\cdot}] ,$$

which is region IV. In this region no oxygen dependency is observed (see Mizusaki et al. [4]) and a constant concentration of oxygen vacancies exists. Thus with reduction, we expect to see ionic conductivity increasing as we enter region III and then maximize to a constant in region IV (as illustrated in fig. 4).

As the oxygen activity decreases further, eventually the oxide again begins to lose oxygen due to the Mn^{3+} → Mn^{2+} transition yielding the reaction

$$2Mn_{Mn}^{\times} + O_O \underset{\text{oxid.}}{\overset{\text{red}}{\rightleftharpoons}} 2Mn_{Mn}' + V_O^{\cdot\cdot} + \tfrac{1}{2}O_2 .$$
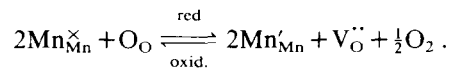
This reaction can generate more oxygen vacancies,
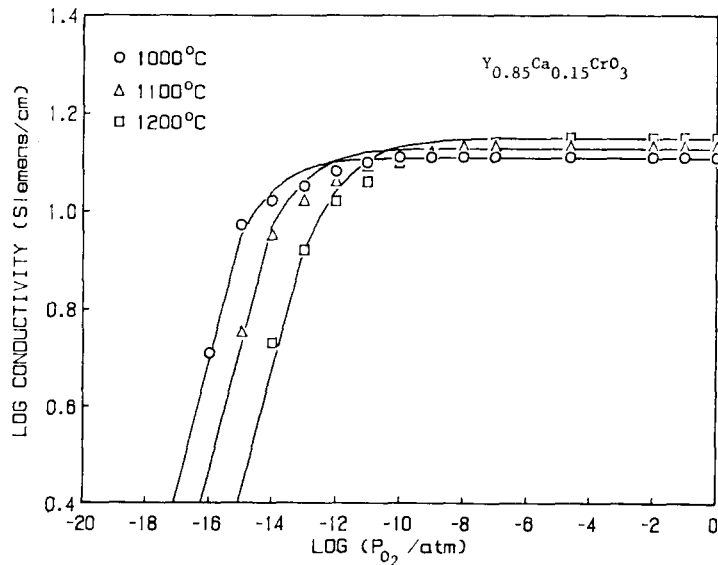

Fig. 2. Log conductivity vs. Log P$_{O2}$ for Y$_{0.85}$Ca$_{0.15}$CrO$_3$ at various temperatures. The solid lines are calculated.
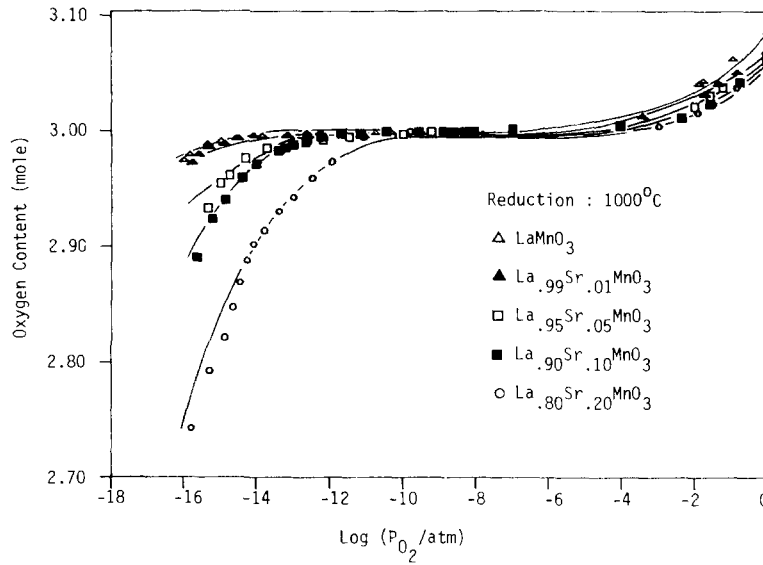
Fig. 3. Moles oxygen weight loss per mole sample vs. Log P_{O2} for various Sr-dopant levels. The solid lines are calculated from model.
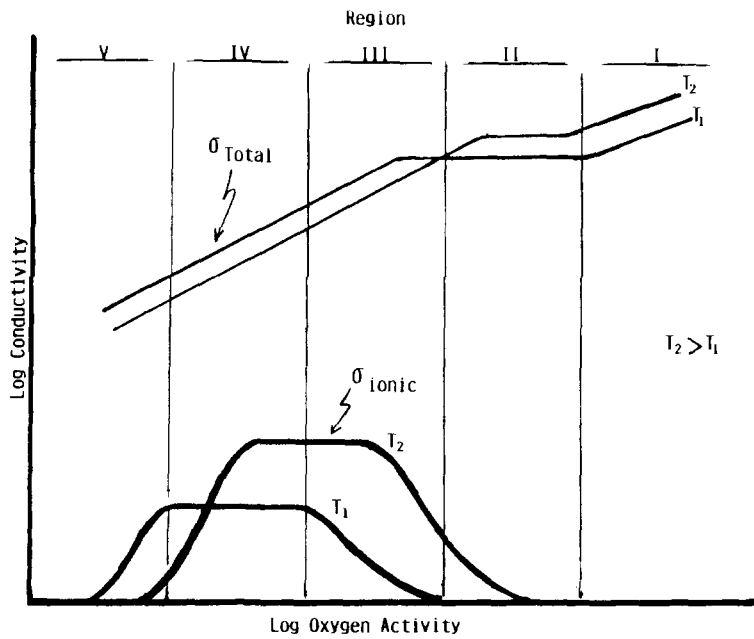
Fig. 4. Total electrical conductivity and ionic conductivity as function of oxygen activity and temperature of acceptor doped LaBO$_3$, where the B site is occupied by a transition metal ion.

however in the case of LaMnO$_3$, the perovskite structure cannot accomodate a very high Mn^{2+} concentration before the structure dissociates into La$_2$O$_3$, MnO, SrMnO$_3$ and La$_2$MnO$_4$. When this occurs, the oxygen vacancy concentration decreases to zero.

According to information available [3] all of the

$LaBO_3$ series behave similar to $LaMnO_3$ in the respect that dissociation occurs as soon as about 10–30% of the B^{3+} reduces to B^{2+}. Thus region V can be considered to represent the limit where the oxygen vacancy concentration becomes negligible and the ionic as well as the electronic conductivities become undefined.

Table 1 shows the available data regarding the locations of regions III, IV and V for the $LaBO_3$ series. An inspection of the table reveals that the maximum oxygen activity at which oxygen vacancies begin to form (region III), in a rare earth perovskite oxide ($LaBO_3$) with the B site being occupied by either a single transition element (Cr to Ni), or mixtures thereof, is influenced by the position of the cation in the periodic table, temperature and acceptor dopant concentration. Figs. 2 and 3 illustrate the influence of acceptor concentration and temperature on the position of region III respectively. As can be seen that region III shifts to higher oxygen activity with increase in either temperature or acceptor concentration.

For all practical purposes, region V (which is defined by the oxygen activity where dissociation occurs) is the limit of the existence of oxygen vacancies. Thus the oxygen activity range over which high oxygen vacancy concentration exists lies in region III and IV. (As illustrated in fig. 4.) It is within this region that we postulate the presence of maximum

mixed conductivity. We have neither confirmed this experimentally nor found any data confirming this by others.

Our studies plus others [1–4] suggest that the onset of regions III and V are very dependent upon both the position of the B ion in the periodic Table (number of 3d electrons) and the acceptor concentration. As shown in table 1 and fig. 5, the onset of both regions III and V occurs at higher oxygen activity as the number of 3d electrons of the B site ion increases and also with addition of acceptors. For example at 1000°C undoped $LaCrO_3$ has no oxygen vacancies under any conditions. However, the introduction of either Mg or Sr causes region III to appear at about 10^{-10} atm oxygen with region IV extending to $< 10^{-20}$ atm. $LaFeO_3$ also has few oxygen vacancies, but the introduction of Sr causes region III to start near 1 atm oxygen with region IV extending to 10^{-17} atm oxygen. In the case of Sr doped $LaCoO_3$ and $LaNiO_3$, region III exists at 1 atm oxygen however, dissociation occurs at 10^{-7} and $10^{-0.6}$ atm oxygen respectively. Similar to our observations a relationship between the electrolytic evolution of oxygen and the number of 3d electrons in the B site ion has been reported by Bockris and Otagawa [9]. In this study they show that the catalytic activity of $LaBO_3$ is related to the electronic configuration of the B ion. Much research is focussed in the area of relating electronic configuration and stoichiometry to mixed conductivity and SOFC electrode stability. Most of this work is ongoing and little is available in the open literature.

3. Applications

3.1. Solid oxide fuel cell

As electrode materials, perovskites find a wide range of applications in particular in SOFC. Perhaps the most significant limitations are imposed on the cathode and interconnect material. Because of the severe working conditions, chemical and the thermal stability are required along with adequate electronic conductivity, porosity and compatibility with the solid electrolyte. Some of the complex perovskite oxides were suggested e.g. $PrCoO_3$, $LaFeO_3$, $LaMnO_3$ and $LaCoO_3$, their conductivity was enhanced by A

Table 1
Approximate oxygen activity where regions III, IV and V begin at 1000°C.

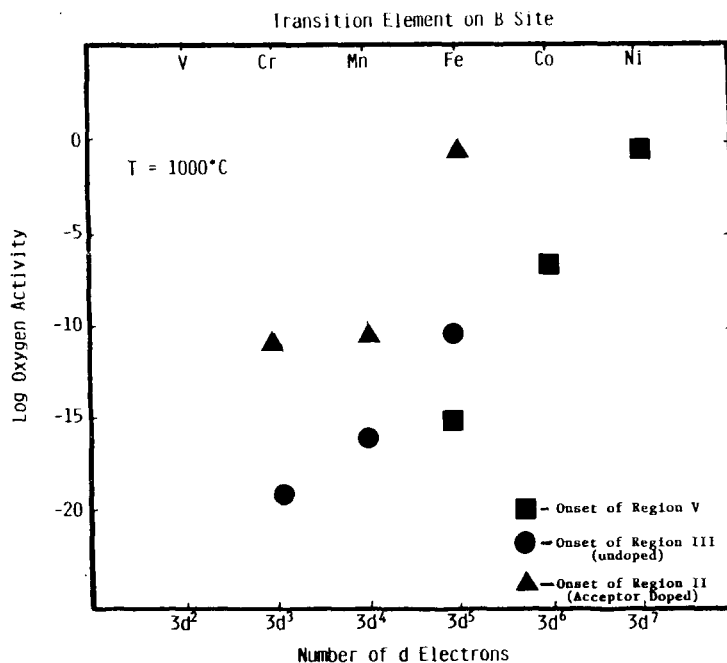| Composition	Region III (atm)	Region IV (atm)	Region V (atm)	Ref.
$LaVO_3$	$< 10^{-20}$	–	$< 10^{-20}$	[3]
$LaCrO_3$	$< 10^{-18}$	$< 10^{-20}$	$< 10^{-20}$	[3]
$LaCr_{0.95}Mg_{0.05}O_3$	10^{-12}	$< 10^{-20}$	–	[6]
$LaCr_{0.9}Mg_{0.1}O_3$	10^{-11}	$< 10^{-20}$	–	[6]
$La_{0.9}Sr_{0.1}CrO_3$	10^{-11}	$< 10^{-20}$	–	[5]
$La_{0.7}Sr_{0.3}CrO_3$	10^{-9}	$< 10^{-20}$	–	[5]
$LaMnO_3$	10^{-16}	–	$10^{-16/15}$	[8]
$La_{0.9}Sr_{0.1}MnO_3$	10^{-13}	10^{-15}	10^{-16}	[8]
$La_{0.8}Sr_{0.2}MnO_3$	10^{-11}	10^{-14}	10^{-16}	[8]
$LaFeO_3$	10^{-11}	–	10^{-17}	[4]
$La_{0.9}Sr_{0.1}FeO_3$	10^{-1}	–	10^{-17}	[4]
$La_{0.75}Sr_{0.25}FeO_3$	$> 10^{0}$	10^{-5}	10^{-14}	[4]
$LaCoO_3$	–	–	10^{-7}	[3]
$LaNiO_3$	–	–	$10^{-0.6}$	[3]

Fig. 5. Oxygen activity where oxygen vacancies start to form (Region III) and where the perovskite $LaBO_3$ starts to dissociate (Region V) as function of the number of 3d electrons of the transition metal ion on the B site at 1000°C.

site doping of alkaline earth ions [10]. Ohno et al. [11] suggested $La_{1-x}M_xCoO_3$ perovskite compounds as promising materials for oxygen electrode applications since they possess semiconducting characteristics at lower temperatures and metallic conductivity at higher temperatures. The calcium substituted compounds are stable with regard to the thermal expansion whereas the strontium substituted compounds possess metallic conductivity throughout the temperature range studied (for $x > 0.3$). To date the most satisfactory and widely used material as SOFC cathode is strontium doped $LaMnO_3$ in which the electronic charge is provided by creating Mn^{4+} and the ionic component attributed to oxygen vacancies [12]. Intensive research on this material has been conducted in our laboratories. A review of its defect chemistry is given by Anderson et al. [8] and its properties clearly outlined [13]. The thermal expansion is shown in table 2. A 10–20 m/o strontium doped $LaMnO_3$ with total conductivity of ≈ 110 S/cm at 1000°C appears to satisfy fuel cell requirements [2]. Priestnall and Steele [14] have recently suggested the use of strontium doped

Table 2
Thermal expansion of $La_{0.99-x}Sr_xMnO_3$ (25 to 1100°C) [13].

Composition	$(\times 10^{-6}/°C)$
$La_{0.99}MnO_3$	11.2 ± 0.3
$La_{0.94}Sr_{0.05}MnO_3$	11.7
$La_{0.89}Sr_{0.10}MnO_3$	12.0
$La_{0.79}Sr_{0.20}MnO_3$	12.4
$La_{0.69}Sr_{0.30}MnO_3$	12.8

lanthanum copper oxides. Cobalt bronzes e.g. Na_xCoO_2 are also applied as electrode materials in electrochemical cells operating on the basis of intercalation of alkali ions. These compounds exhibit high ionic conductivity and also appreciable electronic conductivity (mixed conductors) due to direct overlap of the 3 d-orbitals of the layered CoO_6 octahedra. Stoklosa et al. [15] suggested te presence of oxygen defects in the cobalt sublattice and that Co^{3+} is present on substitutional sodium sites.

The importance of mixed conducting double oxides appears to be clearly emphasized in their application as SOFC cathodes where the charge trans-

fer reaction $[\frac{1}{2}O_2$ (gas) $+2e$ (electrode)$=O^{2-}$ (electrolyte)] would occur over the entire electrode surface when the electrons and ions are mobile rather than having this reaction restricted to the gas–electrode–electrolyte interface (electronic conductors only). Thus polarization losses at the electrode/electrolyte interface will be reduced significantly due to the large increase in charge transfer reaction area. Mixed conductivity was reported in the system Y_2O_3-stabilized ZrO_2–TiO_2 solid solutions [16] whereby the dissolution of TiO_2 significantly increased the percentage of electronic conductivity in this oxygen ion conductor. The results indicate that this material may be attractive for electrode applications in SOFC. Alteration of the extent of ionic and electronic components may also occur by dispersion of oxide particles rather than by substitutional doping [17,18]. The range of ionic conductivity may be altered depending on the dopant. Arai et al. [19] found that in CaO doped CeO_2, the ionic conductivity was extended to lower P_{O2} as the dopant content increased. Ideally, (for optimum cell performance); the same oxide should be used as electrolyte and electrode; this can only be achieved by controlling both ionic and electronic components through appropriate doping. Research is currently being directed towards this goal, however, ZrO_2 and $LaMnO_3$ are still being used for the electrolyte and cathode respectively in SOFC's.

The most significant interconnect material is doped $LaCrO_3$ where electronic compensation occurs by Cr^{4+} formation at high oxygen activities and ionic compensation occurs by $V_O^{..}$ formation at low oxygen activities [5,6]. Due to its stability against reduction in the fuel side of the cell $LaCrO_3$ is the oxide of choice. Several other oxides such as $YCrO_3$ are being considered, but none have had the success of La-CrO_3. There are two major problems with the use of $LaCrO_3$: (1) Thermal expansion mismatch with ZrO_2, (2) poor sinterability in oxidizing conditions. The thermal expansion mismatch is tractable through alteration of the composition (see tables 3 and 4).

The sintering problem is much more serious. [Studies within our group have shown that.] La-CrO_3 is difficult to sinter in air at temperatures low enough to be compatible with the other SOFC components. Typically, the sintering of $LaCrO_3$ involves temperatures as high as 1775°C and oxygen activities in the 10^{-12} to 10^{-9} range [20]. For practical

Table 3
Thermal expansion coefficients of Mg and Sr-doped $La_{0.99}CrO_3$ [a].

Compounds	Thermal expansion coefficient ($\times 10^{-6}/°C$) [b]
$La_{0.99}CrO_3$	9.4
$La_{0.99}Cr_{0.98}Mg_{0.02}O_3$	9.4
$La_{0.99}Cr_{0.95}Mg_{0.05}O_3$	9.5
$La_{0.99}Cr_{0.90}Mg_{0.10}O_3$	9.4
$La_{0.99}Cr_{0.85}Mg_{0.15}O_3$	9.5
$La_{0.97}Sr_{0.02}CrO_3$	10.2
$La_{0.94}Sr_{0.05}CrO_3$	10.8
$La_{0.89}Sr_{0.10}CrO_3$	10.7
$La_{0.84}Sr_{0.15}CrO_3$	10.8
$La_{0.79}Sr_{0.20}CrO_3$	11.1
YSZ	10.3

[a] After ref. [13]
[b] Temperature range from 350 to 1000°C

Table 4
Thermal expansion coefficient (TEC) of $LaCrO_3$ as a function of dopants between 25–1100°C.

Dopant	TEC ($\times 10^{-6}/°C$) [a]
$LaCrO_3$	9.5
10 % Mg–$LaCrO_3$	9.5
2% Sr	10.2
10% Co	13.1
20% Co	13.6
30% Co	15.9
10 Co, 10 Ca	12.3
10 Co, 20 Ca	11.1
10 Co, 30 Ca	10.4
YSZ	10.3

[a] 5% standard deviation.

applications under such extreme conditions its fabrication is both uneconomical and detrimental to other components which may have to be co-sintered with $LaCrO_3$. Thus, it would be desirable to process $LaCrO_3$ at lower temperature in an air atmosphere.

A number of investigators have and are addressing this sintering problem. I will not try to discuss them all. The work by Meadowcroft [21] showed that the sintered density of $La_{0.84}Sr_{0.16}CrO_3$ increased when excess Sr was added in the form of $SrCO_3$ before sintering. The maximum beneficial effect was observed when 4–6 mol% $SrCO_3$ was added. This was probably due to the formation of $SrCrO_3$ at intermediate

temperatures followed by melting and liquid-phase sintering. Flandermeyer et al. [22] used low melting oxide eutectics as well as La, Y and Mg fluorides up to 8–10 wt% to increase density of sintered compacts.

More recent studies by our group have shown that powder from the $La_{1-x}Ca_xCr_{1-y}Co_yO_3$ system with $0.1 < x < 0.3$ and $0.1 < y < 0.25$ can be densified in air at temperatures $< 1400°C$ by the presence of a transient liquid [23]. this work is still in progress. Yokokawa and co-workers at the Tsukuba Research Center [24] in Japan have also been intensely studying this problem.

3.2. Oxygen separation membranes

Stringent requirements are imposed on these membranes for oxygen pumping devices. They are expected to have an optimum range of mixed conductivity, high degree of oxygen nonstoichiometry, structural stability and TEC compatibility throughout a wide range of oxygen activity. Sr doped La-CoO₃ used as oxygen electrode [25] in SOFC's has been suggested for this application. Makor et al. [26] reported that $La_{0.84}Sr_{0.16}CoO_3$ possesses ionic conductivity an order of magnitude higher than YSZ and its electronic conductivity is at least ten folds higher than that of strontium-doped LaMnO₃. However, the observed increase in conductivity was associated with a substantial increase in the thermal expansion coefficient. Moreover, cobaltites are not stable in the reducing gas environment. Other systems with lower cobalt content have been suggested. The $La_{1-x}M_xMn_{1-y}Co_yO_3$ (M=Ca or Sr) system is known for its high ionic and electronic conductivity as well as its electrocatalytic activity [27]. The $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ system is also found to be attractive for oxygen delivery applications [11], an increased oxygen flux in this system was correlated to the extent of mixed conductivity. Several problems need to be addressed before significant applications are evolved. For example, the stability of these oxides towards reduction at the anode is a serious problem. As was mentioned earlier, the best mixed conductors contain cobalt which reduces easily. Thus structural integrity is a serious problem. Another problem is thermal expansion. Most of the mixed conductors have thermal expansion coefficients which exceed $15 \times 10^{-6}/°C$. These are so high that

before thermal and structural stability can be achieved they must be altered to lower values. There are a number of studies currently being conducted in this area. It appears that materials in this area have a bright future.

4. Conclusions

(i) p-type perovskite oxides do satisfy many of the requirements for SOFC and oxygen separation membranes.

(ii) LaCrO₃ is satisfactory for an interconnect in the SOFC, however, fabrication presents a problem. There is a need for an oxide which can be cobalt-sintered with the other cell components.

(iii) LaMnO₃ is satisfactory as a cathode for the SOFC, however, an oxide which is more stable towards reduction and has an ionic transport number greater than 0.001 would be useful.

(iv) Mixed ionic conductors have potential as oxygen separation membranes. The precise compositions are application driven and have not been fully developed.

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