THERMAL EXPANSION STUDIES ON CATHODE AND INTERCONNECT OXIDES *

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ABSTRACT

The thermal expansion of both the cathode and interconnect of the high temperature solid oxide fuel cell is reviewed. The influence of dopants such as Al, Mg and Sr are discussed. Data are presented which suggest that Sr doped LaCrO$_3$ matches the thermal expansion of zirconia best, but this composition is more susceptible to expansion upon reduction than Mg doped LaCrO$_3$. Data also show that Sr doped LaMnO$_3$ has too high of a thermal expansion coefficient and that to make a structurally sound cathode, alternate compositions need to be considered.

1. INTRODUCTION

High temperature solid oxide fuel cells (SOFC) are fabricated as a composite of four different oxides:

1. Y stabilized ZrO$_2$ (Y-PSZ) as electrolyte,
2. Ni-ZrO$_2$ cermet as anode,
3. La$_{1-x}$Sr$_x$MnO$_3$ (LSM) as cathode, and
4. La$_{1-x}$Sr$_x$CrO$_3$ (LSC) or LaCr$_{1-x}$Mg$_x$O$_3$ (LMC) as interconnect.

It is important that the thermal expansion coefficients (TEC's) of all components are the same if the SOFC is to remain stable during thermal cycling. Since the electrolyte, Y-PSZ is fixed in this cell with a TEC of about 10.3 x 10$^{-6}$/°C, the TEC's of the other components must be adjusted to match that of Y-PSZ.

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In this report the influence of cation stoichiometry, dopant and dopant concentration on the TEC of the cathode and interconnect oxides, LSM and LSC or LMC respectively are reviewed.

2. EXPERIMENTAL

The required compositions were prepared with a chemical preparation technique which allowed precise compositional control and produced highly sinterable powders of $<$0.1$\mu$m crystallite size.$^{(1)}$ The compositions were then dry pressed and sintered into disc-shaped and bar-shaped test specimens whose densities all exceeded 93% of theoretical density with no surface porosity. X-ray diffraction analysis showed that all of the compositions were single phase. Thus it was felt that the preparation technique was such that the thermal expansion measurements should reflect variation in dopant content or cation stoichiometry rather than extraneous influences which may result from the preparation process.

3. RESULTS AND DISCUSSION

A. LaMnO$_3$

Table I tabulates the average TEC's measured for LSM as function of Sr content. As can be seen the TEC of LSM is greater than that of Y-PSZ particularly for the Sr content of 10-20 m% which is currently being used. With such large differences in TEC's, cracking at the Y-PSZ-LSM interfaces may occur during thermal cycling. However, this does not appear to be a problem, probably due to the porosity of the cathode. This is a potential problem and the differences in TEC's should be corrected.

In order to lower the TEC of LSM, substitutions with smaller cations will have to be made. The addition of either Ca or Y for La will probably lower the TEC. Compositions with these additives are being fabricated and the results will be discussed in a later report.

B. LaCrO$_3$

1. Pure LaCrO$_3$

From room temperature to about 240°C, LaCrO$_3$ is orthorhombic with a TEC of about $6.7 \times 10^{-6}/^\circ C$. At approximately 240°C the structure becomes rhombohedral with a TEC of about $9.2 \times 10^{-6}/^\circ C$. As can be seen in figure 1, the TEC is not influenced by the cation stoichiometry$^{(2)}$ at least over a range of $\pm 10$ m% variation of La.

No phase equilibria studies in the La$_2$O$_3$-Cr$_2$O$_3$ system show any appreciable Cr$_2$O$_3$ or La$_2$O$_3$ solubility into LaCrO$_3$. Paulikov et. al.$^{(3)}$ conducted a detailed study of the Gd$_2$O$_3$-Cr$_2$O$_3$ system and found
no apparent solubility. Because of the similarity of the two rare earths, Gd and La, they generalized that LaCrO$_3$ existed only in the stoichiometric state. Another study by Berjoan$^{(4)}$ also detected no excess cation solubility in LaCrO$_3$, although excess Cr$_2$O$_3$ volatilization precluded any precise high temperature X-ray diffraction measurements between the limits of La$_.9$CrO$_3$ and La$_1.1$CrO$_3$.

Khattak and Cox$^{(5)}$ studied samples heated to 500°C in air. No solubility was found in excess La$_2$O$_3$ formulations. In excess Cr$_2$O$_3$ material, the corundum phase was not detected until the La/Cr ratio was lower than 0.985.

However, as can be seen in figure 2, the temperature over which the orthorhombic to rhombohedral transformation occurs is dependent upon La content. The onset temperature of the transformation ranges from 240°C to 251°C for La/Cr ratios of 0.9 and 1.1 respectively. The transformation is somewhat sluggish, it is small ($<2 \times 10^{-2}$%) and occurs over about a 10°C temperature range. Upon cooling, the onset of the transformation is depressed by about 10°C. The extent of the hysteresis does not appear to be dependent upon the La content.

2. LaCr$_{1-x}$Al$_x$O$_3$

Aluminum ion is isovalent with Cr so only alters the electrical conductivity by a dilution effect. However, Al additions do markedly change the TEC.

The thermal expansion as function of Al content is shown in figure 3. As can be seen the addition of Al does two things: 1) increases the thermal expansion coefficient of the rhombohedral phase from $9.1 \times 10^{-6}/°C$ to $11.3 \times 10^{-6}/°C$ as it increases from 0 to 100 m%; and 2) shifts the orthorhombic to rhombohedral transformation temperature to lower temperatures. Figures 4 and 5, illustrate the temperature shift of the transformation temperature. No measurements were made below room temperature so only specimens containing less than 15 m% Al could be measured. An extrapolation of the data suggests that 13 m% of Al is sufficient to shift the transformation temperature to room temperature. About 30 m% Al is required for the TEC to match that of Y-PSZ.

3. La$_{1-x}$Sr$_x$CrO$_3$

The addition of Sr to LaCrO$_3$ also shifts the orthorhombic to rhombohedral transformation to lower temperature. As can be seen in figure 6, as little as 10 m% Sr is sufficient to shift the transformation to below room temperature. From Table II, it is evident that only 5 m% Sr will increase the TEC to that of Y-PSZ. This makes Sr to be very attractive dopant for LaCrO$_3$. 131
4. LaCr$_{1-x}$Mg$_x$O$_3$

Magnesium has long been used as an acceptor dopant to increase the conductivity of LaCrO$_3$. However, its addition does little to the TEC as can be seen in figure 7 and Table II. Neither the orthorhombic-rhombohedral transformation nor the average TEC's show much dependence on Mg content. Part of the reason that Mg is not very effective is that it has limited solubility in LaCrO$_3$. This is particularly evident if excess B cation exists (figure 8). Evidently, in the presence of excess B cation, the Mg reacts with Cr to form MgCr$_2$O$_4$ until the A to B ratio becomes unity. This suggests, a possible phase diagram for MgO-La$_2$O$_3$-Cr$_2$O$_3$ at 1000°C as shown in figure 9. At this temperature the maximum Mg solubility is about 20%, but as can be seen it depends upon the A to B ratio.

5. Influence of Oxygen Activity on Lattice Dimensions

A study was made in which the expansion (or contraction) and lattice parameter changes resulting from cycling Sr and Mg-doped LaCrO$_3$ from 10$^{-20}$ to 1 atm oxygen at temperatures as high as 1200°C were determined. The dimensional change measurements were made in a controlled atmosphere dilatometer at 1000°C as dense specimens were oxidized and reduced. Results of these measurements are illustrated in figures 10 and 11. As can be seen, the Mg-doped specimens experience about 5 times less expansion with reduction than do the Sr-doped specimens.

Room temperature lattice parameter measurements were also made on powdered specimens which were quenched from a given atm and 1200°C. The atmosphere was maintained during quenching. These data agreed with the dilatometer measurements in that expansion of the lattice occurred as oxygen was lost from the lattice (see figure 12). This suggests that when used as an interconnect Sr doped LaCrO$_3$ is more susceptible to cracking and leaking due to expansion at the fuel interface than that containing Mg.

4. CONCLUSIONS

1. The TEC's of both LaCrO$_3$ and LaMnO$_3$ do not match that of Y-PSZ.

2. The addition of either Al or Sr to LaCrO$_3$ can adjust the TEC to that of Y-PSZ.

3. The addition of Mg to LaCrO$_3$ does not alter the TEC with the highest value occurring for 10-15 m% Mg addition $\sim$9.6 x 10$^{-6}$/°C.

4. The addition of Sr to LaMnO$_3$ increases the TEC from the base value of about 11.3 x 10$^{-6}$/°C.
5. In order to lower the TEC of LaMnO$_3$, additives other than Sr must be employed. Experience suggests that either Y or Ca additions are likely candidates but there are no data to quantify this supposition.

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### TABLE I

Thermal Expansion of $\text{La}_{99-x}\text{Sr}_x\text{MnO}_3$

(25 to 1100°C)

| Composition       | $\alpha \times 10^6$/°C |
|-------------------|--------------------------|
| $\text{La}_{99}\text{MnO}_3$ | 11.2 ± 0.3               |
| $\text{La}_{94}\text{Sr}_{0.05}\text{MnO}_3$ | 11.7                   |
| $\text{La}_{89}\text{Sr}_{0.10}\text{MnO}_3$ | 12.0                   |
| $\text{La}_{79}\text{Sr}_{0.20}\text{MnO}_3$ | 12.4                   |
| $\text{La}_{69}\text{Sr}_{0.30}\text{MnO}_3$ | 12.8                   |

### TABLE II

Thermal Expansion Coefficients of Mg and Sr-Doped $\text{La}_{99}\text{CrO}_3$

| Compounds          | Thermal Expansion Coefficient ($\times 10^{-6}$/°C) |
|--------------------|----------------------------------------------------|
| $\text{La}_{99}\text{CrO}_3$          | 9.48                                      |
| $\text{La}_{99}\text{Cr}_{0.98}\text{Mg}_{0.02}\text{O}_3$ | 9.46                                      |
| $\text{La}_{99}\text{Cr}_{0.95}\text{Mg}_{0.05}\text{O}_3$ | 9.57                                      |
| $\text{La}_{99}\text{Cr}_{0.90}\text{Mg}_{0.10}\text{O}_3$ | 9.48                                      |
| $\text{La}_{99}\text{Cr}_{0.85}\text{Mg}_{0.15}\text{O}_3$ | 9.55                                      |
| $\text{La}_{97}\text{Sr}_{0.02}\text{CrO}_3$      | 10.24                                     |
| $\text{La}_{94}\text{Sr}_{0.05}\text{CrO}_3$      | 10.89                                     |
| $\text{La}_{89}\text{Sr}_{0.10}\text{CrO}_3$      | 10.74                                     |
| $\text{La}_{84}\text{Sr}_{0.15}\text{CrO}_3$      | 10.84                                     |
| $\text{La}_{79}\text{Sr}_{0.20}\text{CrO}_3$      | 11.10                                     |
| Y-PSZ              | 10.3                                      |

*Temperature range from 350 to 1000°C.*

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Figure 1. Thermal expansion of La$_{1-x}$CrO$_3$.

Figure 2. Dependence of orthorhombic-rhombohedral transformation upon La/Cr ratio.
Figure 3. Thermal expansion coefficient of La$_{0.9}$\((\text{Mg}_{0.05}\text{Cr}_{1-x}\text{Al}_x)_{0.95}\text{O}_{2.83})$ as a function of Al content.

Figure 4. Temperature of onset of orthorhombic-rhombohedral transformation.
Figure 5. Thermal expansion of La$_{0.95}$Mg$_{0.05}$Cr$_{1-x}$Al$_x$O$_3$.

Figure 6. Relative thermal expansion for La$_{0.99-x}$Sr$_x$CrO$_3$. 

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Figure 7. Relative thermal expansion for $\text{La}_{0.99}\text{Cr}_{1-y}\text{Mg}_y\text{O}_3$. (dimensions at 45°C)

Figure 8. Mg solubility in $\text{La}_y\text{Cr}_{1-x}\text{Mg}_x\text{O}_3$ at 1000°C.
Figure 9. MgO-La\textsubscript{2}O\textsubscript{3}-Cr\textsubscript{2}O\textsubscript{3} phase diagram at 1000°C.

Figure 10. Relative dimensional change as a function of Log $P_{O_2}$ for La\textsubscript{0.99}Mg\textsubscript{0.15}Cr\textsubscript{0.85}O\textsubscript{3}. (ref. = dimension at $P_{O_2} = 0.2$ atm.; 1000°C)
Figure 11. Relative dimensional change as function of Log P$_{O_2}$ for La$_{.79}$Sr$_{.20}$CrO$_3$.

Figure 12. c lattice parameter of Mg-doped La$_{.99}$CrO$_3$ quenched from 1200°C, different oxygen atmospheres.