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Effect of cation substitution on the thermal expansion coefficient of LaCrO_3

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High-temperature solid-oxide fuel cells (SOFCs) have been investigated extensively for several years, because they have the potential of converting chemical energy into electrical energy. High-temperature SOFCs are fabricated as composites of four different oxides: Y-stabilized ZrO_2 (Y-PSZ) as electrolyte; Ni- ZrO_2 cermet as anode; $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) as cathode; and $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_3$ (LMC) as interconnect.

The typical operating temperature of an SOFC is from about 800 to about 1200 °C. Therefore, SOFCs must be able to withstand occasional thermal cycling between 25 and 1200 °C. During these thermal cycles all of the components must have a close match of thermal expansion coefficients (TECs) in order to eliminate mechanical stresses, which can cause component layer cracking, with resultant leakage of oxygen and fuel, and degradation of the electrical characteristics of the cell. Very importantly, the interconnect must have a TEC close to that of the solid electrolyte and the cathode. Thermal expansion mismatch between the LaCrO_3 and Y- ZrO_2 appears to be the most severe problem. Table I compares the TEC of Y-PSZ and various LaCrO_3 compositions [1]. As can be seen, the TEC of Mg-doped LaCrO_3 cannot be made to match that of Y-PSZ for any Mg content. This work addressed this problem and the control of the TEC of LaCrO_3 by substitution of Co for Cr and Ca for La without the deterioration of either the electrical conductivity or the high-temperature stability is discussed.

Specimens in the (La,Ca)(Cr,Co) O_3 system were prepared by a polymer precursor method similar to that first described by Pechini [2]. The starting chemicals were La and Ca carbonates and Cr and Co

nitrate. All chemicals were reagent grade materials and were standardized by thermogravimetric methods to determine the actual cation contents. The desired compositions were prepared by dissolving measured amounts of selected carbonates and nitrates in solutions of citric acid, ethylene glycol and water. The mixtures were heated on a hotplate at about 95 °C until polymerization had occurred. Subsequent heating at higher temperatures resulted in the composition of the polymer resin and allowed conversion into the desired oxide. Final calcination was done at 850 °C for 8 h. The resultant powders were milled and subjected to X-ray diffraction to ensure that they were single phase. Powders were pressed into bars with the aid of poly(vinyl alcohol) and water binder. A compaction pressure of 2000 kg cm⁻² yielded 0.6 cm × 0.4 cm × 3.0 cm bars with a density of about 50% theoretical. Densification was conducted at 1500 °C for 10 h in an SiC heated furnace. The linear TEC was determined by using the data obtained from an Orton automatic dilatometer coupled with a data-acquisition system. Measurements were made on specimens with dimensions of 0.3 cm × 0.3 cm × 2.5 cm which were heated at 5 °C min⁻¹ from room temperature to 1100 °C in air.

The measured TECs are given in Tables II and III as a function of the Co and Ca substitution. As can be seen from Table II, the TEC increases linearly with Co substitution. This must be due to the high TEC of LaCoO_3 , which was reported to be approximately $22 \times 10^{-6} \text{ °C}^{-1}$ [3]. The TEC of compositions $\text{LaCr}_{1-y}\text{Co}_y\text{O}_3$ with $y > 0.5$ changed little with a further increase in the Co content and remained close to $(20\text{--}23) \times 10^{-6} \text{ °C}^{-1}$. However, when the Co content was further decreased, the TEC values decreased to $13.1 \times 10^{-6} \text{ °C}^{-1}$ at

TABLE I TECs of cell components and interconnects $\text{LaCr}_{1-y}\text{Mg}_y\text{O}_3$ (350–1000 °C) [1]

Composition (y)	TEC ($\times 10^{-6} \text{ °C}^{-1}$)
0	9.48
0.02	9.46
0.05 Interconnect	9.57
0.10	9.48
0.15	9.55
Y-PSZ Electrolyte	10.30
$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ Cathode	12.40

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TABLE II TEC as a function of y for $\text{LaCr}_{1-y}\text{Co}_y\text{O}_3$ (25–1100 °C)

Composition (y)	TEC ($\times 10^{-6} \text{ °C}^{-1}$)
0	9.5
0.10	13.1
0.20	13.6
0.30	15.9
0.50	21.8
0.70	22.3
0.90	22.8
1.00	23.2

TABLE III TEC as a function of x and y for $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$ (25–1100 °C)

Composition (x)	TEC ($\times 10^{-6} \text{ }^\circ\text{C}^{-1}$)
$\text{La}_{1-x}\text{Ca}_x\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$	
0	13.1
0.10	12.3
0.20	11.1
0.30	10.4
$\text{La}_{1-x}\text{Ca}_x\text{Cr}_{0.8}\text{Co}_{0.2}\text{O}_3$	
0	13.6
0.10	12.3
0.20	11.5
0.30	11.4

$y = 0.1$. The results show that the TEC of compositions can be altered from 9.5×10^{-6} to $23.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ by the substitution of Co for Cr.

It has been found that substitution of Co for Cr into LaCrO_3 imparts good thermal expansion matching characteristics, enables LaCrO_3 to sinter in air at temperatures below 1400 °C [4] and improves the electronic conductivity at 1000 °C [5].

Additional Ca substitution for La decreased the TEC of the compositions (see Table III). The TEC of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ was $10.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. This value matches the TEC of Y-PSZ. Therefore, additional Ca substitution provides even better TEC matching characteristics and electronic conductivity [4] without harming the other desired properties of the LaCrO_3 [5]. Therefore, the TEC of the LaCrO_3 can be altered to match those of the other SOFC

components by the substitution of Co for Cr and Ca for La. The substitution of Ca for La in the $\text{LaCr}_{1-y}\text{Co}_y\text{O}_3$ resulted in the formation of Cr^{4+} and Co^{4+} in order to maintain electrical neutrality. Formation of both Cr^{4+} and Co^{4+} decreases the unit-cell volume, since in these valence states the radii of Cr^{4+} and Co^{4+} ions are markedly lower than those of Cr^{3+} and Co^{3+} . The decrease in TEC with increasing Ca content is probably associated with the formation of Cr^{4+} and Co^{4+} ions.

The TEC of LaCrO_3 can be increased to match those of the other SOFC components by the substitution of Co and Ca. Additional Ca and Co substitution even provides better electronic conductivity and sinterability in air without substantially harming the other desired properties [4, 5].

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