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Preparation and characterization of ceramic interconnect $La_{0.8}Ca_{0.2}Cr_{0.9}M_{0.1}O_{3-\delta}$ (M = Al, Co, Cu, Fe) for IT-SOFCs

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ABSTRACT

The lattice parameters, electrical conductivity, activation energy, mechanical properties, and microstructure of $(La_{0.8}Ca_{0.2})CrO_{3-\delta}$-based specimens were investigated systematically in this paper. The tolerance factors for $(La_{0.8}Ca_{0.2})CrO_{3-\delta}$-based specimens were all greater than 0.9, indicating the perovskite was not distorted with different cations (Al^{3+}, Co^{3+}, Cu^{2+}, Fe^{3+}) substitution for B site of $(La_{0.8}Ca_{0.2})CrO_{3-\delta}$. $(La_{0.8}Ca_{0.2})Cr_{0.9}Co_{0.1}O_{3-\delta}$ specimen revealed the maximum electrical conductivity, $\sigma_{850\ ^\circ C} = 59.59$ S/cm with minimum activation energy, $E_a = 11.2$ kJ/mol among $(La_{0.8}Ca_{0.2})CrO_{3-\delta}$-based specimens. The grain size seemed dependent on doping species and the grain sizes were distributed in the range of 2.4–5.6 μm for $(La_{0.8}Ca_{0.2})CrO_{3-\delta}$-based specimens. The rate of grain growth was proportional to the boundary mobility M_b, which was related to the diffusion coefficient of doping cation. $(La_{0.8}Ca_{0.2})CrO_{3-\delta}$-based specimens revealed variety in microhardness, in the range of 4.33–9.85 GPa and the fracture toughness were distributed in the range of 3.52–4.33 MPa $m^{1/2}$. Based on the results in terms of grain size and mechanical properties, we concluded that the microhardness and fracture toughness were dependent on the dopant ions. The $(La_{0.8}Ca_{0.2})Cr_{0.9}Co_{0.1}O_{3-\delta}$ specimen shows high electrical conductivity and mechanical properties Consequently, it is a promising candidate as an interconnect material for intermediate temperature solid oxide fuel cell (IT-SOFC) applications.

1. Introduction

Solid oxide fuel cells (SOFCs) are regarded as highly efficient power generation systems for future application [1–3]. Although polymer electrolyte membrane (PEM) fuel cells are generally preferred for vehicle propulsion, SOFCs, having high tolerance to a variety of fuel sources, are being developed for auxiliary power units (APU) in automotive applications [4]. Many of the challenges in the development of SOFCs can be met with improved materials. Some literature suggests that electrolyte conductivity and electrode catalytic activity should be improved to develop high performance and low cost SOFCs [5–12]. The interconnect materials, which provide the conductive path for electrical current to pass between the electrodes and to the external circuit, are critical materials in SOFCs. Regardless of planar or tubular cell configuration, the role of an interconnect material is actually twofold: it provides an electrical connection between the anode of one individual cell to the cathode of the adjoining one, and it acts as a physical barrier to protect the air electrode material from the reducing environment of the fuel on the fuel electrode side, and prevents the fuel electrode material from being in contact with the oxidizing atmosphere of the air electrode side [13–15].

Lanthanum chromite substituted with alkaline metals (Ca or Sr) has been widely used for interconnection materials in the present generation of SOFCs [16,17]. However, there are

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several problems associated with these perovskite materials: (i) poor sinterability in air due to the volatilization of Cr; (ii) insufficiently high electrical conductivity; and (iii) mismatching of the thermal expansion coefficients (TECs) with other SOFC components. To reduce the previously mentioned disadvantages, some researchers have studied this material by substituting alkaline earth metal ions or transition metal ions at the La and Cr sites, respectively [18–22].

Materials used in an SOFC system may be susceptible to fracture because of thermal stress and mechanical stress during cell fabrication and operation. The stresses to which the ceramic components are subjected can arise from: (i) residual stresses from manufacturing; (ii) temperature gradient; (iii) differential thermal expansion coefficients; (iv) external mechanical loading; and (v) oxygen activity gradients [23]. Generally, some mixture of all these sources of stress may be present in SOFC components. The magnitude of the stresses depends on the material properties, the operating conditions, and the geometry of the SOFC design. Thus, the mechanical behavior of an SOFC component is very important. According to the literature, Ca substitutions effectively reduce the sintering temperature and match the TECs to other SOFCs components [24]. In this study, ionic substitutions were carried out on A sites for Ca, and B sites for M (M = Al, Co, Cu, or Fe). The effects of different dopants substituted for the B sites of $La_{0.8}Ca_{0.2}Cr_{0.9}(M)_{0.1}O_{3-\delta}$ on the electrical conductivity and mechanical properties were systematically investigated. Moreover, the crystal structure and microstructure were also determined. In this study, the Weibull distribution is used to illustrate the strength distribution of a ceramic, which is used for calculations of failure probability for small stress. The statistical strength values obtained from the testing of ceramics were analyzed using the cumulative probability parameter, $F(\sigma)$.

2. Experimental methods

2.1. Sample synthesis

The $La_{0.8}Ca_{0.2}Cr_{0.9}M_{0.1}O_{3-\delta}$ (M = Al, Co, Cu, Fe) powders used for sintering characteristics were prepared by the solid-state technique. Stoichiometric amounts of lanthanum oxide (La_2O_3, 99.9%), calcium carbonate ($CaCO_3$, 99.9%), chromium oxide (Cr_2O_3, 99.9%), aluminum oxide (Al_2O_3, 99.9%), cobalt oxide (Co_3O_4, 99.9%), copper oxide (CuO, 99.9%), and ferric oxide (Fe_2O_3, 99.9%) powders (as seen in Table 1) were mixed with distilled water for 12 h and then calcined in air at 1000 °C for 4 h.

Table 1 – Composition and abbreviation of $(La_{0.8}Ca_{0.2})Cr_{0.9}M_{0.1}O_{3-\delta}$ specimens.

Composition	Abbreviation
$(La_{0.8}Ca_{0.2})CrO_{3-\delta}$	LCCO
$(La_{0.8}Ca_{0.2})Cr_{0.9}Al_{0.1}O_{3-\delta}$	LCCO(Al)
$(La_{0.8}Ca_{0.2})Cr_{0.9}Co_{0.1}O_{3-\delta}$	LCCO(Co)
$(La_{0.8}Ca_{0.2})Cr_{0.9}Cu_{0.1}O_{3-\delta}$	LCCO(Cu)
$(La_{0.8}Ca_{0.2})Cr_{0.9}Fe_{0.1}O_{3-\delta}$	LCCO(Fe)

The powder samples were then pelletized. The pellets were dry pressed at 100 MPa using as-prepared powder for sintering. Sintering was carried out in air at 1500 °C for 6 h with a programmed heating rate of 5 °C/min. The sintered samples were over 90% of the theoretical density in all the specimens. Rectangular bar specimens (5 mm × 5 mm × 10 mm) were used for electrical conductivity measurements.

2.2. Characterization measurements

A computer interface x-ray powder diffractometer (XRD; Model Rigaku D/Max-II, Tokyo, Japan) with Cu K_α radiation (λ = 0.15418 nm) was used to identify the crystalline phase. The morphological characterization of the $(La_{0.8}Ca_{0.2})(Cr_{0.9}M_{0.1})O_{3-\delta}$ (M = Al, Co, Cu, Fe) was carried out using a scanning electron microscope (SEM; Hitachi 3500H, Tokyo, Japan). The electrical conductivity measurements were made at various temperatures in the range 300–850 °C in air by the direct current (DC) four-probe technique. Four Ag leads were attached to the sample with Ag paste and fired at 800 °C. Arrhenius plots (plots of $\ln\sigma T$ versus $10^3/T$) were constructed, and activation energies for conduction were computed. Activation energy for conduction is obtained by plotting the electrical conductivity data in the Arrhenius relation for thermally activated conduction. It was calculated according to the following equation:

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where T is absolute temperature, E_a is the activation energy for conduction, k is the Boltzmann constant, and σ_0 is a pre-exponential factor [25]. The densities of the sintered ceramics were measured by the Archimedean method.

The Young's modulus was measured by JIS R 1602 using the four-point flexure method. The flexural strength of a test specimen 36 mm in length, 4 mm in width, and 2 mm in height was measured at room temperature using the four-point flexural method over spans of 30 mm (lower span) and 10 mm (upper span) at a crosshead speed of 0.5 mm/min (Autograph AG-I; Shimadzu, Tokyo, Japan). According to the fracture strength results, we can describe the strength distribution of a ceramic. The most widely used tool is the Weibull distribution, which is used for calculations of failure probability for small stress. The statistical strength values obtained from the testing of ceramics were analyzed using the cumulative probability parameter, $F(\sigma)$. This is the probability of failure at a stress $\leqq\sigma$ and is given as follows.

$$\frac{1}{1-F(\sigma)} = \exp\left(\frac{\sigma}{\sigma_0}\right)^m \quad (2)$$

where m is the Weibull modulus, which is the slope obtained from a plot of $\ln\{\ln[1/(1-F(\sigma))]\}$ against $\ln(\sigma)$ curves. The σ_0 is a scale parameter with the same dimensions as σ. The estimator of the cumulative probability parameter was calculated by

$$F_i = \frac{i-0.5}{n} \quad (3)$$

where the ith result in the set of n samples in assigned a cumulative probability of failure, F_i. This was done by