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A modified liquid-phase-assisted sintering mechanism for $La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-\delta}$—A high density, redox-stable perovskite interconnect for solid oxide fuel cells

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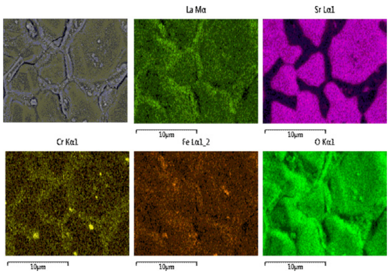
HIGHLIGHTS

- A modified liquid-phase-assisted sintering mechanism is employed.
- A distinct transient liquid phase forms during the sintering process.
- Relative density of 96.6% is successfully obtained for La0.8Sr0.2Cr0.5Fe0.5O$_{3-\delta}$.
- La0.8Sr0.2Cr0.5Fe0.5O$_{3-\delta}$ is proposed as a promising interconnect for SOFCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Fe-doped lanthanum strontium chromites, i.e., $La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-\delta}$ ($x = 0.1$, 0.2, 0.3, 0.4, and 0.5), are synthesised and evaluated as potential interconnect materials for SOFCs. A modified liquid-phase-assisted sintering mechanism is employed to improve the sintering abilities of $La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-\delta}$ powders. A distinct transient liquid phase forms during the sintering process, which spreads into a uniform layer and covers the grain boundaries, thereby enhancing densification. Additionally, it is determined that the amount of liquid phase formed during liquid-phase-assisted sintering significantly affects the densification of doped lanthanum chromites. Relative densities of 94.6% and 96.6% are successfully obtained for $La_{0.8}Sr_{0.2}Cr_{0.6}Fe_{0.4}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$, respectively. Furthermore, these compounds are also redox-stable after being heated to 900 °C in flowing H_2 for 6 h. The electrical conductivity increases with Fe-doping levels, and the conductivity of $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ is measured to be 21.88 S cm^{-1} in air and 6.45 S cm^{-1} in 5% H_2/Ar at 800 °C. Therefore, dense $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ is a promising interconnect alternative for solid oxide fuel cells.

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted considerable interest as a new, clean power generation system with high efficiency. The fuel flexibility of SOFCs makes them an ideal candidate for the effective use of fossil fuels [1–3]. Tubular and planar stack designs are currently the two main SOFC concepts being developed. Tubular SOFCs have certain advantages over planar SOFCs, including ease of sealing and the ability to endure thermal stress caused by rapid heating [4–6]. Unfortunately, only ceramic interconnects can be used in tubular SOFCs [7]. The interconnect, which provides the conductive path for electrical current and separates the fuel gas

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from the oxidant, is an essential part of the SOFC stack. Therefore, the interconnect should be dense, sufficiently conductive, and stable in both oxidising and reducing atmospheres under high temperatures. Because of these strict requirements, only a few materials can be used for SOFC interconnects. $LaCrO_3$-based perovskites, which exhibit high thermal and chemical stability in dual oxidation–reduction atmospheres and good electrical conductivity, are the most promising materials [8–10]. However, the poor sinterability of these compounds in air, because of increased rates of chromium evaporation, imposes a major constraint to their fabrication and utility. Various methods have been suggested to improve the sinterability of doped lanthanum chromite powders, including adding sintering aids [11,12], sintering in a reducing atmosphere [13], using chromium deficient non-stoichiometric composition [14,15], and substituting lanthanum with other elements [12,16]. Nevertheless, adding sintering aids and sintering in a reducing atmosphere increases fabrication complexity and manufacturing costs, whereas using a chromium deficient non-stoichiometric composition causes compositional inhomogeneity. It was determined that the presence of low-melting Ca-rich secondary phases, such as $CaCrO_4$ or $Ca_n(CrO_3)_m$, support the sintering of $La(Ca)CrO_3$ by a liquid-phase-assisted sintering mechanism. However, excess A-site elements tend to react with the zirconia electrolyte during sintering, which produces undesirable secondary phases, such as $La_2Zr_2O_7$ and $CaZrO_3$ [17,18]. Moreover, heavy Ca-doping reduces the chemical and dimensional stability in reducing environments, which decomposes the perovskite structure in fuel conditions [19]. Additionally, chemical expansion causes internal stress and deformation under large oxygen partial pressure gradients [20]. Therefore, an alternative interconnect material is required to overcome the technical limitations of acceptor-doped lanthanum chromite.

To the best of our knowledge, there have been few investigations on aliovalent cation doping of B (Cr) sites for interconnect development. Thus, we hypothesise that doping the B-site with large cations will enhance the diffusion of larger A-site cations during the sintering process. Additionally, doping on the B-site could enhance other properties that may resolve the problems that were previously mentioned [21]. For example, Tao and coauthors [22] have reported that $La_{0.75}Sr_{0.25}Cr_{1-x}Fe_xO_3$ with $x \leq 0.5$ is stable in dry 5% H_2 at 900 °C. Liu et al. [23] successfully prepared $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ) and $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCF) dual-phase composite hollow fibres for oxygen permeation membranes in which oxide ions were transported through YSZ and electrons were transported through LSCF. Furthermore, the ionic conductivity of $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.6}Fe_{0.4}O_{3-\delta}$ was determined to be 0.079 S cm^{-1} at 1223 K with $p(O_2) = 10^{-17}$ atm [24], which is smaller than the ionic conductivity of YSZ (0.1 S cm^{-1}) [1]. Based on these results, and if it has a sufficient density (the accepted density for a ceramic interconnect is 94% [25,26]), Fe-doped lanthanum strontium chromite is expected to satisfy the requirements for use in SOFC interconnects.

In the present work, $La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-\delta}$ ($x = 0.1$, 0.2, 0.3, 0.4, and 0.5) was synthesised and characterised. Relative densities of 94.6% and 96.6% were successfully obtained by a modified liquid-phase-assisted sintering mechanism for $La_{0.8}Sr_{0.2}Cr_{0.6}Fe_{0.4}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$, respectively. The microstructure, electrical conductivities, thermal expansion coefficients, and other properties of $La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-\delta}$ were also investigated. An optimised composition for use in a SOFC interconnect is proposed. The oxygen nonstoichiometry (δ) of $La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-\delta}$ is important because it is closely correlated to the electrochemical properties, mechanical properties, and stability of the material. However, in the present work, we focused on the densification of $La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-\delta}$, which is an extremely critical parameter for the interconnect. The effect of δ will be investigated in future studies.

2. Experimental section

All $La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-\delta}$ (x = 0.1, 0.2, 0.3, 0.4, 0.5) specimens were synthesised individually using the sol–gel method. Metal ion nitrate solutions were prepared from La_2O_3, $SrCO_3$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$. First, La_2O_3 and $SrCO_3$ were dissolved in diluted nitric acid, and $Fe(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were dissolved in de-ionised separately in water. Next, the metal nitrate solutions were mixed together in a proper ratio. An excess of citric acid was added, and the pH of the solution was carefully adjusted to the required level with NH_4OH. The mixtures were placed in a water bath at 80 °C with constant stirring for approximately 3 h to evaporate excess water and obtain a gel. The as-prepared gel was dried at 200 °C and calcined in a temperature range from 900 to 1200 °C for 4 h in air. The crystal structures of the synthesised powder specimens were determined by X-ray diffraction (XRD) with Cu Kα radiation (D8 Advance, Bruker AXS, Germany; 40 kV, 30 mA) at room temperature. To estimate the lattice parameters, the measured XRD patterns were refined using Rietveld refinement. The morphology of the sintered samples was characterised with a field emission scanning electron microscope (S-4800, Hitachi, Japan). Thermal expansion coefficients (TECs) were determined using a TMA 402 F1 Hyperion (Netzsch, Germany).

For the purpose of convenience, $La_{0.8}Sr_{0.2}Cr_{0.9}Fe_{0.1}O_{3-\delta}$, $La_{0.8}Sr_{0.2}Cr_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.8}Sr_{0.2}Cr_{0.7}Fe_{0.3}O_{3-\delta}$, $La_{0.8}Sr_{0.2}Cr_{0.6}Fe_{0.4}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ are abbreviated as Fe 0.1, Fe 0.2, Fe 0.3, Fe 0.4 and Fe 0.5, respectively, throughout this paper.

3. Results and discussion

3.1. Crystal structure

The XRD patterns taken at room temperature of Fe 0.5 powders calcined at 900, 1000, 1100, 1200 °C are shown in Fig. 1. The Fe 0.5 specimens are shown as representative results; the other compositions exhibited similar characteristics. The XRD patterns reveal that although the samples were calcined at different temperatures they all exhibit the perovskite structure. Because of low solubility, an impure $SrCrO_4$ phase was observed (JCPDF card 73-1082) for samples calcined below 1200 °C [14,17,20,26]. For samples calcined at 1200 °C, $SrCrO_4$ dissolved into the perovskite [30] and a pure phase of perovskite powders remained. Notably, when higher calcination temperatures were used, less $SrCrO_4$ was detected (estimated from the peak intensities of $SrCrO_4$ in Fig. 1), which

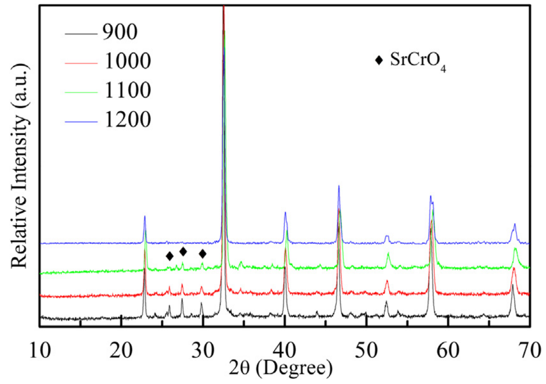

Fig. 1. XRD patterns of Fe 0.5 from powders calcined from 900 °C to 1200 °C.