La_{0.8}Ca_{0.2}CrO₃ Interconnect Materials for Solid Oxide Fuel Cells: Combustion Synthesis and Reduced-Temperature Sintering

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ABSTRACT :

Sub-micrometer La_{0.8}Ca_{0.2}CrO₃ powders for ceramic interconnects of solid oxide fuel cells were synthesized by the aqueous combustion process. The materials were prepared from the precursor solutions with different glycine (fuel)-to-nitrate (oxidant) ratios (ϕ). Single-phase La_{0.8}Ca_{0.2}CrO₃ powders with a perovskite structure were obtained after combustion when ϕ was equal to or larger than 0.480. Especially, the stoichiometric precursor with $\phi = 0.555$ yielded the spherical La_{0.8}Ca_{0.2}CrO₃ particles with 150-250 nm diameters after calcination at 1000°C. When compared with the powders synthesized by the solid-state reaction, the combustion-derived, fine powders exhibited improved sinterability, leading to near-full densification at 1400°C in oxidizing atmospheres. Moreover, a small quantity of glass additives was used to reduce the sintering temperature, and considerable densification was indeed achieved at temperatures as low as 1100°C.

Keywords : Solid oxide fuel cell, Interconnect, Lanthanum chromite, Combustion synthesis, Sintering

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1. Introduction

Interconnects in solid oxide fuel cells (SOFCs) connect electrically the unit cells and separate the fuel from the oxidant in the adjoining cells. The key requirements of the interconnects are (i) high electronic conductivity, (ii) chemical stability in both oxidizing and reducing atmospheres, (iii) low gas permeability, and (iv) chemical/thermal compatibility with other cell components.¹⁻³⁾

Lanthanum chromites (LaCrO₃) with a perovskite structure have become the interconnect material of choice in most SOFC stack developments, since they satisfy the requirements mentioned above.³⁾ However,

the chromites are quite difficult to sinter to high densities even at temperatures above 1600°C in oxidizing atmospheres. This is because sintering proceeds mainly via the evaporation-condensation mechanism of gaseous Cr-O species rather than by the solid-state mass transfer.^{4,5)} Various strategies have been explored to enhance densification, including use of dopants, chromium deficiency, sintering aids and controlled atmospheres.^{1,6-8)} One of the technical approaches that have been widely implemented is to dope LaCrO₃ with Ca on La sites. Liquid-phase calcium chromium oxides being formed during sintering would suppress the vaporization of Cr-O species and accelerate the densification rate.

Different types of synthesis techniques, such as solid-state reaction,⁶⁾ co-precipitation,⁹⁾ hydrothermal,¹⁰⁾ combustion,¹¹⁾ and sol-gel methods,¹²⁾ have been developed to prepare La_{1-x}Ca_xCrO₃ powders. Among

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these, the aqueous combustion method has been known to be effective for synthesizing fine $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powders with the required levels of purity and chemical homogeneity. The combustion technique utilizes a self-sustained reaction between oxidant and fuel. The process involves the dissolution of oxidant (metal nitrates) and fuel (typically, amino acid glycine) in an aqueous solution, followed by the evaporation of excess water at elevated temperatures. On further heating, the reaction medium self-ignites to produce the oxide product ashes. The ashes consist of very fine oxide powders that are suitable for densification during sintering. For example, Nair *et al.* have shown that the powders prepared through the combustion method could be sintered to near-full density at temperatures as low as 1350°C in air.¹¹⁾

In the aqueous combustion process, glycine forms complexes with metal ions to increase solubility. More importantly, it acts as a fuel and controls the flame temperature and the combustion rate.¹³⁾ The objective of this paper is to study the effect of fuel (glycine) concentration on the $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powder characteristics. The powders were synthesized by the combustion technique from the precursor solutions with different molar ratios of glycine to nitrates. The combustion-derived powders were sintered at 1400°C in air and then they were subjected to density measurements and electrical characterizations. Furthermore, the $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders were sintered with a glass additive in an attempt to lower the sintering temperature down to 1100°C.

2. Experimental

2.1. Powder synthesis and sintering

$\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ materials were prepared by the aqueous combustion process as follows: stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Aldrich), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99%, Aldrich) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, Aldrich) were dissolved in distilled water. A desired amount of glycine ($\text{NH}_2\text{CH}_2\text{COOH}$, 98%, Aldrich) was then added into the mixed nitrate solution under stirring conditions. The molar ratio of glycine to nitrates, denoted as ϕ , in the solution was varied between 0.320 and 0.795. The precursor solution was heated slowly to 70°C to evaporate excess water and to form a viscous gel. After further heating to 130°C, the gel ignited spontaneously and the oxide ashes were produced as a result of combustion. Finally the collected ashes were calcined at temperature $T_c = 600$ or 1000°C for 5 h. For comparison, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$

powders were synthesized by a solid-state reaction route as follows: stoichiometric amounts of La_2O_3 (99.9%, Aldrich), CaCO_3 (99.9%, Aldrich), and Cr_2O_3 (99.9%, Aldrich) were thoroughly mixed by a ball-milling process. The precursor mixture was then heat-treated in air at 1500°C for 5 h.

The synthesized powders were uniaxially pressed into a bar under a pressure of 50 MPa and then isostatically pressed under a pressure of 350 MPa using a cold isostatic press (CIP). The powder compact was then sintered at 1400°C for 5 h in air. In addition, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ was sintered with a glass additive at reduced temperatures, *i.e.* 1100 and 1200°C for 5 h. The glass additive used contains SrO , B_2O_3 , La_2O_3 , SiO_2 and Al_2O_3 .

2.2. Materials characterization

In order to identify the crystal structures of the synthesized powder specimens, X-ray diffraction (XRD) patterns were recorded with an automated diffractometer (2500 D/MAX, Rigaku) using Cu K_α radiation. The measurements were conducted over a scanning angle range of 20°–80° at a scan rate of 5° min⁻¹. To determine the particle size and morphology, scanning electron microscopy (SEM) was performed using a high-resolution Hitach X-4900 system. The electrical conductivity of the sintered body was measured in both air and 30 vol.% H_2 in N_2 by a DC four-probe technique (Keithley 2400). The sample was heated to 900°C at a rate of 5°C min⁻¹, and then was held for 24 h. After that, the conductivity was measured over a temperature range of 500–900°C. Three-point bending test of the sintered sample was conducted at room temperature using an Instron 5544A. A crosshead speed was 2 mm min⁻¹.

3. Results and Discussion

One of the primary functions of glycine is to serve as a fuel for the combustion reaction. Therefore, the flame temperature and the combustion rate strongly depend on the glycine concentration, *i.e.* glycine-to-nitrate ratio (ϕ), in the precursor solution. According to propellant chemistry, the ‘stoichiometric’ redox reaction occurs when the total oxidizing valency of metal nitrates is the same as the total reducing valency of fuel.^{14–16)} This refers to the case where $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ is produced directly from the combustion reaction between glycine and nitrates requiring no additional ambient oxygen. The value of ϕ for the stoichiometric reaction corresponds to 0.555 for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$. In order to study the effect

of ϕ on the powder characteristics, the powders were synthesized with fuel-deficient ($\phi < 0.555$), stoichiometric ($\phi = 0.555$) and fuel-rich ($\phi > 0.555$) ratios.

Fig. 1 presents the XRD patterns for the as-combusted powders (oxide product ashes) that were obtained from the precursor solutions with different ϕ values. The XRD data indicate that the crystal structure of the oxide product is highly dependent on the value of ϕ . The as-combusted powder obtained using $\phi = 0.320$ exhibited a completely amorphous structure and only carbonaceous leftovers remained after combustion, as shown in Fig. 1(a). The combustion reaction with $\phi = 0.400$ resulted in a mixture of perovskite phase and secondary phases corresponding to CaCrO_m and/or LaCrO_n . It is generally known that the flame temperature reaches a maximum at a certain ϕ value being slightly lower or higher than the stoichiometric value.¹⁴⁾ Figs. 1(a) and (b) suggest that in the case of $\phi < 0.480$ the flame temperature is not high enough to form a single phase, crystalline $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$. Pure $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders were obtained when ϕ was equal to or higher than 0.480. The measured XRD patterns in Figs. 1(c)-(e) fit well with the data calculated based on an orthorhombic perovskite structure with space group $Pnma$. As the ϕ value increased from 0.440 to 0.795, the diffraction peaks became sharper indicating increased crystallinity.

The as-combusted powders with $\phi = 0.480, 0.555$

and 0.795 were calcined at either 600 or 1000°C for 5 h. Illustrated in Fig. 2 are the SEM micrographs of the as-calcined powders. As shown in Figs. 2(a), (c) and (e), all $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders calcined at 600°C were composed of nano-crystallites in thin-sheeted, soft agglomerates, regardless of the ϕ value. Fig. 2 shows that the stoichiometric precursor with $\phi = 0.555$ resulted in smaller primary particles with more uniform size distribution as compared with the fuel-deficient ($\phi = 0.480$) and fuel-rich ($\phi = 0.795$) precursors. This means that the stoichiometric ratio of glycine to nitrate yielded the most favorable conditions for producing fine, crystalline $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ particles: (i) the flame temperature was high enough to form crystalline particles and (ii) the combustion rate is so fast that the significant particle growth was inhibited. The formation of larger particles from the fuel-rich precursor might be attributed to more sluggish combustion reaction at a higher fuel concentration.¹¹⁾ As presented in Figs. 2(b), (d) and (f), the calcination at 1000°C resulted in relatively large particles that were loosely bound together. In particular, the spherical $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ particles as small as 150-250 nm were obtained with $\phi = 0.555$. Such fine powders are expected to exhibit sintering characteristics suitable for densification.

Fig. 3 depicts the powder XRD patterns for

Fig. 1. XRD patterns for the as-combusted $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders obtained from the precursor solutions with different glycine-to-nitrate ratios (ϕ).

Fig. 2. SEM micrographs of the as-calcined $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders. The glycine-to-nitrate ratio (ϕ) and the calcination temperature (T_c) are indicated in the figure.

Fig. 3. XRD patterns for the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders calcined at 1000°C .

$\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ calcined at 1000°C . Additional peaks, indicated by 'x', appeared in all of the diffraction patterns, which indicated the formation of calcium chromium oxides such as CaCrO_4 and/or CaCr_2O_4 during high-temperature heat-treatment. This result is quite well consistent with the previous reports.^{11,17} During sintering, traces of calcium chromium oxides could melt, disperse along the grain boundaries and thus enhance densification, as reported in the previous studies.^{11,17} The $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders prepared from the stoichiometric precursor solution ($\phi = 0.555$) were used for the following studies on the sinterability and the electrical characterizations.

In order to examine the effect of powder characteristics on the sinterability, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders were also prepared by a conventional solid-state reaction route. La_2O_3 , CaCO_3 and Cr_2O_3 precursors were used. The SEM micrograph in Fig. 4 shows that the powders synthesized by the solid-state method consisted of larger particles (approximately 1–2 μm) when compared with the powders obtained by the combustion process. Both the materials were sintered at 1400°C in air, and then the relative density, *i.e.* a percentage of the theoretical density, was measured by the Archimedes' method. The relative density of the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ was estimated to be 97.37%, which was higher than that of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ prepared by the solid-state method (95.32%). This confirms that the fine powders synthesized by the combustion method exhibit

Fig. 4. SEM image of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders synthesized by the solid-state reaction process.

Fig. 5. Temperature dependence of the electrical conductivity (σ) measured on the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$. The measurements were performed in air and 30 vol.% H_2 in N_2 .

improved sinterability, leading to near-full densification.

Fig. 5 presents the temperature dependence of the electrical conductivity (σ) determined from the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ in air and H_2/N_2 . The σ values at 800°C are listed in Table 1. The relationship between $\ln(\sigma T)$ vs. $1/T$ was linear, as predicted by the following equation derived for the small polaron conduction:

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

where A is the proportional factor, T the absolute temperature, k the Boltzmann constant, and E_a the activation energy for conduction. From the slopes of the $\ln(\sigma T)$

Table 1. Electrical conductivity determined from $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ in air and 30 vol.% H_2 in N_2 .

Synthesis method	Electrical conductivity σ at 800°C (S cm^{-1})	
	Air	30 vol.% H_2 in N_2
Combustion reaction	18.5	1.14
Solid-state reaction	15.8	0.76

vs. $1/T$ plots, the E_a values were calculated to be 10.0 kJ mol^{-1} in air and 27.1 kJ mol^{-1} in H_2/N_2 .

Under oxidizing conditions, Ca doping on La sites results in a charge-compensating transition of Cr^{3+} to Cr^{4+} , *i.e.* hole formation, thereby enhancing the electronic conductivity. Under reducing conditions, on the other hand, charge compensation should occur by the formation of oxygen vacancies. The oxygen loss reduces the charge carrier concentration and, thereby, decreases the conductivity.^{1,3)} As a matter of fact, the σ values in H_2/N_2 were measured to be lower by more than one order of magnitude over the whole temperature range, compared with σ in air. It should be noted that the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ exhibited higher conductivity than $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ prepared by the solid-state reaction (see Table 1). This could be ascribed to a higher degree of densification of the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, as confirmed from the density measurements.

Several attempts have been made to fully densify lanthanum chromites at reduced temperatures in oxidizing atmospheres by introducing sintering aids such as oxides and fluorides with low-melting points.^{1,18)} In a recent study, we have shown that a small amount of glass could act as a reactive additive to encourage densification of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$.¹⁹⁾ A wide variety of results have been obtained depending on the glass amount, constituent and properties, *e.g.* softening point. In the present work, 5 wt.% of the glass additives were introduced for sintering of the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$. The glass additive had the constituents of SrO , B_2O_3 , La_2O_3 , SiO_2 and Al_2O_3 .

Fig. 6 compares the SEM micrographs of the fractured surfaces of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ sintered without and with the glass additive. The samples were sintered at either 1100 or 1200°C for 5 h in air. As shown in Fig. 6(a), little grain growth occurred in pure $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ during sintering at 1100°C, resulting in a very porous body. Fig. 6(b) shows that the degree of densification increased upon firing at 1200°C, but many small pores still remained on grain intersections. When sintering was conducted at 1100°C in the presence of the glass additive, on the other hand,

Fig. 6. SEM micrographs of the fractured surfaces of the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ sintered (a, b) without and (c, d) with the glass additive. The samples were sintered at either 1100 or 1200°C. **Fig. 7.** Typical flexural stress-strain curves for the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ sintered at 1100°C in the absence and presence of the glass additive.

the sintered body exhibited a densely packed array of larger grains without residual pores. The fractured surface of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ sintered with the additive at 1200°C showed a glassy appearance in some regions, but the compositional analysis indicated no significant changes in the overall composition.

In addition to the SEM observations, the measurement of mechanical strength may provide further evidence proving the glass-assisted densification. Fig. 7 presents typical flexural stress-strain curves for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ sintered at 1100°C in the absence and presence of the glass additive. The ultimate flexural strength of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ sintered with the glass additive was 113.5 MPa, which was much higher than that of pure

$\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ (22.8 MPa). Here, the ultimate flexural strength was determined at the point of failure on the stress-strain curve. This indicates that densification can be remarkably improved with the glass additive even at temperatures as low as 1100°C. The preliminary results presented in Figs. 6 and 7 suggest that a minor quantity of glass additives can pull the $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ particles together and enhance mass transport during sintering, giving rise to accelerated densification at reduced temperatures. Further work is in progress to optimize the additive constituents, amount, sintering conditions in order to mitigate possible degradation of electrical properties due to the incorporated glass species.

4. Conclusions

Fine $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders were synthesized by the aqueous combustion method with different glycine-to-nitrate ratios (ϕ). The XRD results indicated that the crystal structure of the as-combusted powders were strongly dependent on the ϕ value. The value of $\phi \geq 0.480$ was a necessary condition for the formation of single-phase $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ after combustion. The stoichiometric precursor with $\phi = 0.555$ resulted in smaller particles with more uniform size distribution as compared with the fuel-deficient ($\phi = 0.480$) and fuel-rich ($\phi = 0.795$) precursors. The stoichiometric precursor ($\phi = 0.555$) yielded the spherical $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ particles as small as 150–250 nm after calcination at 1000°C. When compared with the powders synthesized by the solid-state reaction, the combustion-derived powders exhibited improved sinterability, leading to near-full densification at 1400°C in air, and thus they showed higher electrical conductivity in both oxidizing and reducing atmospheres. Moreover, a small quantity of glass additives gave rise to considerable densification of the combustion-derived $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ at temperatures as low as 1100°C.

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