

Effects of Calcium and Lithium Additions on the Densification and Electrical Conductivity of Gadolinia-Doped Ceria

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Abstract

This work investigates the effects of small additions of lithium and calcium on the densification and electrical conductivity of ceria-10 mol% gadolinia. Solid electrolytes co-doped with 1.5 mol% lithium or calcium were prepared by the coprecipitation method. Pressureless sintering of compacts was carried out in the 1250-1500°C range. The sintered density increased for specimens containing the additives allowing for reducing the sintering temperature by about 150°C in order to obtain similar values. The additives enhanced the grain growth process. The grain size distribution of specimens containing calcium and sintered at 1350°C for 4 h, for example, is comparable to that of pure gadolinia-doped ceria sintered at 1500°C for 4 h. The grain conductivity of specimens containing additives is similar to that of pure gadolinia-doped ceria. Both additives exert an important effect on the grain boundary conductivity as determined by impedance spectroscopy measurements.

Keywords: Ceria, solid electrolyte, coprecipitation, densification, electrical conductivity.

Introduction

Over the last years, efforts have been made to lower the operating temperature of solid oxide fuel cells to the so-called intermediate temperature (< 750°C) range. This goal has contributed to the discovering and designing of new oxide-ion conductors.^{1,2} At present, however, the most developed solid electrolyte with sufficient electrical conductivity to operate in that temperature range are those based on doped ceria.

Several cations may be incorporated into the cubic lattice of ceria solid electrolytes as co-additives to act as sintering aid. A recent review on this subject³ revealed that transition metal oxides such as Cu, Co, Fe and Mn, along with Li reduce the sintering temperature of gadolinia-doped ceria, while Ca, Mg and Ni have little effect on densification. In that study the effect of the additives on electrical conductivity was not investigated.

Cho et al.⁴ have shown that small amounts of CaO scavenge the intergranular silicious phase in gadolinia-doped ceria containing 500 ppm of SiO₂ leading to an increase in grain boundary conduction. However, the effect of calcium addition on electrical conductivity in low-silica gadolinia-doped ceria is unknown.

In this work, powders of gadolinia-doped ceria containing 1.5 mol% of Ca or Li were prepared by the oxalate coprecipitation technique. The effects of these co-additives in the densification and electrical conductivity of the solid electrolyte were systematically investigated.

Experimental

Cerium oxide containing 10 mol% gadolinia and 1.5 mol% lithium (CGLi) or calcium (CGCa) were prepared by the oxalate coprecipitation method. Cerium nitrate hexahydrate (99.99%, Aldrich), gadolinium oxide (99.99%, Strem Chemicals), lithium carbonate (99%, Alfa Aesar) and calcium carbonate (reagent grade, Vetec), were used as starting materials. Ammonium hydroxide, oxalic acid, absolute ethanol, iso-propanol and *n*-butanol (P.A. grade) were also employed during synthesis. Full description of the synthesis procedures may be found elsewhere.⁵ For comparison purposes Ce_{0.9}Gd_{0.1}O_{1.95}, GDC, (Fuel Cell Materials) was used as standard material.

The coprecipitated powders were calcined at 400°C (CGLi) or 700°C (CGCa). Powder compacts were sintered at several dwell temperatures and times in air.

Sintered specimens density was determined by the water immersion technique. Microstructural characterization was performed on polished and thermally etched surfaces in a scanning electron microscope (Philips, XL30). The mean grain size was determined by the intercept method. Electrical conductivity measurements were carried out by impedance spectroscopy (HP 4192A) in the 5 Hz-13 MHz and 1300-400°C frequency and temperature ranges, with 100 mV of applied signal and using silver as electrode material.

Results and Discussion

The sintered density of GDC specimens as a function of dwell time at 1500°C is listed in table 1.

Table 1 Values of sintered density, D_{hid} , of GDC specimens.

Time (h)	D_{hid} (g.cm ⁻³)
2	6.22
4	6.78
6	6.77

Increase in the density occurs up to 4 h at 1500°C. Table 2 lists values of density for co-doped specimens.

Table 2 Values of sintered density at several dwell temperatures and dwell time of 4 h for co-doped specimens.

Temperature (°C)	D_{hid} (g.cm ⁻³)	
	CGCa	CGLi
1300	6.82	6.69
1350	6.73	6.78
1400	6.84	7.12
1450	7.15	7.18
1500	7.13	7.16

The density increases up to 1450°C and is higher for specimens containing Li. At 1350°C all specimens have densities of about 94% of the theoretical value. These results evidence that both additives act as sintering aids to gadolinia-doped ceria.

Fig. 1 shows a scanning electron microscopy micrograph of a polished and thermally etched surface of GDC specimen sintered at 1500°C for 2 h. It can be seen a wide distribution of grain sizes. There are small fractions of pores and grain pullout.

Micrographs of co-doped specimens are shown in Fig. 2. These specimens were sintered at (a) 1350, (b) 1400 and (c) 1500°C for 4 h. The pore fraction decreases with increasing the dwell temperature, as expected. The porosity and grain pullout are higher after sintering at 1350°C. Specimens sintered at 1400 and 1500°C are dense, but the grain growth is accelerated compared to specimens sintered at lower temperatures.

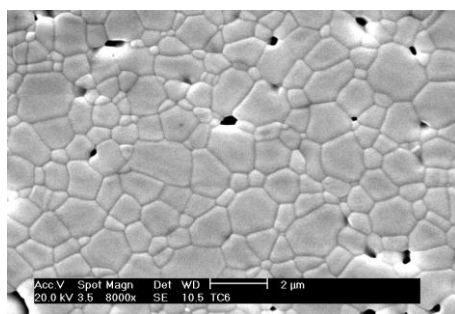


Fig. 1 Scanning electron microscopy micrograph of commercial gadolinia-doped ceria.

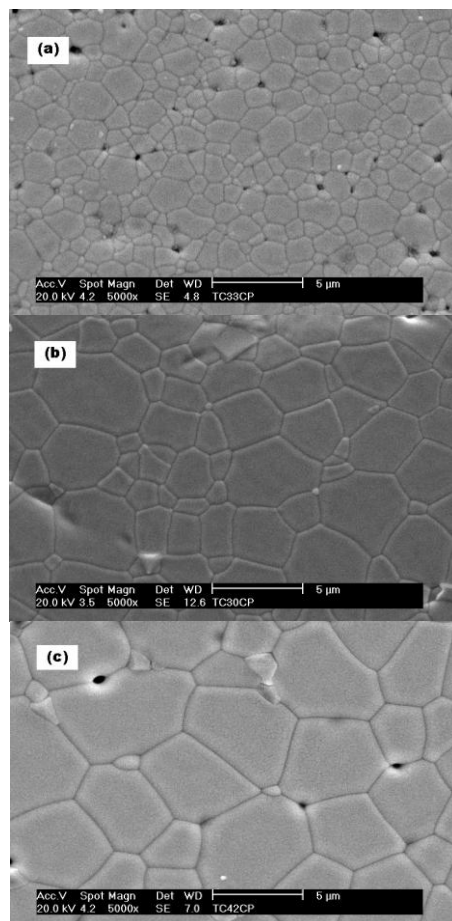


Fig. 2 Scanning electron microscopy micrographs of CGCa specimens sintered at (a) 1350, (b) 1400 and (c) 1500°C for 4 h.

Fig. 3 shows scanning electron microscopy micrographs of specimens containing lithium as co-dopant sintered at (a) 1350, (b) 1400 and (c) 1500°C for 4 h. It can be seen that lithium addition does not change substantially the microstructure of gadolinia-doped ceria (Fig. 1). All micrographs show a small fraction of porosity and angular grains. The main difference is the grain size. In general, the higher is the dwell temperature the higher is the grain size. However, in specimens with lithium addition, the grain size is similar to that of the commercial material without additive.

Table 3 lists values of mean grain size, G , of selected sintered specimens.

Table 3 Mean grain size of pure and 1.5 mol% additives containing gadolinia-doped ceria. Dwell times were 2 and 4 h for commercial and co-doped specimens, respectively.

Temperature (°C)	G_{CGCa} (μm)	G_{CGLi} (μm)	G_{GDC} (μm)
1350	1.61	0.91	-
1400	3.39	1.14	-
1500	6.17	1.78	1.54

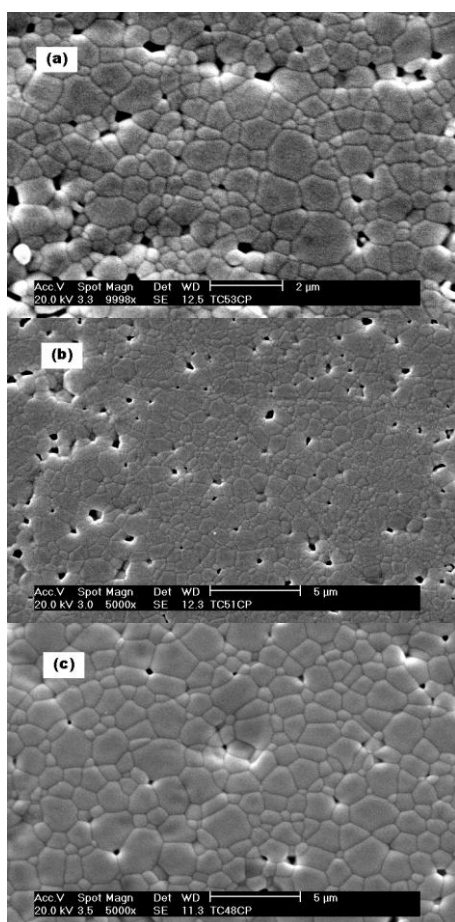


Fig. 3 Scanning electron microscopy micrographs of CaGLi specimens sintered at (a) 1350, (b) 1400 and (c) 1500°C for 4 h.

The medium grain size of specimens containing calcium is considerably higher than those of other specimens. Therefore, calcium acts as both a sintering aid and promotes an accelerated grain growth.

Addition of lithium also enhanced the gadolinia-doped ceria densification. In this case, due to its relative low melting point the densification should occur by liquid phase sintering.³

Fig. 4 shows the Arrhenius plots of electrical conductivity of pure and calcium co-doped specimens. The grain conductivity (Fig. 4 top) of the commercial material is higher than those of specimens containing calcium sintered at both 1350 and 1500°C.

It is worth to note that the grain conductivity of specimens containing calcium sintered at 1350°C is higher than that sintered at 1500°C. This result suggests that calcium addition may induce dopant (gadolinium) segregation. This would explain the comparatively lower value of grain conductivity.

The grain boundary conductivity (Fig. 4 bottom) of co-doped specimens is also lower than that of gadolinia-doped ceria. This result agrees with the hypothesis of possible dopant segregation and formation of a secondary and less conductive phase at the grain boundaries.

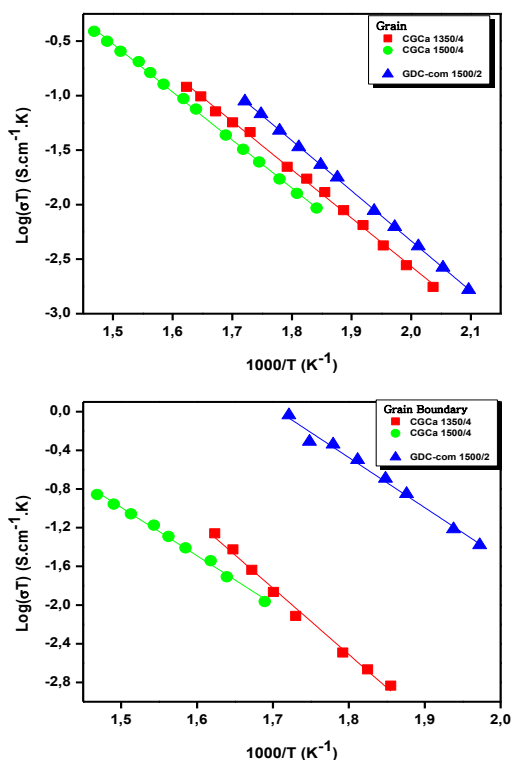


Fig. 4 Arrhenius plots of grain (top) and grain boundary (bottom) conductivity of calcium co-doped specimens.

Fig. 5 shows the Arrhenius plots of grain (top) and grain boundary (bottom) conductivity of specimens containing lithium sintered at 1400 and 1500°C, and that of the commercial material at 1500°C, for comparison purposes.

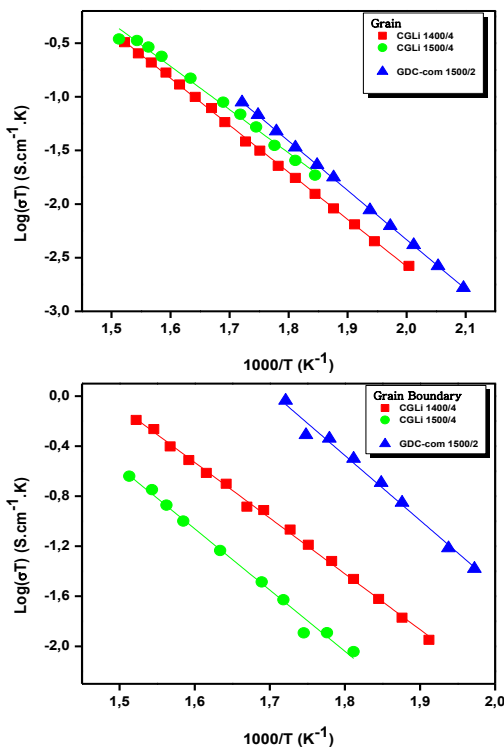


Fig. 5 Arrhenius plots of grain (top) and grain boundary (bottom) conductivity of lithium co-doped specimens.

The grain conductivity (Fig. 5 top) of co-doped specimens increases with increasing the dwell temperature. There is a negligible difference between the grain conductivity of the commercial gadolinia-doped ceria and the coprecipitated one containing lithium and sintered at 1500°C. This means that lithium has a very low solubility into the ceria matrix.

The grain boundary conductivity (Fig. 5 bottom) is lower for co-doped specimens due to lithium segregation at the grain boundaries.

Conclusions

Dense specimens of gadolinia-doped ceria containing 1.5 mol% calcium or lithium were successfully prepared by the coprecipitation technique followed by conventional sintering.

Calcium and lithium additives act as sintering aid to gadolinia-doped ceria. The grain growth is enhanced in specimens containing calcium. All specimens exhibited lower grain and grain boundary conductivities compared to pure gadolinia-doped ceria. Lithium exerts less influence than calcium in the electrical conductivity of GDC.

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