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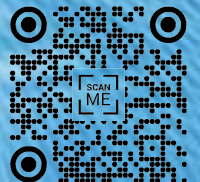
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## OPTIMIZATION OF LOW-GRADE CGO TRANSPORT PROPERTIES FOR SOFC APPLICATIONS

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### ABSTRACT

Grain boundaries are frequently responsible for a poor performance of gadolinium-doped ceria-based electrolytes, due to a low ionic conductivity, orders of magnitude smaller than the bulk conductivity. Silica, the dominant impurity in many low-grade ceramics, namely, in ceria-based materials, has a detrimental effect on grain boundaries conductivity. Several previous works had explored the silica-scavenging effect. In the present work, we exploit an alternative approach using the addition of 5% (w/w) of  $Y_2O_3$ , as silica scavenging agent, and sintering by hot pressing at low temperature to minimize bulk dissolution of yttrium in the CGO lattice. Gadolinium-doped ceria-based powders were co-fired with additions of 1% (w/w) of silica, and silica and yttrium oxide to test the silica scavenging role of yttrium. The samples were prepared by hot press at low temperature (1000°C) and were characterized by impedance spectroscopy as a function of temperature in air, in order to de-convolute different microstructural contributions to the overall electrical behaviour. Combined information obtained from structural, microstructural, and electrical characterization allowed one to study the impact of new phases on the resulting ceria-based solid electrolytes.

**Keywords:** Ceria, Yttria, Scavenge effect, Heterogeneities, Hot press.

### INTRODUCTION

The threat of global warming due to burning fossil fuels and clean-up challenges from using nuclear power have resulted in rise of environmental consciousness and tremendous efforts on seeking alternative power sources in the whole world. The fuel cell is one attractive alternative that can produce clean and efficient electricity to meet the environmental challenges and is a radically different way of making electrical power from a variety of fuels. The major requirement for current carrying devices like solid oxide fuel cell (SOFCs) is the fast ion conduction in solid electrolytes, which is the combined result of large concentrations of ionic defects and high ionic mobility. Materials with the fluorite-type structure are amongst the most effective oxygen-ion conductors. The fluorite structure shows comparatively high oxygen-ion mobility and accepts high levels of anionic disorder, which can be introduced to compensate for aliovalent metal doping [1,2]. One of the most used fluorite-type oxides is yttria stabilized zirconia (YSZ), which, due to the relatively low ionic conductivity, requires an operating temperature range reasonably high, and consequently the use of expensive complementary materials. Reducing the operating temperature allows the use of cheaper construction materials and more reliable seals. Thus, new materials have been investigated to lower the operating temperature to 500/700°C, which includes new electrolyte materials [3] with higher ionic conductivity. The recommended use of low-grade ceramics, much cheaper than the high purity oxides, has silica as predominant constituent of the grain boundary region. Doped ceria is one of the most recognized electrolytes in the intermediate temperature range (IT-SOFCs), and shows much higher ionic conductivity than that of the well-established yttria-stabilized zirconia (YSZ) [4, 5]. However, the grain boundary behaviour usually dominates the total conductivity of ceria-based electrolytes in intermediate temperature range [4-6]. Due to the presence of thin siliceous films, the grain boundary has a blocking effect to the transport of oxygen ions across the electrolyte. In the well-established stabilized zirconia system, there have been many studies [7–13] aimed at improving grain-boundary conduction by engineering the grain-boundary phase. The principal approaches are the scavenging of the siliceous phase by the addition of  $Al_2O_3$  [7–11], the gathering of a Si-containing phase into a discrete configuration [11,12] and the dewetting of the intergranular phase by crystallization [13]. However, alumina additions to CGO ceramics showed a detrimental effect attributed to the formation of another non-conductive phase,  $GdAlO_3$  [14]. Another attempt with CGO ceramics involved additions of lanthanum oxide, as scavenging agent, which proved to be effective on removing the siliceous phases from the grain boundaries [15].

In the present work, we exploit an alternative approach to optimize the total conductivity of CGO electrolytes, using the addition of 5% (w/w) of  $Y_2O_3$ , as silica scavenging agent, and sintering by hot pressing at low temperature to minimize bulk dissolution of yttrium in the CGO lattice and hence promoting the formation of heterogeneous microstructures.

## EXPERIMENTAL

Ceramic samples were prepared using commercially high purity powders as starting materials (Table 1). CGO5 was used as a reference material to compare with the prepared compositions. All samples were prepared using conventional ceramic solid state processing route. To obtain dense ceramics, the powders were sintered by hot press (HP) at 1000°C for 2 h with 65 MPa. To study the temperature effect, a posterior thermal treatment was done at 1100°C and 1400°C for 2h. The density was calculated using Archimedes method. The samples were analysed by x-ray diffraction (XRD) and SEM/EDS. The relative density (RD) was obtained using the density from Archimedes method and from XRD The bulk and grain boundary resistances were obtained by ac impedance spectroscopy in air, using HP Impedance Analyzer. The electrical measurements were performed in air between 1000°C and 300°C, in the frequency range of 20 -10<sup>6</sup> Hz. The same analyser was used to assess the oxygen partial pressure (pO<sub>2</sub>) dependence of the total conductivity, during isothermal measurements carried out between 800 and 1000°C, with pO<sub>2</sub> changing from about 10<sup>-15</sup> Pa to air, using a gas mixture of 5%H<sub>2</sub> and 95% of N<sub>2</sub>.

## RESULTS AND DISCUSSION

Structural characterization by XRD confirms a CGO single phase material with the fluorite type structure, without detection of silica and yttrium oxide. SEM/EDS analysis also show a homogeneous distribution of Si and Y over all the samples, suggestion an incorporation of this elements into the CGO lattice. Slight increase of the lattice parameter (Table 1) also suggests the formation of solid solution.

Table 1. Prepared samples notation, composition, thermal treatment, and obtained relative density (RD) and lattice parameter (a<sub>0</sub>).

Sample	Composition	Thermal treatment	RD (%)	a <sub>0</sub> (Å)
CGO5	Ce <sub>0,95</sub> Gd <sub>0,05</sub> O <sub>2-δ</sub>	HP	92.42	5.416535
CGO5 Si	Ce <sub>0,95</sub> Gd <sub>0,05</sub> O <sub>2-δ</sub> +1%(w/w) SiO <sub>2</sub>	HP	77.56	5.4176936
CGO5 Si 1100	Ce <sub>0,95</sub> Gd <sub>0,05</sub> O <sub>2-δ</sub> +1%(w/w) SiO <sub>2</sub>	HP + 1100°C 2h	93.36	5.4157112
CGO5 Si 1400	Ce <sub>0,95</sub> Gd <sub>0,05</sub> O <sub>2-δ</sub> +1%(w/w) SiO <sub>2</sub>	HP + 1400°C 2h	95.97	5.4139509
CGO5 Si 5Y	Ce <sub>0,95</sub> Gd <sub>0,05</sub> O <sub>2-δ</sub> +1%(w/w) SiO <sub>2</sub> +5% (w/w) Y <sub>2</sub> O <sub>3</sub>	HP	83.97	5.417249
CGO5 Si 5Y 1100	Ce <sub>0,95</sub> Gd <sub>0,05</sub> O <sub>2-δ</sub> +1%(w/w) SiO <sub>2</sub> +5% (w/w) Y <sub>2</sub> O <sub>3</sub>	HP + 1100°C 2h	85.44	5.41408
CGO5 Si 5Y 1400	Ce <sub>0,95</sub> Gd <sub>0,05</sub> O <sub>2-δ</sub> +1%(w/w) SiO <sub>2</sub> +5% (w/w) Y <sub>2</sub> O <sub>3</sub>	HP + 1400°C 2h	93.44	5.412672

Silica addition significantly decrease the specific grain boundary conductivity, which suggests the presence of this impurity on the grain boundary (Fig.1A). Specific grain boundary conductivity partially recovers with the addition of yttria for all temperatures of thermal treatment. This effect on the specific grain boundary conductivity denotes that Si and Y have a preferential effect on grain boundaries.

The oxygen partial pressure dependence of the total conductivity shows the well-known behaviour of CGO based materials, with an ionic plateau for high oxygen partial pressures and an onset of n-type conductivity for low oxygen partial pressure. Silica as a negative effect on both types of conductivities, while yttria addition reveals some recover of the ionic conductivity and no significative effect on the n-type conductivity.

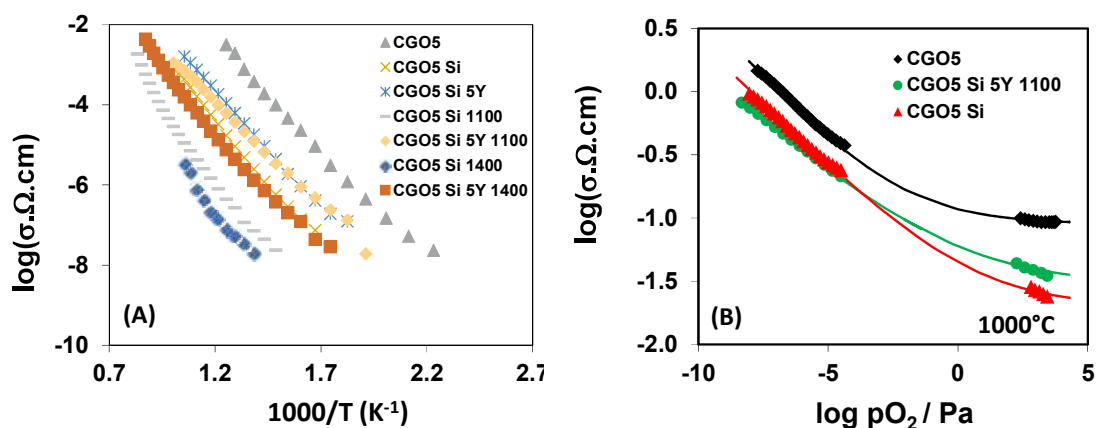


Fig. 1. Arrhenius plot of specific grain boundary conductivity (A) and oxygen partial pressure dependence of total conductivity (B).

## CONCLUSIONS

Samples of gadolinium-doped ceria-based electrolytes were thermal treated at different temperatures (1100 and 1400°C) after hot press at 1000°C. High density ( $\geq 90\%$ ) was achieved with almost all the samples. Addition of small amounts of impurity of silica reduces the total conductivity when compared with pure ceramic sample. However, addition of yttria increases total conductivity when compared with samples without yttria. This effect is related with the partial recover of specific grain boundary conductivity, suggesting a preferential location of Si and Y cations on grain boundaries.

## ACKNOWLEDGEMENT

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