NATIONAL HYDROGEN ASSOCIATION TURKEY

OntarioTech UNIVERSITY

International Association for Hydrogen Energy

Proceedings of WHEC-2022

Bridging Continents by H_2

WHEC-2022

23rd World Hydrogen Energy Conference

Onsite and Online

June 26-30, 2022

Istanbul Congress Center, Istanbul, Turkey

Editors:
Ibrahim Dincer
Can Ozgur Çolpan
Mehmet Akif Ezan

www.whecistanbul.org
info@whecistanbul.org

ISBN: 978-625-00-0843-0

WHEC-2022
23rd World Hydrogen Energy Conference
June 26-30, 2022 - Istanbul

ELECTRICAL CONDUCTIVITY OF Y-DOPED CGO BASED MATERIALS SINTERED BY HOT PRESS

[1]*Devaraj Ramasamy*, [1]*Eduarda Gomes*, [1]*António A.L. Ferreira*, [1,2*]*João C.C. Abrantes*
[1]proMetheus, Instituto Politécnico de Viana do Castelo, 4900-347 Viana do Castelo, Portugal
[2]CICECO Aveiro Institute of Materials, Universidade de Aveiro, 3810-193I Aveiro, Portugal

*Corresponding author e-mail: jabrantes@estg.ipvc.pt

ABSTRACT

Commercial ceria–gadolinia powders were used to prepare dense CGO (5 mol% Gd) samples, by hot press method at relatively low temperature (1000°C). To study the effect of post-sintering, further the as-sintered bodies were subjected into different thermal treatments 1100ºC-1400ºC. The sintered samples were characterized by impedance spectroscopy as a function of temperature in air, in order to identify each microstructural contribution to the overall electrical behaviour. Scanning electron microscopy shows that the increase in the temperature of thermal treatment leads to grain growth. Electrical properties were studied with different oxygen partial pressures and ion blocking methods. Y_2O_3 (5 wt%) additions were used to seek the grain boundaries heterogeneities effects in CGO material, prepared by hot press and subjected into post sintering thermal treatments. Electrical conductivities of CGO samples were analysed with and without Y_2O_3 additions.

Keywords: SOFC, Hot press, CGO, Electrical conductivity, Heterogeneities.

INTRODUCTION

The electrolyte is a crucial component of solid-state electrochemical systems, in which ions must diffuse between electrodes. Gadolinium doped cerium oxide (CGO) electrolytes have an extraordinary range of applications, which include solid oxide fuel cells (SOFC), electrolysers, oxygen sensors, oxygen permeation membrane systems, oxygen storage capacitors, pumps and photo catalysts, mostly, due to its unique properties, such as high electrical conductivity (high mobility of oxygen ions) and catalytic activity (large oxygen storage capacity) compared to those of conventional zirconia-based electrolytes. However, a high material cost or insufficient performance of CGO may prevent commercial success in some of these applications [1-3]. It is noted that the contribution of grain-boundary resistivity to the overall resistivity of CGO based materials are known to be 2-3 orders of magnitude higher than the grain-interior resistivity, due to the depletion of oxygen vacancies near the grain-boundary, due to the formation of a space charge layer. Though, promising properties of CGO can be obtained by selecting the proper concentration of oxygen vacancies in the crystal structure, as well as the fitting microstructure, since both have a direct and decisive effect on functional properties [4-5]. However, it is challenging to obtain homogeneous microstructures with full densification for ceria-based materials, since CGO has a poor sinterability due to its high refractoriness. It is also expected that ionic conductivity of ceria-based electrolytes might be optimized by engineering core–shell microstructures, with higher contents of trivalent additive at the shell [6].

In this work, we assess and correlate the sinterability, microstructural evolution, and electrical properties of CGO samples with and without addition of Y_2O_3, prepared by hot press method.

MATERIALS AND METHODS

Commercially available $Ce_{0,95}Gd_{0,05}O_{2-\delta}$ (Praxair) and Y_2O_3 (Alfa Aesar) high purity powders were used as starting materials. Doped Y_2O_3 (5 wt%) into $Ce_{0,95}Gd_{0,05}O_{2-\delta}$ powder was prepared using conventional solid-state reaction method. The $Ce_{0,95}Gd_{0,05}O_{2-\delta}$ powders with and without Y_2O_3, were sintered by hot-press method in an alumina die under 60 MPa at 1000ºC for 2h, 5˚C/min heating and 10ºC/min cooling rate were used. The sintered samples are labelled CGO5 and CGO5 5Y. In order to study the effect of post-sintering, further the as-sintered bodies were subjected into different thermal treatment at 1100˚C and 1400˚C for 2h. The samples were named CGO5-1100˚C, CGO5 5-1100˚C and so on. Scanning electron microscopy was used to characterize microstructure features of sintered ceramic samples. The total conductivity measurements were performed on dense pellets prepared by hot-press and post thermal treatment, using an AC impedance spectroscopy in air HP Impedance Analyzer. The pellets were painted on both sides with porous platinum electrodes and fired at 900ºC. All measurements were carried out from 1000 to 100°C with 25°C steps, in the frequency range of 20 -10^6 Hz. In order to obtain the n-type conductivity, a dense CGO based samples were painted with a Pt electrode and then sealed against a dense alumina disk with glass ceramic seal, to achieve gas tightness required for ion blocking measurements. This electrode was polarized cathodically, at different values of applied voltage and the corresponding current was measured.

RESULTS AND DISCUSSION

The morphology of CGO samples sintered at 1000˚C by hot press and with post thermal treatment at 1100˚C and 1400˚C are presented in Fig.1. The ceramics sintered at 1000˚C show relatively small grains and a further increase in temperature of thermal treatment leads to grain growth. Along with, CGO ceramic thermal treated at 1400ºC achieved large grains.

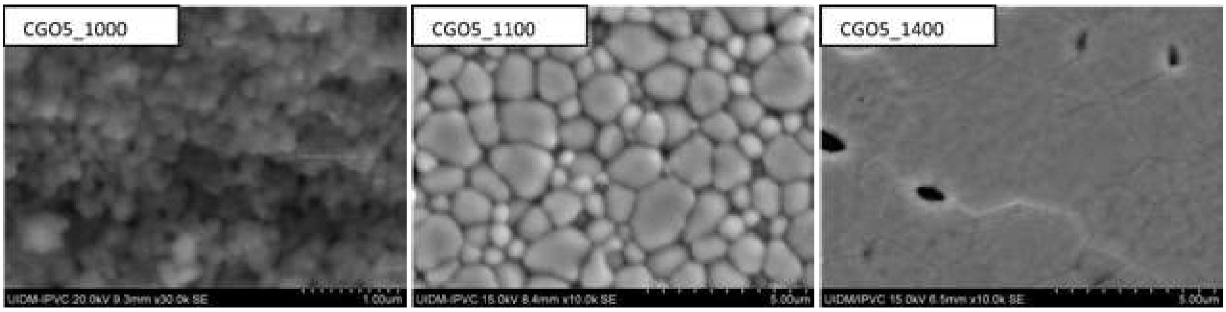

Fig. 1. SEM micrographs of CGO ceramics: sintered at 1000ºC, 1100ºC and 1400ºC.

Specific grain boundary conductivity of selected samples was determined and is showed in Fig. 2. In order to understand the effect of hot press approach, CGO sample prepared by conventional sintering at 1400˚C is also included. Sample prepared by hot press at 1000ºC with and without Y_2O_3 shows higher specific grain boundary conductivity than CGO from conventional sintering. Thermal treatments of the samples between 1100°C and 1400ºC have a negative effect on specific grain boundary conductivity, with the worst value observed at the temperature of 1400ºC, which suggest a degradation of properties of the grain boundary with the increase of the thermal treatment temperature. The thermal treatment temperature effect it is much evident for Y-doped samples than for the pure CGO, which suggest a dissolution of Y into the grain interior for higher temperatures.

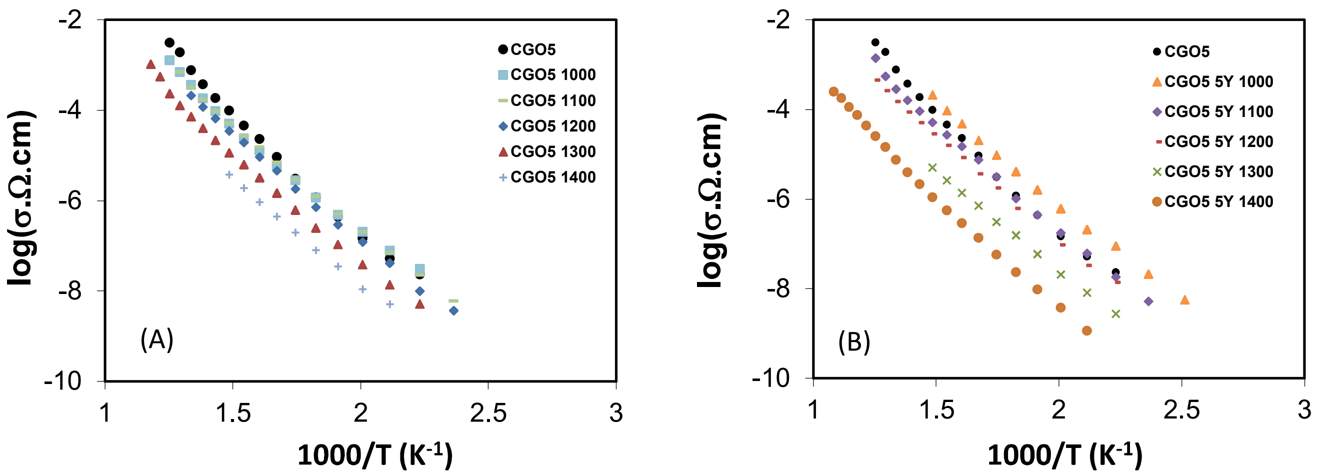

Fig. 2. Arrhenius plot of specific grain boundary conductivity of CGO (A) and CGO 5Y; (B) ceramics with post thermal treatment 1100ºC and 1400ºC.

The oxygen partial pressure dependence of the total conductivity and ion blocking measurements, 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 (Fig.3).

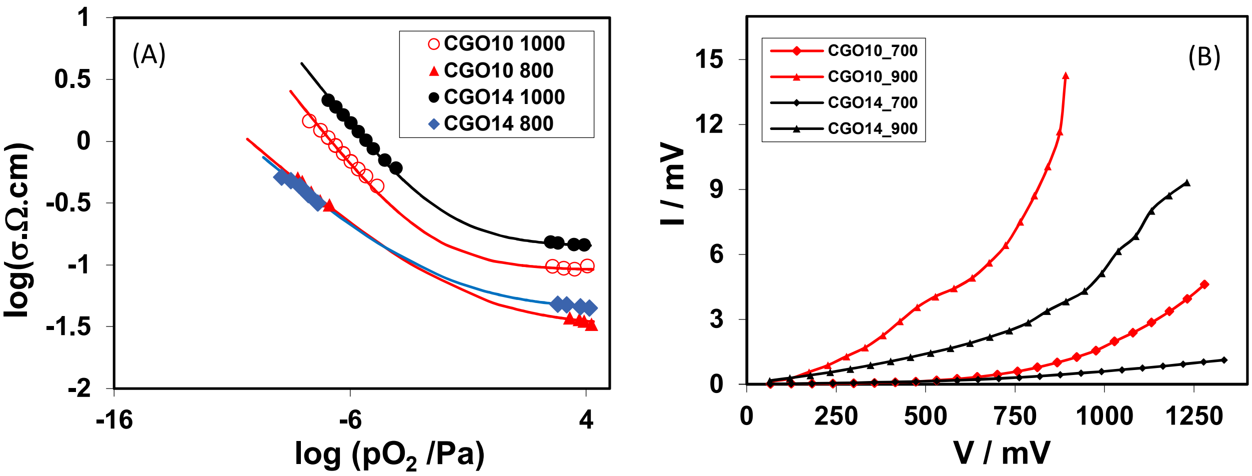

Fig. 3. Electrical conductivity as a function of the oxygen partial pressure(A) and ion blocking results (B) for of CGO based ceramics sintered at 1000˚C and 1400°C.

CONCLUSIONS

The present studies have shown that, using hot press sintering method, the widely used gadolinia doped ceria (CGO) electrolyte ceramics could be densified at relatively lower temperature 1000°C-1100°C with favourable performance, namely with higher electrical conductivities of the grain boundaries, when compared with traditional materials obtained at higher sintering temperature (≥1400˚C).

ACKNOWLEDGEMENT

This work was supported by the project HEALING (POCI-01-0145-FEDER-032036) and within the scope of the project proMetheus – Research Unit on Materials, Energy and Environment for Sustainability, FCT Ref. UID/05975/2020, financed by national funds through the FCT/MCTES.

REFERENCES

1. Inaba H, Tagawa H. 1996. Ceria-based solid electrolytes. Solid State Ionics. 83:1–16.
2. Steele BCH. 2000. Appraisal of Ce1-yGdyO2-y/2 electrolytes for IT-SOFC operation at 500°C. Solid State Ionics. 129:95–110.
3. Guo X, Zhang ZL.2003. Grain size dependent grain boundary defect structure: case of doped zirconia, Acta Mater. 51:2539–2547.
4. Tian CY, Chan SW. 2000. Ionic conductivities, sintering temperatures and microstructures of bulk ceramic CeO2 doped with Y2O3. Solid State Ionics. 134:89–102.
5. Cho YH, Cho PS, Auchterlonie G, Kim DK, Lee JH, Kim DY, Park HM, Drennan J.2007. Enhancement of grain-boundary conduction in gadolinia-doped ceria by the scavenging of highly resistive siliceous phase, Acta Mater. 55:4807-4815.
6. Tanaka R, Oliveira WS, Brandão A, Abrantes JCC, Frade JR.2012. Grain boundary conductivity of heterogeneous ceria gadolinia, Electrochimica Acta 85:116-121.