IONIC CONDUCTIVITY AND CRYSTALLOGRAPHIC INDEX OF CERIA DOPED WITH YTTRIA AND DYSPROSIA

S. K. Tadokoro, R. Muccillo, E. N. S. Muccillo
Centro Multidisciplinar para o Desenvolvimento de Materiais Cerâmicos
Instituto de Pesquisas Energéticas e Nucleares – CCTM
C. P. 11049, S. Paulo, SP, 05422-970, Brazil

ABSTRACT

Ce\textsubscript{1-x}(Y\textsubscript{0.5}Dy\textsubscript{0.5})\textsubscript{2-x} solid solutions with 0.030 ≤ x ≤ 0.150 were prepared by the precipitation of the corresponding cation hydroxides. The main purposes of this work were to verify the effect of combined addition of yttrium and dysprosium oxides on the ionic conductivity of ceria, and to evaluate the application of the crystallographic index model in the studied dopant content range. X-ray diffraction and scanning electron microscopy results evidence the homogeneous nature of the synthesized materials. The grain conductivity of the sintered pellets at a fixed temperature increases with increasing dopant content up to x = 0.045, and then decreases for higher concentrations. These results show that the addition of a codopant influences the composition at which the maximum value of conductivity is attained. Moreover, the crystallographic index model seems to be unsuitable to describe the behavior of the ionic conductivity of either grain or grain boundaries when the total dopant content is relatively low.

INTRODUCTION

Cation-doped ceria with a fluorite structure is a potential solid electrolyte because of its high oxygen-ion conductivity (1,2). These solid solutions contain a number of oxygen vacancies in the crystal lattice which are produced by partial replacement of the host cation by aliovalent cations. These materials are potential candidates as solid electrolytes in intermediate temperature solid oxide fuel cells (3,4). Over the last few years, many efforts have been carried out to increase the ionic conductivity in ceria-based solid solutions by means of co-doping (5-12). The increase in ionic conductivity in double-doped solid solutions is believed to occur as a consequence of the reduction in the residual lattice strain produced by cation substitution. In most cases, the ionic conductivity of codoped systems has been studied for total dopant contents near that of the maximum conductivity of single-doped solid solutions (5,6,8,9,11,12). The application of a crystallographic index for improvement of the electrolytic properties of solid electrolytes, however, has been restricted to relatively high total dopant contents (7,10). These studies have indeed demonstrated some improvement in the ionic conductivity compared to values of singly-doped materials.

In this study, the ionic conductivity of ceria codoped with yttria and dysprosia was studied by impedance spectroscopy. The main purposes of this work were to verify the
effect of dopants on the grain and grain boundary conductivity of ceria matrix, and to evaluate the use of the crystallographic index model in the low total dopant contents range.

**EXPERIMENTAL**

**Sample Preparation**

Ce$_{1-x}$(Y$_{0.5}$Dy$_{0.5}$)$_x$O$_{2.8}$ solid solutions with $x = 0.010, 0.030, 0.045, 0.065, 0.080$ and $0.150$ were synthesized by the aqueous precipitation of cerium, yttrium and dysprosium hydroxides. Cerium nitrate hexahydrate (99.99%, Aldrich), yttrium oxide (99.99%, Sigma Chem. Co.), and dysprosium oxide (99%, Merck) were used as starting materials. Precipitated gels were washed with diluted ammonium hydroxide solution and partially dehydrated with absolute ethanol and isopropyl alcohol. Dehydrated materials were distilled with n-butyl alcohol and dried in a rotoevaporator. The thermal decomposition of powders was carried out at 400°C/2 h. Further details on the synthesis of solid solutions may be found elsewhere (13). Cylindrical pellets were obtained by uniaxial pressing and sintering at 1450°C/4 h.

**Sample Characterization**

The crystalline phase characterization was carried out by room temperature X-ray diffraction experiments, using a diffractometer (D8 Advance, Bruker-AXS) operating at 40 kV and 40 mA with Cu K$_\alpha$ radiation. Typical experimental conditions were 20°≤ 2θ≤80°, and 0.05° step size and 2 s of counting time. Microstructure features were observed in a scanning electron microscope (XL30, Philips) using secondary electrons.

The electrical conductivity of solid solutions was studied by impedance spectroscopy using a LF impedance analyzer (4192A, Hewlett Packard) in the 5 Hz to 13 MHz frequency range. Isothermal measurements were performed over the 150°C to 450°C temperature range. The amplitude of the applied ac signal was 50 mV. Impedance data were analyzed by equivalent electrical circuit fitting. Opposite pellet surfaces were coated with silver paste and baked at 400°C to burn out the binder material and to ensure good electrical contact of the electrodes with the electrolyte for these measurements.

**RESULTS AND DISCUSSION**

**Microstructural Characterization**

Results will be shown for all sample compositions except for that with $x = 0.010$. Pellets with this total dopant content cracked during sintering, although special care was taken by using low heating and cooling rates.

Fig. 1 shows X-ray diffraction patterns of sintered pellets with $x = 0.080$ and 0.150. All diffraction patterns exhibit sharp peaks usually assigned to a well-crystallized material. Patterns of doped pellets are qualitatively unchanged with that of cerium oxide (cubic fluorite-type structure, space group Fm3m). No reflections were detected that could be
attributed either to isolated yttrium oxide and dysprosium oxide, or to the solid solution of yttrium and dysprosium oxides.

![X-ray diffraction patterns of Ce$_{1-x}$(Y$_{0.5}$Dy$_{0.5}$)$_{x}$O$_{2-δ}$ with $x = 0.080$ and $0.150$.](image)

Figure 1. X-ray diffraction patterns of Ce$_{1-x}$(Y$_{0.5}$Dy$_{0.5}$)$_{x}$O$_{2-δ}$ with $x = 0.080$ and $0.150$.

These solid electrolytes exhibit similar microstructure characteristics, exemplified by the scanning electron microscopy, SEM, micrographs shown in Fig. 2.

![SEM micrographs of sintered pellets of Ce$_{1-x}$(Y$_{0.5}$Dy$_{0.5}$)$_{x}$O$_{2-δ}$ with $x = 0.080$ (top) and 0.150 (bottom).](image)

Figure 2. SEM micrographs of sintered pellets of Ce$_{1-x}$(Y$_{0.5}$Dy$_{0.5}$)$_{x}$O$_{2-δ}$ with $x = 0.080$ (top) and 0.150 (bottom).
The main observed microstructure features are negligible porosity (intra- and intergranular pores) and grains with similar shape and size. Relative density values of samples were higher than 94%, and average grain sizes were in the 1.4 to 2.4 μm range.

**Impedance Spectroscopy**

Impedance spectroscopy diagrams of sintered pellets show two well-resolved semicircles in $-Z'' \times Z'$ plots. Typical impedance diagrams are shown in Fig. 3 at a temperature of 232°C. As the relative amplitudes of these semicircles are quite different, this figure was divided to show specific frequency regions: high-frequency (top) and low-frequency (bottom). The high-frequency semicircle in these solid solutions describes the grain ($g$) resistance and capacitance relaxation. The low-frequency semicircle is related to blocking effects at grain boundaries ($ig$). It may be seen in these plots that there is a characteristic evolution of the grain and grain boundary impedance with total dopant content.

![Impedance diagrams](image)

**Figure 3.** Impedance diagrams of $\text{Ce}_{1-x}(\text{Y}_{0.5}\text{Dy}_{0.5})_x\text{O}_2$ with $x = 0.030, 0.045, 0.065$ and 0.150. Temperature of measurement: 232°C.

Apparent activation energy values obtained from Arrhenius plots for the grain conductivity increase with increasing the total dopant content (from 0.77 to 0.94 eV). In contrast, the activation energy for the blocking effect is nearly constant (~ 0.95 eV), except for the pellet with $x = 0.030$, for which the activation energy is 1.05 eV. Considering that the grain conductivity is much higher than the grain boundary conductivity, the ionic conductivity in these solid electrolytes is dominated by the bulk contribution to the total conductivity.

The evolution of the grain conductivity, $\sigma_g$, at 300°C with $x$ in $\text{Ce}_{1-x}(\text{Y}_{0.5}\text{Dy}_{0.5})_x\text{O}_2$ is shown in Fig. 4.
There is an increase of the grain conductivity from $x = 0.030$ to 0.045, and beyond this dopant content, $\sigma_g$ steadily decreases. This result shows that codoping with dysprosia displaces the maximum conductivity to lower dopant contents when compared to the $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2.5}$ solid solution. The overall behavior of the isothermal conductivity is similar to that of single-doped solid electrolytes (14).

In the studied range of dopant content, the crystallographic index, calculated from equations 2 and 3 in (7), varied from 0.737 to 0.765. According to that model, the ionic conductivity of a given solid electrolyte should increase with increasing crystallographic index. This effect was observed to occur for a number of ceramic electrolytes (7,10) for dopant contents higher than 0.170. The behavior of the grain and grain boundary conductivity with the crystallographic index is shown in Fig. 5.

The results in this figure show that the grain boundary conductivity increases with the increase of the crystallographic index reaching a steady state value for $x = 0.080$. The grain conductivity presents the same behavior as that shown in Fig. 4.
In the study of codoped ceria solid solutions (10), the improvement of the ionic conductivity with increasing crystallographic index was attributed to a reduction in size of micro-domains formed in codoped systems compared to those formed in single-doped materials. It then proved the close relationship between microstructure and electrical properties. Results shown here demonstrate that for low dopant contents, microstructure effects, like the formation of micro-domains, are not of primary concern to the ionic conductivity. Other factors, such as concentration of anionic vacancies and ionic radius of codopants, should be responsible for the electrical properties in solid electrolytes.

CONCLUSIONS

Homogeneous and single-phase solid solutions of $\text{Ce}_{1-x}(\text{Y}_{0.5}\text{Dy}_{0.5})_x\text{O}_{2-\delta}$ with $0.030 \leq x \leq 0.150$ were synthesized by the hydroxide precipitation method. Impedance spectroscopy results show a displacement of the maximum grain conductivity to lower dopant content in the codoped materials. The apparent activation energy for grain conduction increases with increasing dopant content. The crystallographic index model is not suitable to explain results of the ionic conductivity in these low-dopant content solid electrolytes.

ACKNOWLEDGEMENTS

The authors acknowledge FAPESP, CNPq (300394/94-7 and 306496/88) and CNEN for financial support. S. K. Tadokoro acknowledges FAPESP (00/08908-1) for the scholarship.

REFERENCES

1. H. L. Tuller and A. S. Nowick, *J. Electrochem. Soc.*, 122, 255 (1975).
2. T. Kudo and H. Obayashi, *J. Electrochem. Soc.*, 123, 415 (1976).
3. R. Doshi, V. L. Richards, J. D. Carter, X. Wang and M. Krumpelt, *J. Electrochem. Soc.*, 146, 1273 (1999).
4. B. C. H. Steele, *Solid State Ionics*, 129, 95 (2000).
5. J. M. Ralph, J. Przydatek, J. A. Kiener and T. Seguelong, *Ber. Bunsenges. Phys. Chem.*, 101, 1403 (1997).
6. J. Van herle, D. Seneviratne and A. J. McEvoy, *J. Eur. Ceram. Soc.*, 19, 836 (1999).
7. T. Mori, T. Ikegami and H. Yamamura, *J. Electrochem. Soc.*, 146, 4380 (1999).
8. N. Kim, B.-H. Kim and D. Lee, *J. Power Sources*, 90, 139 (2000).
9. H. Yamamura, E. Katoh and K. Kakinuma, *J. Ceram. Soc. Jpn.*, 110, 1021 (2002).
10. T. Mori, J. Drennan, J.-H. Lee, J.-G. Li and T. Ikegami, *Solid State Ionics*, 154-155, 461 (2002).
11. R. Yinzhe, J. Kai, W. Haixia, M. Jian and S. Qiang, *J. Rare Earths*, 21, 461 (2003).
12. S. Zha, C. Xia and G. Meng, *J. Power Sources*, 115, 44 (2003).
13. S. K. Tadokoro and E. N. S. Muccillo, *J. Alloy. Comp.*, 374, 190 (2004).
14. C. B. Choudhary, H. S. Maiti and E. C. Subbarao, *Solid Electrolytes and Their Applications*, E. C. Subbarao, Editor, p. 1, Plenum Press, New York, (1980).