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Ceria-yttria-based solid electrolytes for intermediate temperature solid oxide fuel cell

M. DUDEK[*], J. MOLENDA

AGH University of Science and Technology, Faculty of Materials Science and Ceramics
al. Mickiewicza 30, 30-059, Cracow, Poland

Pure ceria and ceria-yttria solid solution powders with formula $Ce_{1-x}Y_xO_2$, where $0 < x < 0.30$ were prepared by the coprecipitation-calcination method. The samples were sintered at 1250–1600 °C for 2 hours. The XRD method was used to determine cell parameters of the samples. Their electrical properties were investigated by ac impedance spectroscopy in the temperature range of 100–700 °C in air. It was found that the electrical conductivity, fracture toughness, and flexural strength of the samples increase with yttria concentration and reach a maximum for $Ce_{0.85}Y_{0.15}O_2$. The obtained material seems to be a promising solid electrolyte for IT-SOFC.

Key words: *ceria; solid electrolyte; electrical properties; mechanical properties; zirconia*

1. Introduction

Solid oxide fuel cells (SOFC) are very attractive due to their high efficiency and very low pollutant emission. Until now, solid oxide fuel cell systems have been based mainly on yttria-stabilized zirconia (YSZ) ceramics, because of their nearly pure oxygen conductivity in oxidizing and reducing atmospheres as well as good mechanical properties [1]. ZrO_2-based electrolytes, however, require high operating temperatures – over 900 °C – in order to maintain high oxygen ionic conductivity. Such high operating temperatures result in large fabrication costs and accelerate the degradation of the fuel cell systems [2, 3]. Recently, intensive research has been conducted aiming at reducing the operating temperature of SOFC to 700–650 °C. Ceria-based solid solutions have been regarded as being the most promising electrolytes for intermediate temperature SOFC (IT-SOFC), since their ionic conductivities are higher than that of YSZ in the intermediate temperature range [4]. The ionic conductivity of ceria-based solid electrolytes doped with various cations (e.g., Ca^{2+}, Sr^{2+}, Y^{3+}, La^{3+}, Gd^{3+} and

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[*] Corresponding author, e-mail: potoczek@uci.agh.edu.pl

Sm^{3+}) at various dopant concentrations has been extensively investigated [5, 6]. Literature data on the electrical and mechanical properties of ceria-based electrolytes versus dopant types and concentrations, however, are often inconsistent and contradictory. In spite of such interest in ceria-based materials, there has not been any systematic research on the influence of yttria on the structure, microstructure, and consequently the electrical and mechanical properties of CeO_2-based materials. The microstructures of sintered samples, which are affected both by chemical composition and preparation conditions, have a strong influence on the material characteristics. Fine-grained, dense microstructures usually lead to an improvement of the mechanical and electrical properties. This is due to the role that grain boundaries play both in fracture propagation and the conductivity of materials.

The aim of this work was to study the influence of yttria concentration and preparation conditions on the microstructure of yttria-ceria based ceramics and hence on their mechanical and electrical properties.

2. Experimental

A co-precipitation method was used to prepare pure ceria and yttria-ceria solid solutions with the formula of $Ce_{1-x}Y_xO_2$, where $0< x <0.30$. Aqueous solutions of cerium nitrate with an appropriate amount of yttrium nitrate were introduced into the ammonia solution. The resulting gels were washed with water, dried, and calcined in the temperature range of 400–800 °C for 1 hour. The ground powders were cold pressed isostatically under 200 Pa and then sintered in air at 1250–1600 °C for 2 hours. The phase composition of all powders and sintered samples was characterized by X-ray diffraction analysis. The crystalline size of the powders was estimated by the line broadening analysis, using the reflection from (110) plane. The specific surface area of the powders was measured by the one-point BET technique. The Archimedean method was used to determine the apparent density of the studied samples. Scanning electron microscopy was used to observe the microstructure of the materials obtained. The Vickers hardness (HV) and fracture toughness (K_{IC}) were determined by the Vickers indentation method. The Palmquist crack model and Niihara equation were applied [7]. Specimens for three-point flexural tests were cut from the plates and their surface polished. The electrical properties of yttria-ceria-based solutions were investigated by ac impedance spectroscopy in the temperature range of 100–750 °C and at the frequencies from 1 Hz to 10 MHz.

3. Results and discussion

Phases of pure ceria and ceria-yttria solid solution with the formula of $Ce_{1-x}Y_xO_2$ (with $0< x <0.30$) were detected by the XRD analysis in the powders and samples sintered. The properties of pure and yttria-doped ceria powders are listed in Table 1.

Table 1. Average crystallite sizes of pure CeO_2 and $Ce_{1-x}Y_xO_2$ powders determined by XRD and BET specific surface measurements

x	D_{hkl}, nm	D_{BET}, nm
0	30.0	35.0
0.10	25.0	28.8
0.15	17.3	18.3
0.20	12.8	13.6
0.25	14.1	15.9

The data presented in Table 1 indicate a decrease in the crystallite size of the $Ce_{1-x}Y_xO_2$ solid solutions with increasing yttrium concentration. The consistency of sizes determined by X-ray diffraction analysis and BET specific surface measurements suggests that the powders are composed of isometric and not agglomerated crystallites. Generally, all samples sintered at temperatures 1400–1500 °C achieved a relative density exceeding 98% of the theoretical value. Concentrations of yttria higher than $x = 0.20$ in $Ce_{1-x}Y_xO_2$ solid solutions led to lower densities, because of an increase in close porosity. The unit cell parameter decreased with increasing yttria content (Fig. 1) in good agreement with effective ionic radii considerations, taking into account that $r_{Ce^{4+}} = 0.111$ nm and $r_{Y^{3+}} = 0.089$ nm [8].

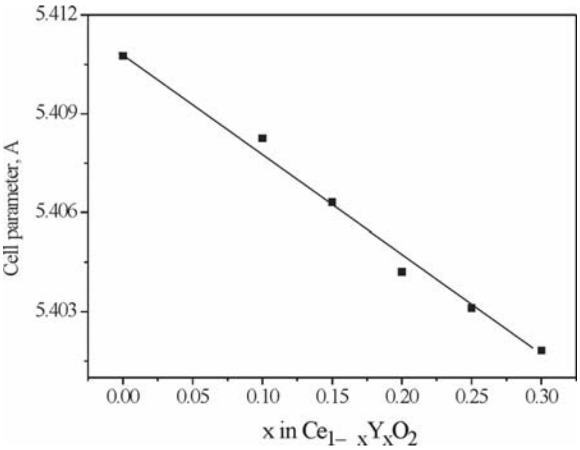

Fig. 1. Changes of cell parameters versus yttria concentrations in $Ce_{1-x}Y_xO_2$

Figure 2 shows a typical microstructure of a pure CeO_2 sample sintered at 1400 °C. The ceria average grain sizes decreased in the $Ce_{1-x}Y_xO_2$ materials sintered at this temperature from about 1.0 μm to 0.60 μm with increasing yttria content. Above 1500 °C, a significant grain growth was observed in all sintered samples. The samples sintered at temperatures of 1500–1600 °C exhibited average grain sizes in the range of 2.8–5.0 μm.

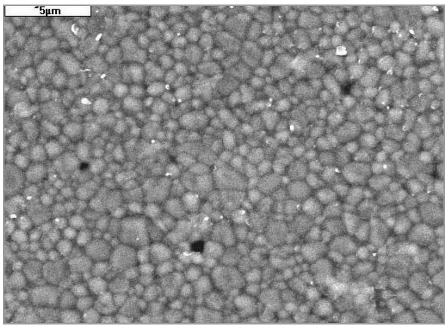

Fig. 2. Microstructure of pure CeO_2 sample sintered at 1400 °C

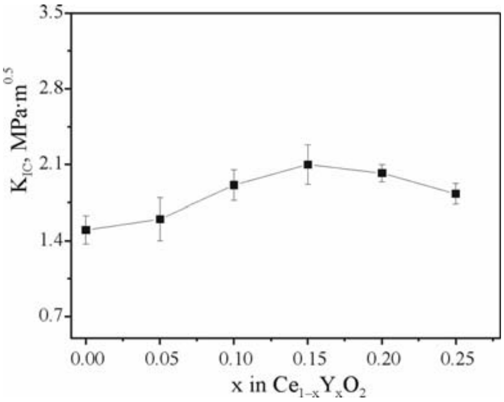

Fig. 3. Influence of yttria concentration on fracture toughness K_{IC} of $Ce_{1-x}Y_xO_2$ samples

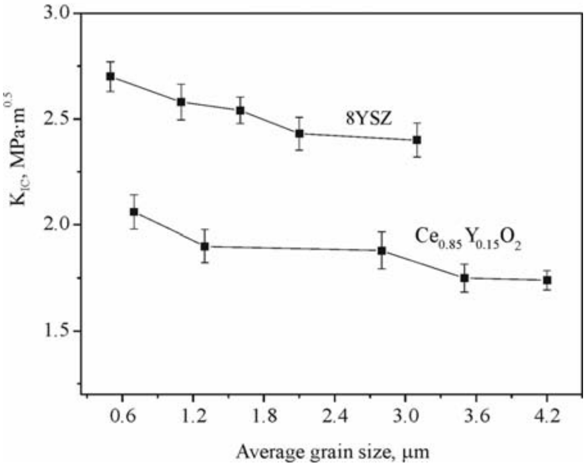

Fig. 4. Influence of grain size on fracture toughness K_{IC} of $Ce_{0.85}Y_{0.15}O_2$ and 8YSZ solid electrolyte

K_{IC} measurements revealed a small increase in fracture toughness with increasing yttria concentration in solid solutions for $x = 0.15–0.20$ (Fig. 3). For higher concentrations of yttria, a rather small decrease was observed, which could be attributed to the presence of small amounts of closed porosity in the investigated samples. The effect of grain size on the fracture toughness of the samples is also presented in Fig. 4. In order to compare the influence of microstructure on the changes in the fracture toughness of yttria-ceria based solid solutions, the diagram shows these changes together with the grain size for the 8YSZ sample, which up to now has been in common use as a solid electrolyte in oxide fuel cells. In both cases, one can observe a very slight increase in fracture toughness along with a decrease in grain size to about 0.5–0.7 µm. Without going into further details of the microscopic observations, one can state that the cracks propagate along grain boundaries and across grain interiors in the investigated materials. The very small increase in the fracture toughness of the fine-grained microstructure was caused by a slight deflection in the fracture course through the inter-granular boundaries. Table 2 presents other mechanical properties (hardness and flexural strength) which are important in the usage of yttria-doped ceria as a solid electrolyte in SOFC. A comparison of the data indicates a slight improvement of the mechanical characteristics with increasing yttria content in the $Ce_{1-x}Y_xO_2$ solid solutions which, however, have slightly worse mechanical properties than the 8YSZ electrolyte.

Table 2. Mechanical properties of selected materials based on ceria and zirconia

Material	*HV*,GPa	σ, MPa
CeO_2	7.80 ±0.15	101 ± 14
$Ce_{0.9}Y_{0.1}O_2$	8.13 ±0.11	130 ± 12
$Ce_{0.85}Y_{0.15}O_2$	8.90 ±0.16	144 ± 11
8YSZ	12.83 ±0.16	212 ± 17

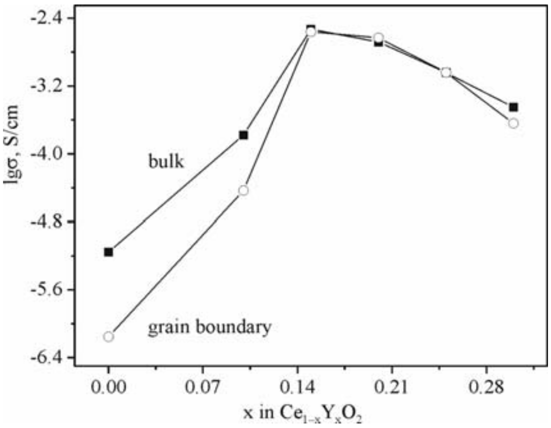

Fig. 5. The bulk conductivity and grain boundary conductivity of $Ce_{1-x}Y_xO_2$ as a function of dopant concentration x

Figure 5 shows the dependence of the bulk conductivity and grain boundary conductivity of the $Ce_{1-x}Y_xO_2$ system on dopant concentration x at 500 °C. The analysis of the conductivities of all investigated samples shows that the bulk conductivity reaches a maximum of $3.0 \cdot 10^{-3}$ S/cm at 500 °C for $x = 0.15$. This is in good agreement with the results reported in [9]. Other data, however, indicate a maximum conductivity corresponding to $x = 0.2$ or even $x = 0.08–0.12$ [10, 11].

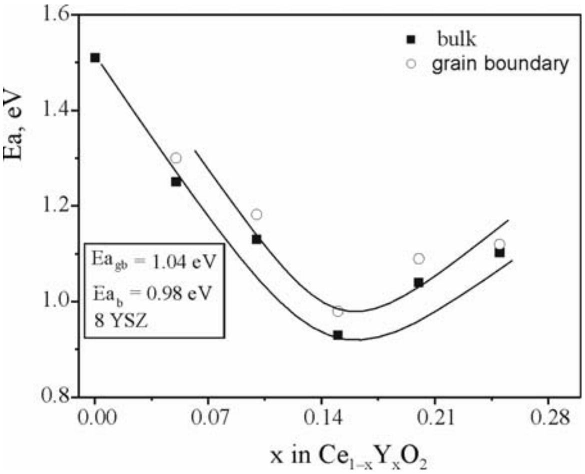

Fig. 6. The energy activation of bulk
and grain boundary conductivity of $Ce_{1-x}Y_xO_2$ samples

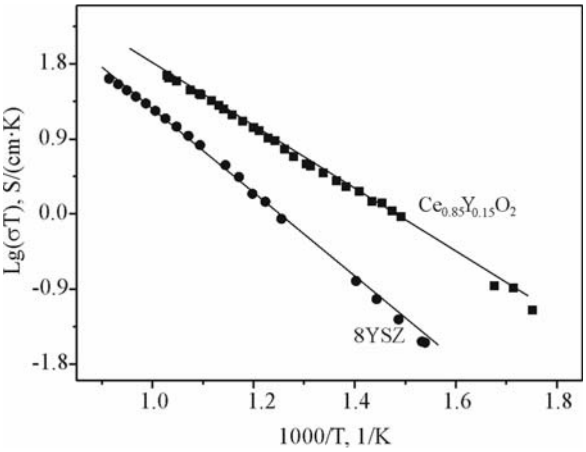

Fig. 7. Temperature dependence of the total conductivity
of $Ce_{0.85}Y_{0.15}O_2$ and 8YSZ samples

The grain boundary conductivities of $Ce_{1-x}Y_xO_2$ also increase with Y_2O_3 content and reach a maximum for $x = 0.15$ in the investigated temperature range. In both cases, the maximum in grain boundary and bulk conductivity corresponds to a minimum energy activation of electrical conductivity (Fig. 6). The temperature dependences of the total conductivity for a sample with $x = 0.15$ as well as for 8YSZ are shown in Figure 7. A single straight line represents the Arrhenius plot of total conductivities for both samples. The total conductivity of $Ce_{1-x}Y_xO_2$ reaches a maximum (6.0×10^{-2} S/cm at 700 °C) for $x = 0.15$. This value is nearly 50% higher than the total conductivity of 8 YSZ at 700 °C (1.2×10^{-2} S/cm). The obtained values of electrical conductivity and activation energy indicate that $Ce_{0.85}Y_{0.15}O_2$ can be a suitable electrolyte for solid oxide fuel cells operating in the temperature range of 600–700 °C. In both investigated electrolytes, an increase in the sintering temperature led to a decrease in the total electrical conductivity. This can be related to microstructural changes in ceria and zirconia samples, consisting in grain size and porosity development.

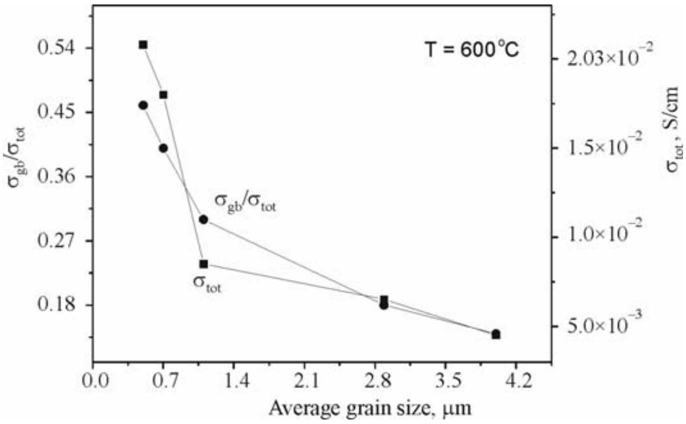

Fig. 8. Changes of the grain boundary conductivity to total conductivity and total conductivity as a function of grain size in $Ce_{0.85}Y_{0.15}O_2$ sample

The plot in Figure 8 shows the ratio of grain boundary and total conductivity (σ_g/σ_t) versus average grain size for the $Ce_{0.85}Y_{0.15}O_2$ sample. As expected, an increase in grain size caused a decrease in the relative fraction of grain boundary conductivity and total electrical conductivity.

4. Conclusions

Pure ceria and yttria-doped ceria solid solution powders with thea formula of $Ce_{1-x}Y_xO_2$ ($0 < x < 0.30$) were successfully synthesized by the calcination-coprecipitaion method. It was found that the electrical conductivity, fracture toughness and flexural strength of the investigated materials increase with the yttria doping concentration and reaches a maximum for $Ce_{0.85}Y_{0.15}O_2$. Contrary to mechanical properties, the electrical conductivity of ceria-based electrolytes can be improved simply by controlling the grain size. The obtained values of electrical conductivity and energy activation for $Ce_{0.85}Y_{0.15}O_2$ with an average grain size of 0.5 µm show that the prepared material is a promising solid electrolyte for IT-SOFC systems operating in the temperature range 600–700 °C.

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