

Effect of the tantalum oxide addition in the phase composition and electrical conductivity in the zirconium-10% mol Scandia

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Abstract

Scandia-stabilized zirconia (ScSZ) based compositions are alternative electrolyte systems to the conventional yttria stabilized zirconia (YSZ) for solid oxide fuel cells (SOFCs) operating at intermediate temperatures (500-700 °C). ScSZ exhibits higher ionic conductivity ($\sim 10 \text{ mS.cm}^{-1}$) than YSZ and has a high ionic transference number (~ 1.0) under reducing conditions. However, the cubic-rhombohedral phase transition at $\sim 600^\circ\text{C}$ causes a considerable decrease in ionic conductivity, hindering its use in technological applications. The introduction of a second additive promotes the stabilization of the cubic phase at room temperature and suppresses the deleterious phase transition. In this work the effect of the addition of small amounts (up to 0.50 mol%) of tantalum oxide in the phase composition and in the electrical conductivity of the zirconia-10% mol scandia is investigated. Double doping samples were prepared by the conventional mixing method followed by solid state reaction. The compacts obtained by uniaxial pressing were sintered in air at 1500°C for 5 h. Samples containing at least 0.40 mol% of additive showed stabilization of the cubic phase at room temperature. The impedance spectroscopy results showed an increase in grain conductivity for compositions containing at least 0.35 mol% tantalum oxide. These results show that it is possible to use tantalum oxide in small amounts to suppress the cubic-rhombohedral phase transition, and to increase the zirconia-scandia electrical conductivity at low temperatures.

Keywords: Solid electrolytes, zirconia, additives, phase transition.

Introduction

One class of functional materials with wide application range is ion conductors. Oxygen ion conductors are used in several applications such as: chemical species sensors, oxygen pumps, oxygen permeable membranes and fuel cells for energy production [1, 2].

The oxides known for longer and more studied as conductors of oxygen ions are those of fluorite structure, which consist of a cubic lattice of oxygen ions with alternating centers occupied by cations. The cations are arranged in a cubic face-centered structure with anions occupying tetrahedral positions. This results in an open structure with wide empty spaces[3].

Scandia Stabilized zirconia (ScSZ) has high ionic conductivity, and can reach up to 2.5 times the ionic conductivity of Ytria Stabilized Zirconia (YSZ) at the same temperature [4, 5]. ScSZ also has low electronic conductivity and high chemical stability compared to other oxygen ion conductors [6].

The ScSZ exhibits similar chemical and thermodynamic properties to YSZ, and its interfacial interactions with the materials used in the electrodes for SOFC can be given as studied. For these reasons ScSZ presents high potential for application in electrochemical devices. Its cost will probably also be reduced in coming years, with the entry of several countries into the production of its inputs [7].

The phase diagram of the solid solution of zirconia-scandia presents a composition of complex phases depending on the content of the scandium and, therefore, several studies with the introduction of a second additive to assist in the stabilization of the cubic phase fluorite, chemical stability and ionic conductivity are being carried out. Several rare earth oxides and transition metals, such as Gd_2O_3 , CeO_2 , Cr_2O_3 , Dy_2O_3 , and Nb_2O_5 , showed promising results [4, 8-11].

In this work the main objective was to verify the effect of small additions of Eu_2O_3 in the composition phase and in the ionic conductivity of zirconia-10% mol Scandia, considering that a second additive consisting of rare earth oxide often favors the stabilization of the conducting phase at room temperature, in addition to allowing maintenance in the concentration of oxygen vacancies.

Materials and Methods

The starting materials used are zirconia-10 mol% scandium (10ScSZ, DKKK) and Tantalum oxide (99.99%, Aldrich Chemicals). Ta₂O₅ was used as an additive. The nominal levels used were 0.25; 0.35; 0.40; 0.45 and 0.50 mol%.

The compositions were prepared by the oxides mixing method followed by solid state reaction. The starting materials were dried, stoichiometrically weighed, on an analytical balance (Mettler, H315) and then mixed and homogenized in an agate mortar, filled with isopropyl alcohol, until the drying point.

Cylindrical compacts were prepared by uniaxial press (10 MPa). Sintered at 1500 ° C for 5 h with heating rate of 5 ° C / min followed by rapid cooling (30 ° C / min) to ~ 700 ° C.

The pellets densities were determined geometrically and by the method of immersion in distilled water using the Archimedes principle. The apparent density was compared to the calculated theoretical density (rhombohedral phase: 5.731 g / cm³, cubic phase: 5.740 g / cm³ [12]).

The dimensions of the samples were measured with an analytical micrometer (Tesa). Ten measurements of diameter and 10 of thickness were made. The mass was determined on an analytical scale (Mettler, H315), which was also used to determine the 10 measurements of dry, wet and immersed masses by the water immersion method.

The apparent porosity was determined from the data obtained for the density measurements according to ASTM C20-00 [13].

The sintered pellets were analyzed by X-ray diffraction (Bruker-AXS, D8 Advance) to determine the crystallographic phases. The angular range used was 20 ° to 80 °, with step of 0,05 ° and 4 s of exposure time. Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) was used. The identification was made with the aid of PDF files (rhombohedral phase β PDF: 89-5482 and cubic phase PDF: 89-5483). Differential scanning calorimetry (Netsch, Pegasus 404) analyzes were carried out to determine the temperature of rhombohedral cubic phases transformation in the heating and cooling of the samples. The heating rate used was 10 ° C / min and the analyzes were done in a synthetic air atmosphere.

The ionic conductivity was determined by impedance spectroscopy. Measurements were made from 345 to 585 ° C, in the frequency range of 5 Hz

to 13 MHz, with a voltage of 200 mV. An HP 4192A impedance analyzer coupled to an HP 362 controller was used to monitor the temperature. A K-type thermocouple (Cromel / Alumel) positioned near the samples was used. For the measurements, silver electrodes were deposited on the faces of the pellets. The data obtained in the electrical measurements were collected and analyzed through a computer program [14].

Results and Discussion

The green relative density of the compacts was measured geometrically, and values of approximately 40% were found for all samples.

Table I summarizes the results of geometric density, density by the immersion method and the apparent porosity of samples containing Ta₂O₅. The introduction of this additive did not alter the relative density or apparent porosity of the solid solution.

Note that the apparent porosity has low values. However, a difference between the densities measured by the two methods is observed. This may be related to the formation of closed pores, which are characteristic of the cubic phase.

In this table, the relative density values were calculated in relation to the rhombohedral phase density for the samples without additive and with up to 0.5 mol% of the additive; and the density of the cubic phase for the other compositions. The reason for this is shown below.

Table I: Relative values of geometric density (ρ_g) and density by the immersion method (ρ_h), and apparent porosity (Pa) of samples of 10ScSZ without additive and with 0.25; 0.35; 0.40; 0.45 and 0.50 mol% Ta₂O₅, sintered at 1500 ° C for 5h.

Ta ₂ O ₅ (% mol)	ρ_g (%)	ρ_h (%)	Pa (%)
0.25%	96.67 (1.97)	95.92 (8.09)	1.25 (0.17)
0.35%	97.12 (1.29)	95.63 (6.60)	1.18 (0.18)
0.40%	96.35 (1.84)	96.82 (5.22)	0.58 (0.37)
0.45%	97.66 (0.73)	97.90 (6.46)	1.4 (0.12)
0.50%	97.07 (1.57)	96.78 (6.75)	2.4 (0.78)

Figure 1 shows the X-ray diffractograms of the samples of 10ScSZ without additives and 0.25; 0.35; 0.40; 0.45 and 0.50 mol% Ta₂O₅ sintered at 1500 ° C for 5 h. It is possible to observe that with the increase of Ta₂O₅ the fraction of rhombohedral phase decreases and that of the cubic phase increases. The addition of 0.40 mol% Ta₂O₅ completely stabilizes the cubic phase, as it can be

observed in Figure 1b, which corresponds to the enlargement of the diffraction profiles in the angular range of 48 to 54°.

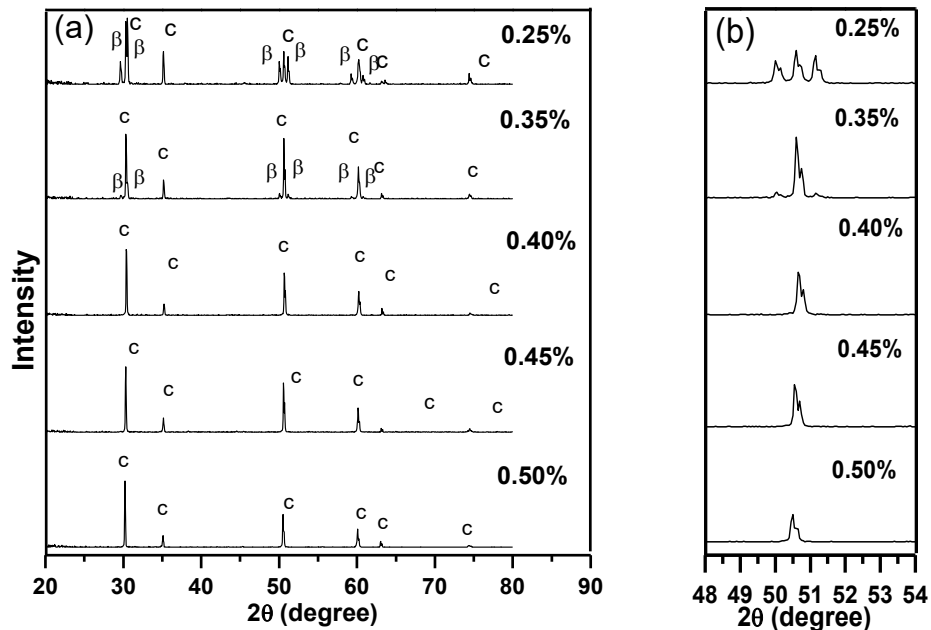


Figure 1: X-ray diffraction patterns of samples containing 0.25, 0.35, 0.40, 0.45 and, 0.50% mol Ta₂O₅, sintered at 1500°C/5 h. (a) 20 a 80° e (b) 48 a 54°. β: β-romboedral phase (PDF: 89-5482), c: cubic phase (PDF:89-5483).

Figure 2 shows the graph of total electrical conductivity of 10ScSZ samples without and containing various Ta₂O₅ contents. In this figure, for comparison purposes, the Arrhenius graph of the total electrical conductivity of the sample 10ScSZ (without additive) sintered at 1500 ° C is also shown.

All samples have a single straight segment. This result is further evidence that this sample shows a mixture of cubic and rhombohedral phases.

As can be seen, the electrical conductivity increases substantially (~ 2 orders of magnitude) with the introduction of Ta₂O₅.

Samples containing from 0.35 to 0.50 mol% Ta₂O₅, where the cubic phase is the majority, presented very close conductivity values. The sample with 0.25 mol% Ta₂O₅, with phase mixing, presented intermediate conductivity values, but still higher than those obtained for the 10ScSZ sample.

These results also show that there was formation of a solid solution of Ta⁵⁺ in the zirconia-escandia matrix. This is also verified by the frequency variation graphs as a function of temperature.

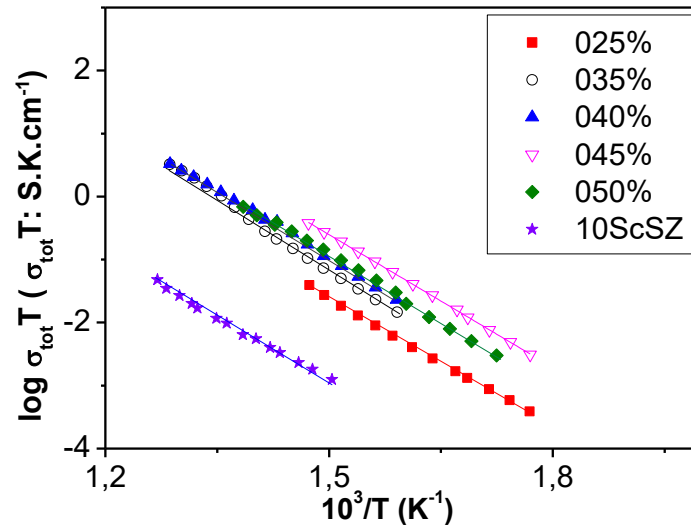


Figure 2: Arrhenius plots of the electrical conductivity of 10ScSZ samples without and with several contents of Ta₂O₅ sintered at 1500°C/5h.

Conclusions

Samples containing small additions of Ta₂O₅ have low apparent porosity and high density.

The increase of the Ta₂O₅ content favored the stabilization of the cubic phase at room temperature, shown by X-ray diffraction and differential scanning calorimetry. The stabilization of the cubic phase occurred at Ta₂O₅ levels close to 0.40 mol%.

The intragranular electrical conductivity of samples containing Ta₂O₅ is approximately 2 orders of magnitude higher than that of the sample without additives at low temperatures.

The total electrical conductivity, in the measurement temperature range, also increases considerably with the addition of Ta₂O₅. This additive proved to be efficient for the stabilization of the cubic phase at room temperature and suppression of the cubic-rhombohedral phase transition in zirconia-escandia.

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