

Improved ionic conductivity of zirconia-scandia with niobia addition



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ABSTRACT

The ionic conductivity and the crystalline structure of ZrO_2 -10 mol% Sc_2O_3 -x mol% Nb_2O_5 solid electrolytes were investigated for x=0.25, 0.5 and 1. Dense specimens with relative densities higher than 95% were prepared by solid state reaction and sintered at 1500 °C for 5 h. Full stabilization of the cubic structure at room temperature was obtained for compounds with x=0.5 and 1, whereas the cubic and rhombohedral structures coexist for x=0.25. The highest ionic conductivity in codoped system was found for specimen containing 0.5 mol% niobium pentoxide, with the same order of magnitude as that of the parent solid electrolyte (zirconia-10 mol% scandia) in the high temperature range (above 600 °C). Preliminary investigation on phase stability shows that the isothermal conductivity of the new solid electrolyte remained constant up to 100 h at 600 °C. Niobium pentoxide addition was found to improve the overall ionic conductivity of zirconia-scandia solid electrolyte.

1. Introduction

Over the last years enhancement of the ionic conductivity of oxide-ion conductors has been one of the main issues to improve their performance foreseeing technological applications [1,2]. That improvement has been shown to be accomplished by suitable choices and/or changes of composition, ceramic processing and microstructure [3].

Zirconia-based solid electrolytes, especially 8 mol% yttria-stabilized zirconia (8YSZ), are among the most investigated oxide-ion conductors, because of the combination of their mechanical and electrical properties [1,2,4]. Nevertheless, the development of solid oxide fuel cells operating at intermediate temperatures (below 800 °C) requires solid electrolytes with oxide-ion conductivity higher than that of 8YSZ. The ionic conductivity of 10 mol% scandia stabilized zirconia (10ScSZ) is approximately twice that of 8YSZ [1,5], turning this system a potential candidate for that application. The comparatively high ionic conductivity found in this solid electrolyte is attributed to a lower defect association enthalpy and to the similarity of the ionic radii of Zr^{4+} (0.084 nm) and Sc^{3+} (0.087 nm) in eight-fold coordination [6]. Notwithstanding the attractive ionic conductivity of 10ScSZ, its low phase stability, accounting for the reversible cubic-to-rhombohedral phase transition below 600 °C, is a restrictive factor for the use of this solid electrolyte in electrochemical devices [7].

According to literature, full stabilization of the high symmetry cubic structure of 10ScSZ at room temperature can be achieved by decreasing the grain size to the nanoscale [8–10] or by introducing a second additive [7,11–17]. These reports show as general features an increase

of the ionic conductivity at low temperatures (< 600 °C), but lower high temperature (≥ 600 °C) conductivity compared to that of the parent electrolyte (10ScSZ). In most of these studies, the additive was a trivalent cation. Another parameter playing a role for obtaining high ionic conductivity is the ionic size of the additive cation. As a consequence, the highest ionic conductivity in ternary systems was found for 10ScSZ containing 1 mol% cerium oxide ($r_{Ce^{4+}} = 0.097$ nm) [14].

Addition of pentavalent cation has been explored recently. In a previous work, we have shown by high temperature X-ray diffraction that addition of only 0.5 mol% Nb_2O_5 to 10ScSZ synthesized by coprecipitation, allowed for suppression of the cubic-to-rhombohedral phase transition [17]. It has been demonstrated that oxidation state of niobium is 5+ in scandia-zirconia solid solutions [11]. In this work, we investigate the effects of small amounts of niobium pentoxide on phase stability and ionic conductivity by X-ray diffraction and impedance spectroscopy, respectively, of zirconia-scandia electrolyte prepared by solid state reactions.

2. Experimental

2.1. Sample preparation

ZrO_2 -10 mol% Sc_2O_3 , 10ScSZ (Daichi Kigenso Kagaku Kogyo, DKKK, Japan) and Nb_2O_5 (Companhia Brasileira de Metalurgia e Mineração, CBMM, Brazil, 99.99%) were used as starting materials. Solid electrolytes of ZrO_2 : 10 mol% Sc_2O_3 -x mol% Nb_2O_5 with x=0.25,

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0.5 and 1 nominal contents were prepared by the conventional method of solid state reaction. Stoichiometric amounts of the dried starting oxides were mixed in isopropyl alcohol in an agate mortar for 15 min followed by drying in an oven at 40 °C for 1 h.

Disc-shaped (ϕ 5 mm and 3 mm thickness) doped ($x=0.25, 0.5$ and 1) and undoped (10ScSZ) specimens were prepared by uniaxial (50 MPa) and cold isostatic (100 MPa) pressing with average relative green density of 45%. Sintering was carried out in a box-type furnace (Lindberg BlueM) in the 1400–1550 °C range for 2–10 h with 5 °C/min heating rate and cooling down to room temperature by turning off the furnace. Preliminary study on stability of the cubic phase was conducted by further annealing of sintered specimens at 600 °C up to 100 h in air.

2.2. Characterization methods

The apparent density of sintered solid electrolytes was determined by the water immersion method and compared to the theoretical density (5.90 g/cm according to PDF 64–9607). Phase characterization was performed by X-ray diffraction, XRD (Bruker-AXS, D8 Advance) using Ni-filtered Cu K α radiation ($\lambda=1.5405$ Å) in the 20–80° 2 θ range, with 0.05° step size. Indexing of the XRD patterns were done by comparison of the experimental profile with those of PDF64-9607 and 64–9610 files for cubic (c) and rhombohedral (β) phases, respectively.

The microstructure of sintered specimens was observed by field emission scanning electron microscopy, FESEM (FEI, Inspect F50) on polished and thermally etched surfaces. The average grain size, G , was estimated by the intercept method [18] on a population of about 1000 grains. The electrical conductivity of specimens sintered at 1500 °C for 5 h was determined by impedance spectroscopy measurements (HP, 4192 A), with 200 mV of applied signal in the 5 Hz to 13 MHz frequency range. Data were collected in impedance mode in the 450–800 °C range. For phase stability experiments, resistance measurements were carried out at 700 °C, after specific times of annealing at 600 °C. Silver and platinum pastes were applied onto the large surfaces of specimens and fired at 400 °C for 1 h and 800 °C for 1 h, respectively, to act as electrode for electrical conductivity measurements.

3. Results and discussion

3.1. Phase composition, densification and microstructure

Fig. 1 shows room temperature X-ray diffraction patterns of specimens with and without niobium pentoxide sintered at several dwell temperatures and times. All specimens containing 0.25 mol% Nb₂O₅ (Fig. 1a) exhibit the main reflections of the cubic fluorite-like structure ($Fm-3m$ space group), and those of the β -rhombohedral phase ($R3$ space group). Increasing dwell temperature as well as dwell time increases the intensity of cubic phase reflections. Full stabilization of the cubic structure is found for 0.5 (Fig. 1a) and 1 mol% (Fig. 1b) Nb₂O₅ with marginal influence on lattice parameter as reported previously [11]. It is to be noted that the minimum amount of niobium pentoxide required for cubic phase stabilization is the same (about 0.5 mol%), regardless the method of solid solution preparation [17]. Indeed, the melting point of Nb₂O₅ (1512 °C) is close to the sintering temperature (1400–1550 °C), which helps its solubilization in the zirconia matrix.

Specimens containing 1 mol% Nb₂O₅ are fully stabilized at any sintering profile, except for the lowest dwell temperature and time. In contrast, 10ScSZ solid electrolyte displays only the characteristic reflections of the β -rhombohedral phase (Fig. 1b).

The phase composition of all specimens and their relative densities are summarized in Table 1. Relative density values are high (above 95%), except for 1 mol% Nb₂O₅ sintered at the lowest dwell temperature (1400 °C). In addition, a net tendency of the density to decrease with increasing niobium pentoxide contents is observed, as previously

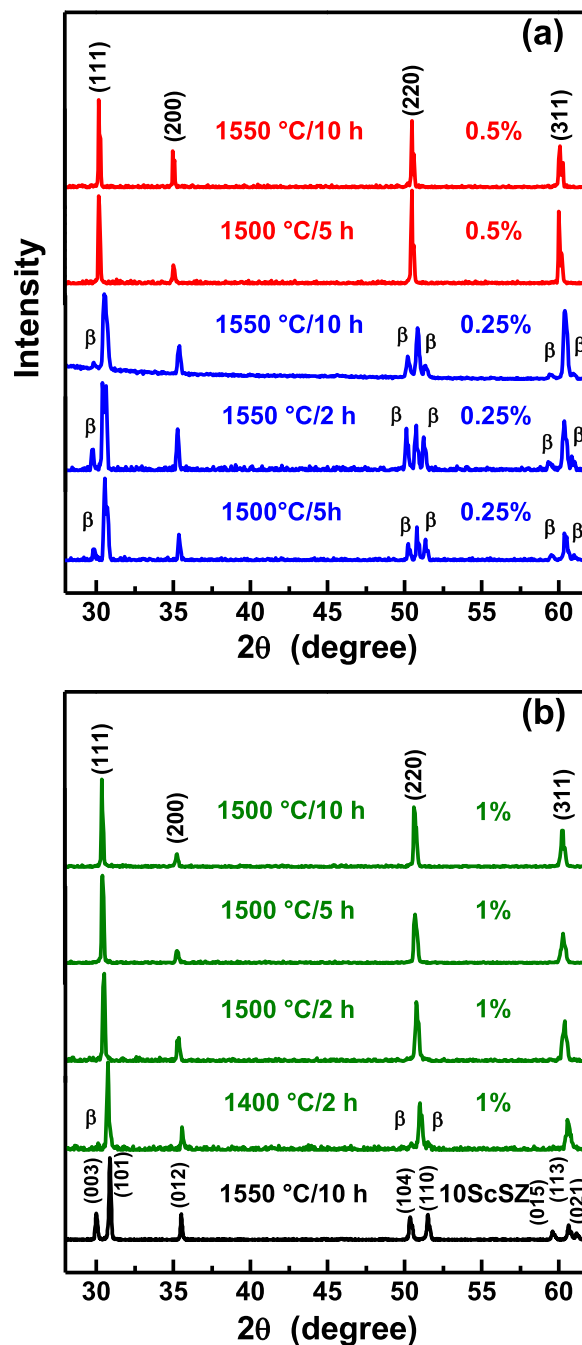


Fig. 1. X-ray diffraction patterns of specimens containing (a) 0.25 and 0.5; and (b) 1 mol % Nb₂O₅ and 10ScSZ.

reported for other additives [13,14].

The effect of Nb₂O₅ on the microstructure of 10ScSZ samples sintered at 1500 °C for 5 h was evaluated by scanning electron microscopy. Similar microstructure features were observed for all investigated compositions. Fig. 2 shows, as example, FESEM micrographs of specimens (a) 10ScSZ and (b) $x=0.5$ mol% Nb₂O₅. Typical features in these micrographs are polygonal grains, with similar grain size distribution, along with negligible porosity. Average grain size values are in the ~7.5 to ~9.5 μ m range.

3.2. Ionic conductivity

Fig. 3 shows $-Z''(\omega)$ versus $Z'(\omega)$ impedance diagrams for all investigated compositions sintered at 1500 °C for 5 h. In these plots,

Table 1

Relative density (in % of the theoretical value) and phase composition of specimens sintered at several dwell temperatures and times.

| T (°C) | t (h) | ρ_R (%) | Phase composition |
|-----------|-------|--------------|-------------------|
| 10ScSZ | | | |
| 1500 | 5 | 98.0 ± 0.5 | β |
| 1550 | 10 | 97.5 ± 0.9 | β |
| 0.25 mol% | | | |
| 1500 | 5 | 98.1 ± 0.5 | c + β |
| 1550 | 2 | 98.4 ± 0.6 | c + β |
| 1550 | 10 | 98.0 ± 0.8 | c + β |
| 0.5 mol% | | | |
| 1500 | 5 | 97.7 ± 0.5 | c |
| 1550 | 10 | 97.9 ± 0.6 | c |
| 1 mol% | | | |
| 1400 | 2 | 86.8 ± 0.3 | c + β |
| 1500 | 2 | 95.7 ± 0.3 | c |
| 1500 | 5 | 95.0 ± 1.2 | c |
| 1500 | 10 | 96.3 ± 0.4 | c |

measured resistances are normalized for specimen dimensions for comparison purposes. The temperature of measurement and the electrode material are indicated in these plots. The shape of the impedance spectroscopy diagrams is similar for doped and undoped specimens, consisting of a high-frequency semicircle assigned to grain resistivity, a low-intensity intermediate-frequency semicircle, attributed to blocking of charge carriers (oxygen vacancies) at grain boundaries, and a low-frequency spike, due to electrolyte/electrode interface reactions.

In the low temperature range, the relative contributions of grains and grain boundaries are easily obtained for specimens containing niobium pentoxide fully cubic stabilized (Fig. 3a) by fitting the impedance diagrams. Indeed, increasing niobium pentoxide content increases the grain boundary blocking effect (Fig. 3a). At 400 °C the grain and grain boundary capacitances for 0.5 mol% Nb₂O₅ containing specimens are approximately 8 pF/cm and 2 nF/cm, respectively. The ionic conductivity at that temperature amounts 1.06×10^{-4} S/cm (grain, σ_g) and 1.56×10^{-4} S/cm (grain boundary, σ_{gb}). For 10ScSZ specimen, deconvolution of the impedance spectroscopy diagrams is not trivial at any temperature independent on the electrode material (Fig. 3a and b), because of the small blocking effect. Then, for this specimen only the total conductivity, σ_T , was evaluated.

The large low-frequency spike detected for 0.5 mol% Nb₂O₅ samples (Fig. 3a and c) is indirect evidence that the total conductivity is predominantly ionic. In these plots, it is remarkable the dominant effect of the grain resistivity over the blocking effect.

The temperature dependence of the grain conductivity, σ_g , of fully

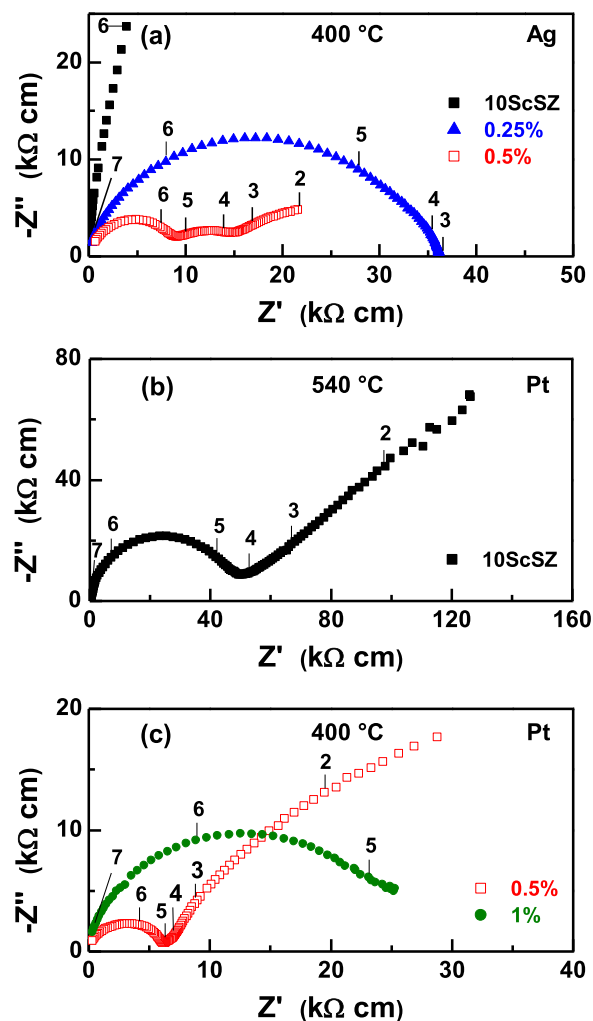


Fig. 3. Impedance spectroscopy diagrams of specimens with (a) silver and (b) and (c) platinum electrodes. Numbers in these plots are the logarithm of the frequency (Hz).

stabilized doped specimens is shown in Fig. 4. The Arrhenius plots of the grain conductivity of solid electrolytes with 0.5 and 1.0 mol% niobium pentoxide shows linear behavior with a change of slope near 550 °C, without any jump in the conductivity value. The same effect has been observed for other ternary systems, and is attributed to association of defects [13]. Our results on the ionic conductivity of niobium oxide doped 10ScSZ may not be compared to those reported in [11], because these compounds exhibit different phase assemblages.

It is well known that additives with valences higher than that of the

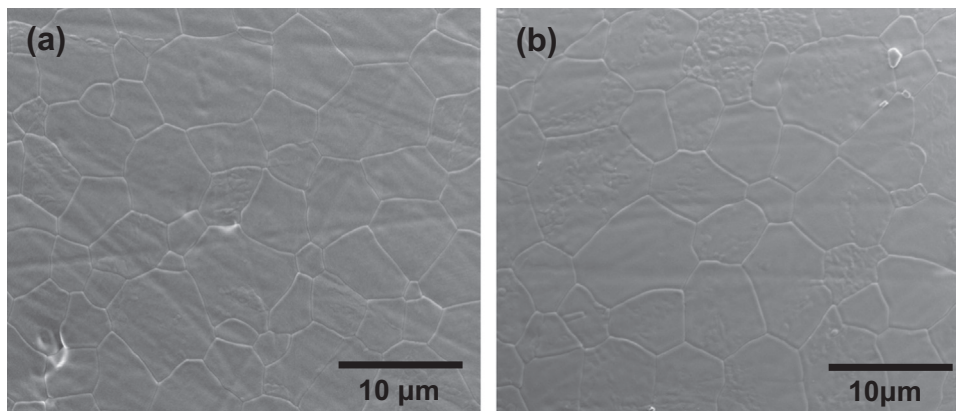


Fig. 2. FESEM micrographs of (a) 10ScSZ and (b) containing 0.5 mol% Nb₂O₅ specimens. Sintering profile: 1500 °C for 5 h.

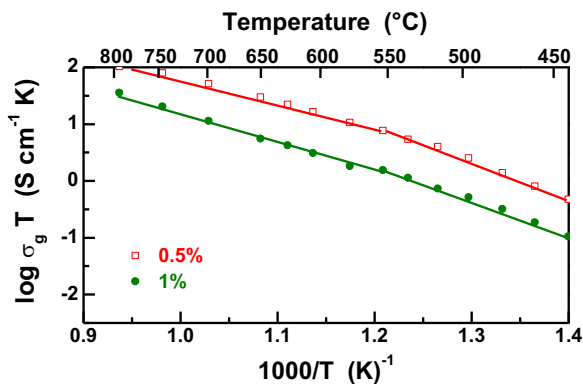


Fig. 4. Arrhenius plots of intragrain conductivity of 10ScSZ with 0.5 and 1 mol% Nb₂O₅.

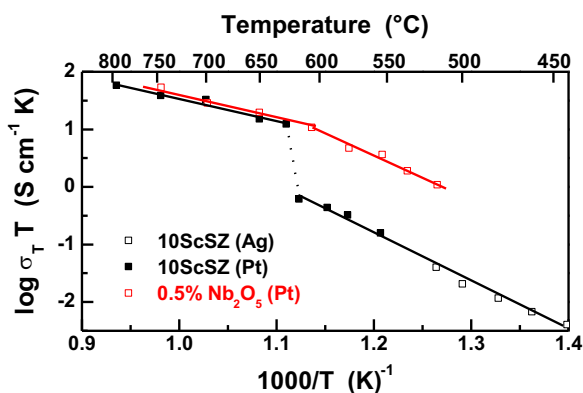


Fig. 5. Arrhenius plots of total ionic conductivity of 10ScSZ with silver and platinum electrodes and 10ScSZ containing 0.5 mol% Nb₂O₅ with platinum electrode.

host cation might introduce an electronic conductivity to the system leading to an increase of the total electrical conductivity. The same holds for multivalent dopants. As shown in Fig. 4, the grain conductivity decreases with increasing the content of Nb₂O₅ from 0.5 to 1.0 mol%. This effect reveals the predominance of the ionic conductivity over the electronic component in the temperature range of measurements, which may be understood taking into account the small contents of Nb₂O₅.

These results are in general agreement with those of 3 mol% iron oxide doped zirconia-scandia. In that case, the electronic conductivity remained low (about 6.3×10^{-6} S/cm) up to an oxygen partial pressure of 10^{-20} bar at 750 °C. In addition, the electronic transference number at that temperature was only 2×10^{-3} [19].

Fig. 5 shows Arrhenius plots of the total (grain and grain boundary) ionic conductivity of specimens without and with 0.5 mol% Nb₂O₅. In the low temperature range, the parent solid electrolyte (10ScSZ) exhibits a comparatively low ionic conductivity characteristic of the β -rhombohedral phase. The improved ionic conductivity obtained for 0.5 mol% Nb₂O₅ containing specimen is attributed to stabilization of the cubic phase. Above 600 °C the ionic conductivity of both specimens is the same within experimental errors. The stabilization of the cubic structure at room temperature and the achievement of high levels of ionic conductivity may be assigned to a combination of several factors, such as the concentration of oxygen vacancies, the ionic radius and the coordination preference of the dopants, the interaction of dopants with oxygen vacancies, and the local environment. Introduction of pentavalent cations in zirconia-based solid electrolytes is expected to decrease the concentration of oxygen vacancies. Nevertheless, the relatively low solubility of Nb⁵⁺ in the zirconia matrix [20] contributes to preserve the ionic conductivity. Moreover, Rietveld refinement of neutron powder diffraction along with molecular dynamic simulation and reverse Monte Carlo modeling indicated that the addition of Nb⁵⁺

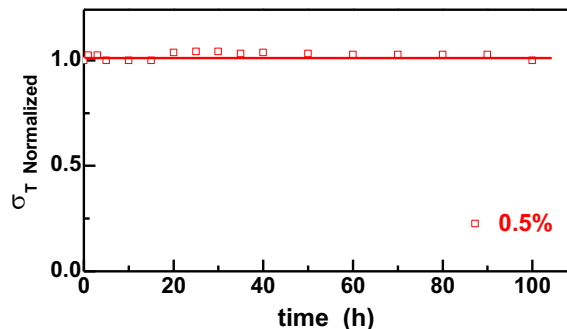


Fig. 6. Isothermal total ionic conductivity of 10ScSZ with 0.5 mol% Nb₂O₅.

to the zirconia matrix leads to an increase in the degree of short range disorder within the anion sublattice [21]. In general, crystalline solids with high levels of lattice disorder exhibit high ionic conductivity.

In a previous study on niobium pentoxide addition to yttria-stabilized zirconia an opposite trend was observed, with reduction of the ionic conductivity [22]. That deleterious effect may be attributed to the increased solubility of Nb⁵⁺ caused by Y³⁺ [23], which seems not take place in the zirconia-scandia system.

Fig. 6 shows the isothermal behavior of the total ionic conductivity with annealing at 600 °C up to 100 h. The measurements of resistance, in this case, were conducted at 700 °C, when the blocking effect at grain boundaries vanishes. As may be noted, there is no significant effect of the annealing on the ionic conductivity. Whereas a degradation of the ionic conductivity of 10ScSZ containing 1 mol% CeO₂ samples occurs within the first 100 h of aging at intermediate temperatures [24]. A systematic study on the isothermal conductivity under different temperatures and atmospheres is under way, and the results will be reported separately.

The overall results show that small amounts of niobium pentoxide allow for obtaining a new solid electrolyte with full stabilization of the cubic structure at room temperature and high ionic conductivity, turning this ternary system promising for application in intermediate temperature solid oxide fuel cells.

4. Conclusions

Stabilization of the cubic structure at room temperature of zirconia-10 mol% scandia is obtained with small additions of niobium pentoxide. The minimum nominal amount required for full phase stabilization is 0.5 mol% Nb₂O₅. For this additive content, the ionic conductivity is found to attain similar values as those of the parent electrolyte (10ScSZ) at temperatures above 600 °C. No noticeable degradation of the ionic conductivity of this system occurs after annealing at 600 °C up to 100 h.

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