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# 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 ( $\geq 600$  °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 ( $r_{Ce^{4+_{VIII}}}=0.097$  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 ( $\phi$  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 $\alpha$  radiation ( $\lambda=1.5405$  Å) in the 20–80° 2 $\theta$  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 ( $\beta$ ) 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% Nb<sub>2</sub>O<sub>5</sub> (Fig. 1a) exhibit the main reflections of the cubic fluorite-like structure ( $Fm-3m$  space group), and those of the  $\beta$ -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) Nb<sub>2</sub>O<sub>5</sub> 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 Nb<sub>2</sub>O<sub>5</sub> (1512 °C) is close to the sintering temperature (1400–1550 °C), which helps its solubilization in the zirconia matrix.

Specimens containing 1 mol% Nb<sub>2</sub>O<sub>5</sub> 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  $\beta$ -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% Nb<sub>2</sub>O<sub>5</sub> 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

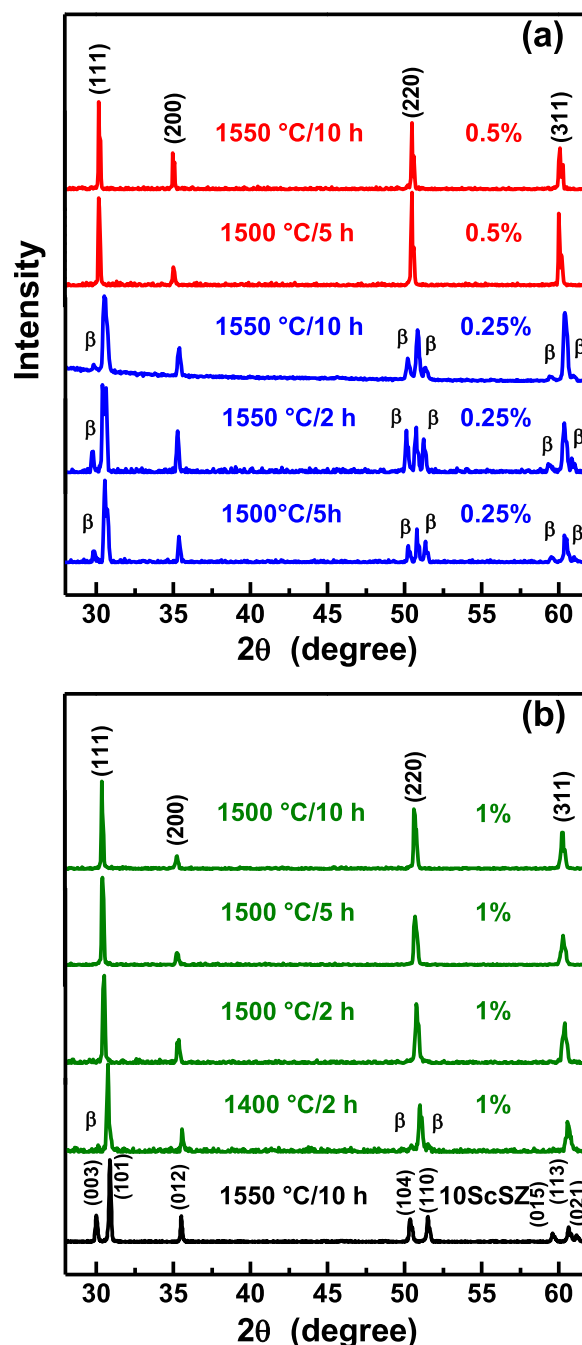


Fig. 1. X-ray diffraction patterns of specimens containing (a) 0.25 and 0.5; and (b) 1 mol % Nb<sub>2</sub>O<sub>5</sub> and 10ScSZ.

reported for other additives [13,14].

The effect of Nb<sub>2</sub>O<sub>5</sub> 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% Nb<sub>2</sub>O<sub>5</sub>. 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  $\mu$ 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,

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