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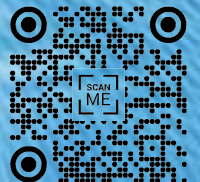
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#327

OPTIMIZATION OF LOW-GRADE TETRAGONAL ZIRCONIA BY PRASEODYMIUM OXIDE ADDITIONS

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ABSTRACT

Zirconia-based materials are still the state of art electrolyte for high temperature electrochemical systems, and for non-electrochemical applications. Their purity is known to affect performance, thus requiring high-grade expensive precursors and additional concerns about contamination during high temperature processing and/or during long term applications at intermediate temperatures, as found for contamination by silica. Thus, the purpose of this work was to demonstrate the scavenging ability of praseodymium oxide to minimize or suppress the impact of contamination by silica.

In the present work, one used TZP precursor powders from Tosoh and Innovnano. Starting materials of both powders contained significant fractions of monoclinic phase, coexisting with tetragonal zirconia, and yielded highly dense samples after sintering at 1450°C/2h. Praseodymium oxide and/or silicon oxide additions did not affect significantly the sintering behaviour. Additions of Pr and Si yielded co-existing tetragonal and cubic phases, as revealed by XRD and Rietveld refinements, with an impact on lattice parameters of the cubic phase.

The electrical characterization showed the expected severe decrease in conductivity after the addition of silicon oxide addition and also showed that this negative impact is at least partially reverted by additions of praseodymium oxide.

Keywords: solid electrolyte, yttria-stabilized zirconia, praseodymium oxide, scavenging, silica impurity

INTRODUCTION

Growing environmental concerns force the search and development of alternative energy technologies. However, the buoyancy in renewable energy production and the mismatch between energy production and demand point to the need for energy storage systems. Therefore, the importance of the study and development of solid electrochemical systems is relevant in deepening the knowledge of solid oxide fuel cells (SOFC), solid oxide electrolysis cells (SOEC) and, more recently, solid oxide reversible cells (rSOC) [1]. The growing importance of the latter cells is related to the finding that the degradation that occurs at the oxygen electrolyte/electrode interface can be delayed with the cell operating in a reversible SOEC/SOFC regime and the degradation that occurs in the SOEC regime can be partially recovered when the cell works in SOFC mode, properly controlling cycle duration [2-4]. One possible approach might be to introduce active components into the reduction. To achieve greater chemical and thermomechanical compatibility, these components can be based on zirconia with the addition of yttria and additions of cations of varying valence such as manganese and praseodymium [5].

MATERIALS AND METHODS

Commercially available Tosoh and Innovnano tetragonal zirconia powder (3% molar percentage of Y₂O₃) (TZP), Pr₂O₃ and SiO₂ high purity powders were used as starting materials. Doped powders were prepared using the conventional solid-state reaction method. The powder mixtures were weighed and mixed through ball milling in ethanol medium using zirconia balls. The prepared slurry was dried in and grounded using agate mortar and pestle until a fine powder was obtained. To study the effect of SiO₂ as impurity and Pr₂O₃ as a scavenging solution, pellets of undoped and doped TZP were unidirectionally pressed at 125 MPa and then sintered at 1450°C for 2 hours with heating and cooling rates of 10°C/min. The densities of sintered samples at various temperatures were calculated by the Archimedes method. X-ray diffraction was used to characterize the phase composition of the as-prepared and thermally treated ceramics, also the lattice parameters were calculated after Rietveld refinements. Scanning electron microscopy and EDS were used to analyse microstructure characterization of sintered ceramic samples. The total conductivity measurements were performed on dense pellets, using an AC impedance spectroscopy in an air atmosphere by HP Impedance Analyzer. The variation of the total conductivity with oxygen partial pressure at a fixed temperature was also made. The pellets were painted on both sides with porous platinum electrodes and sintered at 900°C. All measurements were carried out in the direction of decreasing temperature, from 1000 to 200°C with at 25°C steps in the frequency range of 20 -10⁶ Hz.

RESULTS AND DISCUSSION

The high densification of the samples of all compositions is achieved for the sintering conditions used, see Table 1. There are no remarkable differences in densification with the additions of silica or praseodymium oxide. The high densification is confirmed by SEM, Figure 1, where is also evident the small size of the grains. It is also clear some bimodal distribution of the grain sizes.

Table 1. Sample identification, density and relative density (RD) of the different compositions sintered at 1450°C for 2h.

Notation	TZP provider	at% SiO ₂	at% Pr ₂ O ₃	Density	RD (%)
T	Tosoh	0	0	5.962	98.7
3PT	Tosoh	0	3	5.828	96.5
ST	Tosoh	1	0	5.904	97.7
S3PT	Tosoh	1	3	6.028	99.8
I	Innovnano	0	0	5.818	96.3
3PI	Innovnano	0	3	5.730	94.9
SI	Innovnano	1	0	5.882	97.4
S3PI	Innovnano	1	3	5.546	91.8

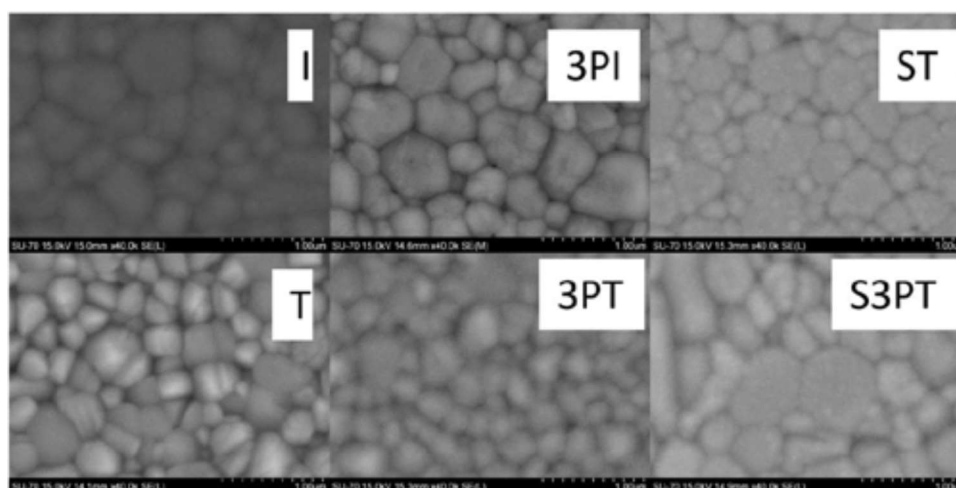


Fig. 1. SEM micrographs of the different studied compositions.

The overall conductivity of the samples is strongly affected by the presence of silica, but not so much with the additions of praseodymium oxide. It is also noticeable that the addition of praseodymium oxide to samples with silica benefits the samples, the conductivity decrease is not so relevant. By the analysis of the bulk and the grain boundary conductivities, it is clear that the more significant variations are seen on the grain boundary conductivity, as illustrated in Figure 2.

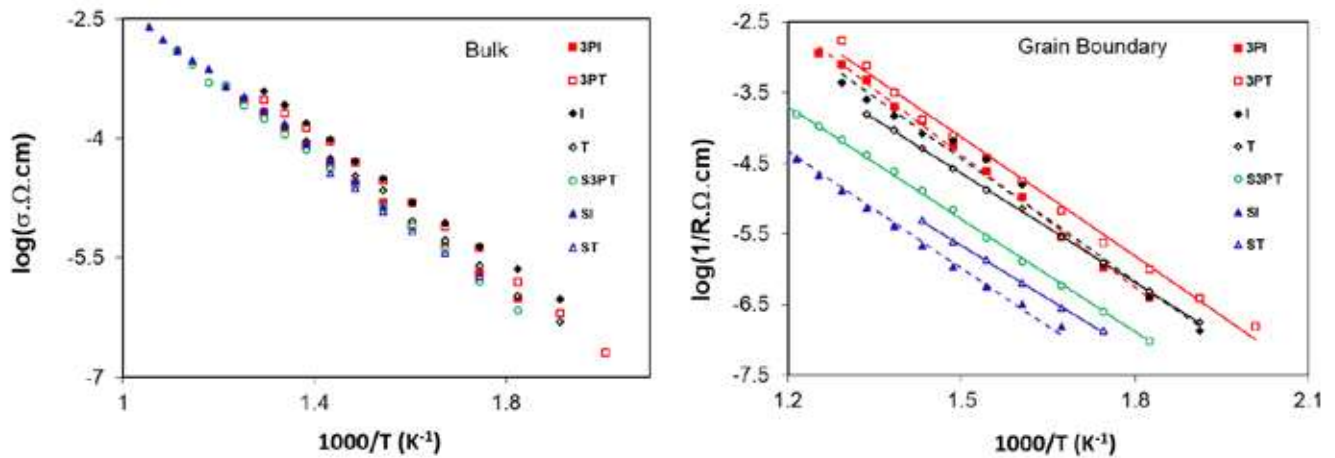


Fig. 2. Bulk and grain boundary conductivities as a function of temperature for the studied compositions.

CONCLUSIONS

The addition of praseodymium oxide to TZP to prevent or diminish the prejudicial results of the impurity silica is a viable hypothesis. The degradation in the conductivity is attenuated and further studies should be carried on to preview the right amount of praseodymium to be added to obtain the maximum effect to correct the deviations promoted by silica and not to alter the properties by itself.

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