Evaluation of the effect of heavy rare earth elements on electrical resistivity of zirconia-yttria ceramics

D. R. R. Lazar; V. Ussui; E. N. S. Muccillo; A. H. A. Bressiani; J. O. A. Paschoal

Instituto de Pesquisas Energéticas e Nucleares
C.P. 11049 Pinheiros – São Paulo, S.P., 05422-970, Brazil
drlazar@ipen.br

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Abstract. The use of yttria concentrates was investigated in this study for synthesis and processing of zirconia based ceramics applied as solid electrolyte materials. Terbium, dysprosium, holmium, erbium and ytterbium are the chemical elements, classified as heavy rare earths, that can be found in those concentrates due to their association with yttrium ores. The ceramic characteristics were compared to zirconia-yttria and zirconia-yttria-heavy rare earth oxide systems, containing 3 and 9 mol% of dopant. Powders were prepared by the coprecipitation route and ceramic processing conditions were established to attain relative densities up to 95%. The characterization of as-sintered pellets was performed by apparent density measurement by Archimedes method, X-ray diffraction, scanning electron microscopy and electrical resistivity measurement by impedance spectroscopy. It was observed that the presence of heavy rare earths in a concentrate containing 85 wt% of yttria has no significant influence on the total ionic resistivity of zirconia based ceramics.

Introduction

Yttria is an oxide commonly used to stabilize the cubic and tetragonal phases of zirconia, at room temperature, preventing the tetragonal → monoclinic phase transformation of pure oxide, which occurs at 1150 °C with a disruptive volume change. Stabilization is accomplished by a partial substitution of Y^{3+} ions for the host lattice cation (Zr^{4+}), creating oxygen vacancies that result to a high ionic conductivity over a wide range of temperature and oxygen pressure. This feature has led zirconia-yttria ceramics suitable for applications as solid electrolytes in electrochemical devices for energy conversion in solid oxide fuel cells and for oxygen determination in steel melts and automobile exhaust [1,2].

It is well known that the maximum in conductivity for zirconia-yttria ceramics is attained at elevated temperatures (~1000 °C) close to the lower limit for fully stabilization of cubic phase, that can be formed with the addition of 8-9 mol% Y_2O_3 [3]. Recently, the development of nanosized materials has shown that zirconia ceramics doped with 2,5-3 mol% Y_2O_3 could also be considered as a promising solid electrolyte [4-6]. This material, commonly referred as yttria-tetragonal zirconia polycrystals (Y-TZP), has remarkable mechanical properties [7] and could achieve higher ionic conductivity in the low temperature domain (400-700 °C), compared to cubic stabilized zirconia (CSZ). The greatest limitation of Y-TZP ceramics is the degradation of mechanical properties in humid environments at relatively low temperatures (200-300 °C) due to the formation of monoclinic phase at the ceramic surface [8]. Besides the dopant concentration, the ionic conductivity is also a function of valence and size of dopant cation [3]. Dopants that can easily change their oxidation state may introduce electronic conductivity on the material (ex. Tb_4O_7) and larger dopant cations can block the migration of vacancies decreasing ionic conductivity [9-11].

In this work, it was evaluated the influence of heavy rare earths oxides, remaining in yttria after an intermediate purification step [12], on the resistivity and microstructure of zirconia-yttria solid electrolyte. For this purpose, zirconia ceramics were prepared from powders doped with 3 and 9 mol% of high purity yttria or concentrates containing 85 and 95 wt% of this oxide.