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Densificação de $BaZr_{0,1}Ce_{0,7}Y_{0,1}Yb_{0,1}O_{3-\gamma}$ para aplicação como eletrólito de Células a Combustível de Óxido Sólido

Densification of $BaZr_{0,1}Ce_{0,7}Y_{0,1}Yb_{0,1}O_{3-\gamma}$ for Solid Oxide Fuel Cell electrolyte

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Abstract: $BaCeM^{III}O_{3-\delta}$ (M^{III} = metals with valence 3+ as Y, Yb, Gd, etc) is the most investigated proton conductive ceramic to be applied as electrolyte in the electrochemical devices as Solid Oxide Fuel Cell (SOFC). Despite their high conductivity, the low chemical stability in the presence of acidic gases (CO_2 and SO_2) requires improvements. The stability can be provided by doping with zirconium [1] and the loss in conductivity due to the presence of zirconium can be retrieved by adding yttrium and ytterbium [2]. The conductivity at the grain interface is also a major factor for an efficient electrolyte, so the synthesis is an important step. One of the synthesis methods used to obtain complex stoichiometry materials is Pechini and their variations as EDTA-Citrate method [3]. However, this class of methods have still hurdles to obtain dense materials due to the difficulty to eliminate carbonates. One way to facilitate the elimination of carbonates is to obtain materials with high surface area. The aim of this work is to synthesize $BaZr_{0,1}Ce_{0,7}Y_{0,1}Yb_{0,1}O_{3-\delta}$ by citrate-EDTA method and evaluate the influence of pH (~5 and ~8) during the precursor synthesis in order to obtain materials with high surface area. After synthesizing the resins, they were heat treated at: 600ºC/4h and 1000ºC/3h (all in air). The obtained ceramic powders were characterized by TG/DTA, XRD, EDX, FTIR and N_2 adsorption at 77K. After, the green ceramic pellets were obtained, they were submitted to the following sintering process: 500ºC/1h, 1000ºC/1h and 1450ºC/3h (all in air). The dense pellets were characterized by XRD, EDX, relative density by Archimedes method, SEM and impedance measurement. Regarding to the powder samples, the TG/DTA results indicated the formation of perovskite phase at the range of 700ºC-1000ºC (endothermic process) and, at same time the carbonate is eliminated (exothermic process). The XRD patterns of materials calcined at 1000ºC/3h showed that EDTA-citrate method provided materials under perovskite type structure when synthesized in boths pHs. The analysis by EDX (materiais obtained in boths pHs and calcined at 1000ºC/3h) confirmed that the compositions are close to the nominal one. The FTIR results indicated the carbonates are still present even calcining at 1000°C/3h, for boths pHs. The N_2 adsorption results showed that the materials synthesized in pH~8 exhibited higher surface area than materials synthesized in pH~5 (22 m^2/g and 9 m^2/g, respectively, for materials calcined at 600ºC/4h). Regarding to the dense materials, the XRD patterns of the pellets synthesized by controlling pH~8 and sintered at 1450ºC/3h showed crystalline structure with higher symmetry (orthorhombic phase) while the XRD patterns of the pellets synthesized at pH~5 showed phase with lower symmetry (monoclinic phase). The analysis by EDX in the samples sintered at 1450ºC/3h confirmed that the composition is close to the nominal one, for boths pHs. The pellets obtained from materials synthetized at pH~8 showed higher relative density than the pellets at pH~5, being 98% and 94%, respectively. The SEM analysis corroborated these results. The impedance spectroscopy showed the total conductivity within the densified material (pH 8) is in the range 11-0,54 mS/cm when measured in wet air at the temperature of 800ºC-400ºC. In other words, considering a current density of 300mA/cm^2 and a thickness of 20 μm, the overpotential is close to 100 mV at 700ºC, showing that the materials prepared by EDTA-citrate method can be used as electrolyte in the intermediate temperature SOFC (IT-SOFC).

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