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Spark-plasma-sintered barium zirconate based proton conductors for solid oxide fuel cell and hydrogen separation applications

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ABSTRACT

Proton conducting ceramics exhibit high levels of bulk proton conductivity at intermediate temperatures (500–700 °C). However, this material class has not been widely utilized in energy conversion and storage applications due to the blocking behavior of the grain boundary proton conduction. A better understanding of proton conduction in these materials requires a systematic study of the sintering conditions that determine microstructure and ultimately the electrical properties. In this work, spark plasma sintering with high heating rates was employed to prepare a state-of-the-art $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY) proton conductor for studies focused on the behavior of proton conduction at the grain boundary interfaces. The ceramics prepared by the SPS method resulted in an ultra-fine grain size of approximately 200 nm. The large grain boundary interfacial area was used as a "tool" to investigate the interfacial conduction in these materials systems. Samples displayed a lowered grain boundary conductivity and a higher activation energy compared with the literature results on conventionally prepared materials. The lower bulk conductivity is interpreted with reference to polymorphs of BZY sintered at different temperatures. The combined effect led to a lower total conductivity of the SPS densified BZY ceramics.

Introduction

Proton conducting oxide materials have been extensively studied due to their unique proton conduction at intermediate temperatures (500–700 °C) [7,10,11,25,29,32]. This materials class has demonstrated potential for use as high temperature H_2 separation membranes to produce purified H_2, as well as for electrolytes in next generation proton conducting solid oxide fuel cells that operate at lower temperatures than the state-of-the-art oxygen ion conducting SOFCs [4,5,26,28,30,32–34]. Among the various compositions of proton conductors, the $BaZrO_3$ based compounds with different dopants and co-dopants have been widely investigated due to their high bulk proton conductivity and high chemical stability [14,20]. Although these proton conducting oxides possess high levels of bulk conductivity, in practice, the total conductivity of such

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materials varies greatly depending on the synthesis methods employed. This implies that the microstructures, especially interfacial microstructures, play a key role in determining the overall performance [27]. Typically, large grained materials show a lower grain boundary resistance and a higher total conductivity. Highly resistive grain boundaries and potential space-charge induced segregations of acceptor dopants at the grain boundaries may play an important role [9]. The work outlined in this manuscript focused on the preparation methods that determine the microstructure of the materials, as well as the impact of the microstructure on the electrical properties.

Spark plasma sintering (SPS) provides a unique way of densifying materials at very low temperatures (at temperatures far below the melting point) via fast heating rates, which suppresses the grain growth during sintering, resulting in a refined microstructure. The lowered sintering temperature also avoids the evaporation of some volatile components during sintering. Different from conventional furnace sintering, SPS heats the materials by applying pressure and electric current directly to the sample simultaneously, so that dense ceramics can be obtained under uniform heating at relatively low sintering temperatures and in short processing times. The SPS method has been widely applied to various SOFC solid electrolytes to obtain dense sintered specimens, such as yttrium doped zirconia, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$, samarium doped ceria, as well as barium zirconate [8,9,12,15,17]. The SPS process was observed to enhance the conductivity of electrolytes in some studies [8,15], while other investigations did not show any improvement in the conductivity [9,13]. Those studies observing an enhanced conductivity reported that ultrafine grain sizes resulted in a modification in the grain boundary characteristics. A change in the grain boundary behavior from a barrier, to a promoter of proton transport was hypothesized [15]. In addition, less impurities in the ceramic phase [12], or improved densification of the materials were offered as additional explanations for the observed results [8]. With regards to the grain boundary conductivity in particular, recent results have indicated that samples sintered at lower temperature possess smaller grain size and higher grain boundary resistivity [13]. Consequently, the sintering conditions of SPS impacts the microstructure and the conductivity of the resulting samples. In this work, the small grain size induced by SPS processing resulted in a large grain boundary area that was used as a "tool" to investigate the interfacial conduction in these materials systems.

In this paper, we investigated the state-of-the-art yttrium doped barium zirconate $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY) proton conductor sintered by the SPS method. BZY powder was prepared by a modified Pechini technique with combined EDTA-citric method resulting in nano-sized starting powders. The ceramics were densified by SPS at different sintering temperatures. The focus was on low temperature sintering in order to obtain fine-grained BZY samples. This also avoided the vaporization of the Ba during high temperature sintering. The phase structures and microscrostructures of the proton conductors, as well as the resulting electrical properties of the proton conducting ceramics were investigated.

Experimental

Sample preparation

The proton conducting ceramic powders were prepared by a modified pechini method reported elsewhere [5,28,30]. $Ba(NO_3)_2$ (Alfa Aesar, 99.95%), $Ce(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.5%), $ZrO(NO_3)_2{\cdot}xH_2O$ (Alfa Aesar, 99.9%), $Y(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.9%) and $Yb(NO_3)_3{\cdot}xH_2O$ (Alfa Aesar, 99.9%) starting chemicals were dissolved in deionized water. The concentration of the metal ions in the individual nitrate was determined by titration. Citric acid (Alfa Aesar, 99%) and ethylenediaminetetraacetic acid (EDTA, Alfa Aesar, 99%) were employed as chelating and complexing agents for each composition. Ammonium hydroxide (Sigma–Aldrich, NH_3 content 28.0–30.0%) was added to promote the dissolution of EDTA. The metal precursors were then stoichiometrically added into the chelating and complexing agents with metal nitrates: citric acid: EDTA molar ratio = 1: 1.5: 1.2. At this stage, ammonium hydroxide was added to keep the precursors soluble in the solution. The solution was heated and stirred for 24 h to achieve a fully chelated gel, followed by heat treatment in a kitchen microwave oven to assist in foaming. The gel was burned into foam during the process and the obtained ashes were subsequently fired at 600 °C for 4 h in air to remove the organic residue. The powder was then calcined at 1100 °C to form pure phase BZY powder samples.

The calcined proton conductor powder samples were then sintered by the SPS method. The powders were filled into a graphite die with a diameter of 12.7 mm, and sintered by the SPS machine (Dr. Sinter 1020, Sumitomo Coal Mining Co.). This process was accomplished by applying a constant 4 MPa axial pressures and an increasing AC current (100 A min^{-1}) simultaneously to the die in dynamic vacuum (~10 Pa), while the temperature of sample was monitored by a pyrometer.

Characterization

The crystal structures of the calcined and sintered samples were recorded on an X-ray diffractometer (Rigaku, Japan) with graphite-monochromatized CuKa radiation ($\lambda = 1.5418$ Å) at a scanning rate of 2° min^{-1} in a 2θ range from 20 to 80°. The diffraction patterns were analyzed by performing Rietveld refinement using the General Structure Analysis System (GSAS) package and the graphical user interface (EXP GUI) [24,25]. The surface microstructure and the cross-sectional morphology of the sintered pellets were characterized by scanning electron microscopy (FESEM, Zeiss Ultra). The relative density of the samples was measured by the Archimedes method. For the conductivity measurements, both surfaces of the sintered pellets were polished, painted with platinum paste (Heraeus, CL11-5349) and baked at 950 °C for 30 min. Platinum wires were then attached to the surface of the platinum layer. Electrical conductivity was measured using an A.C. impedance method with an A.C. amplitude of 10 mV in the frequency range from 0.1 Hz to 8 MHz via an electrochemical station with a built-in impedance analyzer (Zahner IM6 Electrochemical Workstation, ZAHNER-Electrik GmbH & Co., Kronach, Germany). The conductivity measurement was