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Two-step sintering of ultrafine-grained barium cerate proton conducting ceramics

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ABSTRACT

Ultra-fine grained dense $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) ceramics have been successfully prepared via a two-step sintering method. Co-precipitation method has been adopted to prepare nano-sized BZCYYb precursors with an average particle size of 30 nm. By controlling the sintering profile, an average grain size of 184 nm was obtained for dense BZCYYb ceramics via the two-step sintering method, compared to 445 nm for the conventional sintered samples. The two-step sintered BZCYYb samples showed less impurity and an enhanced electrical conductivity compared with the conventional sintered ones. Further, the two-step sintering method was applied to fabricate anode supported solid oxide fuel cells (SOFCs) using BZCYYb as the electrolyte, resulting in dense ultrafine-grained electrolyte membranes and porous anode substrates with fine particles. Due to the reduced ohmic as well as polarization resistances, the maximum power output of the cells fabricated from the two-step sintering method reached 349 mW m^{-2} at 700 °C, significantly improved from 172 mW cm^{-2} for the conventional sintered cells, suggesting that two-step sintering method is very promising for optimizing the microstructure and thus enhancing the electrochemical performances for barium cerate based proton-conducting SOFCs.

1. Introduction

It is widely known that microstructure of the ceramics has significant impact on the performances. In many cases the mechanical and electrical properties can be readily modified just by altering the grain size distributions without changing the compositions of the ceramics [1–3]. Many parameters, such as particle sizes of the reactant materials, fabrication methods, and even the microstructure of the green bodies will affect the final microstructures of the sintered ceramics [4]. In addition, the choice of sintering profiles plays a crucial role to adjust the final microstructure, especially the grain size distributions and densities of the ceramics. To obtain refined microstructure for the ceramic samples, advanced techniques such as spark-plasma sintering and high temperature microwave sintering have been utilized by rapidly heating the samples to high temperatures to prevent or suppress grain growth [5,6]. However, these advanced techniques are usually not assessable or affordable to most researchers and sometimes may induce unwanted heterogeneities [7].

As a promising alternative to prepare fine microstructured dense ceramics, the recently developed two-step sintering method has been proved to be less costly and more efficient [8]. With appropriate sintering profile, the two-step sintering can produce fully densified ceramics with grains constrained down to nanometer size. The mechanism for the two-step sintering method is to suppress the grain boundary migration of the ceramics which occurs at high temperature, while enabling the grain boundary diffusion which occurs at relatively low temperature [8]. The first-stage high temperature sintering step helps eliminate supercritical pores while the second-stage low temperature sintering step suppresses grain growth [4]. This two-step sintering method has been applied with great success in obtaining dense ceramics with unique fine microstructures, including Y_2O_3 and SiC with nanometer-sized grains [8,9], CeO_2 and cubic structured zirconia (8 mol% Y_2O_3 stabilized) with ultrafine grains [10,11], and the perovskite structured barium titanite compound with ultrafine grain size below 200 nm [12].

Barium cerate-based ceramics have been extensively investigated due to their high proton conductivity at intermediate temperatures which can be applied in proton conducting solid oxide fuel cells (SOFCs), steam electrolysers and hydrogen separation membranes [13]. However, very limited reports are available to study the influence of microstructure on the electrochemical properties for the barium cerate-based ceramics. In this study, $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) has been chosen due to its high ionic conductivity and good chemical stability [14]. We have demonstrated for the first time that ultrafine grained dense BZCYYb ceramics can be achieved via a two-step sintering method and

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further evaluated the effect of microstructure on the electrical properties. In addition, the two-step sintering method has been applied to co-sinter an anode–electrolyte bi-layer to fabricate proton conducting SOFCs with significantly improved cell output power density.

2. Experimental

2.1. Powder synthesis and sample preparation

Powder samples of doped barium cerates having the nominal composition of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) were synthesized by a co-precipitation method as reported previously [10]. $Ba(NO_3)_2$ (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%) were used as starting materials and dissolved in deionized water and titrated to determine the concentration of the metal ions. Stoichiometric ratio of each metal ion was taken and mixed with deionized water as precursors and $(NH_4)_2CO_3$ (Fisher Scientific, 95%) was used as the mineralizer. The precursors were dripped into the mineralizer at a rate of 3 mL min^{-1} under stirring. The obtained ivory-colored co-precipitate was washed with de-ionized water and ethanol to obtain a pH value of 7 and then filtered and dried. The obtained raw powders were subsequently calcined at 1100 °C for 5 h in air. The calcined powder was then pulverized and mixed with 5 wt% polyvinyl alcohol (PVA) binder and pressed uniaxially into pellets under 600 MPa (13 mm in diameter and about 1 mm in thickness) for further sintering study.

2.2. Sintering study

The pressed pellets were sintered by a two-step sintering method in which the samples were heated at 5 °C min^{-1} to 600 °C and held for 2 h to remove the organic PVA bonder, followed by heating at a rate of 5 °C min^{-1} to a peak temperature at 1450 °C and held for 1 min to achieve an intermediate density, then cooled at 15 °C min^{-1} to 1300 °C and held for 20 h, during which the ceramic densification was achieved while grain growth was suppressed [8]. As comparison, some pressed pellets were sintered by a conventional sintering method in which the pellets were heated to 600 °C and held for 2 h, followed by heating to 1450 °C at a heating rate of 5 °C min^{-1} and held for 5 h. Some co-precipitate raw powders were also pressed directly into pellets and sintered through a reactive sintering method in which the pellets were heated to 600 °C and held for 2 h, followed by heating to 1450 °C at a heating rate of 5 °C min^{-1} and held for 5 h, where the decomposition of the co-precipitate to form perovskite phase and subsequent sintering of the perovskite powders took place consecutively. The sintered pellets are named as Two-step, Conv., Reactive for samples sintered via two-step sintering method, conventional sintering method, and reactive sintering method, respectively.

2.3. Sample characterization

Crystalline phases of the samples were recorded on a X-ray diffractometer (Rigaku, Japan) with graphite-monochromatized CuKα radiation (λ = 1.5418 Å) using a scan rate of 5° min^{-1} in a 2θ range from 20° to 80°. The sintering behavior of the material was carried out on samples using the same sintering profiles described above by a NETZSCH DIL 402C pushrod dilatometer. The microstructure of the samples was examined by a field emission scanning electron microscopy (FESEM, Zeiss Ultra) and transmission electron microscopy (TEM, Hitachi H-800, 200 kV). The porosities of the sintered pellets were quantified by a mercury porosimetry (Autopore IV, Micromeritics) at pressures ranging from 0.5 psi to 30,000 psi. For the conductivity measurements, both surfaces of the sintered pellets were polished and painted with platinum paste (Heraeus, CL11-5349) followed by baking at 950 °C for 30 min. Platinum wires were then attached to the surface of the platinum layer. Electrical conductivity was measured using A.C. impedance method with A.C. amplitude of 10 mV in the frequency range from 0.1 Hz to 8 MHz using a Zahner IM6 Electrochemical Workstation (ZAHNER-Elektrik GmbH & Co., Kronach, Germany). The conductivity tests were measured in wet air and wet H_2 containing 3 vol% H_2O, obtained by flowing gases through a water bubbler at room temperature.

2.4. Fuel cell fabrication and evaluation

For the electrochemical property measurements, anode supported BZCYYb fuel cells were prepared. The anode substrates containing NiO (J.T. Baker, 99%), BZCYYb and graphite (Alfa Aesar, 99.8%) with weight ratio of 3:2:1 were fabricated by die pressing at 100 MPa, followed by adding BZCYYb powder to the anode substrates and co-pressing the BZCYYb electrolyte powder onto the substrates at 300 MPa to form anode–electrolyte bi-layers [15]. Two-step sintering method with the same sintering profile as the BZCYYb pellets was used to sinter the anode–electrolyte bi-layer. $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN) cathode ink [16] was prepared by ball-milling BCFN powders with V-006 organic solvent (Heraeus Materials, Germany) and then pasted on the BZCYYb electrolyte surface of the sintered NiO-BZCYYb bi-layers, followed by firing at 1000 °C for 2 h to form single cells. The two-step sintered anode supported BZCYYb single cells with the configuration of Ni-BZCYYb|BZCYYb|BCFN were sealed on alumina tubes by a ceramic bond (Ceramabond™ 552, Aremco Products Inc.). Single cells were tested with hydrogen (3 vol% H_2O) as the fuel with a flow rate of 40 mL min^{-1} and ambient air as the oxidant. The cells were first stabilized at 750 °C to allow complete reduction of NiO to Ni. Cell current and voltage characteristics were evaluated by a Versa STAT3-400 electrochemical station in the temperature range of 600–750 °C. AC impedance spectra were measured under open circuit conditions with A.C. amplitude of 10 mV in the frequency range from 0.1 Hz to 1 MHz. The cross-section images of the single cells after electrochemical tests were taken using a field emission scanning electron microscopy (FESEM, Zeiss Ultra). The conventional sintered anode supported BZCYYb single cells with the same configuration were also tested for comparison.

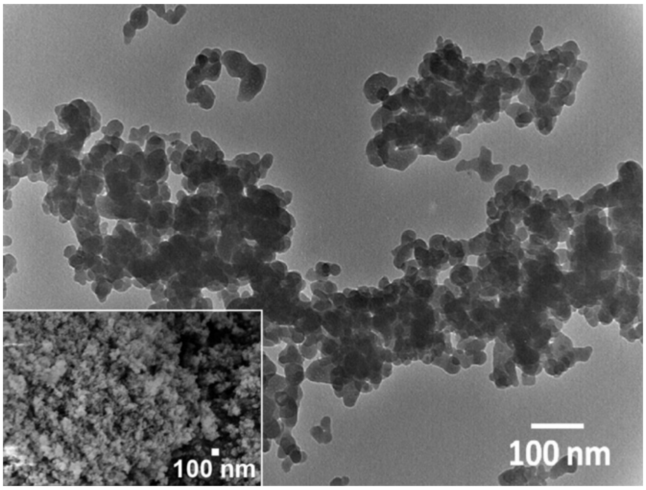

Fig. 1. TEM bright filed image of BZCYYb raw powder prepared by co-precipitation method. Inset is the FESEM picture of the powder.