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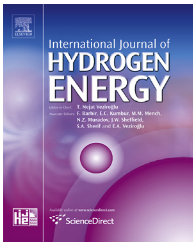

Evaluation of $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ electrolyte prepared by carbonate precipitation for a mixed ion-conducting SOFC

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ABSTRACT

Potential of $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) electrolyte prepared by ammonium carbonate coprecipitation was investigated for application in solid oxide fuel cells (SOFCs). An 8 μm thick BZCY electrolyte layer was deposited on a porous Ni–BZCY anode. A slurry mixture of BZCY–$LaSr_3Co_{1.5}Fe_{1.5}O_{10-\delta}$ (LSCF) was used as the cathode. The ionic conductivities of the BZCY electrolyte were 5.0×10^{-2} and 1.8×10^{-2} S cm^{-1} at 750 and 550 °C, respectively, and the conduction activation energy was 0.42 eV. A fabricated single cell exhibited excellent maximum power densities of 1.39 Wcm^{-2} at 750 °C and 0.72 Wcm^{-2} at 600 °C using hydrogen as fuel. Further the cell was also exposed to CH_4 (70%) and CO_2 (30%) in the anode side as fuel. Under biogas the maximum power densities were 0.79 W cm^{-2} at 750 °C and 0.28 W cm^{-2} at 600 °C. The characteristics of the electrolyte were quantified by measuring the total conductivities across a range of temperatures.

Introduction

Solid-oxide fuel cells (SOFCs) have gained tremendous recognition in the field of renewable energy because they offer to the following advantages: (i) high efficiency, (ii) fuel flexibility, (iii) modularity, (iv) lower pollutant emission, (v) non containment of corrosive liquids [1–3]. Their commercialization is yet to be realized, however, owing to their poor reliability, high cost of manufacturing, and high operating temperature. Yittria-stabilized zirconia (YSZ) has been commonly used as the electrolyte in the fuel cells, but it has a relatively high operating temperature of about 800–1000 °C. High operating temperature electrolytes require expensive materials in the interconnectors of the fuel cells; in addition they cause thermal stress, require a long time to start-up, and consume large input energy [3]. Therefore, new electrolyte materials with low operating temperatures are highly desired.

Recently, proton-conducting electrolytes have been found to operate at low or intermediate temperatures (500–750 °C). SOFCs with proton-conducting electrolytes also have operation advantages; for example, no dilution of fuel can occur at the anode because the generation of water takes place on the cathode surface [3]. Proton-conducting electrolyte materials for SOFCs are primarily based on $BaCeO_3$ and $BaZrO_3$. To improve the chemical and thermal stability of these perovskite-type oxides, they are doped with different trivalent or divalent cations of Y, Yb, Ca, Gd, In, Sm, Nd, Eu, and La [4,5].

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The proton conductivity of doped $BaCeO_3$ is high, but the material shows low chemical stability. On the contrary, $BaZrO_3$ has poor conductivity but high chemical stability. Therefore, solid solutions, consisting of doped $BaCeO_3$ and $BaZrO_3$, such as $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY), are largely designed to attain high chemical stability as well as proton conductivity [6,7]. An excellent value was reported earlier for the conductivity of BZCY at low temperature (9×10^{-3} S cm^{-1} at 500 °C) [8]. Furthermore, it was reported that when methane is used as fuel, proton-conducting SOFCs exhibits better efficiency than conventional SOFCs (oxide-ion conducting). This happens because of the generation of water vapor on the cathode side; in addition it also improved the open-circuit voltage that enhances the SOFC efficiency [9]. A barium zirconate cerate codoped with Y and Yb (BZCYYb) was also reported to exhibit high tolerance to coking and H_2S poisoning [10].

BZCY electrolytes have been prepared from $BaCeO_3$ and $BaZrO_3$ by sol–gel method, coprecipitation, combustion, and solid state reaction, etc. [10–12]. Among these techniques, coprecipitation has been highly acknowledged because it is relatively simple and is well established for mass production of electrolytes with high purity [13]. Synthesis of ceria doped with rare-earth elements using a carbonate precursor has been reported to provide less agglomeration and deliver good dispersion and excellent sinterability [14].

The performance of fuel cells fabricated with BZCY electrolytes is the least reported. To the best of our knowledge, there is no report on the use of biogas as fuel for cells based on these electrolytes. In this study, fine nanocrystalline BZCY electrolyte powders were synthesized by coprecipitation of ammonium carbonate. The electrochemical performance of single cells using hydrogen and biogas as fuel was investigated. The sintering behavior and ionic conductivity of the BZCY electrolytes were also evaluated.

Experimental and procedures

Electrolyte preparation and fabrication of anode-supported single cell

$BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) electrolyte powder was prepared using the coprecipitation method with $Ba(NO_3)_2$ (99%), $ZrO(NO_3)_2 \cdot 6H_2O$ (99%), $Ce(NO_3)_3 \cdot 6H_2O$ (99%) and $Y(NO_3)_3 \cdot 6H_2O$ (99%) from Aldrich, USA as the starting materials, as described in a previous report [15]. The precursor powder was calcined in air at a temperature of 900, 1000, and 1100 °C. Thus electrolyte powder was obtained, which were later pelletized and sintered.

A BZCY powder and NiO nanopowder (<50 nm, Aldrich, USA) were mixed at a weight ratio of 35:65. Next, for 24 h this mixture was ball-milled in presence of ethanol. After that, this fine mixture material was dried for ethanol removal. The dried material was sieved and the product derived was used as an anode powder. It was further pressed into disk shape with a diameter of 31 mm and sintered at 800 °C (for 2 h) to obtain a very rigid anode substrate.

Next, slurry of the electrolyte material was prepared for spin coating. First, BZCY electrolyte powder and an organic vehicle (3% ethyl cellulose and 97% terpinol) were mixed and then sonicated for 48 h. Later, the electrolyte slurry was spin coated onto a Ni–BZCY anode substrate and sintered at 1400 °C for 5 h. For the cathode, BZCY powder and commercial $LaSr_3Co_{1.5}Fe_{1.5}O_{10-\delta}$ (LSCF) (Fuel Cell Materials, Inc., USA) were mixed at weight ratio of 3:7 in the presence of an organic vehicle (6% ethyl cellulose and 94% terpinol). This BZCY–LSCF slurry was pasted on electrolyte face of the cell by screen printing after that it was fired for 2 h at 1000 °C. The thickness of the electrolyte layer was 8 μm while the thickness of the cathode layer was around 30 μm. The active area of the cell was measured to be approximately 0.75 cm^2.

Instruments used for characterization

The particle sizes and the crystallinity of the BZCY powders and pellets sintered at different temperatures were examined by X-ray diffraction (XRD; D/MAX-2200 Rigaku, Japan). The wavelength of Cu $K\alpha$ radiation was 1.5406 Å. The current and voltage of the diffractometer were set at 20 mA and 40 kV, respectively. The scattering angle 2θ was measured in the range of 20–90° at scanning speed of 4° min^{-1}. A scanning electron microscope (SEM; S-4700, Hitachi, Japan) was used to investigate the morphology of BZCY powders and sintered pellets. The single cell cross-sectional morphology was also analyzed. The impedance spectra were measured using an alternating-current (AC) impedance analyzer (1280B, Solatron Analytical, UK) and the frequency range was kept at 0.1 Hz to 1.0 MHz. In addition, the signal amplitude was set at 10 mV. For better connectivity, a platinum paste was coated on either side of the sintered electrolyte pellets to determine the ionic conductivity. Cell tests were carried out by exposing the anode side to wet hydrogen (~3% vol H_2O) and the cathode side to ambient air. The cell was also exposed to biogas (70% CH_4 and 30% CO_2) to check the fuel flexibility of the cells. The current and voltage characteristic curves of single cells were examined as the temperature was varied.

Results and discussion

Analysis of structural properties

X-ray diffraction patterns of BZCY powders that were calcined at different temperatures are shown in Fig. 1(a). The BZCY powder that was calcined at 900 °C exhibited a perovskite-type structure and secondary phases of $BaCO_3$ and CeO_2. However, at 1000 °C or higher temperatures, only BZCY reflection lines related to the perovskite with orthorhombic structure were detected. The formation of perovskite phase at a relatively low temperature indicates the homogeneous precipitation of all the components. XRD patterns of the BZCY pellets sintered at various temperatures are shown in Fig. 1(b). The peak intensities of the sintered pellets were higher than those of powders, which indicate the larger grain sizes of the pellets along with higher degree of crystallinity. The average grain size of electrolyte powder calcined at 1000 °C was found to be around 60 nm as calculated from the Scherrer equation. The sintered pellet specimens (at 1500 °C for 5 h) had a density equivalent to 93–96 % of the theoretical density of the single

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