



Synthesis, structural and electrical studies of $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.65}\text{Zr}_{0.25}\text{Pr}_{0.1}\text{O}_{3-\delta}$ electrolyte materials for solid oxide fuel cells



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ARTICLE INFO

Article history:

Received 26 October 2017

Received in revised form 25 November 2017

Accepted 25 November 2017

Available online 2 December 2017

Keywords:

Solid oxide fuel cell

Proton conducting electrolyte

Chemical stability

Sol-gel synthesis

BaCeO₃

ABSTRACT

This paper is discussed Sr doping effect on the microstructure, chemical stability and conductivity of $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.65}\text{Zr}_{0.25}\text{Pr}_{0.1}\text{O}_{3-\delta}$ ($0 \leq x \leq 0.2$) electrolyte prepared by sol-gel method. The lattice constants and unit cell volumes are found to decrease as Sr atomic percentage increased in accordance with the Vegard law, confirming the formation of solid solution with orthorhombic structure. Among them all the synthesized samples are showed a conductivity with different atmosphere values at 500 °C. $\text{Ba}_{0.92}\text{Sr}_{0.08}\text{Ce}_{0.65}\text{Zr}_{0.25}\text{Pr}_{0.1}\text{O}_{3-\delta}$ recorded highest conductivity with a value of 3.3×10^{-6} S/cm (dry air) & 3.41×10^{-6} S/cm (wet air with 3% relative humidity) at 500 °C due to its smaller lattice volume, larger grain size and lower activation energy that led to excessive increase in conductivity. All pellets exhibited good chemical stability when exposed to air and H₂O atmospheres. This study elucidates that the composition will be a promising electrolyte material for use as SOFC at intermediate temperatures if Sr doping is limited to small amounts.

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Introduction

BaCeO₃ based ceramic materials are one of the protons conducting perovskite oxides to show relatively high electrical conductivity when compared to other perovskite zirconates [1–6]. These oxides are mostly used as the electrolytes in fuel cells, hydrogen pumps and gas sensors [7–12]. At operating temperatures, the electrolyte should satisfy the condition of material having dense structure in order to avoid the mixing between the gases coming from both anode and cathode. Many efforts are focussed to obtain dense samples at lower temperatures either by doping Zr, Y, Yb, Gd or by adding non refractory oxides like ZnO. The electrical transport properties are strongly influenced by size and conductivity of the grains. Thus the microstructure is the key to improve the condition through the bulk and the grain boundary.

In contrast to BaCeO₃, BaZrO₃ is stable under CO₂ and under humid reductive conditions. Partial substitution of Ce⁴⁺ with Zr⁴⁺ provided a partly substituted Ba(CeZr)O₃ with better stability but on the other hand conductivities achieved are not still sufficient for commercial applications where power densities over 0.1 W/cm² are required [13–15]. Among them the available materials, Praseodymium is a soft, malleable, silvery and ductile material in

the lanthanide group and valued for its magnetic, chemical and optical properties like more rare earth elements. It readily forms trivalent Pr (III) ions and more resistant to corrosion in air than europium (Eu), lanthanum (La), cerium (Ce) or neodymium (Nd) with oxidation states +2, +3 and +4. Pr and Ce ions have very similar crystal structure, chemical properties and consequently are compatible in the perovskite crystal structure. Pr readily forms materials containing more than one oxidation state, or so more than cerium, zirconium surpasses the ability for electrochemical activity through transitions between oxidation states of adjacent Pr centers within the lattice. It has been recently shown that perovskite materials doped with praseodymium manifests relatively high conductivity at low and intermediate temperatures. In particular BaPr_(1-g)Gd_gO₃ exhibits conductivity ranging from 5×10^{-3} S/cm at 200 °C to 0.5 S/cm at 700 °C that depicted higher values than the benchmark barium cerates [16–22].

The electrical conductivity of BaCe_{0.8}Pr_{0.2}O_{3-δ} was found to be 3.07×10^{-4} S/cm at 600 °C with a sintering temperature of 1350 °C/12 h [23]. A recent study indicated that introduction of Pr as a dopant in BZY did not reduce its electrical performance. Fabbri et al., developed BaZr_{0.7}Pr_{0.1}Y_{0.2}O_{3-δ} nano structured powders by a combustion method which dramatically improved the sinterability of BZY material with a conductivity of order of 10^{-2} S/cm [24].

Thermodynamically SrCeO₃ is more stable than BaCeO₃ and very few research papers dealt with BaSrCeZrO₃ structures. Thus the present work is aimed to study the effect of strontium by

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partially replacing Ba in the A sites along with co-doping strategy of Pr in B sites of barium cerate-zirconates and examine the chemical stability and conductivity.

Experimental

Powder preparation

The citrate-EDTA complexing sol-gel process is employed for preparing $\text{BaCe}_{0.9}\text{Pr}_{0.1}\text{O}_{3-\delta}$ (BCP), $\text{BaCe}_{0.65}\text{Zr}_{0.25}\text{Pr}_{0.1}\text{O}_{3-\delta}$ (BCZP) and $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.65}\text{Zr}_{0.25}\text{Pr}_{0.1}\text{O}_3$ (BSCZP-1 to BSCZP-4) $x = 0.04, 0.08, 0.16, 0.2$ oxides. The starting materials were commercial $\text{Ba}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (High Media, 99.5%), $\text{Sr}(\text{NO}_3)_2$, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich). Both citric acid and EDTA perform the operation of chelating agents to the precursor solution. The ratio of molar solutions of EDTA: citric acid: total metal cations content is set at 1:2:1. The pH value of the solution is adjusted to be ~ 6 by addition of small amounts of NH_4OH . The mixed solutions were heated to 100°C under continuous stirring over night to remove excess water and promote polymerisation. During continuous heating, the solution becomes more viscous with a change of colour from colourless to dark brown gel form. On further heated to a temperature of $250^\circ\text{C}/24\text{ h}$ in an oven to evaporate residual water and organics, these gels get converted into black powders. The synthesized powders are now calcined at 1100°C (12 h) with a heating rate of $5^\circ\text{C}/\text{min}$. All the samples are coloured in yellow colour which is marked in contrast to the Pr doped materials of chocolate in colour. To obtain dense samples, the resulted fine calcined powders were uniaxially pressed into cylindrical pellets at 5 ton pressure and then sintered (at 1300°C for 5 h at a heating rate of 5°C min^{-1}) in air atmosphere. While sintering small amount of powder is sprinkled on the platinum foil to avoid material evaporation in the process.

Characterization

Thermogravimetric analysis (TGA) is carried out to the dried powder ($T = 250^\circ\text{C}$) by a TA instrument model SDT Q600. The phase identification of the sintered oxides is analysed with a powder diffractometer (PANalytical X-pert Pro) with Ni filtered $\text{Cu-K}\alpha$ radiation and the diffraction angle from 10° to 90° with an interval of $0.01^\circ/\text{min}$. Morphologies of the sintered pellets are examined using Scanning Electron Microscope (JEOL model JSM-6610 LV) in combination with an Energy Dispersion Spectrometer (EDS) to estimate the percentage of elements present in the samples. A FTIR spectrometer (SHIMADZU IR Prestige-21, Singapore) is employed to record the Fourier transform infrared (FTIR) spectra of calcined and sintered BCP, BCZP and $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.65}\text{Zr}_{0.25}\text{Pr}_{0.1}\text{O}_{3-\delta}$ powder in the range of $4000\text{--}400\text{ cm}^{-1}$ to predict the complex, carbonates and oxides formation. The theoretical density of the powders is calculated with the obtained XRD. Fourier transforms Raman spectroscopy is employed to study the vibrational modes of the samples in the range $0\text{--}1200\text{ cm}^{-1}$. LCR measurements from room temperature to 500°C (in dry air and wet air with 3% relative humidity) are performed with (Wayneker P65000 model and Solartron 1260) in the frequency range from 20 to 1 MHz. Silver paste is painted on both sides of the pellet and heated in a furnace at 375°C for half an hour prior to Impedance measurements.

Results and discussion

Thermo gravimetry/differential thermal analysis (TG-DTA)

To evaluate the reaction during the formation of the perovskite phase structure, simultaneous TG-DTA curves of the samples are

conducted from room temperature to 1200°C . Thermal studies reveal that there are three major steps in the decomposition process. They are (1) loss of moisture (b) decomposition of nitrates to corresponding oxides (c) solid state diffusion reaction leading to the formation of perovskite.

Three regions are reflected in TG-DTA of the powder as shown in Fig. 1(a)–(f). The gradual weight loss up to 100°C with corresponding endothermic peaks are due to absorption of water molecules that arises due to storage of preheated sample in the ambient atmosphere. The further weight loss accompanied by two exothermic peaks in DTA reveals that the decomposition of gel takes place in two steps. The weight loss from 100 to 500°C accompanied with small exothermic peak near $300\text{--}550^\circ\text{C}$ which may be due to thermal decomposition of the citrate complex, burning of citrate chains and metal nitrates. The weak endothermic peak near 800°C can be ascribed to a polymorphic phase transformation from orthorhombic to hexagonal in BaCeO_3 . The weight loss from 500 to 1000°C and the exothermic peaks near 900°C is due to co-oxidation [25]. A very small weight loss is observed above 1050°C which is due to thermal decomposition of barium carbonate, with the release of CO_2 for all the samples and formation of perovskite phase [26–28]. This is consistent with the XRD results that $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.65}\text{Zr}_{0.25}\text{Pr}_{0.1}\text{O}_{3-\delta}$ phase only forms upon calcining at 1100°C and above. There is no noticeable weight change when the temperature is higher than 1100°C , indicating that complete decomposition of BaCO_3 and formation of $\text{BaSr}_x\text{Ce}_{0.65}\text{Zr}_{0.25}\text{Pr}_{0.1}\text{O}_{3-\delta}$ compound. A small amount of weight gain is observed above 1100°C for samples which may be due to the formation of BaCO_3 or SrCeO_3 like second phase or due to buoyancy effect owing to the decreasing density of the purge gas (Ar) with temperature. Individual decomposition of the compound with respect to heat treatment is illustrated below in Table 1.

Deanello et al. [29] studied the effect of pH on CeO_2 precipitation for the $\text{Sr}_{0.85}\text{Ce}_{0.15}\text{FeO}_{3-x}$ perovskite system processed by solution combustion synthesis with citric acid and showed that segregation of CeO_2 is substantially reduced with increasing pH. The phase formation in sol gel method may be attributed to the chelating strength of citric acid towards metal ions at different pH conditions. Acids generally dissociate and liberate protons, where ligands can form metal complexes citric acid is a polyprotic acid (H_3A) which has three dissociation constants namely PK_{a1} (3.10), PK_{a2} (4.77) and pk_{a3} (6.4) liberating three protons [29,30] as shown in equations below.



A low pH level (1), the precursor solution is not sufficient to dissociate citric acid and hence the tendency to form metal complexes is lower. On increasing the pH further to 6, liberates the PK_{a2} (4.77) and PK_{a3} (6.4) protons respectively and this further enhances the concentration of metal complex in the solution which favours the formation of the desired phase. Moreover, NH_4OH which is added for controlling pH of the precursor solution, separates to form bonds with nitrate ions and results in the formation of NH_4NO_3 [31]. This compound acts as an additional oxidizer which can further improve the efficiency of combustion reaction.

XRD analysis

The formation of multi component perovskite oxide involves the rearrangement of oxygen ions and cations during the process of synthesis. As solid state reaction requires high calcination tem-

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