Solid State Ionics 202 (2011) 30–35

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Tailoring mixed proton-electronic conductivity of $BaZrO_3$ by Y and Pr co-doping for cathode application in protonic SOFCs

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ARTICLE INFO

Article history:
Received 29 March 2011
Received in revised form 4 August 2011
Accepted 4 August 2011
Available online 25 September 2011

Keywords:
Solid oxide fuel cell
Proton conductor
Barium zirconate
Praseodymium
Mixed conductivity

ABSTRACT

$BaZr_{0.8-x}Pr_xY_{0.2}O_{3-\delta}$ (BZPYx, $0.1 \le x \le 0.4$) perovskite oxides were investigated for application as cathode materials for intermediate temperature solid oxide fuel cells based on proton conducting electrolytes (protonic-SOFCs). The BZPYx reactivity with CO_2 and water vapor was evaluated by thermogravimetric and X-ray diffraction analyses, and good chemical stability was observed for each BZPYx composition. Conductivity measurements of BZPYx sintered pellets were performed as a function of temperature and p_{O_2} in humidified atmospheres, corresponding to cathode operating condition in protonic-SOFCs. Different conductivity values and activation energies were measured depending on the Pr content, suggesting the presence of different charge carriers. For all the compositions, the partial electronic conductivity, calculated from conductivity measurements at different p_{O_2}, increased with increasing the temperature from 500 to 700 °C. Furthermore, the larger the Pr content, the larger the electronic conductivity. $BaZr_{0.7}Pr_{0.1}Y_{0.2}O_{3-\delta}$ and $BaZr_{0.4}Pr_{0.4}Y_{0.2}O_{3-\delta}$ showed mostly pure proton and electron conductivity, respectively, whereas the intermediate compositions showed mixed proton/electronic conductivity. Among the two mixed proton/electronic conductors, $BaZr_{0.6}Pr_{0.3}Y_{0.2}O_{3-\delta}$ presented the larger conductivity, which coupled with its good chemical stability, makes this perovskite oxide a candidate cathode materials for protonic-SOFCs.

1. Introduction

High temperature proton conductors (HTPCs) have emerged as attractive electrolyte materials for reducing the operating temperature of conventional solid oxide fuel cells (SOFCs) down to an intermediate temperature range (IT, 400–700 °C) [1,2]. Compared to the oxygen-ion conducting electrolytes developed in the last decades for IT applications, such as doped ceria or doped lanthanum gallate, HTPCs offer several advantages; primarily, the activation energy for proton conduction is much smaller than the typical activation energy for oxygen migration, allowing the reduction of the operating temperature without a drastic decrease of the ionic conductivity. Furthermore, fuel dilution with water vapor can be avoided since water is produced at the cathode side [3].

Among HTPCs, Y-doped barium zirconate (BZY) has been recently recognized as a promising electrolyte material because of its good chemical stability and high bulk conductivity [4–6]. However, BZY has drawbacks related to its high refractory nature that makes its processing very difficult; dense pellets can be obtained at high sintering temperatures [7–9], which leads to Ba evaporation and conductivity decrease [10,11], or using sintering aids [12], which might be detrimental for proton conductivity [13], and in all cases the grain size is generally smaller than 1 μm. This implies that sintered pellets generally have low total proton conductivity because of the large volume content of poorly conducting grain boundaries [14]. Furthermore, when anode/electrolyte co-sintering is required for film electrolyte-based SOFCs, the high sintering temperatures can lead to detrimental chemical reactions at the electrode/electrolyte interfaces and hinder the anode from preserving its porous microstructure.

In a previous work [15], BZY sinterability was improved by co-doping the Zr sites with 10 mol% of Pr (BZPY10). Dense BZPY10 pellets were obtained by sintering the samples at 1500 °C for 8 h, which is generally 100 °C smaller than the typical sintering temperature required to obtain dense BZY pellets without sintering aids [16,17]. The conductivity of the BZPY10 electrolyte was confirmed to be purely protonic in humidified atmospheres below 700 °C, and it turned to be as large as 10^{-2} S cm^{-1} at 600 °C. BZPY10 was tested as electrolyte material in anode supported SOFCs, showing promising results in the IT operating range.

However, the reduction in SOFC operating temperature causes also large overpotentials at the electrode/electrolyte interfaces. In particular, the cathode plays a critical role in establishing intermediate operating temperatures since the oxygen reduction reaction kinetics are several orders of magnitude slower than the kinetics related to fuel oxidation. Nonetheless, despite the growing attention received by HTPC electrolytes in the last decade, scarce fundamental

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doi:10.1016/j.ssi.2011.08.019

studies have been performed on cathodes specifically designed for SOFCs based on HTPC electrolytes [18]. Therefore, the development of an efficient, purposely-tailored cathode material is crucial for improving the performance of IT-SOFCs based on HTPC electrolytes. A mixed proton/electronic conducting cathode should be the most desirable material for application with a proton conducting electrolyte, since in this case protons can diffuse within the cathode bulk and react with the O^{2-} ions created by dissociative oxygen adsorption and subsequently oxygen reduction at the cathode surface. This would result in a great enhancement of the electrochemical reaction active area from the electrode/electrolyte interface to the whole cathode specific surface, facilitating by-product water evaporation.

Only few approaches have been reported in the literature towards the development of a mixed proton/electron conducting oxide. Yb-doped barium cerate [19] or $BaCe_{0.8-y}Pr_yGd_{0.2}O_{3-\delta}$ [20] oxides have been reported to show mixed proton/electronic conductivity in wet oxidizing atmosphere, but the poor chemical stability of barium cerates makes these materials useless for practical applications.

In this work, chemically stable mixed proton/electron conducting oxides have been developed and their electrical properties have been evaluated by electrochemical impedance spectroscopy. Starting from the chemically stable Y-doped barium zirconate, which is well known to be a mere proton conductor below 600 °C, the substitution of the Zr with Pr might favor the appearance of electronic conductivity in addition to the protonic one, because of the mixed valence state of Pr [21,22]. The content of Y, which acts as an acceptor dopant to create oxygen vacancies, was fixed at 20 mol%, since this concentration allows the largest proton conductivity for BZY [10]. The Pr content was kept below 40 mol%, since literature data report reaction with CO_2 for higher Pr concentration in $BaZrO_3$–$BaPrO_3$ solid solutions [23,24]. The conducting properties of the different compositions were studied as a function of temperature and oxygen partial pressure by electrochemical impedance spectroscopy under humidified conditions, which corresponds to the operating conditions at the cathode side of a SOFC using a proton conducting electrolyte.

2. Experimental

Powders of $BaZr_{0.8-x}Pr_xY_{0.2}O_{3-\delta}$ (BZPYx, with $x=0.1$, BZP10; $x=0.2$, BZPY20; $x=0.3$, BZPY30; and $x=0.4$, BZPY40) were prepared using a combustion synthesis procedure. Stoichiometric amounts of commercial $Ba(NO_3)_2$ (Wako, 99.9%), $ZrO(NO_3)_2 \cdot 2H_2O$ (Wako, 97%), Pr_6O_{11} (Wako, 99,9), and $Y(NO_3)_3 \cdot 6H_2O$ (Aldrich, 99.99%) were dissolved in an aqueous solution of nitric acid. Citric acid was used as a chelating agent in a 2:1 ratio with respect to the total metal cations. After obtaining a transparent solution, the pH was adjusted between 6 and 8 by adding NH_4OH.

Phase identification of BZPYx powders was carried out using X-ray diffraction (XRD, Rigaku, mod. Ultima III) analysis with Cu Ka radiation. Thermogravimetric (TG) analysis of the BZPYx powders was performed in 100% CO_2 atmosphere to test the chemical stability of the samples in this atmosphere. The powder samples were heated up to 1200 °C, holding this temperature for 1 h, and then cooled down at the same rate of 10 °C/min.

Dense BZPYx pellets, 13 mm in diameter and about 1 mm thick, were obtained by uniaxially pressing the powders at 220 MPa for 1 min and then sintering at 1600 °C for 8 h in air (covering the samples with the same powder to limit Ba evaporation) with a heating rate of 5 °C/min. The chemical stability toward water vapor was tested soaking dense pellets in boiling distilled water for 3 h and then performing XRD analysis. Dilatometric measurements were performed on BZPY30 using a thermal expansion analyzer (DIL 402C, Netzsch) from room temperature to 800 °C at 2 °C/min in flowing air.

For conductivity measurements, two symmetrical porous Ag electrodes were deposited onto both sides of polished BZPYx pellets and heated to 700 °C for 4 h. Electrochemical impedance spectroscopy (EIS) measurements were performed in humidified (~3 vol.% H_2O) air using a multichannel potentiostat (VMP3, Bio-Logic Co.), in the 0.1 Hz–1 MHz frequency range, with an applied ac voltage amplitude of 100 mV. The conductivity was measured between 450 and 700 °C. For the measurements at different oxygen partial pressures, the p_{O2} was varied using various O_2–N_2 and air–N_2 gas mixtures, and monitoring the p_{O_2} of the outlet gas with an oxygen zirconia sensor. ZView software was used to fit the acquired impedance data to equivalent circuits.

3. Results and discussion

Fig. 1a shows the XRD patterns of the BZPYx powders synthesized by wet combustion method and calcined at 1100 °C for 6 h in air. A single phase was observed for all the BZPYx compositions, with a shift of the reflection lines toward smaller angles with increasing the Pr content, consistently with the larger ionic radius of Pr^{4+} ($R=0.85$ Å) compared to Zr^{4+} ($R=0.72$ Å) in six-fold coordination [23–25]. Table 1 reports the cubic lattice parameter, the tolerance factor, and the average crystallite size calculated using the Scherrer equation for the BZPYx synthesized powders. The listed lattice parameter values confirm that the Pr amount increase led to an increase in the unit cell volume, consistently with the Pr substitution in the Zr sites. The tolerance factor (t) decreases from 0.979 to 0.962 with increasing the Pr content from 10 to 40 mol%, respectively. Cubic symmetry is generally observed for $0.95 \leq t \leq 1.04$ [26], consistently with the XRD patterns in Fig. 1. The crystallite size was similar for each composition, ranging between 12 and 17 nm. Fig. 1b shows the XRD patterns of the BZPYx pellets sintered at 1600 °C for 8 h in air. For all the BZPYx samples, a single phase was retained also after high temperature sintering. The XRD peaks of the BZPYx pellets compared to those of calcined powders became narrower due to the increase in crystallite size after sintering, without any significant shift in the peak positions.

Fig. 2 shows typical SEM micrographs of the sintered BZPYx pellet fractured surface. Each sample showed a dense microstructure, with a

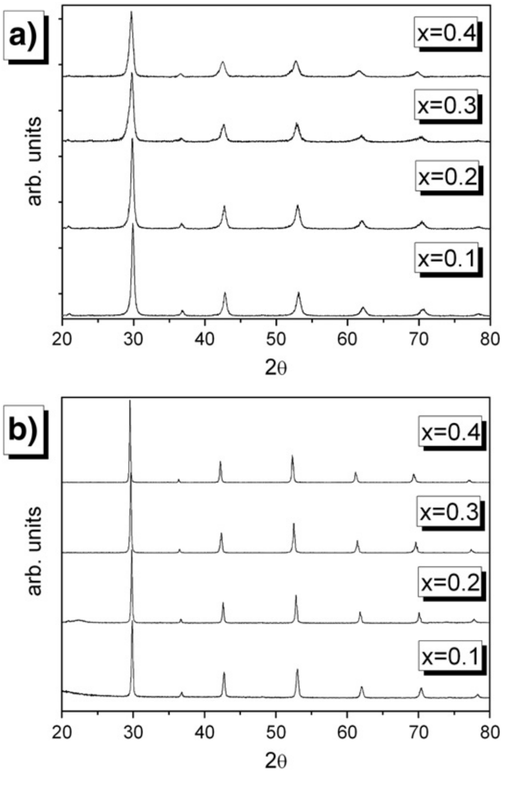

Fig. 1. XRD patterns of $BaZr_{0.7}Pr_{0.1}Y_{0.2}O_{3-\delta}$ ($x=0.1$), $BaZr_{0.6}Pr_{0.2}Y_{0.2}O_{3-\delta}$ ($x=0.2$), $BaZr_{0.5}Pr_{0.3}Y_{0.2}O_{3-\delta}$ ($x=0.3$), and $BaZr_{0.4}Pr_{0.4}Y_{0.2}O_{3-\delta}$ ($x=0.4$) powders calcined at 1100 °C for 6 h in air (a) and pellets sintered at 1600 °C for 8 h in air (b).