Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 5017–5025

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

A novel composite cathode $La_{0.6}Sr_{0.4}CoO_{3-\delta}$–$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ for intermediate temperature solid oxide fuel cells

Mao Sen Wang[a], Jian Xin Wang[a,*], Chang Rong He[a], Ye Jian Xue[a], He Miao[a], Qin Wang[b], Wei Guo Wang[a,*]

[a]Division of Fuel Cell and Energy Technology, Ningbo Institute of Materials, Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, PR China
[b]Department of Microelectronic Science and Engineering, Faculty of Science, Ningbo University, Ningbo 315211, PR China

Received 17 October 2014; received in revised form 3 December 2014; accepted 11 December 2014
Available online 18 December 2014

Abstract

In this study, $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) was incorporated into $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) to form a composite cathode LSC–BZCYYb. The X-ray diffraction (XRD) results demonstrate that BZCYYb has an extremely desirable chemical compatibility with LSC below 1200 °C. The thermal expansion coefficient (TEC) measurements indicate that incorporating 30 wt% BZCYYb enables the TEC of the composite cathode to be significantly reduced to $14.7 \times 10^{-6}\ K^{-1}$ from $20 \times 10^{-6}\ K^{-1}$ (LSC). The influence of the sintering temperature, composition and thickness on the microstructure as well as the electrochemical properties of the LSC–BZCYYb cathode were investigated. A Scanning electron microscope (SEM) testing shows that the LSC–BZCYYb cathode sintered at 950 °C has an optimum microstructure with good adhesion to the GDC interlayer and higher porosity. Electrochemical measurements reveal that 0.7LSC–0.3BZCYYb sintered at 950 °C with a thickness of approximately 20 μm possesses the minimum activation energy ($E_a = 1.32$ eV) and polarization resistance (R_p), measuring approximately $0.116\ \Omega\ cm^2$ at 650 °C. This study confirms that the composite 0.7LSC–0.3BZCYYb cathode has the great potential to be a cathode material for intermediate temperature solid oxide fuel cells.

Keywords: Composite cathode; LSC–BZCYYb; TEC; Polarization resistance; Intermediate temperature solid oxide fuel cells

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted increasing attention worldwide as a future green energy conversion device, due to its reliability, durability, high fuel efficiency, environment friendly aspects and fuel flexibility [1–4]. In general, SOFCs demand relatively high operating temperatures (>800 °C), which could promote catalytic activity of the electrode and rapid reaction kinetic while also benefiting the internal reforming of the hydrocarbon fuels [5]. However, excessive operating temperature makes the performance of the cell degrade rapidly attributed to interdiffusion of chemical components and reaction that interconnects and seals oxidation corrosion at high temperatures. In view of the material durability and system stability, the operating temperature must be significantly reduced [6,7]. Consequently, the intermediate temperature solid oxide fuel cells have become a hot new research topic.

Reducing the operating temperature of SOFCs produces two negative impacts [8,9]: (1) the polarization resistance of the electrode (mainly the cathode) reaction increases; and (2) the ionic conductivity of the electrolyte decreases. The key to overcome these problems is to investigate novel cathode materials with high electrocatalytic activity and electrolytes with higher ionic conductivity. To our knowledge, gadolinium-doped ceria

---

*Corresponding authors.
Tel.: +86 574 87910735; fax: +86 574 87910728.
E-mail address: jxwang@nimte.ac.cn (J.X. Wang).

http://dx.doi.org/10.1016/j.ceramint.2014.12.069
0272-8842/

$Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) and proton conductor $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) have considerable ionic conductivity in the intermediate temperature range (500–700 °C) [10–12]. The resistive contribution of the electrolyte can be reduced significantly by using electrolyte materials such as GDC and BZCYYb, so the critical challenge has been focused on the cathode. Lanthanum–strontium cobaltite (LSC, $La_{1-x}Sr_xCoO_{3-\delta}$, especially $La_{0.6}Sr_{0.4}CoO_{3-\delta}$) [13,14] is considered a potentially promising cathode material due to its substantial catalytic activity and conductivity at lower temperatures compared with congeneric materials such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [11,15]. The conductivity of LSCF has been reported to be only approximately 284 S cm^{-1} at 700 °C [16], whereas the conductivity of LSC is 2204 S cm^{-1} at 600 °C [17]. Furthermore, LSC is revealed to be very compatible with GDC at high operating temperatures, although LSC would exhibit unwanted reactions in contact with yttria-stabilized zirconia (YSZ) at temperatures higher than 900 °C. Consequently, LSC as a cathode will remain stable with electrolyte YSZ by embedding an interlayer of GDC.

Unfortunately, the thermal expansion coefficient (TEC) of LSC ($\sim 20 \times 10^{-6}$ K^{-1}) is much higher than the TECs of YSZ and GDC ($\sim 12 \times 10^{-6}$ K^{-1}) [5,18]. The mismatch in TEC may leads to cracks and delamination between the cathode and the electrolyte. To overcome this issue, researchers incorporated the electrolyte into LSC to form a composite cathode [19,20]. BZCYYb is a promising electrolyte material below 750 °C displaying the highest ionic conductivity of all known electrolyte materials for SOFCs such as LSGM, GDC, YSZ, etc. [10,12] Meanwhile, BZCYYb reveals considerable thermal stability in the range of the SOFC operating temperature. The TEC of BZCYYb is approximately 12×10^{-6} K^{-1} much lower than the TEC of LSC. In addition, BZCYYb as a proton conductor incorporating into LSC forms a composite cathode with mixed proton–electron conductors (able to conduct protons, oxygen vacancies and electronic defects). This way will extend the triple phase boundary (TPB) from the interface to the entire cathode, which will significantly accelerate the charge transfer reaction and restrain the cathode polarization effect [21,22]. Given these elements, the composite cathode LSC–BZCYYb seems to possess significant potential application value.

In this study, the chemical and thermal compatibility between LSC and BZCYYb was studied. The electrochemical properties of the LSC–BZCYYb composite cathode were studied in detail on symmetrical cells. It is reported by the group of Liu MeiLin that the cell with configuration Ni–BZCYYb/YSZ/LSCF was demonstrated excellent tolerance to coking [12]. YSZ was considered as electrolyte to investigate the application prospect of LSC–BZCYYb cathode in YSZ-based SOFC. Next research steps include the substitution of BZCYYb for YSZ. In view of the application to the YSZ electrolyte, a symmetrical composite cathode LSC–BZCYYb was fabricated on YSZ tape with a GDC interlayer. Various sintering temperatures were adopted to study the effect on the interfacial reaction and the electrochemical properties. The influence of cathode composition ratio and thickness on cathode performance was also investigated.

2. Experimental

2.1. Powder synthesis and characterization

In this study, three types of powders were involved, including LSC, BZCYYb and GDC. These powders were prepared by three different methods, described briefly below:

The LSC powders were prepared by a modified citrate-EDTA method [17]. La_2O_3 (99.99% Sinopharm), $Sr(NO_3)_2$ (99.99% Sinopharm) and $Co(NO_3)_2 \cdot 6H_2O$ (99.99% Sinopharm) were used as source materials. The three types of powder (La_2O_3, $Sr(NO_3)_2$, and $Co(NO_3)_2 \cdot 6H_2O$ in stoichiometric ratios) were dissolved in nitric acid. The solution was heated in a water bath at 75 °C. Next, a certain amount of citric acid (CA) and EDTA with molar ratios to metallic ion content of 1.5:0.5:1 was added to the solution in sequence. The pH value of the solution was adjusted to 0.5 by adding ammonia. A definite amount of polyethylene glycol (PEG) was added as a surfactant. The solution was heated and stirred continuously in a water bath for 6 h to evaporate the water. Next, the gel-like precursors that were obtained were dried at 110 °C for 12 h and 250 °C for 5 h later. Finally, the black ash was heated at 900 °C for 3 h.

The BZCYYb powders were synthesized by a solid–liquid composite method [23]. CeO_2 (99.99% Aladdin), $Zr(NO_3)_4$ (99.99% Aladdin), $Y(NO_3)_3 \cdot 6H_2O$ (99.99% Aladdin), $Yb(NO_3)_3$ (99.99% Aladdin), and $Ba(Ac)_2 \cdot 4H_2O$ (99.99% Aladdin) were used as source materials. A certain amount of polyvinyl pyrrolidone (PVP) was used as a surfactant. The four types powder (CeO_2, $Zr(NO_3)_4$, $Y(NO_3)_3 \cdot 6H_2O$, and $Ba(Ac)_2 \cdot 4H_2O$) in stoichiometric ratios were ball-milled for 19 h together with the surfactant PVP, dried at 380 °C for 4 h and crushed. Next, the precursors were calcined at 950 °C for 2 h. Finally, the goal powders were obtained.

The GDC powders were prepared by an acetic–acrylic polymer-pyrolysis method [24]. Gd_2O_3 (99.99%, Aladdin) and $Ce(Ac)_3$ (99.9%, Aladdin) were used as source materials. Acetic acid water solution was used as the solvent, and acrylic acid was used as the polymerized monomer. A stoichiometric amount of Gd_2O_3 was dissolved in acetic acid and cerium acetate hydrate was added subsequently to obtain a mixed acetic aqueous solution. An amount of acrylic acid with the molar ratio to metallic ions $L/M=0.5$ was added to the solution, and a little ethylene glycol (EG) was added as the surfactant. The solution was heated and stirred in a water bath at 80 °C for 5 h to evaporate the water. Next, the gel-like precursors were dried at 110 °C for 12 h and later 250 °C for 6 h later. Finally, the yellow ash that was obtained was heated in a muffle furnace at different temperatures.

The composition and purity of the powders that were obtained were measured by XRF (Rigaku ZSXPrimus II). Phase formation and chemical compatibility of the aforementioned powders were characterized by means of X-ray diffraction (XRD) in a Bruker D8 Advance with Cu Kα radiation from 10° to 90°. The microstructures of the powders were investigated by field emission scanning electron microscopy (FESEM, Hitachi SU70). Specific surface areas of the synthesized powders were measured