Applied Surface Science xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Full length article

Electrochemical properties of composite cathodes using Sm doped layered perovskite for intermediate temperature-operating solid oxide fuel cell

Seung-Wook Baek[a], Abul K. Azad[b], John T.S. Irvine[c], Won Seok Choi[d], Hyunil Kang[d], Jung Hyun Kim[e,*]

[a] Center for Energy Materials Metrology, Division of Industrial Metrology, Korea Research Institute of Standards and Science (KRISS), 267 Gajeong-Ro, Yuseong-Gu, Daejeon 305-340, Republic of Korea
[b] Faculty of Integrated Technologies, University Brunei Darussalam, Jalan Tunku Link, Gadong BE1410, Brunei Darussalam
[c] School of Chemistry, University of St. Andrews, St.Andrews, Fife KY16 9ST, United Kingdom
[d] Department of Electrical Engineering, Hanbat National University, 125, Dongseo-Daero, Yuseong-Gu, Daejeon 305-719, Republic of Korea
[e] Department of Advanced Materials Science and Engineering, Hanbat National University, 125, Dongseo-Daero, Yusung-Gu, Daejeon 305-719, Republic of Korea

ARTICLE INFO

Article history:
Received 24 September 2016
Received in revised form 22 February 2017
Accepted 23 February 2017
Available online xxx

Keywords:
Intermediate temperature-operating solid oxide fuel cell
Layered peorvksite
Area specific resistance
Percolation
Composite cathode

ABSTRACT

$SmBaCo_2O_{5+d}$ (SBCO) showed the lowest observed Area Specific Resistance (ASR) value in the $LnBaCo_2O_{5+d}$ (Ln: Pr, Nd, Sm, and Gd) oxide system for the overall temperature ranges tested. The ASR of a composite cathode (mixture of SBCO and $Ce_{0.9}Gd_{0.1}O_{2-d}$) on a $Ce_{0.9}Gd_{0.1}O_{2-d}$ (CGO91) electrolyte decreased with respect to the CGO91 content; the percolation limit was also achieved for a 50 wt% SBCO and 50 wt% CGO91 (SBCO50) composite cathode.

The ASRs of SBCO50 on the dense CGO91 electrolyte in the overall temperature range of 500–750 °C were relatively lower than those of SBCO50 on the CGO91 coated dense 8 mol% yttria-stabilized zirconia (8YSZ) electrolyte for the same temperature range. From 750 °C and for all higher temperatures tested, however, the ASRs of SBCO50 on the CGO91 coated dense 8YSZ electrolyte were lower than those of the CGO91 electrolyte.

The maximum power densities of SBCO50 on the Ni-8YSZ/8YSZ/CGO91 buffer layer were 1.034 W cm^{-2} and 0.611 W cm^{-2} at 800 °C and 700 °C.

1. Introduction

Recently, Intermediate Temperature-operating Solid Oxide Fuel Cells (IT-SOFCs) have been focused on because Solid Oxide Fuel Cells (SOFCs) operated at high operating temperature ranges over 800 °C have problems of thermal degradation, thermal expansion mismatch and high fabrication cost. However, cathode overpotential has dramatically increased at the intermediate operating temperature ranges and has typically been the major source of voltage loss in IT-SOFC operation. Therefore, most research on IT-SOFCs had been devoted to cathode materials [1–3].

One candidate cathode material using ionic and electronic conductors (MIECs), a layered perovskite with the general formula $LnBaCo_2O_{5+d}$ (Ln: lanthanides $0 < d < 1$), has recently been a subject of interest for cathode materials for IT-SOFCs because of its high oxygen transport properties, excellent oxygen surface exchange coefficients and superior oxide ionic diffusivity [4,5].

Our group has shown that layered perovskite materials are promising cathode materials for application to IT-SOFCs at temperatures between 500 °C and 700 °C [6–9]. For example, the maximum electrical conductivity value of SBCO was 570 S cm^{-1} at 200 °C; this material also showed a metal–insulator transition (MIT) phenomenon at about 200 °C. The Area Specific Resistance (ASR) results for single phase SBCO and for a composite cathode comprised of 50 wt% SBCO and 50 wt% CGO91 were 0.13 and 0.05 Ω cm^2 at 700 °C. The coefficients of thermal expansion (CTE) of the SBCO of 19.7×10^{-6} K^{-1} and 20.0×10^{-6} K^{-1} at 600 and 700 °C dropped to 12.5×10^{-6} K^{-1} and 12.7×10^{-6} K^{-1} at 600 and 700 °C, which values are similar to the value of the CGO91 electrolyte [7].

In this work, the electrochemical properties of a composite cathode prepared using SBCO with various weight percentages of CGO91 (from 0 wt% to 70 wt%) were investigated for direct applica-

* Corresponding author.
E-mail addresses: jhkim2011@hanbat.ac.kr, jhkim1870@gmail.com (J.H. Kim).

http://dx.doi.org/10.1016/j.apsusc.2017.02.211
0169-4332/

tion as IT-SOFC cathode material. Significantly, the ASR properties when using two types of electrolytes (CGO91 and CGO91 coated 8 mol% Y_2O_3 stabilized ZrO_2 (8YSZ)) are also investigated for the operating temperature conditions. In addition, the power densities when using a single phase cathode and composite cathodes on a Ni-8YSZ/8YSZ/CGO91 buffer layer were also measured for cathode application of IT-SOFC.

2. Experimental

2.1. Sample preparation and phase synthesis

Layered perovskites with general chemical compositions of $LnBaCo_2O_{5+d}$ (Ln: lanthanides) were prepared by general solid state reaction using high purity oxides (Praseodymium oxide (Pr_6O_{11}, Aldrich, 99.9%), Neodymium oxide (Nd_2O_3, Aldrich, 99.9%), Samarium oxide (Sm_2O_3, Aldrich, 99.9%), Gadolinium oxide (Gd_2O_3, Aldrich, 99.9%) and Cobalt oxide (Co_3O_4, Aldrich, 99.9%)) and carbonate (barium carbonate, ($BaCO_3$, Aldrich, 99.9%)). These oxides and carbonate were heat-treated at 300 °C for 2 h to achieve dehydration of the raw materials. After weighing the powders for exact stoichiometry with respect to the molar ratio of lanthanide oxides, barium carbonate and cobalt oxide, the samples were calcined in two steps. In the case of the first calcination process, the powders were mixed and ground in a mortar and pestle. Then, in order to decompose the carbonate, they were placed in a muffle furnace and heated at various ramp rates from room temperature to 1000 °C for 8 h as a first calcination. The temperature for the first calcination was increased in 3 steps, for example 300, to 500–750 °C before reaching 1000 °C. After finishing the cooling process to room temperature, the samples were ground and ball-milled for 24 h with zirconia media in acetone. In the second step, samples were heated at 1100 °C for 36 h at an increment of 5 °C/min and were then cooled to room temperature.

X-ray diffraction (XRD) patterns of the prepared samples were obtained in a Philips diffractometer using Cu radiation (λ = 0.15418 nm). The obtained data were matched with the reference data for identification of the crystal structures.

2.2. Half cell fabrication and test

For the fabrication of symmetric half cells that could be used to perform electrochemical characterizations, 10 mol% gadolinia doped ceria ($Ce_{0.9}Gd_{0.1}O_{2-d}$, CGO91, Praxair Specialty Ceramics, 99.9%) and 8 mol% Y_2O_3 stabilized ZrO_2 (8YSZ, Tosoh) were used as electrolytes. These electrolytes were prepared by pressing the powders into pellets with circular shapes at 2×10^3 kg/m^2 and sintering them at 1400 °C for 4 h. The final dimensions of the sintered CGO91 electrolyte pellets were approximately 21 mm diameter and 2 mm thickness. For the CGO91 buffer layer coated 8YSZ electrolyte, CGO91 slurry was prepared with vehicle systems comprised of α-Terpineol and Butvar, spin coated onto the surface of the sintered 8YSZ and then heat treated at 1300 °C for 3 h.

Single phase cathodes and composite cathodes with CGO91 powders were also used for electrochemical measurements. Vehicle systems comprised of α-Terpineol and Butvar were prepared and then cathodes were mixed with vehicles. The characteristics of the initial single phase cathodes and of the composite phase cathodes are summarized in Table 1. These cathodes were coated onto the electrolytes using screen printing to form symmetrical half cells. These half cells were sintered for 1 h at 1000 °C in order to form a porous electrode structure well bonded to the electrolyte. The final surface area of the symmetric cells was about 1.09 cm^2.

Measurements of the ASRs of the cathodes were conducted in air at open circuit voltage (OCV) as a function of temperature between 500 and 850 °C, with an increment of 50 °C. An AC four-probe method using a Solartron 1260 was used to measure the electrochemical properties. Impedance measurements were conducted in a frequency range of 5 MHz to 100 mHz; the amplitude of the applied voltage was 20 mV under OCV. The ASRs, measured from the differences between the first intercept in the vicinity of the high frequency and the last intercept at low frequency, were divided in two because the tested cells had two symmetrical electrodes.

Table 1
Chemical compositions and their initials in this research.

Compositions	Initials
$PrBaCo_2O_{5+d}$	PBCO
$NdBaCo_2O_{5+d}$	NBCO
$SmBaCo_2O_{5+d}$	SBCO
$GdBaCo_2O_{5+d}$	GBCO
30 wt% SBCO and 70 wt% CGO91	SBCO70
40 wt% SBCO and 60 wt% CGO91	SBCO60
50 wt% SBCO and 50 wt% CGO91	SBCO50
60 wt% SBCO and 40 wt% CGO91	SBCO40
70 wt% SBCO and 30 wt% CGO91	SBCO30
80 wt% SBCO and 20 wt% CGO91	SBCO20
90 wt% SBCO and 10 wt% CGO91	SBCO10

2.3. Single cell fabrication and test

Anode substrates of SOFC comprised of 8YSZ and NiO (Alfa, 99.9%) powders were provided by the Korea Electric Power Research Institute (KEPRI), as previously reported and as can be found in the literature [10]. After coating the CGO91 slurry on the anode substrates of SOFC with a spin coater, a buffer layer (CGO91 slurry) coated sample was sintered at 1300 °C for 3 h. $SmBaCo_2O_{5+d}$ (SBCO) and 50 wt% SBCO–50 wt% CGO91 (SBCO50) cathodes were also screen-printed and then heat-treated on CGO91 coated anode substrates at 1000 °C for 1 h.

Power densities multiplied by voltage and current were measured as a function of applied current density using a Solatron 1286 with a 4 lead configuration under 5% H_2/N_2 from 600 °C to 800 °C with a water bubbling system. 3% H_2O humidified H_2 was supplied to the anode chamber by bubbling through deionized water at a flow rate of 100 sccm. Air was also fed into the cathode chamber as the oxidant gas. When supplying hydrogen gas and the oxidant gas, mass flow controllers were used to control the gas flow rates. Pt-paste and Pt-mesh were used for current collection. Pt mesh, having a surface area of 1.09 cm^2, was placed on the cathodes; Pt paste was also used between the mesh and each electrode as a current collector.

3. Results and discussion

3.1. Electrochemical properties of $LnBaCo_2O_{5+d}$

Fig. 1 shows the relationships of the Area Specific Resistances (ASRs) to the various lanthanide replacements in the $LnBaCo_2O_{5+d}$ (Ln: Pr, Nd, Sm, and Gd) oxide systems as a function of temperature in the range of 500–850 °C. The ASRs of $PrBaCo_2O_{5+d}$ (PBCO) at 600, 650 and 700 °C are 1.209, 0.475 and 0.233 Ω cm^2 and the values of $NdBaCo_2O_{5+d}$ (NBCO) in this same tested temperature range are 0.606, 0.438 and 0.259 Ω cm^2. In addition, $GdBaCo_2O_{5+d}$ (GBCO) shows ASR values of 13.749, 4.943 and 1.945 Ω cm^2 at 600, 650 and 700 °C. Finally, the ASRs of $SmBaCo_2O_{5+d}$ (SBCO) in the same measured temperature range are 0.603, 0.283 and 0.131 Ω cm^2. Consequently, from these summarized ASR values, as well as from the results shown in Fig. 1, it can be asserted that the Sm doped layered perovskite (SBCO) shows the lowest observed ASR values in the $LnBaCo_2O_{5+d}$ (Ln: Pr, Nd, Sm, and Gd) oxide systems; there-

Please cite this article in press as: S.-W. Baek, et al., Electrochemical properties of composite cathodes using Sm doped layered perovskite for intermediate temperature-operating solid oxide fuel cell, Appl. Surf. Sci. (2017), http://dx.doi.org/10.1016/j.apsusc.2017.02.211