INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

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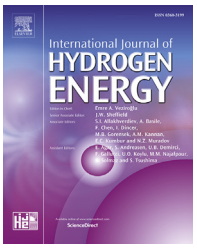

Synthesis and characterization of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Ni_{0.1}O_{3-\delta}$ cathode for intermediate-temperature solid oxide fuel cells

Biao Wang [a,b], *Guohui Long* [c], *Yunfei Li* [d], *Hongbao Jia* [a], *Dongchao Qiu* [a], *Jian Wang* [a], *Gaobin Liu* [e], *Kaiming Wang* [a], *Yuan Ji* [b,*]

[a] *School of Science, University of Science and Technology Liaoning, Anshan 114051, PR China*
[b] *Key Laboratory of Physics and Technology for Advanced Batteries, Ministry of Education, College of Physics, Jilin University, Changchun, 130012, PR China*
[c] *College of Life Sciences, Jilin Agricultural University, Changchun, 130118, PR China*
[d] *Foundation of Department, Shenyang University of Technology, Liaoyang, Liaoyang, 111003, PR China*
[e] *School of High Temperature Materials and Magnesium Resources Engineering, University of Science and Technology Liaoning, Anshan 114051, PR China*

ARTICLE INFO

Article history:
Received 6 December 2017
Received in revised form
8 February 2018
Accepted 9 February 2018
Available online xxx

Keywords:
Solid oxide fuel cells
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Ni_{0.1}O_{3-\delta}$
Cathode
Electrochemical performance

ABSTRACT

Perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Ni_{0.1}O_{3-\delta}$ (BSCFNi) oxide is synthesized and characterized as a cathode material for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The X-ray diffraction (XRD) spectra show that BSCFNi is chemical compatible with $La_{0.9}Sr_{0.1}Ga_{0.83}Mg_{0.17}O_{2.865}$(LSGM) electrolyte below 950 °C, but weak reaction is observed between BSCFNi cathode and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte after calcined at 950 °C for 10 h. The XPS results indicate that transition metal cations in BSCFNi sample exist two different valence states, i.e., $Co^{4+/3+}$, $Fe^{4+/3+}$ and $Ni^{3+/2+}$. The average thermal expansion coefficient (TEC) of BSCFNi is 18.7 × 10^{-6} K^{-1} between 200 °C and 850 °C in air. The maximum electrical conductivity reaches 35.3 Scm^{-1} at 425 °C in air. The polarization resistance of BSCFNi cathode on LSGM and SDC electrolytes are 0.033 and 0.066 Ωcm^2 at 800 °C, respectively. The maximum power density of LSGM electrolyte-supported single cell with BSCFNi cathode reaches 690 $mWcm^{-2}$ at 800 °C. These primarily results indicate that BSCFNi is a candidate cathode material for IT-SOFCs.

Introduction

As an all solid state electrochemical reactor, Solid Oxide Fuel Cells(SOFCs) can produce electricity energy between fuel gas (hydrogen or natural gas) and oxygen gas in an efficient and environment friendly manner [1,2]. In order to decrease the cost of SOFCs, reducing the operating temperature is desirable as it would allow replacement of the expensive ceramic interconnects by cheaper stainless steel. However, any reduction of the operational temperature will also reduce the catalytic activity of the electrode, especially for cathode [3,4]. Traditional cathode $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) is almost a pure

* *Corresponding author.*
E-mail address: jiyuan@jlu.edu.cn (Y. Ji).
https://doi.org/10.1016/j.ijhydene.2018.02.056
0360-3199/

electron conductor and does not provide satisfying electrochemical performance in intermediate-temperature range (500–800 °C) [5,6]. The oxygen reduction reaction of LSM cathode is restricted to an area close to three phase boundary (TPB) and dramatically increases polarization resistance at intermediate temperature. Therefore, it is very important to explore novel cathode materials with high catalytic activity for developing intermediate-temperature SOFCs (IT-SOFCs).

In recent years, simple perovskite oxide materials with general formula ABO_3 (A = La, Pr, Sm, Gd, Ba, Sr, Ca, etc; B= Mn, Co, Fe, Ni, etc) have been extensively studied as possible cathode materials in IT-SOFCs because of its high electrical conductivity and high catalytic activity for oxygen reduction reaction [7–11]. Among these perovskite materials, mixed ionic and electronic conductors (MIEC) can extend the active oxygen reduction reaction sites from the three phase boundary (gas, electrode and electrolyte interface) to the entire cathode surface [4]. MIEC materials exhibit better catalytic activity for oxygen reduction reaction and oxygen-ions transmission than pure electron conductor, which can significantly reduce the polarization resistance. MIEC materials of perovskite oxides $Ln_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (Ln = La, Pr, Nd, Sm, Gd), $Ba_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$, and layered perovskite oxides $LnBaCo_2O_{5+\delta}$ (Ln = Pr, La, Nd, Sm, Gd) have been investigated as possible cathode materials for application in IT-SOFCs [12–15]. For various MIEC materials, Shao and Haile [16] presented that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode is regarded as the most promising IT-SOFCs cathode material because of its high electrochemical performance. Subsequently, the properties of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode and its derivatives have been extensively studied [17–20].

In fact, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was originally proposed as an oxygen-permeable material [21]. The high and long-term stability is beneficial to oxygen reduction reaction of cathode. Compared with Co or Fe, Ni has lower oxidation state; the partial substitution of Ni for Co or Fe can create oxygen vacancies and improve oxygen-permeable flux. Teraokoa et al. [22] mentioned that preserving the perovskite structure was important for high oxygen permeability of material. Therefore, we can assume that the low content of Ni partial substitution Co or Fe can preserve perovskite structure and obtain a certain concentration of oxygen vacancies. Moreover, Babakhani et al. [23] also demonstrated that among these series of materials $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}R_{0.1}O_{3-\delta}$ (R = Al, Mn, Fe, Ce, Cr, Co, Ni), Ni was the most effective dopant for improving permeation oxygen and long-term stability. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Ni_{0.1}O_{3-\delta}$ (BSCFNi) has the highest permeation oxygen, which is about 3.19 ml min^{-1} cm^{-2} under air/He gradient at 950 °C [24]. The high permeation oxygen is beneficial to improve the oxygen reduction reaction as SOFC cathode material. To the best of our knowledge, the performance of BSCFNi as a cathode material has not been reported to date. Therefore, it is necessary to investigate the feasibility of BSCFNi as IT-SOFCs cathode material. The phase structure, chemical compatibility, electrical conductivity, thermal expansion coefficient (TEC), and the electrochemical performance of BSCFNi cathode on $La_{0.9}Sr_{0.1}Ga_{0.83}Mg_{0.17}O_{2.865}$ (LSGM) and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolytes have been systematically investigated.

Experimental

Powder preparation

Cathode powder $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Ni_{0.1}O_{3-\delta}$ (BSCFNi) was synthesized by EDTA-Citrate complexing method. Stoichiometric amounts of $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_2{\cdot}9H_2O$, and $Ni(NO_3)_2{\cdot}6H_2O$ were used as start materials, and the specific synthesis processes refer to our previous work [25]. The finally resulting powders were calcined at 1000 °C for 10 h in air. Electrolyte SDC and LSGM were prepared by sol-gel and solid state reaction method, respectively. Anode $Ni_{0.9}Cu_{0.1}O$ was prepared by glycine-nitrate combustion process.

Characterization of materials

Crystalline phase structure and chemical compatibility of the BSCFNi sample were characterized by X-ray diffraction(XRD) (Rigaku-D-Max Ra system operating at 12 kW with Cu K_α radiation, $\lambda = 0.15418nm$), scanning range from 20° to 80° with 0.02° increment in 2θ at room temperature. X-ray photoelectron spectra (XPS) measurements were performed using a VG scientific ESCALAB MK II X-ray photoelectron spectrometer and an Al Kα(1486.6ev) radiation source at room temperature. The thermal expansion coefficient (TEC) of BSCFNi sample was measured from 200 °C to 850 °C using Al_2O_3 sample holder and calibration reference, and heating rate of 5 °C min^{-1} by using a Netzsch DIL 402C dilatometer in air. The electrical conductivity of cathode was measured by Van der Pauw method from 300 °C to 850 °C in air.

Fabrication cell

Symmetrical cell of BSCFNi cathode on SDC and LSGM electrolytes were fabricated. Electrolyte powders of SDC were dry-pressed into pellets and calcined at 1400 °C for 10 h in air. Electrolyte powders of LSGM were calcined and grinded repeatedly, and finally LSGM powders were calcined at 1450 °C for 20 h in air. The thickness of SDC and LSGM ceramic disk was controlled at 0.3 mm. The BSCFNi cathode slurries were printed onto both sides of the SDC and LSGM electrolyte by screen printing method and calcined at 950 °C for 2 h. The effective electrode area of cell was kept on 0.16 cm^2. Sliver paste mesh as a current collector was painted on the electrode surface. The AC impedance spectra was measured by Iviumstat electrochemical analyzer. Measurement was performed under open-circuit condition with 10mv AC signal amplitude, and the frequency range from 0.1 Hz to10^6 Hz. For LSGM electrolyte-supported single cell, in order to prevent the reaction between Ni and LSGM, a SDC buffer layer was first printed onto the anode side of LSGM electrolyte and calcined at 1300 °C for 1 h. Then the composite anode $Ni_{0.9}Cu_{0.1}O$–SDC (3:2 by weight) was printed on SDC buffer layer and calcined at 1000 °C for 5 h. The BSCFNi cathode layer was printed on the opposite side of the LSGM electrolyte and calcined at 950 °C for 2 h. For SDC electrolyte-supported single cell, the composite anode $Ni_{0.9}Cu_{0.1}O$–SDC was first printed on SDC electrolyte and calcined at 1000 °C for 5 h. Then BSCFNi cathode layer was printed on the opposite side of the SDC electrolyte and

Please cite this article in press as: Wang B, et al., Synthesis and characterization of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Ni_{0.1}O_{3-\delta}$ cathode for intermediate-temperature solid oxide fuel cells, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.056