Journal of Power Sources 195 (2010) 1859–1861

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

Electrochemical performance of novel cobalt-free oxide $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ for solid oxide fuel cell cathode

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ARTICLE INFO

Article history:
Received 30 June 2009
Received in revised form
18 September 2009
Accepted 30 September 2009
Available online 13 November 2009

Keywords:
Cobalt free
Cathode
Electrochemical performance
Intermediate-temperature solid oxide fuel cell

ABSTRACT

A novel cobalt-free perovskite oxide $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (BSFC) is employed as a cathode material for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The electrical conductivity of BSFC reaches the maximum value of $57\,S\,cm^{-1}$ at 600 °C. Symmetrical electrochemical cell with the configuration of BSFC/SDC/BSFC is applied for the impedance study and area specific resistance (ASR) of BSFC cathode material is as low as $0.137\,\Omega\,cm^2$ at 700 °C. The single cell, consisting of BSFC/SDC/NiO–SDC structure, is assembled and tested from 550 to 700 °C with humidified hydrogen (~3% H_2O) as the fuel and the static air as the oxidant. A maximum power density of $718\,mW\,cm^2$ is obtained at 700 °C for the single cell. Preliminary results demonstrate that the cobalt-free oxide BSFC is a very promising cathode material for application in IT-SOFCs.

1. Introduction

Solid oxide fuel cell (SOFC) is the most efficient device among the energy technology invented so far for the conversion of chemical fuels directly into electrical power, and now it is on the way to practical application and commercialization [1,2]. Nevertheless, the expensive SOFCs system limits the commercial use for its high operating temperature. Nowadays, lowering the operation temperature of SOFCs to around 500–800 °C cannot only significantly improve materials' compatibility for the SOFCs system, but also reduce the capital costs of production and application [3]. However, a key obstacle to reduced-temperature operation of SOFCs is the poor activity of traditional cathode materials such as $La_{1-x}Sr_xMnO_3$ (LSM) [4]. Accordingly, the development of alternative cathode materials with high electrochemical performance is indispensable to make intermediate-temperature SOFCs (IT-SOFCs) technology successful.

Perovskite-type mixed ionic and electronic conductors (MIECs) have been widely investigated as potential cathodes operated in the intermediate temperature range, which tend to exhibit higher ionic conductivities than LSM owing to a greater concentration of oxygen vacancies. Considerable interest is devoted to cobalt-containing perovskite-type oxides, such as $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ [5], $La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ [6] and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [7], etc. Unfortunately, these cobalt-based cathodes often suffer some problems like high thermal expansion coefficients (TECs), high cost of cobalt element and easy evaporation and reduction of cobalt [8,9]. Therefore, the development of cobalt-free perovskite cathodes is highly desired. Large efforts have been made to develop new cobalt-free materials for the cathodes of IT-SOFC, such as $(Pr–Nd)_{0.7}Sr_{0.3}MnO_{3-\delta}$ [10], $La_xSr_{1-x}FeO_{3-\delta}$ [11] and $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ [12], etc.

In this work, we presented the development of the novel cobalt-free material $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (BSFC). The BSFC powder was synthesized via wet chemical method and its electrochemical performance was characterized in detail to investigate its suitability as the cathode of IT-SOFCs.

2. Experimental

The powders involved in this work including $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC), NiO and $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (BSFC) were synthesized by auto ignition process. Taking the synthesis of $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (BSFC) as example, stoichiometric amount of $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Fe(NO_3)_3$ and $Cu(NO_3)_2$ were dissolved in distilled water to form an aqueous solution, and then citric acid was added with the ratio of citric acid/metal mole of 1.5:1, which was used as complexation agent. The solution was then heated till self-combustion occured. The as-synthesized powders were subsequently calcined at 950 °C for 2 h to obtain fine BSFC powders.

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doi:10.1016/j.jpowsour.2009.09.078

Electrical conductivity of BSFC was studied using the standard DC four-probe technique on H.P. multimeter (Model 34401) from 400 to 800 °C. Symmetrical electrochemical cell with the configuration of BSFC/SDC/BSFC applied for the impedance research was measured by Electrochemical Workstation (IM6e, Zahner) (0.1 Hz–100 kHz) from 550 to 700 °C.

The electrochemical performance of BSFC as a cathode for IT-SOFCs was characterized in SDC electrolyte based fuel cell. To make a single cell, the anode-supported SDC bilayer (φ15 mm) was prepared by a dry-pressing method. Anode powders (NiO, SDC, and starch with a weight ratio of 65:35:20) were pre-pressed at 200 MPa as a substrate. Then loose SDC powder, calcined at 800 °C for 2 h to form a pure fluorite oxide, was uniformly distributed onto anode substrate, co-pressed at 250 MPa and sintered subsequently at 1300 °C for 5 h to obtain the SDC membrane. Fine BSFC powder was mixed thoroughly with a 10 wt% ethylcellulose–terpineol binder to prepare the cathode slurry, which was painted on the SDC electrolyte membrane to form a single cell. Afterwards, the cell was fired at 950 °C for 2 h in air. Single cells were tested from 550 to 700 °C in a home-developed-cell-testing system with humidified hydrogen (∼3% H_2O) as fuel and air as oxidant, respectively. The current–voltage curve was obtained by using a galvanostat mode.

3. Results and discussion

Fig. 1a presents XRD pattern of the BSFC powder after calcined at 950 °C for 2 h. Sharp lines reflect a well-developed crystallization and all the peaks can be well indexed as a cubic perovskite structure with the space group of *Pm*3*m* (2 1 1). Fig. 1 also presents the XRD spectra of electrolyte/anode bilayer sintered at 1300 °C for 5 h. It is obvious that there were only peaks corresponding to SDC in the electrolyte membrane (Fig. 1b) and to NiO and SDC in the anode substrate (Fig. 1c) with no peaks attributable to impurities detected.

For perovskite MIECs, the co-presence of electronic holes and oxygen vacancies makes them simultaneously exhibit both electronic and ionic conductivity. As electronic conductivity is at least one order higher than ionic conductivity, the measured values (total conductivity) can be mainly referred to electronic conductivity [8]. Fig. 2 shows the electrical conductivity behaviors of the dense BSFC sample versus the temperature when exposed to an air atmosphere. It is clear that, upon heating, the conductivity increases with the increasing of temperature (p-type semi-conductivity) and reaches the maximum value of 57 S cm^{-1} at about 600 °C, after which, the conductivity begins to decrease (pseudometallic behavior) because of the loss of the lattice oxygen and the reduction of the B-site iron ions at elevated temperature. A similar behavior with lower conductivity value of $Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-\delta}$ (BSZF) has been reported by Wei et al. [8].

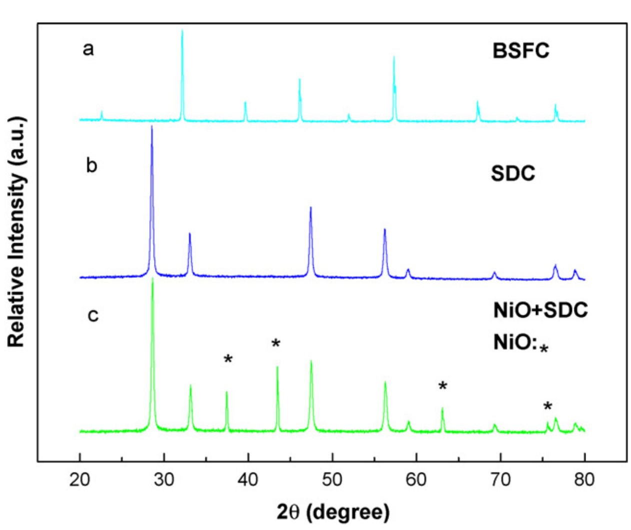

Fig. 1. XRD diffraction patterns of (a) $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (BSFC), (b) $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) membrane and (c) NiO–SDC anode substrate (*: NiO).

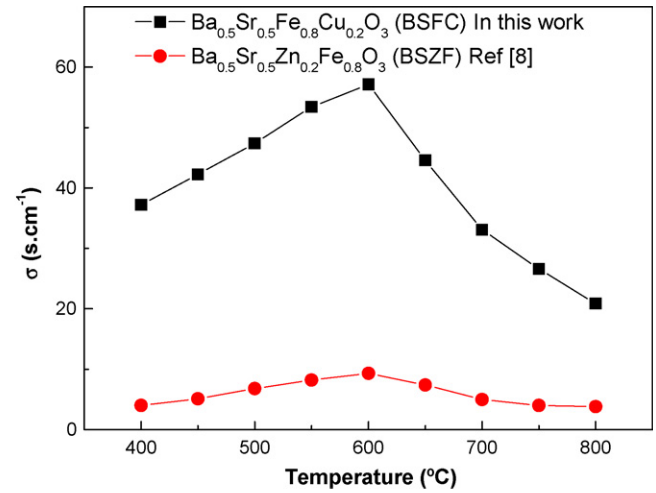

Fig. 2. Temperature dependence of the conductivity for BSFC sample measured at 400–800 °C in air.

In fact, several perovskite electrode materials with low conductivity have been reported with good electrochemical performance. For example, the maximum conductivities of $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) were about 20–60 S cm^{-1} [13] which was very close to BSFC; the conductivity of $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) anode under working condition ($PO_2 = 10^{-20}$ atm) was about 3 S cm^{-1} at 800 °C [14]. According to Wei et al. [8], compared with the electronic conductivity, the ionic conduction related to large oxygen vacancy concentration should be more important for SOFC cathode. And, in the following section, we can found that BSFC cathode exhibits attractive electrochemical performance for oxygen reduction.

A symmetric cell configuration was prepared with SDC serving as the electrolyte. Fig. 3 shows the typical impedance spectra of the symmetrical cell BSFC/SDC/BSFC from 550 to 700 °C in air. The high-frequency intercept of the electrode impedance on the real axis is the ohmic resistance of the symmetric cell, while the difference between the low-frequency and the high-frequency intercepts on the real axis corresponds to the area specific resistance (ASR) of the two interfaces. It is clear that the ASR significantly reduces with the increasing temperature. It is worthy

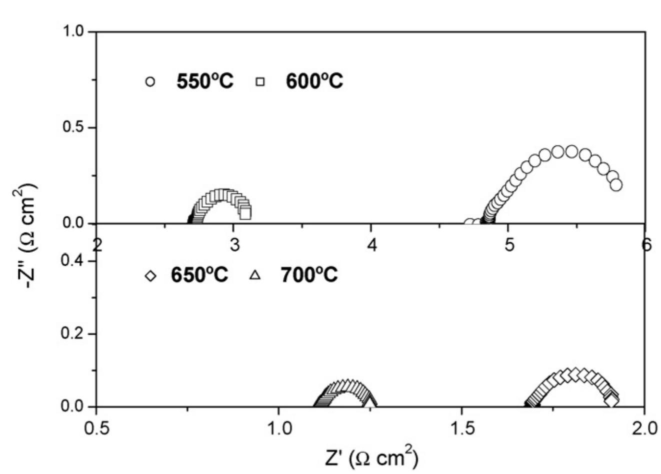

Fig. 3. Impedance spectra of the BSFC cathode with SDC serving as the electrolyte measured at 550–700 °C.

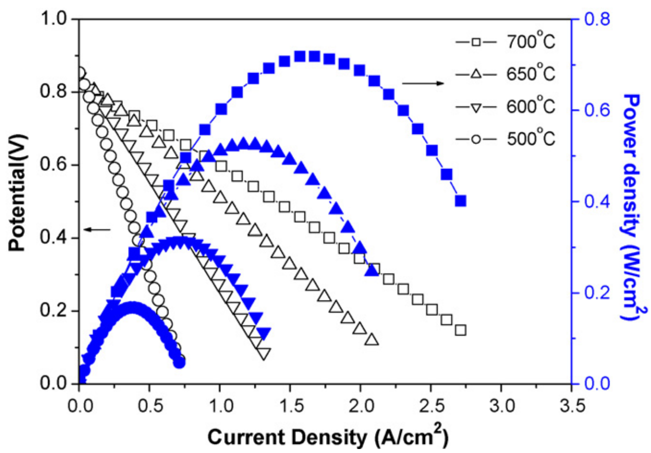

Fig. 4. Cell performance of a single cell (BSFC/SDC/NiO–SDC) under wet hydrogen atmosphere at 550–700 °C.

to note that the ASR of the BSFC cathode is 0.939 Ω cm^2 at 550 °C, 0.365 Ω cm^2 at 600 °C, 0.220 Ω cm^2 at 650 °C and 0.137 Ω cm^2 at 700 °C, respectively. Compared with other cobalt-free cathodes with high performance, such as: $Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-\delta}$ (0.23 Ω cm^2 at 700 °C) [8], $La_{0.6}Sr_{0.4}Ni_{0.2}Fe_{0.8}O_{3-\delta}$ (0.50 Ω cm^2 at 700 °C) [15] and $LaBaCuFeO_{5+\delta}$ (0.21 Ω cm^2 at 700 °C) [16], the ASR of BSFC is much lower. Obviously, the activity of BSFC cathode is higher than traditional LSM and other cobalt-free cathodes. Moreover, the performance of BSFC is also somewhat comparable to other cobalt-containing cathodes, such as: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ – 30 wt% GDC cathode (0.60 Ω cm^2 at 590 °C) [6], $SrCo_{0.9}Sb_{0.1}O_{3-\delta}$ (0.24 Ω cm^2 at 650 °C) [17], $SmBaCo_2O_{5+\delta}$ (0.19 Ω cm^2 at 700 °C) [18]. This implies that BSFC should be a serious potential material as IT-SOFCs cathode with high electrocatalytic activity for the oxygen reduction reactions.

In order to further investigate BSFC as a cathode material for IT-SOFCs, the single BSFC/SDC/Ni–SDC cell was prepared with about 30 μm thick electrolyte. Fig. 4 presents the *I–V* and *I–P* characteristics of the cell measured from 550 to 700 °C with humidified hydrogen (~3% H_2O) as the fuel. The maximum power densities of 718, 524, 314 and 168 mW cm^2 are obtained at 700, 650, 600 and 550 °C, respectively. Obviously, the performance of the cell with BSFC cathode is well compared with other cobalt-free cathodes, which are measured under almost the same conditions, such as: $Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-\delta}$ (392 mW cm^2 at 650 °C) [8] and $LaBaCuFeO_{5+\delta}$ (87 mW cm^2 at 600 °C) [16]. High power densities demonstrate that BSFC could become a promising cobalt-free cathode for IT-SOFCs, which is in good agreement with the results of impedance measurement discussed above.

4. Conclusions

In this study, a novel cobalt-free BSFC, instead of the traditional cobalt-containing perovskite-type cathode materials, was prepared by auto ignition process for IT-SOFCs. The ASR of BSFC cathode on SDC electrolyte investigated by the EIS is as low as 0.137 Ω cm^2 at 700 °C, which displays high performance. The maximum power density of the BSFC/SDC/NiO–SDC cell with about 30 μm thick electrolyte is 718 mW cm^2 at 700 °C, implies that the simple perovskite oxide BSFC might be best applied as a cobalt-free cathode material for intermediate-temperature SOFCs.

Acknowledgments

The authors gratefully acknowledge the support of this research by National Natural Science Foundation of China under contract (No. 50572099 and No. 50730002) and National High-tech R&D Program of China (Grant No.: AA2060140001).

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