Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 160 (2006) 1217–1220
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

A screen-printed $Ce_{0.8}Sm_{0.2}O_{1.9}$ film solid oxide fuel cell with a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode

Yaohui Zhang [a], Xiqiang Huang [a], Zhe Lu [a], Zhiguo Liu [a], Xiaodong Ge [a], Jiahuan Xu [a], Xianshuang Xin [a], Xueqing Sha [a], Wenhui Su [a,b,c,*]

[a] *Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150001, People's Republic of China*
[b] *Department of Condensed Matter Physics, Jilin University, Changchun 130022, People's Republic of China*
[c] *International Center for Materials Physics, Academia, Shenyang 110015, People's Republic of China*

Received 13 January 2006; received in revised form 10 February 2006; accepted 10 February 2006
Available online 29 March 2006

Abstract

Screen-printing technology was developed to fabricate $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) electrolyte films onto porous NiO–SDC green anode substrates. After sintering at 1400 °C for 4 h, a gas-tight SDC film with a thickness of 12 μm was obtained. A novel cathode material of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was subsequently applied onto the sintered SDC electrolyte film also by screen-printing and sintered at 970 °C for 3 h to get a single cell. A fuel cell of Ni–SDC/SDC (12 μm)/$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ provides the maximum power densities of 1280, 1080, 670, 370, 180 and 73 mW cm^{-2} at 650, 600, 555, 505, 455 and 405 °C, respectively, using hydrogen as fuel and stationary air as oxidant. When dry methane was used as fuel, the maximum power densities are 876, 568, 346 and 114 mW cm^{-2} at 650, 600, 555 and 505 °C, respectively. The present fuel cell shows excellent performance at lowered temperatures.

Keywords: Solid oxide fuel cells; Screen-printing; Electrolyte films; $Ce_{0.8}Sm_{0.2}O_{1.9}$; $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted more and more attention in recent decades because of their high energy conversion efficiency, flexibility of fuels and reduced pollution [1,2]. The traditional Yttria-stabilized zirconia (YSZ)-supported SOFCs always operates at around 1000 °C for acceptable performance. However, it is difficult to expect a good long-term stability at such a high temperature because of the sintering of the electrodes, the diffusion of material between the cell components and the mismatch of the thermal expansion coefficients (TEC) [3]. From the viewpoint of cost reduction and long-term stability, it is necessary to lower the operating temperature. Anode-supported YSZ thin film SOFCs have been extensively studied and have shown excellent performance at intermediate-temperatures from 600 to 800 °C [4–6]. Substituting doped-cerias for YSZ will further lower the operating temperature because of the higher ionic conductivity of doped-cerias at the lowered temperature [7]. Leng et al. [8] reported that dense $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) electrolyte films could be obtained in situ by a solid-state reaction. A maximum power density of 578 mW cm^{-2} at 600 °C was obtained based on a 10-μm-thick GDC film and a $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$ (LSCF)–GDC cathode. Xia and Liu [9] prepared a 20-μm-thick GDC film by conventional dry-pressing and got a maximum power density of 400 mW cm^{-2} at 600 °C by using $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC)–SDC as the cathode.

It is known that the performance of anode-supported film SOFCs is basically limited by cathode polarization resistance [9,10]. So, a new cathode material is desirable to further improve the performance. Recently, Shao and Haile [11] reported that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) was an excellent cathode material for SOFCs operating at lowered temperatures. Their single fuel cell made of a dry-pressed SDC electrolyte film (20 μm thick) and a BSCF cathode layer exhibited a very high power density of 1010 mW cm^{-2} at 600 °C using moist hydrogen as fuel and airflow as the oxidant.

* Corresponding author. Tel.: +86 451 86418570; fax: +86 451 86412828.
E-mail addresses: hitcrazyzyh@hit.edu.cn, suwenhui@hit.edu.cn (W. Su).

0378-7753/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2006.02.048

Screen-printing [12,13] is a simple and inexpensive technology for fabrication of dense films onto porous substrates. Peng et al. [14] fabricated a dense $Ce_{0.8}Y_{0.2}O_{1.9}$ (YDC) film (15 μm thick) onto a porous NiO–YDC anode by screen-printing. Based on this YDC film and $Sm_{0.5}Sr_{0.5}CoO_3$ cathode, they obtained a maximum power density of 230 mW cm^{-2} at 600 °C. Xia et al. [15] got a $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) electrolyte film with a thickness of 30 μm using a similar screen-printing technology. Combined with a SSC–SDC cathode, their fuel cell provided maximum power densities of 118 and 397 mW cm^{-2} at 500 and 600 °C, respectively.

In this paper, gas-tight $Ce_{0.8}Sm_{0.2}O_{1.9}$ films were fabricated on porous NiO–SDC anode substrates by screen-printing. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ powder was prepared and screen-printed onto the sintered SDC electrolyte films. Using hydrogen as fuel and ambient air as oxidant, a single cell with a 12-μm-thick SDC film exhibited maximum power densities of 1080 and 1280 mW cm^{-2} at 600 and 650 °C, respectively. The excellent fuel cell performance shows a significant improvement when the fabrication of the ceria-based electrolyte film for SOFCs uses screen-printing technology.

2. Experimental

NiO powder was prepared by a precipitation method. Ammonia (analytical reagent, A.R.) was added to a $Ni(NO_3)_2{\cdot}6H_2O$ (A.R.) solution drop by drop to obtain nickel hydroxide deposition. Then, the as-prepared deposition was aged at 70 °C for 40 min. After washing by alcohol and drying at 105 °C, the resultant deposition was finally fired at 400 °C for 2 h to get nickel oxide powder.

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ powder was synthesized by a citric-nitrate process. $Ba(NO_3)_2$ (A.R.), $Sr(NO_3)_2$ (A.R.), $Co(NO_3)_2{\cdot}6H_2O$ (A.R.) and $Fe(NO_3)_3{\cdot}9H_2O$ (A.R.) were used as the starting materials. Stoichiometric amounts of nitrate were dissolved in deionized water and citric acid (A.R.) was added as a complexant. The molar ratio of the total cation concentration to the citric acid was 1:1.15. The solution was evaporated at 75–100 °C to form a dry gel, which was finally fired at 1000 °C for 6 h to get $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ powder.

SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) powder was also prepared by the citric-nitrate process. Stoichiometric amounts of $Ce(NO_3)_3{\cdot}6H_2O$ (A.R.) and Sm_2O_3 (A.R.) were dissolved in diluted HNO_3 (A.R.) and citric acid (A.R.) was added as the complexant. The solution was evaporated and dried to form dry gel. The SDC powder was obtained by firing the dry gel at 750 °C for 2 h.

The as-prepared powder of NiO and SDC was mixed in a weight ratio of 65:35 and ball-milled for 10 h using ethanol as media. To form sufficient porosity in the anode, 15 wt.% starch was added as the pore former. The mixed powders were pressed into pellets of 13 mm in diameter and 0.5 mm in thickness. The green pellets were pre-sintered at 1000 °C for 2 h to strengthen their mechanical property. The sintered pellets were used as the support for the fuel cells.

The SDC ink for printing was made of SDC powder (55 wt.%) and ethyl cellulose-terpineol vehicle (45 wt.%). The SDC ink was screen-printed onto the pre-sintered NiO–SDC anode substrates through a Terylene screen. The mesh count of the screen is 165 wires cm^{-1} and the wire diameter is 30 μm. The screen has an opening size of 30 μm and an open area of 25%. Three printing passes were needed to get an adequate thickness. After drying in air for 10 h, the anode-supported SDC electrolyte films were sintered at 1400 °C for 4 h at a heating rate of 5 °C min^{-1}.

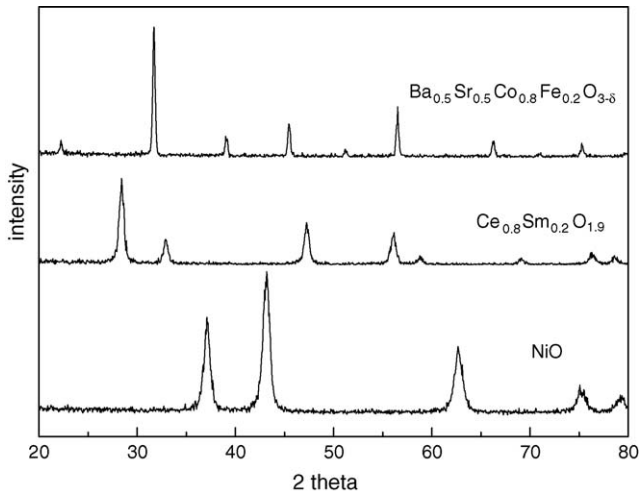

Fig. 1. XRD patterns of as-prepared powders of NiO, $Ce_{0.8}Sm_{0.2}O_{1.9}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$.

The $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode was also screen-printed onto the sintered SDC films and fired at 970 °C for 3 h.

X-ray diffraction (Bede D^1 X-ray diffraction meter) was used to confirm the crystalline structure of the prepared powders. The microstructure and morphology of the screen-printed SDC films were examined by a scanning electron microscope (SEM). The cell performances were measured using a SI 1260 impedance/gain-phase analyzer in combination with an SI1287 electrochemical interface (Solartron Instruments, Hampshire, UK). A four-probe configuration was adopted in the electrochemical testing. Hydrogen (100 ml min^{-1}) and dry methane (60 ml min^{-1}) was used as fuel, respectively, while the ambient air was used as oxidant.

3. Results and discussion

As shown in Fig. 1, the as-prepared powder of NiO shows the expected phase structure without impurity phases. The X-ray pattern for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ matches well with the diffraction data for a perovskite phase while the pattern for $Sm_{0.2}Ce_{0.8}O_{1.9}$ shows the standard cubic fluorite structure.

Fig. 2 shows the cross-sectional microstructure of a single cell and the surface of a screen-printed SDC film. As can be seen from Fig. 2a, the SDC film adheres well to both the Ni–SDC anode substrate and the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode. The SDC film is 12 μm thick with somewhat closed pinholes in cross-section. From Fig. 2b, the SDC thin films are composed of grains of irregular shapes without obvious cracks or pinholes.

Fig. 3 shows the performance of the single cell with a 12-μm-thick SDC film from 405 to 650 °C. When hydrogen (100 ml min^{-1}) was used as fuel and ambient air as oxidant, the maximum power densities were 1280, 1080, 670, 370, 180 and

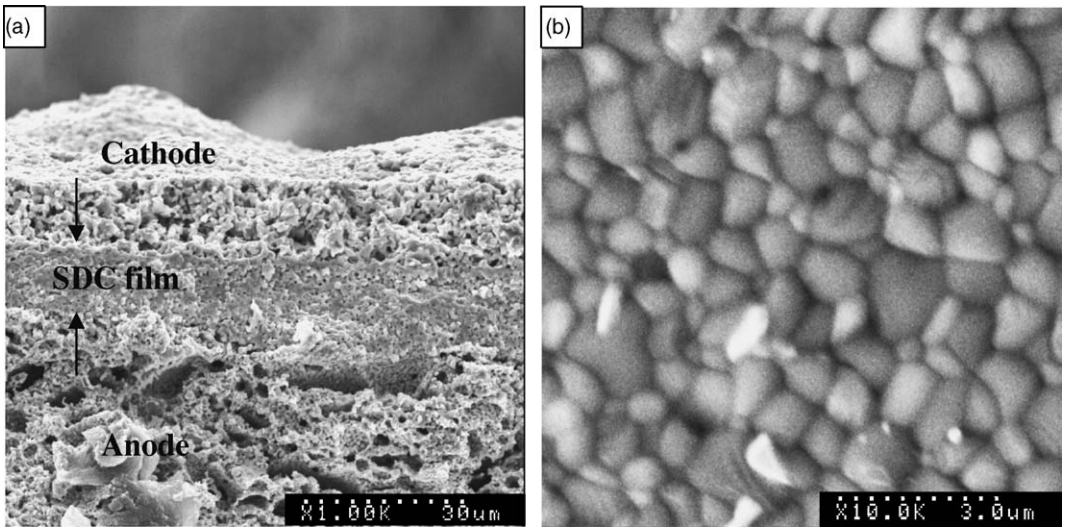

Fig. 2. SEM micrographs of the cell and the SDC film: (a) cross-section of the cell with a 12-μm-thick SDC film and (b) surface of an anode-supported SDC film.

73 mW cm^{-2} at 650, 600, 555, 505, 455 and 405 °C, respectively. It is gratifying that the performance of the present cell at 600 °C is as high as that obtained with the state-of-the-art anode-supported YSZ film of SOFCs at 750–800 °C.

Fig. 4 shows a comparison of the maximum power density between the present cell and prior reports. It can be seen that the present cell can provide the highest power density among the cells listed in Fig. 4. Since the cells have similar structures, similar ceria-based electrolyte films and comparable film thickness, the distinct difference in power density can be ascribed to the cathode used. The present cell exhibits the highest power density, which implies that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ possesses a better cathode performance at lower temperature than that for $Sm_{0.5}Sr_{0.5}CoO_3$ and $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$ [11].

Fig. 5 shows the cell performance from 505 to 650 °C using dry methane as fuel and ambient air as oxidant. The maximum power densities were 876, 568, 346 and 114 mW cm^{-2} at 650, 600, 555 and 505 °C, respectively. Xia et al. [15] operated a screen-printed SDC film (30 μm thick) SOFCs using moist

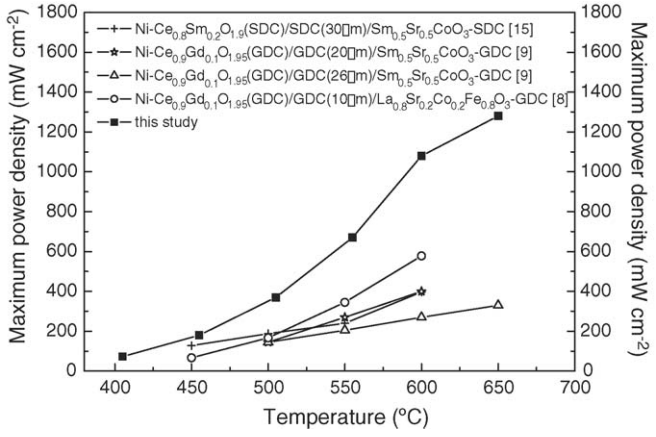

Fig. 4. Maximum power density as a function of the test temperature for the present cell compared with prior reports.

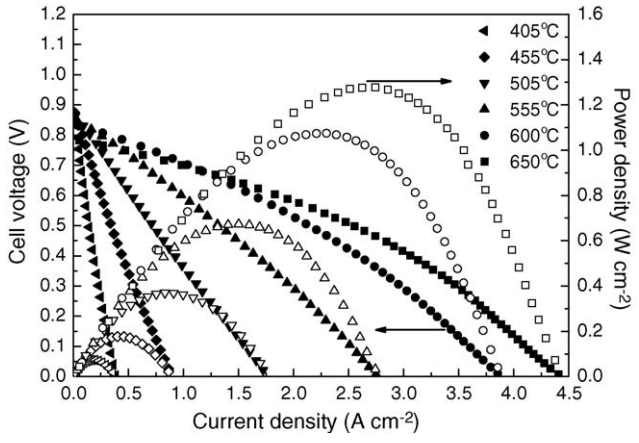

Fig. 3. Performance of the single cell with a 12-μm-thick SDC film from 405 to 650 °C. Hydrogen was used as the fuel (100 ml min^{-1}) and ambient air as the oxidant.

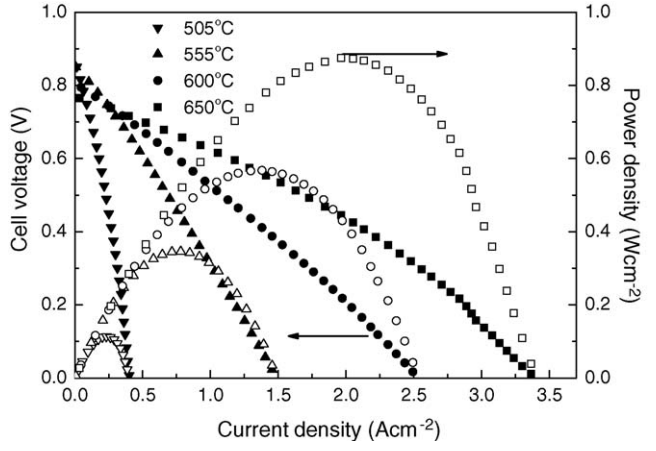

Fig. 5. Performance of the single cell with a 12-μm-thick SDC film from 505 to 650 °C. Dry methane was used as fuel (60 ml min^{-1}) and ambient air as oxidant.

methane as fuel and obtained the maximum power density of 304 mW cm^{-2} at 600 °C. This value is obviously lower than our result.

4. Conclusion

A 12-μm-thick $Ce_{0.8}Sm_{0.2}O_{1.9}$ electrolyte film was successfully fabricated onto an anode substrate by screen-printing technology. Combined with a novel $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode, a single cell of Ni–SDC/SDC (12 μm)/$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ provided a maximum power density of 1080 mW cm^{-2} at 600 °C, using hydrogen as fuel and stationary air as oxidant. When dry methane was used as the fuel, the maximum power densities were 876 and 568 mW cm^{-2} at 650 and 600 °C, respectively. The power densities reported in this paper are obviously higher than prior reports on screen-printed doped-ceria film SOFCs. This initial cell performance indicates that, with an optimized cathode material, it is a realistic goal to fabricate a high performance SDC film SOFC capable of operating at low temperature using a low-cost screen-printing technology. Detailed investigations related to the fuel cell impedance, electrode polarization and long-term stability will be carried out in the near future.

Acknowledgment

Financial support from the National Natural Science Foundation of China (grant no. 10504005) is gratefully acknowledged.

References

[1] N.Q. Minh, J. Am. Ceram. Soc. 76 (3) (1993) 563–588.
[2] B.C.H. Steele, Nature 400 (1999) 619–621.
[3] S.D. Souza, S.J. Visco, L.C. De Jonghe, Solid State Ionics 98 (1997) 57–61.
[4] V.A.C. Haanappel, J. Mertens, D. Rutenbeck, C. Tropartz, W. Herzhof, D. Sebold, F. Tietz, J. Power Sources 141 (2005) 216–226.
[5] R. Zheng, X.M. Zhou, S.R. Wang, T.L. Wen, C.X. Ding, J. Power Sources 140 (2005) 217–225.
[6] Y.J. Leng, S.H. Chan, K.A. Khor, S.P. Jiang, Int. J. Hydrogen Energy 29 (2004) 1025–1033.
[7] Y. Ji, J. Liu, T.M. He, L.G. Cong, J.X. Wang, W.H. Su, J. Alloys Compd. 353 (2003) 257–262.
[8] Y.J. Leng, S.H. Chan, S.P. Jiang, K.A. Khor, Solid State Ionics 170 (2004) 9–15.
[9] C.R. Xia, M.L. Liu, Solid State Ionics 144 (2001) 249–255.
[10] J. Liu, S.A. Barnett, J. Am. Ceram. Soc. 85 (12) (2002) 3096–3098.
[11] Z.P. Shao, S.M. Haile, Nature 431 (2004) 170–173.
[12] W.F. Chu, Solid State Ionics 52 (1992) 243–248.
[13] P.V. Dollen, S. Barnett, J. Am. Ceram. Soc. 88 (12) (2005) 3361–3368.
[14] R.R. Peng, C.R. Xia, X.Q. Liu, D.K. Peng, G.Y. Meng, Solid State Ionics 152/153 (2002) 561–565.
[15] C.R. Xia, L. Chen, M.L. Liu, Electrochem. Solid-State Lett. 4 (5) (2001) A52–A54.