



# Improvement of output performance of solid oxide fuel cell by optimizing Ni/samaria-doped ceria anode functional layer

Na Ai<sup>a</sup>, Zhe Lü<sup>a</sup>, Jinke Tang<sup>b</sup>, Kongfa Chen<sup>a</sup>, Xiqiang Huang<sup>a</sup>, Wenhui Su<sup>a,c,\*</sup>

<sup>a</sup> Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150001, China

<sup>b</sup> Department of Physics, University of New Orleans, New Orleans, LA 70148, United States

<sup>c</sup> International Center for Material Physics, Academia, Shenyang 110015, China

## ARTICLE INFO

### Article history:

Received 29 April 2008

Received in revised form 7 June 2008

Accepted 9 June 2008

Available online 20 June 2008

### Keywords:

Chemical composition

Anode functional layer

Three-phase boundary

Slurry spin coating

Solid oxide fuel cell

## ABSTRACT

Anode functional layers (AFLs) were fabricated using slurry spin coating method on anode substrates to improve the performance of cells based on samaria-doped ceria (SDC) films. The effects of the chemical compositions of AFL and AFL thickness on the performance of solid oxide fuel cell anodes were investigated by studying their effect on the ohmic loss, electrode overpotential, and output performance of cells in different atmospheres. With humidified hydrogen used as fuel and oxygen as oxidant, the cell with an 8- $\mu\text{m}$ -thick AFL (NiO:SDC = 6:4) exhibited excellent maximum power densities of 3.41, 2.89, 1.46 and 0.80 W cm<sup>-2</sup> at 650, 600, 550 and 500 °C, respectively.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Low temperature solid oxide fuel cells (SOFCs) are very attractive in recent years for their potential to bring down fabrication cost. Anode-supported thin film SOFC is one of the most efficient cells which can reduce the ohmic loss resulting from the electrolyte [1]. Since electrolyte has been substantially reduced in thickness to film, it is of course very important to study the properties of an electrode because it is a primary factor which limits the output performance of a cell. Due to incomplete densification and loss of oxygen caused by reduction of NiO, the pores produced in a thick anode are not enough when submicro-sized NiO particles are used in an anode, which leads to a reduced overall reaction rate [2,3]. So, various organic pore-formers have been used to facilitate gas diffusion. However, these pore-formers also cause some defects in the interface between anode and electrolyte film [4].

Most of the electrocatalyses related to the redox reaction occur next to electrolyte in an effective anode thickness of an anode substrate [5]. The anode functional layer (AFL) fabricated on the anode substrate could increase the length of three-phase boundaries

(TPBs), thereby lowering the polarization of an anode. Moreover, a fine AFL structure has its effect on the deposition process and the mechanical property of an electrolyte film [3]. The lower porosity of an AFL could also reduce the impact of fuel on SDC film and enhance the long-term stability of cell system. Therefore, the electrochemical and physical properties of AFLs play an important role in determining the performance of a cell. This is why much work has been done on the effect of AFLs on cell performance [6–8]. We reported a pilot study on the effect of AFL on cell performance and presented and discussed the fabrication of electrolyte film of low temperature SOFC [4]. In this paper, we shall present what we have done recently to improve the output performance of cells by optimizing a Ni/samaria-doped ceria AFL.

## 2. Experimental

Fig. 1 shows the schematic preparation procedure of a cell. Nickel oxide (NiO) powders were synthesized by precipitation method and calcined at 400 °C for 2 h [2]. Electrolyte Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> (SDC) powders were prepared by glycine-nitrate process (GNP) and calcined at 800 °C for 2 h. Anode powder was prepared by mixing NiO, SDC and pore-former (wheat flour) at a weight ratio of 52:28:20. The anode powder was compacted into pellets with 13 mm in diameter, and anode substrates were obtained by

\* Corresponding author. Tel.: +86 451 86418420; fax: +86 451 86412828.  
E-mail addresses: [suwenhui@hit.edu.cn](mailto:suwenhui@hit.edu.cn), [ina396@163.com](mailto:ina396@163.com) (W. Su).

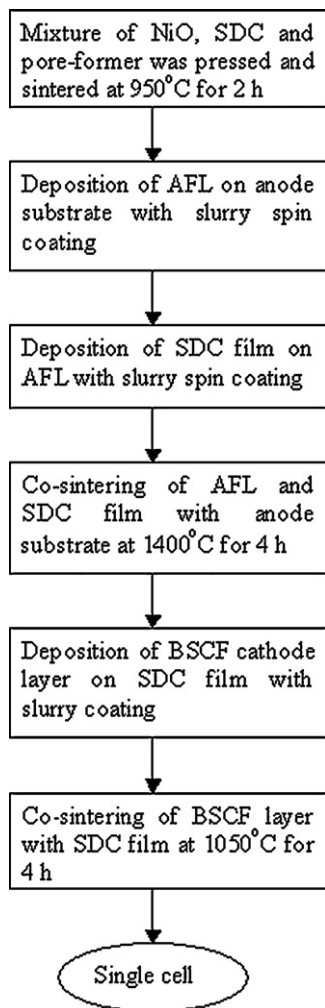


Fig. 1. The schematic representation of the fabricating procedure of cell.

calcining the pellets at 950 °C for 2 h. AFLs were fabricated by spin coating slurries containing NiO and SDC at different weight ratios onto one side of anode disks. SDC films were fabricated by slurry spin coating on the AFLs [4], and co-sintered with the anode structure at 1400 °C for 4 h. A  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) cathode layer was fabricated on the SDC film, and then sintered at 1050 °C for 4 h.

A cell without AFL was denoted as Cell-0, and the cells with AFLs containing NiO and SDC at weight ratios of 4:6, 6:4 and 8:2 were denoted as Cell-1, Cell-2 and Cell-3, respectively. The remaining cell fabrication process was the same. The cells fabricated were tested under the same conditions so that the effect of AFLs on the output performance of cells could be evaluated.

Silver paste, DAD-87 supplied by Shanghai Research Institute of Synthetic Resin was used as both current collector and sealant. The electrochemical properties of cells were tested using four-probe method in an electrical furnace. With anodes in situ reduced at 600 °C, these cells were measured for their  $I$ - $V$  characteristics and ac impedance spectra with an electrochemical interface Solartron SI 1287 and an impedance analyzer SI 1260 at a temperature in the range of 500–650 °C.

Upon completion of the test, SDC matrixes were attained by removing nickel from AFL by acid leaching. The anode sample was soaked in a diluted  $\text{HNO}_3$  solution at 80 °C for 2 h. Porous SDC matrixes were obtained by rinsing and drying. The samples were characterized using scanning electron microscope (Hitachi S-570).

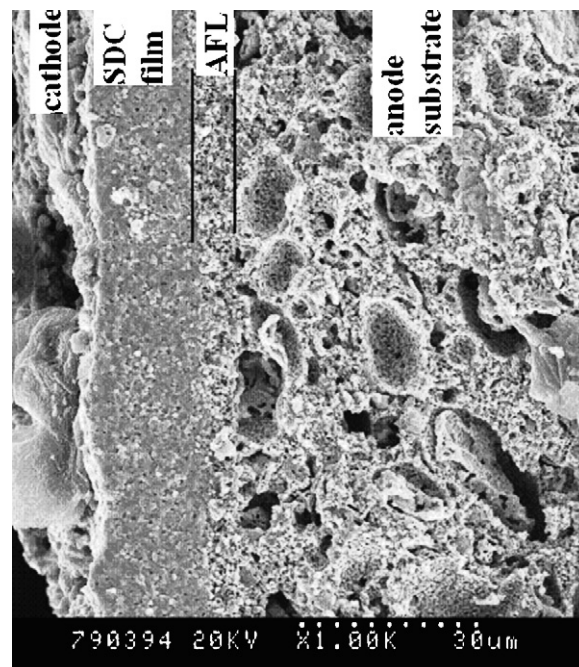


Fig. 2. SEM micrograph of a cell with an AFL structure after operation.

### 3. Results and discussion

It can be seen from Fig. 2 that the 18- $\mu\text{m}$ -thick dense SDC film is in close contact with the 8- $\mu\text{m}$ -thick AFL, and the flour produced pores are up to 20  $\mu\text{m}$  in size in the microstructure of anode substrate. Although the continuous pores could offer a pathway for reactant and resultant to diffuse, these pores would cause reduction in both ionic and electronic conductivities [3]. Moreover, these pores would diminish the overall three-phase boundary (TPB) areas in the effective thickness of the reaction area adjacent to the SDC film and reduce the area available for chemical reaction. The Ni/SDC anode substrate is 0.58-mm-thick and its porosity is 65.7%.

As shown in Fig. 3, the particles and the pores are uniformly distributed on the surface of AFLs with various compositions. By comparing the structure of AFLs before and after reduction, it can be seen that the bigger grains are SDC and the smaller dispersed grains are Ni. The SDC phase forms a well-proportioned ceramic skeleton with Ni grains uniformly distributed in AFLs. A porous network is formed by the spaces between the necked NiO and SDC powders. The larger pores in AFLs were produced by incomplete sintering densification, while the smaller ones around the Ni grains were produced by reduction of NiO to Ni. It can be easily concluded that a high NiO ratio in the green AFL results in more micropores after reduction of NiO. The porosities of Ni/SDC AFLs are 22.3, 30.2 and 37.8% when the original weight ratios of NiO to SDC in the AFLs are 4/6, 6/4 and 8/2, respectively.

Different compositions of the AFLs cause electronic and ionic conductivities, activity for electrochemical reactions and porosity for reaction gas transport [9]. They are all important parameters having effect on anode performance. Cells with different AFLs were investigated to find the suitable composition of AFL. In order to find a suitable AFL composition, the anode substrates, cathodes and SDC films were fabricated using the same processes and the cells were tested under the same conditions, so the difference in cell performance can be attributed to the difference in AFL composition.

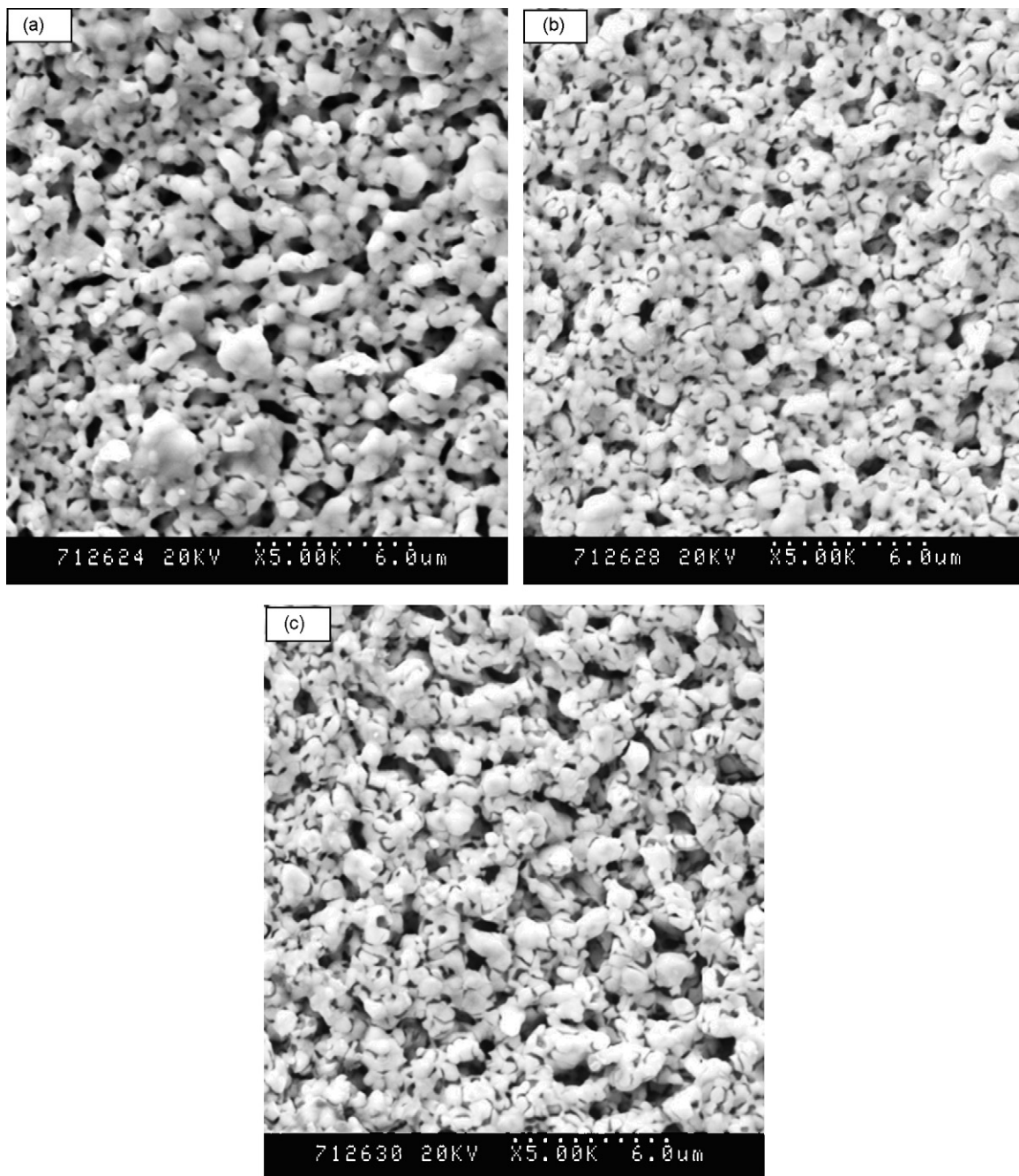
It can be seen from Fig. 4 that the open circuit voltages (OCV) of cells are very close to each other, which means the effect of AFL on the gas impermeability is approximately the same. However, the

$I$ - $V$  curves are quite different from each other at high current densities. The performance of the cells with AFLs is better than that of the cell without AFL. The maximum power densities (MPDs) of cells from Cell-0 to Cell-3 tested at 600 °C are 0.93, 1.04, 1.28 and 1.03  $W\text{ cm}^{-2}$ , respectively. Cell-2 exhibits the best output performance among the cells with AFLs, and its output performance is 38% higher than that of Cell-0. The  $I$ - $V$  curves of Cell-1 and Cell-3 are very close to each other at a low current density, while the voltage of Cell-1 begins to drop more rapidly at a current density higher than 2.5  $A\text{ cm}^{-2}$ .

Polarization indicates a voltage drop within a cell which limits the output voltage of a fuel cell and reduces the area-specific output power at a given current density. It should be noted that the

impedance spectra under open circuit conditions reflect the cell performance at a very low output current density only. In order to identify the cause for the difference in performance between cells, the polarizations of cells can be divided into ohmic loss and electrode overpotential as shown in Fig. 5. Ohmic losses are obtained from the impedance spectra measured at different voltages, and the electrode overpotentials are obtained by subtracting ohmic losses from  $I$ - $V$  characteristics.

It can be seen from Fig. 5 that the AFLs could usually reduce both the ohmic loss and electrode overpotential of cells. The total ohmic resistance includes ohmic resistances of electrolyte film and electrodes and contact resistances between neighboring cell components. SEM observations indicate that the thicknesses of SDC



**Fig. 3.** Surface-sectional views of the AFLs with different weight ratio of Ni:SDC (a) 4:6; (b) 6:4; (c) 8:2 after reducing; (d) weight ratio Ni:SDC=6:4 before reducing; (e) weight ratio Ni:SDC=6:4 after removing Ni structure.



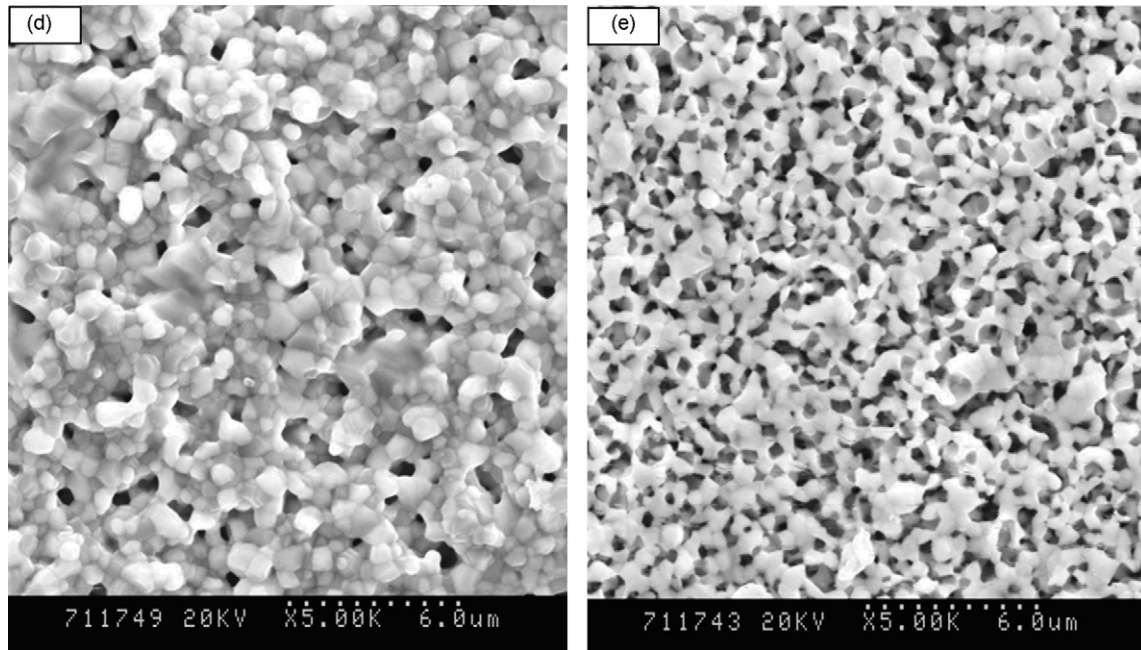


Fig. 3. (Continued).

films are almost the same. So the difference in ohmic losses is possibly attributed to the difference between AFLs. It is generally accepted that the electronic conductivity of an anode increases as the weight ratio of Ni increases. Moreover, according to Koide et al.'s study [10], the weight ratio of Ni has its effect on the contact resistance between electrolyte and anode due to the difference in the cross-sectional areas of Ni. The addition of AFL reduces the contact resistance between AFL and SDC film, which leads to the reduction of ohmic resistance. The ohmic loss of Cell-0 is similar to Cell-1, despite the weight ratio of NiO in Cell-0 is 25% higher than that in the AFL of Cell-1. The possible causes are Cell-1 has more cross-sectional area of Ni and higher electrical conductivity of fine AFL structure. As shown in Fig. 5a, except Cell-3 the ohmic resistance of all the other cells decreases as the weight ratio of Ni in AFL increases, despite the weight ratio of the Ni in the AFL of Cell-3 is the highest of all the samples. The possible cause is the cracks developed between AFL and electrolyte of Cell-3. Due to the different chemical compositions in AFLs, the thermal characteristic of AFLs would be quite different [11]. The weight ratio of SDC in the

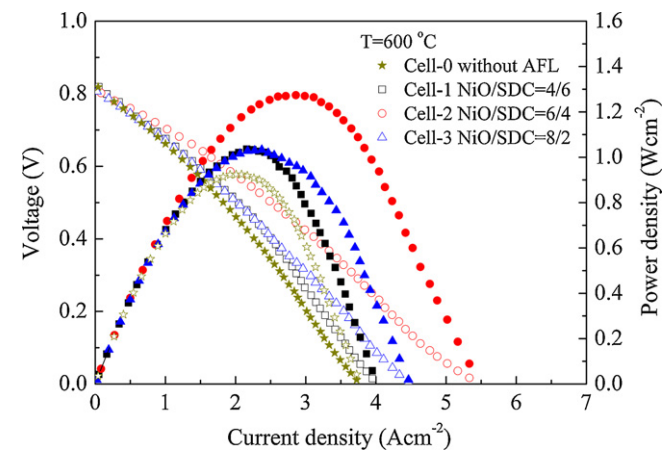
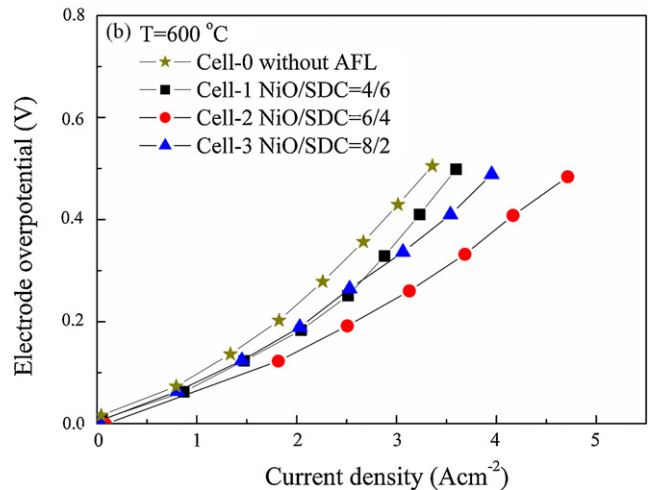
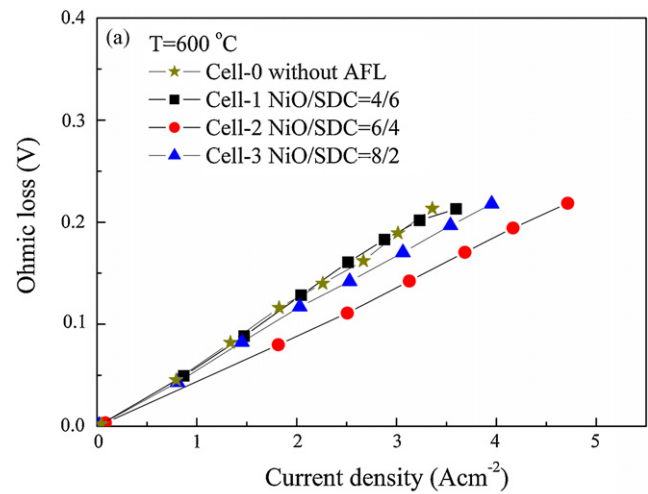


Fig. 4. Performances of the cells operated at 600 °C with the cathodes exposed to stationary air.

Fig. 5. (a) Ohmic loss versus current density and (b) electrode overpotential versus current density at 600 °C.

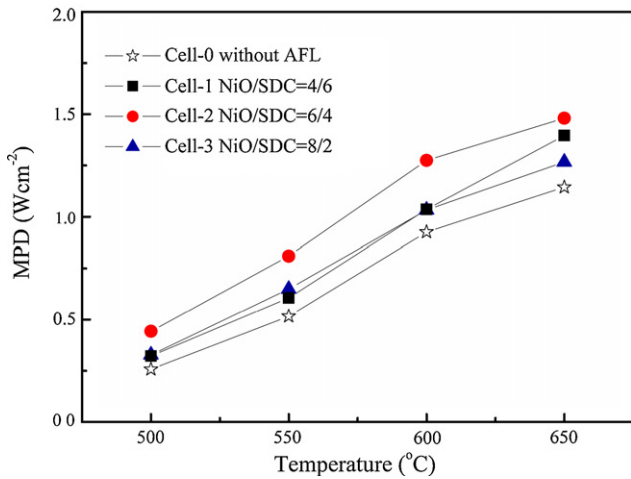


Fig. 6. Maximum power densities of cells at different temperatures when cathodes were exposed to the stationary air.

AFL of Cell-3 is the lowest of all the other cells. Some cracks can be developed in the co-sintering process and/or heating process during measurement at the interface between SDC film and AFL of Cell-3. In addition, the in situ reduction of NiO initiates stress at the interface between electrolyte and anode [12]. So, the interface of SDC film and AFL of Cell-3 is subject to a higher stress because more NiO is required to reduce. Therefore, some hairlines and fine cracks might be developed in the interface between SDC film and AFL in Cell-3. These defects increase the contact resistance, which

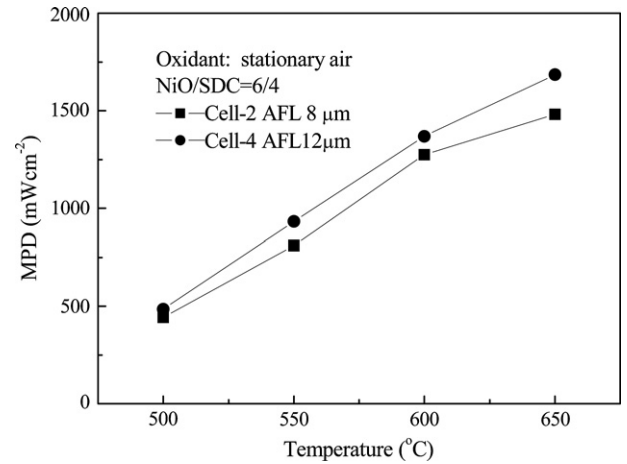


Fig. 8. Comparison result of the maximum power density of the cells with different AFL thickness when the stationary air was used as oxidant.

leads to a larger ohmic loss in Cell-3. All these justify the necessity to optimize the chemical composition of AFLs so that a good balance could be achieved between the decreasing contact resistance and the improved thermal compatibility. It can be seen from Fig. 5a that 6:4 is the suitable weight ratio of NiO:SDC for reducing the ohmic loss in AFLs.

It can be seen from Fig. 5b that AFL structure is effective in reducing the electrode overpotential. When a cell is working, electrochemical reaction takes place near TPB, and an electrode with a

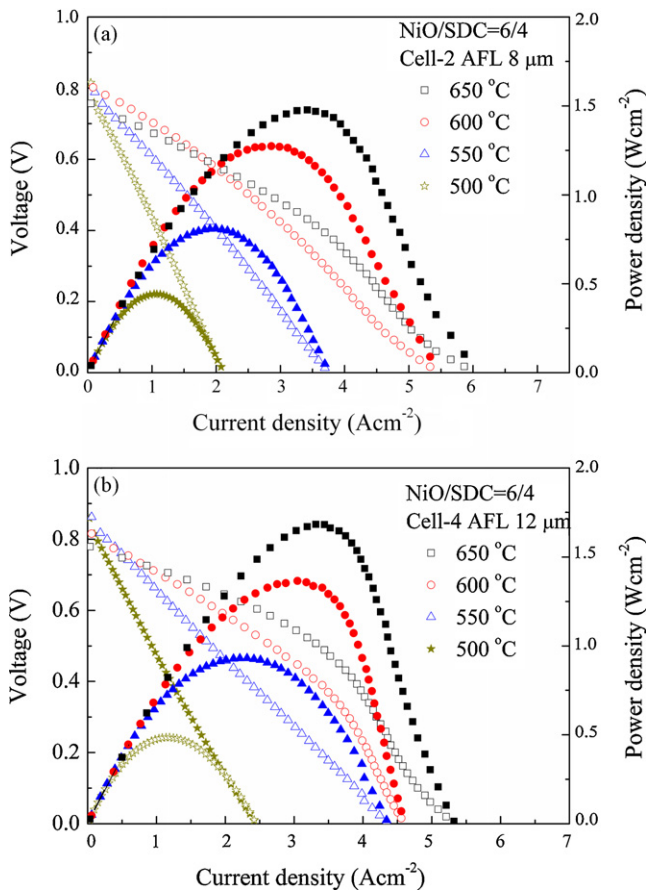


Fig. 7. *I*-*V* characteristics of the cells with different AFL thickness when the cathodes were exposed to the stationary air.

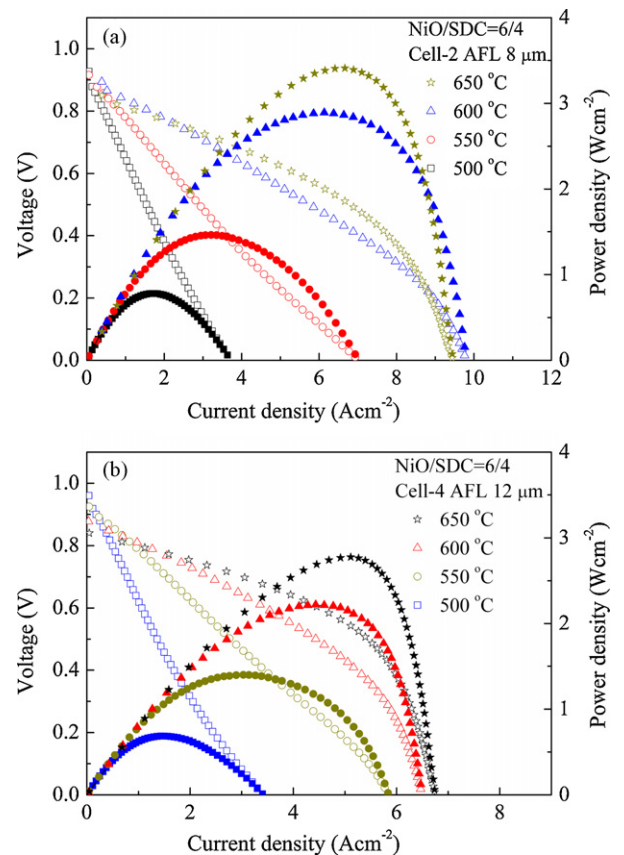
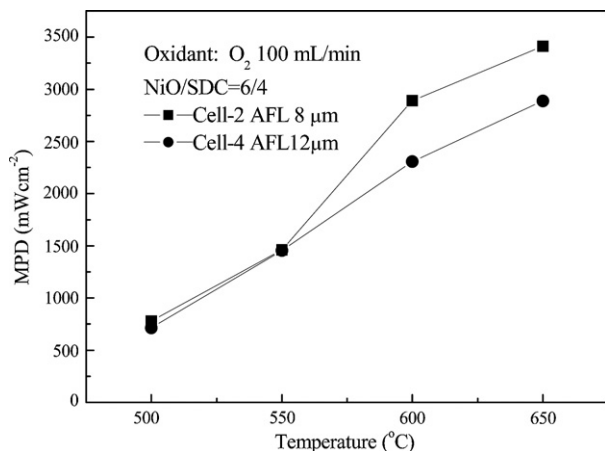


Fig. 9. *I*-*V* characteristics of the cells with different AFL thicknesses when the oxidant was an  $\text{O}_2$  flow at  $100 \text{ ml min}^{-1}$ .



**Fig. 10.** Comparison result of the maximum power density of the cells with different AFL thicknesses when the oxidant was  $O_2$  at  $100 \text{ ml min}^{-1}$ .

larger TPB length shows a lower electrode overpotential [13]. The AFLs reduce the electrode polarization resistance by increasing TPB, thereby enhancing the electrochemical reaction rate, which leads to a better anode performance [3]. The electrode overpotentials of Cell-1 and Cell-3 are quite close to each other at a low current density, and the overpotential of Cell-1 is bigger than that of Cell-3 at a current density higher than  $2.7 \text{ A cm}^{-2}$ , because the higher proportion of NiO in the AFL of Cell-3 produces more pores than those in Cell-1. It is that fine grain size, large surface area, adequate porosity, sufficient nickel content and good distribution of Ni and electrolyte particles in an anode are essential to improve the output performance of an anode [14]. Comparing the microstructure shown in Fig. 3 and the electrode overpotentials of cells shown in Fig. 5b, it could be concluded that the microstructure of the AFL (NiO:SDC = 6:4) in Cell-2 satisfies all the requirements for achieving high anode performance. The AFL in Cell-2 could increase the TPB while supply sufficient porosity for the diffusion of reactant and resultant.

It can be seen from Fig. 6 that the cells with AFLs all exhibit better outputs than the cell without an AFL (Cell-0) over the studied temperature range, with humidified hydrogen as fuel and stationary air as oxidant. Cell-2 ( $8 \mu\text{m}$  AFL, NiO:SDC = 6:4) exhibits excellent MPDs of 1.48, 1.28, 0.81 and  $0.44 \text{ W cm}^{-2}$  at 650, 600, 550 and  $500^\circ\text{C}$ , respectively, which suggests it is possible to develop an intermediate temperature SOFC by optimizing an anode.

In order to determine the effective thickness of an AFL, we fabricated Cell-4 with a  $\sim 12 \mu\text{m}$  AFL (NiO:SDC = 6:4) and tested in the same way as Cell-2. The  $I$ - $V$  characteristics of the two cells with different AFL thicknesses are as shown in Fig. 7. The OCVs of Cell-4 are a little higher than that of Cell-2, which means thicker AFL could increase the gas impermeability of cell. With a thicker AFL, the MPDs of Cell-4 are increased to 1.69, 1.37, 0.93 and  $0.49 \text{ W cm}^{-2}$  at 650, 600, 550 and  $500^\circ\text{C}$ , respectively. It can be seen from this that the increase in AFL thickness increases the number of TPBs of anodes, thereby improving the outputs performance of a cell. On the other hand, the increase in AFL thickness also makes the transport of gases across the fine anode more difficult, which causes serious concentration polarization at a high current density.

Then we introduce an oxygen flow at  $100 \text{ ml min}^{-1}$  to the cathodes while we maintain the flowing rate of humidified hydrogen. Compared with the performance of the cells with air as oxidant, the output performance of both cells with oxygen as oxidant is significantly improved as shown in Fig. 9. It's quite unusual that Cell-2 exhibits better cell performance than Cell-4, especially at a

temperature above  $550^\circ\text{C}$ . The thicker AFL of Cell-4 could increase TPB for reaction, while lowering the gas diffusion rate. With oxygen as oxidant, the oxygen reduction reaction at the cathode is fast, and the performance of cathode is substantially improved. In this case, a shorter gas transport path associated with a thinner anode is needed to warrant rapid gases diffusion. Otherwise, the shortage of fuel gas and the abundance of vapor in the effective anode layer adjacent to the electrolyte would cause a rapid voltage drop. This is the reason why Cell-4 with a thicker AFL exhibits a lower performance. On the other hand, it can be seen from Fig. 10 that Cell-4 exhibits a slightly lower performance than Cell-2 at a temperature below  $550^\circ\text{C}$ , since the gas diffusion rate is high enough for the cell at a lower temperature.

It can be seen from Figs. 8 and 10 that it is possible to use a thicker AFL, e.g., above  $12 \mu\text{m}$  when air is used as oxidant, or a thinner AFL, e.g., below  $8 \mu\text{m}$  when oxygen is used as oxidant to achieve a good output performance. In a word, in order to get better cell performance, a balance should be achieved by increasing TPB and/or reducing gas transfer rate.

#### 4. Conclusions

It can be seen from the results and discussion above that:

On the basis of different composite of NiO and SDC, the anode functional layers were fabricated on the porous anode substrates. The  $I$ - $V$  curves suggested that the AFLs could reduce the electrode polarization effectively, and 6:4 is the suitable weight ratio of NiO:SDC in AFL for reducing both the ohmic loss and electrode polarization. The performance of cells with the cathodes exposed in different atmospheres showed the optimized effective thickness was determined by the combined effects between the TPB and gas diffusion rate. Moreover, better cell performance can be expected by adjusting the thickness and porosity of AFL structure and the anode substrate in the further investigation.

#### Acknowledgements

The authors thank the financial supports from the Ministry of Science and Technology of China under contract no. 2007AA05Z139.

#### References

- [1] J.-W. Kim, A.V. Virkar, K.-Z. Fung, K. Mehta, S.C. Singhai, *J. Electrochem. Soc.* 146 (1999) 67–78.
- [2] K.F. Chen, Z. Lü, X.J. Chen, N. Ai, X.Q. Huang, B. Wei, J.Y. Hu, W.H. Su, *J. Alloys Compd.* 454 (2008) 447–453.
- [3] J.J. Haslam, A.-Q. Pham, B.W. Chung, J.F. DiCarlo, R.S. Glass, *J. Am. Ceram. Soc.* 88 (2005) 513–518.
- [4] N. Ai, Z. Lü, K.F. Chen, X.Q. Huang, X.B. Du, W.H. Su, *J. Power Sources* 171 (2007) 489–494.
- [5] A. Abudula, M. Ihara, H. Komiyama, K. Yamada, *Solid-State Ionics* 86–88 (1996) 1203–1209.
- [6] S.D. Kim, S.H. Hyun, J. Moon, J.-H. Kim, R.H. Song, *J. Power Sources* 139 (2005) 67–72.
- [7] R.N. Basu, G. Blass, H.P. Buchkremer, D. Stöver, F. Tietz, E. Wessel, I.C. Vinke, *J. Eur. Ceram. Soc.* 25 (2005) 463–471.
- [8] E. Wanzenberg, F. Tietz, P. Panjan, D. Stöver, *Solid-State Ionics* 159 (2003) 1–8.
- [9] C. Sun, U. Stimming, *J. Power Sources* 171 (2007), pp. 274–260.
- [10] H. Koide, Y. Someya, T. Yoshida, T. Maruyama, *Solid-State Ionics* 132 (2000) 253–260.
- [11] R.M.C. Clemmer, S.F. Corbin, *Solid-State Ionics* 166 (2004) 251–259.
- [12] P. Charpentier, P. Fragnaud, D.M. Schleich, E. Gehain, *Solid-State Ionics* 135 (2000) 373–383.
- [13] J. Mizwaki, H. Tagawa, T. Saito, T. Yamamura, K. Kamitani, K. Hirano, S. Ehara, T. Takagi, T. Hikita, M. Ippommatsu, S. Nakagawa, K. Hashimoto, *Solid-State Ionics* 52 (1994) 70–71.
- [14] S.W. Zha, W. Rauch, M.L. Liu, *Solid-State Ionics* 166 (2004) 241–250.