Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 2599–2603

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of Bi_2O_3 on the electrochemical performance of $LaBaCo_2O_{5+\delta}$ cathode for intermediate-temperature solid oxide fuel cells

Ruifeng Li, Dalei Wang, Lin Ge, Shoucheng He, Han Chen, Lucun Guo*

College of Materials Science and Engineering, Nanjing University of Technology, No. 5 Xinmofan Road, Nanjing, Jiangsu 210009, PR China

Received 6 October 2013; received in revised form 17 October 2013; accepted 17 October 2013
Available online 26 October 2013

Abstract

The $LaBaCo_2O_{5+\delta}-x$ wt.% Bi_2O_3 (LBCO-$x$$Bi_2O_3$, $x=10$, 20, 30, and 40) were prepared as composite cathodes for intermediate-temperature solid oxide fuel cells (IT-SOFCs) via the conventional mechanical mixing method. The effect of Bi_2O_3 on polarization resistance, overpotential, and long-term stability of the LBCO cathode was investigated. An effective sintering aid for LBCO cathode, Bi_2O_3 not only lowers its sintering temperature by ~200 °C, but also improves the electrochemical performance within the intermediate temperature range of 600–800 °C. Electrochemical impedance spectroscopy measurements showed that the addition of 20 wt% Bi_2O_3 to LBCO exhibited the lowest area-specific resistance of 0.020 Ω cm^2 at 800 °C in air, which was about a seventh of that of the LBCO cathode at the same condition. At a current density of 0.2 A cm^{-2}, the cathodic overpotential of LBCO-20Bi_2O_3 was about 12.6 mV at 700 °C, while the corresponding value for LBCO was 51.0 mV. Compared to B_2O_3–Bi_2O_3–PbO frit, the addition of Bi_2O_3 significantly improved the long-term stability of cathode. Therefore, LBCO-20Bi_2O_3 can be a promising cathode for IT-SOFCs.

Keywords: A. Mixing; B. Microstructure; C. Impedance; E. Fuel cells

1. Introduction

As an all-solid-state electrochemical system, solid oxide fuel cells (SOFCs) can directly convert the chemical energy of fuel into electricity in an efficient and clean way, which usually operated at temperatures as high as 1000 °C [1–4]. Lowering their operating temperature to an intermediate temperature range of 600–800 °C has been widely investigated in recent years, and this process is considered as a very promising method to widen the practical application of SOFCs [5–11]. However, the cathodic electrochemical performance decreases with decreasing operating temperature, which directly affects the overall performance of the system [4,11–14]. Therefore, the development of high-performance cathodes with low polarization losses, high electrocatalytic activity for oxide reduction reaction, and good long-term stability within the intermediate temperature range has become increasingly critical.

Our previous study [14,15] proved that the B_2O_3–Bi_2O_3–PbO frit is proved to be effective in lowering the sintering temperature of $LaBaCo_2O_{5+\delta}-x$ wt.% Ag and $LaBaCo_2O_{5+\delta}$ cathodes and in improving their electrochemical performance within the intermediate temperature range. However, the long-term stability of these composite cathodes poses a challenge because of the relatively low melting temperature of B_2O_3–Bi_2O_3–PbO frit (~550 °C). Moreover, the use of Pb, especially at such high temperatures, is not recommended given the worsening pollution in the environment.

Therefore, looking for new sintering aids for the cathode is important. The key factor determining a material could be used as sintering aid is considered that the material should be able to lower the sintering temperature of cathode without sacrificing the performance (mainly including electrochemical performance and long-term stability), maintain the structural stability within an intermediate temperature range, cause no damage to the porous structure of the cathode, and have good chemical compatibility with other components.

Based on the above mentioned considerations, Bi_2O_3 was chosen as the sintering aid for $LaBaCo_2O_{5+\delta}$ cathode for IT-SOFCs in this study. As a good ionic conductor, Bi_2O_3 has been investigated as a potential oxide ion-conducting solid electrolyte for SOFCs [16–18]. The melting point of Bi_2O_3 is about 825 °C, making it can remain the structural stability

---

*Corresponding author. Tel.: +86 25 83587261; fax: +86 25 83306152.
E-mail address: lc-guo@163.com (L. Guo).

0272-8842/$ - see front matter Crown Copyright © 2013 Published by Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.10.074

within intermediate temperature range of 600–800 °C. Attempts were made to investigate the effects of Bi_2O_3 on the polarization resistance, cathodic overpotential, and long-term stability of $LaBaCo_2O_{5+\delta}$ cathode via AC impedance and cyclic voltammetry (CV) techniques.

2. Experimental

La_2O_3 (99.9%), $BaCO_3$ (99.0%), Co_2O_3 (99.0%), Sm_2O_3 (99.99%), and CeO_2 (99.99%) were used as starting materials. The detailed synthetic process of $LaBaCo_2O_{5+\delta}$ (LBCO) cathode and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte powders, and the preparation of dense SDC pellets were described in our previous study [15].

LBCO and Bi_2O_3 (99.0%) powder was mixed with an appropriate mass ratio of ethyl cellulose and terpinol, which was painted via the screen painting method onto both sides of the SDC pellets with a circle pattern (about 10 mm diameter) and then calcined at 900 °C in air. The current collector, Ag paste, was painted onto the cathode surface and calcined at 770 °C.

The electrochemical impedance spectroscopy (EIS) were performed using PARSTAT 2273 electrochemical workstation under open circuit voltage from 600 °C to 800 °C in air, and with excitation potentials of 10 mV and frequency range of 100 kHz–0.1 Hz. The impedance spectra were fitted and analyzed using the ZsimpWin software. The polarization analysis was carried out on a three-electrode cell at 700 °C. As reference electrode, Ag paste was prepared with a ring shape, to ensure a sufficient distance between the Ag paste and the working electrode (at least twice the thickness of the SDC electrolyte).

The long-term stability of the cathode was also characterized via EIS. The impedance spectra of the same cathode sample before and after 3000 min of aging at 800 °C in air were compared with each other to evaluate the cathode stability. Moreover, the microstructure was characterized by scanning electron microscopy (SEM, JEOL, JSM-5900, Tokyo, Japan). To avoid electrostatic effect, the surface of the sample was coated with gold before the test.

3. Results and discussion

3.1. Crystal structure and chemical compatibility

To investigate the phase reaction between the cathode and Bi_2O_3, the mixed powders consisting of LBCO and 20 wt% Bi_2O_3 were calcined at 800 °C for 2 h and 3000 min in air. As shown in Fig. 1, $La_{0.19}Bi_{0.81}O_{1.5}$ and bismuth oxide were observed at 2θ values between about 26 °C and 30 °C, whereas the LBCO structure remained unchanged. The peak height of the new phases hardly changed after 3000 min of aging at 800 °C. The influence of all the new phases on the cathode performance is considered to be negligible because of their little content and relatively random distribution.

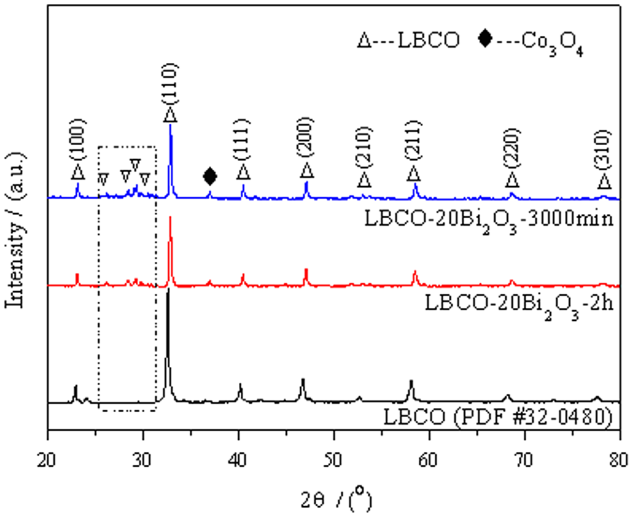

Fig. 1. XRD patterns of the LBCO cathode calcined at 1100 °C for 2 h and LBCO-20 Bi_2O_3 calcined at 800 °C for 2 h and 3000 min.

3.2. Electrochemical impedance spectroscopy

Fig. 2 shows the AC impedance spectra of LBCO-$x$$Bi_2O_3$ cathodes measured at 700 °C and 800 °C in air. The impedance spectra were fitted to the equivalent circuit $LR_{ohm}(R_pQ)$, where L is the high-frequency inductance, R_{ohm} is the ohmic resistance, R_p is the polarization resistance and corresponds to the differences between real-axes intercepts, and Q is the corresponding constant phase elements. For simplification, LBCO-$x$$Bi_2O_3$ (x=10, 20, 30, and 40 wt%) is the LBCO cathode with different amounts of Bi_2O_3, and x denotes the Bi_2O_3 fraction in the LBCO-$x$$Bi_2O_3$ mixed powder.

As shown in Fig. 2, the R_p of LBCO-$x$$Bi_2O_3$ first decreased at each measured temperature, reached the minimum at 20 wt% Bi_2O_3, and then increased with increasing Bi_2O_3 content. This tendency can be explained as follows: when the Bi_2O_3 content is about 10 wt%, LBCO-10Bi_2O_3 can hardly form a relatively dense cathode functional layer after sintering at 900 °C (the sintering temperature of LBCO is about 1100 °C in air [15]), and a high R_p was observed. For LBCO-20 Bi_2O_3, the improved performance can be attributed to the optimized microstructure and the high ionic conductivity of Bi_2O_3. An appropriate amount of Bi_2O_3 (~20 wt%) makes the LBCO-$x$$Bi_2O_3$ sample after sintering at 900 °C to form a optimum structure with reasonable porosity and shows good adhesion to SDC electrolyte. In addition, with the addition of high ionic conductive Bi_2O_3, the triple phase boundary (TPB) areas were extended to the whole cathode layer, resulting in an improvement in the electrochemical performance. However, when the Bi_2O_3 content was increased above 30 wt%, the excessive amount of Bi_2O_3 makes the LBCO-$x$$Bi_2O_3$ sample to form a too dense structure (not beneficial for the transport of the electron and gas), leading to a sharp increase of R_p.

The area-specific resistance (ASR) of the cathode is the size-related parameter based on the geometric area of the cathode and the polarization resistance R_p. The R_p of a single cathode is half that of the obtained R_p in Fig. 2 because the two-electrode configuration was used in our experiments. Therefore, the ASR value is defined as follows:

$$\text{ASR} = \frac{R_P}{2} \times \text{cathode area} \qquad (1)$$

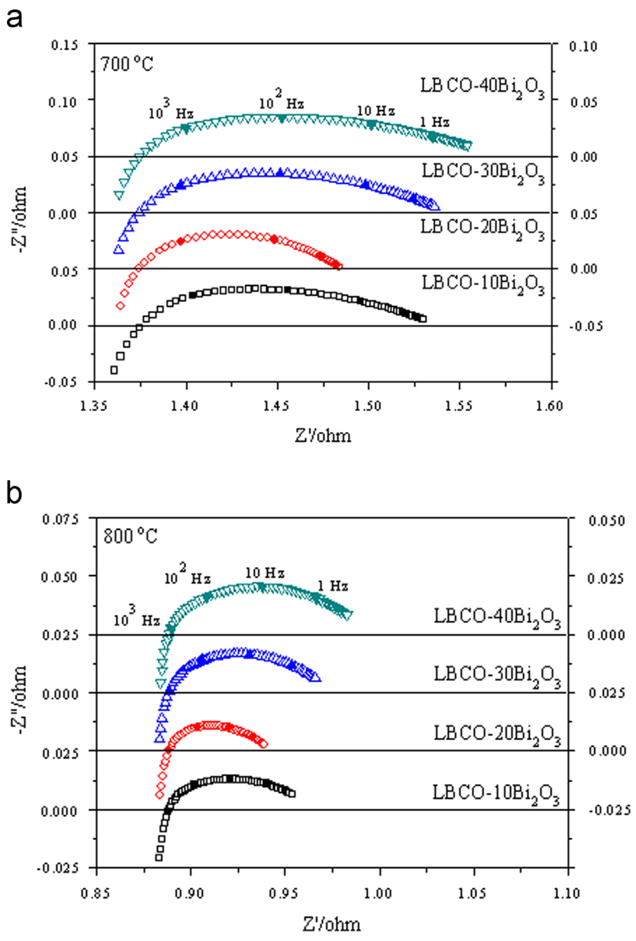

Fig. 2. Impedance spectra of LBCO-xBi_2O_3 cathodes under open circuit potential at 700 and 800 °C in air.

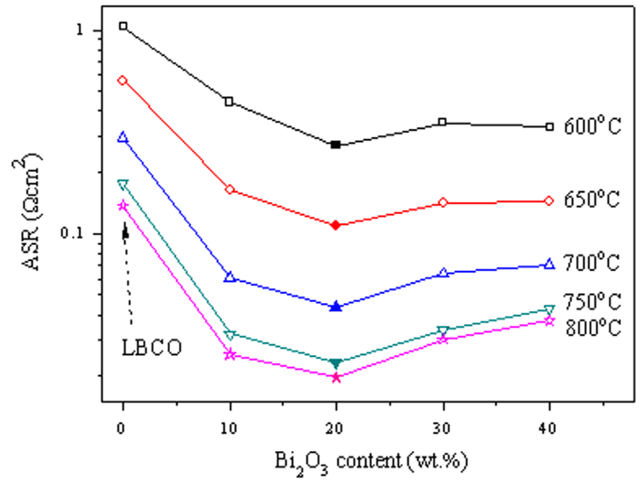

Fig. 3. ASR values of LBCO-xBi_2O_3 cathodes at 600–800 °C

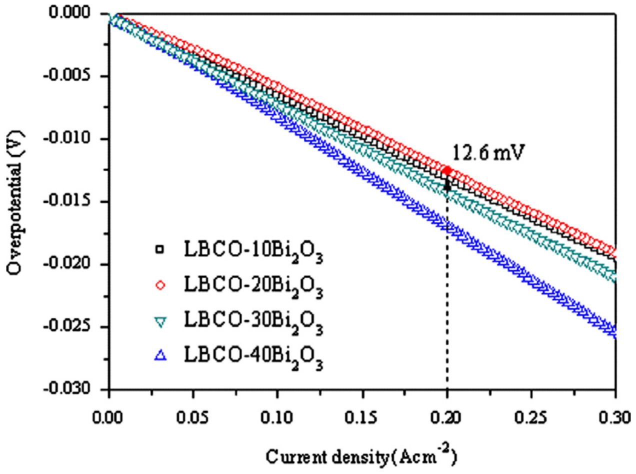

Fig. 4. Polarization curves for LBCO-x Bi_2O_3 cathodes at 700 °C in air.

Fig. 3 shows the ASR of LBCO and LBCO-xBi_2O_3 cathodes measured from 600 °C to 800 °C in air. The ASR values for each sample decreased with increasing temperature, and this tendency is consistent with the results in Fig. 2. The LBCO-20Bi_2O_3 exhibited the lowest ASR at the same temperature, indicating it showed the best electrochemical performance within the studied range. For LBCO-20Bi_2O_3, the lowest ASR was 0.020 Ω cm^2 at 800 °C, a value much lower than the LBCO cathode of 0.137 Ω cm^2 at the same condition.

The LBCO-xBi_2O_3 cathodes sintered at 900 °C had lower ASR values than LBCO sintered at 1100 °C measured at the same temperature. High sintering temperatures always resulted in a remarkable grain growth of cathode particles, which resulted in a decrease in electrocatalytic activity for the oxygen reduction reaction (ORR). Similar phenomena have been already reported by us [14].

3.3. Cathodic polarization analysis

Fig. 4 shows the cathodic polarization overpotential of LBCO-xBi_2O_3 as a function of current density at 700 °C in air. At the same current density, the polarization overpotential of LBCO-xBi_2O_3 initially decreased when the Bi_2O_3 content was increased to 20 wt% and then increased with further increasing Bi_2O_3 content. This tendency was consistent with the result shown in Fig. 2. At a current density of 0.2 A cm^{-2}, the cathodic overpotential values were about 13.0, 12.6, 14.2, and 17.0 mV for LBCO-xBi_2O_3 ($x=10$, 20, 30, and 40 wt%), respectively, whereas the value for LBCO was 51.0 mV [15]. Thus, addition of Bi_2O_3 to the cathode can effectively reduce the cathodic polarization overpotential.

3.4. Long-term stability

The long-term stability is an important factor to evaluate the cathode performance. As is well known, the performance stability is closely related to the microstructural stability.

The B_2O_3–Bi_2O_3–PbO frit is an effective sintering aid for $LaBaCo_2O_{5+\delta}$ [14] and $LaBaCo_2O_{5+\delta}-x$ wt.% Ag [15] cathodes. However, the long-term stability of these composite cathodes is poor. For $LaBaCo_2O_{5+\delta}-30$ wt.% Ag with 2.5 wt% B_2O_3–Bi_2O_3–PbO frit, the ASR value had an increase of 21 ± 0.2% after 3000 min of aging at 800 °C, that for $LaBaCo_2O_{5+\delta}$ with 5 wt% B_2O_3–Bi_2O_3–PbO frit is 17 ± 0.3%. The increased ASR was ascribed to the unstable microstructure within the intermediate temperature range because of the low melting temperature of B_2O_3–Bi_2O_3–PbO frit (~550 °C).

Fig. 5 shows the impedance spectra of LBCO-20Bi_2O_3 cathode before and after 3000 min of aging at 800 °C in air. Obviously, the two impedance spectra almost overlapped with each other, indicating that the LBCO-20Bi_2O_3 exhibited a relatively stable performance. The LBCO-20Bi_2O_3 based on SDC electrolyte before and after aging at 800 °C in Fig. 6 had the same kind of morphology and particle size, indicating a high structural stability. It seems reasonable to conclude that extending the operating time does not damage the porous structure of the LBCO-20Bi_2O_3 cathode.

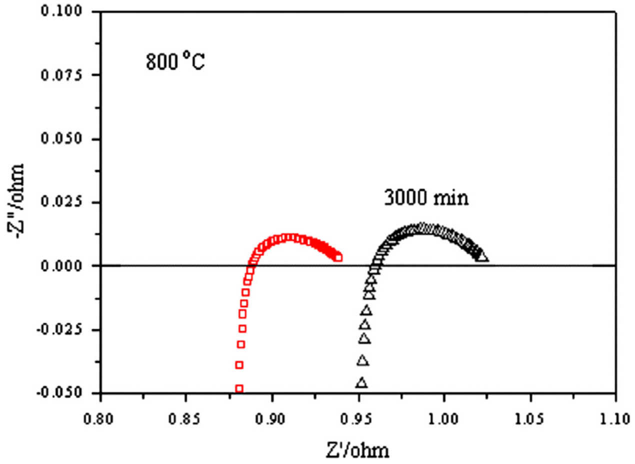

Fig. 5. Impedance spectra of LBCO-20Bi_2O_3 before and after 3000 min of aging at 800 °C in air.

Compared to the cathodes with B_2O_3–Bi_2O_3–PbO frit, the ASR of LBCO-20Bi_2O_3 had a much smaller increase after 3000 min of aging at 800 °C and showed a better long-term stability. In addition, the ASR of LBCO-20Bi_2O_3 after 3000 min of aging was about 0.0216 Ω cm^2 at 800 °C, which was still much lower than that of the LBCO cathode in Fig. 3.

The melting temperature of sintering aids for cathode must be a little higher than the typical IT-SOFCs operating temperature to maintain the structural stability of the cathode in actual application. Although further studies are needed, the LBCO-20Bi_2O_3 cathode can be a promising cathode material for IT-SOFCs.

4. Conclusions

The effect of Bi_2O_3 on the electrochemical performance and long-term stability of the cathode for IT-SOFCs was systematically investigated in this study. The addition of Bi_2O_3 to the

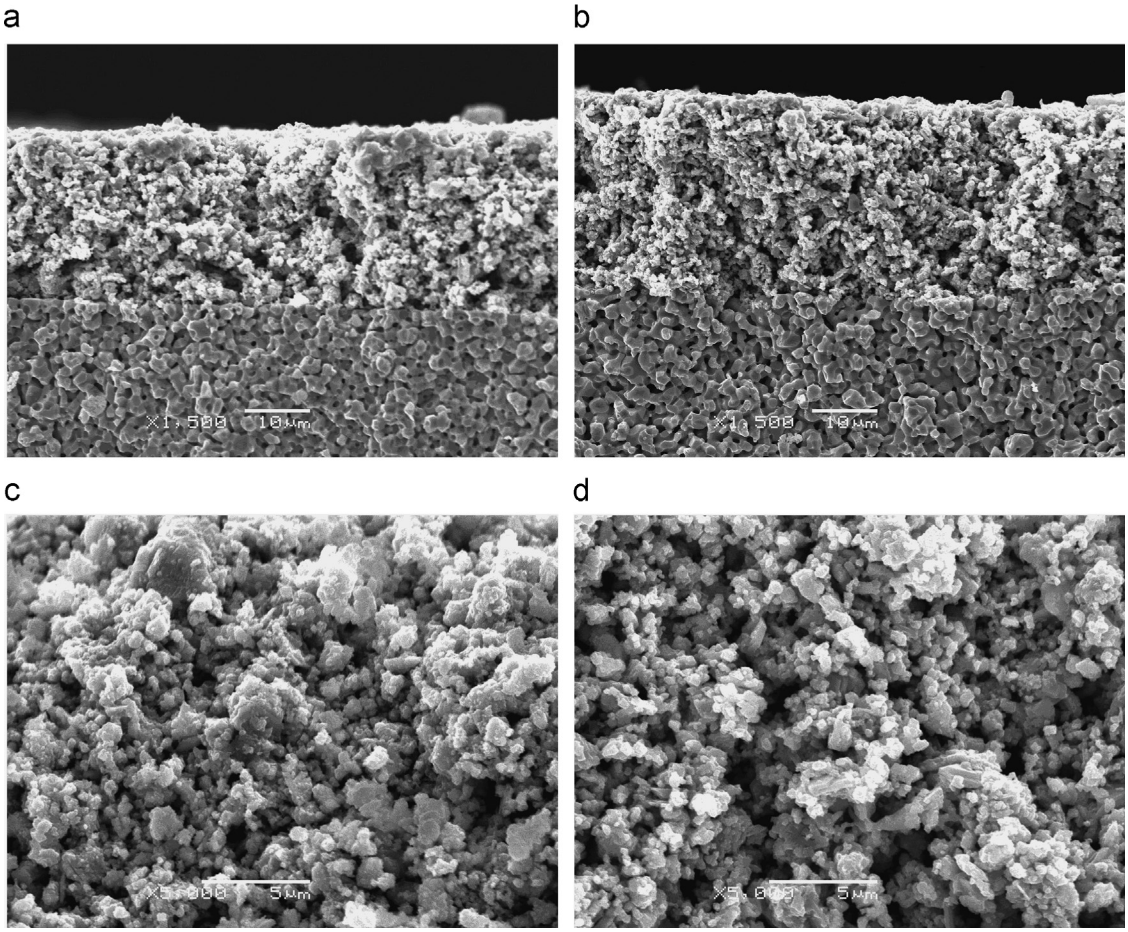

Fig. 6. Cross-sectional SEM images of LBCO-20Bi_2O_3 based on SDC electrolyte before ((a) and (c)) and after ((b) and (d)) 3000 min of aging at 800 °C in air.

cathode can effectively lower the sintering temperature and improve the electrochemical performance of the cathode within 600–800 °C. According to the experimental results, the ASR and overpotential of LBCO$-x$Bi$_2$O$_3$ composite cathode first decreased and then increased with increasing Bi$_2$O$_3$ content, and the optimal content was 20 wt%. For LBCO-20Bi$_2$O$_3$, its ASR was about a seventh of that of the LBCO cathode at 800 °C, and the cathodic overpotential at a current density of 0.2 A cm^{-2} had an approximate decrease of 75.3% at 700 °C. By contrast with B$_2$O$_3$–Bi$_2$O$_3$–PbO frit, the addition of Bi$_2$O$_3$ significantly improved the long-term stability of the cathode. The LBCO-20Bi$_2$O$_3$ can be a potential cathode material for IT-SOFCs through the characterization of electrochemical performance and long-term stability.

Acknowledgements

The project was financially funded by the Graduate Science and Technology Innovation Foundation of Jiangsu (CXZZ12_0413), the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions, and Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT, IRT1146). In addition, the authors are sincerely grateful to Jiale Zhao and Lushun Gu for their experimental assistance.

References

[1] N.Q. Minh, Ceramic fuel cells, J. Am. Ceram. Soc. 76 (1993) 563–588.

[2] S.C. Singhal, Advances in solid oxide fuel cell technology, Solid State Ionics 135 (2000) 305–313.

[3] T. Horita, K. Yamaji, N. Sakai, H. Yokokawa, A. Weber, E. Ivers-Tiffée, Oxygen reduction mechanism at porous La1-*x*Sr*x*CoO3-d cathodes/La0.8Sr0.2Ga0.8Mg0.2O2.8 electrolyte interface for solid oxide fuel cells, Electrochim. Acta 46 (2001) 183–1845.

[4] M. Muranaka, K. Sasaki, A. Suzuki, T. Terai, LSCF-Ag cerment cathode for intermediate temperature solid oxide fuel cells, J. Electrochem. Soc. 156 (6) (2009) B743–747.

[5] D.J.L. Brett, A. Atkinson, N.P. Brandon, S.J. Skinner, Intermediate temperature solid oxide fuel cells, Chem. Soc. Rev. 37 (2008) 1568–1578.

[6] A. Tarancón, S.J. Skinner, R.J. Chater, F. Hernández-Ramírez, J.A. Kilner, Layered perovskites as promising cathodes for intermediate temperature solid oxide fuel cells, J. Mater. Chem. 17 (2007) 3175–3181.

[7] S. Geng, J. Zhu, P.B. Michael, U.A. Harlan, X. Zhou, Z. Yang, A low-Cr metallic interconnect for intermediate-temperature solid oxide fuel cells, J. Power Sources 172 (2007) 775–781.

[8] Y. Zheng, S. He, L. Ge, M. Zhou, H. Chen, L. Guo, Effect of Sr on Sm-doped ceria electrolyte, Int. J. Hydrogen Energy 36 (2011) 5128–5135.

[9] C.M. Lapa, D.P.F. de Souza, F.M.L. Figueiredo, F.M.B. Marques, Two-step sintering ceria-based electrolytes, Int. J. Hydrogen Energy 35 (2010) 2737–2741.

[10] Y.C. Yang, Y.C. Chen, Influences of the processes on the microstructures and properties of the plasma sprayed IT-SOFC anode, J. Eur. Ceram. Soc 31 (2011) 3109–3118.

[11] V. Dusastre, J.A Kilner, Optimisation of composite cathodes for intermediate temperature SOFC applications, Solid State Ionics 126 (1999) 163–174.

[12] D. Chen, R. Ran, K. Zhang, J. Wang, Z. Shao, Intermediate-temperature electrochemical performance of a polycrystalline PrBaCo2O5 + δ cathode on samarium-doped ceria electrolyte, J. Power Sources 188 (2009) 96–105.

[13] H.C. Yu, F. Zhao, A.V. Virkar, K.Z. Fung, Electrochemical characterization and performance evaluation of intermediate temperature solid oxide fuel cell with La0.75Sr0.25CuO2.5 − δ cathode, J. Power Sources 152 (2005) 22–26.

[14] R. Li, L. Ge, S. He, H. Chen, L. Guo, Effect of B$_2$O$_3$–Bi$_2$O$_3$–PbO frit on the performance of LaBaCo$_2$O$_{5+\delta}$ cathode for intermediate-temperature solid oxide fuel cells, Int. J. Hydrogen Energy 37 (2012) 16117–16122.

[15] R. Li, L. Gao, L. Ge, Y. Zheng, M. Zhou, H. Chen, L. Guo, Performance of LaBaCo$_2$O$_{5+\delta}$-Ag with B$_2$O$_3$–Bi$_2$O$_3$–PbO frit composite cathodes for intermediate-temperature solid oxide fuel cells, J. Power Sources 196 (2011) 9939–9945.

[16] P. Shuk, H.-D. Wiemhöfer, U. Guth, W. Göpel, M. Greenblatt, Oxide ion conducting solid electrolytes based on Bi$_2$O$_3$, Solid State Ionics 89 (1996) 179–196.

[17] N.M. Sammes, G.A. Tompsett, H. Näfe, F. Aldinger, Bismuth based oxide electrolytes-structure and ionic conductivity, J. Eur. Ceram. Soc. 19 (1999) 1801–1826.

[18] T. Suzuki, T. Yamazaki, K. Kaku, M. Ikegami, An application of oxide and silver electrode on the BaO-doped Bi2O3 electrolyte, Solid State Ionics 15 (1985) 241–246.