

Short communication

# Development of Ag-(BaO)<sub>0.11</sub>(Bi<sub>2</sub>O<sub>3</sub>)<sub>0.89</sub> composite cathodes for intermediate temperature solid oxide fuel cells

Shouguo Huang<sup>\*</sup>, Zheng Zong, Chunqiu Peng

Ministry of Education Key Laboratory of Opto-electronic Information Acquisition and Manipulation,  
School of Physics and Materials Science, Anhui University, Hefei, Anhui 230039, PR China

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## Abstract

The electrochemical performances of Ag-(BaO)<sub>0.11</sub>(Bi<sub>2</sub>O<sub>3</sub>)<sub>0.89</sub> (BSB) composite cathodes on Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> electrolytes have been investigated for intermediate temperature solid oxide fuel cells (ITSOFCs) using ac impedance spectroscopy from 500 to 700 °C. Results indicate that the electrochemical properties of these composites are quite sensitive to the composition and the microstructure of the cathode. The optimum BSB addition (50% by volume) to Ag resulted in about 20 times lower area specific resistance (ASR) at 650 °C. The ASR values for the Ag50-BSB and Ag cathodes were 0.32 and 6.5 Ω cm<sup>2</sup> at 650 °C, respectively. The high performances of Ag-BSB cathodes are determined by the high catalytic activity for oxygen dissociation and ionic conductivity of BSB, and by the excellent catalytic activity for oxygen reduction of silver. The maximum power density of the Ag50-BSB cathode was 224 mWcm<sup>-2</sup> at 650 °C, which classify this composite as a promising material for ITSOFC. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Sintering; Electrical conductivity; Fuel cell materials; Composites; Cathode

## 1. Introduction

Solid oxide fuel cells (SOFCs) have become of great interest as a potential economical, clean and efficient means of producing electricity in a variety of commercial and industrial applications [1–3]. However, traditional SOFC systems based on yttria-stabilized zirconia (YSZ) electrolytes must operate at high temperature (1000 °C) which places considerable restrictions on the materials that can be used in both cell construction and in the balance of plant. To overcome these problems, it has been widely accepted that the operating temperature of the device should be lowered. This has led to the development of intermediate temperature SOFC (ITSOFC) operating at 500–700 °C. Furthermore, it is widely established that the performance of ITSOFCs is strongly dependent on cathode area specific resistance (ASR), which must be minimized to optimize the ITSOFC power densities [4,5]. Hence, there is interest in improving cathodes for ITSOFCs.

Interest is currently being expressed in porous cathodes fabricated from LaCoO<sub>3</sub> perovskite oxides with high electronic conductivities referred as mixed electronic and ionic conductors, such as La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub>, La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3</sub> (LSCF), Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub>, Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> (BSCF) [6–14]. These doped LaCoO<sub>3</sub> compositions and their composites exhibit good cathode performances at 500–700 °C. For example, the ASR of the BSCF cathode was as low as 0.055–0.07 Ω cm<sup>2</sup>, and peak power density of the cell with BSCF cathode was about 1010 mWcm<sup>-2</sup> at 600 °C [14]. Unfortunately, these materials do not completely meet all the technological requirements (ionic conductivity, mechanical stability, thermal expansion, cost), which prevent the rapid commercialization of the ITSOFC system.

Silver is much less expensive than platinum, gold, and palladium and has excellent catalytic activity for oxygen reduction. It is known that the melting point of silver is only 960 °C, which limits the operating temperature of SOFCs when silver is used as cathodes. However, it should be stable when silver as cathode material or additive is used for SOFC operated at intermediate temperature, especially for those at temperature below 700 °C [15,16]. Moreover, one commonly used means for improving cathode performance is to add silver into an electrode material.

<sup>\*</sup> Corresponding author. Tel.: +86 551 5108557; fax: +86 551 5846849.  
E-mail address: [huangsg@ustc.edu](mailto:huangsg@ustc.edu) (S. Huang).

For example, the ASR of the Ag-LSCF-Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.9</sub> (CGO) cathode have been studied and found to be promising cathode materials for ITSOFC using CGO or YSZ electrolytes [17,18].

Conductors based on bismuth oxide have much high oxygen-ion conductivity, and the conductivity of bismuth oxide is about two orders of magnitude higher than that of stabilized zirconia [19]. A further and determining advantage of Bi<sub>2</sub>O<sub>3</sub> is its favorable catalytic effect on the oxygen dissociation reaction, which is always the first and often limiting step in every electrochemical process involving oxygen transfer. Reports showed that bismuth oxide is stable at intermediate temperature when PO<sub>2</sub> > 10<sup>-10</sup> atm [20]. To enhance the oxygen-ion conducting of silver, oxygen-ion conductors of stabilized bismuth oxide were added to form Ag-Bi<sub>0.75</sub>Y<sub>0.25</sub>O<sub>1.5</sub> composite electrodes for YSZ, SDC (Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub>) and BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3</sub>-based solid oxide fuel cells [21–23].

In this study we present Ag-(BaO)<sub>0.11</sub>(Bi<sub>2</sub>O<sub>3</sub>)<sub>0.89</sub> (BSB) as a new cathode from viewpoint of cost reduction, using low-cost raw materials and the low-cost fabrication of ceramic structures. The aim of the present study was to obtain more detailed information about the composite cathode system Ag-BSB. A wide range of Ag-BSB composite cathode was fabricated. SDC electrolytes were used in order to determine the feasibility of using these cathodes with this standard electrolyte material. The electrochemical properties of these cathodes were investigated and correlated with the compositions and microstructures.

## 2. Experiment

The (BaO)<sub>0.11</sub>(Bi<sub>2</sub>O<sub>3</sub>)<sub>0.89</sub> powders were prepared by a solid-state reaction. First, Bi<sub>2</sub>O<sub>3</sub> (99.9%) and BaO (99.9%) powders were mixed and then calcined in air at 720 °C for 5 h. The calcined powders were milled in plastic pots with zirconia balls and C<sub>2</sub>H<sub>5</sub>OH for 24 h, and then dried.

A pure silver slurry was made, in addition to four slurries containing 30, 40, 50, and 60 vol.% BSB. These slurries were ball-milled for 24 h, and then screen-printed onto both sides of Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (SDC) pellets (15 mm diameter, 0.6 mm thickness, sintering at 1400 °C). Each slurry contained the desired amount of Ag and BSB, along with 3 wt.% polyvinyl buteral-76 binder, and 25 wt.% sodium-free corn oil. Methyl ethyl ketone was used as the solvent. The samples were sintered at 600 °C for 2 h. SDC powders were synthesized using an oxalate co-precipitation method [24], and fired at 750 °C for 2 h. La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> powders were prepared by a solid-state reaction, and fired at 1200 °C for 5 h.

Single planar anode-supported thin-film electrolyte fuel cells were fabricated using a dual dry-pressing method for the measurement of cathode property [25]. The anode, formed from a 60:40 wt.% mixture of NiO and SDC powders was dry-pressed into a pellet, and then SDC powders were distributed on the anode surface and co-pressed with the anode. The resultant bilayer was calcined at 1350 °C for 5 h. Ag50-BSB (50:50 by volume) and LSCF50-SDC were screen-printed on the electrolyte (SDC) surface, respectively. The cell with Ag50-BSB was sintered at 600 °C for 2 h, and with LSCF50-SDC was sintered at 950 °C for 2 h. Before measurement of the power density,

NiO was reduced to Ni in a H<sub>2</sub> stream at 1000 °C for 1 h. Pure O<sub>2</sub> (99.9%) and hydrogen humidified with 3 vol.% H<sub>2</sub>O were fed to the cathode and the anode side, respectively.

AC impedance spectroscopy measurements were carried out using a CHI604A analyzer. The frequency range was from 0.01 to 100 kHz with signal amplitude of 10 mV. Measurements were taken over a temperature range of 500–750 °C in air. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to observe the morphology, structure and phase purity.

## 3. Results and discussion

Fig. 1 shows typical cross-SEM microstructures of an Ag50-BSB cathode on a SDC electrolyte, sintered at 600 °C for 2 h. High porous electrodes were apparent. The electrode microstructure appeared uniform, and the Ag and BSB particles appear to good bonding and continuous contact with each other. Meanwhile, the Ag and BSB particles appear to have bonded well at the Ag50-BSB/SDC interface. The thickness of the cathode layer was found to be 45–50 μm.

The ASR of a composite cathode can be decreased in two ways: increasing the triple phase boundaries by control of the microstructure combined with a contiguous ionic conducting phase, which allows electrochemical reactions to occur within the cathode; improving the kinetics of oxygen exchange and diffusion. Transport properties in a composite cathode, such as electrical conductivity, are especially sensitive not only to the amount of each phase, but also to the degree to which phases are connected. This is illustrated in Fig. 2, where the ASR as a function of Ag volume fraction for a composite containing an electrical phase (Ag) and an ionic phase (BSB).

In general, the values of the ASRs decreased as the BSB concentration increased to 50 vol.%. The excellent performance of Ag-BSB is due to the fact that it is a mixed-conducting oxide, which provides multiple pathways for the oxygen ions to

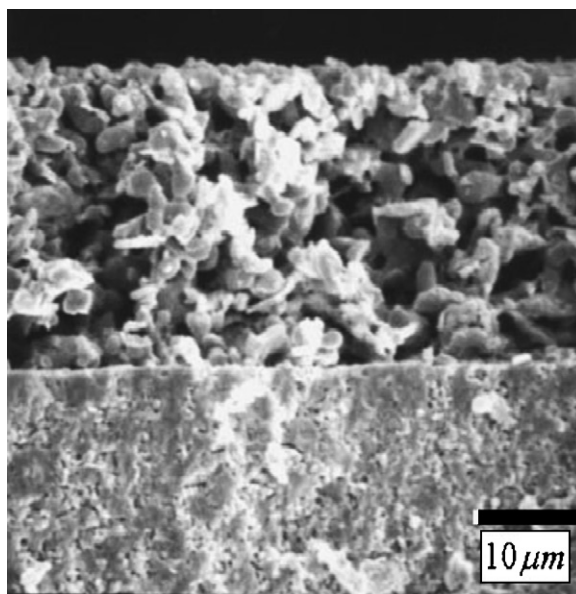


Fig. 1. SEM images of Ag50-BSB cathodes sintered at 600 °C for 2 h.

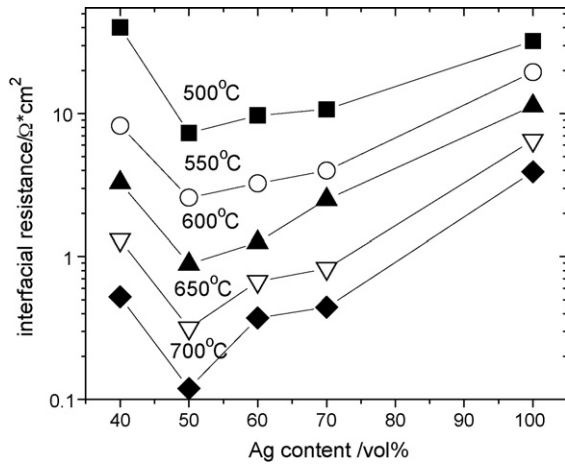


Fig. 2. ASR of Ag-BSB cathodes as a function of the volume fraction of Ag.

migrate to the electrode/electrolyte interface. Hence, it is conceivable that the ASR of the optimized composite electrode was decreased by extending the triple phase boundary line (tpbl), which resulted in much lower overpotentials toward oxygen reduction and by increasing the oxygen diffusion upon addition of an ionic conducting phase (BSB).

The ASRs of Ag-BSB cathodes increased rapidly for further increases in BSB content above 50 vol.%. The increase of ASR may be due to a decrease in the continuity of the Ag phase in the composite, and hence a decrease in electrical conductivity. The optimum BSB addition (50% by volume) to Ag resulted in about twenty times lower ASR at 650 °C. The ASR values for the Ag50-BSB and Ag cathodes were 0.32 and 6.5  $\Omega\text{ cm}^2$  at 650 °C, respectively. The observed high performances of the composite electrodes at 50 vol.% electrolytes can be interpreted with the effective medium percolation theory [26,27], which predicts the ambipolar transport behavior of composite consisted of mixed ionic–electronic conductors as a function of the volume fraction of each of the randomly distributed constituent phases.

The performance of the composite cathodes is dictated by the sum of resistance associated with each component, the rates of interfacial reactions such as gas diffusion, oxygen adsorption and dissociation, charge-transfer (oxygen reduction) and oxygen-ion diffusion. It is generally recognized that the slow interfacial (charge-transfer) reaction rate at the electrocatalyst–electrolyte interfaces often limits performance. Fig. 3 shows typical impedance spectra for Ag and Ag-BSB cathodes tested at 650 °C in air. The spectrum for pure Ag (Fig. 3a) appeared to be a single depressed arc, but fits to the spectra using a nonlinear least squares fitting program (EQUIVCRT) [28], suggesting that two arcs were present. The low-frequency arc was larger than the high-frequency arc, indicating oxygen diffusion processes probably limited the electrode reaction [29].

Fig. 3b–e shows the results for different Ag-BSB compositions. The overall size of the impedance arcs decreased with increasing BSB content  $X$ . The only exception was for  $X=60\%$ , where the arcs became larger than for  $X=30\text{--}50\%$ . The high-frequency arc was larger than the low-frequency arc with increasing BSB content in the composites, indicating charge transfer processes probably limited the electrode reac-

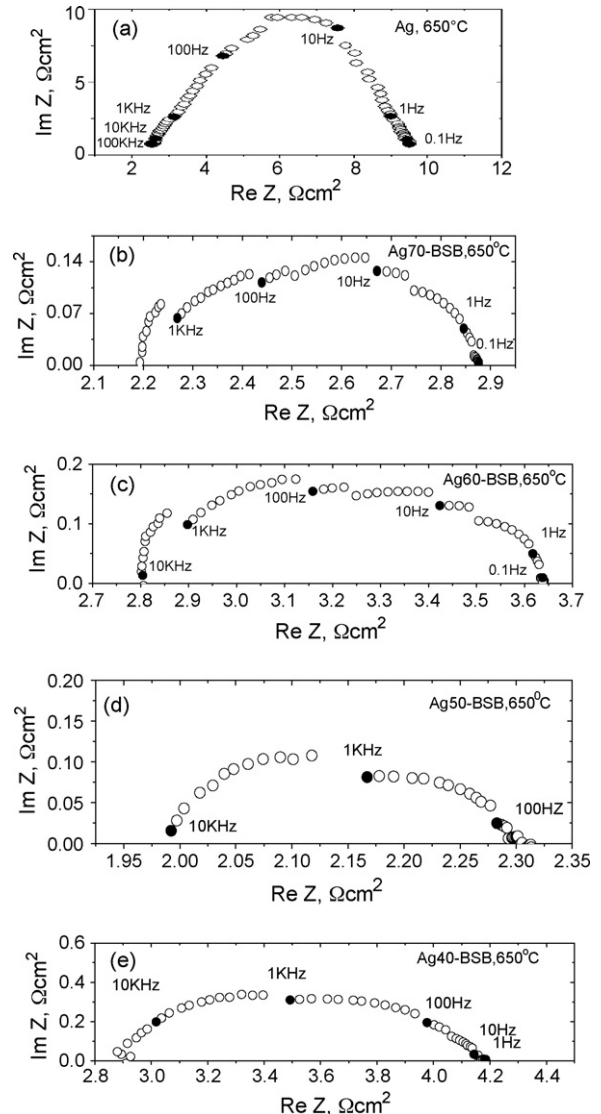


Fig. 3. AC impedance spectra at 650 °C for Ag-BSB composite cathodes.

tion. Meanwhile the above results indicated that BSB had good catalytic activity for oxygen dissociation. In addition, the performances of Ag-BSB composite cathodes can be explained by using the combination of two materials with different rate-limiting processes may allow a “short circuiting” of the limiting steps of each. For example, BSB may provide rapid mass transport, while silver may provide sites for efficient charge transfer and surface exchange.

A few mechanisms may explain the enhanced electrode performance produced by the BSB addition. However, it seems likely that the high oxygen dissociation activity and ionic conductivity of BSB played a key role by expanding the electrochemical reaction zone further from the electrode/electrolyte interface.

The issue of cathode microstructure has raised questions as to the stability of Ag-BSB composite under ITSOFC operating conditions because of the relatively low melting points of both BSB and silver. Fig. 4 shows the long-term stability of Ag50-BSB cathode. The value of the ASR showed little change over



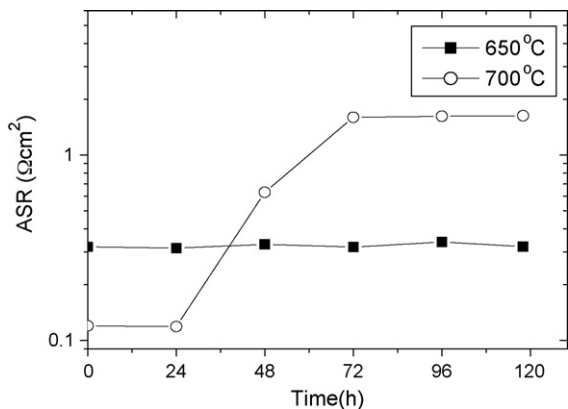


Fig. 4. ASRs as a function of testing times for Ag50-BSB cathodes.

the entire 120 h test at 650 °C. This result indicated Ag50-BSB cathode has good stability at 650 °C. However, the values of ASR increased rapidly as the stability was tested at 700 °C for 48 h. That is, continued growth of Ag and BSB phases would decrease the porosity due to over-sintering (coarsening) of the microstructure and increase the cathode resistance over time (see Fig. 5). X-ray diffraction on each of the samples sintered at 700 °C for 120 h showed no new phases except for Ag, BSB and SDC phases. While long-term tests are needed, this result is promising because Ag50-BSB cathodes would most likely be used for ITSOFCs designed to operate at below 650 °C.

Fig. 6 shows the current voltage characteristics and the corresponding power densities for two fuel cells using the Ag50-BSB cathode and LSCF50-SDC cathode, respectively. The maximum power density for the cell with the Ag50-BSB cathode was 224 mWcm<sup>-2</sup> at 650 °C, while that with the LSCF50-SDC cathode was only 182 mWcm<sup>-2</sup>. Power densities of a cell are a function of its internal resistances, which are the sum of the cathodic and anodic ASRs and the ohmic resistance of the elec-

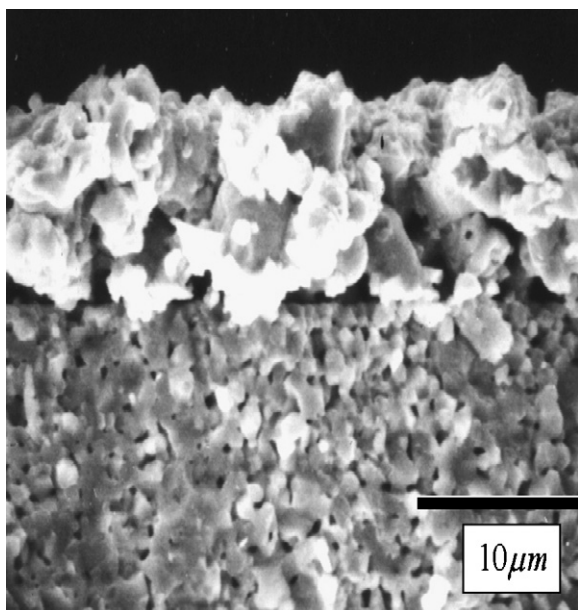


Fig. 5. SEM images of Ag50-BSB cathodes tested for 48 h at 700 °C.

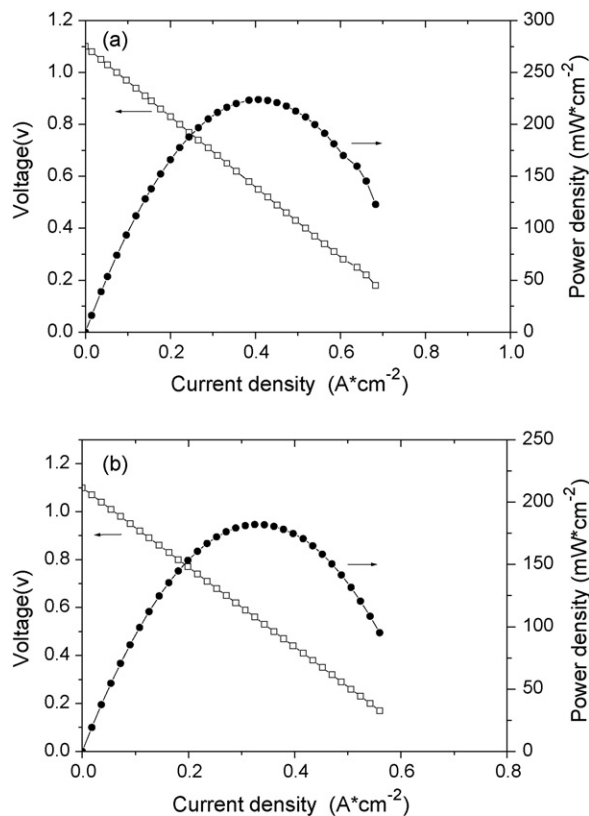


Fig. 6. Cell voltage and power density as functions of current density. (a) With Ag50-BSB cathode; (b) with LSCF50-SDC cathode.

trolyte. The anodic and electrolyte resistances of the above two cells can be reasonably assumed identical, because the anode and electrolyte are fabricated with the same procedures. So the relative higher power densities infer better performance of Ag50-BSB cathode.

It should be noted that bismuth oxide is a favorable catalyst for oxygen dissociation reaction, which will certainly improve the silver catalytic activity for the oxygen reduction at the cathode. Further study should be conducted to distinguish the effect between the enhancement on oxygen-ion conducting and the improvement of catalytic activity for oxygen reduction.

#### 4. Conclusion

The area specific resistances of new composite cathode materials were measured and found to exhibit good performance at low operating temperature depending on the volume fraction of BSB. The composite contain 50% in volume BSB exhibited the lowest interfacial resistance or the highest catalytic activity for oxygen dissociation and reduction, which classify this composite as a promising material for ITSOFC.

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