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Composite cathode based on yttria stabilized bismuth oxide for low-temperature solid oxide fuel cells

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Composites consisting of silver and yttria stabilized bismuth oxide (YSB) have been investigated as cathodes for low-temperature honeycomb solid oxide fuel cells with stabilized zirconia as electrolytes. At 600 °C, the interfacial polarization resistances of a porous YSB–Ag cathode is about 0.3 Ω cm^2, more than one order of magnitude smaller than those of other reported cathodes on stabilized zirconia. For example, the interfacial resistances of a traditional YSZ–lanthanum maganites composite cathode is about 11.4 Ω cm^2 at 600 °C. Impedance analysis indicated that the performance of an YSB–Ag composite cathode fired at 850 °C for 2 h is severely limited by gas transport due to insufficient porosity. The high performance of the YSB–Ag cathodes is very encouraging for developing honeycomb fuel cells to be operated at temperatures below 600 °C. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1542933]

Stabilized zirconias are the most commonly used electrolytes in solid oxide fuel cells (SOFCs) because of their excellent mechanical strength and outstanding thermal/chemical stabilities in both oxidizing and reducing atmospheres. Due to their limited ionic conductivities, however, SOFCs based on a zirconia electrolyte must be operated at high temperatures (800–1000 °C) to overcome Ohmic losses. Recent advancements in deposition of thin film electrolytes makes it possible to reduce the operating temperature to 600 °C and below.[1–3] For example, with hydrogen as fuel and air as oxidant, calculated power densities over 400 mWcm^{-2} at 600 °C are expected with a 30-μm-thick scandia stabilized zirconia electrolyte, assuming that the anodic and cathodic interfacial polarization resistances are 0.2 and 0.3 Ω cm^2, respectively. Further, the power densities of SOFCs based on thin films of stabilized zirconia can be enhanced by using a honeycomb design.[4,5] While the anodic interfacial resistance is relatively small, the cathodic interfacial resistance is very large; it actually determines the performance of SOFCs operated at low temperatures (below 600 °C).[6]

One of the advantages of low-temperature SOFC is the potential for dramatic cost reduction. If SOFCs can be operated below 600 °C, for example, many components (such as the interconnect and heat exchangers) can be fabricated from much less expensive materials. Additional benefits of lower operating temperature include greater system reliability, longer operational life, and increased potential for mobile applications and for cost-effective fabrication.[7]

The development of cathode materials for SOFCs based on yttria-stabilized zirconia (YSZ) has mainly focused on strontium-doped lanthanum manganites (LSM) because of the thermal and chemical compatibilies with YSZ. However, single phase LSM does not have acceptable performance due to its low oxygen-ion conductivity. The addition of a second phase of higher ionic conductivity to LSM may extend the active area over which the oxygen reduction reaction can take place. Composite cathodes consisting of LSM and YSZ or gadolinia doped ceria (GDC) are studied and better performances were achieved at high temperatures. For example, interfacial resistance as low as 0.49 Ω cm^2 at 750 °C was reported for the interface between a LSM-GDC cathode and a YSZ electrolyte.[8] Recently, interfacial polarization resistance as low as 0.7 Ω cm^2 was observed for a functionally graded cathode based on LSM and YSZ[9] at 900°C. However, the interfacial resistances increased dramatically as the operating temperature is reduced to below 600 °C. It is very likely that only limited improvements of LSM cathodes are achievable because the coefficients for oxygen surface exchange and oxygen diffusion in LSM are relatively low.[6] To efficiently operate a zirconia-based SOFC at 600 °C or below, it is necessary to develop cathode materials with high catalytic activity for oxygen reduction and with high oxygen ion conductivity for oxygen transport through the composite cathode.

Among the oxygen ion conductors developed, bismuth oxides have showed favorable catalytic effects on the oxygen disassociation reaction,[10] which is often the rate limiting step in many electrochemical process involving oxygen reduction, such as the one in an SOFC. Besides, bismuth oxides exhibit conductivities about two orders of magnitude higher than those of stabilized zirconia. In this work, yttria doped bismuth oxides were investigated as the ionic conducting phase in a composite cathode for stabilized zirconia. Silver was used to enhance the electronic conductivity of the composite electrodes.

Yttria stabilized bismuth oxide (Y$_{0.25}$Bi$_{0.75}$O$_{1.5}$) (YSB) was synthesized using a coprecipitation method. Stoichiometric amount of Bi(NO$_3$)$_3$5H$_2$O (Aldrich 98%) and Y(NO$_3$)$_3$6H$_2$O (Aldrich 99.9%) were dissolved in a dilute nitric acid solution, which was then added drop by drop to an oxalic acid solution to form white precipitates. The precipitates were collected by filtration, dried at 120 °C overnight,

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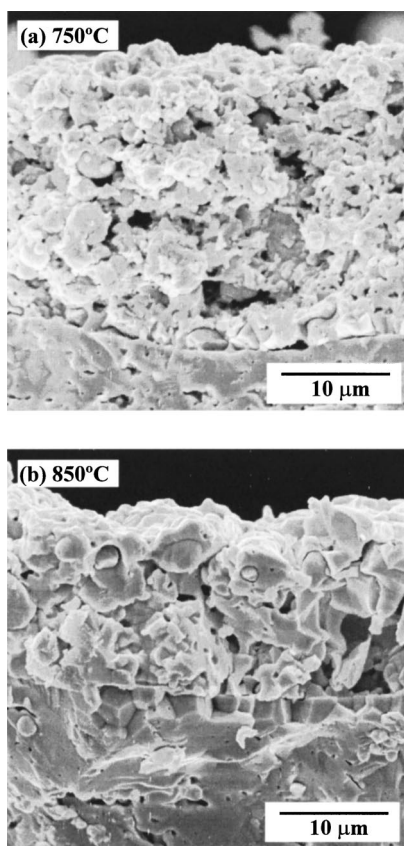[a]Author to whom correspondence should be addressed; electronic mail: meilin.liu@mse.gatech.edu

FIG. 1. Cross-sectional views of two YSB–Ag composite cathodes fired at (a) 750 and (b) 850 °C.

FIG. 2. Interfacial polarization resistances of a YSB–Ag composite cathode, functionally graded cathodes, GDC–LSM, and YSZ–LSM composite cathodes.

and fired at 900 °C for 5 h to form crystalline YSB with fluorite structure as confirmed by x-ray diffraction. Silver oxide (Aldrich 99%), used as the source for electronic conducting component, was mixed with YSB powder at a weight ratio of $YSB:Ag_2O=40:60$. The mixed powders were made into a slurry by ball milling for 24 h with an organic binder and acetone. The slurries were subsequently coated onto the inner channels of a fired YSZ honeycomb with wall thickness of about 300 μm.[4,5] The coated electrode layer was dried at 120 °C for 2 h and subsequently fired at 750 or 850 °C for 2 h with a heating and cooling rate of 5 and 10 °C per minute, respectively.

Electrochemical impedance measurements were carried out using a Solartron 1255 HF frequency response analyzer in combination with a Solartron 1286 electrochemical interface. Silver wires were attached to the electrodes with a silver paste, and a thermocouple was positioned close to the sample to monitor the sample temperature, usually increasing from 500 to 750 °C in 50 °C interval. Impedance spectra were typically obtained in the frequency range from 1 MHz to 10 mHz with an applied ac voltage amplitude of 10 mV. All data was taken 30 min after the desired temperature was reached. The interfacial impedances as determined from the spectra were corrected for electrode area (0.16×3.0 cm^2) and divided by two (symmetric cell) to obtain the area specific polarization resistance (Ω cm^2).

Shown in Fig. 1 are the cross-section views of two YSB–Ag composites fired at different temperatures. It can be seen that the composite electrode fired at 750 °C has high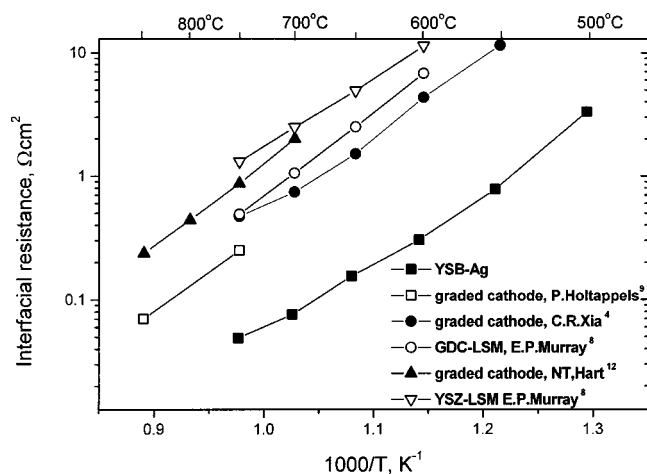 porosity and consists of small grains. In contrast, the composite electrode fired at 850 °C has isolated pores and consists of large grains. The average thicknesses of the two electrodes are about 25 and 12 μm, respectively.

The interfacial polarization resistances are determined from the impedance spectra of symmetric cells as described elsewhere.[4] Shown in Fig. 2 is the temperature dependence of interfacial polarization resistances measured without dc bias for a YSB–Ag cathode fired at 750 °C. Also shown in Fig. 2 are the interfacial polarization resistances of other composite cathodes (YSZ–LSM, GDC–LSM)[8] and recently developed functionally graded cathodes.[4,9,11,12] Clearly, the YSB–Ag cathode displays much smaller interfacial polarization resistances than other cathodes. At 600 °C, for example, the interfacial polarization resistance of YSB–Ag is only 0.30 Ω cm^2, compared to 4.3 Ω cm^2 for a graded cathode,[4] 6.8 Ω cm^2 for a GDC–LSM composite,[8] and 11.4 Ω cm^2 for a YSZ–LSM composite,[8] implying about one order of magnitude improvement. The performance of a mixed-conducting electrode is determined by the ionic and electronic conductivities of the electrode, catalytic activities at the triple phase boundary and electrode surfaces, and the rate of gas transport through the porous electrodes. It is well know that LSM, LSCF, Ag, and most other electrode materials have adequate electronic conductivities. Likewise, transport of gases species through the porous cathodes is usually rapid, and thus the effect of concentration polarization is significantly only when the porosity of the electrode is inadequate or the cell is operated at very high current densities. Often, it is found that the overall performance of a mixed-conducting electrode depends critically on the ionic transport properties and on the catalytic properties for oxygen reduction.[13] The relatively high oxygen ion conductivity of YSB[14] (0.070 S cm^{-1} at 600 °C), compared to GDC[15] (0.017 S cm^{-1}) and YSZ[16] (0.0045 S cm^{-1}), is clearly an important reason that the YSB–Ag composite electrode shows much lower interfacial resistances than the composites consisting of YSZ, GDC, LSM, and LSCF. Moreover, another possible reason is the catalytic effect of YSB on the oxygen disassociation, which is often the limiting step in oxygen reduction at the cathode.[6,10] For YSZ–LSM and GDC–LSCF it is suggested that the oxygen disassociation
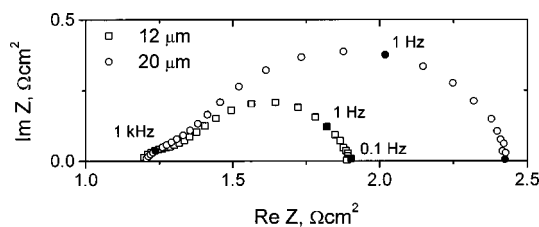
FIG. 3. Impedance spectra measured at 600 °C for two YSB–Ag composite cathodes of different thickness (12 and 25 μm) sintered at 850 °C for 2 h.

rate have to be enhanced by at least two orders of magnitude to account for the desired cathodic performance at low temperature.[6] While there is no data available for direct comparison in catalytic activity for oxygen reduction between YSB and YSZ or GDC, previous work on bismuth oxide based materials demonstrated that the activity of bismuth oxide surface is higher than that of noble metals. This effect was clearly demonstrated using a bismuth lead oxide electrolyte, which was shown to easily support high current densities using a special cell design in which the electronic surface conductivity was provided by means of a thin gold grid co-sintered with the electrolyte.[17,18] It should be noted that silver could also contribute to the observed enhancement in performance since silver is also a very good oxygen reduction catalyst.

Shown in Fig. 3 are two typical impedance spectra measured at 600 °C for two YSB–Ag composite electrodes fired at 850 °C for 2 h. The cross-section view of the 12-μm-thick cathode is shown in Fig. 1(b). The interfacial polarization resistance seems to be proportional to the thickness of the electrodes, indicating that the overall interfacial impedances were determined primarily by the resistance to gas transport through the electrodes. Each spectrum consists of two semicircles from visual inspection. The resistances corresponding to the low frequency semicircle are 0.57 and 1.09 Ω cm^2 for the cathodes with thickness of 12 and 20μm, respectively.

Shown in Figs. 4(a) and 4(b) are the impedance spectra measured at 600 °C for two porous YSB–Ag composite electrodes fired at 750 °C with average thickness of 12 and 25 μm, respectively. The two spectra are almost identical, indicating that their electrochemical performances are indepen-
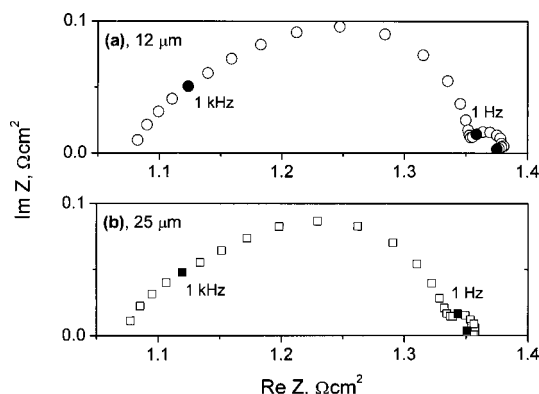
dent of their thickness. The electrochemical performances are determined critically by its TPBs, which are related to its structures and microstructures. Since the two electrodes have the same structures except thickness, it can be concluded that the gas transport is efficient through the YSB–Ag composites thinner than 25 μm; it can also be concluded that the active or useful thickness of the electrode is smaller than 12 μm.

While the long-term stability of bismuth oxide-based cathodes in SOFCs is yet to be studied, many previous studies seem to suggest that YSB is stable under the operating conditions studied. For example, it is reported that YSB is chemically stable in partial pressure of oxygen as low as 10^{-13}, 10^{-14}, and 10^{-20} atm under different conditions, as discussed in a review article on bismuth based oxide electrolytes.[14] Also, the interface between YSZ and YSB seems to be clean and there was no detectible evidence suggesting any reactions between YSZ and YSB; this is consistent with previous studies reported in the literature.[19,20] However, the microstructural stability of the YSB–Ag composite electrode could be a concern because of the relatively low melting points of both YSB and silver. Thus, YSB–Ag composite electrode is an excellent cathode only for low-temperature SOFCs.

[1] E. P. Murray, T. Tsai, and S. A. Barnett, Nature (London) **400**, 649 (1999).
[2] Y. Jiang and A. V. Virkar, J. Electrochem. Soc. **148**, A706 (2001).
[3] S. Souza, S. J. Visco, and L. C. Jonghe, J. Electrochem. Soc. **144**, L35 (1997).
[4] C. R. Xia, W. Rauch, W. Wellborn, and M. L. Liu, Electrochem. Solid-State Lett. **5**, A217 (2002).
[5] C. R. Xia, W. Rauch, J. Cochran, J. Lee, and M. L. Liu, Proceeding of 1st International Conference on Materials Processing for Properties and Performance (MP3), Aug. 1, 2002, Singapore.
[6] B. C. H. Steele, K. M. Hori, and S. Uchino, Solid State Ionics **135**, 445 (2000).
[7] C. Xia and M. Liu, Adv. Mater. **14**, 521 (2002).
[8] E. P. Murray and S. A. Barnett, Solid State Ionics **143**, 265 (2001).
[9] P. Holtappels and C. Bagger, J. Eur. Ceram. Soc. **22**, 41 (2002).
[10] J. C. Boivin and G. Mairesse, Chem. Mater. **10**, 2870 (1998).
[11] N. T. Hart, N. P. Brandon, M. J. Day, and J. E. Shemilt, J. Mater. Sci. **36**, 1077 (2001).
[12] N. T. Hart, N. P. Brandon, M. J. Day, and N. Lapena-Rey, J. Power Sources **106**, 42 (2002).
[13] M. L. Liu, J. Electrochem. Soc. **145**, 142 (1998).
[14] N. M. Sammes, G. A. Tompsett, H. Nafe, and F. Aldinger, J. Eur. Ceram. Soc. **19**, 1801 (1999).
[15] C. R. Xia and M. L. Liu, Solid State Ionics **152-153**, 423 (2002).
[16] S. P. S. Badwal, F. T. Ciacchi, S. Rajendran, and J. Drennan, Solid State Ionics **109**, 167 (1998).
[17] M. Dumelie, G. Nowogrocki, and C. J. Boivin, Br. Ceram. Proc. **43**, 151 (1988).
[18] M. Dumelie, G. Nowogrocki, and C. J. Boivin, Solid State Ionics **28–30**, 524 (1988).
[19] M. J. Miyayama, T. Nishi, and H. Yanagida, J. Mater. Sci. **22**, 2624 (1987).
[20] K. Keizer, A. J. Burggraaf, and G. deWith, J. Mater. Sci. **17**, 1095 (1982).

FIG. 4. Impedance spectra measured at 600 °C for two YSB–Ag composite cathodes of different thickness (12 and 25 μm) sintered at 750 °C for 2 h.