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Electrochemical performances of Ag–$(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ composite cathodes

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Abstract

The electrochemical performances of Ag–$Y_{0.25}Bi_{0.75}O_{1.5}$ (YSB) composite cathodes on $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) electrolytes have been investigated at intermediate temperature using AC impedance spectroscopy. The results indicated that the electrochemical performances of these composites are quite sensitive to the compositions and the microstructures of the cathode. The optimum YSB addition to Ag resulted in 10 times lower area specific resistance. The ASR of Ag-50 vol.% YSB was about 0.12 Ωcm^2 at 700 °C as compared to 3.9 Ωcm^2 for Ag cathodes. The observed high performance of Ag–YSB composite cathodes might be due to the high oxygen-ion conductivity of YSB and its high catalytic activity for oxygen reduction.

Keywords: Electrode materials; Fuel cells; Ionic conduction; Electrochemical impedance spectroscopy; Microstructure

1. Introduction

Solid oxide fuel cells (SOFCs) are energy conversion devices that convert chemical energy directly into electric power with high conversion efficiency and negligible pollution. While the operating temperature of SOFC should be lowered in order to minimize the stringent requirements at the high temperature operation. This has lead to the development of intermediate temperature SOFC (ITSOFC) operating at 500–800 °C [1,2]. Meanwhile, the performance of ITSOFCs is strongly dependent on the cathode–electrolyte interface, since the interfacial polarization of solid-state cells increases rapidly as the temperature is decreased [3,4].

The cathodes for ITSOFCs should have high electrical conductivities, adequate porosity for gas transport, good compatibility with the electrolyte and long-term stability. Doped $LaCoO_3$ cathodes and their composites have good performances at intermediate temperature, such as (La, Sr)(Co, Fe)O_3 [5,6], (Sm, Sr)CoO_3 [7–9] and (Ba, Sr)(Co, Fe)O_3 [10–12]. Unfortunately, these materials do not completely meet all the technological requirements (thermal expansion, ionic conductivity, mechanical stability and cost), which prevent the rapid commercialization of the ITSOFC system.

Metal composite cathodes are potential candidates for ITSOFCs, especially silver composite cathodes. Silver is an excellent electronic conductor and widely used as electrodes for various electrochemical devices [13,14]. 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. Conductors based on bismuth oxide have much high oxygen-ion conductivity; the conductivity of bismuth oxide is about two orders of magnitude higher than that of stabilized zirconia (YSZ) [15]. Meanwhile bismuth oxide is excellent in disassociation oxygen. Reports showed that bismuth oxide is stable at intermediate temperature when $p(O_2) > 10^{-10}$ atm [16]. To enhance the oxygen-ion conducting of silver, oxygen-ion conductors of stabilized bismuth oxide were added to form composite electrodes for YSZ and $BaCe_{0.8}Gd_{0.2}O_3$-based solid oxide fuel cells [17,18]. Studies indicate that Ag–$Y_{0.25}Bi_{0.75}O_{1.5}$ (YSB) cathodes have good performances on YSZ [19,20]. However, details and data concerning the electrochemical properties of Ag–YSB

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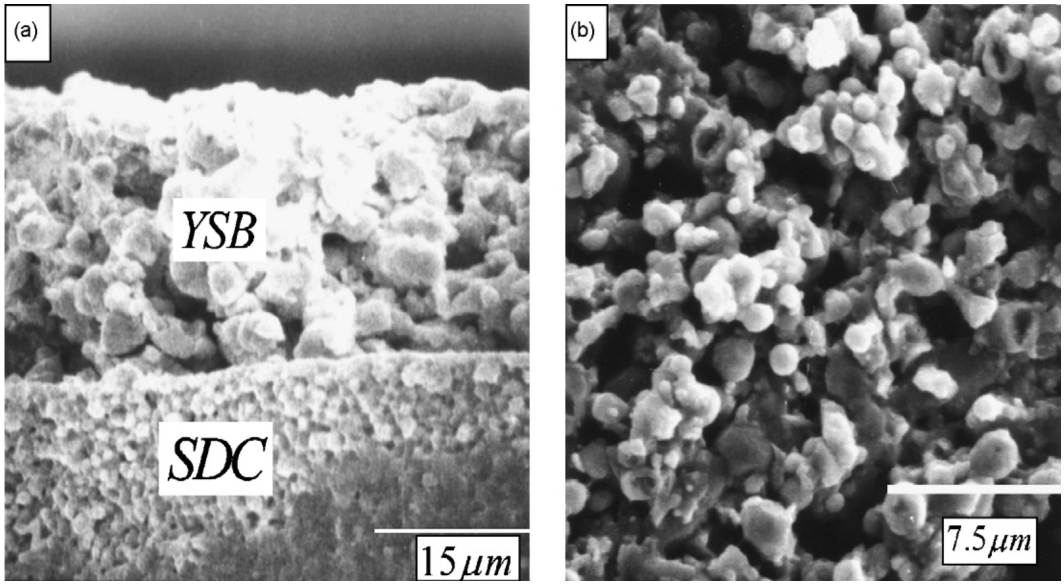

Fig. 1. SEM images of the Ag–50YSB cathode sintering at 600°C for 2 h: (a) cross-section, (b) surface.

cathodes on $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) electrolyte were still scarce.

In this study, composites consisting of Ag and YSB were investigated as cathodes for ITSOFC with SDC as electrolytes. The electrochemical properties of these cathodes were investigated and correlated with the compositions and microstructures.

2. Experimental

Yttrium stabilized bismuth ($Y_{0.25}Bi_{0.75}O_{1.5}$, YSB) powders were synthesized using an oxalate co-precipitation method. Stoichiometric amount of $Bi(NO_3)_3{\cdot}5H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ 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 80 °C for 24 h, and fired at 900 °C for 5 h. Silver oxide was mixed with YSB powder at volume ratios of YSB:Ag = 6:4, 5:5, 4:6, 3:7, 2:8 and 1:9. The mixed powders were made into slurries by ball-milling for 24 h with methyl ethyl ketone. Ethanol was used as solvent. The slurries were printed on each side of $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) pellets (15 mm diameter, 0.6 mm thickness, sintering at 1400 °C). The symmetrical cell was sintered at 600 °C for 2 h in air, to form two nominally identical electrodes for electrochemical testing. SDC powders were also synthesized using an oxalate co-precipitation method, and then fired at 750 °C for 2 h.

AC impedance spectroscopy measurements were carried out using a CH604A electrochemistry analyzer (SHANGHAI CHENHUA). A thermocouple was positioned close to the sample to monitor the sample temperature, increasing from 500 to 700 °C at 50 °C interval. The frequency range was 0.01–100 KHz with a signal amplitude of 10 mV. All data were taken 30 min after the desired temperature was reached. A scanning electron microscope (SEM, Hitch 650) was used to detect the microstructure of the sintered pellets.

3. Results and discussion

Fig. 1 shows typical cross-sectional and surface SEM images of Ag–50YSB (50:50 by volume) cathodes. Fig. 1a shows Ag–50YSB cathode sintered at 600 °C for 2 h, thickness of the cathode layer was found to be 15–25 μm. High porous electrodes were apparent, and the cathode layer has a better contact with the electrolyte to ensure a better current collection. Fig. 1b shows the Ag–50YSB interface at higher magnification which clearly indicated that the electrode microstructure appeared uniform and porous. The cathode particles are well necked which average 1–3 μm.

It is known that silver is a good catalyst for oxygen reduction. However, ASRs of silver electrodes for SDC electrolytes are relatively high at intermediate temperatures. For example, it is 3.9 Ωcm^2 at 700 °C. This value is much higher than that expected for cathode ASR, lower than 0.15 Ωcm^2 at operating temperature. To improve the performance of electrodes, adding second phase electrolytes to the electrochemical catalysts has been widely used for many years to develop SOFCs with high performance. YSB was thus added into Ag to form Ag–YSB composite electrodes. Shown in Fig. 2 is the effect of YSB addition on the ASR measured at temperature between 500 and 700 °C. It was noted that the addition of YSB could dramatically improve the electrochemical performance of Ag, namely decrease the

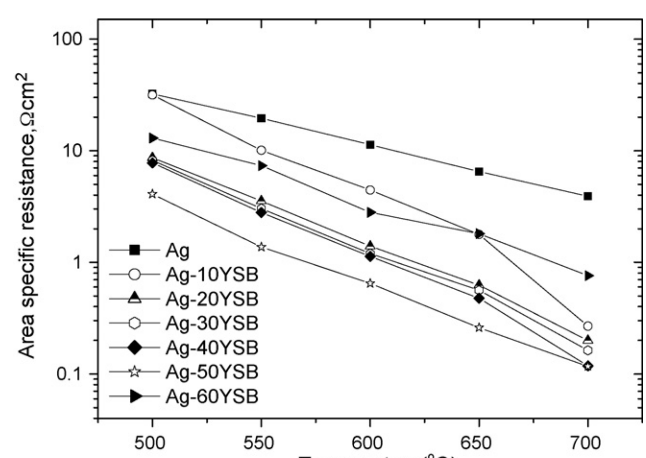

Fig. 2. Temperature dependence of the area specific resistances for pure Ag and Ag–YSB cathodes.