Journal of Power Sources 194 (2009) 625–630

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

$La_{0.84}Sr_{0.16}MnO_{3-\delta}$ cathodes impregnated with $Bi_{1.4}Er_{0.6}O_3$ for intermediate-temperature solid oxide fuel cells

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ARTICLE INFO

Article history:
Received 7 May 2009
Received in revised form 18 June 2009
Accepted 19 June 2009
Available online 30 June 2009

Keywords:
Intermediate-temperature solid oxide fuel cells
Composite cathode
Impedance spectroscopy
Ion-impregnation
Bismuth oxides

ABSTRACT

$La_{0.84}Sr_{0.16}MnO_{3-\delta}$–$Bi_{1.4}Er_{0.6}O_3$ (LSM–ESB) composite cathodes are fabricated by impregnating LSM electronic conducting matrix with the ion-conducting ESB for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The performance of LSM–ESB cathodes is investigated at temperatures below 750 °C by AC impedance spectroscopy. The ion-impregnation of ESB significantly enhances the electrocatalytic activity of the LSM electrodes for the oxygen reduction reactions, and the ion-impregnated LSM–ESB composite cathodes show excellent performance. At 750 °C, the value of the cathode polarization resistance (R_p) is only 0.11 $\Omega\,cm^2$ for an ion-impregnated LSM–ESB cathode, which also shows high stability during a period of 200 h. For the performance testing of single cells, the maximum power density is 0.74 $W\,cm^{-2}$ at 700 °C for a cell with the LSM–ESB cathode. The results demonstrate the ion-impregnated LSM–ESB is one of the promising cathode materials for intermediate-temperature solid oxide fuel cells.

1. Introduction

$La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) is regarded as one of the most promising cathode materials for use in the production of high-temperature solid oxide fuel cells (SOFCs) because of its high thermal and chemical stability, relatively good compatibility with zirconia-based electrolytes [1,2]. However, the electrochemical activity of the LSM-based cathodes decreases substantially with decreasing cell operating temperatures and the cathode polarization resistance dominates the cell resistance at intermediate temperatures. Therefore, it is critical to improve the LSM cathode performance in order to improve the cell performance at intermediate temperatures. Many researchers have investigated the properties of LSM-based cathodes [3–6], and it is reported that the rate-determining step of the oxygen reduction on LSM cathodes is the adsorption and surface diffusion of oxygen. Some other researchers suggested that the charge transfer reaction is the rate-determining step for the oxygen reduction reaction on LSM cathodes. However, all of them suggested that the performance of cathodes is closely related to the length of the triple phase boundary (TPB). It is reported that the composite cathodes can availably increase the length of TPB and improve their electrochemical performance [7–9], and the addition of an oxygen ion conductor into LSM to form a composite cathode is a general method. For instance, cathode polarization resistances (area specific resistances) were 2.49 and 0.75 $\Omega\,cm^2$ at 700 °C for a LSM–YSZ cathode and a LSM–GDC cathode, respectively, which were 25 and 7.5% of the value for the LSM polarization resistance [9]. And the superior performance of the LSM–GDC composite cathode over that of LSM–YSZ was attributed to the higher ionic conductivity as well as the higher oxygen surface exchange coefficient of GDC compared with that of YSZ.

Doped bismuth oxides have been investigated recently as possible component of composite cathodes in IT-SOFCs [10–12]. Doped bismuth oxides have high levels of oxygen ion conductivity [13–15]. For instance, Er_2O_3-stabilized Bi_2O_3 (ESB) has the highest level of oxygen ion conductivity (0.37 $S\,cm^{-1}$ at 973 K). In addition, the oxygen surface exchange coefficient of stabilized bismuth oxide is comparable to that of other electrolytes [16]. Thus, ESB is expected to improve the electrode performance by playing the role of GDC or YSZ in composite cathodes.

Now, a more effective ion-impregnating method has been proposed to fabricate the composite cathodes [17–20]. It is an effective way to deposit electrocatalytic oxides into the porous LSM matrix without diminishing the advantages of stability and compatibility of LSM materials with zirconia-based electrolytes. In this work, LSM–ESB composite cathodes for intermediate-temperature solid oxide fuel cells (IT-SOFCs) based on the SSZ ($(ZrO_2)_{0.89}(Sc_2O_3)_{0.05}(CeO_2)_{0.01}$) electrolytes were fabricated with a two-step fabricating process including screen-printing and ion-impregnating, and the electrochemical behavior at the cathode/electrolyte was investigated by AC impedance analyses. Besides, the performance of anode-supported single cells using LSM–ESB as cathode materials was also evaluated.

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doi:10.1016/j.jpowsour.2009.06.070

2. Experimental

The $La_{0.84}Sr_{0.16}MnO_{3-\delta}$ (LSM) powder was synthesized by autoignition of citrate–nitrate gel as reported previously [21]. $La(NO_3)_3 \cdot 6H_2O$(>99.0%), $Sr(NO_3)_2$ (>99.5%), and $Mn(NO_3)_2 \cdot 4H_2O$ (>99.0%) in stoichiometric proportions were mixed together in a water-bath at 80 °C. When they were dissolved completely, a certain amount of citric acid was introduced to form the LSM precursor solution. The solution was heated on a hot plate till autoignition occurred, resulting in a black powder. Then the powder was sintered in air at 850 °C for 5 h to form the expected perovskite phase.

To prepare the cathode, LSM was mixed with an appropriate amount of graphite (30 wt.%) and ball-milled for 24 h to form a uniform electrode powder. Using the screen-printing method, the LSM electrode precursor was printed to the SSZ ($(ZrO_2)_{0.89}(Sc_2O_3)_{0.05}(CeO_2)_{0.01}$) substrates and then sintered at 1200 °C for 2 h in air to form porous LSM frames. The ESB particles were coated onto the inner surface of the porous LSM frames with an ion-impregnation process. An aqueous solution containing $Er(NO_3)_3$ and $Bi(NO_3)_3$ (Er^{3+}:Bi^{3+} = 3:7) was dropped onto the top of the LSM frame, dried at room temperature, and heated at 700 °C for 2 h to form $Bi_{1.4}Er_{0.6}O_3$ (ESB) particles. The mass of the electrode before and after the impregnation treatment was measured to determine the impregnated oxide loadings. The procedure was repeated to increase the ESB loadings. The impregnated ESB loadings in LSM–ESB composite cathodes were 30, 40, 50 and 60 wt.% (named LSM–ESB30, LSM–ESB40, LSM–ESB50 and LSM–ESB60, respectively).

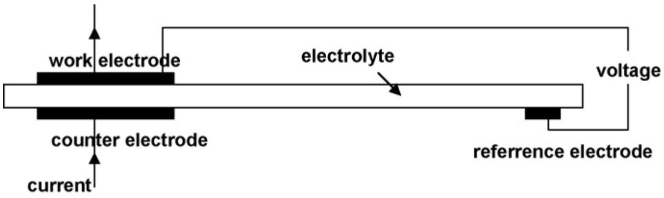

Fig. 1. The schematic configuration of the three-electrode cell.

The polarization resistance was measured by two-electrode impedance method using symmetric cells, using an AC impedance spectroscopy (ZAHNER IM6e) with a 20 mV AC signal, over a frequency range of 0.05 Hz to 1 MHz. The area of every cathode was 1.0 cm^2. A three-electrode cell configuration was used to measure the overpotential of the LSM–ESB electrodes as shown in Fig. 1. A LSM–ESB working electrode was fabricated with the same process as forenamed, and the area of the working electrode was also 1.0 cm^2. The counter electrode was formed by applying the Pt paste to the opposite side of the working electrode on the SSZ electrolyte, and the Pt reference electrode was deposited beyond the counter electrode. Both counter and reference electrodes were fired at 800 °C for 2 h. The electrode overpotential was measured at 650 °C by a combination of EIS and DC polarization. The overpotential, η, was calculated by the following equation:

$$\eta = U_{WR} - iR_{ohm}, \tag{1}$$

where U_{WR} is the voltage between the working electrode and the reference electrode, obtained when passing a current, i, through the cell. R_{ohm} is the ohmic resistance obtained from the high frequency real axis intercept of the impedance spectra. A single cell was prepared with the LSM–ESB50 composite cathode on the anode-supported SSZ film. The performance of the single cell was measured from 600 to 700 °C with humidified hydrogen (a water

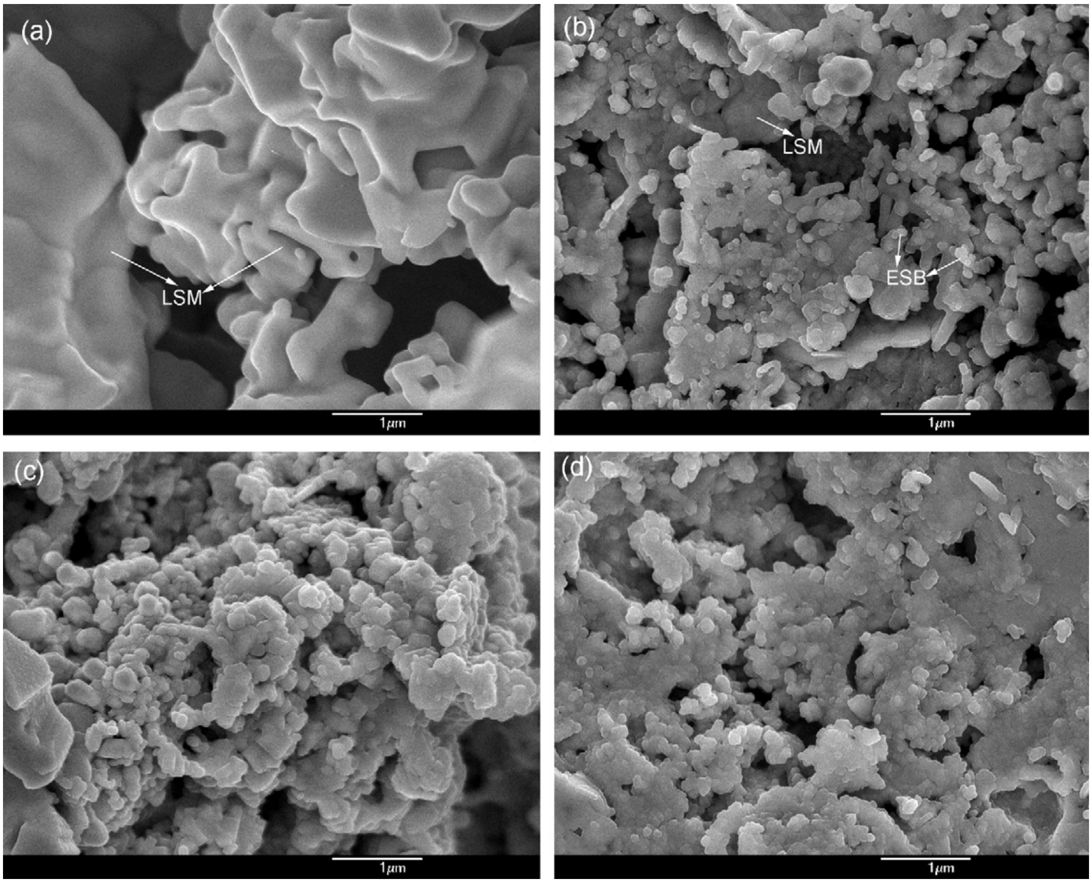

Fig. 2. Typical fracture cross-section SEM images of pure LSM (a), LSM–ESB40 (b), LSM–ESB50 (c) and LSM–ESB60 (d) composite cathodes.