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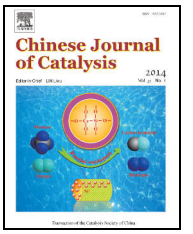

Article

High performance $La_{0.8}Sr_{0.2}MnO_3$-coated $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ cathode prepared by a novel solid-solution method for intermediate temperature solid oxide fuel cells

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ABSTRACT

$La_{0.8}Sr_{0.2}MnO_3$ (LSM)-coated $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) composite powder (LSM-BSCF) was synthesized by a novel solid-solution method and investigated electrochemically as a cathode material for intermediate temperature solid oxide fuel cells. The cathode combined the merits of LSM and BSCF cathodes through an extended triple phase boundary and stabilized microstructure and demonstrated a polarization resistance between 0.61 and 0.09 Ω cm² at 600 to 750 °C. Compared with high performance cathodes prepared by solution impregnation, this LSM-BSCF cathode greatly improved performance stability.

1. Introduction

The solid oxide fuel cell (SOFC) is recognized as an environmental friendly power generation technology for the 21st century. The state-of-the-art cathode material Sr-doped $LaMnO_3$ (LSM) has been widely used for SOFCs operated at temperatures near 1000 °C owing to its high electrochemical activity, electronic conductivity, and structural stability as well as compatibility with the commonly used electrolyte Y_2O_3 stabilized ZrO_2 (YSZ). However, LSM is almost a pure electronic conductor with negligible oxygen ion conductivity [1]. This limits its application as a cathode material for intermediate temperature SOFCs (IT-SOFCs) by rapidly increasing the polarization resistance when the temperature is reduced to the intermediate range of 600 to 800 °C. Efforts have been made to improve the electrochemical performance of LSM at intermediate temperatures by fabricating composite cathodes consisting of LSM and electrolyte materials [2–6]. Low cathode polarization resistance has been obtained by mixing LSM and Gd-doped CeO_2 (GDC, 0.49 Ω cm² at 750 °C [3]) or impregnating GDC into LSM (0.21 Ω cm² at 700 °C [5]); however, polarization resistance as high as 3.25 Ω cm² was also reported for a cell with conventionally mixed LSM/YSZ composite cathode at 750 °C [6]. While many other mixed electronic and ionic conducting perovskite cathode materials have been developed, such as $La_xSr_{1-x}Co_yFe_{1-y}O_3$ (LSCF) and $Ba_xSr_{1-x}Co_yFe_{1-y}O_3$ (BSCF), their use in IT-SOFCs has been hindered by performance degradation. Efforts have been made to improve the performance stability of LSCF by infiltration with LSM [7], and the CO_2 tolerance of BSCF by coating with $La_2NiO_{4+\delta}$ (LN) [8].

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$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is a mixed electronic and ionic conductor with high oxygen surface exchange coefficient [9], oxygen vacancy diffusion rate (7.3×10^{-5} cm^2/s at 775 °C) and ionic conductivity (> Sm-doped CeO_2, SDC) [10]. The electronic conductivity of BSCF is approximately 43 S/cm at 500–900 °C [11]. This value is significantly smaller than that of LSM-based perovskites (190 S/cm at 900 °C for $La_{0.8}Sr_{0.2}MnO_3$ [12]). In addition, the performance of BSCF is not stable because the enrichment of Sr_2O_3 and BaO on the surface leads to the formation of carbonates in the presence of CO_2 [9,13,14]. To combine the high electronic conductivity and stability of LSM with the high ionic conductivity and electrochemical activity of BSCF, an LSM scaffold was impregnated with BSCF to form a composite cathode that achieved a low cathode polarization resistance of 0.18 Ω cm^2 at 800 °C [15]. While the solution impregnation method has been confirmed to be effective for fabricating high-performance electrodes [16–20], the microstructure of such impregnated cathodes is not stable due to continuous growth of the impregnated particles at operating temperature, leading to cathode performance degradation [15]. In addition, implementation of this method adds complexity and increased cost to the cell fabrication process.

The purpose of the present study is to enhance the performance of LSM and stabilize the performance of BSCF for their use as cathode materials in IT-SOFCs, while also avoiding the above-mentioned disadvantages of LSM and BSCF composite cathodes prepared by solution impregnation. To meet this goal, a novel simple method for preparing LSM-coated BSCF composite powder (designated as LSM-BSCF) was developed. The method allows the powder composition to be easily controlled to incorporate the merits of BSCF and LSM, and the cathode microstructure to be stabilized to ensure a high and stable performance.

2. Experimental

For the preparation of the LSM-BSCF powder, BSCF powder was synthesized by the EDTA-citrate-metal complexing method [21]. Ba, Sr, Co, and Fe nitrates (AR, 99%, Aladdin Industrial Corporation) were dissolved proportionally into distilled water, to which EDTA (AR, 99.5%, Sinopharm Chemical Reagent) dissolved in NH_3 solution and solid citric acid (AR, 99.5%, Sinopharm Chemical Reagent) were added in a 1:1:2 molar ratio of the metals, EDTA, and citric acid. NH_4OH was used to adjust the pH to 7–8 before the solution was evaporated at 80 °C to form a dark-red gel. The obtained gel was calcined at 900 °C for 5 h in air, followed by ball-milling at room temperature to obtain BSCF powder with an average particle size of 1 μm. The LSM-BSCF powder was prepared by a novel solid-solution method. LSM ($La_{0.8}Sr_{0.2}MnO_3$) solution was prepared according to the same procedure described above and mixed with the BSCF powder under stirring at 80 °C. The mixture was further dried at 150 °C for 12 h prior to final firing at 800 °C for 4 h in air to obtain LSM-BSCF powder containing 50% LSM and 50% BSCF.

To evaluate the electrochemical performance of the LSM-BSCF cathode, an electrochemical cell was prepared with a dense GDC ($Gd_{0.1}Ce_{0.9}O_{1.95}$) electrolyte substrate of ⌀ 22 mm × 1.2 mm in size. The cathode (working electrode), which had a thickness of 10 μm and an active area of 0.5 cm^2, was fabricated by screen-printing the LSM-BSCF slurry onto one side of the substrate and sintering at 1000 °C for 2 h in air. Pt paste was painted on the top surface of the cathode as the current collector and on the other side of the substrate as the counter and reference electrodes. The round counter electrode was positioned symmetrically opposite to the cathode, and the ring-shaped reference electrode was placed at the edge of the electrolyte. Electrochemical impedance spectra (EIS) of the LSM-BSCF cathode were acquired with the three-electrode cell using an impedance/gain phase analyzer (Solartron 1260) and an electrochemical interface analyzer (Solartron 1287) in air at open circuit and temperatures of 600–750 °C. To evaluate the performance stability, a cathodic current of 200 mA/cm^2 was applied at 650 °C for more than 5 h. R_P was measured every 10 min for the first 30 min, and then every 30 min thereafter at open circuit. The phase and microstructure of the LSM-BSCF cathode were examined by X-ray diffraction (XRD; PANalytical B.V.) and scanning electron microscopy (SEM; Sirion 200) before and after the impedance measurements.

3. Results and discussion

Figure 1 shows the XRD pattern of the LSM-BSCF cathode on the GDC electrolyte prior to EIS measurements. The peak positions were matched with the JCPDS files 00-053-0058 and 01-075-0161 for $La_{0.8}Sr_{0.2}MnO_3$ and GDC, respectively, and that reported in the literature for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ [22], suggesting that the cathode fired on the GDC substrate at 1000 °C for 2 h in air consisted of perovskite LSM and BSCF without other unexpected phases. Figure 2 demonstrates the cross-sectional microstructure of the LSM-BSCF cathode before and after polarization at 200 mA/cm^2 and 650 °C for 5 h. The LSM-BSCF cathode consisted of fine LSM particles (smaller than 100 nm) coated on microsized BSCF and exhibited both macro- and meso-pores, which are beneficial for both gas transport and surface reaction in the cathode as well as issues related to the CO_2-sensitivity of BSCF [14]. Compared with that of the impregnated cathodes [15,23–25], the microstructure of the

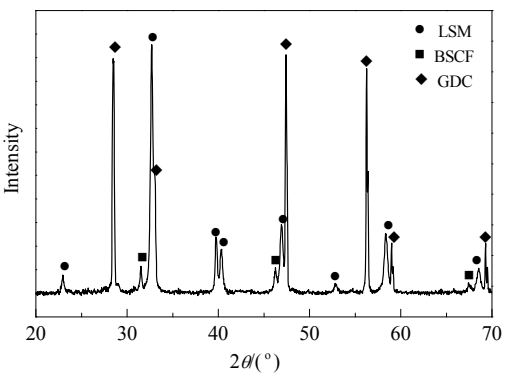

Fig. 1. XRD pattern of the LSM-BSCF composite cathode prepared on GDC electrolyte by sintering at 1000 °C in air for 2 h.