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High performance $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ -coated $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ cathode prepared by a novel solid-solution method for intermediate temperature solid oxide fuel cells

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ABSTRACT

$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM)-coated $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (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 $\Omega \text{ cm}^2$ at 600 to 750 °C. Compared with high performance cathodes prepared by solution impregnation, this LSM-BSCF cathode greatly improved performance stability.

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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 $\Omega \text{ cm}^2$ at 750 °C [3]) or impregnating GDC into LSM (0.21 $\Omega \text{ cm}^2$ at 700 °C [5]); however, polarization resistance as high as 3.25 $\Omega \text{ cm}^2$ 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 $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_3$ (LSCF) and $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_3$ (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 $\text{La}_2\text{NiO}_{4+\delta}$ (LN) [8].

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Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) is a mixed electronic and ionic conductor with high oxygen surface exchange coefficient [9], oxygen vacancy diffusion rate (7.3×10^{-5} cm²/s at 775 °C) and ionic conductivity (> Sm-doped CeO₂, 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}MnO₃ [12]). In addition, the performance of BSCF is not stable because the enrichment of Sr₂O₃ and BaO on the surface leads to the formation of carbonates in the presence of CO₂ [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 cm² 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 NH₃ 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. NH₄OH 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}MnO₃) 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 cm², 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/cm² 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}MnO₃ and GDC, respectively, and that reported in the literature for Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ [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/cm² and 650 °C for 5 h. The LSM-BSCF cathode consisted of fine LSM particles (smaller than 100 nm) coated on micro-sized 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 CO₂-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.

Fig. 2. Cross-sectional microstructure of the LSM-BSCF cathode before (a) and after (b) polarization tests at 650 °C and 200 mA/cm² for 5 h.

LSM-BSCF cathode was much more stable because it was established by firing at 1000 °C, and therefore a durable high performance was anticipated.

Figure 3(a) shows the initial open circuit EIS of the LSM-BSCF cathode measured in air at various temperatures

Fig. 3. Initial open circuit impedance spectra (a) and derived polarization resistances (b) of the LSM-BSCF cathode obtained at 600 to 750 °C.

from 600 to 750 °C. The spectra were characterized by a depressed arc, from which cathode polarization resistance R_p was derived as shown in Fig. 3(b). The R_p was 0.61, 0.44, 0.18, and 0.09 $\Omega \text{ cm}^2$ at 600, 650, 700, and 750 °C, respectively. These values are significantly smaller than those reported for pure LSM cathodes ($> 1.13 \Omega \text{ cm}^2$ between 600 and 750 °C [3]), conventionally mixed LSM/GDC ($> 0.34 \Omega \text{ cm}^2$ between 600 and 750 °C [3]) and LSM/YSZ ($> 1.31 \Omega \text{ cm}^2$ between 600 and 750 °C [3]) cathodes, GDC-modified LSM cathodes ($> 0.68 \Omega \text{ cm}^2$ at 750 °C [26]), and BSCF-impregnated LSM cathodes (0.18 $\Omega \text{ cm}^2$ at 800 °C [15]). BSCF is a mixed electronic and ionic conductor that has an extremely high oxygen exchange coefficient and ionic conductivity owing to its extremely high oxygen vacancy diffusion rate. LSM is an electronic conductor that facilitates electron transport for oxygen ionization. Therefore, the present LSM-BSCF cathode presents a unique combination of the merits of LSM and BSCF, extending the active reaction region (triple phase boundary) into the bulk from the interface of LSM and GDC and enhancing the oxygen reduction reaction.

Performance stability is an unsolved issue for BSCF cathodes; Ba and Sr are segregated on the cathode surfaces to form carbonates during exposure to CO₂ [9,13,14]. However, this stability problem can be alleviated by coating with LSM. Figure 4 shows the dependence of polarization resistance (R_p) and overpotential (η) of the LSM-BSCF cathode on testing time at 200 mA/cm² and 650 °C. R_p initially decreased from 0.44 to 0.39 $\Omega \text{ cm}^2$; this behavior is similar to that of GDC-modified LSM cathodes [26] and is considered to be related to the activation effect of the cathodic current on establishing the electronic and ionic paths. When the testing time was extended, R_p was found to increase from 0.39 to 0.72 $\Omega \text{ cm}^2$ in less than 3 h and then slowly increase to 0.80 $\Omega \text{ cm}^2$ by the end of the test. Correspondingly, η increased in a similar way. Such a slow rate of increase in R_p and η is ascribed to the stabilized cathode microstructure (Fig. 2(b)). This result is very different from that obtained with solution-impregnated cathodes such as the BSCF-impregnated LSM composite cathode, for which R_p was reported to consistently increase from 0.47 to 2.4 $\Omega \text{ cm}^2$ within 90 h at 700 °C due to significant growth of BSCF particles [15].

Fig. 4. Change in polarization resistance (R_p) and overpotential (η) of the LSM-BSCF cathode at 200 mA/cm² and 650 °C over the testing period.

Graphical Abstract

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$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM)-coated $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) composite powder (LSM-BSCF) synthesized by a novel solid-solution method, exhibited an extended triple phase boundary, reduced LSM polarization resistance, and stabilized microstructure as of the cathode.

4. Conclusions

The present LSM-BSCF cathode, which was fabricated from LSM-BSCF powder prepared by a novel solid-solution method, demonstrated a polarization resistance of 0.61, 0.44, 0.18, and $0.09 \Omega \text{ cm}^2$ at 600, 650, 700, and 750 °C, respectively, significantly lower than the results reported for most of the LSM/YSZ (or GDC) and LSM/BSCF composite cathodes in the literature. Such high performance is attributed to the unique combination of the merits of LSM and BSCF in the composite, which extended the active reaction region and enhanced the oxygen reduction activity. In addition, the stabilized cathode microstructure greatly enhanced the stability of the cathode performance.

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固-溶法制备中温固体氧化物燃料电池高性能

$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ - $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 阴极

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摘要: 研究了新型固溶法合成 $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) 包覆 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) 复合粉体 (LSM-BSCF), 并探讨了其作为中温固体氧化物燃料电池阴极材料的电化学性能。LSM-BSCF 阴极结合了 LSM 和 BSCF 阴极的优点, 不仅增大了三相界面, 而且稳定了

微观结构. 当温度为600–750 °C时, 其极化阻抗为 $0.61\text{--}0.09\ \Omega\cdot\text{cm}^2$. 与溶液注入法制备的高性能电极相比, 极大地提高了性能稳定性.

关键词: 固体氧化物燃料电池; 中温; $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ - $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 复合阴极; 极化电阻; 性能稳定性

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