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Promoted CO_2-poisoning resistance of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$-coated $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode for intermediate temperature solid oxide fuel cells

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HIGHLIGHTS

- Core-shell structure cathode was prepared by the solution impregnation technology.
- The prepared cathode has excellent CO_2-poisoning resistance.
- The LSM shell prevents the poisoning reaction and maintains the good ORR activity.

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ABSTRACT

The solution impregnation technology was used to prepare a novel core-shell structure cathode for intermediate temperature solid oxide fuel cells (IT-SOFCs). The core was composed of porous $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) backbone with high oxygen conductivity, while the dense shell consisted of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) high catalytic activity and the excellent CO_2-poisoning resistance. The presence of the dense LSM shell prevented the BSCF cathode from being poisoned by CO_2, and improved its electrochemical performance. The best performance was achieved when the BSCF cathode was impregnated twice in the LSM precursor solution and coated by LSM shell.

1. Introduction

Solid oxide fuel cells (SOFCs), which can convert the chemical energy in fuels directly to electricity with high efficiency, low emissions and excellent fuel flexibility [1,2], have attracted widespread attention in recent years. Current research activities focus on developing electrode materials operating at intermediate temperature (650–850 °C) in order to meet the requirements of the commercialization of cost and stability [3]. The lower operating temperature can make SOFCs get more applications in the field of mobile power supply, transportation and so on [4]. However, it will cause some negative effects with the temperature decrease. The most striking phenomena is the increase of the cathode polarization resistance (R_p) [5], which leads to the deterioration of the SOFCs' performance. The R_p of cathode is still the bottleneck of intermediate temperature SOFCs (IT-SOFCs) in terms of current technology [6]. Therefore, understanding the cathode reaction process, developing cathode materials with good performance for IT-SOFCs are very important for the development of IT-SOFCs.

The classical LSM cathode has excellent oxygen reduction catalyst performance, high electronic conductivity as well as the chemical and thermal compatible with the common used electrolyte yttria stabilized zirconia (YSZ) at high temperature [7–9]. However, the ionic conductivity of LSM is negligible at intermediate temperature [10], leading to sharp increase of R_p [11], and limiting its application in IT-SOFCs. Therefore, many efforts have been made

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to improve its application for IT-SOFCs by fabricating the LSM/electrolyte composite cathodes [12,13]. Recently, the perovskite oxide materials with mixed ionic and electronic conducting (MIEC) such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [14] and BSCF have been widely studied as cathode materials for IT-SOFCs because of their outstanding electrochemical performance. Among this materials, BSCF exists the best performance reported by Shao and Haile [15]. The high activity of BSCF which allows SOFCs to work with high power density can be ascribed to the highly improved oxygen surface exchange rate and MIEC. As demonstrated by Baumann [16], the electrochemical surface exchange resistance of BSCF is much lower than that of LSCF. The presence of barium and strontium, however, makes BSCF very sensitive to CO_2 at operating temperature [17]. It is found that the peak power output of SOFC with BSCF cathode is nearly halved at 600 °C when the CO_2 concentration is as low as 0.85% in the cathode atmosphere [18].

A solution impregnation technique has recently been introduced in SOFCs electrodes and shows great promise in the development of nanostructure electrodes [19]. Generally the impregnation is deposited as a collection of discrete "islands" over the cathode surface, or as a continuous thin film [20]. The precursor solution, containing the stoichiometric metal salt, proper amount surfactants and chelating agent, is introduced into a prepared backbone. The solution impregnation technique has many advantages: (a) the electrode coating introduced by impregnation is sintered at lower temperature, (b) the introduced solution may be engineer to allow control of the backbone morphology, (c) the unique properties of backbone and coating can be effectively utilized, offering the multi-functionality electrodes [21]. Li et al. [20] impregnated $Ce_{0.8}Sm_{0.2}O_{1.9}$ and $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ onto LSCF, promoting the oxygen surface exchange coefficient and the ORR kinetics of the LSCF cathode. Liu et al. [22,23] successfully prepared the LSM-coated LSCF cathode by the solution impregnation technique, suppressing the Sr-enrichment and improving the durability and performance of the LSCF cathode.

Cathode material must meet the comprehensive requirements of high MIEC, high oxygen reduction reaction (ORR) catalytic activity, high stability and high CO_2 resistivity under the working conditions [9]. However, the current single-phase cathode materials can't fulfill all these rigorous requirements at the same time. Therefore, a novel core-shell structured cathode is proposed: the core is made of material with high oxygen bulk diffusivity and electrical conductivity, while the shell is composed of material with high oxygen surface exchange rate and CO_2-poisoning resistance. In this study, BSCF is selected as the core material and the LSM is used as the shell material. By the solution impregnation method, LSM was coated densely onto the porous BSCF backbone to optimize the electrochemical performance and CO_2-poisoning resistance of BSCF for their utilization in IT-SOFCs.

2. Experimental details

2.1. Synthesis and characterization of BSCF

The BSCF powder was synthesized by the EDTA-citrate-metal mixing method. Appropriate amounts of Ba, Sr, Co and Fe nitrates (AR, 99%, Aladdin Industrial Corporation) were dissolved into distilled water. EDTA was dissolved into ammonia and mixed into the metal ions solution, and then the citric acid was added. The molar ratio of the metal ions, EDTA, and citric acid was 1: 1: 2. NH_4OH was used to adjust the pH to 7–8 and the solution was stirred in the oil bath pot at 80 °C to form a dark-red gel. The obtained gel was dried at 180 °C to form the black-bread precursor. The precursor was sintered at 900 °C for 4 h in air, followed by ball-milling to obtain the BSCF powder with an average particle size of 500 nm. The BSCF particles of nanometer sizes were used to fabricate the cathodes in order to increase the three-phase boundary (TPB) [24].

The phase analysis of BSCF was analyzed by X-Ray Diffraction (XRD, Panalytical X'Pert). XRD was operated at 40 kV and 40 mA, with Cu-K_α radiation. The samples were the form of powder or block, and the spectra was collected over the angular range $20^\circ < 2\theta < 80^\circ$.

2.2. Half cell fabrication and performance test

The prepared BSCF powder was mixed with binder and activated carbon powder, followed by manually grinding in a mortar to obtain the BSCF cathode paste. The activated carbon powder was acted as the pore former to control the porosity. The obtained cathode paste was screen printed on one side of electrolyte pellet and sintered at 1000 °C for 2 h in air to prepare the half cells. After being sintered, the cathode had a thickness of 10 μm and an active area of 0.5 cm^2.

To prepare the precursor solution, appropriate amounts of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Mn(NO_3)_2 \cdot 4H_2O$ (AR, 99%, Aladdin Industrial Corporation) were dissolved in a mixture of distilled water and isopropyl alcohol (1: 4, vol/vol) to prepare 0.05 mol L^{-1} LSM precursor solution. Glycine was added as the chelating agent which the molar ratio of it to LSM was 1.5: 1, in order to control the phase formation and morphology. Polyvinyl pyrrolidone (PVP, Aladdin Industrial Corporation) was used (~5 wt% relative to the amount of LSM) as the surfactant to improve the wetting of the solution onto the BSCF backbone. The mixture was stirred 6 h before the impregnation process. A small amount of solution was sintered according to a two-step procedure: up to 400 °C for 1 h to decompose the glycine and the PVP, and then up to 800 °C for 2 h. The phase analysis of LSM was also analyzed by XRD.

LSM precursor solution was impregnated onto the as-prepared porous BSCF backbone with a micro syringe 1–4 times, respectively. Then the half cells were placed under vacuum for 1 h in order to let LSM solution have good contact with the entire backbone. By calculating, LSM was about 2 wt% relative to the amount of BSCF when impregnating 1 time. The half cells after impregnation were sintered according to the two-step procedure to obtain the desired crystalline phase of LSM. To evaluate the cathode electrochemical performances, Pt paste was painted on the top surface of the cathode as the current collector. The cathode side, the other side of the GDC pellet and the ring-shaped edge of the electrolyte were working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively. Polarization impedance of the cathodes was acquired by using the impedance/gain phase analyzer (Solartron 1260) and an electrochemical interface analyzer (Solartron 1287) in air at open circuit and temperatures of 600–750 °C. The frequency range was 0.1 Hz–100 kHz and the signal amplitude was 10 mV. The microstructure of the cathodes was examined by scanning electron microscopy (SEM, Sirion 200).

3. Results and discussion

3.1. Phase and structure

SOFC cathode should be chemically compatible with the electrolyte under the operation and fabrication conditions. The electrolyte material used in this study is $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC), which is found to have good chemical compatibility with a wide variety of electrodes, including many well-investigated cobalt-containing materials [25]. The XRD patterns of the BSCF, LSM, GDC and their mixed powder sintered at 1000 °C for 2 h in air are presented in Fig. 1. The spectrums show that the pure perovskite phases of BSCF