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Liquid plasma sprayed nano-network $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_3$/$Ce_{0.8}Gd_{0.2}O_2$ composite as a high-performance cathode for intermediate-temperature solid oxide fuel cells

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HIGHLIGHTS

- Liquid plasm spraying was applied to prepare LSCF/GDC composite cathodes.
- The optimized cathode prepared by 15 g L^{-1} suspension has a nano-network structure.
- The cathode prepared by 15 g L^{-1} suspension exhibits R_p of 0.1 Ω cm^2 at 600 °C.
- The optimized cathode shows a good stability at 650 °C for more than 350 h.

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ABSTRACT

Here, we investigate the feasibility of using a liquid plasma spray process as a novel method for the cost-effective fabrication of a nanonetwork of $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC) composite as a high-performance cathode for intermediate-temperature solid oxide fuel cells. A suspension containing well-dispersed nanosized GDC particles in an LSCF precursor solution is designed as the feedstock. The effects of GDC concentration in the suspension on the phase composition, microstructure, and electrochemical performance of the resulting cathode are studied. When the GDC concentration increases to 15 g L^{-1}, the nanosized GDC particles distribute uniformly and continuously on the LSCF backbone to form a porous network structure. The electrochemical studies further indicate that the cathode polarization decreased with the increase in GDC concentration from 0 g L^{-1} to 15 g L^{-1}, whereas a further increase in the GDC concentration increases the cathode polarization instead. At 600 and 750 °C, the cathode prepared using 15 g L^{-1} GDC concentration exhibits an impressive area-specific polarization resistance (R_p) of 0.1 Ω cm^2 and 0.009 Ω cm^2, respectively. Finally, the R_p of the optimal cathode almost does not change after the isothermal dwelling at 650 °C for 350 h.

1. Introduction

Solid oxide fuel cells (SOFCs) convert chemical energy stored in a fuel to electricity with many advantages such as fuel flexibility, high efficiency, low emission, and environmental friendliness [1–4]. To commercialize the SOFC technology, a major research effort in recent years has been to reduce the operating temperature to below 700 °C [5], where cost and reliability, the two main challenges of SOFC technology, can be best met [4,6–10]. However, lowering the operating temperature would not only increase the electrolyte resistance, but also decrease the kinetics of electrode reactions, resulting in an appreciable increase in the cell resistance [11,12]. With the use of thin-film electrolytes, the performance of intermediate-temperature SOFCs (IT-SOFCs) has become more limited by cathode polarization. Therefore, a critical step towards

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IT-SOFCs is the development of new materials [13–15] or novel microstructures with a low polarization loss [16,17].

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)-based cathodes have been extensively investigated for IT-SOFCs because of significantly higher mixed ionic and electronic conductivity in the temperature range 600–800 °C [18,19]. $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) [20], $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC) [21], and a precious metal such as Pt, Pd, and Ag [22–24] have been commonly blended with LSCF to further increase the performance by increasing oxygen reduction reaction (ORR)-active triple-phase boundary (TPB). Many studies have clearly indicated that the polarization resistance of LSCF/GDC composite cathode is several times lower than that of the pure LSCF cathode [25,26]. Moreover, the cathode performance is not only affected by the material itself, but also by the microstructure, Which is mainly controlled by the fabrication process. The most common fabrication methods for LSCF-based composite cathodes follow either a screen printing or an infiltration approach [27–29]. In particular, the nanostructures obtained by the infiltration method yield a low polarization resistance in the IT-range. In this method, a porous LSCF backbone is first prepared by the screen printing or tape casting method. Then, the backbone is infiltrated with the GDC or SDC precursor solution. After the firing, the precursor decomposes into GDC or SDC nanoparticles on the surface of the LSCF backbone. One disadvantage of this method is the high temperature (>900 °C) required for sintering the porous LSCF backbone in an oxidation atmosphere, which is not suitable for metal-supported SOFCs. Moreover, the infiltration process is tedious and production unfriendly, requiring many steps to achieve the desired mass loading. Therefore, alternative fabrication processes should be developed to prepare high-performance LSCF-based composite cathodes at low temperatures and with a low cost.

Suspension plasma spraying (SPS) and solution precursor plasma spraying (SPPS) techniques have been recently developed for the cost-effective fabrication of SOFCs. Plasma spraying (PS) is a widely proven low-cost, large-scale industrial coating process. One of the advantages of PS for SOFCs is the fact that the sprayed cells are ready for assembly, and further processing of the coatings at higher temperatures is not required after the deposition [30,31]. However, conventional plasma sprayed ceramic deposits always show a lamellar structure [32,33]. The deposit unit always has a diameter of >20 μm and thickness of >1 μm. Hence, it is difficult for conventional PS to deposit nanostructured coatings. SPS and SPPS are two derivatives of conventional PS where a liquid solution is used instead of solid particles as the feedstock. The advantage of SPS and SPPS over the conventional PS is the ability to fabricate nanostructures; this is critical for increasing the ORR activity of IT-SOFCs. We have previously demonstrated that SPS can be used to deposit a high-performance composite anode [34]. However, to the best of our knowledge, only a few studies have been reported on the fabrication of LSCF-based composite cathode by SPS [35]. Particularly for SPPS, impure phases are frequently formed during the spraying process when two types of liquid precursors are mixed, thus making it difficult for SPPS deposition for composite cathode application.

We recently observed that high-performance LSCF/GDC composite cathodes can be deposited by a combination of SPS and SPPS. In this study, nanosized GDC particles were added to the LSCF precursor solution, affording a suspension as the feedstock. The precursor solution may react to LSCF under the heating of a plasma gas, whereas GDC particles adhere to LSCF, forming composite agglomerates in the final deposits. Compared to the high melting point of GDC (~2500 °C), LSCF with a much lower melting point (~1890 °C) is easier to sinter and melt during the spraying. Therefore, the LSCF may form backbones with larger connected grains; nanosized GDC particles adhere to them, forming a network structure, and providing more TPBs.

In this study, the phase composition, microstructure, and electrochemical performance of SPS–SPPS-derived LSCF/GDC composition cathodes for IT-SOFCs were systematically characterized.

2. Experimental

Stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$ (99.99%, SCRC), $Sr(NO_3)_2 \cdot 6H_2O$ (99.99%, SCRC), $Co(NO_3)_2 \cdot 6H_2O$ (99.99%, SCRC), and $Fe(NO_3)_3 \cdot 9H_2O$ (99.99%, SCRC) were dissolved in a water/alcohol (99.7%, Ante) solvent (1:1 vol%), affording a nitrate solution of 0.05 M concentration. Nanosized GDC particles (~50 nm, Fuel cell materials, USA) were then added to the precursor solution, affording a suspension. The GDC concentration of the suspension was controlled at 0, 5, 10, 15, and 20 g L^{-1}. The prepared suspension was sprayed using a conventional air plasma spraying system (GDP-80, Jiujiang, China). Fig. 1 shows the schematic diagram of the spraying process. The suspension was injected into the plasma jet using a peristaltic pump (Qdos 30, England). The parameters for spraying LSCF/GDC cathodes are shown in Table 1.

Sc_2O_3-stabilized ZrO_2 (ScSZ) pellet was used as the substrate for deposition; ScSZ served as the electrolyte because of its high ionic conductivity at intermediate temperatures (600–800 °C). To prepare ScSZ substrates, ScSZ powders (~300 nm, TERIO, Qingdao, China) were pressed into pellets with a diameter of 15 mm under a pressure of 100 MPa. The pellets were then densified at 1400 °C for 5 h. The final products had a diameter of 13 mm and a thickness of ~1 mm. The density of the sintered pellets reached more than 97% (tested by Archimedes method).

To characterize the cathode performance, symmetric cells of the LSCF/GDC|ScSZ|LSCF/GDC were prepared by depositing approximately 20–30 μm thick LSCF/GDC composite on both sides of the ScSZ substrates with a diameter of 8 mm. Prior to the electrochemical characterization, silver paste/meshes were attached as the current collectors for the symmetric cells and annealed at 700 °C in air for 2 h. The electrochemical impedance spectroscopy (EIS) of the symmetrical cells was then carried out using a Solartron SI 1260/1287 impedance analyzer in ambient air under open-circuit voltage (OCV) conditions. The sweeping frequency range was 0.1–10^5 Hz at an amplitude of alternating circuit (AC) voltage of 20 mV.

The phase compositions of the prepared cathodes were investigated by X-ray diffraction (XRD) analysis (X'Pert PRO, PANalytical, Netherlands). The microstructures of the cathodes were analyzed using a scanning electron microscope (SEM, TESCAN MIRA 3 LMH, Czech). The distribution and content of GDC in the final cathodes were quantified by energy-dispersive X-ray (EDX) analysis.

3. Results and discussion

3.1. Phase composition and microstructure

Fig. 2 shows the XRD patterns of the cathodes deposited by

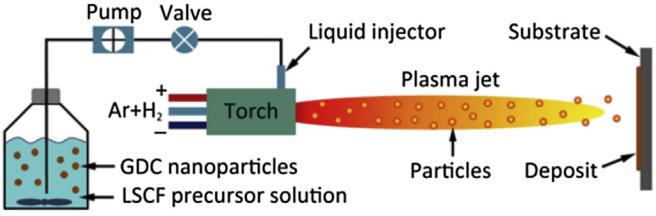

Fig. 1. Schematic diagram of the spray process.