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Full Length Article

Enhanced sintering behavior of LSGM electrolyte and its performance for solid oxide fuel cells deposited by vacuum cold spray

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ABSTRACT

How to obtain dense $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) electrolyte at low sintering temperature (<1300 °C) is a challenge to improve solid oxide fuel cell (SOFC) performance at intermediate operation temperature. In this study, a double-layer design method for vacuum cold spray (VCS) prepared-LSGM electrolyte assisted with two-step sintering at a low temperature was proposed. The sintering behavior of VCS deposited LSGM layers at 1200 °C was investigated. The LSGM layers became denser in most regions except the appearance of some cracks. Subsequently, the effect of a second LSGM layer on the sintered top layer was studied to block cracks. Results showed that the co-sintered layer with a thickness of approximately 5 μm presented a maximum open circuit voltage of ~0.956 V at 650 °C and a maximum power density of 592 mW/cm^2 at 750 °C. Result indicates that the sintering assisted VCS is a promising method to prepare the LSGM electrolyte applied in intermediate temperature SOFCs.

1. Introduction

Solid oxide fuel cell (SOFC) have attracted considerable attention in recent years as a power conversion system, owing to its high-energy conversion efficiency, fuel flexibility and low pollution emissions as well. However, a high operating temperature (>1000 °C) of the SOFC brings up some challengeable problems, e.g., limited material choices for the electrode and the electrolyte, cell sealing and a high manufacturing cost [1,2]. Therefore, significant efforts have been made to decrease the operating temperature of SOFC. Towards this orientation, intermediate temperature solid oxide fuel cell (IT-SOFC, 600–800 °C) appears to be an alternative choice for the development of SOFC. Challenges to develop the IT-SOFC are at least twofold. The first is material choices for both the electrode and the electrolyte. As a traditional material choice for the electrolyte, yttria-stabilized zirconia (YSZ) with an ionic conductivity of 0.14 S/cm at 1000 °C is widely used at high temperatures [3,4]. However, the ionic conductivity of YSZ decreases dramatically below 800 °C. Therefore, it is of great importance to find a new electrolyte material, which can remain a high ionic conductivity even at the intermediate temperature. Fortunately, some material choices, e.g., gadolinia/samaria-doped ceria (GDC/SDC) [5,6], stablized-Bi_2O_3 [7], as well as strontium- and magnesium- doped lanthanum gallate (LSGM) [8,9], have been developed as potential electrolyte candidates for the SOFC applied at low temperatures. In the case of the GDC/SDC, one main limitation is its mixed ionic and electronic conduction, which is caused by the reduction of ceria from Ce^{4+} to Ce^{3+} when it is exposed to reduced atmosphere [5]. In the case of the Bi_2O_3-based material, it is challengeable to overcome its phase instability in reduced atmosphere and the evaporation of bismuth oxide at the operating temperature, although it remains a high ionic conductivity at the low temperatures [7]. In contrast, it seems that the LSGM with a perovskite structure potentially leads the material choice of electrolyte, owing to its high ionic conductivity (~0.1 S/cm at 800 °C), negligible electron conductivity, as well as high stability over a wide oxygen partial pressure range [8,9].

The second challenge for the IT-SOFC is the fabrication method for electrolyte. Conventional fabrication methods for the LSGM electrolyte include dip-coating [10], screen printing [11], and sol-gel method [12]. Nevertheless, the aforementioned methods are often aided with high temperature sintering at 1350–1500 °C to obtain dense LSGM films [10–12]. Unfortunately, undesirable chemical reaction between the electrolyte with other cell components at these high temperatures significantly deteriorates the cell performance. For instance, the interfacial reaction between Ni-based anode and the LSGM occurs above 1350 °C, which results

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in unexpected degradation of the cell performance [13–15]. Air plasma spraying (APS) seems to be another potential method to prepare the LSGM electrolyte. As reported previously, the LSGM electrolyte with a thickness of approximately 55 μm was successfully fabricated by the APS [16]. They effectively controlled the Ga evaporation by optimizing the process parameter and the spray powder. Consequently, an excellent performance of the IT-SOFC with a plasma-sprayed LSGM electrolyte was achieved. In addition, the APS method can eliminate the interfacial reaction between electrolyte and electrode at a high temperature. However, the APS is relatively difficult to prepare a thin electrolyte layer (e.g., <20 μm) with low ohmic resistance, which is required to assemble the IT-SOFC with excellent performance. Therefore, it is necessary to develop a low temperature deposition process to fabricate the thin electrolyte with both lower ohmic resistance and less depletion of Ga.

Vacuum cold spray [17], also known as aerosol deposition [18], has been widely used to deposit thin ceramic films. During the VCS, ceramic particles are firstly injected into the vacuum chamber by a pressure difference between powder feeder and deposition chamber. Subsequently, these particles are deposited on substrate through post-deformation or fragmentation upon impact in their solid states at room temperature [18]. Numerous investigations on preparing films by the VCS have been documented, such as the Al_2O_3 coating applied for the integral radio-frequency modulus [19], the nano-structured TiN-SiC composite coatings applied as electrical conductors [20], the porous nano-crystalline TiO_2 photoanode coatings in dye-sensitized solar cells [21,22], as well as the hydroxyapatite/graphene coating for biomedical application [23]. Based on these investigations, it is obvious that the VCS is more readily to deposit meso-porous nanostructured coatings, since the VCS-prepared coatings often exhibit nano-grain sizes. However, regarding the preparation of electrolyte applied in the SOFC, it is still much challengeable to obtain a dense coating using the VCS. Moreover, the mechanisms concerning the deformation and the subsequent deposition were still unclear. Therefore, it is highly necessary to further optimize the deposition process of the VCS, with the aim to prepare dense thin films applied for the SOFC.

Lakshmi et al. [24] obtained dense bulk ScSZ with nanocrystalline powders through low temperature sintering at 1250 °C (the sintering temperature of the micro-sized scandium-stabilized zirconia is 1400–1500 °C [25,26]), indicating that the sintering temperature of a ceramic material can be lowered when it is composed of nano-sized particles or nanograins. As reported by Morales et al. [27] in their review article, the advantages of lowering the sintering temperature of LSGM include: avoiding the volatilization of gallium oxide, preventing interface reaction and lowering the manufacturing temperature of SOFCs. They also summarized that the methods for lowering sintering temperature include adopting some processing techniques and using sintering additives. Raghvendra et al. [9] obtained dense $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM1020) samples without the secondary phases, which were synthesized by an ethylene-glycol method following by sintering at 1400 °C. Morales et al. [28] also synthesized a pure perovskite LSGM1520 via the ethylene-glycol method at a relatively lower sintering temperature of 1350 °C. Moreover, it has been reported that the interfacial reaction between the NiO and the LSGM can be neglected at a temperature below 1300 °C [14,15]. Therefore, it may be potentially possible to densify the VCS-prepared mesoporous LSGM coating, which is composed of nanosized particles, through a post-sintering process at a lower temperature (e.g., <1300 °C).

In the present study, a double-layer method deposited by the VCS was developed to prepare the thin LSGM layer. Subsequently, a post-sintering process at a low temperature of 1200 °C (the common sintering temperature of the LSGM is above 1400 °C [29,30]) was carried out to further enhance the densification of the VCS-prepared LSGM coatings. Finally, the cell performance of an anode-supported SOFC was evaluated by using the densified LSGM layer as an electrolyte membrance.

Table 1
Deposition parameters of the vacuum cold spray.

Parameter	Unit	Value
Chamber pressure	Pa	250
He gas flow rate	L/min	6.5
Distance from nozzle exit to substrate	mm	5
Nozzle traversal speed	mm/s	30
Nozzle orifice size	mm × mm	2.5 × 0.2
Spray passes	times	2, 4, 8

2. Experimental

2.1. Materials

A commercially available powder $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) (Tian-yao. Inc., Qingdao, China) was used as the starting powder. The morphology and the particle size distribution of the starting powder are shown in Fig. 1. It can be observed that the powder exhibits an angular morphology (see Fig. 1a) and that the average particle size was ~1.5 μm (see Fig. 1b). An anode-supported SOFC was used as the substrate to investigate the power generation performance. The disk-shaped anode, which is composed of NiO-8YSZ (50 vol.% NiO), was prepared by a tape casting process. In order to avoid chemical reaction between the Ni and the LSGM, a $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) layer (2–3 μm) was coated preferentially on the NiO/YSZ substrate by using the tape casting.

2.2. Preparation of LSGM coating and sintering procedure

LSGM coatings were deposited using a VCS-2000 vacuum cold spray system developed in our laboratory. As reported previously [31,32], the system consists of a vacuum chamber, an aerosol chamber, a carrier gas unit, a two dimensional workable, and a control unit. As soon as the pressure in the vacuum chamber reaches 20 Pa, the powders carried by helium gas are injected into the vacuum chamber via an accelerating nozzle. Through the movement of the nozzle back and forth, the powders impact on substrate to form a relatively uniform coating. Additionally, during deposition, the chamber pressure is controlled as a constant value of 250 Pa. Deposition parameters of the VCS are shown in Table 1. Different thicknesses of the LSGM coatings can be obtained by changing the scanning passes [31,33]. In this study, a coating obtained by *n* spray passes was termed as the C*n*. For instance, a coating deposited by 2 spray passes corresponds to the C2. After deposition, the obtained LSGM layers were further sintered at 1200 °C for 5 h.

2.3. Characterization of the LSGM coating

Surface and cross-sectional morphologies of the LSGM coatings were examined by using a scanning electron microscope (SEM) system (TESCAN MIRA 3 LMH, Czech Republic). Grain size was measured using a linear intercept method based on the SEM images of the coating surface. At least 10 SEM images were used to estimate the average grain size. Back scattered electron (BSE) images were used to characterize fractured cross-sections of the different coatings. Porosities of the co-sintered LSGM coatings and the GDC buffer layer were characterized by image analysis. At least 10 BSE images were used to determine the average porosity.

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