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Scandia-stabilized zirconia electrolyte with improved interlamellar bonding by high-velocity plasma spraying for high performance solid oxide fuel cells

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HIGHLIGHTS

- ► High-velocity plasma-sprayed ScSZ electrolyte was used directly to SOFC.
- ► In-flight particle diagnostics are employed to select the optimal spray parameters.
- ► ScSZ prepared by SAPS exhibits higher gas tightness than conventional APS.
- ► Electrolyte gas tightness is improved by the increasing of deposition temperature.
- ► Output power density is increased about 70% with the growth of long columnar crystal.

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ABSTRACT

A main challenge of conventional atmospheric plasma spraying (APS) in the application for SOFCs is how to fabricate the dense electrolyte which can be used directly. In this study, supersonic atmospheric plasma spraying (SAPS), one of the high-velocity plasma spraying technologies, was used to prepare scandia-stabilized zirconia (ScSZ) electrolyte to enhance the performance of SOFCs by decreasing the porosity and improving the ionic conductivity with the continuous growth of columnar grains across splat interfaces. The temperature and velocity of in-flight ScSZ particles were measured, and the influences of deposition temperature on the microstructure and cell output performance were investigated. Results showed that the as-sprayed ScSZ prepared by SAPS exhibited higher gas tightness than conventional APS by approximately one order of magnitude. With the increase of deposition temperature from 200 °C to 600 °C, the microstructure of ScSZ electrolyte changed from the traditional lamellar structure with limited interface bonding to the long columnar crystal structure, and the maximum output power densities of the cells with 60 μm ScSZ electrolyte prepared by SAPS increased by more than 70% with the increase of deposition temperature from 200 °C to 600 °C and reached 995 mW cm^{-2} at 1000 °C.

1. Introduction

Solid oxide fuel cells (SOFCs) have been widely investigated as an efficient and environmentally friendly alternative to conventional power generation using fossil fuels. The performance of SOFCs is generally limited by the internal ohmic losses and the electrochemical-catalytic activity of electrodes [1]. Electrolytes have the lowest electrical conductivity among all functional layers in SOFCs, especially at low temperature [2,3]. Therefore, the use of an electrolyte with high electrical conductivity is one of the effective approaches to improve the performance of SOFCs. Scandia-stabilized zirconia (ScSZ) is one of the zirconia-based electrolyte materials that exhibit higher electrical conductivity than other zirconia-based materials. The maximum electrical conductivity of ScSZ bulk is approximately 0.36 S cm^{-1} at 1000 °C, in comparison to 0.16 S cm^{-1} of yttria-stabilized zirconia (YSZ), which has been extensively used in SOFCs [4]. Moreover, ScSZ conductivity at 780 °C is comparable to that of YSZ at 1000 °C [1]. The activation energy for the transport of oxygen ions in the ScSZ materials is also lower than in YSZ materials [1]. Many studies have shown that SOFCs that use ScSZ as electrolytes exhibited better performance than SOFCs using YSZ electrolytes [5,6].

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The fabrication process of electrolytes also plays an important role in the SOFC's commercial applications. Atmospheric plasma spraying (APS) is one of the most promising processing methods for the production of the components used in SOFCs; APS has many cost-effective characteristics, including its flexibility and easy automation features, compared with the film-formation processes of electrochemical vapor deposition (EVD) [7], vacuum plasma spraying (VPS) [8], and sol–gel method [9]. Compared with conventional coating technologies, such as tape casting [10], screen printing [11], and dip coating [12], plasma-sprayed electrolyte does not need sintering at a high temperature which will easily introduce many defects, such as warp, crackle and pores for the cells with a large area.

However, the ceramic coatings deposited by traditional APS have high porosity, and the pores in the coating are linked with the unbonded interfaces and microcracks. Because of these features, traditional APS ceramic coating may not be suitable for SOFCs electrolytes, directly [13–17]. Instead, a sintering process, which is described as the "thermal spraying-sintering process", has been investigated following plasma spraying, to obtain improved gas tightness, a thinner layer, and higher electric conductivity of the electrolyte [18,19]. However, the high-temperature sintering process usually causes other problems, including interface reactions, increased cost, and unsuitability for metal-supported SOFCs. Furthermore, the YSZ electrolyte deposited by vacuum plasma spraying (VPS) exhibited acceptable performance [20,21]. Comparing VPS with traditional APS for spraying electrolytes, the main improvements of VPS over APS are a relatively high in-flight particle velocity and temperature obtainable, in addition to the low-pressure atmosphere for deposition. The dense YSZ electrolyte can be fabricated by a three-cathode APS torch, which also showed a relatively high in-flight particle velocity and temperature [22]. Three key parameters influence the coating microstructure and properties: in-flight particle velocity, temperature, and particle size. For the powders with a determined size range, only particle velocity and temperature have strong influences on the coatings microstructure [23]. Many previous investigations showed that the density of the coatings can be significantly improved with the boost of particle velocity when the temperature of particle prior deposition exceeds the melting point. Therefore, a high-velocity thermal spray process is preferable for deposition of dense electrolyte.

As one of the high-velocity plasma spraying technologies, supersonic atmospheric plasma spraying (SAPS) is characterized by high velocity of supersonic plasma jet, which is much higher than that of conventional APS. Furthermore, it works at atmospheric pressure and has operating costs similar to those of traditional APS. Therefore, SAPS will be a potential process for the future fabrication of high performance electrolytes for SOFCs, due to its features of high velocity and temperature.

The gas-leakage channels in the plasma-sprayed ceramic coatings consisted of pores, microcracks, and unbonded interfaces. Although the particle velocity significantly affects the porosity of the coatings, it has limited influence on the cohesive bonding of plasma-sprayed coating [15]. The mean bonding ratio at the interfaces between splats of ceramic coatings deposited by conventional APS or VPS is less than 1/3 of the total apparent interface area; this has a significant influence on ionic conductivity and gas tightness of as-sprayed electrolyte [24].

Recently, another parameter that influences the cohesive bonding of the coatings has been identified [24]: the deposition temperature is the coating surface temperature prior droplet impact during deposition. Our previous research [24] showed that with the increase of deposition temperature, the microstructure of YSZ coatings deposited by APS changed from the typical lamellar structure to the continuous columnar crystal structure. This structural change led to the increased lamellar interface bonding and, subsequently, the increased ionic conductivity of the plasma-sprayed YSZ. Therefore, the electrolyte prepared at a high deposition temperature may exhibit improved performance, with high ionic conductivity and gas tightness.

The purpose of this study was to fabricate a dense electrolyte that can be used directly for SOFCs by high-velocity plasma spraying. The performance of as-sprayed electrolyte would be improved by three aspects. Firstly, ScSZ with a high ionic conductivity was used as the electrolyte material. Then, the ScSZ electrolyte was prepared by SAPS to increase the density and the gas tightness due to the high in-flight particle velocity and temperature. Finally, the ScSZ electrolyte was further improved by the growth of long columnar crystal structures at a relatively high deposition temperature. Therefore, in this study, the ScSZ electrolyte was deposited at different temperatures by SAPS to examine the effect of the deposition temperature on microstructure and gas-leakage rate of ScSZ deposit and SOFC performance. The influences of spray distance on the ScSZ particle velocity and temperature were investigated to examine the factors that control cell performance.

2. Experimental

2.1. Material feedstock

In this study, a fuse-crushed 10 mol% Sc_2O_3-stabilized ZrO_2 doped with 1 mol% CeO_2 and 0.1 mol% Al_2O_3 powder (Fujimi Co., Japan) was used as the electrolyte feedstock. By the addition of CeO_2 [25] and $A1_2O_3$ [26], the 10 mol% Sc_2O_3-stabilized ZrO_2 showed a cubic phase at room temperature and had no phase transformation with the increase of temperature. The powder has a size range of 5–25 μm and shows an irregular shape (Fig. 1a). Commercially available 8 mol% YSZ powder (Fujimi Co., Japan, $-25 + 5$ μm) was also used for comparison to ScSZ. Results from our previous study [27] suggested that plasma-sprayed anode with NiO/YSZ agglomerated powders had a long three-phase boundary (TPB) and exhibited a good performance. Therefore, in order to prepare an anode with sufficient TPB and high electron and ionic conductivity, the agglomerates of NiO particles less than 5 μm with ScSZ particles less than 10 μm were used as the feedstock powders to deposit the anode. The agglomerated powders had a particle size of 50–70 μm (Fig. 1b). In this study, plasma-sprayed $La_{0.8}Sr_{0.2}MnO_3$ (LSM) was used as the cathode. Although the LSM showed relatively low catalytic activity for oxygen reduction at the lower temperatures, it had good chemical and physical compatibility with zirconia-based electrolyte material even at 1000 °C [1]. Therefore, we used commercially available agglomerated LSM powders with a size range of 30–70 μm (Fig. 1c) for the preparation of the cathode to investigate the cells performance.

2.2. In-flight particle diagnostics

The surface temperature and velocity of in-flight ScSZ particles were measured by the spray watch system (spray watch-2i CCD system, Oseir, Finland). In this study, experiments were carried out using a SAPS system (HEPJ-100, 80 kW class) and APS system (GPD-80, Jiujiang, 80 kW class). The anode nozzle of the SAPS torch was designed as a Laval nozzle, which had a throat diameter of 4 mm and exit diameter of 5.5 mm. The spray distance was increased from 70 mm to 140 mm for the SAPS and from 60 mm to 110 mm for the APS to investigate the temperature and velocity of in-flight ScSZ particles (Table 1). An optimal spray distance, in which the particles had a higher temperature and velocity, was selected to fabricate the electrolyte.