Atmospheric plasma-sprayed $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) electrolyte membranes for intermediate-temperature solid oxide fuel cells

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Abstract:

The high co-sintering temperature of BZCYYb electrolyte membranes supported by anode substrates usually causes a series of problems including undesirable electrolyte-anode reactions/diffusion and Ba-evaporation, posing a challenge for seeking alternative fabrication approaches. In this study, BZCYYb electrolyte membranes supported by anode substrates are fabricated by a large-scale and cost-effective atmospheric plasma spraying (APS) process. The 25 μm thick BZCYYb membrane has negligible electrolyte-anode reactions/diffusion due to the APS process free of high-temperature co-firing. The Ba-evaporation problem is also resolved during APS process because of the adoption of

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large-grained BZCYYb feedstock powders. After 15 cycles of post-densification treatment by infiltrating, the plasma-sprayed BZCYYb membrane is dense enough for electrolyte application. The single cell based on dense plasma-sprayed BZCYYb electrolyte membrane shows a peak power density of 0.35 W cm^{-2} at 750°C using 3 vol. % humidified H_2 as fuel and ambient air as oxidant.

Keywords: Atmospheric plasma spraying; solid oxide fuel cell; doped barium cerate; electrolyte membranes; post-densification.

1. Introduction

Solid oxide fuel cells (SOFCs) hold promise to be the most efficient and environmentally benign system for power generation from a wide variety of readily available fuels, including coal gas, natural gas and gasified carbonaceous solid fuels (e.g. municipal solid waste and biomass).^[1-7] With the development of SOFCs progresses, one of the concerns for the commercialization of SOFCs technologies is to reduce the operating temperature to less than 800°C to reduce fuel cell costs.^[8] However, one challenge associated with lowering the SOFCs operating temperature is the significant decrease of the ionic conductivity of the solid state electrolyte.^[9, 10] Thus, it is necessary to develop an electrolyte of high ionic conductivity for applications of intermediate-temperature solid oxide fuel cells (IT-SOFCs).

In recent years, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb), a proton and oxygen ion mixed conductor, has been regarded as a promising electrolyte for IT-SOFCs because of its superior ionic conductivity ($\sim 0.01 \text{ S cm}^{-1}$ in humidified O_2 at 500°C) and adequate stability under typical fuel cell operating conditions.^[5] However, the densification of BZCYYb electrolyte requires a high sintering temperature ($>1550^{\circ}\text{C}$)

and a long holding time (>10 h).^[5] Such sintering conditions may result in a series of problems such as abnormal grain growth, dramatically mechanical properties degrade and undesirable electrolyte-electrode reactions/diffusion during co-firing,^[11] making the fabrication of BZCYYb thin films supported by an electrode (anode or cathode) difficult. In addition, Ba evaporation during high temperature sintering for extended times may also reduce the conductivity of the electrolyte.^[12-14] S. Wang et al.^[15] have successfully fabricated dense BZCYYb electrolyte membranes at a relatively low temperature (1300°C) by a two-step sintering method, but the long holding time (20 h) leads to a low cell efficiency. For large-scale production, it is highly desirable to develop a cost-effective approach for the fabrication of dense BZCYYb membranes on anode substrates without high-temperature firing.

Atmospheric plasma spraying (APS), a proven low-cost, large-scale industrial production process, has been developed and used for fabrication of SOFCs due to its characteristic fast deposition rate.^[16] Some electrolytes, such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) and yttria-stabilized zirconia (YSZ) have been produced using APS.^[17-22] The unique advantage of APS is that thin electrolyte membranes can be prepared on an electrode or metal substrate without high-temperature firing.^[17] However, APS-sprayed coatings are generally not suitable for direct use as electrolytes in SOFCs due to their high gas permeability.^[20] Some post-densification processes including sintering^[23, 24] and infiltration^[20, 22] have been attempted to densify the as-prepared film. Infiltration of metal nitrate solutions has been proven to be a more effective method for post-densification. For example,

plasma-sprayed YSZ electrolyte coatings can be densified to a gas permeability level satisfactory for the operation of SOFCs by infiltrating yttrium and zirconium nitrate solutions into the coating followed by heat-treatment at 400°C. [25, 26] Therefore, the post-densification treatment through infiltration makes it possible to fabricate dense plasma-sprayed electrolyte membranes.

In this study, APS was employed to fabricate BZCYYb electrolyte membranes on porous NiO-BZCYYb anode substrates. To our knowledge, plasma-sprayed BZCYYb electrolyte membranes were obtained for the first time. To densify the plasma-sprayed BZCYYb membranes, metal nitrate solutions according to the stoichiometry of BZCYYb were infiltrated into the membranes followed by heat-treatment with several repeated cycles. Finally, single cells based on dense plasma-sprayed BZCYYb electrolyte membranes were fabricated and evaluated.

2. Experimental

2.1 BZCYYb powder synthesis

In our previous study of LSGM, [17] we found that Ga-evaporation during the APS process leads to the formation of Ga-deficient splats, thus dramatically reducing the ionic conductivity of the APS-fabricated LSGM film. Considering the similar characteristics of Ba-evaporation in the BZCYYb electrolyte to Ga-evaporation in the LSGM electrolyte, [14] Ba-deficient splats may also be formed during the APS process. In the LSGM study we found that element evaporation could be avoided by increasing the size of the feedstock powders. [17] Therefore, large-grained BZCYYb powders were used in this study. BZCYYb primary powders were prepared by a traditional

solid state reaction (SSR) method as described elsewhere. ^[5] The primary powders were then pressed into pellets, crushed into aggregated particles, sieved to separate small particles and fired at 1350°C for 5 h. As a result, BZCYYb feedstock powders with a size distribution of 30-80 µm are obtained as shown in Fig. 1.

2.2 NiO-BZCYYb anode substrate fabrication

NiO (Alfa Aesar, USA), BZCYYb (synthesized by SSR method ^[5]) and corn starch (Sigma, USA) powders with a weight ratio of 65:35:10 were ball-milled in ethanol for 24 h and subsequently dried. The mixed powders were uniaxially pressed into pellets with the size of 0.6 mm in thickness and 13 mm in diameter under a pressure of 300 MPa and subsequently fired at 1400°C for 5 h in air to form the anode substrates.

2.3 Atmospheric plasma sprayed BZCYYb membranes

A commercial plasma spray system (GDP-80, Jiujiang, China) was used to deposit BZCYYb coatings with the spray parameters listed in Table 1. The BZCYYb electrolyte membranes were deposited on NiO-BZCYYb anode substrates which were preheated up to 400°C.

The phase of the electrolyte membrane and anode substrates was characterized by X-ray diffraction analysis (XRD, X'Pert PRO Alpha-1, Cu Kα 1). The cross-sectional morphologies were observed using a field emission scanning electron microscopy (FE-SEM, LEO 1530).

2.4 Post-densification process

The densification of plasma-sprayed BZCYYb electrolyte membranes was performed by infiltrating barium nitrate ($\text{Ba}(\text{NO}_3)_2$), zirconium dinitrate

($\text{ZrO}((\text{NO}_3)_2 \cdot 3\text{H}_2\text{O})$), cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), and ytterbium nitrate ($\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) solutions. The solution of nitrates with a concentration of 30 wt. % was made using deionized water, corresponding to a final composition of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ after decomposition of nitrates. Glycine was added into the nitrate solutions as a chelating agent with a glycine/nitrate molar ratio of 2:1. To examine the phase structure of decomposed nitrates in the BZCYYb coatings, the mixed solutions were slowly dried to get precursor powders and then calcined at different temperatures. The calcined powders were characterized by XRD (X'Pert PRO Alpha-1, Cu $\text{K}\alpha$ 1).

For each infiltration cycle, 50 μL nitrate solutions were dropped on the top surface of BZCYYb electrolyte membranes supported by anode substrates in ambient atmosphere for 20 min to enable the solutions to fill into the pores in the coatings sufficiently. The samples were placed on a hotplate ($\sim 80^\circ\text{C}$) for the duration of the infiltration process to avoid formation of precipitation caused by the poor solubility of barium nitrate in water. Then, the samples were heated to 1000°C and held for 5 h for the nitrates to decompose. After 15 densification cycles, the surface of the BZCYYb electrolyte was wiped clean for the fabrication of single cells. The microstructure of the coatings after post-densification treatment was characterized by FE-SEM (LEO 1530).

2.5 Fabrication and characterization of single cells

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) cathode ink was prepared by ball-milling LSCF powders (Alfa Aesar, USA) with V-006 organic solvent (Heraeus, USA) and acetone.

The LSCF ink was screen-printed on the surface of BZCYYb electrolyte membranes supported by NiO-BZCYYb anode substrates, followed by firing at 1080°C for 2 h to form single cells. The effective cathode area was 0.31 cm².

The cross-sectional view of the single cells was characterized using FE-SEM (LEO 1530). The current density-voltage curves and electrochemical impedance spectra (EIS) of the cells were measured with a four probe method using a multi-channel Versa STAT (Princeton Applied Research) at the operating temperatures ranging from 650 to 750°C. NiO paste and silver paste were employed as current collectors on the anode and the cathode side, respectively. Silver wires were used as the lead wires. During cell measurement, humidified H₂ (with 3 vol. % H₂O) was used as the fuel while the cathode side was exposed to ambient air. Gas flow rate of H₂ was controlled at 40 sccm by a precision volume flow controller (APEX, Alicat Scientific). The cells were first stabilized at 750°C for 30 min to allow complete reduction of NiO to Ni. The EIS was performed under open circuit condition with 10 mV AC amplitude and the frequency range of the measurement was from 1 MHz to 0.1 Hz.

3. Results and discussion

Shown in Fig. 2(a) is the fractured cross-sectional morphology of the as-sprayed BZCYYb deposits. It is clear that some voids are present in the deposited film. During the thermal spray process, individual droplets typically experience rapid flattening, cooling and solidification. When one layer is deposited by a single pass, the surface of the previously deposited layer acts as the substrate. ^[18, 22] The voids in the deposit result from the insufficient filling and incomplete wetting of molten liquid on the

previously formed deposited surface. ^[27] On the other hand, some voids maybe result from the semi-molten particles because these particles are too large and have a porous structure. Also, it can be recognized that the deposit exhibits two types of typical microstructure. In a few regions, the deposit shows a typical lamellar structure with some non-bounded interfaces (as indicated by arrows A). However, on the large-scale, the deposit shows a long continuous columnar crystal structure (as indicated by arrows B). In this region, the length of columnar crystals reaches more than 5 μm , indicating that the effective bonding is formed through several lamellas. Such long columnar grains are formed by the growth of the grains of solidifying liquid splat through heterogeneous nucleation on the previously deposited splats. In our previous study, ^[28, 29] we found that there is a critical deposition temperature for the spray molten droplet to bond completely with the previous deposited splats, which is referred to as the critical bonding temperature. Usually, for ceramic materials, the critical bonding temperature is proportional to the melting point of the material. For example, the critical bonding temperatures for LSGM (melting point: 1700°C ^[17]), Al_2O_3 (melting point: 2050°C ^[30]), and YSZ (melting point: ~2700°C ^[31]) are about 300, 500, and 680°C, respectively. For BZCYYb, the melting point is regarded to be slightly higher than that of BaCeO_3 (1743°C) ^[32] and much lower than that of BaZrO_3 (2705°C) ^[33] because of the high molar content of Ce and low molar content of Zr. The deposition temperature during spraying process in this study (400°C) is near to the critical bonding temperature (300°C for LSGM, 500°C for Al_2O_3). Therefore, most regions of the deposits are bonded well. It is noted that some vertical cracks (as

indicated by arrow C in Fig. 2(a)) are presented in the deposit, which is attributed to the quenching stress evolved during the rapid solidification of molten droplets. Finally, as shown by the arrows in Fig. 2(b), the plasma-sprayed electrolyte is bonded well with the anode substrate.

Typically, the pores created by the APS process include non-bonded interfaces and vertical cracks which are linked to form interconnected channels, leading to gas or liquid penetration throughout the deposited film. Although the long columnar grains may be beneficial for fast ionic conductivity, the pores and non-bonded interfaces may block many of the direct ion transport pathways in the electrolyte. Therefore, in order to improve the gas tightness and ionic conductivity, the post-densification infiltration process is necessary.

Shown in Fig. 3 are the XRD patterns of the as-prepared anode substrate and the plasma-sprayed BZCYYb electrolyte. It shows only NiO and peaks corresponding to BZCYYb phases in the anode substrate, and only BZCYYb phases in electrolyte coatings, indicating that there are no reactions or decomposition during the spraying process. Moreover, the pure phase in electrolyte membranes illustrates that Ba-evaporation is effectively avoided during the APS process, which is attributed to the large-grained BZCYYb feedstock powders. As reported in our previous work^[17], the element evaporation depends mainly on the difference of kinematic viscosities between the molten particles and surrounding media in plasma jet. Since the larger particles reach the full molten state slow with a smaller velocity difference from the plasma jet, the vortex flow effect becomes negligible, thus the Ba evaporation

becomes negligible.

Shown in Fig. 4 is the fractured cross-sectional morphology of plasma-sprayed BZCYYb electrolyte membranes after 15 cycles of post-densification treatment. It can be clearly observed that the electrolyte membranes are fully densified, indicating that the decomposed nitrates effectively fill the interconnected pores. The interfaces between the consecutive layers in post-densified deposits are evidently well bonded together. It is clear that the porosity of the APS deposited film decreases and the vertical cracks disappear after the post-densification process. The remarkable improvement of non-bonded interfaces, pores, and vertical cracks may make a great contribution for increased gas tightness and ionic conductivity of the infiltrated APS-deposited films. In our previous study, ^[26] we found that the gas permeability of the plasma-sprayed YSZ electrolyte could be reduced from $2.9 \times 10^{-6} \text{ cm}^4 \text{ gf}^{-1} \text{ s}^{-1}$ to $2.5 \times 10^{-7} \text{ cm}^4 \text{ gf}^{-1} \text{ s}^{-1}$ by post-infiltration treatment, while electrical conductivity was increased by ~30%. Also, the decomposed nitrates bond well with the deposit, despite a few isolated nanopores present at the interface of the APS-deposited film and the infiltrated BZCYYb. It has been proven that the isolated nanopores have no adverse effect on the gas tightness of post-densified deposits. ^[22]

Owing to the limited amount of the decomposed nitrates in the plasma-sprayed electrolyte, it is difficult to determine its phase composition from the bulk deposit. Therefore, the dried precursor powders are calcined at different temperatures to determine the phase composition. The XRD patterns of the precursor powders after calcining at various temperatures are shown in Fig. 5. The pure orthorhombic

structure of the perovskite-type BaCeO_3 is obtained when the calcination is carried out at 1000°C for 5h, while some secondary phases are observed at lower temperatures (900°C and 950°C). The results imply that the decomposed nitrates in the current work are pure BZCYYb.

Shown in Fig. 6 is a cross-sectional image of the as-prepared cells. It can be observed that the BZCYYb electrolyte membrane with a thickness of $\sim 25\ \mu\text{m}$ is quite dense and crack-free, which may be responsible for the high OCV as to be described later. In addition, the interface between the BZCYYb electrolyte and LSCF cathode is not flat due to the plasma-sprayed deposit characteristics. Such interface is expected to extend TPBs (triple phase boundaries, where electronic-conducting phase, ionic-conducting phase and gas meet) length for cathode electrochemical reactions.

The electrochemical performance of the as-prepared cells is obtained at operating temperatures ranging from 650 to 750°C with humidified H_2 as the fuel and ambient air as the oxidant. As shown in Fig. 7, the OCV values of the cell are 1.02, 0.99, and 0.96 V at 650 , 700 , and 750°C , respectively, which are similar to that of the cells based on dense BZCYYb electrolytes fabricated by spin-coating.^[34] The high OCV values show that the plasma-sprayed BZCYYb electrolyte membrane after post-densification treatment is sufficiently dense, consistent with the SEM image in Fig. 6. The peak power densities of single cells are 0.11 , 0.24 , and $0.35\ \text{W cm}^{-2}$ at 650 , 700 , and 750°C , respectively.

Shown in Fig. 8 is the impedance spectra of the single cells measured at different temperatures under open circuit conditions. The cell ohmic resistances (R_{ohm}) derived

from the spectra interception with the real-axis at high frequencies are 0.83, 0.71 and $0.59 \Omega \cdot \text{cm}^2$ at 650, 700, and 750°C, respectively, higher than that of solution-coated BZCYYb electrolyte membranes with thickness of 10 μm ($0.06 \Omega \cdot \text{cm}^2$ at 750°C) [34].

At testing temperatures, the polarization resistances are much lower than the ohmic resistances, thus high ohmic resistance is regarded as the main limiting factor for such lower cell performance in the current work. Assuming that the R_{ohm} is caused solely by the electrolyte resistance, the plasma-sprayed BZCYYb electrolyte membrane exhibits an electrical conductivity of 0.004 S cm^{-1} at 750°C. This conductivity is ~24% of the conductivity of the solution-coated BZCYYb electrolyte membrane (0.017 S cm^{-1} at 750°C) [34]. The result is similar with other reports for YSZ deposits. [21, 31] Although the electrical conductivity of plasma-sprayed electrolyte is generally lower than that of the bulk materials because of its deposit characteristics, it can be further improved by improving the non-bonded interface and increasing the size of columnar grains. [18, 19] For instance, the improved plasma-sprayed LSGM electrolyte membranes can reach an ionic conductivity as high as 78% of the bulk conductivity by optimizing APS parameters. Therefore, the ionic conductivity of plasma-sprayed BZCYYb electrolyte membranes can be improved as following optimizations: 1) decreasing the porosity of the spraying powders; 2) increasing the deposition temperature to more than 600°C.

4. Conclusions

BZCYYb is regarded as a promising electrolyte for IT-SOFCs due to its superior ionic conductivity and adequate stability under typical fuel cell operating conditions.

However, the long-time high-temperature firing of BZCYYb causes a series of problems including electrolyte-anode reactions/diffusion and Ba-evaporation. APS was applied to fabricate BZCYYb electrolyte membranes on an anode substrate for the first time. The undesirable electrolyte-anode diffusions/reactions were avoided because of the lack of long-time high-temperature firing in the APS process. Also, Ba-evaporation was avoided during APS process, which was attributed to the adoption of large-grained BZCYYb feedstock powders. A post-APS deposition treatment was successfully employed using nitrate solution infiltration to densify the coating microstructure and improve gas permeability. Single cells based on dense BZCYYb electrolyte membranes showed a peak power density of 0.35 W cm^{-2} at 750°C . Although the ionic conductivity of plasma-sprayed BZCYYb electrolyte membranes was lower than that of solution-coated BZCYYb electrolyte membranes, the conductivity can be further improved by optimizing the APS parameters. APS was shown to be a promising approach for the cost-effective fabrication of IT-SOFCs.

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Figure captions

Fig. 1 SEM image of BZCYYb feedstock powders

Fig. 2(a) SEM images of a cross-sectional view of BZCYYb deposits on a NiO-BZCYYb anode

Fig. 2(b) SEM images of a cross-sectional view of the electrolyte and anode interface

Fig. 3 XRD patterns of NiO-BZCYYb anode and plasma sprayed-BZCYYb electrolyte membranes

Fig. 4 The SEM image of a high-magnification view of plasma-sprayed BZCYYb coatings after 15 cycles of post-densification treatment.

Fig. 5 XRD patterns of BZCYYb powders calcined at various temperatures

Fig. 6 SEM image of a cross-sectional view of the as-prepared single cell

Fig. 7 Electrochemical performance of the as-prepared cell with humidified hydrogen at different temperatures

Fig. 8 Impedance spectra of the as-prepared cell with humidified hydrogen at different temperatures

Table 1 Typical plasma spray parameters

Parameters	Unit	Values
Plasma arc power	kW	45.5
Arc voltage	V	70
Arc current	A	650
Flow rate of primary gas (Ar)	slpm	45
Pressure of primary gas (Ar)	MPa	0.8
Flow rate of secondary gas (H ₂)	slpm	7.5
Pressure of secondary gas (H ₂)	MPa	0.4
Powder feed rate	g min ⁻¹	10
Spray distance	mm	75
Robot move speed	m s ⁻¹	0.6