Abstract

In this report, a strategic approach for preparation of dense 8YSZ electrolyte layer on porous NiO-YSZ substrate was proposed. Porosity in the substrate was introduced by mixing corn starch with the starting NiO-YSZ powder. By varying the content of corn starch, porosity and sintering shrinkage of the sintered substrates were studied. The porous substrates were deposited with an electrolyte layer using the Electrophoretic Deposition (EPD) technique. The difference in total sintering shrinkage between the substrate and that of YSZ electrolyte layer was found to be the major cause of cracks and pores in the electrolyte films. Finally, by optimizing the preparation conditions of the porous NiO-YSZ substrates, a dense YSZ film as thin as 2 μm was successfully fabricated.

1. Introduction

Solid oxide fuel cells (SOFCs) are regarded as a promising power generation technology for the future. The attractiveness of SOFC is its efficient and clean production of electricity from a variety of fuels. 8 mol% yttria stabilized zirconia ceramics (8YSZ) are the most common electrolyte in SOFCs owing to its high oxygen ion conductivity and chemical stability over a wide range of temperatures and oxygen partial pressures [1]. However, it requires sufficiently high operating temperature around 1000°C to achieve the required ionic conductivity of 0.1 S/cm [2]. Current development of SOFCs is focused on lowering the operating temperatures to 600–800°C, since the advantages of a reduced-temperature
operation for SOFCs include wider material selection, better long-term performance, system compactness and potentially reduced fuel cell costs [3]. In order to reduce the operating temperature, one needs either to use materials with higher ionic conductivity, or to reduce the thickness of the electrolyte. The second approach is a favorite way for practical applications, because cheap, reliable and mature electrolyte materials can be used. An anode supported electrolyte thin film configuration has been widely studied. It was claimed that a thinner electrolyte film resulted in lower ohmic losses during cell operation, preferably [4]. NiO-YSZ is usually used as the anode substrate with YSZ thin film.

Electrophoretic deposition (EPD) process is one of the promising candidates for forming thin film of electrolyte on a porous support. EPD is described as a colloidal processing method in which charged particles dispersed in a liquid medium are attracted and deposited onto an oppositely charged conductive electrode on application of a dc electric field [5]. It has the advantages of short formation time, little restriction in the shape of deposition substrate, suitability for mass production, suitability for deposition of laminates. In addition, EPD offers easy control of the thickness and morphology of the deposited films through simple adjustment of the deposition time and applied potential.

Prerequisite of substrate for a successful EPD are: (1) the substrate should be electrically conductive. However, non-conducting substrate such as NiO-YSZ can be provided electrical conductivity by graphite-coated before EPD process; (2) in case of non-conducting substrate, it must show enough porosity to provide conductive path during deposition process [6]; (3) sintering shrinkage of the substrate should be close to that of electrolyte film. It has to be noted that matching in the sintering shrinkage between an anode substrate and electrolyte is very important for producing a dense electrolyte film. To comply with these requirements, preparation conditions of the NiO-YSZ substrate must be optimized.

This report studied preparation of the porous NiO-YSZ anode for using as a substrate for EPD. Effective parameters on pore shape, porosity, and sintering shrinkage have been investigated. The preparation conditions were studied first using commercial NiO-YSZ powder and then these results were used as the starting point for tuning the sintering shrinkage of the substrate.

2. Experimental

2.1. Preparation of NiO-YSZ substrate

In order to investigate the effect of processing parameters, preliminary experiments were carried out on the commercial powder of NiO-YSZ (NiO:YSZ, wt. ratio = 50:50, American Elements). Corn starch (Sigma-Aldrich) was used as a pore former. Various weight percent values of corn starch (15%, 20%, and 25%, abbreviated as Anode-Ax, x = wt% of corn strach) were prepared to observe the variation of the porosity. Corn starch was mixed with NiO-YSZ powder by ball-milling for 24 h in ethanol medium. Then the mixed powders were dried at 80°C. Porous NiO-YSZ anode substrates were fabricated by pressing the mixed powders at 100 MPa in a 1.5 cm diameter stainless steel die. Finally, the pressed composites were pre-sintered at 900-1100°C for 4 h to remove pore former and provide strength for handling. The dimensions of the green and sintered samples were measured to determine the shrinkage. Porosity of the sintered substrates (1400°C, 2h) was measured by Archimedes method.

For tuning sintering shrinkage between electrolyte and anode substrate, 3 compositions of substrate were varied in order to determine condition that accurately matched the shrinkage profile of the electrolyte layer. Their composition details were shown in Table 1.
Table 1. Compositions of different types of the anode.

<table>
<thead>
<tr>
<th>Anode substrate</th>
<th>Sources of powder</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiO YSZ (commercial)</td>
<td>NiO (commercial)</td>
<td>YSZ (in-house)</td>
<td>Corn starch (wt%)</td>
<td></td>
</tr>
<tr>
<td>Anode-A15</td>
<td>✓</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Anode-B15</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Anode-B25</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Anode-B35</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
<td>35</td>
<td></td>
</tr>
</tbody>
</table>

2.2. Electrophoretic deposition

The in-house nanocrystalline YSZ powder was prepared by modified solvothermal technique. The detailed experiments have been reported in the previous work [7]. The suspension was prepared by mixing YSZ powders in ethanol solvent using ball-milling for 24 h. The powder concentration of the EPD suspension was 10 g/l, which was prepared with a dilution of the milling mixture with ethanol. A suitable amount of PVB (average Mw = 170,000 - 250,000, Aldrich) was then added as a binder. The suspensions were ultrasonicated for 30 min and then allowed to settle of large agglomerated particles for 48 h before EPD process. For EPD process, stainless steel was used as the positive electrode. The negative electrode was connected to a copper sheet which attached to the graphite layer side of the NiO-YSZ substrate. The two electrodes were kept parallel with a distance of 10 mm. EPD coating experiments were carried out at constant apply voltages of 10 V and deposition time of 3 minutes using the upper stable suspension. The deposited films were co-sintered at 1400°C for 2 h with heating rate of 1°C/min.

The morphology of the green and sintered films were evaluated using Scanning Electron Microscope (SEM).

3. Results and discussion

3.1. Effect of corn starch content on porosity and sintering shrinkage of anode substrate

This part of experiment was done by ball milling for 24 h using 25, 20 and 15 wt% of corn starch. The value of relative shrinkage of the different anode substrates from pre-sintering temperature to sintering temperature and porosity of the sintered samples were shown in Table 2. It showed that the porosity was increased with increasing of corn starch content. The initial porosity of sintered NiO–YSZ composite should be around 20 vol%. Due to in the reduction of NiO to Ni about 41.1% of the initial volume of NiO is transferred to the pores, and that the final porosity of the anode is approximately 40% of the total volume of the composite following the requirement. Consequently, 15 wt% corn starch sample showed suitable porosity to use as a substrate.

Pre-sintering of the substrate was required to remove pore former and generate porosity and guarantee the strength of the substrate. Since the substrates must be pre-sintered before EPD process, sintering changes in the substrate did not occur before the pre-sintering temperature when co-sintering with the electrolyte layer. Thus, the substrate that exhibits similar final shrinkage with the electrolyte layer will be selected. It can be seen that the lower pre-sintering temperature resulted in the increasing of the final shrinkage of the substrate. However, pre-sintering at 900°C was not enough to provide mechanical strength of the substrate for easy handing due to the weak adhesion between particles. When increasing the pre-sintering temperature to 1100°C, the final shrinkage of the substrate reached only
~20%. It was expected that the final shrinkage of the substrate should be higher than 20% to achieve dense microstructure of the electrolyte film. Therefore, pre-sintering at 1000°C was selected to prepare the Anode-A15 substrate before EPD process.

The above results also indicated that increasing corn starch content could increase the porosity of the substrate, but it could hardly influence the sintering shrinkage with increasing the corn strach content. As can be observed from Table 2, the linear shrinkages are quite similar in the substrates in spite of the variation in the corn starch content.

Table 2. The relative shrinkage of the different anode substrates and 8YSZ samples as a function of pre-sintering temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative shrinkage (%)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>900-1400°C</td>
<td>1000-1400°C</td>
</tr>
<tr>
<td>Anode-A25</td>
<td>25.87</td>
<td>22.71</td>
</tr>
<tr>
<td>Anode-A20</td>
<td>25.13</td>
<td>22.17</td>
</tr>
<tr>
<td>Anode-A15</td>
<td>25.55</td>
<td>22.66</td>
</tr>
</tbody>
</table>

3.2. Sintering behavior of YSZ electrolyte and NiO-YSZ substrate

To obtain more information for the sintering behavior of each material, the linear shrinkage was measured. Data of the sintering shrinkage were obtained in Fig.1. It show that the sintering shrinkage of YSZ electrolyte increased to 32% after sintering at 1200°C, and it remained relatively constant with further increases in sintering temperature. This suggested that the YSZ electrolyte could densify at a sintering temperature as low as 1200°C. Compared to the YSZ electrolyte, the shrinkage of Anode-A15 appeared lower in the temperature range 1000-1400°C. In practical, shrinkage of the substrate in this temperature range should be matched to the electrolyte layer in order to avoid defects after co-sintering process. As a consequence, adjusting the shrinkage of the substrate was necessary to investigate.

The shrinkage behavior of substrate can be tuned by several factors such as precursor materials, preparation process, pre-sintering temperature of anode, and co-sintering temperature. Much works has been done to solve the problem associated with the mismatched sintering profiles of anode and YSZ films by adding composite pore former to anode [9], by adjusting the pre-sintering temperature of anodes [10], by adjusting the particle size of precursor powders in anodes [11], by adjusting the pressure for press the pellets [12]. Among these approaches, reducing the particle size of the precursor powders was the most effective way to increase the shrinkage of the substrate. The other approaches were used to fine-tune the shrinkage.

With the propose of matching of shrinkage between the substrate and electrolyte, in-house YSZ nanopowder was mixed with commercial NiO nanopowder (240 nm) to favor the shrinkage. It can be seen that Anode-B15 and Anode-B25 yielded a higher shrinkage of ~31% at 1400°C, which was comparable to the YSZ electrolyte. It was expected that using these two substrates, dense YSZ film could be achived.
3.3. Microstructure of sintered films

Fig. 2 shows surface and cross section micrographs of the YSZ thin film after sintering at 1400°C by using different substrates. It can be seen that the YSZ film on the Anode-A15 substrate exhibited many open pores. This clearly demonstrated that large different sintering shrinkage between electrolyte and substrate led to low densification of the electrolyte layer (See Fig. 1). On the otherhand, deposition YSZ film on both of Anode-B15 and Anode-B25, the denser microstructure with thickness around 2 μm were obtained as expected due to similar sintering shrinkage at 1400°C. However, cross section micrograph of the Anode-B15 sample showed insufficient porosity of the substrate. Such microstructure might results in low gas permeability. Further, more amount of corn starch in the sample of Anode-B25 could increase the porosity of the substrate to enhance gas transport.

It was obvious that increasing of porosity of the substrate not affected densification of electrolyte films. On the other hand, the sintering shrinkage of anode has greatly affected densification of electrolyte films made by the co-sintering of anode-electrolyte double layers.

4. Conclusion

This study provided a guide line for preparation anode substrate. Different content of corn starch (pore former) were investigated in order to study their influence on the porosity of the porous NiO-YSZ substrate for EPD process. The choice was done on the basis of their porosity and sintering shrinkage. Reducing particle size of the precursor powders of the substrate was an effective way to increase the sintering shrinkage. Matching in the sintering shrinkage between electrolyte and substrate was found to be important for obtained dense electrolyte.
Fig. 2 SEM micrographs of surface and cross section of YSZ films on different substrate (a, b) Anode-A15, (c, d) Anode-B15 and (e, f) Anode-B25.

Acknowledgements

The authors would like to thank the financial support from Thailand Graduated Institute of Science and Technology (TGIST) and Maefahluang university.
References


