Thickness variations in electrolytes for planar solid oxide fuel cells

Ching-Ti Kao a,b, Wei-Hsing Tuan a and Shu-Wei Chang a

a Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan; b Chemistry and Environment Research Lab, Taiwan Power Research Institute, New Taipei City, Taiwan

ABSTRACT
Shape uniformity is one of the key factors for determining the performance of planar solid oxide fuel cells. Three parameters must be considered to acquire a full picture of shape uniformity: the extent of warpage, surface roughness and thickness variations. The present study examines the thickness variations of yttria-stabilized zirconia electrolytes after sintering. An optical technique has been successfully developed to determine the thickness variations, which are closely related to microstructure uniformity. A warm isostatic pressing lamination technique can be used to reduce thickness variations.

1. Introduction
The success of manufacturing a planar solid oxide fuel cell (SOFC) depends on control of its shape uniformity. Three important parameters, the extent of warpage, surface roughness and thickness variations, are key factors in addressing shape uniformity. A definition of the extent of warpage and surface roughness is given in Figure 1(a). The extent of warpage is usually expressed in terms of the radius of electrolytes. Since the size of electrolyte is in the range of hundreds of millimeters, the warpage may reach a value of hundreds of micrometers [1,2]. The extent of warpage can be estimated through the use of a caliper warpage is a serious problem. When the warpage is too small to be measured with a caliper, an optical technique was used [3].

Surface roughness is a local deviation in the surface profile (Figure 1). The average surface roughness (Ra) of SOFC electrolytes, for example, may vary within 1 micrometer (µm) [4,5]. The surface roughness of electrolytes is usually small and may not cause much problem. Surface roughness can be measured using a microprofilometer, but it is not possible to apply this technique to determine the surface roughness of a whole electrolyte, which is extremely time-consuming.

The causes of warpage of planar SOFCs have been clearly explained [1,3,6–9], but the thickness variations (Figure 1(b)) of electrolytes have attracted little attention. As demonstrated later, thickness variations do not result from the tape itself, but from the lamination process. The lamination process is a routine method of preparing SOFC electrolytes. Since thickness variations may affect the contact area between electrolytes and electrodes, or the area of the three-phase boundary, they represent an important issue requiring more attention.

The objectives of the present study are as follows:
a. The importance of thickness variations of SOFC electrolytes is addressed.
b. A fast and reliable technique for estimating thickness variations is proposed.
c. The basic reason for thickness variations is suggested.
d. A possible strategy for solving problems related to thickness variations is also proposed.

2. Experimental
A zirconia tape with 8 mol% yttria (yttria-stabilized zirconia (YSZ), 8YSZ-ESL-42401, Electroscience Laboratory, USA) was used in the present study. The thickness of the as-received tape was 125 ± 5 µm. The density of the tape, including the binder, was 3.39 ± 0.08 g/cm³. The size of a green electrolyte punched from the tape was 63 mm × 63 mm. Three tapes were laminated together using two techniques: warm pressing (WP, model 4122, Carver Inc., USA) and warm isostatic pressing (WIP, CH860, Hongchi Co., Taiwan). Table 1 shows the parameters for the lamination techniques. The pressing parameters were the same for the WP and WIP techniques, except that the load was uniaxial for WP and isostatic for WIP. The pressing medium for the WIP process was water. A copper plate with a thickness of 1 mm was used to assist in achieving uniformity of pressure, as demonstrated in Figure 2.

The binder was removed by heating slowly at 0.5°C/min to 900°C in air. The dwell time was 1 h. Cooling from the debinding temperature was
conducted at 2°C/min. Sintering was carried out at 1410°C for 1 h. The heating and cooling rates were 1n and 2°C/min, respectively. In order to avoid warpage of the electrolyte during sintering, alumina substrates with a thickness of 3 mm were used as the top and bottom layers, as demonstrated in Figure 3. The alumina substrates generated a load equivalent to 0.00015 MPa to the laminate.

Phase analysis was conducted using an X-ray diffraction (XRD, Bruke D2 Phaser, Germany) technique; microstructure characterization was performed using scanning electron microscopy (Hitachi S4700, Hitachi Co., Japan). An optical technique (DSX500, Olympus Co., Japan) was used to evaluate the thickness variations. The whole area of a sintered electrolyte was divided into 9 sections (Figure 4), 8 sections near the edges and 1 in the center. Ten spots, each with an area of 1 mm × 1 mm, were chosen randomly within each section. The height of these spots was then recorded. The resolution of the technique was 0.01 µm. Since a sintered electrolyte is relatively large, 50 mm × 50 mm, a technique without establishing a base plain was proposed. Two of the 10 spots within one section were chosen randomly and compared (Figure 4), and the difference between these two spots was considered to reflect the local variation in thickness. The local thickness variation locally, whether near the edge or in the center, could then be estimated. The technique was a fast one. The thickness variations for one sintered electrolyte could be estimated within 1 min.

3. Results and discussion

The green density of the electrolytes prepared by laminating three YSZ tapes together can be found in Table 1. The thicknesses of the electrolytes prepared by the WP and WIP techniques were 370 ± 8 and 370 ± 4 µm, respectively. Though the dimensions and green density of the electrolytes prepared by WP and WIP techniques are similar to each other, the density variation (in terms of the standard deviation) of the electrolytes laminated by the WIP technique is smaller. This implies that the pressure applied by the WIP technique is more uniform.

A small load of ~0.00015 MPa was applied to the top of the electrolytes during sintering (Figure 3). Though the load was small, the warpage of the

Table 1. Processing details for the warm pressing (WP) and warm isostatic pressing (WIP) lamination techniques (the dimensions and density of the electrolyte are also shown).

| Lamination technique | Warm pressing (WP) | Warm isostatic pressing (WIP) |
|----------------------|-------------------|-------------------------------|
| Pressure/MPa         | 60                | 60                            |
| Temperature/holding time | 70°C/30 min | 70°C/30 min |
| Dimensions of a green electrolyte | 63 mm × 63 mm × 63 mm × 370 µm | 370 µm |
| Green density/%      | 54.1 ± 4.3        | 54.7 ± 1.8                    |
| Dimensions of a sintered electrolyte | 50 mm × 50 mm × 50 mm × 315 µm | 315 µm |
| Sintered density/%   | 94.6 ± 1.3        | 94.9 ± 0.4                    |
The final dimensions of sintered electrolytes after sintering was 50 mm × 50 mm. The lineal shrinkage of the electrolytes in the planar direction during sintering was 20% and in the thickness direction 15%. The thickness variations of sintered electrolytes could be estimated first by locating a base plane outside the electrolyte and then measuring the standard deviation for the sintered electrolytes prepared by the WIP technique was also smaller. XRD analysis indicated that the phase of the sintered electrolytes was the cubic phase. No difference was noted in the phases of the electrolytes prepared by the two lamination techniques.

Figure 2. Schematics for the (a) warm pressing (WP) and (b) warm isostatic pressing (WIP) lamination techniques.

Figure 3. A small load was applied on the electrolyte during sintering through the use of alumina substrates.

Figure 4. Definition of the edge and central sections of a sintered YSZ electrolyte. The whole electrolyte is divided into 9 sections, and 10 spots within each section are selected randomly. The size of each spot is 1 mm × 1 mm. Without defining a base plane, the difference between two arbitrary spots (for example, point A and point B) within one section is termed thickness variation (Δthickness). As the shape uniformity within one section is high, the thickness variation should be small.
thickness within the electrolyte. The difference between the thickness of the electrolyte and the base plane reveals the thickness variations of the whole electrolyte. However, local variations in thickness within small sections are also an important issue. Such thickness variations can be determined by comparing the thickness of two nearby spots within a small section, as demonstrated in Figure 4. Adopting such a procedure enables the thickness variations to be estimated within 1 min.

Figure 5 shows the thickness variations for the edge and central regions. The local thickness variations in electrolytes prepared by lamination with the WIP technique are similar for every sections. This indicates that an electrolyte with only small variations in thickness can be obtained after sintering. The thickness variations in the central section are much larger than those in the edge sections, however, as the green electrolyte was laminated using the WP process (Figure 5). Figure 6 shows the surface of a sintered electrolyte prepared using the WP technique. Many pores are to be found in the central section. A sintered electrolyte prepared by the WIP process was dense. Moreover, the microstructure of its central section is similar to its edges section (Figure 7). Use of an image analysis technique shows the porosity in the micrographs in Figure 6(a,b) to be 0.17% and 2.19%, respectively; the porosity in Figure 7(a,b) is 0.17% and 0.05%, respectively.

There is a close relationship between the thickness variations (Figure 5) and the microstructure uniformity (Figures 6 & 7). An electrolyte prepared with the WIP technique, the microstructure is uniform (Figure 7), with only small thickness variations (Figure 5). Many pores are found, however, in the central section of sintered electrolytes prepared using the WP process (Figure 6(b)). The density uniformity of WP electrolytes is poor, and so is their thickness uniformity (Figure 5).

To make sure an electrolyte was flat enough, a load was applied on it during sintering. Though the load was small, 0.00015 MPa, it was sufficient to solve the problem of warpage. Nevertheless, thickness variations can still be detected. The present study focuses mainly on the thickness variations of sintered electrolytes, as defined in Figure 1, since the thickness variations of electrolytes may affect the contact area between electrode and electrolyte. Consequently, the efficiency of the SOFC may be considerably affected by the thickness variations.

Azari applied an optical method to determine the warpage of a circular electrolyte [3]. The technique is fast and reliable. In the present study, an optical technique is used to determine the thickness variations of planar electrolytes. A strong connection between the thickness variations and microstructure is observed. This indicates that density uniformity is the key to achieving shape uniformity. The lamination process plays an important role in ensuring density uniformity. Isostatic pressure can reduce the density variation in green electrolytes and achieves thickness uniformity in sintered electrolytes consequently.
4. Conclusions

In the present study, the importance of thickness variations to planar SOFC electrolytes is investigated. Two important findings are proposed based on our experimental evidence. First, local thickness variations can be measured with an optical technique. Secondly, the density variation can be improved through the use of an isostatic lamination pressing technique. It is the density variation within green electrolytes that leads to differences in shrinkage; the thickness thus varies within a relatively small region. A uniform green compact is essential to produce an electrolyte with shape uniformity. The use of isostatic pressure during the lamination process can ensure a uniform green compact.

Acknowledgments

The present study was supported by the Chemistry and Environment Research Laboratory of Taiwan Power Research Institute, New Taipei City, under contract number 546-2415-0001.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Taiwan Power Research Institute [546-2415-0001].

Figure 7. Typical micrographs of the (a) edge and (b) central sections of sintered electrolytes prepared by the WIP lamination technique.

References

[1] Yamamoto O. Solid oxide fuel cells: fundamental aspects and prospects. Electrochim Acta. 2000;45:2423–2435.
[2] Tietz F, Buchkremer HP, Stover D. Components manufacturing for solid oxide fuel cells. Solid State Ion. 2002;152-153:373–381.
[3] Azari K, Vaghasloo YA. The effect of cell shape on the warpage in solid oxide fuel cells. J Power Sources. 2015;279:67–71.
[4] Talebi T, Haji M, Raissi B. Effect of sintering temperature on the microstructure, roughness and electrochemical impedance of electrophoretically deposited YSZ electrolyte for SOFCs. Int J Hydrogen Energy. 2010;35:9420–9426.
[5] Kim YB, Park JS, Gur TM, et al. Oxygen activation over engineered surface grains on YDC/YSZ interlayered composite electrolyte for LT-SOFC. J Power Sources. 2011;196:10530–10535.
[6] Huijsmans JPP. Ceramics in solid oxide fuel cells. Curr Opin Solid State Mater Sci. 2001;5:317–323.
[7] Hui S, Roller J, Yick S. A brief review of the ionic conductivity enhancement for selected oxide electrolytes. J Power Sources. 2007;172:493–502.
[8] Myung JH, Shin TH, Kim SD, et al. Optimization of Ni–zirconia based anode support for robust and high-performance 5 × 5 cm2 sized SOFC via tape-casting/co-firing technique and nano-structured anode. Int J Hydrogen Energy. 2015;40:2792–2799.
[9] Cologna M, Sglavo VM, Bertoldi M. Sintering and deformation of solid oxide fuel cells produced by sequential tape casting. Int J Appl Ceram Technol. 2010;7:803–813.

ORCID

Ching-Ti Kao @ http://orcid.org/0000-0001-8650-8160