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# Varied layer thickness improves structural properties of YSZ thin film

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**Abstract**

In this study, the Yttrium Stabilized Zirconia (YSZ) thin films were deposited on the sapphire substrate ($Al_2O_3$) by dip-coating method using simple ethanol-based YSZ suspension. The layer thickness of YSZ films were varied by sintering at 1300°C. Phase change and structural evolution in YSZ films were observed by conducting X-ray diffraction (XRD) analyses. The microstructures and the surface morphology of the deposited films were examined using Atomic Force Microscope (AFM) and Field Emission Scanning Electron Microscope (FESEM). The XRD pattern revealed a phase change from cubic to monoclinic with an increase in YSZ layer thickness. The crystallite size was varied in the range of 9.68–42.98 nm with the changes in the layer thickness. Meanwhile, the AFM image analyses showed a layer thickness-dependent variation in the grain size (205.83–373.77 nm) and the RMS surface roughness (16.72–36.44 nm). The FESEM images of the achieved film exhibited the occurrence of a dense morphology. It was concluded that by controlling the layer thickness of the deposited films, their improved structure and morphology can be achieved.

**Keywords**

SOFC, YSZ electrolyte, dip-coating, sapphire substrate, nanostructure

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## Introduction

Lately, intensive studies have been conducted on the electrolyte material of the Solid Oxide Fuel Cell (SOFC). The SOFC is known to have many potentials, for example, generation of low environmental pollution and low-cost ceramic materials and electrochemical generation of electricity with high efficiency.[1] The operating temperature for SOFC is in range of 700°C–1000°C, which is considered a high range of operating temperature. In recent years, a number of researchers have been focusing on lowering this temperature.[2,3] This is because a high operating temperature increases the resistivity level, which decreases the efficiency of SOFC. On the other hand, by lowering the operating temperature, the performance of ionic conductivity of the electrolyte is disrupted. To make a balance, the thickness of electrolyte needs to be decreased.[2]

It is worth mentioning that the materials chosen for electrolyte are important to the cell performance or efficiency. Yttrium stabilized zirconia (YSZ) is the most commonly-used material for SOFC electrolyte due to its high mechanical and chemical stability and high level of hardness.[4] To achieve an effective performance of low-temperature SOFC, the method chosen for the deposition of YSZ thin film must be so practical that YSZ electrolyte could be obtained as thin as possible.[5–8]

Thin YSZ electrolyte can be obtained in many ways, either physical deposition or chemical deposition. Physical deposition (such as sputtering, chemical vapour deposition (CVD), pulsed laser deposition (PLD) and Atomic Laser Deposition (ALD)) can produce a high quality nano-scale YSZ thin film up to $< 100$ nm. However, these physical deposition methods and the equipment required are costly and challenging for commercialized manufacturing environment.[9–13] Chemical deposition is much better and simpler with cost-effective techniques. Dip-coating, as a chemical deposition method, has been used widely for several decades. Moreover, this method can easily control the

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shape and size of electrolyte and electrode of the cell and also can control all the parameters in a way to make a high-quality film. All of the parameters need to be optimized so that films with extremely high uniformity and smaller roughness values could be produced. One coating is enough to produce one layer on the surface.[14,15]

In this work, to prepare good quality YSZ electrolyte thin film on the C-plane of sapphire substrate, the dip-coating method was adopted because of its various notable advantages. Lattice constant between YSZ and sapphire was closely matched within ≈7%. The effects of different layer thicknesses on the microstructures and morphologies of deposited YSZ films were examined. The sintered thin films were characterized using XRD, AFM and FESEM measurements, and the obtained results were analysed and discussed in this paper.

## Materials and methods

### Materials

Zirconium (IV) Oxide Yttria stabilized ( $<$ 100 nm particle size) was purchased from Sigma Aldrich. The 99.98% ethanol was used to dissolve the YSZ powder together with polyethylene glycol (PEG) as a binder. All chemicals were used as received, without further purification.

### Methodology

YSZ electrolyte thin films were fabricated by the dip-coating method. The suspension of YSZ was prepared. The YSZ powder was dissolved in ethanol and mixed with PEG as a binder. The suspension was stirred on the hotplate for 2 h before giving ultrasonic treatment for another 1 h.

C-plane sapphire (0001) was used as substrate for the fabrication of the YSZ thin film. The substrate was ultrasonically cleaned in ethanol followed by acetone and distilled water, in turns. The substrate with a measurement of 10 mm $\times$ 10 mm was placed in the sample holder and dip into the suspension. The time was constantly dip in 60 s. By controlling the withdrawal speeds of dip coating using low speeds, a uniform coating can be achieved. The speed was chosen after the optimization process. The solution temperature also plays an important role; the room temperature is the best for better uniformity in films. One layer was obtained on the substrate and dried for 24 h. The steps were repeated until 10 layers were obtained. The final stage was the sintering process constantly for every sample at 1300°C with the heating rate of 10°C/min, and the dwell time was 2 h. The sintering temperature has a great effect on thin films, specifically on their crystallization and growth.[16–18] Rahimi et al.,[19] it was concluded that YSZ thin film produced using dip-coating method are not suitable for sintering temperature below 1000°C as in this temperature, the film cannot be fully crystallized. This can be concluded from the XRD results.[19] Five samples were obtained with 1-, 2-, 3-, 5- and 10-layer deposition labelled as YSZ1, YSZ2, YSZ3, YSZ5 and YSZ10, respectively.

### Characterizations

The phase structures of the YSZ thin films were characterized by X-ray Diffractometer. Moreover, the morphology, thickness and grain size of the thin films were characterized by means of Atomic Force Microscope (AFM) and Field Emissions Scanning Electron Microscope (FESEM).

## Results and discussion

### YSZ thin film microstructure

Figure 1(a) shows the X-ray Diffraction (XRD) patterns of the YSZ thin films deposited on the sapphire substrate with various coating layers sintered at 1300°C. The XRD measurement was carried out with Cu K$\alpha$ radiation on a Bruker diffractometer under angles ranging from 25° to 90°.

The first two layers were oriented in the (111) direction at cubic structure. The intensity of YSZ2 was higher than that of YSZ1, which shows high crystallinity in YSZ2. However, as the layer deposition increased to ten layers, the pattern showed a monoclinic structure of YSZ. The (111) peak slowly disappeared as the layer deposition goes up to 3 and clearly vanished when the layer increased to 5 and 10. This phenomenon indicated that the thickness of the film deposition was a critical parameter in the crystallinity of the YSZ thin film and the phase structure of the film. Monoclinic is where the rare zirconium oxide mineral ($Zr_2O$) at room temperature and it is called Baddeleyite.[20] To stabilize the pure $Zr_2O$, it was reported that cubic phase has a higher conductivity compared to tetragonal and monoclinic due to the equal number of vacant oxygen sites in all crystalline lattice directions, which helps SOFC to perform well.[21]

Figure 1(b) shows the reduction of the peak broadening for orientation (111) that happened for YSZ1 and YSZ2 and pure powder was considered as the reference. These two samples show the highest intensity of the peak. This was attributed to the change of crystallite size. Figure 1(b) also shows that the peak is shifted slightly to the left. This can explain the change to the lattice parameter.

Table 1 summarizes the thickness depending on the value of crystallite size (D) and the lattice parameter ($a$).

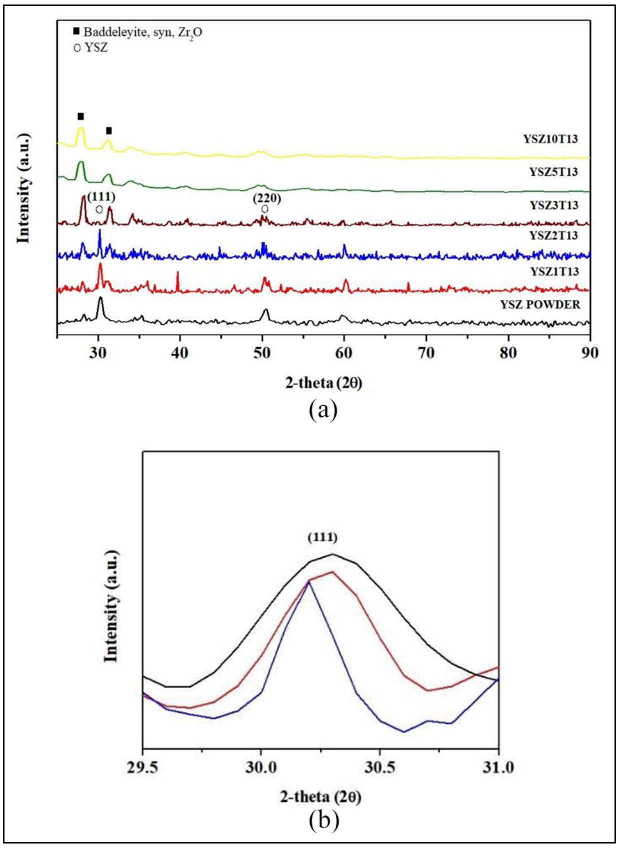


**Figure 1.** (a) The XRD pattern of the studied YSZ thin film with different layer depositions and (b) magnified view corresponding to the highest intensity peak at (111) for YSZ1 and YSZ2 with a referral of YSZ pure powder.

The decrement of crystallite size from 21.47 to 19.68 nm for YSZ was due to defect in the structure.

### *Atomic force microscope analysis*

Figure 2 shows the three-dimensional AFM images of the YSZ thin films with various thickness layers sintered at 1300°C. YSZ1, YSZ2 and YSZ3 show homogeneous surface with uniform grain sizes. The different thickness deposition act on the grains size of the YSZ films despite the presence of several pores. Grain growth of the YSZ thin films is clearly shown. It can be observed that uniformity of the grains size from AFM analysis supports the crystallite size from XRD. The grain size decreases from 270.85 to 205.83 nm for YSZ2 and increases to 249.70 nm for YSZ3. There is no uniformity in the size of the grains appearing on the surface of YSZ5 and YSZ10. Thicker deposition of thin film may disturb the grain growth of the film and cause the film to appear as monoclinic phase and not suitable for SOFC application. Root mean square (RMS) roughness and average roughness (Ra) are also two important parameters measured from AFM analysis. The roughness also linearly decreases with grain size. By increasing from two to three layers of deposition, RMS and Ra increased from 16.72 to 29.73 nm and 13.00 to 22.66 nm, respectively. To obtain the smoothest surface, the thickness of the film needs to be optimized because the surface roughness affects the performance of YSZ films.

**Table 1.** Estimated values of crystallite sizes and lattice parameter of the prepared YSZ thin films.

| Sample code | *D* (nm) | *a* (nm) |
|---|---|---|
| YSZ1 | 21.47 | 5.1074 |
| YSZ2 | 19.68 | 5.1289 |
| YSZ3 | 42.98 | 5.1597 |
| YSZ5 | 15.88 | 5.1891 |
| YSZ10 | 9.68 | 5.3221 |

Table 2 summarizes the layer thickness with estimated grain size and root mean square (RMS) roughness of the studied YSZ thin film.

### *Field emission scanning electron microscope analysis*

The surface morphology and the cross-sectional microstructure of the YSZ thin film are shown in Figure 3(a) to (e). The FESEM images of YSZ1, YSZ2, YSZ3, YSZ4, and YSZ5 show the columnar structure. It can be observed as well that fully dense dip-coated YSZ thin films can be obtained regardless of how many layers are deposited on the substrate. The average grain size for each sample was measured and shown in Table 3. A size reduction occurred in YSZ2 from 265.23 to 170.21 nm. The grain size increased again in YSZ3 from 170.21 to 208.35 nm. The grain size continued to increase to 220.32 and 237.56 nm for YSZ5 and YSZ10, respectively. Unfortunately, the thickness of the film for YSZ1, YSZ2 and YSZ3 can be seen clearly from the images. However, the thickness was estimated to be around 1 μm. For YSZ5 and YSZ10, better images could be captured; their average thicknesses were 1.5 and 5.438 μm, respectively.

The mechanical strength of the film was determined by the grain size homogeneity and uniformity. Smaller grains could delay the dislocation better than the larger ones because the fine grains had bigger fatigue resistance. Thus, it was suitable for excellent ionic transport performance. Figure 3 indicates that the optimization layer deposition is two layers deposition because the grain size is smaller compared to that of the other films.

## Conclusions

The YSZ thin films of different layer thicknesses were grown on the sapphire substrate by dip-coating method and sintered at 1300°C. As-deposited thin films were characterized by diverse techniques. The crystalline phases of thin films showed that cubic is the most stable phase for electrolyte to be used in SOFC. The surface roughness and the morphology analyses revealed that the grain size of YSZ thin film increased with an

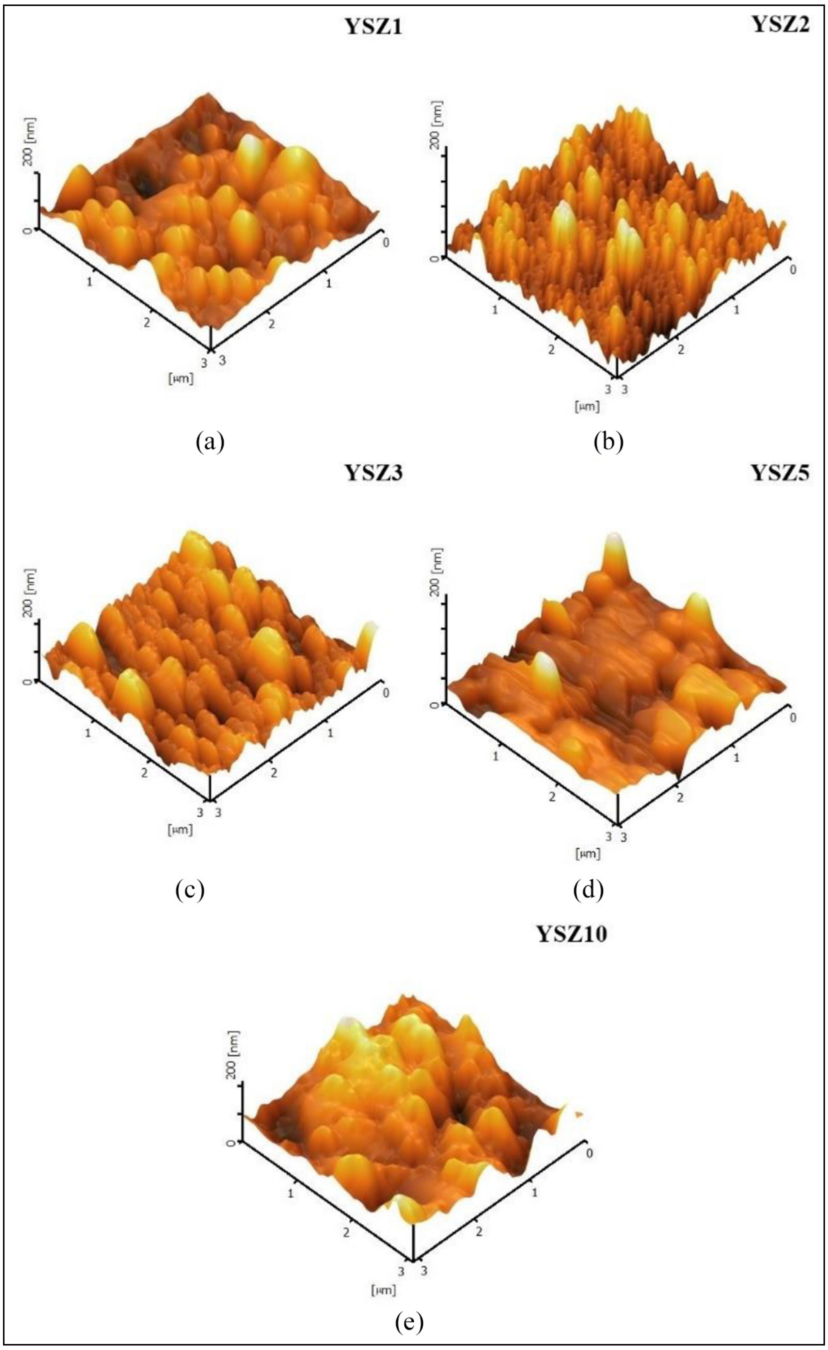


**Figure 2.** 3D AFM images of: (a) YSZ1, (b) YSZ2, (c) YSZ3, (d) YSZ5 and (e) YSZ10.

**Table 2.** Estimated values of RMS roughness and grain size of the prepared YSZ thin films.

| Samples | Grain size (nm) | RMS (nm) | Ra (nm) |
|---|---|---|---|
| YSZ1 | 270.85 | 28.31 | 22.50 |
| YSZ2 | 205.83 | 16.72 | 13.00 |
| YSZ3 | 249.70 | 29.73 | 22.66 |
| YSZ5 | 333.77 | 35.52 | 23.74 |
| YSZ10 | 351.01 | 36.44 | 29.56 |

**Table 3.** Estimated average value of grain size of the prepared YSZ thin films.

| Samples | Grains size (nm) |
|---|---|
| YSZ1 | 265.23 |
| YSZ2 | 170.21 |
| YSZ3 | 208.35 |
| YSZ5 | 220.32 |
| YSZ10 | 237.56 |

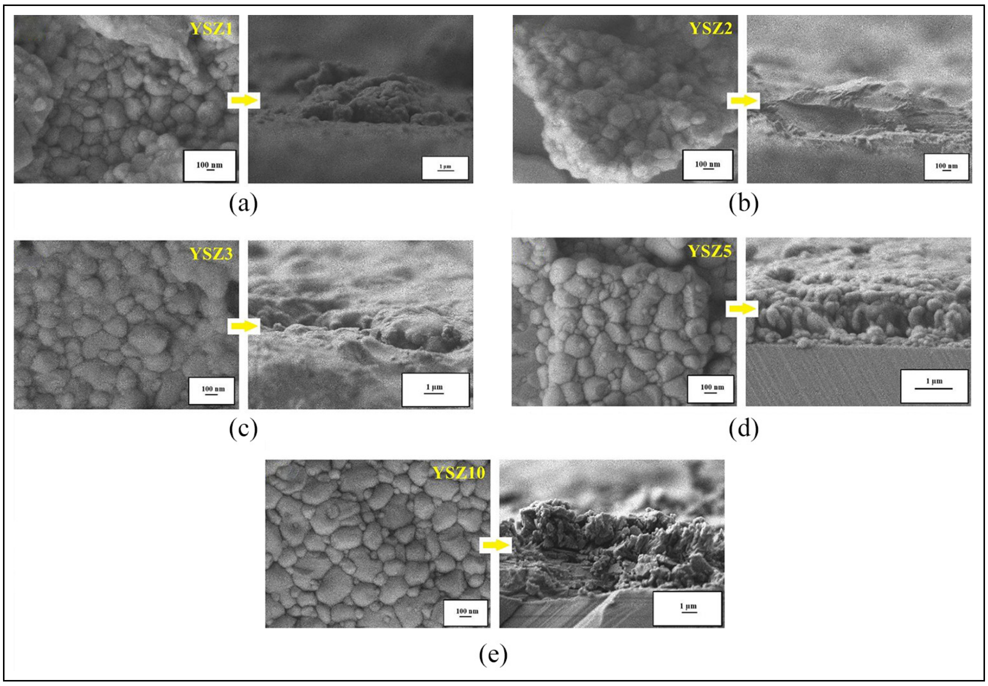


**Figure 3.** Top view (left) and cross-sectional view (right) of FESEM images for: (a) YSZ1, (b) YSZ2, (c) YSZ3, (d) YSZ5 and (e) YSZ10.

increase in the layer thickness. YSZ2 film with two layers showed the optimum results. It was demonstrated that the morphology and structures of the YSZ thin films can be tuned by adjusting the layer thickness. The findings of this study can be useful for the development of high performance YSZ electrolyte in SOFC. Thin film SOFC can operate at intermediate and low operating temperatures without performance issue such as high fabrication cost, limited choice of materials and less durability. High operating temperature can limit the progress of the SOFC manufacturing process.

## Declaration of conflicting interests

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