

## Fabrication of yttria stabilized zirconia films as the electrolyte of micro fuel cells by aerosol flame deposition

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The aerosol flame deposition technique using an oxy-hydrogen flame was employed to prepare thin films of yttria-stabilized zirconia from liquid sources. Spherical and dense yttria stabilized zirconia particles were synthesized in the submicrometre range and the particle size distribution was controlled by changing the concentration of the precursor solution and flame conditions. The crystallinity of the synthesized soot powder was reasonably good even in the as-prepared state and an additional heat treatment improved the crystallinity to a level comparable to that of the conventional solid state reaction. The mean diameter of particles was approximately 400-600 nm depending on the precursor solution and the flame conditions. Transmission Electron Microscopy revealed that particles were polycrystalline composed of approximately 20 nm sized grains. It was demonstrated that the aerosol flame deposition technique is a promising approach to realize inexpensive continuous process technology fabricating micro-solid oxide fuel cell devices, since this technique realized a reasonable deposition rate with relatively simple and inexpensive equipment operating under ambient conditions.

**Key words:** YSZ, aerosol flame, fuel cell.

### Introduction

In the past decades, solid oxide fuel cells (SOFC) have been of great interest to researchers working in the field of solid-state ionics and advanced ceramic materials. A SOFC is a new way of producing electrical power from a variety of fuels, in which oxygen is transported via the vacancy mechanism through a dense ceramic electrolyte, normally yttria-stabilized zirconia (YSZ). Recently, a major issue in SOFC is the reduction of operation temperature since the high operation temperature invokes various thermomechanical problems in cell materials and the cell system, and in the management of fuel cell system. Among the various approaches to solve this problem, the employment of a thin film type electrolyte is a direct and simple approach while the appropriate method to fabricate the thin film is not fully demonstrated yet [1, 2]. Since this approach also enables the realization of "micro" or "mini" SOFC, the necessity for thin film type electrolyte becomes increasingly important in the fuel cell industry.

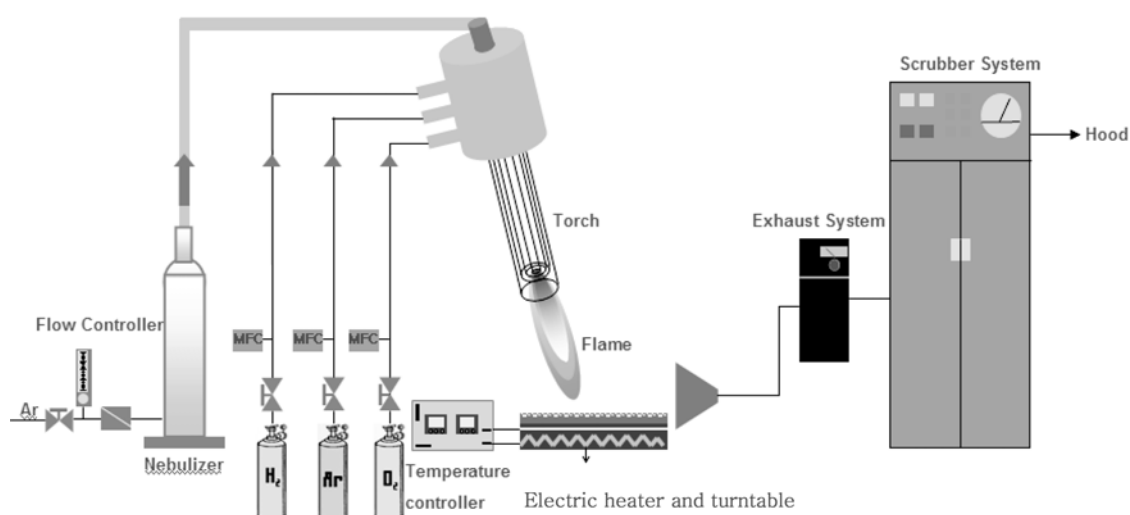
For the SOFC electrolyte, stabilized cubic zirconia with 8 mol% yttrium oxide (so called "8YSZ") is still the essential material because it has sufficient ionic conductivity at planar SOFC operating temperatures (about  $10^{-2}$  S/cm<sup>-1</sup> at 800 °C) [3, 4]. YSZ has various

excellent properties as an electrolyte for a SOFC, such as high heat resistance, high mechanical strength, chemical durability, and high ionic conductivity at high temperature. YSZ is more advantageous compared to a ceria (CeO<sub>2</sub>)-based electrolyte, another common candidate of electrolyte, in terms of high temperature mechanical strength and stability.

To realize a micro or mini SOFC, it is essential to develop new technology to fabricate the thin film of each component of a SOFC, namely the electrolyte and electrode assembly including catalysts and current collectors. It would be desirable if all these components were fabricated in a continuous process with a simple apparatus for low manufacturing cost. Aerosol flame deposition is promising for synthesis and deposition of a broad spectrum of inorganic nano-particles since liquid precursors can be used instead of gaseous precursors. The deposition rate of this technique is very high (0.1-1 μm/minute) compared to conventional thin film deposition techniques such as electrochemical deposition (EVD), plasma spray, sputtering, spray pyrolysis, Aerosol-assisted metal-organic chemical vapor deposition and sol-gel [5-10]. Furthermore, this technique does not require a vacuum and hence the deposition apparatus is relatively simple. By contrast, this technique requires high temperature heat treatment to densify the as-deposited film since the synthesized materials are in the form of particles or porous soot [11-13]. In spite of this shortcoming, it is believed that this technique is very useful for the fabrication of oxide films 1-10 μm thick.

In this paper, we report the preparation procedure of

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**Fig. 1.** A schematic diagram of the experimental apparatus for aerosol flame deposition for the synthesis of YSZ.

particles and films of YSZ by the aerosol flame deposition technique for application as an electrolyte layer of a micro or mini SOFC.

## Experiments

A schematic of the experimental apparatus for the synthesis and deposition of YSZ particles is shown in Fig. 1. The experimental apparatus consists of an aerosol generator, a deposition chamber, and a gas delivery system. The aerosol generation was performed by an ultrasonic nebulizer employing a 1.7 MHz resonator, which is known to generate an aerosol of  $\sim 1 \mu\text{m}$  diameter. The aerosol generated from the liquid-type source material is transported by the Ar carrier gas to the high temperature oxy-hydrogen flame for pyrolysis and hydrolysis, and intense thermal oxidation takes place within the flame to produce normally nano-sized oxide particles in an extremely short time, normally less than 0.5s. The deposition chamber includes a rotating stage with linear motion controlled by a computer program assuring uniform deposition during the rotation. The quartz torch producing the flame was constructed by several concentric tubes whose diameters were designed to match the flow velocity at the end of torch so that eventually a laminar flow of mixed gases could be formed. The fuel gases used to produce the flame were  $\text{H}_2$  and  $\text{O}_2$ , which produced a flame with maximum  $\sim 1800^\circ\text{C}$ .

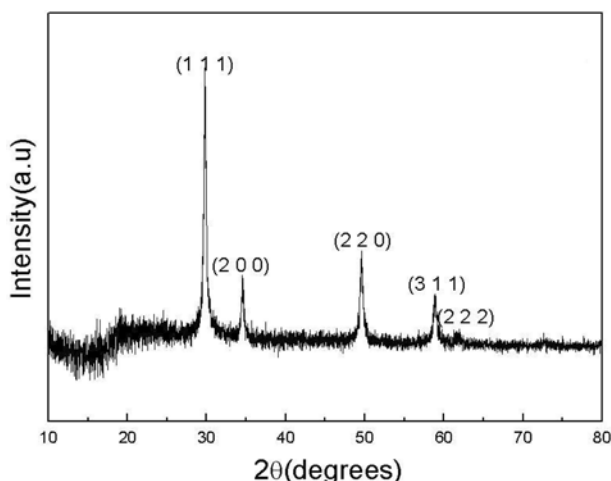
Yttria-stabilized zirconia (YSZ) powder was prepared from an ethanol (99.9%) based solution containing zirconium(IV) n-propoxide  $\text{Zr}(\text{n-C}_3\text{H}_7\text{O})_4$  (in n-propanol, 70%, Aldrich) and yttrium nitrate  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.9%, Aldrich). Source reagents were dissolved in ethanol and a small quantity of nitric acid was added to aid complete dissolution of these constituents. A Zr/Y ratio of 0.84:0.16 was chosen with total precursor concentrations (Zr+Y) of 0.1, 0.2, and 0.3 M.

The flow rate of source material was dependent on the Ar carrier gas flow rate, the ultrasonic resonator intensity, and the solution concentration. In this study, the Ar carrier gas flow rate (1 l/minute) and the ultrasonic resonator intensity were fixed. Submicrometer YSZ particles were deposited on Si substrates with  $1 \mu\text{m}$  thermally grown  $\text{SiO}_2$  on silicon. To ensure uniform deposition, a Si substrate was placed on the rotating stage, which was kept at about  $150^\circ\text{C}$  to eliminate  $\text{H}_2\text{O}$  formed by the fuel reaction producing the flame. To consolidate the soot, samples were placed in an electric furnace and heated up to  $1400^\circ\text{C}$  for more than 2 hours or in a microwave furnace for 5 minutes.

The morphology and size distribution of the particles prepared and the thin films were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was used to observe the microstructure of individual particles. X-ray diffraction [Rigaku D/max-2500, with  $\text{CuK}_\alpha$  X-ray radiation 40 mA 100 mV] was used to confirm the crystallographic state of synthesized particles and thin films.

## Results and Discussion

The XRD pattern of synthesized soot (Fig. 2) exhibited only the diffraction peaks of the cubic structured YSZ, suggesting that a fully-stabilized cubic phase  $\text{ZrO}_2$  was successfully synthesized directly from the liquid precursor solution. The composition of YSZ was  $\text{Y}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$  when judged based on the comparison to the data in JCPDS. SEM analysis of the deposited YSZ powders from the precursor solution reveals that the zirconia particles are spherical, the particles size sub-micrometer, as shown in Fig. 3. The particle sizes were measured around 0.2 to  $0.6 \mu\text{m}$ . The synthesis method used in this study differs to that in the previous report in the fuel type used to supply the heat for thermal reaction. The synthesis temperature was estimated to be

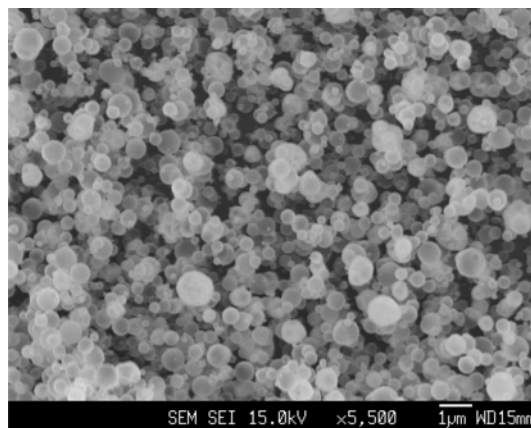


**Fig. 2.** XRD pattern of YSZ powder deposited on a Si wafer substrate. YSZ powder was synthesized at a H<sub>2</sub> flow rate 2 l/minute, O<sub>2</sub> flow rate 2 l/minute, Ar flow rate 1 l/minute, turntable temperature at 150 °C, the concentration of source materials in the precursor solution 0.2 mol%.

1300-1800 °C which is much higher than that in the conventional flame synthesis or spray pyrolysis process. Liquid droplets generated by the ultrasonic system explosively broke into much smaller droplets due to the extremely high temperature of the flame and subsequent instantaneous evaporation of solvent in high temperature flame produced the solid particles in a very short time. Then, these seed particles were deposited on the substrate at the end of the flame by thermophoresis. Thus, the particle size of YSZ synthesized in this study was smaller than that in a previous report and the particle morphology was more spherical. The particle size decreased with increasing deposition temperature, which was controlled by changing the flow rate of fuel gas, especially hydrogen. Since the spherical solid particles were formed instantaneously and the residence time of these particles inside the flame was short, the degree of particle agglomeration was also significantly lower in this study compared to that of a previous report. The size distribution of synthesized YSZ particles was dependent on the concentration of precursor solution as shown in Fig. 4. The particle size is largely dependant on the aerosol droplet size and the concentration of source liquid as predicted by Lang [14]. The particle size gradually increased with increasing concentration of the precursor solution. Once the droplet size of the aerosol,  $D_{droplet}$ , generated by the ultrasonic nebulizer is determined, the size of the particle,  $d_p$ , transformed from this aerosol droplet is expressed on the following equation:

$$d_p = \left[ \frac{MS_s}{1000\rho_s} \right]^{1/3} D_{droplet} \quad (1)$$

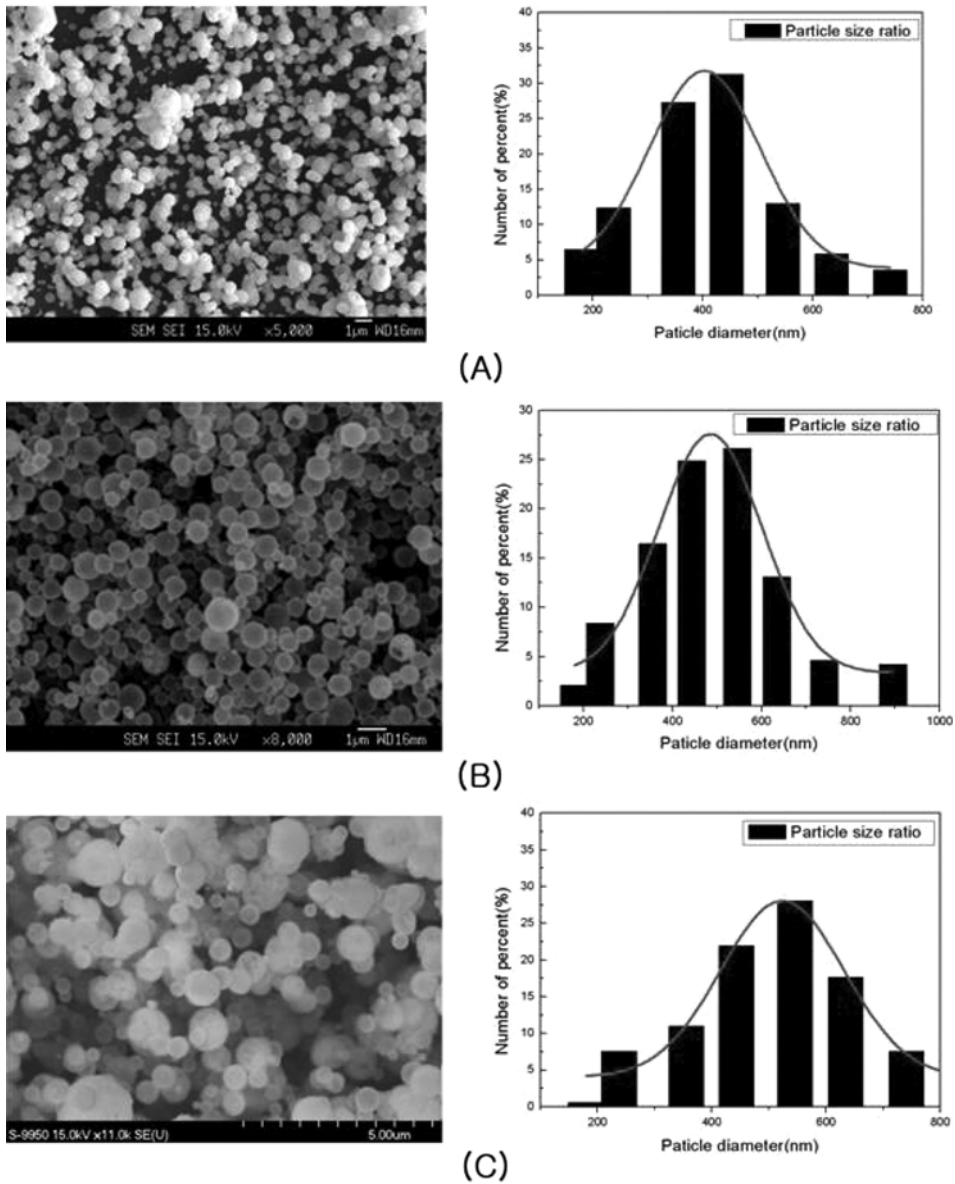
where  $M$  and  $\rho_s$  are the molecular weight and theoretical density of the particle material, and  $C_s$  is the



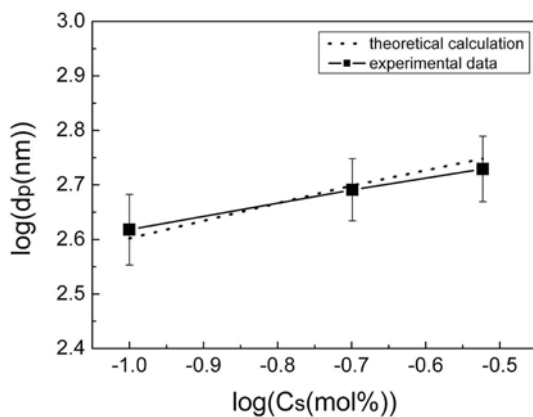
**Fig. 3.** SEM micrograph of YSZ particles synthesized by aerosol flame deposition. YSZ powder was synthesized at H<sub>2</sub> flow rate 2 l/minute, O<sub>2</sub> flow rate 2 l/minute, Ar flow rate 1 l/minute, turntable temperature at 150 °C, the concentration of source materials in the precursor solution 0.2 mol%.

concentration of source materials in the precursor solution. This equation assumes that there is no complex aerosol dynamics such as the breaking up of large droplets and Brownian coagulations of particles. In Figure 5, the concentration dependence of particle size is compared to that in equation (1) and one can see that theory successfully predicts the variation of mean particle size as a function of  $C_s$ . Nevertheless, the concentration dependency (the slope of linear fitted line) was slightly lower than 1/3 and this suggests that there are other parameters determining the particle size in the real experiments such as the change of the viscosity of the precursor solution, the breaking up of droplets, and the coagulation of particles within the flame. However, it is clear that the particle size can be controlled by simply changing the concentration of the precursor solution, even though it is less effective than the control of droplet size ( $d_p \sim D_{droplet}$ ). The fitted result in Figure 5 also suggests that the aerosol breaking and the particle coagulation do not strongly affect the final particle size in this materials system, which is probably due to the low vapor pressure of YSZ. Another problem with the control of particle size by changing the concentration of the precursor solution is that the deposition rate or the efficiency of particle formation changes concurrently. Indeed, it was observed that the deposition rate of YSZ soot increased with an increase in the concentration of the precursor solution. Therefore, it is clear that the control of droplet size is a more efficient way to control the particle size since it does not sacrifice the deposition rate.

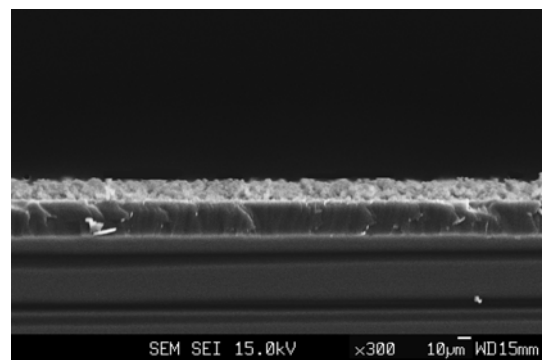
YSZ was first deposited on a Si wafer in the form of porous soot as shown in Fig. 6. The thickness of soot layer was 22 μm and the deposition rate was approximately 1.2 μm/min. Figure 7 shows the deposition rate as a function of the concentration of source materials in the precursor solution. As expected, the deposition rate increased with increasing precursor solution concen-



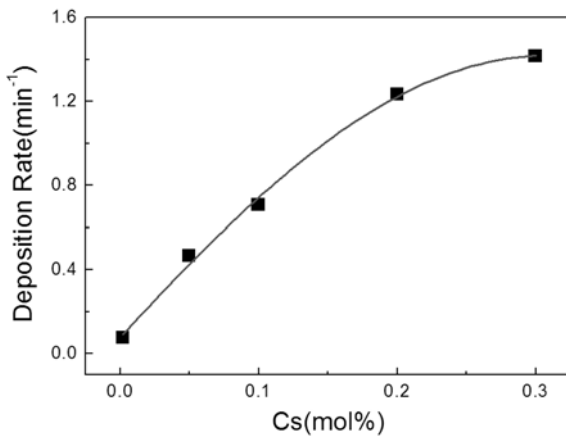
**Fig. 4.** Particle size distribution of the YSZ powders synthesized from 0.1, 0.2 and 0.3 mol precursor solutions. YSZ powder was synthesized at H<sub>2</sub> flow rate 2 l/minut, O<sub>2</sub> flow rate 2 l/minut, Ar flow rate 1 l/minut, turn table temperature at 150 °C, the concentration of source materials in the precursor solution 0.2 mol%.



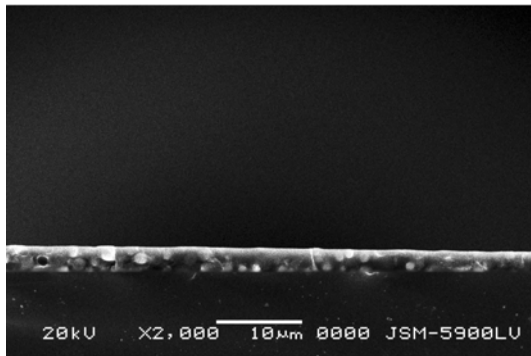
**Fig. 5.** The variation of mean particle size as a function of the concentration of source materials in the precursor solution. The dotted line is the theoretical calculation by Lang’s model [14].



**Fig. 6.** Cross sectional SEM image of a YSZ film deposited on a Si-wafer by aerosol flame deposition. YSZ powder was synthesized at H<sub>2</sub> flow rate 2 l/minut, O<sub>2</sub> flow rate 2 l/minut, Ar flow rate 1 l/minut, turntable temperature at 150 °C, the concentration of source materials in the precursor solution 0.2 mol%.



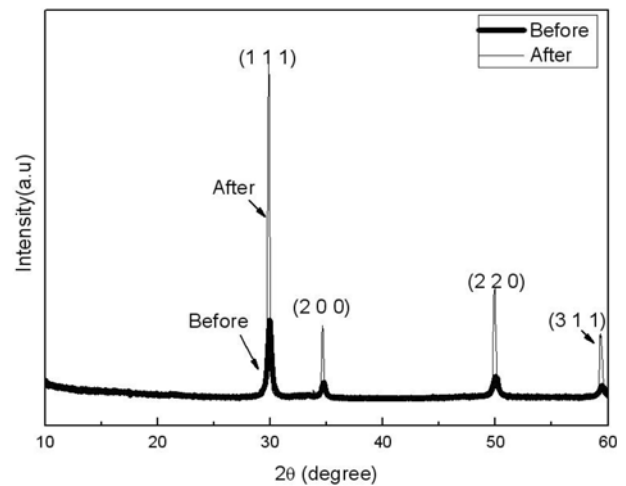
**Fig. 7.** Deposition rate of YSZ films as a function of the concentration of source materials in the precursor solution.



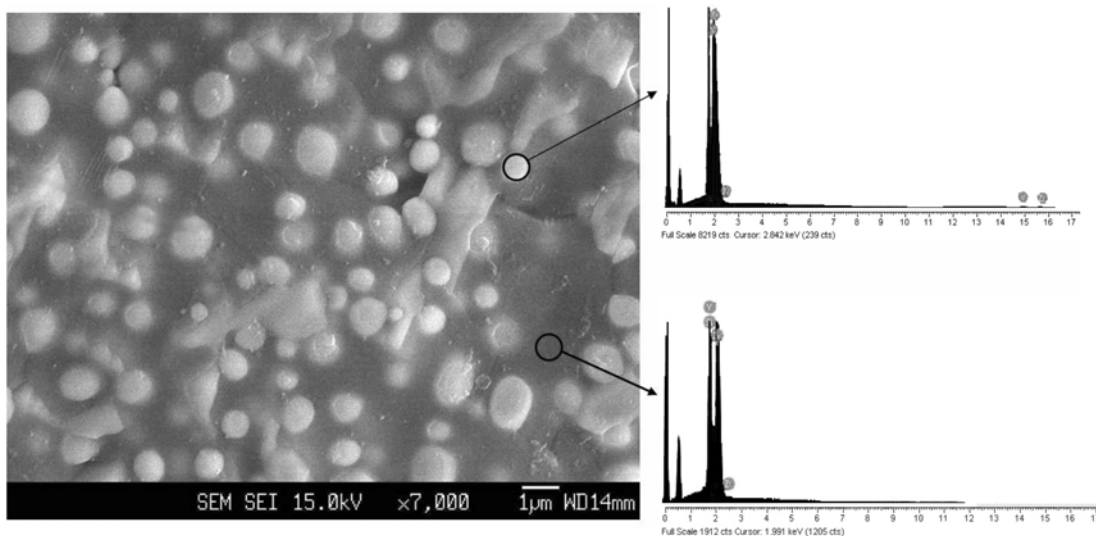
**Fig. 8.** Cross sectional SEM image of YSZ film deposited on a Si-wafer after sintering at 1400 °C for 2 h. YSZ powder was synthesized at H<sub>2</sub> flow rate 2 l/minut, O<sub>2</sub> flow rate 2 l/minut, Ar flow rate 1 l/minut, turntable temperature at 150 °C, the concentration of source materials in the precursor solution 0.2 mol%.

tration due to the increased amount of source materials contained in aerosol droplets.

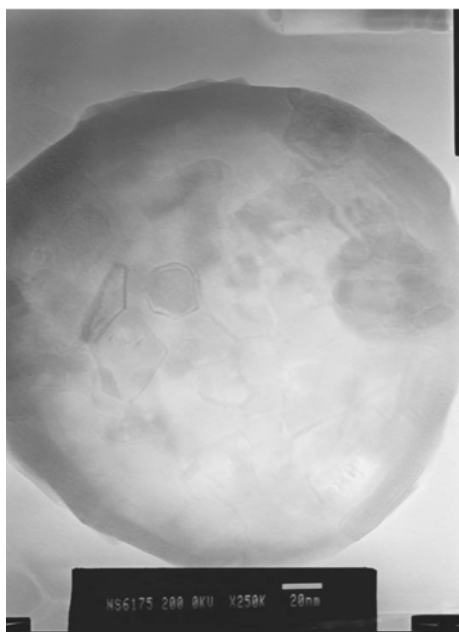
This soot layer shrunk into a dense thin film by the high temperature sintering (1400 °C, 2 h) in a furnace and the volume shrinkage ratio was approximately 10 as shown in Fig. 8. Figure 9 shows an image of the surface of a YSZ film sintered at 1400 °C for 2 hours, in which white spherical particles are the particles not fully sintered. The number density of the white particle was reduced by increasing the sintering temperature or sintering time. Although the film was fully densified, the white particles were not completely eliminated even after 2 hours sintering probably due to their large initial particle size. The dark portion surrounding white particle is thought to be formed by material transport during the high temperature sintering and it filled the pores between original particles in the soot film. The surface of the dense film was slightly rough since the size of the white particles was comparable to the thickness of dense film. Therefore, it is necessary to reduce the soot



**Fig. 10.** The comparison of XRD patterns of YSZ measured before and after sintering at 1400 °C for 2 h.



**Fig. 9.** The morphology of a YSZ film deposited on a Si-wafer after sintering at 1400 °C for 2 h and the EDS spectra of the white and the dark spots. YSZ powder was synthesized at H<sub>2</sub> flow rate 2 l/minut, O<sub>2</sub> flow rate 2 l/minut, Ar flow rate 1 l/minut, turntable temperature at 150 °C, the concentration of source materials in the precursor solution 0.2 mol% .



**Fig. 11.** TEM image of a YSZ particle synthesized by aerosol flame deposition. YSZ powder was synthesized at a  $\text{H}_2$  flow rate 2 l/minut,  $\text{O}_2$  flow rate 2 l/minut, Ar flow rate 1 l/minut, turntable temperature at  $150^\circ\text{C}$ , the concentration of source materials in the precursor solution 0.2 mol%.

particle size to fabricate a completely uniform and smooth film, though it is not a prerequisite in a fuel cell device since the rough surface of electrode enhances the electrochemical reaction by increasing the interfacial area. The compositional analysis by energy dispersive spectroscopy shown in Fig. 9 reveals that the chemical composition of the dark portion is not different from that of the white particles and this result suggests that a normal sintering process occurred. Particles originally formed during the deposition seem to be porous on the nano scale even though their crystallinity is fairly good. The porous nature of synthesized particles seems to be maintained even during the sintering process.

Figure 10 shows the difference in the XRD crystalline peak pattern measured before and after sintering of the YSZ film. After sintering, the FWHM of each peak became narrower and the peak intensity was increased, which is ascribed to the enhanced crystallinity. A TEM image of a synthesized particle (Fig. 11) also revealed that the particles are polycrystalline composed of tiny grains whose size is approximately 20 nm.

## Conclusions

Aerosol Flame Deposition (AFD) technology, a novel aerosol technique, has been demonstrated to be useful for the production of submicrometer YSZ powders. The YSZ particles synthesized by this method were spherical, solid, and free of agglomeration. The crystallinity of particles was also excellent even without additional heat treatment and the polycrystalline particles were composed of 20 nm grains. A very good deposition rate was achieved and the thickness of the YSZ film after sintering was approximately  $4\ \mu\text{m}$ .

However, for completely uniform films with smooth surfaces, the porosity of the starting film should be controlled to be low enough, which can be achieved by a smaller particle size. This is a technical challenge to be attempted in future and the authors are currently seeking an appropriate method to generate a smaller droplet size.

## Acknowledgements

This work was supported by the Seoul Research and Business Development Program (Grant No 10583).

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