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Yttria stabilized zirconia films deposited by electro-spray deposition for solid oxide fuel cells

Yongsub Yoon, Jongmo Im and Dongwook Shin*
Division of Material Science & Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul, Korea

Solid oxide fuel cells(SOFCs) are interesting as an energy conversion system of the future with high efficiency and environmental cleanness. To fabricate the micro-fuel cell for mobile applications, it is essential to develop a process for the deposition of dense electrolyte films. In this study, for a micro-SOFC application, YSZ electrolyte films were prepared by an electro-spray deposition (ESD) method. The deposition parameters studied were deposition temperature, distance between nozzle and substrate, solution concentration and DC voltage. Depending on these parameters, the surfaces were remarkably changed from cracked or rough surfaces to smooth and dense films. Dense films was prepared with the conditions of a nozzle-substrate distance of 4 cm, a deposition temperature of 150 °C, a deposition time of 4 minutes, and a voltage of 16 kV.

Key words: SOFC, Electrolyte, ESD, YSZ.

Introduction

A solid oxide fuel cell (SOFC) is suggested as one of the solutions for the energy exhaustion problem in the future. SOFCs have the advantages of high over cell efficiency and a versatility of fuel in comparison with other fuel cells such as molt carbonate fuel cell and polymer electrolyte membrane fuel cell [1]. However, the high operation temperature of SOFCs(700-900 °C) is known to be the cause that each material or stack become unstable when operated for an extended period of time, which has lead to effort to lower the operation temperature [2]. A thin electrolyte film is a plausible solution to reduce the operation temperature. Regarding the fabrication of thin electrolyte films, many reports are found in the literature such as the use of chemical vapor deposition [3], pulsed laser deposition [4] and sputtering [5]. The electro-spray deposition system is a method of fabricating oxide films by injecting a precursor solution through spray nozzles and depositing with evaporation droplets on substrates at a high temperature. In this study, to fabricate thin and dense electrolyte films and to enhance the efficiency of a SOFC, YSZ electrolyte layer were deposited on silicon substrates by the ESD method. The deposited YSZ films were surveyed for their surface morphology and structure.

Experiments

Fig. 1 is a schematic of the electro-spray deposition (ESD) system employed in this study. The ESD system is composed of a syringe pump, a spray nozzle, a DC voltage power supply, and a hot table. The syringe pump is used to control the flow of the precursor solution into the nozzle. A stainless steel nozzle with an outer diameter of 0.31 mm was employed to spray the solution with an applied voltage of 8-20 kV.

The precursor solution was prepared by dissolving yttrium acetate hydrate and zirconyl nitrate powders into methanol. The composition of the precursor was set to be 8 mol% Y_2O_3-92 mol% ZrO_2 to deposit a film with the maximum ionic conductivity [2]. The concentration of precursor solution and the flow rate were fixed at 0.1 M and 1.8 ml/h. The experimental variables were the distance between nozzle and substrate, the temperature of the substrate, and the deposition time. The prepared as-deposited films were sintered at 400-1200 °C.

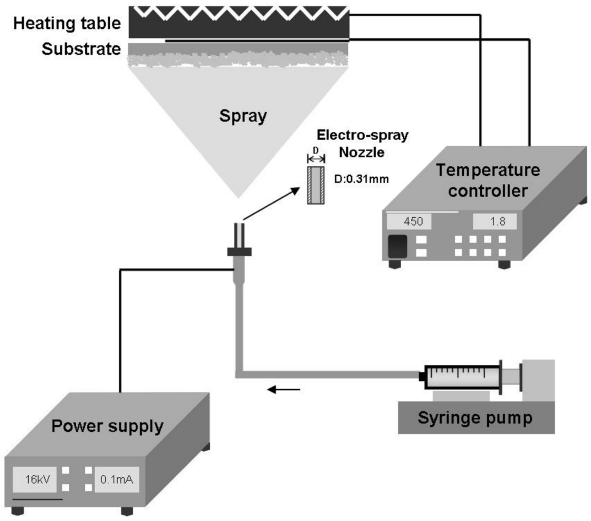

Fig. 1. ESD system set-up.

*Corresponding author:
Tel : +82-2-2220-0503
Fax: +82-2-2220-4011
E-mail: dwshin@hanyang.ac.kr

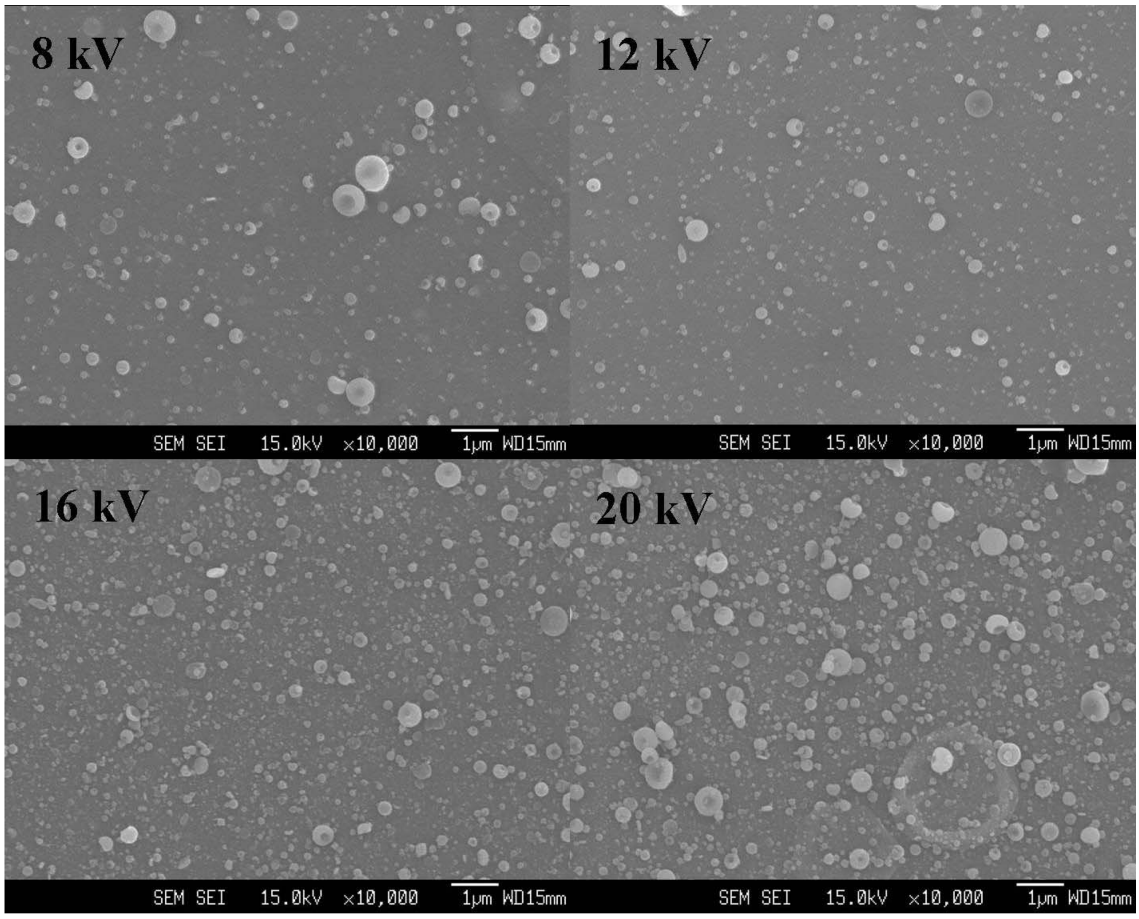

Fig. 2. SEM images of YSZ particles deposited on silicon substrates by electro-spray deposition at a nozzle-substrate distance of 4 cm, a deposition time of 30 seconds, a substrate temperature of 150 °C, a solution flow rate of 1.8 ml/h, and nozzle voltages of 8, 12, 16, and 20 kV.

Results and Discussion

To investigate the effects of the nozzle voltage, YSZ was deposited on silicon substrates with positive nozzle voltages of 8, 12, 16, and 20 kV. While other factors were fixed; the nozzle-substrate distance was 4 cm, the deposition time was 30 seconds, and the substrate temperature was 150 °C. The effects of a positive nozzle voltage on the microstructure of the as-deposited YSZ films are summarized in Fig. 2. It was thought that the size of particles decreased on increasing the positive voltage from 8 kV to 16 kV. It is assumed that the higher positive voltage increases the repulsive force between liquid precursor droplets, which results in this exceeding the surface tension of the droplets. Therefore, increasing the positive voltage is believed to form finer droplets and prevent droplets from coalescence. Wei *et al*. [6] demonstrated that a higher electrical field usually generates finer atomized aerosol droplets and uniform surfaces. However, on increasing the positive voltage from 16 kV to 20 kV, the average size of particles was increased, and the number of particle was increased. As claimed by Fu *et al*. [7], higher electric field strength resulted in a higher speed of the droplets and a shorter time between the nozzle and substrate. It might be thought that the hollow, large particles were fabricated because the strong electric field from a nozzle voltage of 20 kV reduced the evaporation time. Consequently, it is demonstrated that a nozzle voltage of 16 kV was optimum for the generation of smaller droplets, which lead to the formation of smaller particles, and the voltage were fixed as 16 kV.

Fig. 3 are the surface morphologies of YSZ films deposited with nozzle-substrate distances of 3, 3.5, 4, 4.5, and 5 cm at a nozzle voltage of 16 kV, a deposition time of 2 minutes, and a substrate temperature of 150 °C. When the distance was 3 and 3.5 cm, most droplets landed on the substrate with incompletely evaporated solvent. This might be thought to form a wet YSZ as-deposit, which results in the generation of severe cracks due to thermal shrinkage during the fast drying process. At a distance of 4 cm, the cracks in the film disappeared and the film was formed from particles. As the distance become larger to 5 cm, the quantity of particles was reduced due to the droplets spreading in all directions, and the films disappeared due to the droplets completely evaporating over the longer distances. Therefore, it was concluded from this result that a nozzle-substrate distance of 4 cm is the optimum for dense films.

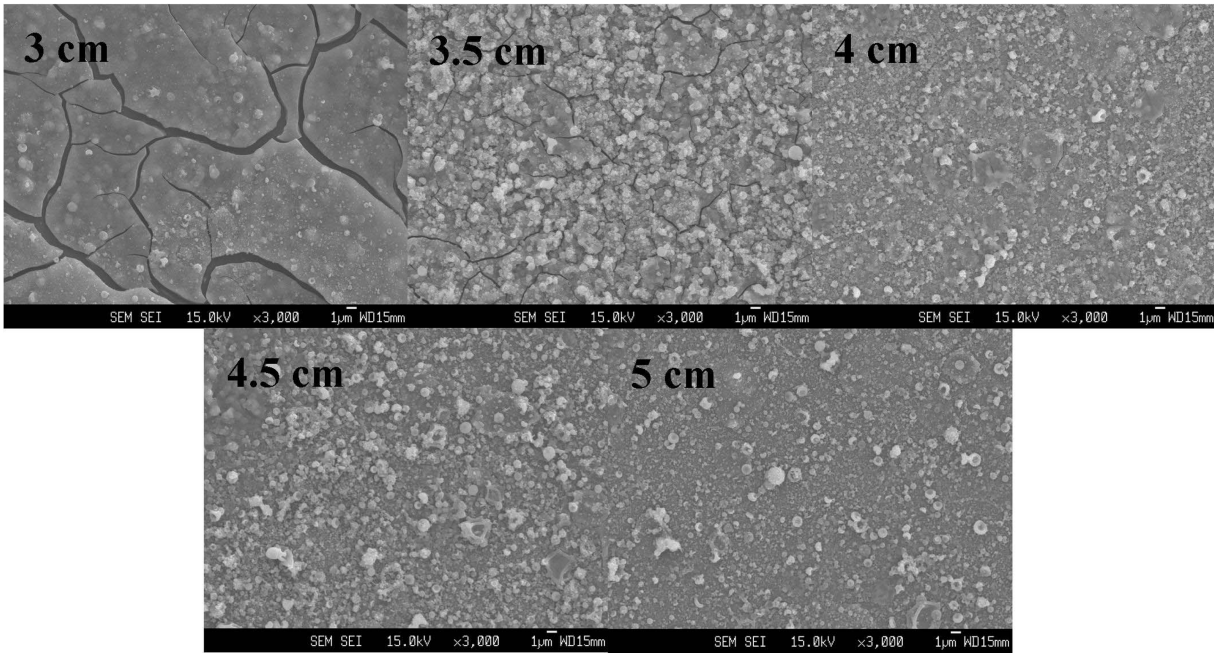

Fig. 3. SEM images of YSZ films deposited on silicon substrates by electro-spray deposition at a substrate temperature of 150 °C, a nozzle voltage of 16 kV, a deposition time of 2 minutes, a solution flow rate of 1.8 ml/h, and nozzle-substrate distances of 3, 3.5, 4, 4.5, 5 cm.

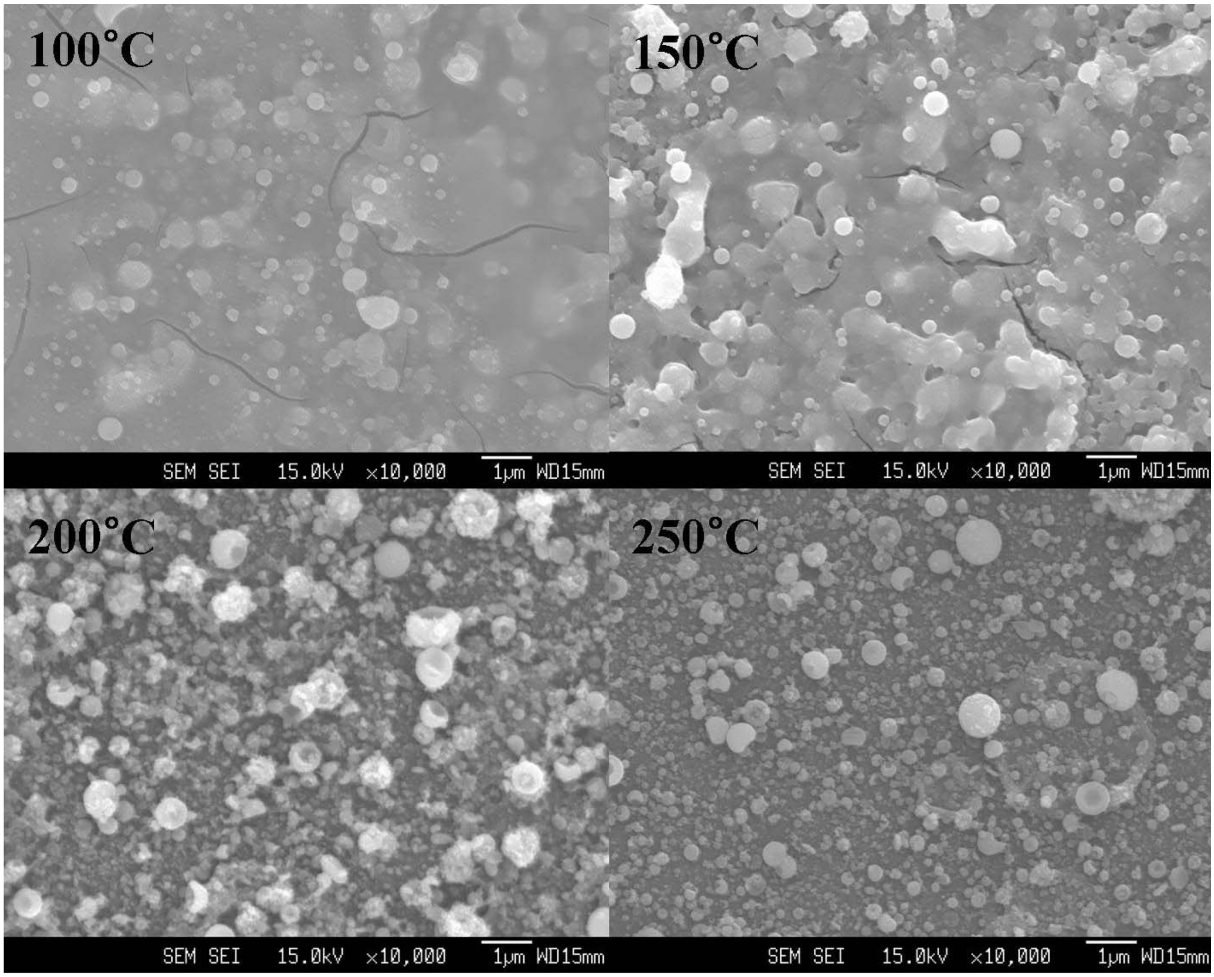

Fig. 4. SEM images of YSZ films deposited on silicon substrates by electro-spray deposition at a nozzle-substrate distance of 4 cm, a nozzle voltage of 16 kV, a deposition time of 4 minutes, a solution flow rate of 1.8 ml/h, and substrate temperatures of 100, 150, 200 and 250 °C.

Fig. 4 shows the effect of the substrate temperature during a deposition time of 4 minutes. At 100 °C, the deposition temperature was too low to evaporate the solvent from landing droplets. On the other hand, at 200 and 250 °C, the surfaces were covered by particles. At 200 °C, hollow particles were produced, and above this temperature hollow particles were not found. Neagu *et al*. [8] demonstrated that cracked films were deposited at a low temperature and particles were fabricated at a high temperature. As claimed by them, dense and crack-free films were deposited at a middle temperature between low temperature and high temperature. Dense YSZ films were deposited on the substrate at 150 °C as a middle temperature, and then heated to sintering temperatures of 400, 600, 800, 1000, and 1200 °C.

Fig. 5 gives X-ray diffraction patterns of YSZ films deposited at a nozzle voltage of 16 kV, a deposition time of 4 minutes, a substrate temperature of 150 °C, and a nozzle-substrate distance of 4 cm. The YSZ film sintered at 400 °C exhibited an amorphous diffraction pattern. Bohac and Gauckler [9] explained that the oxide films deposited by spray deposition experience the following steps; (1) the spreads of liquid droplets, (2) solvent evaporation leading to the formation of solid films, (3) a chemical reaction and burnout of the organic residue, and (4) nucleation and growth of the oxide films. According to this explanation the organic residue in the YSZ film was not evaporated until 400 °C, and the crystallization started in the range between 400-600 °C. The crystallinity was enhanced by increasing the temperature to 1000 °C and the peak intensities were not increased above 1000 °C

Conclusion

An ESD system was employed to deposit YSZ electrolyte films and the experimental conditions for obtaining the dense films were investigated. The morphologies of the deposited films were remarkably changed by the evaporation of liquid droplets. In the deposition mechanisms of films by ESD, the droplets were deposited as mixtures of the particles by complete evaporation and films by incomplete evaporation. Dense films was prepared with the conditions of a nozzle-substrate distance of 4 cm, a deposition temperature of 150 °C, a deposition time of 4 minutes, and a voltage power of 16 kV. The crystallinity of YSZ films became higher with an increase of the sintering temperature to 1000 °C.

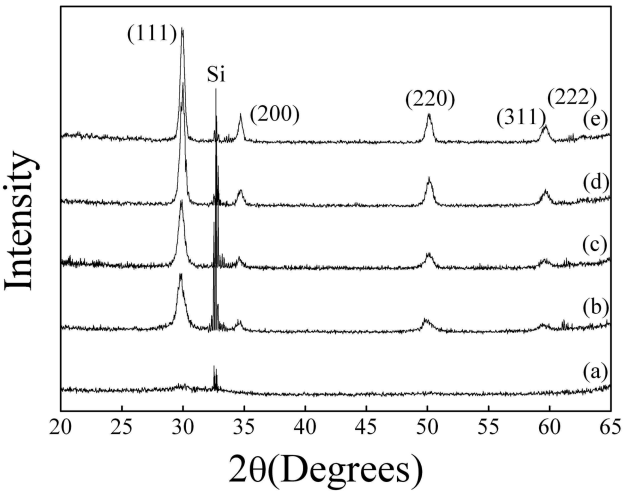

Fig. 5. X-ray diffraction patterns of YSZ films sintered at (a) 400, (b) 600, (c) 800, (d) 1000 and (e) 1200 °C.

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