

Fabrication of nickel oxide-yttria stabilized zirconia films by electrostatic spray deposition

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The commonly used NiO-YSZ cermet is known to have many desirable properties for the anode of solid oxide fuel cells (SOFCs), such as high electronic and ionic conductivity, high electrochemical activity, and good microstructural stability. When used as an anode of an SOFC, the critical factor determining the performance of the NiO-YSZ composite material is the porosity and pore size to ensure a large enough effective surface area for electrochemical oxidation. In this study, electrostatic spray deposition (ESD) was applied to fabricate a porous film of a NiO-YSZ cermet. An ESD system has several advantages over the conventional thick film process, such as creating a uniform coating for large areas, in expensive and simple equipment, high synthesis efficiency, fast deposition rate, a diversity of raw materials selection, operation at atmospheric conditions, and easy control of deposition rate and film thickness. A solution of NiO-YSZ (NiO- 8 mol% yttria stabilized zirconia) in methanol was sprayed onto the anode substrate surface at 350–500 °C by ESD. The Porosity and microstructure were controlled by changing the deposition process parameters and the sintering temperature. The deposition parameters studied were substrate temperature, distance between nozzle and substrate, deposition time and DC voltage.

Key words: NiO-YSZ, SOFC, ESD.

Introduction

Solid Oxide Fuel Cells (SOFCs) have received much attention as energy conversion systems owing to their high efficiency and environmentally-friendly nature, as well as their ability to convert chemical energy to electrical energy directly with a variety of fuels. Due to the rapid development of materials science and technology SOFCs are expected to be commercialized very soon [1].

The most frequently used SOFC systems employ yttria stabilized zirconia (YSZ) as an electrolyte, cermet like nickel oxide-yttria stabilized zirconia (NiO-YSZ) as an anode, conducting oxides like lanthanum manganites, $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ ($\text{M} = \text{Sr}, \text{Ba}$) or LaCoO_3 as a cathode and LaCrO_3 as an interconnect [2].

The commonly used NiO-YSZ cermet is known to have many desirable properties for use in SOFC anodes, such as high electronic and ionic conductivity, high electrochemical activity and good microstructural stability [3]. The NiO-component acts as an electronic conductor and fuel catalyst, while the YSZ phase serves as a supporting matrix to adhere the nickel to the electrolyte. These processes ensures their uniform dispersion and prevents coalescence, [2] provides a catalyst substrate and improves the stability of the anode [4].

The fabrication of anode cermets entails the mixing of coarse and fine YSZ particles with NiO nanoparticles,

where coarse YSZ is used to match the thermal expansion coefficient of the anode to the electrolyte while fine particles are employed to prevent the NiO particles from agglomeration and co-sintering [4]. This anode composition minimizes delamination of components due to thermal expansion mismatch as well as maintaining the desired porosity in the electrode. NiO-8YSZ is widely used as an anode material in SOFCs.

We have applied the electrostatic spray deposition (ESD) technique because it is particularly advantageous in tailoring the film morphology of a large variety of ceramic thin films. The ESD technique was originally developed for advanced-battery electrodes and may be applied to film deposition of NiO-YSZ electrolyte onto a substrate, as demonstrated in an earlier study [8].

The effect of separate ESD parameters on the NiO-YSZ film morphology was previously presented [8]. The aim of our study is to define the domain of the process parameters (substrate temperature, nozzle-to-substrate distance, deposition time, and voltage power) where porous NiO-YSZ anode layers may be obtained and to find a method to realize a film with a gradient porosity.

Experimental

Fig. 1 shows a schematic of the ESD apparatus employed in this study. It consists basically of a nozzle with a pump delivering the precursor solution of NiO-YSZ to the syringe at a measured rate. Syringe needles with 0.03 mm inner diameter have been used as nozzles. A hot plate was employed to heat the substrate and a high voltage power

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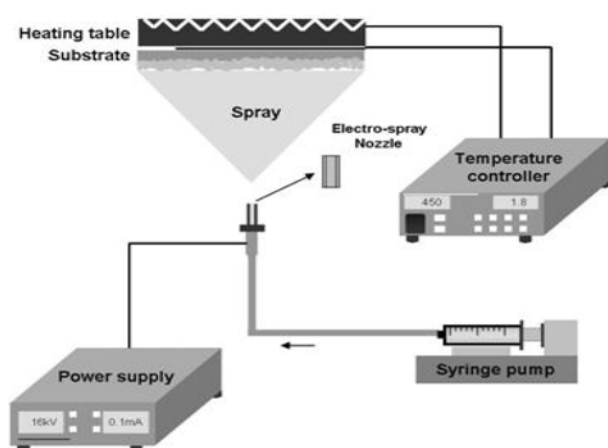


Fig. 1. Schematic of the ESD apparatus.

supply was applied between the nozzle (positive polarity) and the target substrate at ground potential. The distance between the nozzle and target on the substrate was adjustable. In this study, the nozzle was pointed upward and the substrate fixed onto the hot plate, pointed downward.

A precursor solution was prepared by dissolving nickel nitrate hexahydrate (Junsei Chemical Co., Japan), yttrium acetate hydrate (Aldrich Chemical Co., U.S.A) and zirconyl nitrate hydrate (Aldrich Chemical Co., U.S.A) powders into methanol. The composition of the NiO-YSZ composite powder was mixed in a weight ratio 6 : 4 wt.%. In addition, the composition of the precursor was a mixture of 8 mol% Y_2O_3 and 92 mol% ZrO_2 . The concentration of the precursor solution was 0.1 mol/l. The experimental variables were the distance between the nozzle and substrate, the substrate temperature, the

deposition time, and the voltage power. The solution was sprayed onto silicon substrates. The nozzle-to-substrate distance was varied from 40 mm to 55 mm. The temperature of the substrate was altered changed from 350 °C to 500 °C. The deposition time was altered from 90 s to 180 s. The solution was atomized by a high voltage (12 kV to 18 kV) power supply. The voltage was chosen in order to maintain a cone-jet atomization regime. The prepared as-deposited films were sintered by a microwave furnace at 1200 °C for 5 minutes. The Morphology of the films was observed by scanning electron microscopy (SEM) and the crystallinity was analysed using an X-ray diffractometer with $CuK\alpha$ radiation.

Results and Discussion

ESD is a method of liquid atomization by electrical forces, and the process of ESD may be divided into three main steps: atomization of the solution at the nozzle tip, transport of the droplets between the nozzle and the substrate, and formation of the coating on the substrate. Detailed physicochemical reactions of these steps are influenced by the process parameters.

Influence of the nozzle to substrate distance

Fig. 2 shows typical SEM micrographs of NiO-YSZ films deposited by electrostatic spray deposition at a nozzle-to-substrate distance from 40 mm to 55 mm. The same quantity of solution is sprayed over a larger area of the substrate if the distance is increased and vice versa [8]. Simultaneously, a larger quantity of solvent evaporates during the transport phase if a longer distance is used.

As shown in Fig. 2, when the distance was 40 mm,

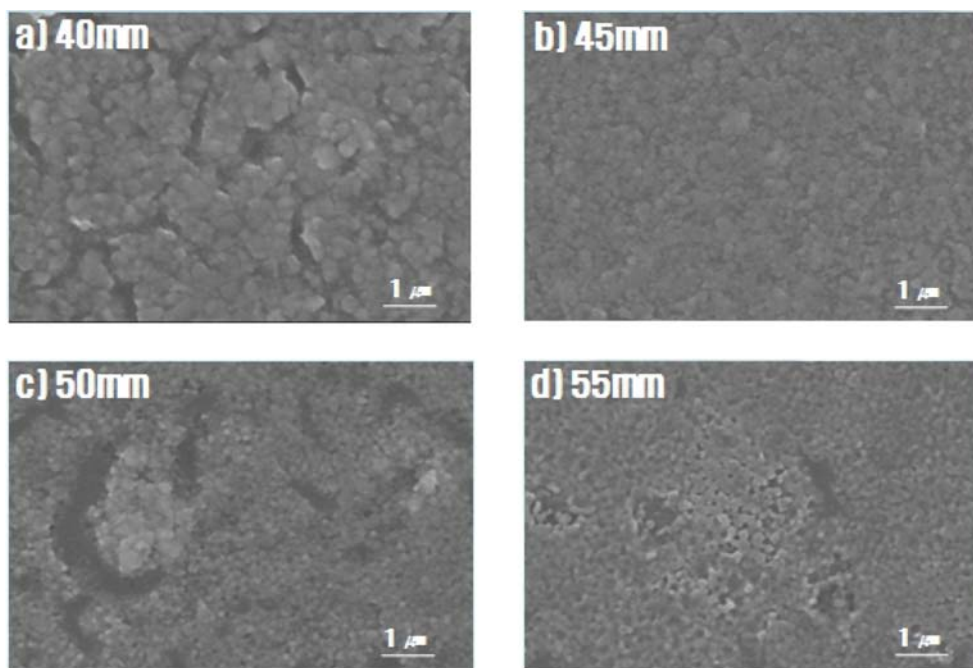


Fig. 2. SEM micrographs of NiO-YSZ films deposited by electrostatic spray deposition. The substrate temperature was 400 °C, the voltage 17 kV, the deposition time 180 s, the solution flow rate 4.0 ml/h, and nozzle-to-substrate distance, a) 40 mm, b) 45 mm, c) 50 mm, d) 55 mm.

most droplets were deposited on the substrate with incompletely evaporated solvent. The particle size became smaller with increasing distance. At a distance longer than 45 mm, the size of the particles was reduced due to the gravity effect and the evaporation of the solvent during the flight of longer distances.

Influence of the substrate temperature

Fig. 3 shows typical SEM micrographs of NiO-YSZ films deposited by electrostatic spray deposition at substrate temperature from 350 °C to 500 °C. As shown in Fig. 3, the roughness and porosity of the films increased with

increasing substrate temperature.

When the substrate temperature was less than 400 °C, wet particles were deposited because of the low evaporation rate of solvent during the transport of the droplets. With increasing temperature, the evaporation of solvents became very fast. When the optimum temperature of the substrate was more than 450 °C, the coating layer was uniform and porous. It is considered that a porous film was formed because of fast evaporation of the solvent.

Influence of the deposition time

Fig. 4 shows typical SEM micrograph of NiO-YSZ

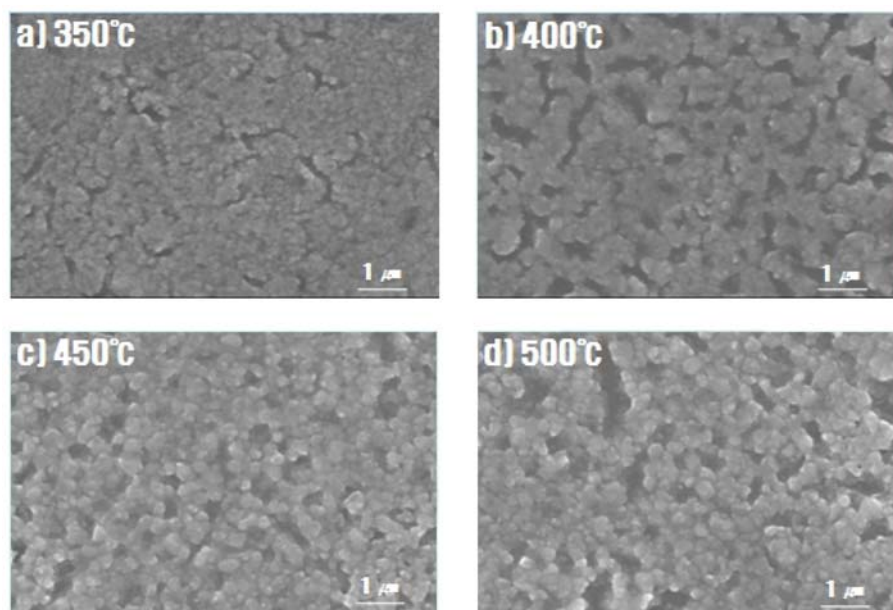


Fig. 3. SEM micrographs of NiO-YSZ films deposited by electrostatic spray deposition. The nozzle-to-substrate distance was 40 mm, the voltage 17 kV, the deposition time 180 s, the solution flow rate 4.0 ml/h, and substrate temperature, a) 350 °C, b) 400 °C, c) 450 °C, d) 500 °C.

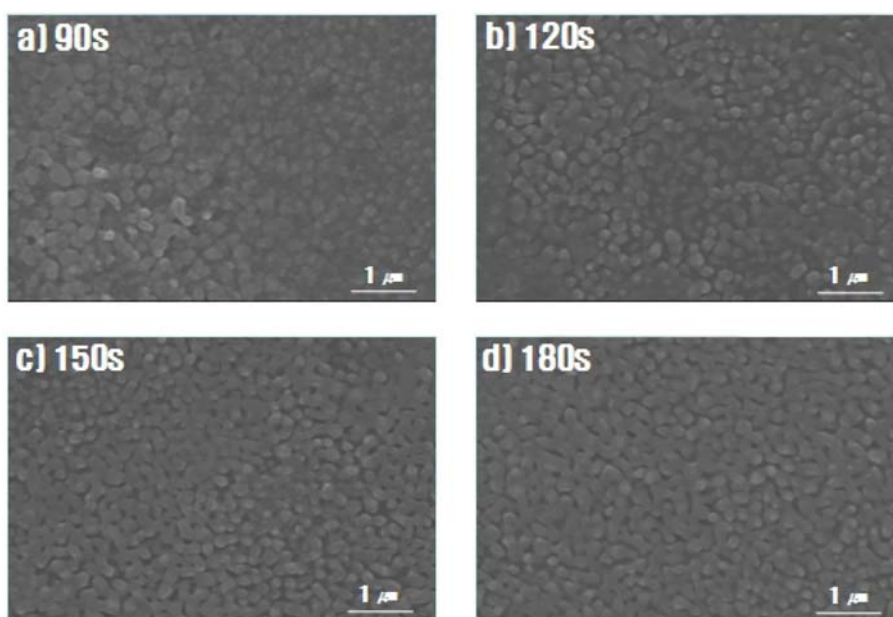


Fig. 4. SEM micrographs of NiO-YSZ films deposited by electrostatic spray deposition. The substrate temperature was 400 °C, the nozzle-to-substrate distance 40 mm, the voltage 17 kV, the solution flow rate 4.0 ml/h, and deposition time, a) 90 s, b) 120 s, c) 150 s, d) 180 s.

films deposited by electrostatic spray deposition at deposition times from 90 s to 180 s. As shown in Fig. 4, at a deposition time of 90 s, a dense morphology appears. At an increased deposition time, a porous microstructure was observed. Because the spreading rate of the droplets was different in reaching the silicon substrate, when the deposition process started, a thin film layer was formed on the substrate. Usually, on a silicon substrate, the spreading rate is larger than on the thin film layer. Therefore, droplets were well spread on the silicon substrate. For shorter deposition times, deposits were generated and dense layers were generated. This effect can be explained by the incomplete evaporation of liquid droplets. On the other hand, with a longer the deposition time, porous microstructures were observed. This generation was attributed to the dry layer formed by the completely evaporated droplets. When the deposition time was less than 120 s, liquid droplets were well spread on the incomplete evaporated wet film. On the other hand, when the deposition time was more than 150 s, liquid droplets were not well spread on the complete evaporated film.

Influence of the voltage

Fig. 5 shows typical SEM micrographs of NiO-YSZ films deposited by electrostatic spray deposition at voltages from 12 kV to 18 kV. As shown in Fig. 5, when the voltage power was 18 kV, a porous microstructure was visible on most parts. Increasing the voltage power caused, porosity to clearly appear. The atomizer nozzle is usually made in the form of a metal capillary, which is biased by a high voltage. The shear stress on the liquid surface, due to the established electric field, causes its disinte-

gration into droplets [14]. The droplets obtained by this method can be extremely small, in special cases down to nanometres. The advantage of ESD is that droplets are highly charged, up to a fraction of the Rayleigh limit. The Rayleigh limit is the magnitude of a charge on a drop, which overcomes the surface tension force that leads to the drop fission [14]. This charge is given by the following equation:

$$Q_R = 2\pi(16\sigma_l\epsilon_0r^3)^{\frac{1}{2}} \quad (1)$$

in which σ_l is the liquid surface tension, ϵ_0 is the electric permittivity of free space, and r is the droplet radius [14]. The charge and size of the droplets can be controlled to some extent by the voltage applied to the nozzle. Charged droplets are self-dispersing in space due to the mutual Coulomb repulsion, resulting in the absence of droplet agglomeration. Therefore, this is believed to form finer droplets and prevent the droplets from coalescence.

Fig. 6 shows the XRD patterns of NiO (60%)-8YSZ films prepared at various sintering temperatures from 1200 °C to 1350 °C.

As shown in Fig. 6, the crystallinity of NiO-YSZ films increased with an increase in the sintering temperature. The intensity of the XRD peaks corresponding to the NiO phase increased with an increase in the sintering temperature of NiO as expected.

Conclusions

The ESD system has proved to be a versatile tool for

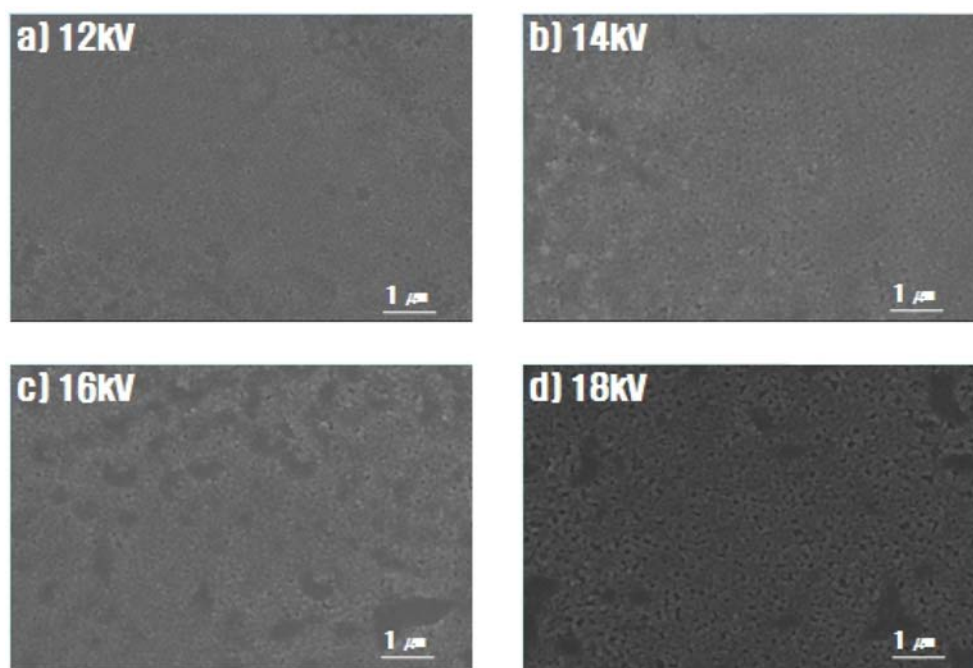


Fig. 5. SEM micrographs of NiO-YSZ films deposited by electrostatic spray deposition. The substrate temperature was 400 °C, the nozzle to substrate distance 40 mm, the deposition time 180 s, the solution flow rate 4.0 ml/h, and voltage, a) 12 kV, b) 14 kV, c) 16 kV, d) 18 kV.

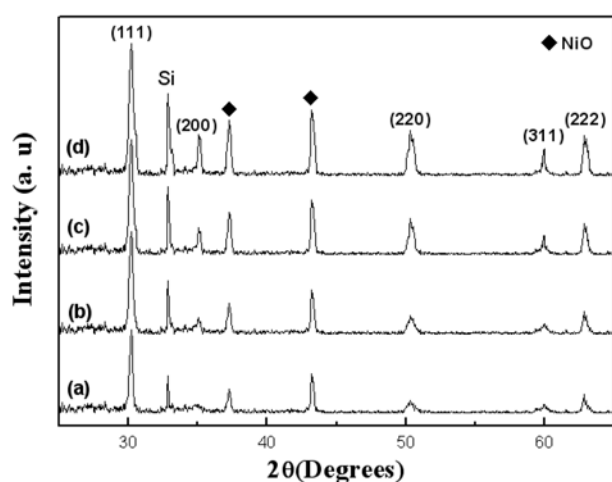


Fig. 6. X-ray diffraction patterns of NiO-YSZ films sintered at a) 1200 °C, b) 1250 °C, c) 1300 °C, d) 1350 °C.

various material processing technologies. This, and previous studies have demonstrated that ESD can be a cost-effective method for manufacturing thin and porous NiO-YSZ films for SOFC applications. The main process parameters studied in our ESD experiments were the substrate temperature, nozzle-to-substrate distance, deposition time, and voltage power. In these experiments the most porous films were observed at a nozzle-to-substrate distance of 55 mm, a substrate temperature of 500 °C, a deposition time of 180 s, and a voltage power of 18 kV. Moreover, it was observed that the degree of crystallinity of NiO-YSZ films became higher by increasing the sintering temperature from 1200 °C to 1350 °C. The ESD system has advantages of uniform coating of large areas, inexpensive equipment, a simple device, high efficiency, a fast deposition rate, a diversity of raw materials selection, operation at atmospheric conditions, and easy control of deposition rate and film thickness. Advances in ESD

applications in thin film deposition will certainly continue in the near future, particularly in nanotechnology and SOFC.

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