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Fabrication of NiO/YSZ anode for solid oxide fuel cells by aerosol flame deposition

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Abstract

Nickel oxide/yttria stabilized zirconia (NiO/YSZ) powder and thin film have been synthesized by aerosol flame deposition (AFD). The nano-sized and spherical NiO/YSZ particles were synthesized and the particle size distribution was controlled by changing processing parameters such as the concentration of the precursor solution. The synthesized powder was composed of YSZ particles of a few hundred nm size and NiO particles of a few tens nm size, which is ideal for the catalysis and reaction of hydrogen offering tremendous amount of three phase boundary. The electrical conductivity of 70% NiO/YSZ exhibited typical metallic behavior and was 10^{-1} S/cm at 700 °C which is adequate for the anode of solid oxide fuel cell.

Keywords: Composites; Porosity; Impedance; Electrical conductivity; Fuel cells

1. Introduction

Solid oxide fuel cells (SOFC) are of current interest as a small/medium power system owing to their high efficiency and comprehensive range of application. Thin film electrodes and electrolyte enables the miniaturization of solid oxide fuel cells and maximization of efficiency. Furthermore, thin film type SOFC will reduce the operation temperature of cell and ease the various problems generated by high temperature operation such as gas sealing and material degradation.

Anode material for SOFC is required to have not only good electronic conductivity but also good ionic conductivity at the same time. To satisfy this requirement, anode electrode should have plenty of three phase boundary (TPB) that is a point among fuel gas, electrode and electrolyte. However, single-layered film type anode will exhibit low performance due to the lack of TPB area and an increase of the polarization resistance during long-term operation. Therefore, the multi-layered porous anode may be a practical approach to solve this problem.[1] The multi-layered anodes have a gradient of particle size, contents of Ni and YSZ and porosity. This system shows a good O^{2-} ionic conductivity by increasing TPB area near YSZ electrolyte and the flow rate of oxygen gas through many pores in the electrolyte. The conventional thin film technique such as sputtering, however, has difficulty to fabricate porous thin film. Therefore, when considering a thin film type SOFC, the new fabrication technique realizing porous film with gradient structure should be developed.

In this study, aerosol flame deposition (AFD) techniques were used to synthesize NiO/YSZ particle and the basic characteristics of synthesized particle and film will be reported.

2. Experimental

Schematically shown in Fig. 1 is a AFD (aerosol flame deposition) system used in this work. AFD system consists of a gas delivery unit, a precursor supply unit including a nebulization system, a reactor containing a torch and rotating wafer stage. In the AFD process, a solution precursor was prepared by dissolving the desired precursors into a solvent and then is atomized into micro-sized aerosol by nebulizer. The flow rate of precursor was controlled by the flow rate of Ar carrier gas. The essential part of the whole system is the combustion unit, which is made from four concentric quartz tubes, creating three ports for source gas and fuel gases for flame. The nebulized aerosol of precursor solution is supplied to the center tube of the torch while hydrogen, argon shield and oxygen are supplied through three ports having different diameters producing the laminar flows of mixture gas. The hydrogen dispersion gas was supplied through an annual gap of 1.5 mm width having an inner radius of 10 mm

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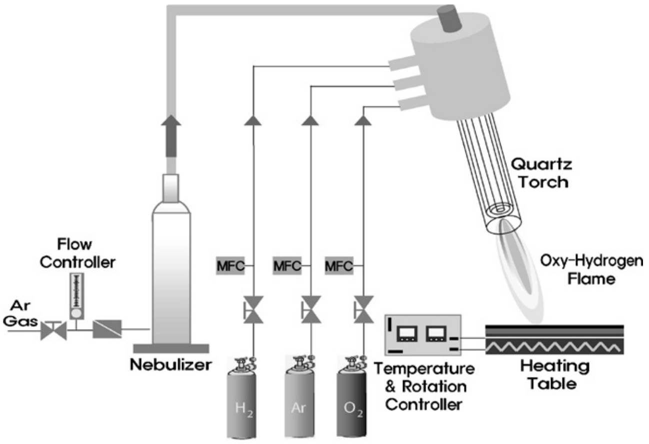

Fig. 1. Experimental set-up of AFD using a nebulizer making precursor solution into aerosol and oxygen–hydrogen torch.

from the center of the torch. The precursor solution atomized by a nebulizer was fed into an oxyhydrogen flame where the aerosol droplets undergo evaporation, oxidation and precipitation of particle in the submicron size range. Substrate is heated on a turn-table to prevent the condensation of water on wafer formed during fuel reaction.

Precursor solution was prepared by dissolving yttrium acetate hydrate, zirconyl nitrate and nickel(II) nitrate hexahydrate powders into methanol. The composition of YSZ was controlled by the composition of precursor solution and set to be 8 mol% Y_2O_3–92 mol% ZrO_2 to maximize the ionic conductivity.[2]

First, NiO/YSZ of composition with 80NiO/20YSZ was synthesized using precursor solutions in the concentration from 0.05 to 1.5 M. Particles was deposited on a silicon wafer for a short time and sintered at 1300 °C. The microscopic features of the prepared particles were characterized using a scanning electron microscope. X-ray diffraction of 1 M 80NiO/YSZ was performed with a scanning step of 0.014°. The electrometer with a furnace was applied to measure conductivities of NiO/YSZ pellets with NiO content varying 40 and 70 mol%. NiO–YSZ pellet of disk shape with 1cm diameter and 0.1 cm thickness was prepared by dry-press and sintered at 900 °C for 10 h, Pt paste was used as an electrode material. Impedance was typically acquired in the frequency range from 0.1 Hz to 1 MHz with a Solartron Si-1260.

3. Results and discussion

Shown in Fig. 2 are the micrographs of 80NiO/YSZ synthesized with precursor solutions concentration from 0.05 to 1.5 M. One can see clearly from Fig. 2(a) that the synthesized particles are composed of particles with two different sizes. It is believed that the relatively large particles are YSZ particles while the smaller ones are NiO. In Fig. 3, NiO particles were formed with typically a few tens of nm since it is completely evaporated and ionized to gas plasma in the oxyhydrogen flame due to relatively low melting temperature and high vapor pressure and precipitates by gas phase homogeneous nucleation. In

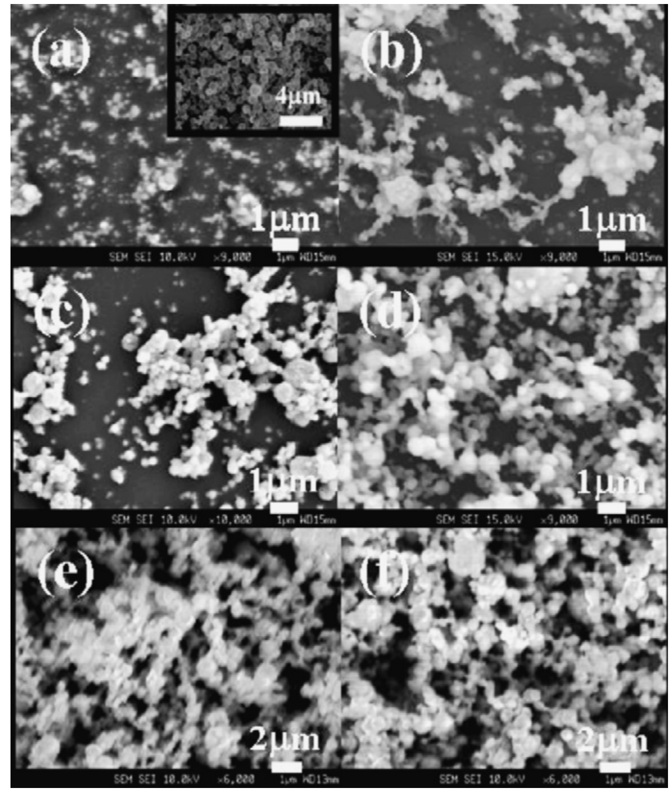

Fig. 2. SEM images of 80NiO/YSZ of the powder synthesized from the precursor solution with the concentration of (a) 0.05 mol% and YSZ, (b) 0.1 mol%, (c) 0.2 mol%, (d) 0.5 mol%, (e) 1 mol%, and (f) 1.5 mol%.

other hand, since the YSZ particles were formed by the direct evaporation of solvent and subsequent collapsing of droplets of precursor solution, the size is relatively large. This is clearly seen from the inset figure in Fig. 2(a), which is the YSZ particle synthesized without Ni source. The particle sizes of two different particles were increased with increasing the precursor solution concentration. The growth of small particles is believed due to intensive Brownian coagulation between precipitated particles, while the growth of large particles is due to increased amount of precursor within each aerosol droplets. The growth of large particles may be explained by Lang's theory.[9] The particle size,

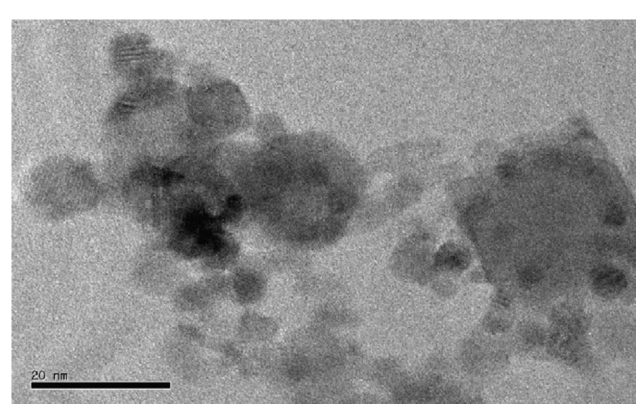

Fig. 3. TEM image of nano-sized particles of 80NiO–YSZ synthesized with 0.05 mol% precursor solution.

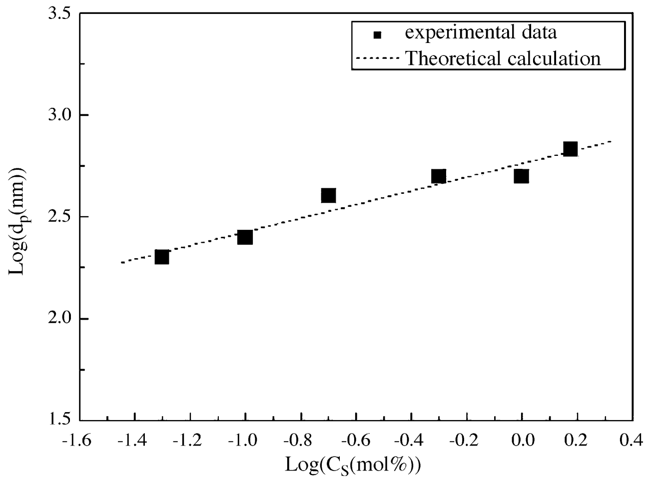

Fig. 4. The precursor solution concentration dependency of particle size. The dotted line is the calculated data based on the Lang's theory.

d_p, is expressed by Eq. (1):

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

where $D_{droplet}$ is the droplet size of aerosol generated by ultrasonic nebulizer, M and ρ_s are the molecular weight and theoretical density of the particle material, and C_s is the concentration of source materials in the precursor solution. This theory predicts the slope in $\log(d_p)$ versus C_s plot is 1/3 and the experimental data in this work produced the slope of ∼1/2 as shown in Fig. 4. This suggests that there are other parameters determining the particle size in the real experiments such as the change of the viscosity of precursor solution, breaking up of droplet, the coagulation of particles within the flame. As the electrolyte thickness decreases, the overall cell polarization losses are increasingly dominated by the losses of the electrochemical reactions at electrodes like anodes and cathodes. Therefore, it becomes increasingly important to lower those losses of electrodes by employing smaller particle size and increased TPB points.[3] Because the electrolytes with nano-sized particle have a

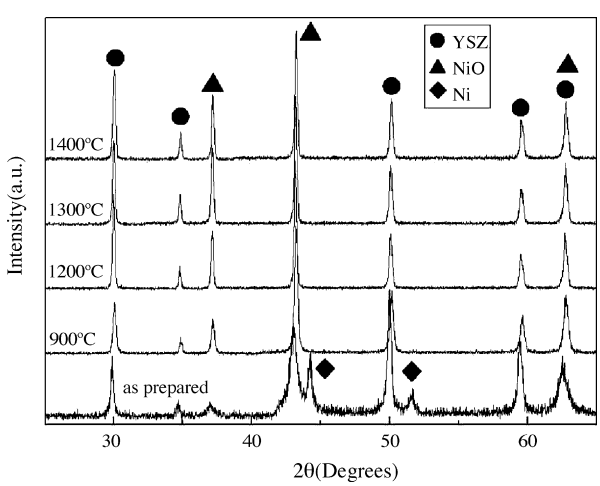

Fig. 5. XRD patterns of synthesized 80NiO/20YSZ sintered at various temperatures.

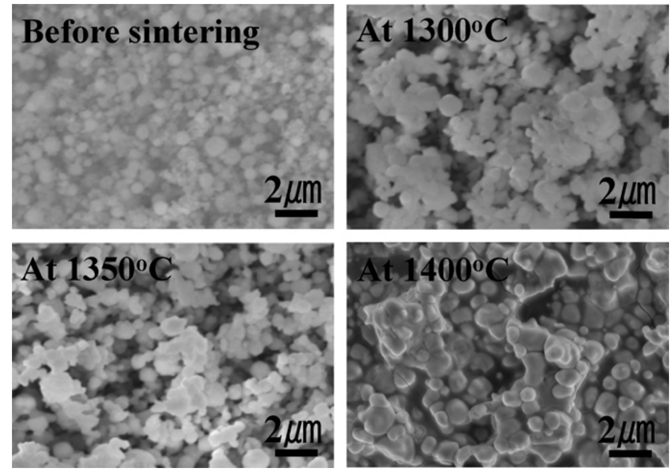

Fig. 6. SEM surface micrographs of 80NiO/YSZ sintered at various temperatures.

good electrochemical efficiency at low temperature,[4,5] the film composed of nano-sized particle similar to the specimen produced in this work would be extremely useful for thin film type SOFC.

Shown in Fig. 5 are the XRD patterns of 80NiO/20YSZ electrodes sintered at various temperatures. As-deposited films before sintering showed Ni metal peaks as well as NiO. Ni metal was synthesized during pyrolysis reaction in the flame due to preferred reaction of YSZ. YSZ peaks exhibited low intensities, suggesting the crystallinity of prepared particles was not fully developed. NiO/YSZ films sintered at 900 °C or more showed fully developed crystalline state and Ni was fully oxidized to NiO.

Shown in Fig. 6 are the microstructures of the 80NiO/YSZ anode sintered at a various sintering temperatures. In general, the films deposited by AFD were very porous in as-deposited state. After sintering process, however, the adhesion between NiO/YSZ particles and with silicon substrate was improved. Pore size and porosity could be controlled by adjusting sintering

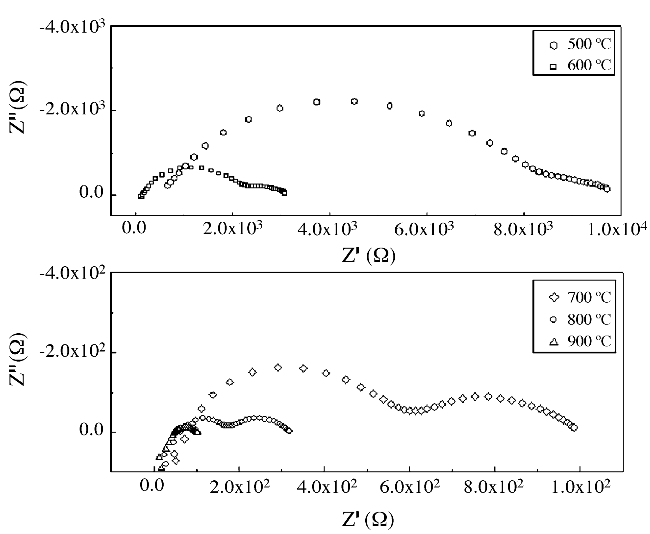

Fig. 7. Typical examples of impedance spectra of 40NiO/YSZ composite samples.

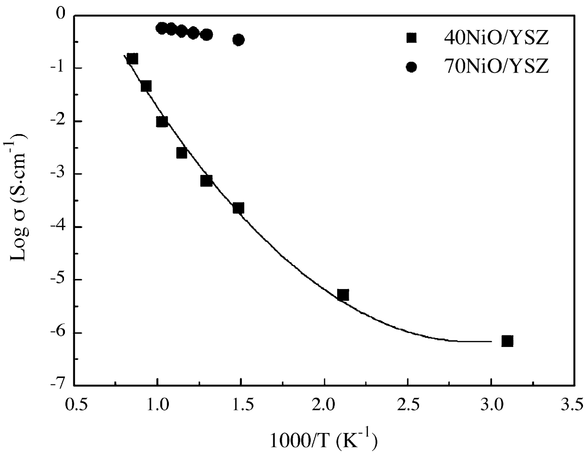

Fig. 8. Electrical conductivity of 40 and 70NiO/YSZ composite as functions of the inverse of temperature.

temperature. The shrinkage happened normally in vertical direction of film. It has been reported that YSZ particles build bridges between particles forming YSZ networks at temperatures over 1400 °C and YSZ sintered at this temperatures showed desirable electrochemical performance.[6,7] NiO/YSZ particles synthesized in this work also showed similar neck formation when sintered as shown in Fig. 6.

Fig. 7 shows the impedance spectra of 40 mol% NiO/YSZ composites measured at various temperatures. Generally, the spectra exhibited two overlapped semicircles.[8] The impedance components originated by grain itself at high frequency were not measured due to the frequency limit of instrument. Therefore, two semicircles shown in the figure can be assigned to the grain boundary and interface components. Fig. 8 is electrical conductivities of 40 and 70NiO/YSZ composites as functions of the inverse of temperature. 40NiO/YSZ composites exhibited typical mixed conduction mechanism, metallic conduction by NiO and ionic conduction by YSZ, while 70NiO/YSZ composites exhibited typical metallic conduction by NiO. The conductivity of 40NiO/YSZ pellets increased from 10^{-6} to 10^{-1} S/cm in the temperature range of 600–900 °C. The conductivity of 70NiO/YSZ pellets reached to 10^{-1} S/cm at 700 °C, which is adequate for an anode of fuel cell.

4. Conclusions

AFD system has been successfully applied to the fabrication of highly porous and nano-structured NiO/YSZ anodes for solid oxide fuel cells. The effects of sintering temperature and precursor concentration in AFD were studied. First, XRD patterns were showed that NiO/YSZ particle was sufficiently crystallized. The control of sintering temperature could adjust microstructures like porosity, particle size, connection and adhesion. At the higher Sintering temperature, porosity was increased and connection and adhesion was better. On the other hands, particle size was influenced by precursor solution concentration. The sizes of NiO/YSZ particles synthesized with low concentration were 50–500 nm. The conductivity of 70NiO/YSZ was 10^{-1} S/cm at 700 °C

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