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Microstructure and electrical conductivity of NiO–YSZ nano-powder synthesized by aerosol flame deposition

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Abstract

The aerosol flame deposition (AFD) process was capable of producing mixed metal oxide powders with 10–500 nm size from low-cost liquid precursors. The nickel oxide–yttria stabilized zirconia (NiO–YSZ) powders used as an anode of SOFC has been synthesised by using AFD process. It was demonstrated that this process is suitable for fabricating the nano-sized and spherical NiO–YSZ particles capable of enhancing three phase boundary areas. The synthesis process was studied by changing processing parameters such as the concentration and the composition ratio of the precursor solution and the flow rates of the flame gases. The sufficiently crystallized and spherically shaped NiO–YSZ particles were synthesized successfully and the size distribution was bimodal when observed by TEM. As changing contents of Ni and YSZ, the conductivities of NiO–YSZ pellet exhibited a typical mixed conductor behaviour of which the ionic conduction is in high temperature range and the electronic conduction is in lower temperature range.

Keywords: B. Nanocomposites; C. Electrical properties; C. Impedance; Aerosol flame deposition (AFD)

1. Introduction

Solid oxide fuel cell (SOFC) is suggested as one of the solutions for energy exhaustion problem in the future. SOFCs have the advantages of high efficiency and stable solid states in comparison with other fuel cells like MCFC and PEMFC. But high operation temperature of SOFCs (700–900 °C) is known to be a cause that each materials or stacks become unstable when operated for an extended period of time. Therefore, it is natural to try to reduce the operation temperature of these cells and this necessity invokes the searches of the electrolytes of higher ionic conductivity at low temperature or thinner electrolyte layer to reduce the apparent resistance. Souza et al. [1] and Nomura et al. [2] deposited 10 micro-sized YSZ thin film on Ni pellets by each colloidal deposition method and electrostatic spray deposition method. The electrical conductivity of electrolyte prepared by Nomura et al. showed 0.1 $\Omega^{-1}\,cm^{-1}$ at 1000 °C. Will et al. [3] synthesized YSZ thin films of a few micro-sized thickness by CVD and PVD.

In the other hand, anode requires porous microstructure and the interfaces between ionic conducting particles and electronic conducting particles. Therefore, fully dense thin film type anode would be inferior in terms of interfacial area for catalytic action and gaseous permeation inside of film. In porous type anode film, the particle size, the porosity and the composition of NiO (or Ni)/YSZ are typical factors affecting characteristics of the anode and several reports on this subject could be found in literature [4–6]. In NiO/YSZ anodes, electrical properties like the polarization resistance are explained that it is associated with the area of three phase boundary (TPB) [7]. TPB is an area where NiO, YSZ and pores coexist as paths for electrons, oxygen ions and hydrogen gases, respectively. In this boundary, the electrochemical reactions take place by combining electrons with oxygen ions of YSZ and hydrogen gases of pores. Accordingly, to maximize the performance of anode, it is desirable that NiO/YSZ particle is smaller, preferably nano-scale, while maintaining the connectivity between particles and the reasonable porosity. The cheap and reliable fabrication method to prepare the porous film containing nano-sized mixed particles and TPB, however, is not available currently. The conventional thin film technology is not adequate to prepare nano-porous film and their deposition rate is too low to prepare

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the film with the thickness of a few micrometers. It is not feasible to use the conventional powder technologies, on the other hand, for the preparation of this thick film. Therefore, if one tries to prepare the film composed of nano-sized particles with TPB and adequate porosity, new method has to be proposed. If a reliable and cheap process for this type of film is established, the realization of micro or ''mini'' solid oxide fuel cell will be a step closer to real applications.

In this study, aerosol flame deposition (AFD) method was applied to synthesize NiO/YSZ nano-powders by depositing on a wafer in a hope to apply to micro-SOFCs. Microstructures and basic electrical characteristics of synthesized NiO/YSZ were studied by changing several process parameters such as precursor concentration, sintering temperature, and atmosphere for the heat treatment.

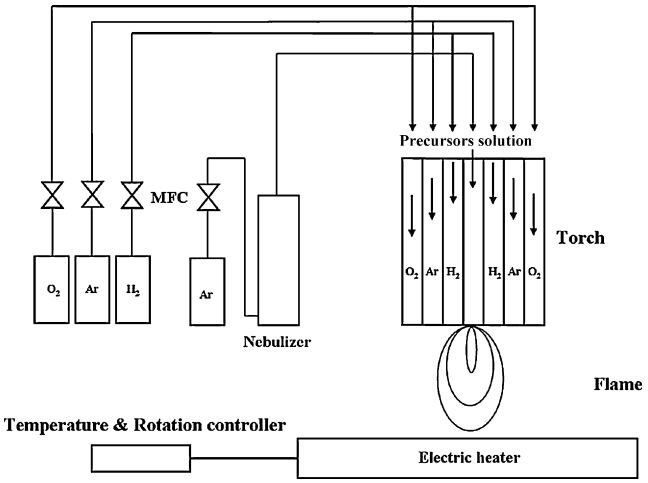

Fig. 1. Schematics of AFD system.

2. Experimental procedure

Fig. 1 is the schematics of the aerosol flame deposition (AFD) system employed in this study. 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 combustion unit, made from four concentric quartz tubes, creates 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 from the center of the torch. The precursor solution atomized by a nebulizer was fed into an oxygen–hydrogen 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.

NiO/YSZ composite powder film was deposited on a Si or Pt wafer from precursor solutions with the composition of 20–80 mol% of nickel(II) nitrate hexahydrate. The notation for the specimen is presented by xNi–$(1-x)$YSZ, where x is the mol% of each component. Because the deposition rate was controlled by content of precursor solutions, the molar concentration of the solutions was fixed as 1 M. The 80Ni–20YSZ powders were deposited on heated silicon wafers. The powders or films were sintered at 900 °C for 10 h in the air and reduced at 900 °C for 2 h in 5% H_2–95% Ar gas mixture.

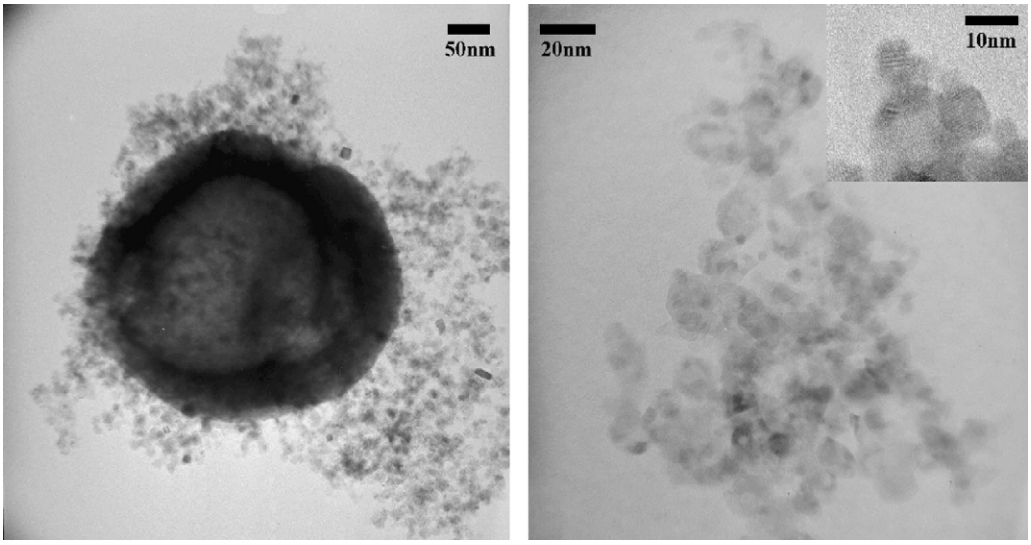

Fig. 2. TEM images of 60Ni–YSZ particles synthesized by AFD. The image in the right shows magnified images of small particles and the inserted figure shows the lattice image of the small particles.

The microstructural features of the prepared particles were characterized using a scanning electron microscope (MIRERO, AIS-2100). The exact shape and size of nano-sized particles were observed by a transmission electron microscope (JEOL, JEM-2010). The variation of crystalline phase was checked by a X-ray diffraction (Rigaku, M2500) for 1 M 60NiO–40YSZ specimen with a scanning step of 0.014°. An impedance analyzer (Solatron, SI-1260) arranged with an electric furnace was applied to measure conductivities of NiO/YSZ pellets with the various Ni content prepared from precursor solution with 20, 40, 60 and 80 mol% of Ni source. 60Ni–YSZ pellet of disk shape with 1 cm 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 10 MHz to 0.01 Hz.

3. Results and discussion

Fig. 2(a) shows a typical TEM image of NiO–YSZ particles prepared by AFD. The image contains particles with two drastically different size ranges, which reflects the bimodal size distribution. It was determined from the direct two-dimensional projection image that the size of large particles is in the range 300–600 nm, while that of small particles was in the range of 10–20 nm as shown in the magnified TEM image of Fig. 2(b). The crystallinity of small particles can be clearly seen from the lattice image in the inserted figure of Fig. 2(b). It was observed that the morphology of large particles was mostly sphere shape while that of smaller particles was less rounded. The experimental evidences for the formation mechanisms of these large and small particles are not obtained yet. However, it is inferred that the large particles are formed from the direct condensation of aerosol droplet by the thermal heat of the flame, while the small particles are formed by the gaseous plasma formation from the vaporized species and subsequent precipitation under the supersaturated atmosphere at the lower temperature region of the flame. The formation of plasma could be observed from the intense color change of the flame from blue to yellowish orange when the precursor source was supplied.

Fig. 3 shows the variation of X-ray diffraction patterns of NiO (or Ni)–YSZ samples prepared at various heat treatment conditions. Before heat treatment, the peaks assigned to Ni metal were appeared as a minor phase as well as YSZ and NiO. The short reaction time due to short residence time within the oxygen–hydrogen flame might be a major cause of this non-oxidized particle formation. In other words, the Ni metal ions in the thermal plasma could not have enough time to be oxidized and this situation would be more evident under a high concentration of Ni in the precursor source. One can easily predict that Ni peaks disappeared after a high temperature sintering and grew after a reductive heat treatment under hydrogen atmosphere. As expected, NiO in the synthesized powder was easily converted to Ni metal under the reduction atmosphere such as a real operation condition exposed to hydrogen sources [9].

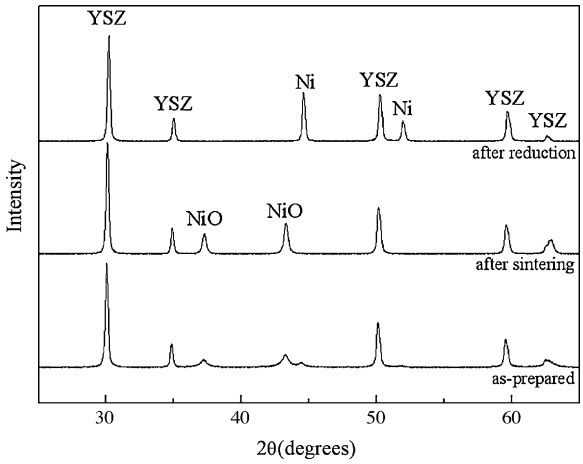

Fig. 3. XRD patterns of the synthesized 60Ni–40YSZ powder. Sintering was performed at 900 °C for 10 h in air and the reduction was performed at 900 °C for 2 h in 5% H_2–95% Ar gas mixture.

Fig. 4 is SEM images of 60Ni–YSZ synthesized from a 1 M precursor solution after various heat treatments. Although the appreciable change in particle size or shape was hardly observed, the particle neck growth/surface smoothening and the surface roughening were noticeable after the sintering in the air and the reduction atmosphere, respectively. This interesting surface roughening might be attributed to the precipitation or growth of Ni metal on the surface of particles and a further study is needed on this subject. It is shown from this figure that the TPB characteristics could be altered by the reduction treatment as well as the oxidation state of Ni related phases.

The electrical conductivities of the specimens sintered in the air are shown in Fig. 5. Conductivity was generally increased with increasing Ni content of precursor solution. Most of specimen exhibited mixed conductivities containing an ionic and

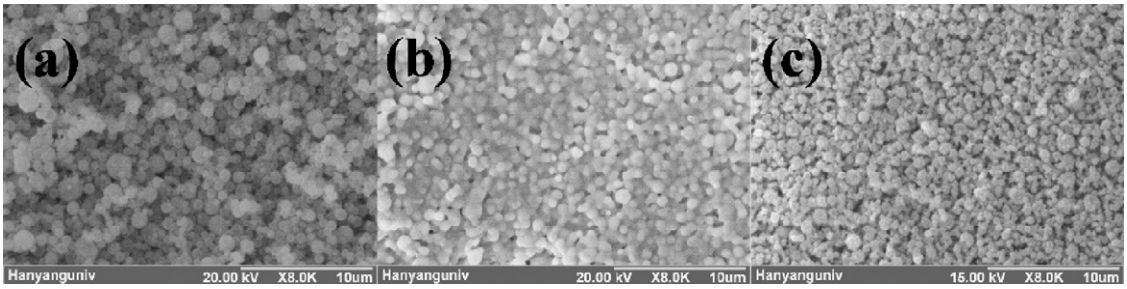

Fig. 4. SEM images of 60Ni–YSZ. (a) As-prepared, (b) after the sintering at 900 °C for 10 h in air, and (c) after the reduction treatment at 900 °C for 2 h in 5% H_2–95% Ar gas mixture.

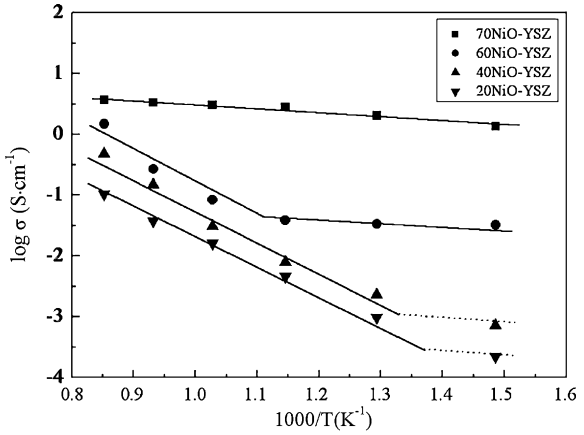

Fig. 5. Arrhenius plots of the conductivity of the pellet type specimens with various Ni contents.

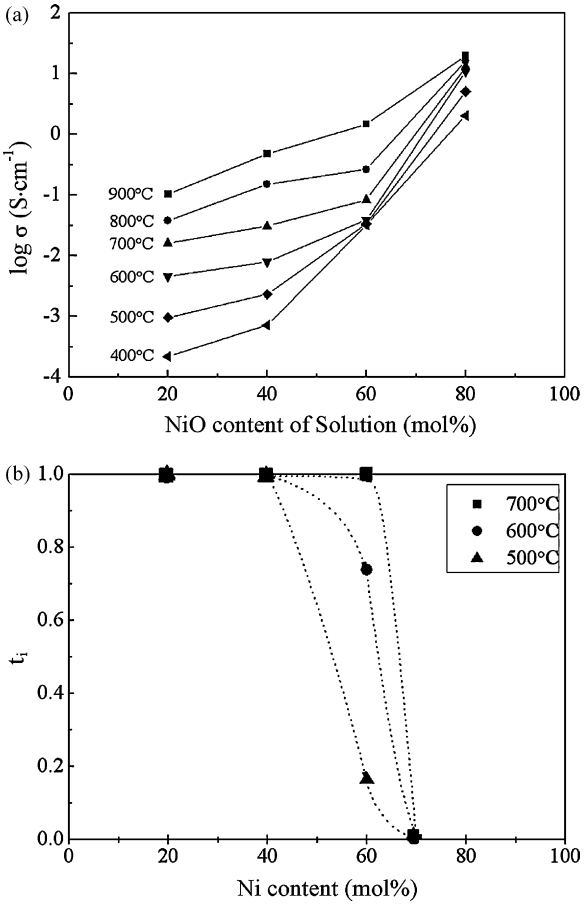

Fig. 6. (a) Conductivity of the NiO–YSZ composites measured as functions of Ni concentration of precursor solution. (b) Ionic transport number (t_i) of the NiO–YSZ composites prepared from the precursor solution with various Ni content.

an electronic component. It is clear that the ionic component has higher activation energy of ∼37.5 kJ/mol [10,11], while the electronic component has lower activation energy of ∼6.0 kJ/mol [8]. As expected, the electronic component was increased with increasing Ni content [12]. From Fig. 6(a), it can be clearly seen that the conduction mechanism is changed from the ionic in 20Ni–80YSZ to electronic in 80Ni–20YSZ. The guideline to separate the region with different mechanisms is not accurate. This is merely for eye guide. The transport number or ionic component, t_i, is shown in Fig. 6(b) exhibited a typical sigmoid type transition curve, which represents the transient or mixed conduction mechanism.

4. Conclusions

For synthesis of NiO–YSZ powders, the AFD system has been successfully applied. The bimodal size distribution was observed and the average sizes resided at tens and hundreds of nm. XRD patterns showed that as-prepared NiO–YSZ particle was sufficiently crystallized, and the coexisting Ni metal was converted into pure NiO or NiO also could be reduced into Ni after sintering under an oxidizing or reducing atmosphere. Interestingly, the reduction treatment roughened the surface of the particles, presumably due to the growth of Ni metal nano-particle. Further study is needed to clarify the exact phase and composition of these nano-particulates. The conductivity and its mechanism of NiO–YSZ composites were controlled by changing precursor solution composition and the conduction mechanism could be changed from ionic to electronic in the synthesized powder with different compositions.

In this study, it was demonstrated that AFD is one of the good candidate for cheap and reliable synthesis method for Ni–YSZ anode. Especially, when a film type anode is designed to apply to a SOFC, the usefulness of this method is believed to be more evident.

References

[1] S. Souza, S.J. Visco, L.C. Jonghe, Thin-film solid oxide fuel cell with high performance at low temperature, Solid State Ionics 98 (1997) 57–61.
[2] H. Nomura, S. Parekh, J.R. Selman, S. Al-hallaj, Fabrication of YSZ electrolyte using electrostatic spray deposition (ESD), I: a comprehensive parametric study, J. Appl. Electrochem. 35 (2005) 61–67.
[3] J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perednis, L.J. Gauckler, Fabricaion of thin electrolytes for second-generation solid oxide fuel cells, Solid State Ionics 131 (2000) 79–96.
[4] M. Marinšek, K. Zupan, J. Macek, Preparation of Ni–YSZ composite materials for solid oxide fuel cell anodes by the gel-preparation method, J. Power Sources 86 (2000) 383–389.
[5] S.P. Jiang, S.H. Chan, A review of anode materials development in solid oxide fuel cells, J. Mater. Sci. 39 (2004) 4405–4439.
[6] P. Holtappels, C. Sorof, M.C. Verbraeken, S. Rambert, U. Vogt, Fuel Cells 6 (2) (2006) 113–116.
[7] S. Primdahl, B.F. Sørenson, M. Mogensen, Effect of nickel oxide/yttria-stabilized zirconia anode precursor sintering temperature on the properties of solid oxide fuel cells, J. Am. Ceram. Soc. 83 (3) (2000) 489–494.
[8] Y.M. Park, G.M. Choi, Mixed ionic and electronic conduction in YSZ–NiO composite, J. Electrochem. Soc. 146 (3) (1999) 883–889.
[9] F.Y. Shih, K.Z. Fung, H.C. Lin, G.J. Chen, Low-temperature synthesis of nanocrystalline NiO–YSZ powders by succinic acid-assisted combustion, J. Power Sources 160 (2005) 148–154.
[10] J.L. Hertz, H.L. Tuller, Electrochemical characterization of thin films for a micro-solid oxide fuel cells, J. Electroceram. 13 (2004) 663–668.
[11] Y. Zhang, J. Gao, D. Peng, M. Guangyao, X. Liu, Dip-coating thin yttria-stabilized zirconia films for solid oxide fuel cell applications, Ceram. Int. 30 (2004) 1049–1053.
[12] Y. Li, Y. Xie, J. Gong, Y. Chen, Z. Zhang, Preparation of Ni/YSZ materials for SOFC anodes by buffer-solution method, Mater. Sci. Eng. B86 (2001) 119–122.