

Improvement of the stability of NiO–YSZ anode material for solid oxide fuel cell

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Abstract Improvement of long-term stability of 40vol.% NiO–60vol.% yttria-stabilized zirconia (YSZ) anode material in reducing atmosphere and under exposure to thermal shock through the modification of vacancy concentration and pore shape has been investigated for a solid oxide fuel cell. We varied the amount of Y_2O_3 additives from 8 to 10 mol% in YSZ and the type of carbon pore former, from plated activated carbon to spherical carbon black, to improve the strength and the stability of porous NiO–YSZ anode materials. Modifications by varying the amount of Y_2O_3 additives and carbon pore former result in a highly stable anode, even upon exposure to a reducing atmosphere for 1,200 h. In particular, the strengths of the new anode materials are markedly improved at the same porosity level. Higher strengths do not degrade during a longtime durability test in a reducing atmosphere or upon thermal shock testing. The relatively smaller degradation of electrical conductivity of the new anode material is discussed in terms of the possibility of suppression of the disconnectivity of Ni phases during operation of a solid oxide fuel cell.

Introduction

The solid oxide fuel cell (SOFC) is a highly efficient and environmentally compatible energy conversion device that produces electricity from oxygen and hydrogen fuel operated at a higher temperature [1]. The SOFC cell consists of ceramic materials. It is currently considered an attractive candidate for commercialization owing to high-energy efficiencies that can reach up to 60% and more than 70% in the case of integration with a gas turbine system [2, 3].

Recently, it has been recognized that the operating temperature should be lowered to an intermediate temperature range of 500–800 °C, from around 1,000 °C, for the commercialization of SOFC [4, 5]. The low ionic conductivity of the yttria-stabilized zirconia (YSZ) electrolyte at reduced operating temperature has been an obstacle to develop intermediate temperature SOFC. Recently, thin films have been considered, as they offer reduced ohmic loss, lower operating temperature, and the possibility of cost reduction as a result of using metal interconnects [6]. Thus, the use of an anode-supported SOFC is a potential technology of reducing the operating temperature [6, 7], because it can reduce the thickness of the YSZ electrolyte.

As the anode of SOFC contains a large concentration of pores, researchers are interested in the development of a porous anode material with high stability, including high mechanical strength, high thermal shock resistance, and appropriate gas permeability, as well as high electrical conductivity [6–11]. Nickel oxide reduces to the nickel phase in a reducing atmosphere, and thus maintaining the connectivity of the nickel phase is another important issue during longtime operation because the connectivity affects the stability of the anode material [8–10]. Therefore, high stability of the porous anode material in a reducing atmosphere is required for long-time stability.

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In the present study, we controlled the amount of Y_2O_3 additives in YSZ and the type of artificial pore former in an effort to improve the stability and the strength of porous NiO–YSZ materials for the anode support for SOFC. We varied the Y_2O_3 content, at 8 and 10 mol%, and investigated the effects of different carbon types, activated carbon (AC) and carbon black (CB). The mechanical strength, thermal shock resistance, electrical conductivity, and the degradation of strength and/or electrical conductivity after thermal shock and longtime duration testing in a reducing atmosphere, respectively, were evaluated. The effect of Y_2O_3 and carbon additives in terms of stability in the porous NiO–YSZ anode was also discussed.

Experimental

The anodes were prepared from mixtures of NiO (Junsei Chemical, Japan) and YSZ powder at volume ratios of NiO/YSZ=40/60%. Different types of YSZ powders were used, 8 mol% of yttria-stabilized zirconia (TZ-8YS, Tosoh, Japan) or 10 mol% of yttria-stabilized zirconia (MPC-ZY10, Millennium Chemical, Australia). We added 10 wt.% of carbon into this powder mixture as an artificial pore former, AC (YP17, Kuraray Chemical, Japan) to 8 mol% YSZ and CB (L30, LG carbon, Korea) to 10 mol% YSZ, and then performed ball milling for an additional 24 h. In some batches, the same amount of AC was added to 10 mol% YSZ for comparison. Scanning electron microscope (SEM) micrographs of the starting powders for the carbon pore formers are shown in Fig. 1. Whereas the AC consists of hexagonal plated carbon, CB is morphologically characterized by relatively smaller spheres. The milled powders were dried in air for 12 h, dried in a hot oven for 24 h, and sieved with a 60-mesh screen. Finally, we prepared two batches of powder mixtures. We designated the batches using as 8Y-AC (8 mol% YSZ–NiO with AC addition), 10Y-AC (10 mol% YSZ–NiO with AC addition), and 10Y-CB (10 mol% YSZ–NiO with CB addition) according to the amount of Y_2O_3 addition and the type of carbon pore former.

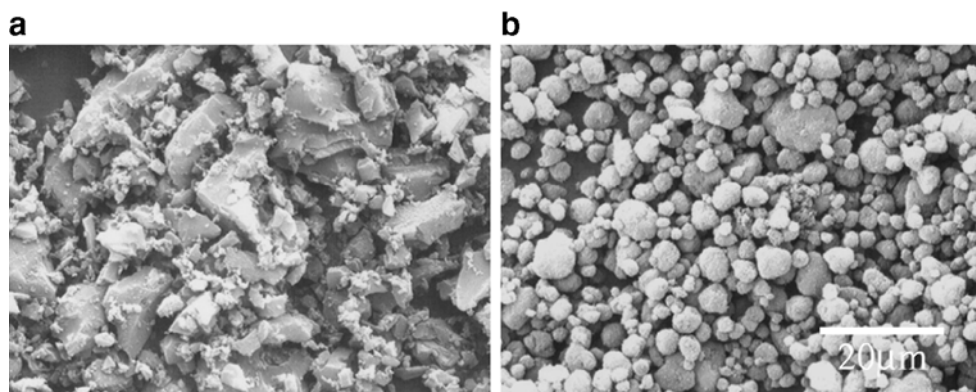
The powder mixtures were pressed uniaxially in a 40×40-mm mold or extruded through a mold with dimensions of 7×5 mm. Some organic additives such as binder, lubricant, and plasticizer were mixed with the ceramic powder. After the mixed batch was aged for 24 h at room temperature, tube-typed anodes were made from the kneaded powder by extrusion forming. The green bodies were dried for 3 days at room temperature so as to remove water and then finally dried again for 1 day at 150 °C in an oven. The dried green bodies were sintered in air at 1,300–1,500 °C for 3 h after removing the added polymers at 600–800 °C.

Long time durability tests were performed for 8Y-AC and 10Y-CB. Figure 2 shows schematic diagrams of the long-term thermal shock and reduction tests. First, the anode samples were thermal shocked from 800 °C to room temperature in air atmosphere. Initially, the temperature of the furnace was raised to 800 °C and maintained for 2 min. The samples were then abruptly drawn out into air and held for 1 min under a blowing fan. The samples were then placed back in the chamber, which was reset to 800 °C and maintained for 2 min. These cycles were repeated to a maximum of 3,000 cycles for the long-term thermal shock test, as shown in Fig. 2a. For the reduction test, the temperature of the furnace was raised to 800 °C in an Ar+4% H_2 atmosphere and maintained for 250, 500, 750, and a maximum of 1,000 h, as shown in Fig. 2b.

Strength tests were conducted on bar specimens in three-point flexure. A minimum of ten specimens of 8×5×4 mm or 3×4×4 mm dimension was cut from the sintered body and edge chamfered. The machined specimens were fractured at a crosshead speed of 3 mm/min using a three-point support on a universal test machine with a span of 25.4 mm at room temperature. The same strength tests were also performed on the reduced and thermal-shocked anode. The strengths were calculated from the beam theory [12].

The fractured and polished surfaces were examined using a SEM and video microscope (i-Camscope, Sometech Vision, Korea) to characterize the microstructure. Porosities of sintered bodies were calculated using the Archimedes

Fig. 1 SEM micrographs of starting powder for pore former, **a** activated carbon and **b** carbon black



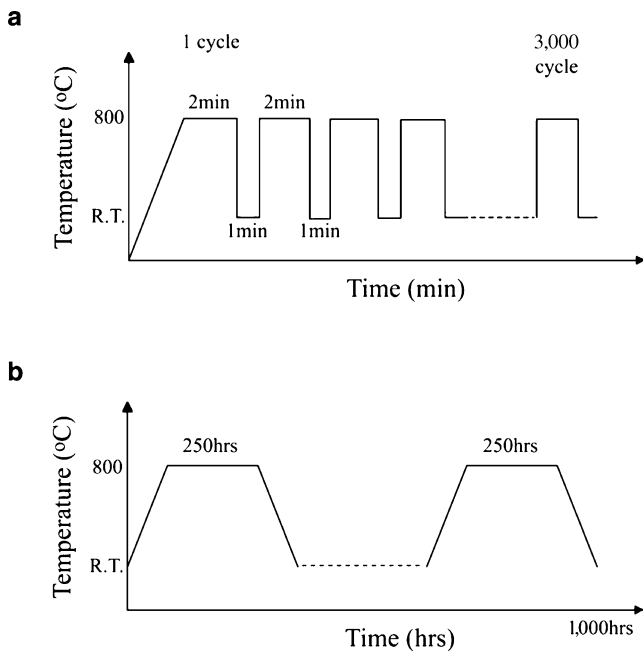


Fig. 2 Experimental schedule of long-term durability tests, **a** thermal shock test conducted in air and **b** long time exposure test in reducing atmosphere (Ar+4% H_2), respectively

method or a mercury porosimeter. Average pore diameters and pore distributions were measured using a mercury porosimeter.

The electrical conductivity was measured using the DC four-probe technique as a function of operating temperature in a range of 700 to 1,000 °C in an Ar+4% H_2 atmosphere. Current in a range of -0.5–0.5 A was supplied, and the voltage drop across the probes was measured with a digital multimeter (Keithley, USA). The electrical conductivity was calculated from the slope of the current–voltage curve.

Results and discussion

Mechanical strength

Figure 3 shows the flexural strengths of porous ZrO_2 anodes for SOFC with different amounts of Y_2O_3 additives and pore preformers as a function of sintering temperature. The flexural strengths of two anode materials, 8Y-AC and 10Y-CB, are compared in Fig. 3. The strength of 8Y-AC is in the similar range with that of literature has been reported [13]. The results show that the strengths of 10Y-CB sintered at the same sintering temperature are higher than those of the 8Y-AC material. Notably, the strength values of 10Y-CB are more than twice those of 8Y-AC material, although they were made at the same sintering temperature.

The strengths of the anode materials, 8Y-AC, 10Y-AC, and 10Y-CB, are plotted as a function of porosity, as shown

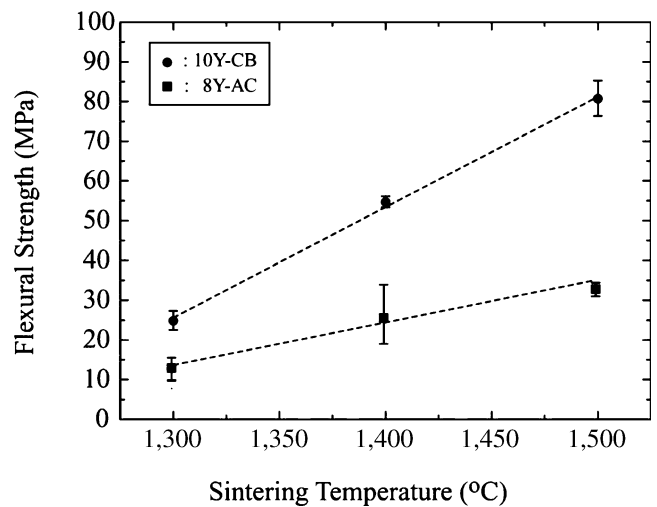


Fig. 3 Flexural strength of NiO–YSZ anode materials with different Y_2O_3 mole ratio, 8 and 10 mol%, and different types of pore formers, activated carbon and carbon black. The strength is plotted as a function of sintering temperature (8Y-AC, 10Y-CB)

in Fig. 4. The strength was improved by increasing the Y_2O_3 amount and by the addition of CB at the same porosity from the comparison between the curves. The results show that the strengths of 10Y-AC sintered at the same porosity level are higher than those of the 8Y-AC material by varying the Y_2O_3 concentration. Moreover, the strengths are much more improved by varying the pore former, indicated in the graph of the 10Y-CB material without changing porosity. Therefore, NiO–10 mol% Y_2O_3 stabilized ZrO_2 material with CB (10Y-CB) can exhibit higher strength while maintaining the same gas permeability.

Generally, sintering temperature controls the porosity of sintered ceramics. Ceramic materials are sintered at higher temperature and thus retain a small pore fraction. Higher strength is measured for materials with small porosity P ,

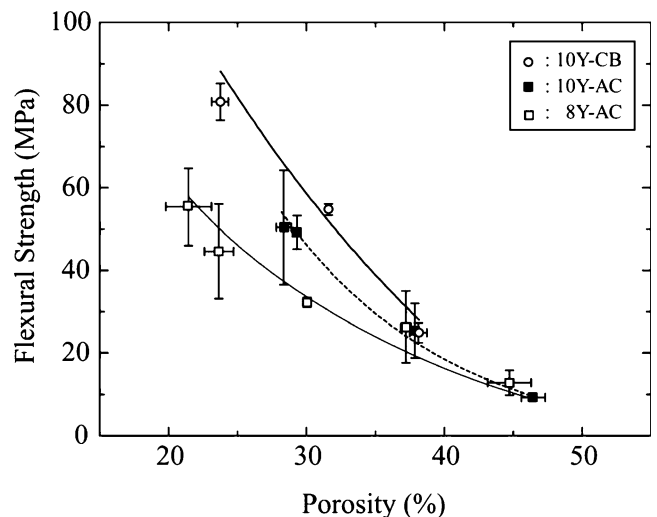


Fig. 4 Flexural strength as a function of porosity in NiO–YSZ anode material (8Y-AC, 10Y-AC, 10Y-CB)

according to the Rice equation [14,15], as indicated in Eq. 1. On the other hand, according to the Carmen–Kozeny equation [16], i.e., Eq. 2, the permeability is higher at higher porosity. High permeability of gas through the porous anode is required for high SOFC efficiency. Therefore, high strength and high porosity are generally contradictable, as indicated in Eqs. 1 and 2.

$$\sigma = \sigma_0 \exp(-bP) \quad (1)$$

with σ as the strength for a material having porosity P , σ_0 for a material having porosity $\sim 0\%$, and b as the experimentally determined constant.

$$K = [1/(\xi S_s^2)] [P^3/(1-P)^2] \quad (2)$$

with K as the permeability, ξ as the proportional constant, and S_s as the specific surface area.

On the other hand, the result of Fig. 4 indicates that the strength can be improved without sacrificing the porosity value by simply changing the type of material. Therefore, it is expected that NiO–10 mol%Y₂O₃-stabilized ZrO₂ material with CB (10Y-CB) is suitable for use as an SOFC anode.

Using SEM, we examined the fractured surface of two materials sintered at 1,500 °C, 8Y-AC and 10Y-AC, as shown in Fig. 5. The average porosity and strength are 31.0 vol.% and 32 MPa for 8Y-AC and 29.0 vol.% and 50 MPa for 10Y-AC, respectively. Fractured surfaces indicate that the fraction of transgranular fracture increases in the 10Y-CB material, as shown in Fig. 5b, relative to the 8Y-AC material. More neck growth occurs in the 10Y-AC material because oxygen vacancies increase to ZrO₂ by the addition of the Y₂O₃ additive. Therefore, the material transport readily occurs during sintering of 10Y-CB via lattice diffusion through the increased oxygen vacancies [17]. The partial sintering between grains caused by the neck growth enhances the intergranular force, which can cause transgranular fracture [18]. The increase in the mode

of transgranular fracture in porous ceramics is clearly related with higher strength.

We also examined the polished surface of two materials sintered at 1,400 °C, 10Y-AC and 10Y-CB, by video microscope, as shown in Fig. 6. The average porosity and strength are 37.5% and 25MPa for 10Y-AC and 32% and 55MPa for 10Y-CB, respectively. The pore geometry of 10Y-CB is finer and more regular and spherical relative to the 10Y-AC material. The anode material with CB added as a pore former consists of relatively small spherical and uniform pores, as indicated in Fig. 6b. On the other hand, the anode with AC presents coarser size, nonuniformity, and irregular pore shapes, as shown in Fig. 6a. According to the Inglis theory [19], when a pore acts as a failure origin, a spherical pore shape can relax the local stress at the tip.

Stability in reducing or thermal shock conditions

We compared the pore distributions of 8Y-AC and 10Y-CB measured by a mercury porosimeter. Figure 7 shows the pore distributions of the two anode materials in Ar+4%H₂ for 48 h at 1,000 °C. It was confirmed that the spherical pore shape of 10Y-CB is maintained during reduction at the same conditions. The total porosities of 8Y-AC and 10Y-CB sintered at 1,400 °C were measured to be 41.7 and 37.1 vol.%, respectively, using a mercury porosimeter. These increasing values are due to the reduction in nickel oxide to nickel [13]. The mean pore size of 10Y-CB was also finer, 0.63 μm, than that of 8Y-AC, 1.38 μm. Small pore size in 10Y-CB is observed in the microstructure, as shown in the SEM image of Fig. 6. Therefore, the key factors influencing the strengths of the anode materials are the small and spherical pores.

The 10Y-CB anode material does not degrade severely, even under long-term thermal shock or reducing conditions, as shown in Fig. 8. The initial high strength of the new anode material is maintained even after exposure in the

Fig. 5 SEM micrographs of NiO–YSZ anode materials with different Y₂O₃ mole ratio, **a** 8 and **b** 10 mol%, sintered at 1,500 °C (8Y-AC, 10Y-AC)

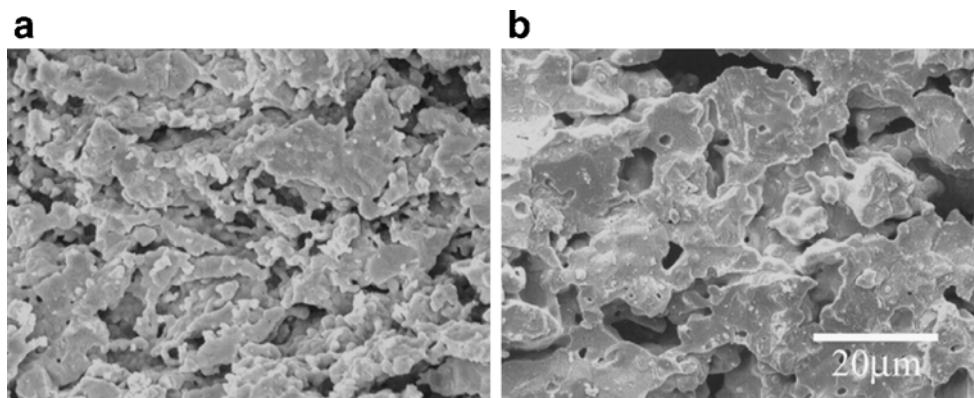
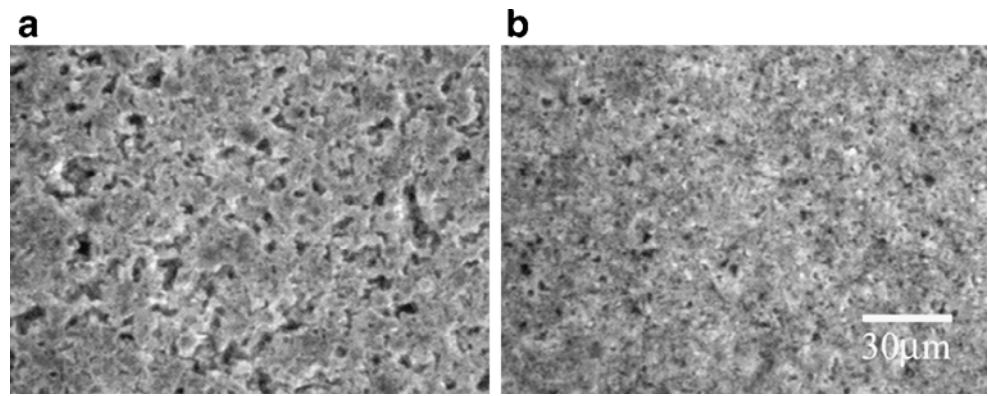


Fig. 6 Optical micrographs of NiO–YSZ anode materials with different types of pore formers, **a** activated carbon and **b** carbon black, sintered at 1,400 °C (10Y-AC, 10Y-CB)



long durability test, as indicated in Fig. 2. Thermal shock testing is important because a SOFC cell can be exposed to thermal shock conditions. Slight strength degradation was observed upon thermal shock testing at 500 or 1,000 cycles, but the degraded strengths recovered quickly to the initial strength at 2,000 or 3,000 cycles. It is thought that the

recovery of strength is related with the release of residual stress during heating or flaw healing [20]. On the other hand, the strengths of the anode materials were reduced, although not critically, upon exposure to the reducing atmosphere relative to the strength degradation from exposure to a thermal shock atmosphere. It was observed

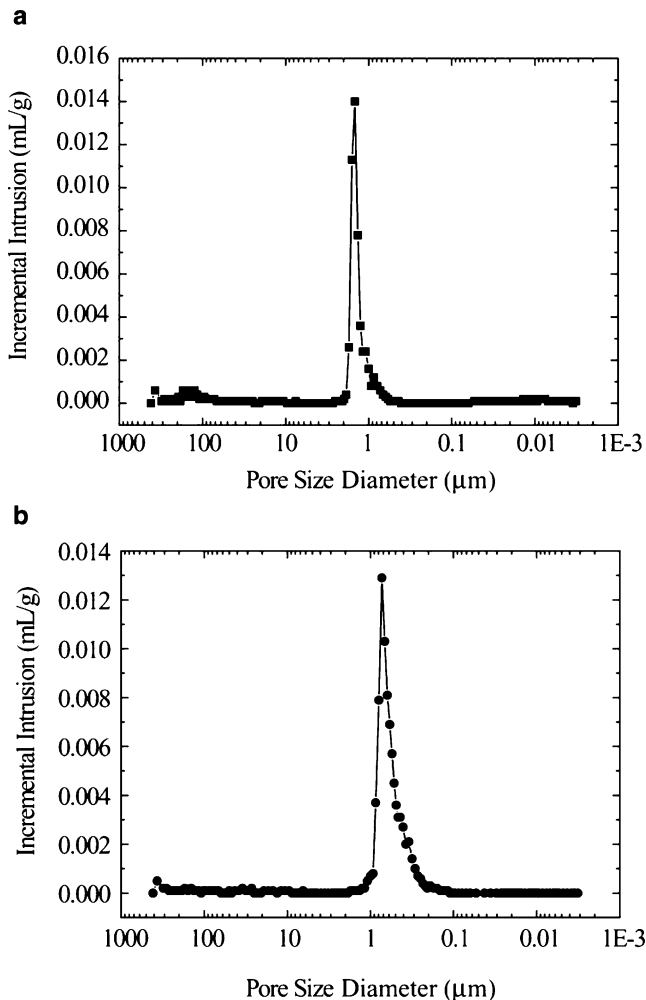


Fig. 7 Pore size distribution in the NiO–YSZ anode materials, **a** 8Y-AC and **b** 10Y-CB sintered at 1,400 °C and reduced at 1,000 °C in Ar+4% H_2 for 48 h

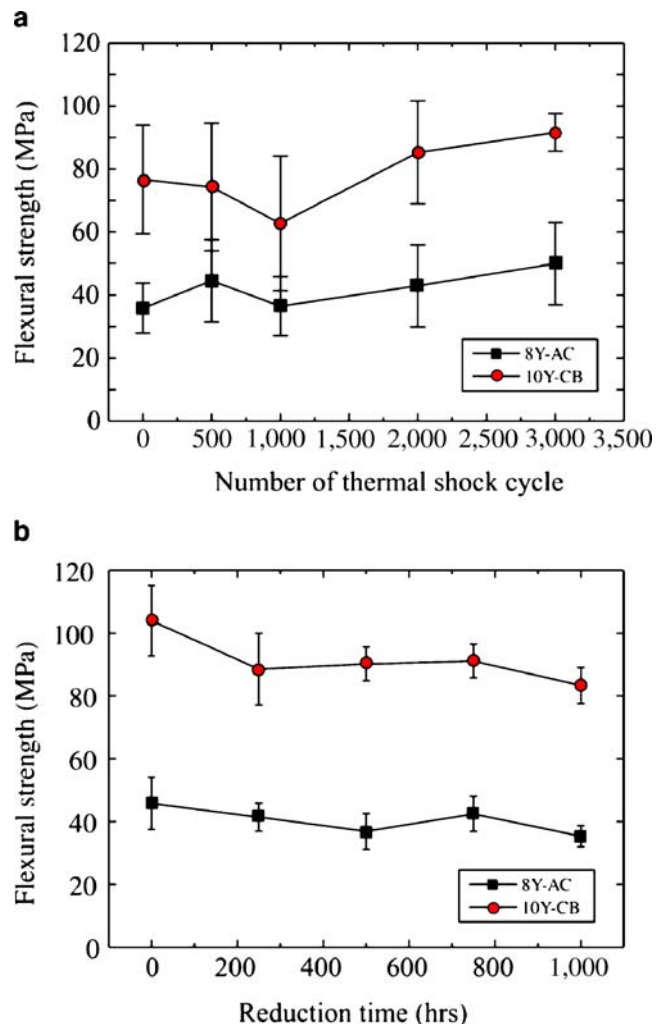


Fig. 8 Flexural strength of **a** NiO–YSZ anode material during thermal shock cycling up to 3,000 cycles and **b** Ni–YSZ anode material after long exposure to reduction (8Y-AC, 10Y-CB)

that the initial strength decreased by about 20% in the reducing condition for 1,000 h, as shown in Fig. 8b. It is thought that the small degradation observed during long-term reduction testing is related to the reduction in nickel oxide to the nickel phase [13], because the increase in pore fraction is indispensable during the reduction to nickel. Nevertheless, evaluating Fig. 8, the long-term duration, greater than 1,000 h, under thermal shock or reducing condition at 800 °C did not result in any measurable change in the strength of NiO–YSZ anode materials.

It is concluded that the NiO–10 mol%YSZ material with added CB is a desirable material for the porous anode support of a SOFC because the porous anode support should have higher flexural strength at the same porosity. It is confirmed that the initial high strength is maintained after the new anode is exposed to thermal shock or reducing conditions greater than 1,000 h. The anodes have high thermal shock resistance as well as resistance against degradation in the reducing atmosphere. Therefore, the porous NiO–10 mol%YSZ anode with CB is favorable owing to its high stability during long-time operation in a reducing atmosphere and/or thermal shock environment under repetitive on–off cycling.

Electrical conductivity

Another important characteristic of the anode material is its electrical conductivity. The anode must possess sufficiently high electrical conductivity for electron flow in a reducing environment at the designated operating temperature. The electrical conductivities of NiO–YSZ anode materials are plotted as a function of temperature in Fig. 9. As a whole, electrical conductivities of 10^1 – 10^3 S/cm were measured,

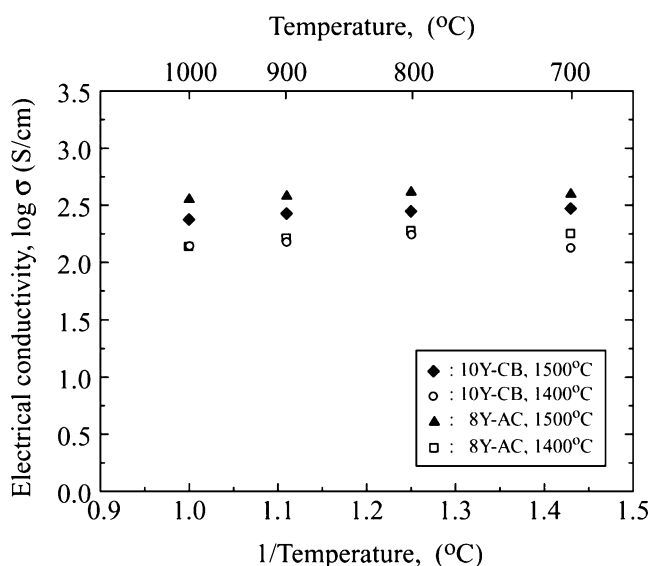


Fig. 9 Electrical conductivity as a function of operation temperature in NiO–YSZ anode materials (8Y-AC, 10Y-CB)

which is in the same range of the literature value [13]. The conduction behavior follows metallic behavior, where conductivity decreases with increasing temperature, indicating that the conduction occurs through Ni connection. Higher electrical conductivities at higher sintering temperature reflect that Ni connectivity depends on sintered density. The electrical conductivities of 10Y-CB are comparable to those of 8Y-AC, which is applicable for the anode of a SOFC from the standpoint of electrical conductivity and in terms of strength and porosity.

The long-term conductivities of anodes sintered at 1,400 °C with varying amounts of Y_2O_3 additives and carbon pore formers at 800 °C of operating temperature are compared in Fig. 10. As expected, both anodes exhibit electrical conductivities that are sufficiently high for a SOFC. The electrical conductivity of 10Y-CB is slightly inferior to that of 8Y-AC before exposure to the reducing atmosphere. However, the degradation of electrical conductivity of the 10Y-CB anode material is not significantly worse than that of 8Y-AC. Thus, the electrical conductivity of 10Y-CB is ultimately higher after longer exposure time in a reducing atmosphere. The deviation of electrical conductivities between the two anode materials according to the exposure time in a reducing atmosphere indicates that the 10Y-CB anode material would offer high stability during the operation of a SOFC at high temperature. The possibility of phase change during long-term exposure at high temperature was not detected by X-ray diffraction analysis in this study. On the other hand, modifications by varying the amount of Y_2O_3 additives and carbon pore formers result in the change of electrical conductivity because it is reported that nickel phases can be disconnected during operation of the SOFC system at high tempera-

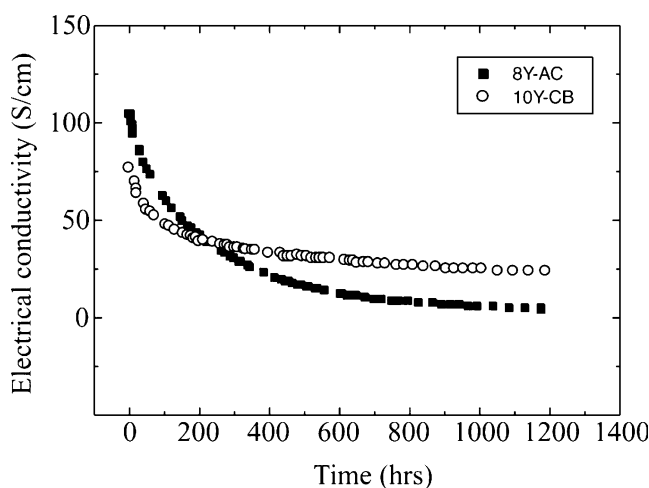


Fig. 10 Electrical conductivity at 800 °C during long-time durability test for 1,200 h in Ar+4%H₂ atmosphere (8Y-AC, 10Y-CB)

ture in a reducing atmosphere [8–10, 19]. Nevertheless, it is noteworthy that the degradation of the electrical conductivity was not critical for the 10Y-CB anode material rather than for 8Y-AC, after exposure to the reducing atmosphere. The result is similar to the prior result that 10 mol%Y₂O₃-added ZrO₂ electrolyte showed high stability after longer exposure time in a reducing atmosphere than 8 mol% Y₂O₃-added ZrO₂ [21].

Conclusions

We varied the yttria content in YSZ, at 8 and 10 mol%, and the carbon pore former, AC and CB, and investigated the effects of vacancy and pore shape variation on the flexural strength, electrical conductivity, and the degradation of those properties in porous NiO–YSZ anode materials for SOFC application.

The strength of the anode materials could be markedly improved without significantly changing the porosity by increasing the amount of Y₂O₃ additives and through the addition of CB as a pore former. The electrical conductivity of NiO–10 mol%Y₂O₃-stabilized ZrO₂ with CB was evaluated to be as high as 10²–10³ S/cm in a temperature range of 700–1,000 °C.

Long time durability tests confirmed that NiO–10 mol% Y₂O₃-stabilized ZrO₂ has high stability during thermal shock testing and in a reducing atmosphere for a maximum of 1,000 h. New NiO–10 mol%Y₂O₃-stabilized ZrO₂ with CB led to higher electrical conductivity after long-term exposure in the reducing atmosphere at high temperature, reflecting the higher stability of the new anode material.

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References

1. Steele BCH, Heinzel A (2001) *Nature* 414:345
2. Yamamoto O (2000) *Electrochim Acta* 45:2423
3. Tiffe EI, Weber A, Herbst D (2001) *J Eur Ceram Soc* 21:1805
4. Choy K, Bai W, Charochochkul S, Steele BCH (1998) *J Power Sources* 71:361
5. Milliken C, Guruswamy S, Khandkar A (1999) *J Electrochem Soc* 146:872
6. Diggiuseppe G, Selman JR (2001) *J Mater Res* 16:2983
7. Yoo YS, Lim HC (2002) *J Power Sources* 4678:1
8. Aruna ST, Muthuraman M, Patil KC (1998) *Solid State Ion* 111:45–51
9. Tamburini UA, Chiodelli G, Arimondi M, Maglia F, Spinolo G, Munir GA (1998) *Solid State Ion* 110:35
10. Skarmoutsos D, Tsoga A, Naoumidis A, Nikolopoulos P (2000) *Solid State Ion* 135:439
11. Kirkpatrick S (1973) *Rev Mod Phys* 45:574
12. Lee KS, Lee SK, Lawn BR (1998) *J Am Ceram Soc* 81:2394
13. Minh NQ, Takahashi T (1995) *Science and technology of ceramic fuel cells*. Elsevier, New York
14. Rice RW (1993) *J Mater Sci* 28:2187
15. Rice RW (1989) *Mater Sci Eng A* 112:215
16. Carman PC (1956) *The flow of gases through porous media*. Academic, New York
17. Yang S, Lee JH, Kim JJ, Lee JS (2004) *Solid State Ion* 172:413
18. Hayashi H, Saitou T, Maruyama N, Inaba H, Kawamura K, Morl M (2005) *Solid State Ion* 176:613
19. Inglis CE (1913) *Trans Inst Naval Archit* 55:219
20. Lee SK, Ando K, Kim YW (2005) *J Am Ceram Soc* 88:3478
21. Gibson IT, Dransfield GP, Irvine JTS (1998) *J Eur Ceram Soc* 18:661