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Fabrication of 80 mm diameter-sized solid oxide fuel cells using a water-based NiO–YSZ slurry

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Abstract

Solid oxide fuel cells (SOFCs) are very attractive for their high energy conversion efficiency and low emissions. Generally, a supported layer of SOFCs is fabricated by tape casting, using an organic solvent. Recently, a slurry based on water instead of an organic solvent has been sought in order to avoid environmental pollution. In this study, the anode of SOFCs was fabricated by aqueous tape casting, and the electrolyte and the cathode were deposited by screen printing. The I–V characteristics of the cell thus obtained were evaluated. As a result, an 80 mm diameter-sized cell with a power density of 0.33 W/cm^2 at 800 °C was successfully fabricated by controlling sintering conditions.

Keywords: Water-based slurry; Fuel cells; Tape casting; Firing

1. Introduction

Solid oxide fuel cells (SOFCs)[1] are very attractive because of their many advantages, e.g., higher energy conversion efficiency, utilisation of high temperature gases and lower emissions, compared with other energy conversion devices.

Tape casting is a low-cost process for making thin and flat substrates, and it is widely used in the electrical industry.[2] In the fabrication of a planar type of cell, a supported layer, such as the anode, is made by tape casting, and other layers, such as the electrolyte and the cathode in the anode supported cell, are deposited by screen printing. In the tape casting process, organic solvent is used in the preparation of the slurry; however, water-based slurries are desired to prevent environmental problems. In recent years, the aqueous tape casting of Y_2O_3 stabilised ZrO_2 (YSZ)[3,4] and Gd_2O_3 doped CeO_2[5] for application to SOFCs has been reported.

In this study, the anode was fabricated using a water-based slurry, and linear shrinkage and the effects of the addition of a pore former to the green sheet were studied to avoid bending and peeling during heat treatment. Then, the electrolyte and the cathode were deposited by screen printing to obtain an 80 mm diameter-sized cell, which was tested in practical use. In addition, the I–V characteristics of the cell thus obtained were evaluated.

2. Experimental

2.1. Materials and chemicals

NiO (Nikko Rica Co., Ltd.) and YSZ (TZ-8YS, Tosoh Co., Ltd.) were used as anode materials. YSZ (TZ-8YS) was also used as an electrolyte material. In addition, $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM, AGC Seimi Chemical Co., Ltd.) and YSZ (TZ-8Y, Tosoh Co., Ltd.), which has lower average diameter and higher specific surface area compared with TZ-8YS, were used in the cathode preparation. The median diameter, D_{50}, measured by a laser scattering particle size distribution analyser (LA-920, HORIBA, Ltd.), and the specific surface areas for NiO, YSZ and LSM are shown in Table 1.

2.2. Cell fabrication procedure

The flowchart for the fabrication of the anode supported planar cell by aqueous tape casting in combination with screen printing is shown in Fig. 1. First, the NiO–YSZ green sheet was

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Table 1
Median diameters and specific surface areas for ceramics powders used in the fabrication.

Ceramics powder	Median diameter, D_{50} (μm)	Specific surface area (m^2/g)
NiO	0.94	–
YSZ (TZ-8YS)	0.38	6.5
YSZ (TZ-8Y)	0.21	13.8
LSM	2.0	2.0

made by tape casting using water-based slurry. After deposition of YSZ electrolyte on the NiO–YSZ green sheet by screen printing, both the anode and the electrolyte were co-fired to obtain a dense electrolyte. Finally, LSM cathode was deposited by screen printing, followed by sintering to fabricate the anode supported planar cell.

2.3. Aqueous tape casting of NiO–YSZ anode

The NiO–YSZ green sheets used as the anodes of SOFCs were fabricated by tape casting. The water-based slurry used in tape casting was prepared as follows.[6,7] Measured NiO and YSZ powders with a weight ratio of NiO/YSZ = 50/50, urethane colloidal and water soluble binders and polyethylene glycol as a plasticiser were dispersed in distilled water using a planetary ball mill (Pulverisette 5, Fritsch Co., Ltd.). The planetary ball mill was operated with a disk speed of 150 rpm for 180 min using ZrO_2 bowls and 10 mm diameter ZrO_2 balls. An antifoaming agent was added to the slurry, followed by mixing for 10 min. Furthermore, the water-based slurry was stirred for 10 min under vacuum to degasify the slurry. The viscosity of resultant slurry was 9.2 Pa s at a shearing rate of $0.35\ s^{-1}$.

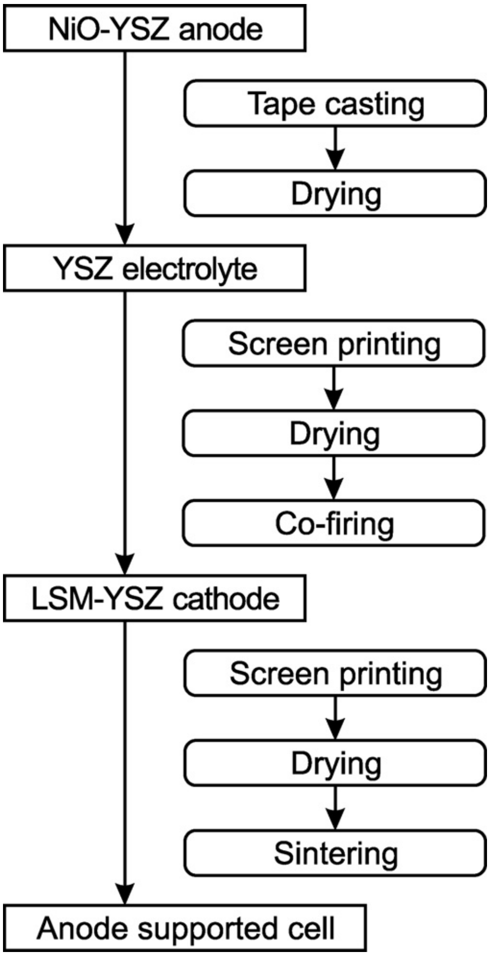

Fig. 1. Flowchart for the fabrication of anode supported planar cells by aqueous tape casting in combination with screen printing.

A tape casting apparatus (IMC-7021, Imoto Machinery Co., Ltd.) equipped with two doctor blades was used for the casting of the NiO–YSZ anode. A width of cast sheet was 200 mm, and the gaps, i.e., the wet thickness of the sheet, at the first and second doctor blades were 2000 and 1250 μm, respectively. The anode sheet was cast on a polyethylene terephthalate film with a sheet velocity of 600 mm/min. After drying for 2 days at room temperature, the NiO–YSZ green sheet was completely dried for 30 min at 80 °C. Then, the NiO–YSZ green sheet was cut to 120 mm × 120 mm for screen printing of the YSZ electrolyte. In addition, a 30 mm × 30 mm sheet was also prepared for measuring the linear shrinkage during heat treatment. Linear shrinkage was calculated from the size change resulting from the heat treatment. Thermal gravimetry (TG) and differential thermal analysis (DTA) were performed to determine the temperature to burn out slip additives in calcining using a thermal analysis apparatus (TGD-9600, ULVAC Inc.).

Graphite is widely used as a pore former to make porous electrodes.[8] Green sheets with added flake graphite (Chuetsu Graphite Works Co., Ltd.), $D_{50} = 7.8$ μm, were also prepared to study the effects on linear shrinkage, water absorption and bulk density. Water absorption and bulk density were measured using kerosene as a liquid, and bulk density was determined by the Archimedes method.

2.4. Screen printing of the electrolyte and the cathode

The YSZ electrolyte was deposited on the NiO–YSZ green sheet by screen printing.[9] The ink preparation for screen printing of YSZ electrolyte was as follows. YSZ and a vehicle (Nisshin Kasei Co., Ltd.) including ethyl cellulose as a binder were dispersed in α-terpineol (Kanto Chemical Co., Inc.) as solvent by a planetary ball mill for 30 min with a disk speed of 300 rpm. The ink for the electrolyte thus obtained was deposited on the NiO–YSZ green sheet using a screen printing apparatus (STF-150A, Tokai Seiki Co., Ltd.). Drying and screen printing of the YSZ electrolyte were repeated 4 or 6 times on the sheet, rotating by 90° after each printing to prevent defects in the electrolyte. After cutting the YSZ-deposited NiO–YSZ green sheet to a 105 mm diameter, the sheet was co-fired to obtain a dense electrolyte.

LSM mixed with YSZ was also deposited on the co-fired NiO–YSZ/YSZ plate. The weight ratio of LSM/YSZ was 50/50. The ink for screen printing the cathode was prepared using the vehicle and α-terpineol. First, LSM and YSZ were pre-mixed for 10 min using an auto mortar and then mixed for 60 min while adding the vehicle and α-terpineol. The cathode, with a 60 mm diameter, was deposited by screen printing and sintered at 1250 °C with a heating rate of 300 °C/h for 4 h to obtain an 80 mm diameter planar cell. A cross-section of the cell thus obtained was observed using a scanning electron microscope (SEM, S-3200N, Hitachi Co., Ltd.) to confirm the structures of the electrolyte and electrodes. Furthermore, the flexural strength and bending of the cell were measured. Flexural strength was measured by 3-point bending with a span of 30 mm on samples with a size of *ca.* 1 mm × 4 mm × 35 mm using a tensile and compression testing machine (AL-100kNB, Minebea Co., Ltd.).

2.5. Evaluation of cell performance

The I–V characteristics of the cell with an anode size of 80 mm diameter were measured by a potentio/galvano stat (VSP, Princeton Applied Research Co., Ltd.) at 700, 750 and 800 °C. In the I–V characteristics measurement, Pt was deposited on the cathode as an electrical collector by screen printing, followed by annealing at 850 °C. As described above, the size of the cathode was 60 mm in diameter, and thus the active area of the cell was 28.26 cm^2. H_2 humidified at room temperature and dry air were used as reduction and oxidation gases, respectively. The flow rate of both gases was 600 mL/min.

3. Results and discussion

3.1. Optimisation of cell fabrication procedure

TG–DTA curves of the NiO–YSZ green sheet without the addition of graphite are shown in Fig. 2. The weight loss of the green sheet due to slip additives, such as binders and a plasticiser, occurred until 500 °C, and some exothermal peaks were also observed with weight loss. This indicates that firing above 500 °C was necessary for burning out slip additives in the pre-heat treatment.

Fig. 3 shows the linear shrinkage of NiO–YSZ and YSZ green sheets, which were fabricated using a water-based slurry by tape casting, during heat treatment between 800 and 1400 °C. In this figure, the shrinkage of the YSZ green sheet started to occur at 1200 °C, while the NiO–YSZ green sheet began to shrink at 1100 °C. In addition, the linear shrinkage of the NiO–YSZ green sheet at 1400 °C corresponded with that of the YSZ green sheet. Although the linear shrinkage at 1000 °C of the NiO–YSZ green sheet with the addition of the pore former was larger, the behavior of linear shrinkage for the green sheet with the addition was similar to that without the addition. Since the flake graphite used as the pore former was burned out around 900 °C and caused the increased porosity of the anode, the structural change started earlier than in the anode without the pore former. In this study, since the difference in the linear shrinkage between the NiO–YSZ and YSZ green sheets was small at 1100 °C, the anode and the electrolyte were pre-fired at 1100 °C with a heating rate of 50 °C/h, followed by co-firing at 1400 °C for 6 h with a YSZ plate, which was put on the NiO–YSZ/YSZ sheet as a weight to prevent bending and peeling. The heating rate during co-firing was 200 °C/h from room temperature to 1100 °C and 100 °C/h to 1400 °C.

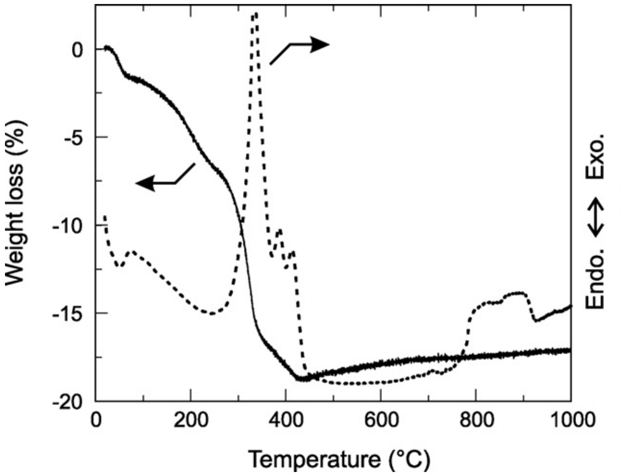

Fig. 2. TG–DTA curves of the NiO–YSZ green sheet without the addition of the pore former.

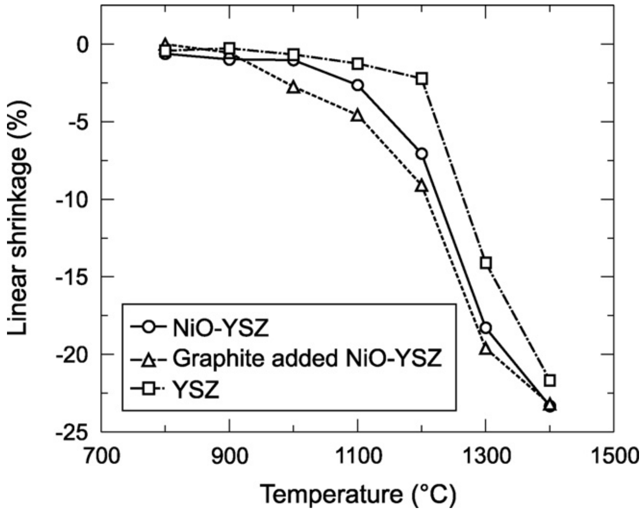

Fig. 3. Linear shrinkages of NiO–YSZ and YSZ green sheets during heat treatment between 800 and 1400 °C.

3.2. Effect of the addition of the pore former

The changes in the water absorption and bulk density as a function of the addition of the pore former are shown in Fig. 4. Here, the amount of pore former added is in percentage with respect to the ceramic powders. The water absorption increased with the addition of graphite as the pore former, while the bulk density decreased. This means that the graphite addition was effective as a pore former. However, in this study, the amount of graphite added was determined as 4 mass% by the occurrence of cracks during drying due to the difficulty of dispersing the graphite in water.

3.3. Evaluation of cell performance

In this study, 80 mm diameter-sized cells were successfully fabricated by aqueous tape casting combined with screen printing. Bending, which was below 400 μm, and peeling were not

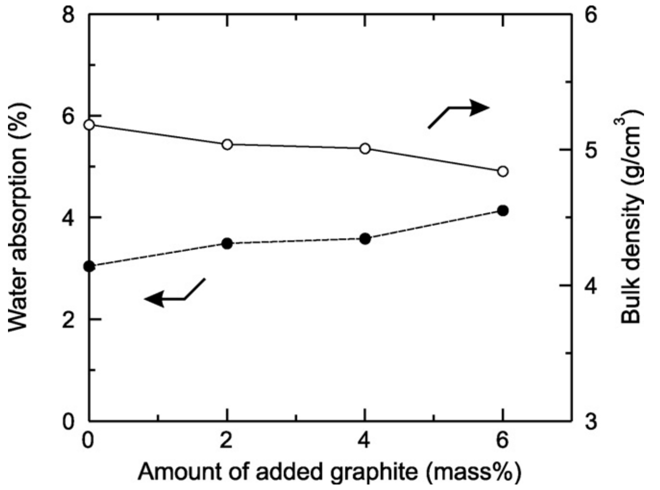

Fig. 4. The change of water absorption and bulk density on the addition of the pore former. The amount of graphite added means percentage with respect to ceramics powders.

observed in these cells due to the adjustment of the linear shrinkage changes between the electrolyte and the anode by controlling sintering conditions, as described above. In addition, the average flexural strength was as high as 165 MPa, so that this cell was easily handled in practical use.

Fig. 5 shows SEM images for the cross-section of the cells with the deposition of the electrolyte (a) 4 and (b) 6 times by screen printing, and after the in situ reduction of the anode in the I–V characteristics measurement. The thickness of the electrolyte was almost proportional to the number of screen printings and was 10 and 15 μm after 4 and 6 times, respectively. This fact indicates that the thickness of the electrolyte was controllable by the number of screen printings.

The I–V and I–P characteristics of the cell are shown in Fig. 6 as a function of operating temperature. The electrolyte of this cell was deposited 4 times by screen printing, and the pore former was not added to the anode. In this figure, the power density increases with increasing operating temperature, and the maximum power density operated at 800 °C is 0.32 W/cm^2. However, the open circuit voltage decreased with increasing operating temperature. The high open circuit voltage, about 1.1 V, indicates that a gas leak from the electrolyte did not occur. Therefore, a dense electrolyte was successfully obtained even with YSZ deposition 4 times by screen printing.

The power densities at 800 °C of all cells fabricated in this study are summarised in Table 2. The highest power density value in this study was as high as 0.33 W/cm^2. There were almost no effects of fabrication conditions, such as the number of screen printings of the electrolyte and the addition of the pore former on power density. The cathode of all cells was same in this study. It may be that other factors, e.g., the cathode performance, were dominant in determining cell performance.

Table 2
Power densities while operating at 800 °C of all cells fabricated in this study.

Number of screen printing in the electrolyte	Pore former in the anode	Power density (W/cm^2)
4 times	Not added	0.33
4 times	Added	0.32
6 times	Added	0.32

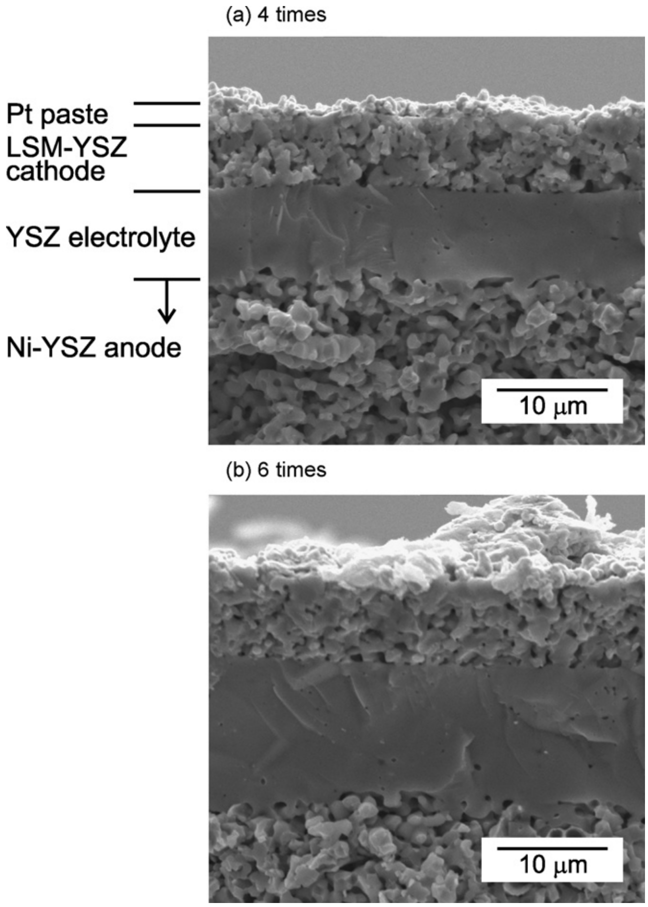

Fig. 5. SEM images for a cross-section of the cell after the in situ reduction of the anode in the measurement of I–V characteristics. The electrolyte was deposited (a) 4 and (b) 6 times by screen printing.

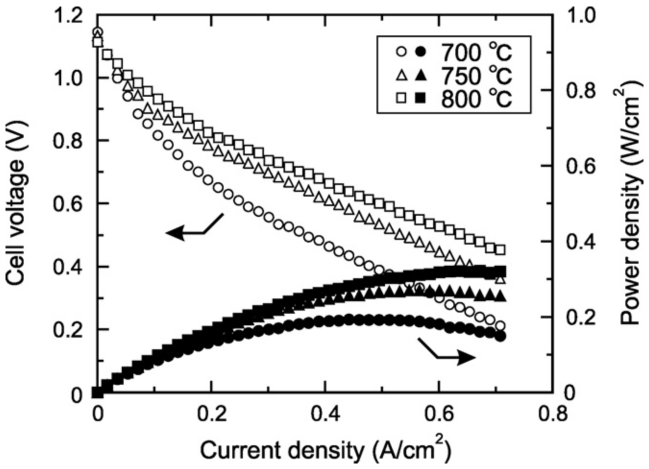

Fig. 6. I–V and I–P characteristics of the cell. The anode was fabricated without the addition of the pore former, and the electrolyte was deposited 4 times by screen printing.

4. Conclusions

The NiO–YSZ anode sheet for SOFCs was made using water-based slurry by tape casting. After deposition of YSZ electrolyte on the NiO–YSZ sheet by screen printing, the NiO–YSZ/YSZ sheet was pre-fired at 1100 °C, followed by co-firing at 1400 °C with a weight on the sheet. By depositing the LSM–YSZ cathode and sintering, an 80 mm diameter-sized planar cell was successfully obtained. Bending and peeling were not observed in the cell due to the adjustment of linear shrinkage changes between the electrolyte and the anode by controlling the sintering conditions in the co-firing process. The open circuit voltage was about 1.1 V; therefore, a gas leak from the electrolyte did not occur even with 4 times YSZ depositions by screen printing. The maximum power density of the 80 mm diameter-sized cell was as high as 0.33 W/cm^2 at 800 °C.

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References

1. Minh, N. Q., Ceramic fuel cells. *J. Am. Ceram. Soc.*, 1993, **76**, 563–588.
2. Mistler, R. E., Tape casting: past, present, potential. *Am. Ceram. Soc. Bull.*, 1998, **77**, 82–86.
3. Snijkers, F., De Wilde, A., Mullens, S. and Luyten, J., Aqueous tape casting of yttria stabilised zirconia using natural product binder. *J. Eur. Ceram. Soc.*, 2004, **24**, 1107–1110.
4. Albano, M. P. and Garrido, L. B., Aqueous tape casting of yttria stabilized zirconia. *Mater. Sci. Eng. A*, 2006, **420**, 171–178.
5. Luo, L. H., Tok, A. I. Y. and Boey, F. Y. C., Aqueous tape casting of 10 mol%-Gd_2O_3-doped CeO_2 nano-particles. *Mater. Sci. Eng. A*, 2006, **429**, 266–271.
6. Moreno, R., The role of slip additives in tape-casting technology: part I-solvents and dispersants. *Am. Ceram. Soc. Bull.*, 1992, **71**, 1521–1531.
7. Moreno, R., The role of slip additives in tape-casting technology: part II-binders and plasticizers. *Am. Ceram. Soc. Bull.*, 1992, **71**, 1647–1657.
8. Yamahara, K., Jacobson, C. P., Visco, S. J. and De Jonghe, L. C., Catalyst-infiltrated supporting cathode for thin-film SOFCs. *Solid State Ionics*, 2005, **176**, 451–456.
9. Dollen, P. V. and Barnett, S., A study of screen printed yttria-stabilized zirconia layers for solid oxide fuel cells. *J. Am. Ceram. Soc.*, 2005, **88**, 3361–3368.