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Changes in the mechanical properties of support materials for segmented-in-series type solid oxide fuel cells as a function of time

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HIGHLIGHTS

- Our aim was to determine the design of support material for segmented-in-series SOFCs.
- We measured the changes in the Young's modulus with time.
- Young's modulus of ternary systems (i.e., $Al_2O_3/TiO_2/MgO$–NiO–YSZ) was measured.
- The behaviour of the Young's modulus depends on the framework composition of the sample.
- SEM analysis of the sample with a mirror polishing exhibits grain boundary sliding.

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ABSTRACT

As the substrate materials for segmented-in-series type solid oxide fuel cells (SOFCs), the mechanical characteristics, such as Young's modulus, of Al_2O_3–NiO–YSZ, TiO_2–NiO–YSZ and MgO–NiO–YSZ were examined under SOFC operating conditions. The Young's modulus for all of the samples decreased at a high temperature. For the Al_2O_3–NiO–YSZ samples, the behaviours of the Young's modulus changed at each process including as-sintered, 100 h reduction and 2000 h reduction. For the TiO_2–NiO–YSZ samples, the Young's modulus behaviour varied between the as-sintered and reduced samples. However, further reduction did not change the behaviour of the Young's modulus. For the MgO–NiO–YSZ samples, the Young's modulus of the samples exhibited a nearly constant behaviour through the sequence of processes from as-sintered to 100 h reduction and 2000 h reduction. Based on the microstructural analysis, the compositions of the framework of the samples and the sliding of the grain boundary strongly affected the Young's modulus.

1. Introduction

Fuel cells can directly convert chemical energy from fuels into electricity and achieve high-energy conversion efficiency compared to existing thermal power generation systems. In all of the fuel cell systems, solid oxide fuel cells (SOFCs) achieve the highest energy conversion efficiency, and they have been actively developed to utilise a limited quantity of fossil fuels [1,2]. Energy devices, such as SOFCs are expected to be operated for an ultra-long term period. The improvement in the power generation efficiency and generation capacity as well as the mechanical durability over an ultra-long term is a challenge for the commercial viability of SOFCs. In particular, understanding the mechanical properties under harsh operating conditions is important [3–8] because a SOFC's conventional operating temperature is very high (i.e., 700 °C–1000 °C).

As shown in Table 1, there are various types of SOFCs with different shapes and supporting substrates. Some authors have previously reported [9–11] that the segmented-in-series (SIS) type SOFCs based on electric insulating materials exhibit high durability against reduction and oxidation (Redox) cycles over a long period of operation. This result indicates that the SIS type SOFCs can be expected to have a long cell stack lifetime. These cell stacks constitute the main portions of the SOFC systems. Fig. 1 shows the schematic of an SIS type SOFCs. In the SIS type SOFCs, the substrate supports multiple single cells, and it has an important role as channels for the fuel supply. Therefore, substrates need to be strong with a high porosity. Because the substrate accounts for a large fraction of the cell stack volume, substrate damage results in breakage of cells. Therefore, understanding the mechanical behaviour is very important for designing substrate materials that exhibit ultra-long term durability. In particular, this substrate component is exposed

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Table 1
Classification of SOFCs.

Type	Substrate	Examples of manufacturing company
Planer type	Anode materials	Topsoe Fuel Cell A/S, SOFCpower, Versa Power Systems, Inc., Ceramic Fuel Cells Limited, NGK Spark Plug Co., Ltd., and more
	Porous metal	Ceres Power
	Electrolyte materials	Hexis Ltd., Bloom Energy Mitsubishi Materials Corporation
Cylindrical type	Anode materials	Acumentrics corporation, TOTO Ltd.
	Cathode materials	Siemens Westinghouse Power Corporation TOTO Ltd.
Flat tubular planer type	Electrical insulating materials	Mitsubishi Heavy Industries, Ltd.
	Anode materials	Kyocera Corporation
	Electrical insulating materials	Kyocera Corporation, Rolls-Royce plc

Table 2
Sample details.

Sample name	Composition materials			Vol%			Mol%		
				NiO	YSZ	Al_2O_3, TiO_2, MgO	NiO	YSZ	Al_2O_3, TiO_2, MgO
ANY	NiO	YSZ	Al_2O_3,	30	35	35	47.8	28.1	24.1
TNY			TiO_2,				44.0	25.8	30.2
MNY			MgO				36.6	21.5	41.9

to a high temperature and reductive atmosphere for long periods. Therefore, understanding the mechanical property of the substrate materials and its variation with time are necessary [12,13].

In this study, we examined the mechanical property variations as a function of the reduction time of various types of substrate materials under SOFC operating conditions to determine the fundamental guiding principle for substrate material design. In detail, we measured the Young's modulus of ternary systems, such as Al_2O_3–NiO–YSZ (ANY), TiO_2–NiO–YSZ (TNY) and MgO–NiO–YSZ (MNY) at each step (i.e., as-sintered, 100 h reduction, and 2000 h reduction). We focused our attention on the Young's modulus because it exhibits a high correlation with internal stress [14–16] and is an important factor for evaluating the long-term reliability of SOFC cells.

2. Experimental setup

2.1. Sample preparation

The samples tested were manufactured from commercial ceramic powders using standard ceramic processing techniques. The sample compositions are shown in Table 2. The ternary systems including Al_2O_3–NiO–YSZ, TiO_2–NiO–YSZ and MgO–NiO–YSZ were prepared by physical mixing and agitating the powders of NiO (0.7 μm, Seido Chemical Industry Corp.), YSZ (1.9 μm, Daiichi Kigenso Kagaku Kogyo Co., Ltd.) and Al_2O_3 (0.3 μm, Sumitomo Chemical Co., Ltd.) or TiO_2 (2.0 μm, Koujundo Chemical Laboratory Co., Ltd.) or MgO, which was obtained by calcination of $Mg(OH)_2$ powders. As previously mentioned, because the substrate plays a role in fuel supply and needs to have a high porosity to ensure the fuel's diffusivity, a pore forming agent (microcrystalline cellulose type, Asahi Kasei Corp.) of 10 mass % was added to the mixture. A solution containing 10 mass % poly-vinyl butyral (BM-1, Sekisui Chemical Co.) in ethanol was added to prepare pellets without cracks. The powders were well mixed using an agate mortar and muddler for 30 min and pressed uniaxially into rectangular pellets with a 12 mm × 70 mm size at a pressure of 640 kg cm^{-2} for 60 s. The pellets were calcined at 1500 °C for 2 h. Then, the pellets were reduced at 800 °C in an atmosphere of 4% H_2 balanced N_2 for 100 h and 2000 h. After each process, we measured the porosity and Young's modulus and performed analyses using an X-ray diffractometer (XRD), a scanning electron microscope (SEM), and an energy dispersive spectroscopy (EDX).

2.2. Experimental equipment

2.2.1. Measurement of Young's modulus

To measure the Young's modulus, a resonance method [17,18] was used in our study. In these measurements, the resonance frequencies of the samples were measured by setting one edge of the platy sample as the fixed end and the other as the free end. The Young's modulus was calculated by using Formula (1) and the measured resonance frequency.

$$E = \frac{4\pi^2 L^4 S \rho}{\alpha^2 I} f \quad (1)$$

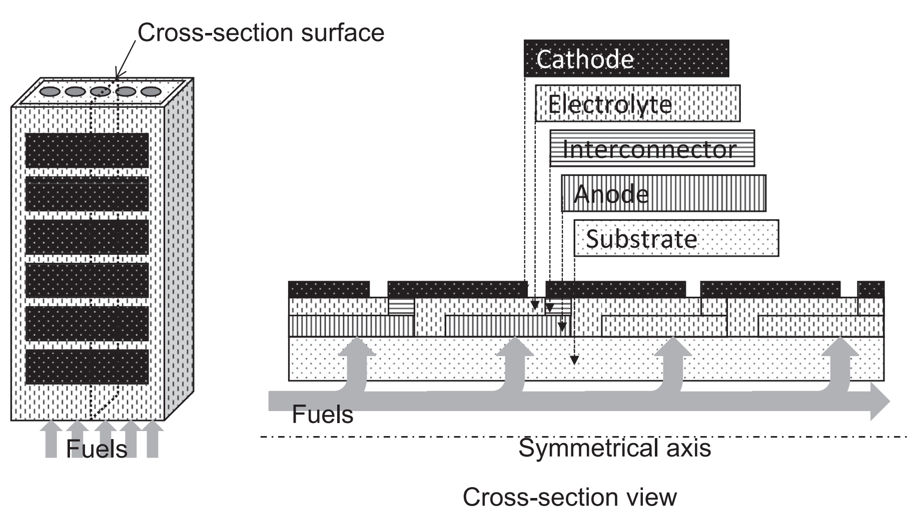

Fig. 1. Schematic of the SIS-type SOFCs.