



# Large gas permeability nickel/alumina substrates with hierarchical pore structure for solid oxide fuel cells derived from particle-stabilized emulsions



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## HIGHLIGHTS

- Hierarchical structure substrates were derived from particle-stabilized emulsions.
- The resulting substrates have a very large gas permeability of  $1.51 \times 10^{-3}$  [m<sup>2</sup>].
- Crack-free substrates exhibit suitable thermal expansion properties.

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## ABSTRACT

A new design of high-porosity substrates with large gas permeability for segmented-in-series solid oxide fuel cells (SIS-SOFCs) is presented in this paper. The use of particle-stabilized emulsions provides high mechanical strength struts and hierarchical pore structures in the substrates. Ni–Al<sub>2</sub>O<sub>3</sub> composites with Ni content of 0–30 vol. % are prepared, and their microstructures, flexural strengths, permeability, bending behavior and thermal expansions are investigated. The results show that porous and crack-free substrates are successfully obtained after sintering at 1450 °C for 5 h. Porosities of the substrates range from 75 to 85 % for an initial oil/water volume ratio in the suspension of 1:1. The flexural strength of the samples investigated are ranging from 7.5 to 9.8 MPa. The resulting porous substrates (30 vol% Ni) exhibit a suitable thermal expansion coefficient for use with a Ni-8YSZ anode and good bending behavior during sintering. Most importantly, these substrates have a very large gas permeability of  $1.51 \times 10^{-3}$  [m<sup>2</sup>].

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## 1. Introduction

Solid oxide fuel cells (SOFCs) have received much recent attention as next-generation alternative energy sources owing to their high efficiency for chemical to electrical energy conversion, cleaner energy production, and practical fuel flexibility [1–4]. Therefore, current efforts are devoted to development of the individual components as well as the integration of its various systems for commercial viability. SOFC cell-stacks, called “flat-tube segmented-in-series (SIS) cell stacks,” have been developed jointly by Tokyo Gas and Kyocera [5]. In SIS-type SOFCs, thick insulating substrates support multiple single cells, and have an important role as fuel supply channels [6,7]. Therefore, substrates need to be strong and have large gas permeability. In particular, in an SIS

cell-stack, due to fuel consumption, the fuel density in downstream cells is lower than in upstream cells. This results in a large concentration of impedances for cells located downstream in the fuel flow path, limited by gas diffusion through small pores between fine particles [8–10]. Pore size is important in allowing sufficiently rapid diffusion of gas to active reaction areas within the electrodes [11,12]. Thus, the design of microstructural features, especially substrate pore structure affecting gas permeability, is very important.

Pore formers such as rice starch, acrylic resin, carbon microspheres, graphite and polyvinyl alcohol [13–17] are generally introduced to increase porosity in electrode or substrate materials. However, pore size is almost the same as or smaller than the grain size of the pore formers, and substrates with high porosity usually have low flexural strengths. Porous materials created by incomplete densification or formed from specific ceramic particle sizes are also satisfactory for fuel cell substrates [18]. However, with these methods, it is often difficult to obtain high porosity; they are

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not as effective in producing large pore pathways within the microstructure, particularly when only fine ceramic particles are used. Other methods such as casting [19–21], injection molding [22], and combustion spray [23] are approaches for changing the microstructure within an electrode or substrate. Although these have been developed and improved to create increasingly more complex features, it is still a challenge to directly prepare high porosity substrates with high strength and large gas permeability by conventional porous ceramic processing. Compared with these conventional methods, using particle-stabilized emulsions [24] as templates has many advantages, such as easy processing and hierarchical pore structure, and the capability to fabricate products with complex shapes and high porosities in addition to high strength.

In general, substrates are prepared with Ni-YSZ cermet to match the thermal expansion coefficients (TEC) of anodes. For reducing production cost, new cermets based on the less expensive oxides,  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$ , were considered as suitable substrate materials in a previous study [25,26]. With a TEC matching 8YSZ, these substrates reduce the cost of cells and avoid thermoelastic bending during cell fabrication and thermal cycling [27].

In this letter, we report the preparation of hierarchical porosity Ni/ $\text{Al}_2\text{O}_3$  substrates from particle-stabilized emulsions. It has been found that these substrates have open cells, with average cell sizes ranging from 5 to 20  $\mu\text{m}$  and especially high porosities within 75%–85%, have large sheet strength, large gas permeability, low production costs and enhanced handling properties. The present study deals especially with the microstructure design and the physical properties of Ni/ $\text{Al}_2\text{O}_3$  substrates. The aim of this work is to investigate the process of using particle-stabilized emulsions as templates to preparation of high porosity ceramic substrates with a tailored microstructure and large gas permeability for segmented-in-series solid oxide fuel cells.

## 2. Experimental

Commercial  $\text{Al}_2\text{O}_3$  (99.99%,  $d_{50} = 0.5 \mu\text{m}$ , Lianyungang Lianlian Chemicals Co., Ltd.) and NiO (>99.9%, Sinopharm Chemical Reagent Beijing Co., Ltd) powders were used as starting materials. The nickel volume-content in the composite and cermet samples are different, and the nickel compositions of the samples used in the present study are summarized in Table 1. The mixtures were ball milled for 6 h. The Ni/ $\text{Al}_2\text{O}_3$  green ceramic body was synthesized using a modified particle-stabilized emulsion [28]. The schematic procedures for preparation of hierarchical porosity Ni/ $\text{Al}_2\text{O}_3$  substrates are illustrated in Fig. 1. The short amphiphile propyl gallate ( $\text{C}_{10}\text{H}_{12}\text{O}_5$ ) (AR), which exhibits high solubility and a high critical micelle concentration (CMC) in the aqueous phase, was used to modify the  $\text{Al}_2\text{O}_3$  and NiO particles *in situ*. A dispersant (the ammonium salt of poly (acrylic acid); 0.5 wt%) was added to the suspension to prevent particles from agglomerating. The other chemicals used in the experiments were deionized water, ammonia (4 M), hydrochloric acid (2 M), and ethanol. Homogenization and de-agglomeration of the suspension were performed by ball-

milling for 24 h using polyethylene milling bottles and agate balls (10 mm in diameter; weight ratio of the balls to suspension = 2:1).

Next, a certain amount of propyl gallate was dissolved in ethanol and added dropwise to the ball-milled suspension while constantly stirring to prevent particle agglomeration. An appropriate volume of octane (AR) was then added as oil to the suspension, which was emulsified using a household mixer at full power for 3 min. A number of oil/water (o/w) emulsions were prepared in this manner. All the emulsions were placed in a culture vessel (2 cm in height and 9 cm in diameter) and left to dry at room temperature for 1 week to allow the oil and water to evaporate. After the emulsions dried, the samples were shaped. Finally, the samples were sintered at 1450 °C in Ar-10%  $\text{H}_2$  for 5 h; the ramp rate from room temperature was 1 °C  $\text{min}^{-1}$ .

The dimensions and weights of sintered samples were measured to determine bulk densities, mass loss and volume shrinkage. The 3-point flexural strengths of the sintered samples (10 mm × 10 mm × 30 mm) were measured with a span length of 20 mm and crosshead speed of 0.5 mm/min on a Reger Universal Testing Machine (Shenzhen, China) at room temperature. In order to evaluate the thermoelastic bending behavior of the substrates caused by temperature changes, a suspension of NiO-YSZ (50:50 wt %) was deposited on the surface of a green support as a thin anode layer by the dip coating method [29]. The disk was then co-fired at 1450 °C in Ar-10%  $\text{H}_2$  for 5 h and a firing rate of 1 °C  $\text{min}^{-1}$ . Phases present in the sintered samples were determined through X-ray diffraction (XRD) analyses (D'Max-Ra12 kW, Ouyatu, Japan), performed using Cu-K $\alpha$  radiation; the scanning rate was 8.0°  $\text{min}^{-1}$ . Morphologies of the samples were investigated by scanning electron microscopy (SEM) (S-4800, Hitachi, Japan), and each phase was identified by an energy dispersive X-ray spectrometer (EDX). The electrical conductivity of these Ni- $\text{Al}_2\text{O}_3$  substrates were tested on a pA meter (HEWLETT PACKARD-4140B) with DC voltage source. Thermal expansion measurements were carried out on 25 mm long substrate specimens in a horizontal pushrod dilatometer (NETZSCH DIL 402 PC) between room temperature and 1100 °C.

## 3. Results and discussion

Fig. 2 shows total mass loss and volume shrinkage of the three different samples heated from room temperature to 1450 °C in Ar-10%  $\text{H}_2$  atmosphere. Volume shrinkage is defined as  $\Delta V_i/V_0$ , where  $\Delta V_i$  is volume change of a sample in the sintering processes, and  $V_0$  is the volume of the green ceramic body. The results indicated that volume shrinkage and mass loss increase with increasing nickel content in the composites. Of all the samples, the ones with 30 vol% Ni fraction showed the highest volume shrinkage of 22.7% and mass loss of –13.9%. Mass loss results mainly from reduction of NiO to Ni. In general, shrinkage during sintering occurs through the removal of pores in a green body as sintering progresses. In this paper, one source of shrinkage is the condensation reaction between matrix grains in struts. As well, and will be shown later, some reduced Ni particles agglomerated into larger particles and were located at the walls of macroporous cells; this reduced the quantity of solid particles on the struts, resulting in further significant volume shrinkage.

To prepare high porosity substrates, which allow good gas access to the electrodes, the ratio of oil/water in the suspension was set at 1:1. Porosities of the Ni/ $\text{Al}_2\text{O}_3$  substrates sintered at 1450 °C in Ar-10%  $\text{H}_2$  atmosphere for 5 h are shown in Fig. 3. As expected, the results showed that all three samples have high total porosity. When the Ni fraction in the initial composites was changed from 5 vol% to 30 vol%, the porosity increased somewhat, from 80% to 85%. In terms of component design, thickness of the support must be

**Table 1**

The nickel compositions of the samples before and after reduction and the particle sizes ( $D_{50}$ ) of the mixed powders.

Composites in air	NiO (wt%)	$\text{Al}_2\text{O}_3$ (wt%)	Ni (vol%)	$D_{50}$ [ $\mu\text{m}$ ]
8 vol% NiO- $\text{Al}_2\text{O}_3$	13.6	86.4	5	0.73
23 vol% NiO- $\text{Al}_2\text{O}_3$	34.5	65.5	15	0.84
36 vol% NiO- $\text{Al}_2\text{O}_3$	50.1	49.9	30	1.10

\* $D_{50}$  is the particle sizes corresponding to a cumulative distribution of 50 mass% of the powder. The  $D_{50}$  value corresponds to the median diameter.

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