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Fabrication and evaluation of a novel wavy Single Chamber Solid Oxide Fuel Cell via in-situ monitoring of curvature evolution

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HIGHLIGHTS

- Uniaxial viscosity of materials using optical method.
- In-situ observation of curvature during co-sintering of multi-layer structure.
- Fabrication of wavy SC-SOFCs using a single step co-sintering process.
- Performance tests, comparison and discussion of both wavy and planar cells.
- Wavy SC-SOFC outperformed planar SC-SOFC under the same operational conditions.

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ABSTRACT

Wavy type Single Chamber Solid Oxide Fuel Cells (SC-SOFCs) are beneficial for improved triple phase boundary conditions contributing to higher performance, compared with planar type SC-SOFCs of the same diameter. This study presents a fabrication process for wavy-type, cathode-supported SC-SOFCs with a single fabrication step via co-sintering of a triple-layer structure consisting of NiO/CGO-CGO-LSCF, with a thickness ratio of 1:3:9 respectively. Curvature evolution occurs due to different sintering behaviour of each layer during the co-sintering process. In-situ observation of each layer during the co-sintering process allows for minimisation of mismatched stresses to avoid unnecessary warping and cracking. Bilayers, consisting of NiO/CGO-CGO and CGO-LSCF, are co-sintered at 1200 °C. In-situ observation, to monitor the shrinkage of each material and the curvature evolution of the structures, is performed using a long focus microscope (Infinity K-2). Monitoring curvature behaviour in real time minimised the development of undesired curvature in the triple-layer structure. Performance testing of wavy cell is carried out in a methane-air mixture (CH_4:O_2 = 1:1). The wavy SC-SOFC generated 0.39 V and 9.7 mW cm^{-2} at 600 °C, which produced 260% and 540% increments in OCV and in maximum power density, respectively, over the planar SC-SOFC under the same operational conditions.

1. Introduction

Fuel cell technology is one of several energy technologies that could free society from fossilised carbon energy inputs and so overcoming any technical difficulties with fuel cell fabrication or operation could have huge dividends. Since Single-Chamber Solid Oxide Fuel Cells (SC-SOFCs) were introduced by Prof. Hibino's group [1–3], many researchers have investigated them primarily due to their inherent advantages such as miniaturisation with simpler structure and reduced manufacturing costs [4–6]. In the operation of SC-SOFCs, single cell or stacks are located in the same gas chamber and exposed to a mixture of fuel (hydrocarbon) and oxidant (air). The design of the fuel cell has inherent simplicity which is aided by having no seals in the fuel cell structure. A wide range of portable electronic devices could benefit from replacing the battery with miniature SC-SOFCs. However, the SC-SOFC electrochemical reaction process is based upon a different catalytic selectivity of the electrodes in a gas mixture condition (cathode for oxygen separation and reduction, anode for electrochemical fuel oxidation) compared to conventional dual chamber SOFCs. The selective catalytic reaction rate of SC-SOFC is quite minimal, and engenders a lower fuel utilisation than that of conventional SOFCs, so renders the novel design less attractive. Therefore, it is necessary to increase the effective reaction area for SC-SOFCs in a gas mixture condition,

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so as to overcome the main disadvantage of SC-SOFCs of low fuel utilisation and low power density per unit volume. Furthermore, thermo-mechanical instability results in the formation of cracks or delamination between layers which further narrows utilisation rates in a variety of applications. In addition, the multi-step fabrication process, used for conventional SOFCs and SC-SOFCs, is difficult to be commercialised.

To cope with the main issue with SC-SOFCs, namely higher performance, researchers have analysed chemical stability and catalytic performance of electrodes in a range of gas mixture conditions [7–9]. The recent examples have achieved power densities of up to 630 mW cm^{-2} using anode-supported configurations, with mixing ratios (R_{mix}) of CH_4:O_2 in excess of 1:1 [10]. One effective way to enhance the performance is to increase the number of triple phase boundary (TPB) sites, which elevates the active electrochemical reactions during the operation of the fuel cell. Researchers have also investigated using different ratios of anode functional layers to enhance electrochemical reaction at TPBs [11,12]. It has been suggested to fabricate a curved SC-SOFC in order to increase the TPB sites and to have a higher effective cell area within the same planar diameter; however, difficulty of fabrication including manufacturing cost and time is one of the main barriers to this suggestion.

In this paper the authors present a novel fabrication method for wavy type SC-SOFCs using co-sintering of multi-layer structure. Compared with typical planar cells, the wavy cell has a higher chemical reaction area due to an increase of effective cell area and so is expected to deliver increased performance per unit diameter compared to planar cells. The shape of the cells can be tailored, subject to curvature development and its manipulation via controlling the sintering conditions, to enhance gas transport in order to enhance gas residual time at electrodes, with the ultimate aim of enhancing the fuel utilisation [13–16]. In addition, the wavy shape allows the cell to absorb thermo-mechanical shock arising from different thermal properties between layers during the redox cycle. The SC-SOFC is a simpler structure than the conventional SOFC. This also applies for the wavy SC-SOFC via co-sintering and leads to a reduction in fabrication steps. Hence if the fuel utilisation and thermo mechanical instabilities can be fully overcome then these wavy type SC-SOFCs could have a wider appeal for a range of portable devices, enabling mass production and commercialisation.

During the sintering process of planar SOFCs, it is well established that a bi-layer structure, consisting of anode and electrolyte layers, is sintered followed by a second sintering step with the cathode layer. The thermo-mechanical behaviour of the anode and electrolyte are similar hence no defects will occur during sintering such as warping, cracking, and delamination. In the second sintering step the cathode layer, which does have different thermo-mechanical properties, shrinks only along the through-thickness direction and thus results in no defects. For a multi-layer structure, co-sintering does result in warping and/or cracking [17–22]. These defects occur due to the different shrinkage rates of the individual layers. The different shrinkage rates result in tensile and compressive stresses being generated at the curved surfaces and result in undesired curvature evolution. This shrinkage behaviour has been delicately monitored throughout this study and an attempt to control the behaviour in order to utilise it and promote a wavy/curved shape has been sought. Consequently, a triple layer structure of thickness ratio 1:3:9 (anode, electrolyte and cathode respectively) was employed to facilitate this curvature evolution in the desired manner. A porous electrolyte (CGO, Gadolinium Doped Ceria) was thus obtained in order to harmonise sintering temperatures for all components, and a cathode (LSCF, Lanthanum Strontium Cobalt Ferrite) supported structure was employed to control the curvature behaviour. It was also a consideration to provide a greater bulk volume of LSCF layer to postpone against deterioration through the anode (NiO/CGO) reduction process prior to the cell test.

The aim of the presented work is to make a more effective wavy type SC-SOFC over a planar SC-SOFC. In order to achieve this aim, the following objectives are set; first, to investigate curvature evolution of bi- and triple-layer structures during co-sintering through in-situ experimental observation; second, to suggest a novel fabrication method for a wavy type SC-SOFC in order to deliver increased electrochemical reaction per unit area; and lastly, to carry out the performance comparison between the wavy and the planar SC-SOFC. Experimental results are presented on shrinkage behaviour of each material followed by the in-situ monitoring of curvature evolution with bi-layer structure. From this triple-layer structure is fabricated so that undesired curvature is minimized during the co-sintering process. Curved triple layer structure can then be fabricated and co-sintered with minimal further curvature (zero-deflection condition). The performance test of wavy type SC-SOFC is presented along with that of planar type including open circuit voltage (OCV) comparison and results are discussed.

2. Experimental procedure

2.1. Materials preparation

Materials used in this study were Ni/CGO for anode, CGO for electrolyte and LSCF for cathode; their specifications are listed in Table 1. Tape-casting process with these materials was carried out with support of Maryland tape-casting company. The thickness of each tape was 20 μm and they were hot pressed at 45 °C under 5 MPa for 5 min to obtain multi-layer structure. In bi-layer structures, one layer of anode and three layers of electrolyte were laminated for anode-electrolyte structure, and three layers of electrolyte and nine layers of cathode were used for electrolyte-cathode structure. For cathode-supported SC-SOFC fabrication, a triple-layer structure was fabricated with one layer of anode, three layers of electrolyte and nine layers of cathode.

After fabrication by hot pressing, the sintering process was performed with single-layer, bi-layer and triple-layer structures. A heating rate of 1 °C min^{-1} was used up to 750 °C for de-binding and then 3 °C min^{-1} up to 1200 °C. During the sintering process, a long-focus camera (Infinity K-2) was used to monitor shrinkage and curvature evolution at a specific temperature. In this study, sintering process was divided into three parts. Section 2.1.1 covers shrinkage measurement in free sintering and vertical sintering, proposed by Cologna [23] to investigate uniaxial viscosity of each material depending on temperatures. Section 2.1.2 covers the estimation of curvature evolution of multi-layer structure derived from mismatched stresses between layers during co-sintering. Section 2.1.3 covers the fabrication of wavy type SC-SOFC with zero-deflection during co-sintering.

2.1.1. Shrinkage measurement

Rectangular specimens with 4 mm (W) × 3 mm (L) were prepared from single-layer tape of each material and leaned on a vertical wall of alumina substrate for the free sintering process, Fig. 1 (a). During the process, shrinkage in the width direction of the specimen was monitored by optical method, following image pro-

Table 1
Specification of materials.

Name	Composition	d_{50} (μm)	S_{BET} (m^2 g^{-1})
NiO/CGO	60 wt% NiO/40 wt% CGO	0.3	4–8
CGO	$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	0.3	5–8
LSCF	$La_{0.6}Sr_{0.4}Co_{0.2}$ $Fe_{0.8}O_{3-\delta}$	1.0	4–8