

# Design and fabrication of three-dimensional solid oxide fuel cells

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## Abstract

A novel design for a three-dimensional (3-D) solid oxide fuel cell (SOFC) along with its method of fabrication is reported. This structure utilizes two 3-D channels that are separated by unique anode/electrolyte/cathode walls that thereby increases the active volumetric surface areas of the electrodes used for the chemical reactions. To implement this structure, a graphite template having one 3-D interconnected channel is successively coated with anode (NiO–YSZ), electrolyte (YSZ), and cathode (LSM–YSZ) slurries, followed by heat-treatment at elevated temperatures. This produces an additional 3-D channel that has the NiO–YSZ layer as a replica of the graphite template, while preserving the pre-existing channel that has the LSM–YSZ layer. The thickness of the NiO–YSZ layer, which provides mechanical stability, is controlled by adjusting the number of dip-coating cycles. Using this approach, it is possible to fabricate a ~10 mm cubic SOFC without any notable defects, as well as to control the microstructures of the NiO–YSZ/YSZ/LSM–YSZ walls.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that convert the chemical energy of gaseous fuels directly into electric energy. These systems provide a much higher specific energy than other types of fuel cell [1,2], as well as high fuel flexibility [3–5]. In principle, a SOFC consists of three key components, namely a fuel electrode, an air electrode, and an electrolyte. In terms of microstructure, the electrolyte must be fully dense to prevent gas mixing, whereas the anode and cathode must be porous to allow gas transport to the reaction sites [1].

Solid oxide fuel cells usually require a high operating temperature in order for the electrolyte to exhibit high ionic conductivity and, consequently, they are rarely viewed as being suitable for powering small portable devices. Nevertheless, a number of research groups are now looking into the possibility of using them for smaller devices [6–10]. This is made possible by decreasing the operating temperature and by improving the power density. More recently, it was demonstrated that the power

density of a planar SOFC, wherein the heat from the oxidation reaction at the anode could maintain the temperature required for the continuous reaction, is sufficient to run an MP3 player [11].

In order to extend their range of applications, SOFCs should have a high power density along with a small physical size, in other words a high volumetric power density. This can be achieved by either improving the material properties used for the components [5,12–14] or by increasing the active surface areas of the electrodes used for the chemical reactions [15]. To date, several designs have been examined for SOFCs, including the tubular and planar types, both to enhance their efficiency and to reduce their manufacturing cost [16]. Each type has its own benefits and drawbacks. For example, the tubular design has rapid start-up capability, excellent thermal shock resistance, and excellent power cycling, but has a much lower current density than the planar design. The flat-tube high power density (HPD) SOFC [17] and the honeycomb SOFC [18] have also been proposed.

In this study, a three-dimensional (3-D) SOFC with a novel structure that can ensure a high volumetric powder density by increasing the active areas of the electrodes is proposed and its method of fabrication is described. To implement this structure, a unit cell is employed that has 3-D connected cylinders that have

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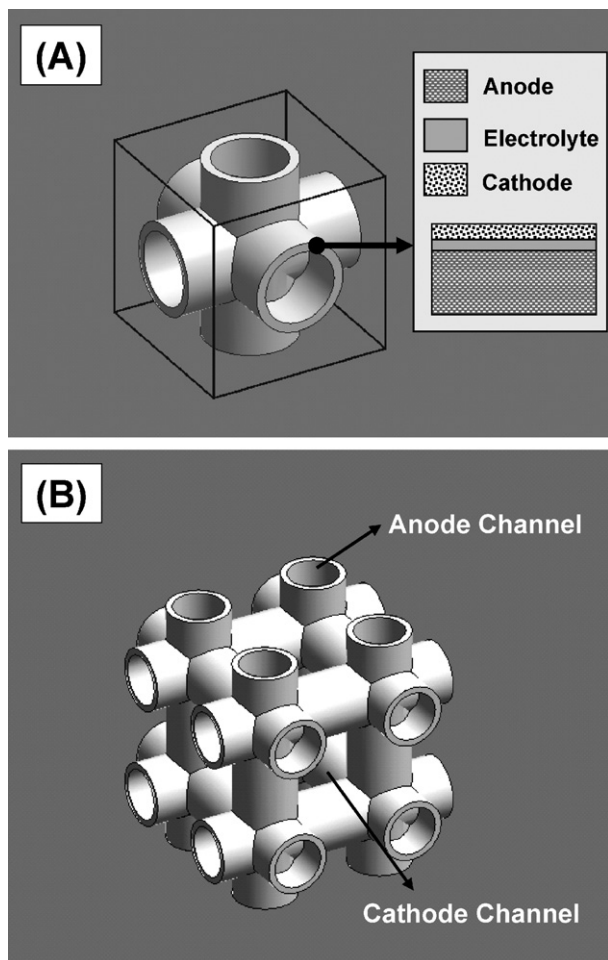


Fig. 1. Schematic illustrations of proposed 3-D SOFC: (A) unit cell with three-dimensionally interconnected cylinders comprised of anode, electrolyte, and cathode layers and (B) 3-D structure with two channels (anode and cathode channels), constructed by placing the unit cells in 3-D pattern.

inside and outside layers made of anode and cathode materials, respectively. These two layers are separated by an electrolyte layer, as shown in Fig. 1(A). In this case, fuel and air can pass independently through the anode and cathode channels and react with the respective materials. A useful 3-D SOFC is achieved by linking the unit cells in a periodic 3-D pattern, as shown in Fig. 1(B). This novel structure allows the volumetric surfaces of the electrodes to be increased compared with conventional 2-D fuel cells [19].

The proposed 3-D SOFC was fabricated by means of a combination of the computer numeric controlled (CNC)-machining and dip-coating processes that was recently developed by the authors to produce highly porous ceramics [20]. In this method, a graphite template with the 3-D interconnected channel was prepared by CNC-machining and then successively dip-coated with anode, electrolyte and cathode slurries, followed by heat-treatment at elevated temperatures to remove the graphite template and to sinter the ceramic walls. This method produced the additional 3-D channel as a replica of the graphite template having the anode layer, while preserving the pre-existing channel having the cathode layer. The processability

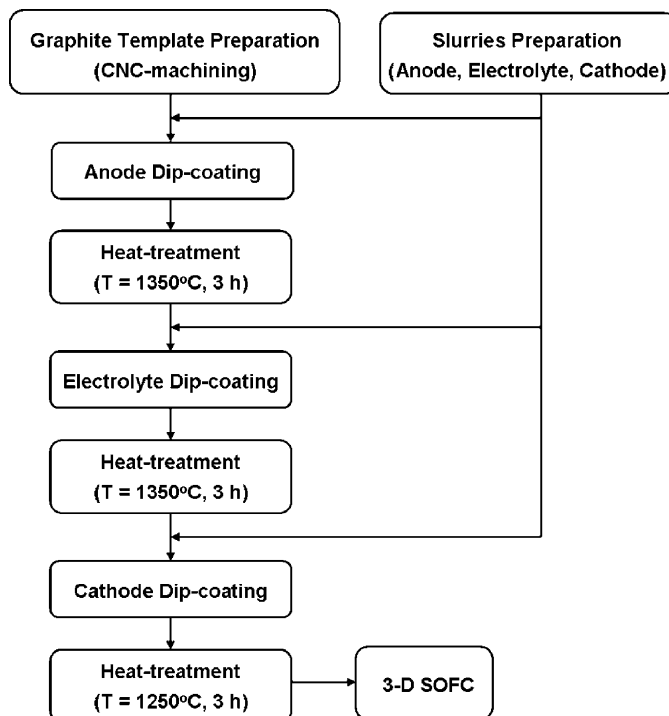


Fig. 2. Flow chart for fabrication of 3-D SOFC using combination of CNC-machining and ceramic dip-coating processes.

of the construction of the 3-D SOFC and its characteristics are addressed.

## 2. Experimental procedure

A flow chart of the fabrication route using a combination of the CNC-machining and the dip-coating processes is shown in Fig. 2. Since an additional 3-D channel is formed by removing the fugitive template, it is crucial to select a suitable material that can be completely removed by heat-treatment and is chemically resistant to the ethanol-based ceramic slurry. In general, polymeric moulds are used as the template because they can readily be produced using various rapid prototyping (RP) methods [21]. However, these materials would experience large volume changes during the heat-treatment which would deteriorate the thin ceramic walls. Thus, in this study, graphite material is chosen as the template because it can easily be machined into complex shapes and removed via thermal oxidation during heat-treatment at elevated temperatures [20].

The graphite template was prepared by machining a solid graphite block (dimensions of 13 mm × 13 mm × 13 mm) using a mini-CNC machine according to a pre-determined design in order to produce an interconnected 3-D channel with a diameter of 1.5 mm, and with a fixed distance between the channels of 1 mm. This simple CNC-machining technique enabled the fabrication of a tightly-controlled channel and graphite wall structure, as shown in Fig. 3(A).

Since the aim of this study is to investigate the usefulness of the novel 3-D SOFC, it was decided to use traditional compositions for the anode, electrolyte, and cathode materials (i.e., anode: 50 wt.% NiO–50 wt.% YSZ; electrolyte: YSZ; cathode:

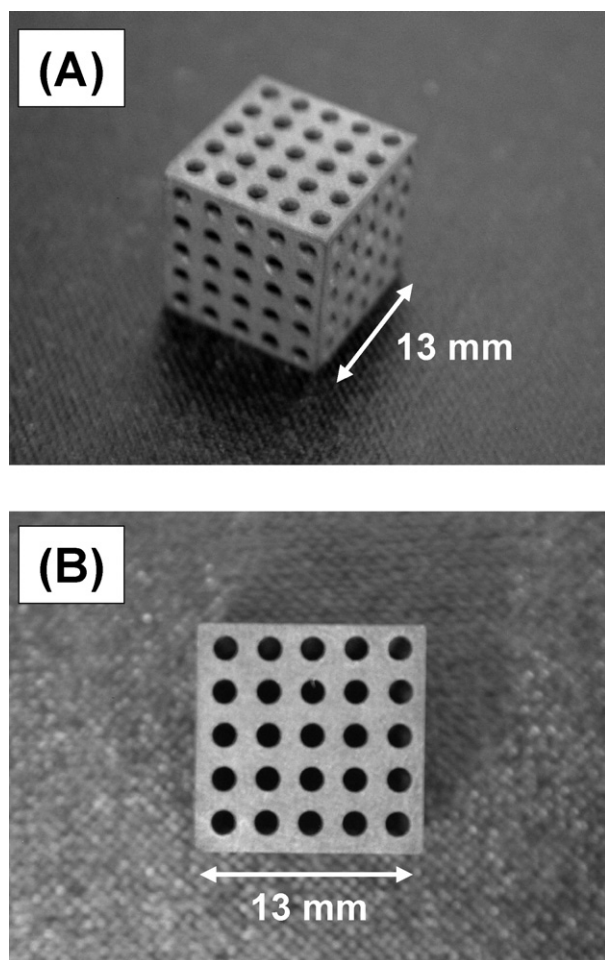


Fig. 3. Optical micrographs of graphite template: (A) 3-D interconnected pore channel and (B) periodic channels separated by graphite walls in plane view.

50 wt.% LSM–50 wt.% YSZ). Commercially available nickel oxide (Wako Pure Chemicals, Osaka, Japan), yttria-stabilized zirconia doped with 8 mol%  $Y_2O_3$  (TZ-8Y; Tosoh Co., Tokyo, Japan), and lanthanum strontium manganate (LSM; Praxair Inc., CT, USA) were used. In addition, carbon black powder (Cabot Black Pearls BP-120; Cabot Corp., Boston, MA, USA) was employed as a fugitive material to produce the pores in the anode and cathode layers.

Three types of ceramic slurry were prepared for the anode, electrolyte, and cathode layers, respectively, by dispersing ceramic powders in ethanol as a solvent containing triethyl phosphate (TEP;  $(C_2H_5)_3PO_4$ , Aldrich, USA) as a dispersant and polyvinylbutyl (PVB, Aldrich) as a binder. The compositions of the ceramic slurries are summarized in Table 1. The mixtures

were then milled for 24 h in a plastic bottle containing zirconia ( $ZrO_2$ ) balls as the media to achieve a stable slurry with a homogenous distribution of the ceramic powders. The viscosities of the prepared slurries were measured using a rheometer (CS-50, Bohlin, East Brunswick, NJ, USA) that had a cone-and-plate measurement geometry.

The prepared graphite template was immersed in the anode slurry and subsequently blown with an air gun to coat its surface uniformly without blocking the channels. After repeating the coating process five times, the sample was dried at  $70^\circ C$  for 10 min to remove the ethanol. The coating-and-drying steps were repeated several times to achieve an anode layer that was sufficiently thick to provide mechanical stability. Thereafter, the anode-coated graphite template was heat-treated at  $900^\circ C$  for 3 h to remove the graphite template, and then at  $1350^\circ C$  for 3 h to sinter the NiO–YSZ walls. This produced a 3-D anode structure that had an additional 3-D channel as a replica of the graphite template. The sintered anode structure was then coated with the electrolyte slurry, followed by heat-treatment at  $1350^\circ C$  for 3 h to sinter the YSZ walls. Thereafter, the cathode (LSM–YSZ) layer was coated using the same dip-coating process, followed by heat-treatment at  $1250^\circ C$  for 3 h. This sequential coating process resulted in the production of unique ceramic walls that were comprised of continuous NiO–YSZ, YSZ, and LSM–YSZ layers. The macro- and microstructures of the samples were characterized with optical microscopy (PMG3, Olympus, Tokyo, Japan) and scanning electron microscopy (SEM, JSM-6330, JEOL Techniques, Tokyo, Japan).

### 3. Results and discussion

The simple process of CNC-machining produced a graphite template with a tightly-controlled 3-D structure, as shown in Fig. 3(A and B). Only a small variation is observed in the sizes of the channels ( $\sim 1.5$  mm) and the graphite walls ( $\sim 1$  mm), so that the channel structure of the 3-D SOFC can be precisely controlled. In addition, an excellent surface finish is obtained without any chipping or cracking, due to the excellent machinability of the graphite itself. It should be noted that it is possible to fabricate other arbitrary 3-D structures as templates by means of the CNC-machining technique or rapid prototyping method, if necessary.

In order to achieve a uniform coating on the surfaces of the graphite scaffold, the slurry should have a low viscosity and good wettability on the graphite material. The desired properties strongly depend on the solid loading, binder content, and the type and amount of the dispersant [22]. It is observed

Table 1  
Compositions of ceramic slurries used for anode, electrolyte, and cathode layers

	Powder				EtOH (g)	PVP (g)	TEP (g)
	NiO (g)	YSZ (g)	LSM (g)	Carbon black (g)			
Anode	20	20		3	130	3	3
Electrolyte		42			130	3	3
Cathode		20	20	4	130	3	3

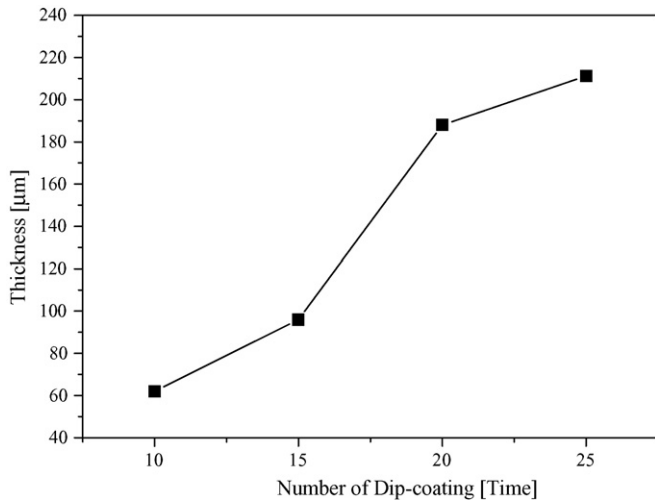


Fig. 4. Thickness of NiO–YSZ layer as function of number of dip-coating cycles after sintering at 1350 °C for 3 h.

that all of the prepared slurries exhibit Newtonian flow with reasonable viscosities, which is a feature that is suitable for the ceramic dip-coating process. These observations indicate that the ceramic particles are homogeneously distributed in the slurry, and thereby allow the production of uniform coating layers.

Since the anode layer has to ensure the mechanical stability of the proposed 3-D SOFC, the thickness of the NiO–YSZ layer is adjusted by varying the number of dip-coating cycles. The change in thickness of the NiO–YSZ walls as a function of the number of dip-coating processes is demonstrated in Fig. 4. The thickness of the wall increases steadily with an increasing number of replication cycles. After repeating the dip-coating procedure 10 times,  $\sim 62 \mu\text{m}$  thick walls are obtained, but still did not have adequate strength. After repeating the dip-coating procedure 25 times, the wall thickness increases to  $\sim 211 \mu\text{m}$ , which gives it sufficient strength for the sequential dip-coating processes and ensures the mechanical stability of the 3-D SOFC.

The prepared 3-D graphite template was uniformly coated with the NiO–YSZ slurry, followed by heat-treatment at 900 °C for 3 h to remove the graphite template, and then at 1350 °C for 3 h to sinter the NiO–YSZ walls. The combination of the graphite template and coating process allows the formation of uniform sintered NiO–YSZ walls without any noticeable defects, such as cracking and distortion, as shown in Fig. 5(A). It should be noted that an additional 3-D channel is newly formed as a replica of the 3-D graphite structure and is surrounded by the NiO–YSZ walls. Thus, this 3-D channel is not visible in the as-fabricated sample. A linear shrinkage of  $\sim 21\%$  is observed after sintering at 1350 °C for 3 h in air. In addition, the NiO–YSZ wall has a porous structure, which results from the use of carbon black as a fugitive material, as shown in Fig. 5(B).

Thereafter, the fabricated 3-D NiO–YSZ structure was uniformly coated with a YSZ slurry, followed by sintering at 1350 °C for 3 h, and then coated again with an LSM–YSZ slurry,

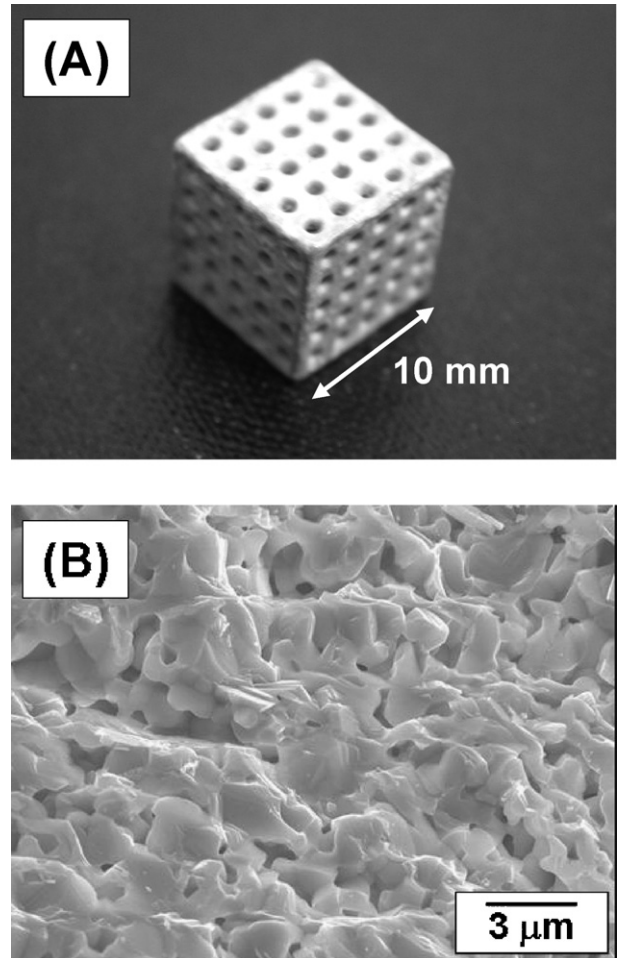


Fig. 5. (A) Optical micrograph of fabricated 3-D NiO–YSZ structure sintered at 1350 °C for 3 h. (B) Scanning electron micrograph showing porous NiO–YSZ layer.

followed by sintering at 1250 °C for 3 h. This sequential dip-coating process allowed for the fabrication of the 3-D SOFC without any noticeable defects, as shown in Fig. 6(A), wherein the outmost layers of the fabricated sample have been ground to expose two channels. Scanning electron micrographs illustrate the 3-D structure more clearly, as shown in Fig. 6(B). The construction of the two periodic channels is visible in Fig. 6(C). The square channel coated with the NiO–YSZ layer is formed as a replica of the graphite template, while the pre-existing cylindrical channel coated with the LSM–YSZ layer is preserved, in such a way as to mimic the original design (Fig. 1(B)).

It should be noted that the outside and inside of the cylinders are uniformly coated with the NiO–YSZ and a LSM–YSZ layers, respectively, and that these two layers are separated by the YSZ layer, as shown in Fig. 7(A and B). The measured thickness of the NiO–YSZ layer is  $\sim 221 \mu\text{m}$ . Even though the mechanical properties of the 3-D SOFC were not measured, it is believed that this structure will have sufficiently high strength to ensure its mechanical stability, especially due to its unique 3-D array of ceramic walls. In addition, a  $\sim 22 \mu\text{m}$  thick LSM–YSZ layer is uniformly coated on the inside of the channel, and this



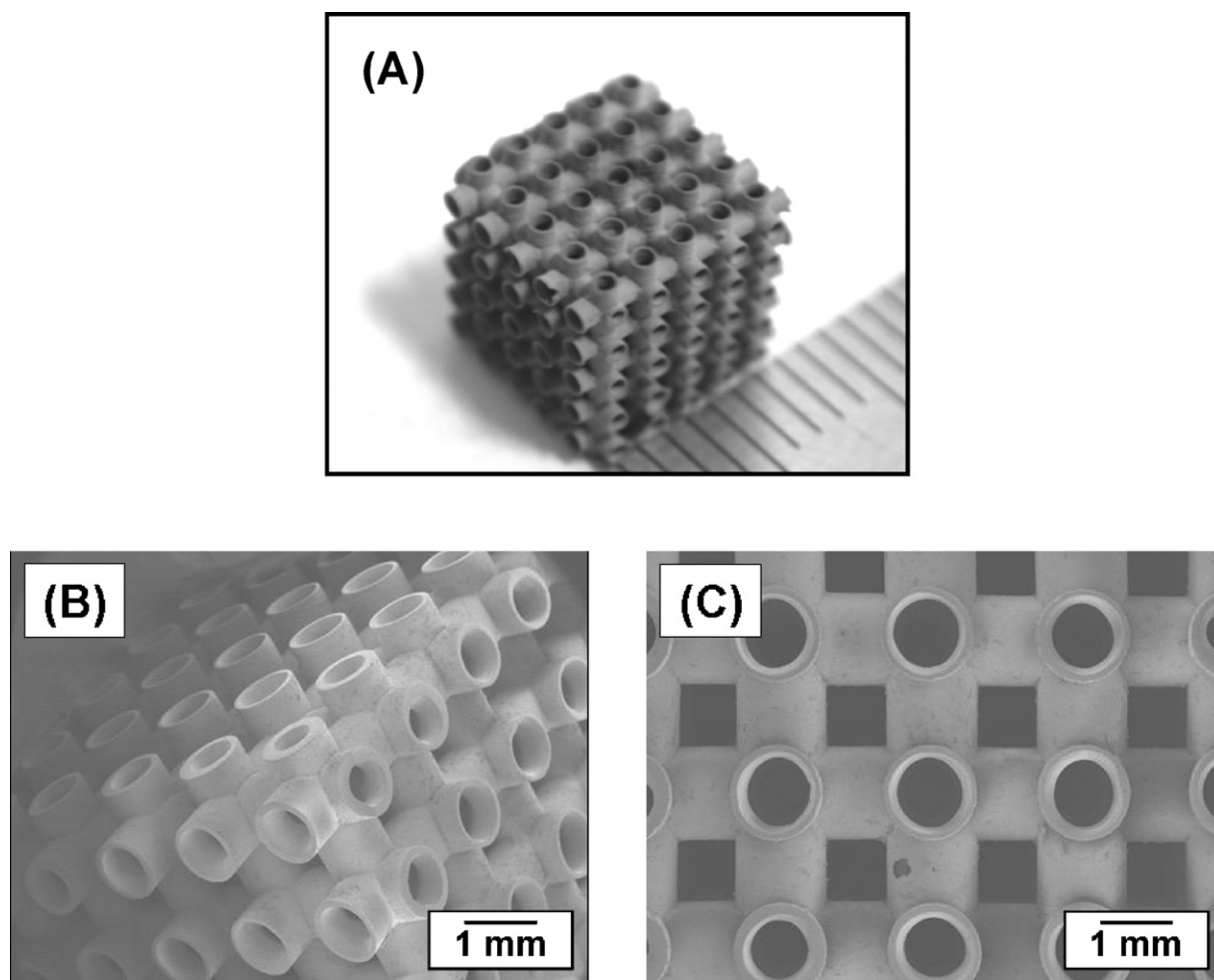


Fig. 6. (A) Optical micrograph of fabricated 3-D SOFC; (B) scanning electron micrograph showing 3-D structure; and (C) micrograph showing two periodic channels used for fuel and air paths, respectively.

is expected to improve the efficiency of the cathodic reduction of oxygen. Between these two layers, the YSZ layer is formed with a thickness as thin as  $\sim 11 \mu\text{m}$  and with good interfacial bonding, as shown in Fig. 7(B). Some pores are visible in the YSZ layer, but this is not expected to hamper significantly its use as an electrolyte to deteriorate the performance of the SOFC as a whole. In addition, the tightly-controlled dip-coating process will likely eliminate defects in the YSZ electrolyte layer. Furthermore, both NiO–YSZ and LSM–YSZ layers exhibit desired porous structures, as shown in Fig. 7(C and D), respectively. These observations indicate that the layers will serve efficiently for the anodic oxidation of fuel and the cathodic reduction of oxygen, respectively. It should also be noted that the thickness of each layer can be adjusted by changing the number of dip-coating cycles.

For powering small portable devices, the single-chamber fuel cell is believed to be the most competitive solution. In this type of SOFC, both the anode and cathode are exposed to the same mixture of fuel and air. This results in a system which is simpler than that of the dual-chamber design which is normally used for conventional SOFCs [12,23,24]. Thus, the unique charac-

teristics of the proposed 3-D SOFC are considered in the light of its use as a single-chamber fuel cell namely: (i) well-known ceramic processing techniques (CNC-machining and ceramic dip-coating) can be used to fabricate the 3-D SOFC, thus keeping the manufacturing costs at a reasonable level; (ii) the unique 3-D structure will notably increase the volumetric surface areas of the active electrodes and thereby result in a higher volumetric power density compared with that of 2-D SOFCs comprised of the same materials, such as in the case of a 3-D battery [20]; (iii) the self-channelled structure will serve as flow paths for the fuel–air mixture, which will enable the device to be very compact; and (iv) the two separate channels will allow the reactions to take place independently at the anode and cathode layers without disturbing each other, and thereby will prevent the problem of electrode poisoning that is often observed in single-chamber fuel cells [11,25]. Despite the attractiveness of such a 3-D SOFC concept, several issues remain to be addressed before it can be made fully practical. Thus, future studies will include the optimization of not only the fabrication techniques and microstructures of the SOFC components, but also the physical–geometrical parameters of the experimental setup.

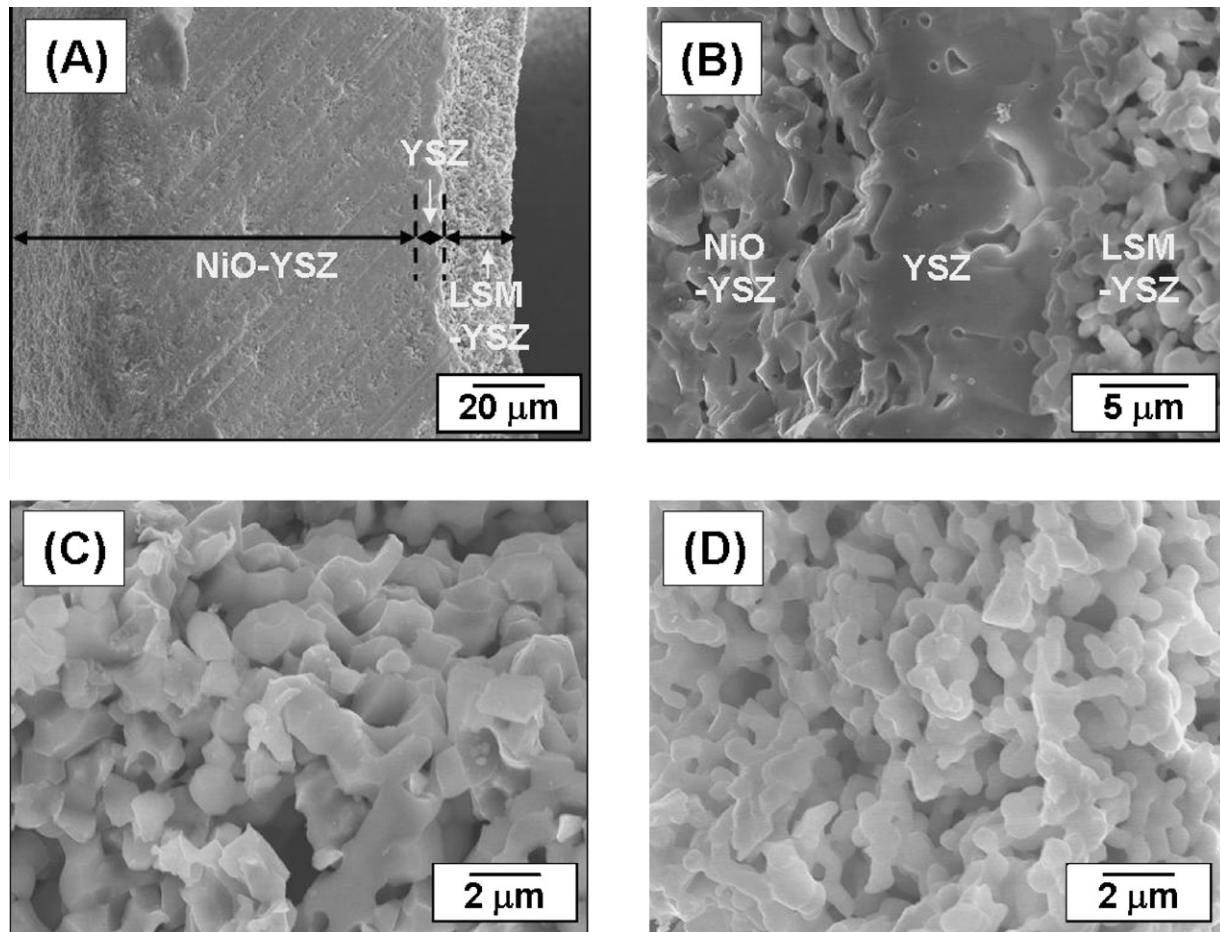


Fig. 7. Scanning electron micrographs: (A) ceramic wall comprised of NiO–YSZ/YSZ/LSM–YSZ layers; (B) YSZ layer between NiO–YSZ and LSM–YSZ layers; (C) porous NiO–YSZ layer; and (D) porous LSM–YSZ layer.

#### 4. Conclusions

A novel 3-D SOFC with two interlaced 3-D channels is designed and fabricated using a combination of the CNC-machining and ceramic dip-coating processes. For its actual fabrication, a graphite template having one three-dimensionally interconnected channel is prepared by CNC-machining and then successively dip-coated with various ceramic slurries (anode, electrolyte, and cathode), followed by heat-treatment at elevated temperatures. The thickness of the NiO–YSZ layer that provides the 3-D SOFC with its mechanical stability is increased up to  $\sim 211 \mu\text{m}$  by repeating the dip-coating cycle 25 times. In addition, the microstructures of the NiO–YSZ, YSZ, and LSM–YSZ layers are controlled by adjusting the sintering temperatures and incorporating carbon black as a fugitive material to produce pores in the electrodes. This new approach allows the fabrication of a 3-D SOFC with dimensions of  $\sim 10 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$  without any noticeable defects, as well as unique NiO–YSZ/YSZ/LSM–YSZ walls. This 3-D SOFC will undoubtedly allow the volumetric surface areas of the electrodes used for chemical reactions to be increased, and thereby will increase the volumetric power density.

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