

Prospective use of the 3D printing technology for the microstructural engineering of Solid Oxide Fuel Cell components

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A cost-effective micro-manufacturing process to accurately build 3D microstructures for their prospective use in the fabrication of Solid Oxide Fuel Cells components has been tested. The 3D printing method, based on the stereolithography, allows solidifying layer by layer a dispersion of ceramic material in a liquid photosensitive organic monomer.

A simple projector, a computer-controlled z-stage and a few PowerPoint slides may be used for the fabrication of a wide range of complex 3D microstructures in few minutes. In this work, 3D ceramic microstructures based on the yttria-stabilized zirconia (YSZ) were successfully fabricated. The microstructured ceramic components produced were stable after sintering at 1400 °C for 4 h. Impedance measurements show that the fabrication process does not have any detrimental effect on the electrical properties of the structured material.

Keywords: 3D printing, YSZ, Deposition methods, Microstructure, Sintering

Potencial uso de la tecnología de impresión 3D para el control microestructural de componentes de Pilas de Combustible de Óxidos Sólidos

Se ha probado un método económico de microfabricación que permite construir con precisión microestructuras 3D para su potencial uso en la producción de componentes de pilas de combustible de óxidos sólidos. El método de impresión 3D basado en la estereolitografía, permite solidificar, capa por capa, una dispersión de material cerámico en un líquido que contiene un monómero orgánico fotosensible.

Un simple proyector, una plataforma vertical automatizada y unas pocas imágenes de PowerPoint pueden ser utilizados para la fabricación de un amplio rango de estructuras complejas 3D en unos pocos minutos. En este trabajo se han fabricado con éxito microestructuras 3D basadas en la zirconia dopada con itria (YSZ). El material cerámico microestructurado producido se mantuvo estable después de sinterizarse a 1400 °C durante 4 h. Las medidas de impedancia demostraron que el proceso de fabricación no tenía ningún efecto perjudicial en las propiedades eléctricas del material estructurado.

Palabras clave: Impresión 3D, YSZ, Métodos de deposición, Microestructura, Sinterizado

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1. INTRODUCTION

The growing concern regarding climate change has led to the development of green technologies mainly based on renewable resources and particularly the applications related to hydrogen.

Hydrogen can be produced from renewable energies, e.g. by photocatalytic water splitting or thermolysis using Concentrating Solar Power and it may be used in off-peak hours to provide power through Solid Oxide Fuel Cells (SOFCs) (1).

Most of the components used in the aforementioned applications are ceramics with outstanding properties that rely on special compositions and microstructures, requiring a precise control throughout the subsequent stages of ceramic

processing. The design of these microstructures may be a key issue, having an impact in parameters such as performance, mechanical stability, optimisation of gas flow-paths to/from the reaction sites, thermal instability and depending on the materials, redox cycling. Furthermore, in most of the cases, the engineered microstructures must be stable at high temperatures, as is the case of the thermal cycles in Concentrating Solar Power when the temperatures may reach values close to 1500 °C, or in YSZ-based components in SOFC technology, which are typically sintered at 1400 °C to produce gas-tight materials (2).

Regarding SOFC technology, the development of alternative approaches to simultaneously control both the macrostructure (flat/tubular configurations) and the microstructure (distribution/patterning of porosity, Triple Phase Boundary (TPB) optimization, thickness of layers, etc.) would be highly desirable. Consequently, a 3D-printing system may be considered as an interesting approach for the production of structured SOFC components.

This type of additive fabrication technology produces 3D complex structures by assembling small elements together into a solid model in shorter periods of time compared to conventional fabrication methods and is usually powered by computer aided design (CAD) (3, 4).

Stereolithography (SLA) can be considered the first of the rapid prototyping technologies (5), and starts by generating a 3D structure using CAD software. The next step involves slicing the 3D structure into a sequence of cross-sectional layers or digital masks. During a fabrication cycle, an ultraviolet laser beam is moved across the surface of a photosensitive polymer to instantly cure the liquid. After one layer is solidified, the polymerized component is re-immersed into the resin to allow the formation of a new thin liquid layer on top. By repeating the cycle, a 3D microstructure is formed from a stack of layers, although a post curing process in an ultraviolet oven is typically required to complete the polymer solidification process.

This type of serial process fabrication is called also vector by vector microstereolithography (V μ SL). The so-produced layers are in the range of the 25-50 μ m, though the technique can be pushed to the limit reaching resolutions down to 75 nm as shown by Kawata *et al.* (6), despite this case was a slow serial process. To overcome the speed limitation and inspired by micro display technologies, a parallel scheme was merged into μ SL, giving rise to the so-called projection microstereolithography (P μ SL). The core of this technology lies on the use of a spatial light modulator as a dynamic mask. It can be either a liquid crystal display (LCD) panel or a digital-light-processing (DLP) (3, 7). An extension of polymer SLA that also utilizes inorganic materials has already been tested by several researchers (4, 7-13).

The aim of this work is to verify the capabilities of the micro-stereolithography to produce 3D microstructures using a dispersion of inorganic powders generally used in SOFCs devices, (YSZ in this work), in a photosensitive polymer solution, with good resolution after sintering at 1400 °C just using a common DLP-projector, an automated z-stage and PowerPoint slides, with the additional advantage that it does not require a post curing process.

2. MATERIALS AND METHODS

2.1. 3D printing system for ceramic materials

Preliminary tests on organic materials were performed with a MiiCraft 3D Printer (Rays Optics Inc). The original procedure for 3D printing was developed by Fang (14) and adapted by Muskin *et al.* (15). We have assembled in our lab a similar 3D system for ceramic materials using a common projector and an automated z-stage.

A micro burette from CRISON (model microBUR 2031) was adapted and used as a z-stage. The minimum layer thickness can be controlled down to 5 μ m.

The light source is produced by an OPTOMA projector (model EX536), XGA 1024x768, 2800 lumens.

A software, based on VisualBasic, was developed to automatically control all the stages of the fabrication process, i.e. automatic control of the z-stage, dwell time between each curing cycle and projection of each digital mask through the projector.

2.2. Starting products

Several organic materials were used as a photo curable resins in our studies: poly(ethylene glycol) diacrylate (MM~575), tetra(ethylene glycol) diacrylate (MM~302), ethylene glycol dimethacrylate (MM~198) and tetraethylene glycol dimethacrylate (MM~330), all of them from Sigma Aldrich. The mechanisms of photo-curing of acrylate resins are known as free radical polymerization and references can be found elsewhere (4, 16, 17).

An ultraviolet sensitive photoinitiator (PI) is required to trigger the polymerization reaction. Phenyl bis (2,4,6-trimethyl benzoyl) known as Irgacure819 (from Sigma Aldrich) was used in all cases. This material exhibits an absorbance maximum between 360-400 nm for 0.1 wt % of PI. This maximum is shifted to higher wavelengths with the PI concentration. A 1 wt % was used in all the samples.

Small quantities of a photo-absorber, 0.05 wt % of Sudan I (Sigma Aldrich) were used to control the light penetration depth in the solution. For samples with inorganic samples no photo-absorber was used.

100 g of each organic curable solution comprises: 98.95 wt % of photo curable resin, 1 wt % of photoinitiator and 0.05 wt % of photo-absorber. All the components were mixed under magnetic stirring for at least 24 h.

8 % mol yttria-stabilized zirconia (100 nm of average grain size) from PI-KEM was used as an inorganic material for the fabrication of 3D microstructures. YSZ powders were added into the organic curable solution and ball-milled for several hours at 150 rpm in zirconia containers. In this work, the solid loading of the YSZ powders ranged between 30 and 40 wt %. The as-prepared dispersion was polymerized under the light radiation coming through the DLP projector. After that, the organic components were removed with shape retention by firing at 900 °C for 1 h, with a ramp rate of 2 °C/min, then, the whole 3D pre-fired structure was sintered at 1400 °C, for 4 h, with a 5 °C/min heating ramp rate.

2.3. Microstructural characterization

The morphology of the 3D structured samples in the green state and sintered were examined using a stereomicroscope Leica Zoom 2000 (Leica Microsystems Inc) and a scanning electron microscope (SEM) (model Jeol LTD, JSM-6300). For SEM studies, all samples were covered with a thin film of sputtered silver to avoid charging problems and to obtain better image definition.

2.4. Electrical characterization

For the conductivity measurements in a YSZ-based 3D microstructure, the sample were sintered at 1400 °C for 4 h with a heating ramp rate of 5 °C/min. The final thickness of the sample was about 175 μ m. Pt-paste (Metalor) electrodes were applied as current collectors on each side of the 3D sample and then fired at 900 °C for 30 min. The geometrical area was 0.196 cm². Impedance

spectra were obtained using a frequency response analyzer (Solartron 1260) under air, in the 0.1 Hz to 1 MHz frequency range with an *ac* signal of 100 mV. The spectra were acquired during the cooling processes between 900 and 600 °C, in 50 °C steps, with a dwell time of 0.5 h between consecutive measurements. The impedance spectra were analyzed with equivalent circuits using the ZView software (18) to study separately the bulk and grain-boundary contributions to the conductivity.

3. RESULTS AND DISCUSSION

Before setting the system for 3D printing of ceramic materials, a commercial 3D printer (MiiCraft) was tested to verify the resolution and reproducibility of details Figure 1(a,b,c).

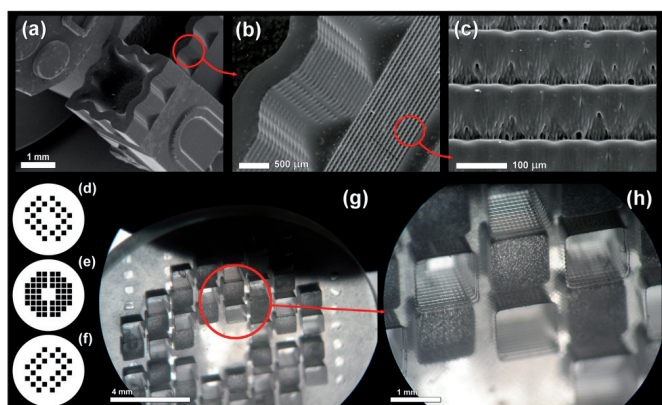


Figure 1. A commercial 3D printer (MiiCraft) was used to verify resolution and reproducibility of details. (a,b,c) complex details using a thickness layer of 100 µm were perfectly reproduced - curing time of 7 s per layer was used. (d,e,f) Digital masks sketched in PowerPoint, used for the fabrication of a special SOFC prototype. (g,h) 3D printed SOFC prototype with a photosensitive polymer.

Given that each sliced layer consists in a black and white image to be sent through the DLP-projector, simple PowerPoint slides Figure 1(d,e,f) were tested for the fabrication of complex structures. For example, for SOFC applications, before the 3D printing in ceramic materials, a prototype can be fabricated in an organic polymer to check the final dimensions, configuration of channels for the gas flows, extension of the geometrical area to increase the power produced, etc. Hence the use of the PowerPoint slides Figure 1(d,e,f) allow the successful fabrication of a 3D structure, in this case a prototype of a SOFC of about 1,5 cm of diameter, Figure 1(g,h), with square channels of 1x1x2 mm³ in both sides corresponding to the anode and cathode compartment. This type of configuration will theoretically allow increasing the geometrical area available for the electrochemical reactions by a factor of 9. The prototype was fabricated with just 20 layers of 100 µm.

For ceramic materials, the liquid monomer phase present in the ceramic dispersion, under the light irradiation, will act as an organic binder, holding the ceramic particles together forming a green ceramic sample. As the radiation will be partially blocked by the particles, the curing depth will be affected, consequently the curing times are longer, typically between 15 and 25 s and no inhibitor was used in all the ceramic-based samples. The black and white images used as sliced model layers, Figure 2(a), were perfectly reproduced in a ceramic based resin with 40 wt % of loading, Figure 2(b,c). This test of a single layer of the ceramic material in the green state is fired up to 1400 °C to remove the

organic material and sinter the YSZ grains together. As can be seen from the SEM images, Figure 2(d,e), the resolution is very good and the microstructure does not exhibit cracks or any other major faults. A magnified image, Figure 2(f), shows a very good contact between the grains keeping the average grain size in the range of 1 µm. The sample shows some porosity and if totally dense samples are required then, the loading of ceramic particles must be over 50 wt %, which in turn is similar to conventional ceramic forming processes (4).

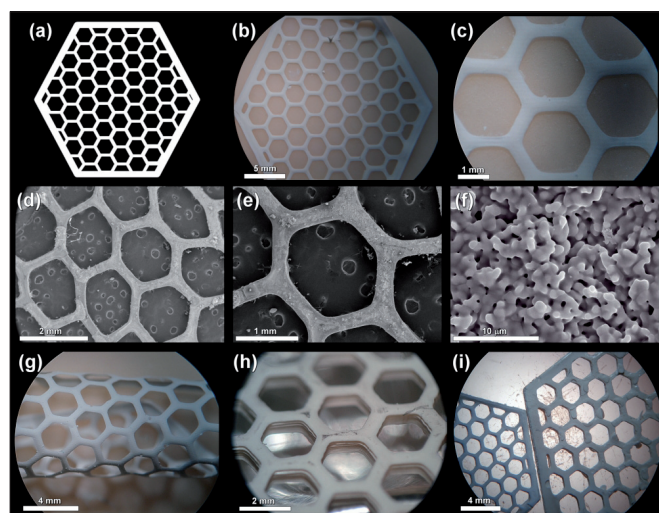


Figure 2. 3D printing of ceramic structures. (a) honeycomb-like model used as a digital mask. (b,c) 3D printed reproduction of the digital mask in the green state - YSZ loading was 40 wt %. (d,e,f) sintered 3D YSZ microstructure at 1400 °C for 4 h - (f) SEM image showing good connectivity between sintered YSZ grains. (g) 3D-printer ceramic samples remain flexible in the green state. (h) Several layers of YSZ were printed to produce a 3D microstructure that after sintering at 1400 °C (i) led to a reduction of about 30 % of the original size.

Another advantage of these 3D samples is that they remain very flexible, in the green state Figure 2(g), and hence they can be further processed before firing. For example, they can be rolled, bended, cut or they can be fixed with other layers, with the same or different morphology, prepared in a range of ceramic materials and be co-fired together, etc. The combination of several layers produces a 3D microstructure, Figure 2(h), which after sintering undergoes a 30 % of volume shrinkage without showing any evidence of cracking or microstructural collapse, Figure 2(i).

Using this procedure, any complex design can be carried out using specialized 3D software or just any simple image processing software to produce black and white images, Figure 3(a,b,c). As can be seen from Figure 3(d,e,f), the complex model represented in Figure 3(a) is reproduced with good quality, after sintering at 1400 °C. In this case just five layers were used, each of them with a final thickness of just 20 µm, Figure 3(f). The same can be applied for the model shown in Figure 3(b), 3D-printed Figure 3(g) and sintered in Figure 3(h).

Finally, thinking about SOFC applications, we tested the possibility to create a thin layer of YSZ, model shown in Figure 3(c). Such thin layer will separate both compartments (anode and cathode sides) and as the thickness should be less than 150 µm then a 300-500 µm layer of supporting anode or cathode is typically needed (19). In our case, we will try to fabricate the supporting layer also in YSZ but with a special configuration, Figure 3(a). The printed 3D structure, after sintering at 1400 °C shows an acceptable resolution, Figure 3(i).

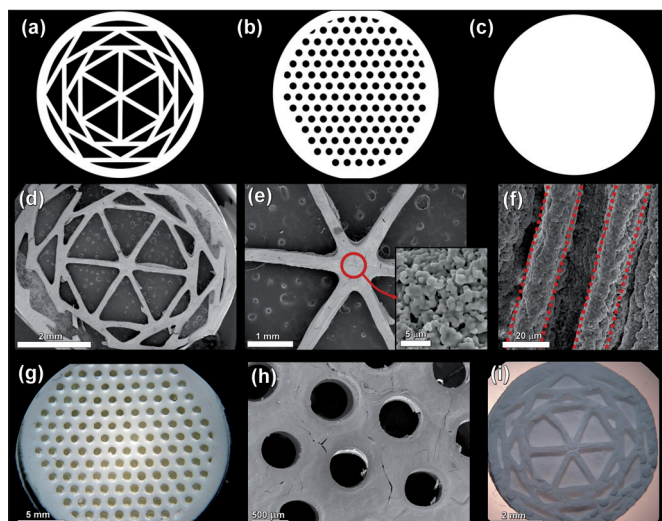


Figure 3. 3D printing of ceramic structures. (a,b,c) digital masks. (d,e,f) 3D reproduction of the digital mask (a), after sintering at 1400 °C for 4 h, 5 layers were printed. Sample broken, shown in (d), when attaching to the SEM sample support due to the very thin layers printed. (f) Each layer has a thickness of about 20 μm . (g) 3D reproduction of the digital mask (b) in the green state and (h) after sintering at 1400 °C for 4 h. (i) A new 3D microstructure printed in YSZ, after sintering at 1400 °C for 4 h, using the combination of digital masks (a) and (c).

TABLE 1. OVERALL CONDUCTIVITY OBTAINED FROM THE IMPEDANCE DIAGRAMS IN AIR, OF THE 3D SAMPLE SINTERED AT 1400 °C FOR 4 H.

T (°C)	1000/T (K ⁻¹)	$\sigma(\Omega^{-1}\text{cm}^{-1})$	ln (σ T)
900	0.852	0.058	4.212
850	0.890	0.053	4.093
800	0.932	0.048	3.935
750	0.977	0.040	3.720
700	1.028	0.030	3.395
650	1.083	0.021	2.959
600	1.145	0.011	2.293

Preliminary electrical characterization of this sample was performed in order to verify that the fabrication process itself would not affect the electrical properties of the material to be structured. The overall conductivity of the sample was obtained for each temperature, by complex impedance spectroscopy, between 600 and 900 °C, and the results are shown in Table 1. The spectra shows the typical behaviour of YSZ samples (20), one arc at high temperatures related to electrode processes and another arc showed when the temperatures are lower than 700 °C, associated with the grain boundary. The conductivities obtained are in good agreement with the typical results published for YSZ films (20), i.e. $\sim 0.05 \text{ S/cm}$ at 900 °C, confirming that the fabrication process does not modify the electrical properties of the 3D-structured material.

4. CONCLUSIONS

A simple 3D printing system comprising just 3 elements was assembled to produce 3D-microstructured ceramic-based materials with any type of complex design for the fabrication of SOFC components.

The prepared 3D samples are flexible in the green state allowing further processing. When sintered at 1400 °C for 4 h the

samples retain shape and resolution of details. Layers as thin as 20 μm have been replicated. Moreover, it has been shown that the fabrication process does not have any detrimental effect in the electrical properties of the structured material.

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