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# Design of industrially scalable microtubular solid oxide fuel cells based on an extruded support

H. Monzón<sup>a</sup>, M.A. Laguna-Bercero<sup>a,\*</sup>, A. Larrea<sup>a</sup>, B.I. Arias<sup>b</sup>, A. Várez<sup>b</sup>,  
B. Levenfeld<sup>b</sup>

<sup>a</sup> Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC – Universidad de Zaragoza, C/ María de Luna 3, E-50018 Zaragoza, Spain

<sup>b</sup> Dpto. Ciencia e Ingeniería de Materiales, Universidad Carlos III de Madrid, Avda. Universidad 30, 28911 Leganés, Spain

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## ABSTRACT

The current work describes the adaptation of an existing lab-scale cell production method for an anode supported microtubular solid oxide fuel cell to an industrially ready and easily scalable method using extruded supports. For this purpose, Ni–YSZ (yttria stabilized zirconia) anode is firstly manufactured by Powder Extrusion Moulding (PEM). Feedstock composition, extruding parameters and binder removal procedure are adapted to obtain the tubular supports. The final conditions for this process were: feedstock solid load of 65 vol%; a combination of solvent debinding in heptane and thermal debinding at 600 °C. Subsequently, the YSZ electrolyte layer is deposited by dip coating and the sintering parameters are optimized to achieve a dense layer at 1500 °C during 2 h. For the cathode, an LSM (lanthanum strontium manganite)–YSZ layer with an active area of ~1 cm<sup>2</sup> is deposited by dip coating. Finally, the electrochemical performance of the cell is measured using pure humidified hydrogen as fuel. The measured power density of the cell at 0.5 V was 0.7 W cm<sup>-2</sup> at 850 °C.

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## 1. Introduction

Fuel cells represent an efficient and clean way of transforming fuel into electric energy [1–3]. By avoiding the chemical-to-heat and heat-to-mechanical energy transformation steps, a high electric energy yield can be achieved. Solid oxide fuel cells (SOFC) are a type of fuel cell in which the electrolyte is an ion conducting ceramic oxide, commonly, yttria stabilized zirconia (YSZ). This material typically reaches an acceptable value of ionic conductivity at working temperatures between 600 and 1000 °C, being 800 °C probably the most extended

working temperature. These high operation temperatures grant fuel molecules enough energy for dissociation to occur in presence of low activity catalysts such as nickel, while lower temperature fuel cells generally need higher catalytic power, usually found in precious metals. Moreover, high temperature operation allows fuel reforming and thus enabling the use of hydrocarbon-based fuels. Fuel reforming can be external, taking advantage of the wasted heat, or internal on nickel in the anode.

Among the different configurations of SOFCs (planar, conventional tubular and micro-tubular), the microtubular configuration overcomes the drawback of the excessive

\* Corresponding author. Tel.: +34 876 555152; fax: +34 976 761957.

E-mail address: [malaguna@unizar.es](mailto:malaguna@unizar.es) (M.A. Laguna-Bercero).

heating and cooling time of the conventional solid oxide cells. The use of small (less than 4 mm) tubes as ceramic support enhances the mechanical strength and thermal shock resistance of the cell [4]. As a consequence, microtubular SOFCs are an excellent candidates for portable applications [5], and their development is only slightly behind the comparable SOFC status [6]. In addition microtubular SOFC can also be used for high temperature steam electrolysis [7,8].

Electrode composition and microstructure play a major role in SOFC electrochemical performance, and those parameters are usually conditioned or limited by the processing path. For this reason, fabrication methods are a major topic in microtubular SOFC research. These methods include cold isostatic pressing [9,10], slip casting [11], extrusion [12–14], gel casting [15], electro-phoretic deposition [16] and phase inversion co-extrusion [17] amongst others. Some features are desired on every production method such as reproducibility, geometrical quality and scalability amongst others. These standards are frequently not met by lab-scale methods and, in some cases, the lack of them can become performance limiting in the resultant cell. Among the aforementioned methods, extrusion is the most promising one for massive substrate production because of its low-cost and well-established technologies. The problems associated with extrusion are mainly related to the binder removal and firing processes. They include lack of straightness, defects in the walls, eccentric shapes, warped and twisted tubes as well as bubble formation [6]. It is also worth mentioning that there is a lack of information in the scientific literature regarding the technical details on the extrusion procedure for microtubular SOFCs.

The current work describes the adaptation of an existing lab-scale cell production method [18] to an industrially ready and easily scalable method using extruded supports. Anode support optimization was carried out via cold isostatic pressing (CIP) on previous works [4,8,19]. Based on these previous studies, the selected final composition for the anode support is: 50% porosity, 25% nickel and 25% YSZ in volume. In the present work, the use of corn starch as pore former is reported in a ceramic powder extrusion process for the first time, producing spherical pores (diameter about 10  $\mu\text{m}$ ). The whole cell fabrication route selected on this study consists of an extruded anode support, whereas both electrolyte and cathode are deposited by dip coating. The new process has numerous advantages such as an increase in the production capacity, in reproducibility and also in the mechanical properties of the green body, which facilitates handling and later processing steps.

## 2. Materials and methods

### 2.1. Anode compounding and extrusion

For the extrusion process, a powder formulation based on NiO (Hart Materials), YSZ (Tosoh) and corn starch as pore former in a composition based on previous studies [4]. Final composition of the anode support is Ni–YSZ ratio of 50:50 (% in volume of solid phase), with porosities near 50%. The binder system consists of polypropylene (supplied by Repsol YPF), paraffin

wax (Panreac) and stearic acid (Panreac). A similar binder system was previously used for manufacturing of YSZ thin tubes [20]. Four powder mixtures were formulated containing 45, 55, 60 and 65 vol% solid loading. Firstly, different feedstock formulations were compounded in a Haake Rheocord 252 mixer with a pair of roller rotor blades at 170 °C and 40 rpm. During the mixing process, the torque values were recorded. In order to determine the optimal feedstock formulation, the rheological characterization was performed in a Thermo-Haake capilar rheometer at 170 °C covering a shear rate from 100 to 10,000  $\text{s}^{-1}$ .

Subsequently, the tubes were extruded using a single screw extruder (Haake Polylab) with a home-designed extrusion die connected to the extruder [20]. Screw speed and temperature profile were tuned in order to obtain an extruded body able to sustain its own weight as well as to avoid deformation before cooling. Extrusion was made vertically into a water bath to reduce the solidification time. A combination of solvent and thermal debinding process was carried out to remove the organic part. Solvent debinding step was then applied to the samples consisting on an n-heptane bath at 60 °C overnight. Thermogravimetric analysis (TGA) was performed under air atmosphere using a Perkin Elmer TGA1 thermogravimetric analyser. Thermal debinding cycle consisted on a heating ramp at 1 °C  $\text{min}^{-1}$  up to 600 °C.

### 2.2. Electrolyte deposition

A dilatometry test was run on a solvent debound sample in order to determine its sintering behaviour using a thermo-mechanical analyser (Setaram, SETSYS 200, France). The same test was run on TZ-8Y and TZ-8YS powders (Tosoh), to be used as the solid electrolyte. Both powders are 8 mol%  $\text{Y}_2\text{O}_3$  in  $\text{ZrO}_2$  (99.9%), presenting average crystallite sizes of 23 and 52 nm respectively.

A suspension was prepared with TZ-8YS powders in an isopropanol–ethanol azeotropic mixture, using PVB (polyvinyl butyral) as binder and Beycostat as dispersant agent. Solvent debound anode support samples were cut into 6.75 cm (in length) samples and dipped 3 times at a drawing rate of 3  $\text{mm s}^{-1}$ . A 5 mm long section was left uncovered on each side of the support to facilitate the later anode electrical contact and sealing. Samples were then sintered at different temperatures (from 1350 to 1600 °C) in order adjust the sintering conditions.

### 2.3. Cathode deposition

After adjusting the sintering conditions for anode-electrolyte half cells, the LSM–YSZ cathodes were deposited. For this purpose, two cathode suspensions were prepared, the first one using a 1:1 (vol%) ratio of LSM (Fuel cell materials) and TZ-8YS (Tosoh), acting as the functional layer, and a second one using a 4:1 ratio of the same materials to enhance current collection. For both suspensions, the dispersing medium and additives were identical to that of the electrolyte suspension. An active area of  $\sim 1 \text{ cm}^2$  of cathode was deposited on each cell, consisting of 2 dips of the 1:1 suspension and 2 dips of the 4:1 suspension, at a 3  $\text{mm s}^{-1}$  drawing rate. Once cathode had been deposited, the cells were sintered at 1150 °C for 90 min.

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