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Microtubular SOFC based on an extruded support

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Abstract

In this work the processing route for an anode supported microtubular solid oxide fuel cell is adjusted. The fuel cell composition and microstructure design is based on previous work. In this work we have developed microtubular cells based on an extruded support. Firstly, Ni-YSZ anode was manufactured by Powder Extrusion Moulding (PEM). Feedstock composition and extruding parameters were adjusted to obtain tubular green bodies. An YSZ layer was then deposited as the electrolyte and the sintering parameters were optimized to obtain a dense layer. An active area of ~1 cm^2 LSM-YSZ was deposited as the cathode and its electrochemical performance was measured using pure hydrogen as fuel, yielding a power output at 0.5V of 0.7Wcm^{-2} at 850^{0}C.

Keywords: *SOFC, Powder Extrusion Moulding, Microtubular*

1 Introduction

Fuel cells represent an efficient and clean way of transforming fuel into electric energy. 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 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^{0}C, being 800^{0}C probably the most extended working temperature. This 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. [1]

Composition and microstructure play a major role in SOFC electrochemical performance, and even once these parameters have been optimized, they are usually conditioned by the processing path. For this reason, some effort must be made in order to adapt an existing lab-scale production method to an easily scalable method such as extrusion. The present work describes the optimization of the processing path of anode supported microtubular cells, based on the design of previous works. Optimized anode has 50% porosity, 25% nickel and 25% YSZ in volume. The used pore former was corn starch, which produces spherical pores (diameter about 10 μm). The lab-scale production method consisted of a isostatically pressed NiO-YSZ anode support, then a spray coated thin YSZ electrolyte and a dip coated cathode, process details are described elsewhere [2]. The process selected on this work is based on an extruded anode support, and 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 in mechanical properties of the green body, which facilitates handling and later processing steps.

2 Experimental

2.1 Anode compounding and extrusion

For the extrusion process we have used a previoulsly optimized powder formulation based on NiO, YSZ and pore-former. The binder system consists of polypropylene, paraffin wax and stearic acid. A similar binder system was previously used for manufacturing of YSZ thin tubes [3]. Four powder mixtures were formulated containing 45, 55, 60 and 65 vol% solid loading. Firstly feedstocks were compounded in a Haake Rheocord 252 mixer with a pair of roller rotor blades at 170ºC and 40 rpm. During mixing process torque values were recorded. Constant values of torque indicate a uniform mixture. On the basis of feedstock rheological properties optimal formulation was selected to act as support for microtubular SOFC. Rheological characterization was performed in a ThermoHaake capilar rheometer at 170^{0}C covering a shear rate from 100 to 10,000s^{-1}.

After selecting the optimal mixture, tubes were extruded using a single screw extruder (Haake Polylab) with a home-designed extrusion die connected to the extruder. Screw speed and temperature profile were tuned in order to obtain an extrud-

ed body able to sustain its own weight and avoid deformation before cooling. Extrusion was made vertically into a water bath to minimize the solidification time. A combination of solvent and thermal debinding process was carried out to remove organic part. Solvent debinding step was then applied to the samples consisting on an n-heptane bath at 60^0C overnight. A TG experiment was run on a sample which had undergone this treatment on an air atmosphere. Thermal cycle consisted on a heating ramp at 1ºC/min up to 600ºC.

2.2 Electrolyte deposition

A dilatometry test was run on a solvent debinded sample in order to determine its sintering behavior on a thermomechanical analyzer (Setaram, SETSYS 200, France). The same test was run on TZP-8Y and TZP-8YS powders (Tosoh Japan), to use as solid electrolyte. Both two powders are 8% mole Y_2O_3 in ZrO_2 (99.9%), but the first one has a finer particle size.

A suspension was prepared with TZP-8YS powders in an isopropanol - ethanol mixture, using PVB (polyvinyl butyral) as binder and Beycostat as dispersant agent. Solvent debinded anode support samples were cut into 6.75 cm samples and dipped 3 times at a drawing rate of 3 mms^{-1}. A 5 mm long section was left uncovered on each side of the support for easiness on the later anode electrical contact. Five samples were then fired at different temperatures 1350, 1400, 1450, 1500 and 1600^0C in order adjust sintering conditions.

2.3 Cathode deposition

Samples resulting in a crack free electrolyte were then deposited an LSM-YSZ cathode for electrochemical testing. For this purpose two cathode suspensions were prepared, one using a 1:1 (%vol) ratio of LSM (Fuel cell materials) and TZP-8YS (Tosoh Japan) 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 the same that in the electrolyte suspension. An active area of ~1 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 mms^{-1} drawing rate. Once cathode had been deposited, the cells were sintered at 1150ºC for 90 min.

2.4 Electrochemical characterization

Electrical contact was made using platinum wire in a four probe setup. Anode contact was made through the uncovered edges and in the cathode by coiling the wire around the deposited section. Pt paste was added to improve electrical contact. Then the cells were sealed to alumina tubes using refractory clay. The cell was placed inside a house made small tubular furnace. Nitrogen was fed to the anode side of the cell during the heating process, at a heating rate of 20^0Cmin^{-1}. Once at 800^0C pure hydrogen was fed to the cell, reducing the anode. Cathode side was open to the atmosphere. j-V and EIS measurements were performed using a VSP Potentiostat/Galvanostat (Princeton Applied Research, Oak Ridge, US).

3 Results and discussion

3.1 Powder extrusion moulding of Ni-YSZ microtubes

As final ceramic microstructure and composition had been optimized in previous work, we have used the same powder formulation and we have prepared different feedstock with different solid powder loading (45, 55, 60 and 65 vol. %). Considering that powder presents pore former and NiO reduction increases the porosity of the compact, we have optimized the feedstock on the basis of a maximum solid loading with appropriated rheological characteristics. This allows us to minimize problems associated with binder removal and shrinkage during densification and to obtain defect-free shapes. Torque measurements showed that all feedstock prepared presented good homogeneity and appropriated torque values.

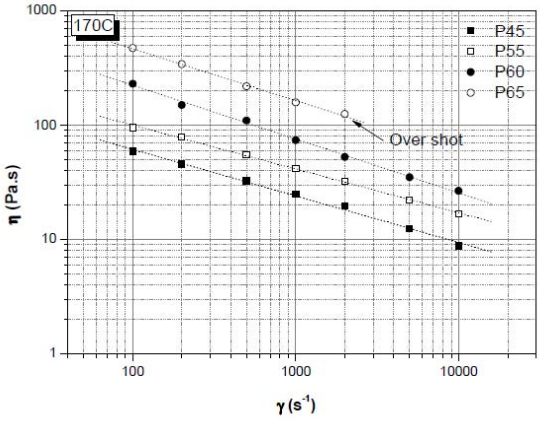


Fig. 1. Viscosity measurements for the tested feedstocks.

All the prepared feedstock presented a thermoplastic behaviour (Fig. 1), which is the most suitable for extrusion process.The viscosity increase with the powder loading, however the reached values were less than 1000 Pa.s which is the desireble for extrusion process.Therefore,feedstock with 65 vol. % of powder loading was determined as optimal.

Figure 2 shows different extruded tubes using feedstock with 55 vol. % of power loading. The dimensions of the tubes were 4 mm outer diameter, around 1 mm wall thickness and 12 cm of length. The extrusion parameters were optimized in order to obtain a homogeneous extrusion profile.

After extrusion process the elimination of polymeric part was carried out. Firstly a conventional thermal debinding was tested. However, blistering occurred in all the samples, even by using very low heating rate. This is a consequence of the violent removal of the most volatile components of the binder system (PW and SA). In order to prevent the presence of these defects a combination of solvent and thermal debinding was carried out. After removal an interconnected pore channel is formed from exterior to interior, which serves as escape path for decomposed gas during subsequent thermal debinding of insoluble binder components.

TGA experiments performed on a solvent debinded sample show two peaks attributable to the elimination of PP, beginning at 177ºC, and corn starch beginning at 240ºC (figure 2). Most of the stearic acid and paraffin wax are previously removed during the solvent debinding step. TGA experiment also shows that organic removal takes place up to approximately 500ºC. Consequently, thermal cycle was programmed to keep at 600ºC for 1h to assure a complete degradation of organic components. Equally, a heating rate of 1ºC/min was used in order to prevent surface cracks and internal bubbles.

3.2 Electrolyte cosintering

Attending to the contraction curve of the YSZ ceramic powders of two tested particle sizes (figure 3), the coarser powder was selected; as it fits better the anode support contraction curve. Samples sintered at 1350 and 1400ºC showed cracking and pinholes respectively, displaying a contraction mismatch between support and thin electrolyte.

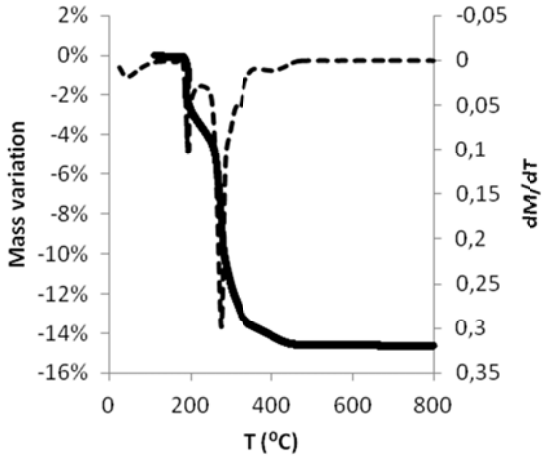


Fig. 2. TG after solvent debinding.

Samples sintered at 1450 and 1500ºC had a smooth uniform appearance. Sample sintered at 1600ºC showed a perfectly smooth and transparent electrolyte, but the cell had bent during sintering and the used crucible showed massive contamination after the process, evidencing a material loss and possible microstructure degradation.

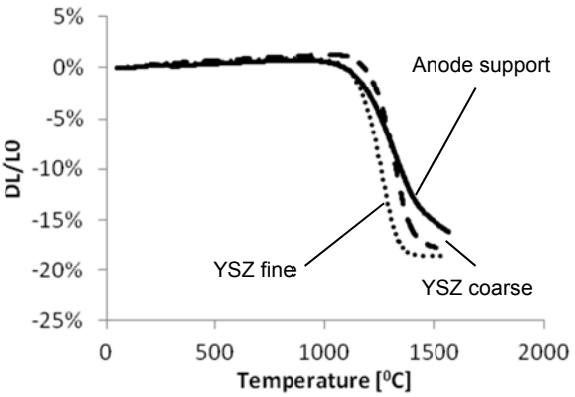
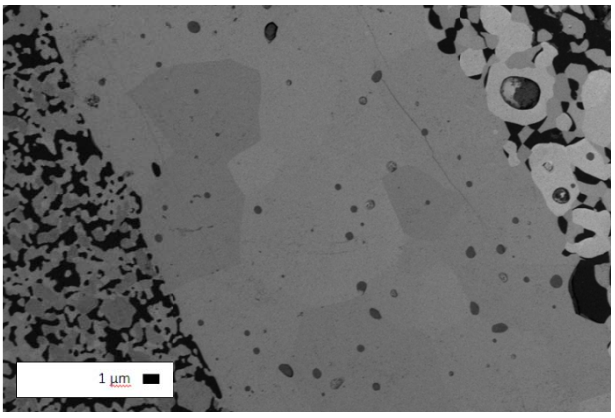


Fig. 3. Contraction curves for extruded material and the proposed electrolyte materials.

Samples sintered at 1450 and 1500ºC were selected and an electrolyte cross section was observed using a Merlin FE-SEM (Carl Zeiss). Figure 4 shows that both samples have some amount of closed porosity, being the overall amount of porosity observed greater for the sample sintered at 1450ºC. Both samples show electrolyte thickness around 22 µm. Additionally the sample sintered at 1450ºC shows zones where sintering happened to a lower extent, probably hindered by internal strain.

3.3 Electrochemical performance

Produced cells were measured at 800 and 850ºC, results of the j-V curves are shown on figure 6. Sample sintered at 1450ºC is clearly outperformed by the one sintered at 1500ºC, power output values at 0.5V and 850ºC are 0.35 and 0.7 Wcm^{-2} respectively (figure 5). EIS measurements reveal a greater ohmic resistance in the sample sintered at 1450ºC, produced by the poor electrolyte sintering.



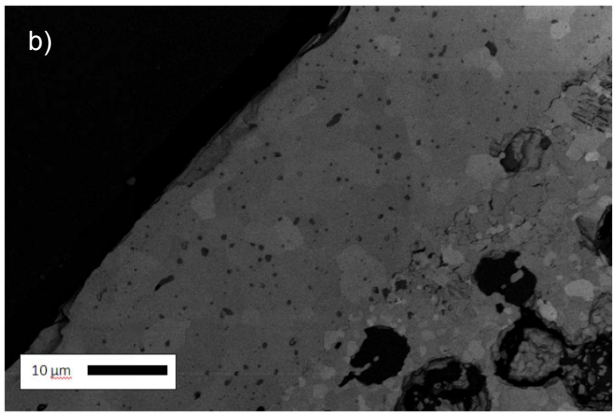


Fig. 4. Electrolyte detail for sample sintered at 1500ºC (a) and 1450ºC (b).

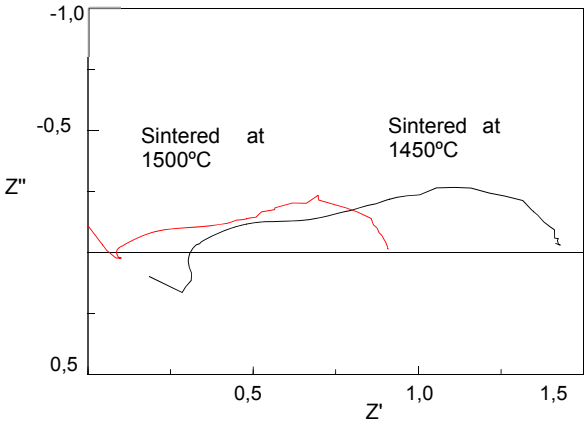


Fig. 5. EIS measurements at 850^{0}C.

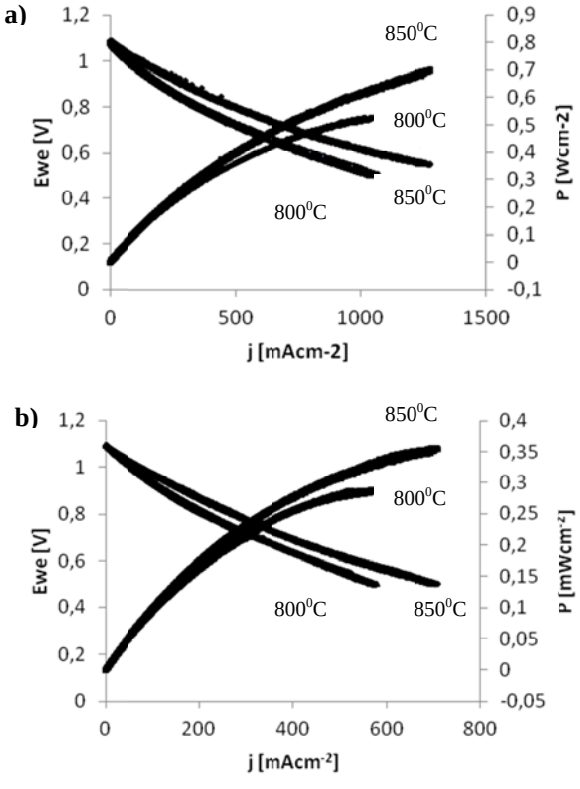


Fig. 6. j-V measurements por the sample sintered at 1500ºC (a) and 1450ºC (b).

4 Conclusions

Powder extrusion moulding was presented in this work as an advantageous technology to obtain a Ni-YSZ porous anode. The production method adaptation has been successful, resulting in a much less time consuming production process, which can be easily scaled up to an industrial production level. Handling of the green bodies has also been significantly improved from the CIP method. A presintering step is no longer needed, as the electrolyte is dipped directly over the solvent debinded body. When using the CIP method the green body is not able to withstand any kind of wetting before sintering. The new method includes then a sintering step less, not only making the method simpler, but also less energy is consumed. Additionally section uniformity has been significantly increased, increasing reproducibility. The j-V and EIS obtained values are similar to state of the art YSZ based SOFC.

5 Acknowledgements

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