Anode Supported Microtubular Solid Oxide Fuel Cells running on Methane

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1 Introduction

Solid Oxide Fuel Cells (SOFCs) are electrochemical devices that convert directly the chemical energy of reactants into electrical energy at high temperature 600-1000ºC [1, 2]. Since the high temperature reduces the electrical losses, those systems have the highest efficiency for fuel cells. In addition to their high efficiency, at this days SOFC are arising as promising systems for power generation because of their ability to cover the electrical demand in a broad range of power densities; from few watts (small units, for portable applications) to several hundreds KiloWatts (big units, for stationary applications) [3, 4]. For both types of applications, SOFCs systems have the great advantage of carring out the internal steam reforming in the fuel chamber when the system is feeded with fuels as Natural Gas, Liquid Petroleum Gases LPGs, methane or alcohols among others [5-7].

At these days there is an increasing interest in microtubular SOFC´s because of the improved advantages such as: higher mechanical and thermal stability, simpler seal requirements, higher power densities per volume unit and shorter times to start-up and shut-down when we compared with planar and tubular conventional designs [8, 9].

The steam reforming reactions that take place into the cells when operating with hydrocarbons are as follows [1, 10, 11]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (1)\ SR$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)\ WGS$$

The Steam Reforming reaction [(1) SR] is highly endothermic whereas the Water Gas Shift reaction [(2) WGS] is slightly exothermic, which means that energy must be supplied to reach the total reaction.

During the operation with the internal reforming of hydrocarbons one of the mayor issues for SOFC is the deposition of elemental carbon. The carbon may be formed by the methane cracking reactions:

$$CH_4 \rightarrow C + 2H_2 \qquad (3)$$
$$2CO \rightarrow C + CO_2 \qquad (4)$$

When the SOFCs are feeded with hydrocarbons is necessary reducing the C_{2+} quantity from fuel gas inlet in order to minimize the carbon deposition. The carbon deposition reduces the efficiency and the lifetime of the cells and stacks and also increases the issues related to redox stability and to presence of thermal and mechanical stresses. This Carbon deposition is dependent of the temperature (increases with temperature) and is also dependent of the Steam/Carbon ratio (S/C). Some papers reported that in order to minimize the carbon formation in the anode catalyst S/C ≥ 1.5 is needed [12-14].

Steam reforming reaction consumes energy but the electrochemical reactions produce energy. Since steam reforming is fastest, the result is the cooling at the fuel inlet and the heating at the fuel outlet. We can conclude that the use of high S/C ratios minimizes the carbon deposition but in contrast the thermal gradients across the cells and stacks are increased.

In this work we have studied the performance of microtubular cells running on methane as fuel. The cells consist on Niquel-Yttria Stabilized Zirconia (Ni-YSZ) microtubular supports with Ytria Stabilized Zirconia (YSZ) as the electrolyte and Lanthanum Strontium Manganite and Ytria Stabilized Zirconia (LSM-YSZ) as the cathode.

2 Experimental

The compositions for the supporting cermet tubes were Ni-YSZ (50 vol% Ni and 50 vol% YSZ). The anode tube dimensions were 12-15 cm length, 400 μm wall thickness and 2.4 mm internal diameter. A 8YSZ electrolyte of 15-20 μm and a LSM-YSZ cathode composite of 50μm were

sequentially deposited on these tubes. The manufacture of the cells was carried out using commercial products: NiO (Aldrich), YSZ (Tosoh), platinum paste (Engelhard 6082A) and LSM-YSZ (Fuel Cell Materials).

In previous works we studied the optimisation of the anode fabrication parameters of YSZ based cells for better gas diffusivity, electrical conductivity and electrochemical performance [15, 16] using H_2 as fuel. Here we have performed the same analysis feeding the cells with methane.

The tubes were manufactured by the following procedure [15, 16]. The commercial NiO powder was conditioned with attrition milling (2-propanol), and mixed in acetone with YSZ and pore generator to achieve porosities up to 40%. The dried precursor powder was used to fabricate the supporting tubes by isostatic pressing at 200MPa. Typically, microtubular supports are prepared by extrusion [17, 18] but in this case the tubes were obtained by cold isostatic pressing (CIP), which makes it possible to alter the anode components easily. The 8YSZ electrolyte layer was deposited by spray coating controlling the thickness by weight measurement. The electrolyte film and the supporting anode were co-sintered at 1400 ºC in air. LSM-YSZ composite cathode layer was deposited by dip coating and then sintered at 1050ºC while the Pt cathode current collector layer was brush painted, and sintered at 850ºC. In all cases an active area of ≈1cm^2 corresponding to about 10 mm tube length was covered with cathode and current colector. In figure 1 we show the appearance of the tubes at each fabrication stage.

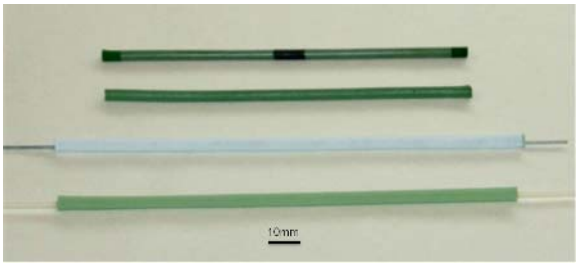

Figure 1. Aspect of the tubes at each stage of the fabrication process.

The electrochemical performance of the cells was measured using four Pt wires, two attached to each electrode to avoid the wire contribution to the overall resistance. The electrochemical test was performed in the 650-850ºC temperature range using two kinds of fuels, pure 97% H_2 and 97% CH_4 mixtures containing 3% H_2O as fuel and stagnant air as oxidizing agent. I-V curves were obtained using an electronic load housing (Department of Scientific Instrumentation, University of La Laguna).

3 Results and discussion

Figure 2 shows the polarization curves measured at the 650-850ºC temperature range with 97% H_2–3% H_2O as fuel gas. The curves were obtained using heating system housing which allows us to minimize the problems associated with the sealing of the anode and cathode chambers. The description of this system can be found in [15].

The Open Circuit Potential (OCP) values, represented in Figure 2 are very close to those predicted by the Nernst equation 1.13-1.09V for 650-850ºC temperature range. These OCP values indicate that the YSZ electrolyte film is tight to gas leaks through all the cells length. The obtained power density values vary from 800mW·cm^{-2} at 850ºC to 200 mW·cm^{-2} at 650ºC. While the Area Specific Resistance values (ASR) vary from 1.83 Ω·cm^2 at 650ºC to 0.35 Ω·cm^2 at 850ºC.

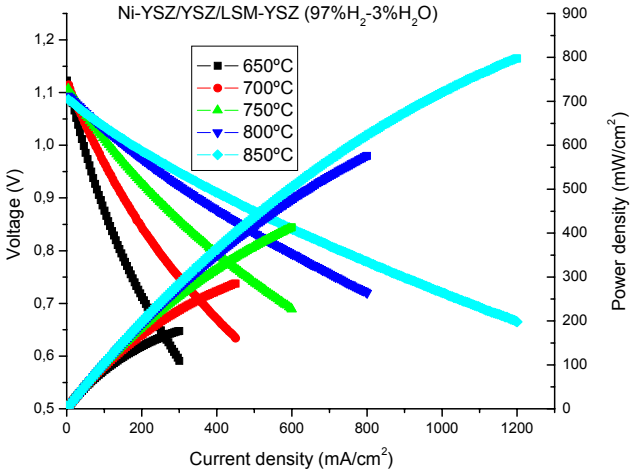

Figure 2. Polarization curves using 97%H_2-3%H_2O as fuel in the anode and stagnant air in the cathode.

In figure 3 we show the polarization curves obtained when we feed the same cells with 97%CH_4-3%H_2O in the Ni-YSZ anode and stagnant air in the LSM-YSZ cathode. In this case we can observe some differences in the OCP values. For higher temperatures (850 and 800ºC) which were firstly measured voltage values are in good agreement with the Nernst equation predictions. However, for the subsequent measurements (750 and 700ºC) the OCP values are lower than those predicted by the Nernst equation. This fast degradation could be explained by the rapid oxidation that takes place in those cells when operating under internal reforming conditions [19].

The obtained power density values operating with methane mixture vary from more than 800mW·cm^{-2} at 850ºC to values over 550 mW·cm^{-2} at 800 and at 0.65V. The calculated Area Specific Resistance values (ASR) vary from 0.76 Ω·cm^2 at 800ºC to 0.37 Ω·cm^2 at 850ºC. As observed from Figures 2 and 3, the obtained power densities using methane the obtained power densities are similar to that obtained when feeding

the same type of cells with humidified hydrogen. However, a rapid degradation of the cell performance was observed, which is originated by carbon deposition in the anode when the cells are operated with methane.

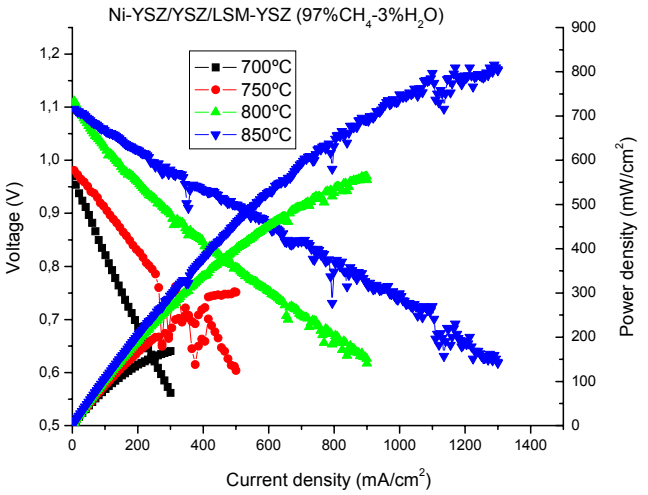

Figure 3. Polarization curves using 97%CH_4-3%H_2O as fuel in the anode and stagnant air in the cathode.

4 Conclusions

The performance of YSZ based microtubular fuel cell has been analysed. Ni-YSZ/YSZ/LSM-YSZ cells have shown a very good performance at 850ºC under methane operation, of about 800mW·cm^{-2} at 0.65V. However, the resistance to internal reforming conditions of these cells is still limited, associated to the rapid deposition of carbon in the Ni-YSZ anode. In order to avoid problem fact high S/C ratios are needed. However, the use of high S/C ratios also enhances the thermal stress of the cells increasing the possibility of tube break. As consecuence the portable testing systems must be improved in order to minimize the temperature gradients along the cells. Another possibility to improve the stability of microtubular cells under internal reforming conditions could be the modification of the anode composition by replacing a small part of the metalic Nickel by metallic Copper as it has been recently reported that the steam reforming rate is reduced without significant reduction in electrochemical performance [20]. Work in that subjet is in progress.

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