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Performance and long term degradation of 7 W micro-tubular solid oxide fuel cells for portable applications

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HIGHLIGHTS

- Microstructural characterization of a large area micro-tubular SOFC.
- Galvanostatic and cycling long-term degradation of mt-SOFC.
- Large area mt-SOFC with a 7 W of total power extracted from a single cell.
- Detailed electrochemical (I–V and EIS analysis) at operation conditions.
- Real portable application for mt-SOFC at 700 °C.

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ABSTRACT

Micro-tubular SOFCs have shown an astonishing thermal shock resistance, many orders of magnitude larger than planar SOFCs, opening the possibility of being used in portable applications. However, only few studies have been devoted to study the degradation of large-area micro-tubular SOFCs. This work presents microstructural, electrochemical and long term degradation studies of single micro-tubular cells fabricated by high shear extrusion, operating in the intermediate range of temperatures (T~700 °C). A maximum power of 7 W per cell has been measured in a wide range of fuel utilizations between 10% and 60% at 700 °C. A degradation rate of 360 mW/1000 h (8%) has been observed for cells operated over more than 1500 h under fuel utilizations of 40%. Higher fuel utilizations lead to strong degradations associated to nickel oxidation/reduction processes. Quick thermal cycling with heating ramp rates of 30 °C /min yielded degradation rates of 440 mW/100 cycles (9%). These reasonable values of degradation under continuous and thermal cycling operation approach the requirements for many portable applications including auxiliary power units or consumer electronics opening this typically forbidden market to the SOFC technology.

1. Introduction

Auxiliary power units (APUs) for portable applications are promising early markets for fuel cell technologies. In particular, fuel cell based APUs are being considered for recreational vehicles, trucks, boats or unmanned aerial vehicles due to their high efficiency, lightweight and high volumetric power density. However, despite solid oxide fuel cells (SOFCs) being the most efficient and fuel flexible among the different types of fuel cells, portable applications have been classically out of the SOFC market mainly due to their poor thermal shock resistance, i.e. slow start-up [1,2]. Recent progress in SOFC technology has clearly shown that this major issue can be addressed by the implementation of alternative geometries based on tubular or thin film configurations [3,4]. Tubular SOFCs show a high thermal shock resistance especially when the diameter is reduced down to the millimeter scale [5]. Kendall et al. recently proved that scaling down the tube diameter below 2 mm potentially reduces the start-up time to less than 1 min and that a 6 mm-diameter micro tubular SOFC (MT-SOFC) does not limit the start-up time with the current Balance of Plant (BoP) [6].

Although electrolyte-supported tubular SOFCs based on well-known electrolytes like yttria stabilized zirconia (YSZ) are probably the best choice in terms of thermomechanical stability [7–11],

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the presence of a thick electrolyte forces the operation of the cell at high temperatures, usually above 800 °C. Operation at high temperatures increases the time and energy consumption during the start-up and accelerates degradation and aging phenomena. However, reducing the temperature below 700 °C greatly limits the fuel flexibility of the system since the existing reforming technologies properly operate above this value [12,13]. Therefore, the upper part of the intermediate range of temperatures (T~700–800 °C) is the most interesting for SOFCs. This range can be covered with anode-supported cells based on few micrometers-thick YSZ electrolytes [10] and mixed ionic-electronic conductor (MIEC) cathodes. A large number of MIEC cathode materials, mainly based on perovskite-type oxides, have been proposed in the last decades to substitute the conventional LSM for intermediate temperature SOFCs (IT-SOFCs) [14]. Among other, lanthanum strontium cobalt ferrite (LSCF) has been highlighted as a good cathode candidate due to its high performance in the IT-range [15,16]. However, due to the incompatibility of YSZ with most of the promising cathode materials for intermediate temperatures, including LSCF, this combination usually requires the implementation of diffusion barrier layers to avoid the formation of insulation phases like $La_2Zr_2O_7$ or $SrZrO_3$ in the electrolyte–electrode interface [17–19]. The quality of this barrier layer becomes essential for the performance of the final device and has been recently matter of comprehensive studies [20]. A thin film dense layer of another compatible electrolyte usually plays this barrier layer role. The most extended choice is doped ceria, e.g. samaria doped ceria (SDC), due to its good oxide-ionic conductivity and excellent chemical compatibility with LSCF. However, recent studies show reactivity of doped ceria and stabilized zirconia at temperatures as low as 1200 °C [21,22] leading to deleterious effects on the SOFC performances. High-enough density must be ensured while avoiding reactivity with the YSZ-electrolyte, this requires fine tuning during the diffusion barrier deposition.

Probably the major goal of the SOFC community in the last years is increasing the durability of the devices operating in real conditions. Although degradation issues have been widely described in numerous scientific publications [23,24], each particular configuration and system has to be analyzed under operating conditions in order to determine the main source of degradation and aging mechanism. Only a few studies have been devoted to analyzing the long term degradation of MT-SOFCs [25–27], even less when considering large-area and high power cells [28].

Several problems of micro-tubular SOFC are still an issue for the final application. The most common degradation phenomenon in micro tubular SOFC is the generation of thermal gradients promoted by the cell operation. When the reaction occurs on the TPB a large amount of thermal energy is released. Only the homogeneity in the TPB density, fuel flow and current collection among the whole tube can avoid the thermal stresses which are able to degrade the cell [8,29]. Small active areas and simple cell geometries make it easier to prevent these inhomogeneities but it is difficult to attain in large area tubular cells. Thermal gradient can be ascribed as the cause of most of the typical degradation process, all of them related to the changes in material volume, microstructure or compositional distribution. Another common degradation issue is the cell layers mismatch, observed when the coefficients of thermal expansion (CTE) of the different materials of the cell are different. The mismatch becomes a major issue during the heating and cooling ramps of the cell, which can occur constantly during portable application, thus causing degradation [25] as experimentally studied and discussed in the present work. The mismatch under thermal cyclic operation can lead to a layer decohesion of the cell causing a dramatic failure of the cell performance.

Another typical problem of the SOFC is Ni coarsening [23,30,31] due to the high mobility of the Ni particles at elevated temperatures and the inhomogeneity on the reduction atmosphere on the anodic chamber. Ni reoxidation can also be related to the water accumulation generated on the TPB. Such water cannot be completely removed from the anode microstructure. In this sense, the redox cycling of the cells is one of the most aggressive degradative processes of the cells. Coupled with redox cycles, fuel utilization has been reported as one of the key factors in cell degradation conditions. Small changes in the percentage of used fuel can have a significant impact on the cell durability [32–34] due to the anode oxidation at high fuel utilizations [35].

When hydrocarbons are used as a fuel [5,25,36], carbon deposition, sulfur poisoning of the anode, due to the sulfur traces of the fuel, and chromium poisoning of the cathode due to the use of steel interconnectors, are other common degradation process of the SOFC systems [5,23].

In the present work, a comprehensive structural and electrochemical characterization of anode-supported MT-SOFCs based on the LSCF/SDC/YSZ/Ni-YSZ configuration is presented. Micro-tubular SOFCs have been tested under stationary working conditions and thermal cycling. Electrochemical Complex Impedance Spectroscopy (EIS) was used in order to decouple the different contributions to the total cell resistance observed in long-term degradations. An aging mechanism is proposed to allow improvement of the next generation devices.

2. Experimental methods

Micro-tubular solid oxide fuel cells employed in this work are supported on Ni-YSZ cermet anode tubes fabricated by high shear extrusion with 5.5 mm of internal diameter and 550 μm in thickness (Fig. 1). A 15 μm-thick YSZ layer covered by a 2 μm-thick SDC film works respectively as electrolyte and diffusion barrier. A 25 μm-thick porous LSCF layer is employed in this work as a MIEC cathode. On the top of the cathode, a homogeneous thick layer of silver is painted to work as a current collector. The total length of the tube is 150 mm, while the active area is reduced to a lateral size of 95 mm. Since the anode tube presents an external diameter of 6.6 mm, a total active area of 19.7 cm^2 should be considered. Top view and cross section images of micro-tubular cells have been obtained by means of a Zeiss Auriga Scanning Electron Microscope provided with Back Scattering Electrons (BSE) and Energy-dispersive X-ray (EDX) detectors.

Fuel cell performance and electrochemical measurements have been carried out in a home-made test station. The test station consists of a furnace box, a gas mixing stage and ac/dc electrical characterization equipment. A gas mixing stage consisting of different El-Flow Bronkhorst mass flow controllers allow control of the H_2 and Ar mixture introduced in the anode side (the cathode operates under open air conditions because convection is sufficient to provide the cathode oxygen). The gas mixture can be controlled to cover the whole range of fuel utilizations keeping a constant total flow of 200 ml/min. For the electrical characterization, a Kepco KLP power source connected in series with a TrueData electronic load is employed to control the applied current in the whole range of operation. A Solartron 1260 impedance analyzer is used for the electrochemical measurements. This configuration allows measurement of I–V galvanostatic curves from OCV to more than 20 A and acquiring Electrochemical Impedance Spectra (EIS) at any applied current from 0 to 20 A.

A specially designed metallic hardware with gas and electrical connections is used as a holder for the tubular cells. The MT-SOFCs are properly sealed by a compressed alumina ceramic felt. Small clamping forces are enough to ensure a proper sealing due to the high pressure applied by the small areas of the cross-sections of the tubes. This especially designed sample holder also allows a control