



Understanding longitudinal degradation mechanisms of large-area micro-tubular solid oxide fuel cells

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ABSTRACT

The degradation mechanism of micro-tubular Solid oxide fuel cells (mSOFC) has been studied as a function of the fuel utilization (FU from 40 to 80%) along the tube (inlet, center and outlet). La_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O₃/Sm_{0.2}Ce_{0.8}O₂/8YSZ/Ni-YSZ pristine cells undergone to different galvanostatic tests were carefully characterized by Raman spectroscopy as well as scanning electron microscopy and energy dispersive X-ray spectroscopy analyses. In this work, remarkable cation diffusion through the barrier layer – electrolyte interface and Ni-reoxidation have been detected as main degradation mechanisms. These phenomena, strongly enhanced by the high fuel utilization, promote Y-segregation through electrolyte and anode, enhancing the reduction of the Ni-percolation paths and, eventually, leading to the reduction of the barrier layer thickness. The most significant microstructural modifications have been identified in the outlet part of the tube where especially harsh operating conditions, in terms of temperature, fuel utilization and polarization gradients, occur. An increase of the total gas flow has shown beneficial effects on the described phenomena reducing the effects of the degradation. Increasing the carrier gas flow allows lower degradation rates for cells operating under high fuel utilization up to 80% for 1000 h.

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1. Introduction

Solid Oxide Fuel Cells (SOFCs) are widely investigated since they appear as environment friendly, high efficiency devices for the ongoing hydrogen-based energy economy [1–5]. Although SOFC technology development is not so mature as its competitors such as proton exchange membrane cells (PEM) or alkaline fuel cells (AFC), it offers better efficiency, i.e. up to 70% in electrical conversion and more than 85% when cogeneration systems are employed [4,5]. In the recent years different studies have showed long term operation of SOFC stacks confirming their enhanced stability and reliability that will facilitate their introduction to the energy market [6–9].

Although different designs and geometries are proposed in order to fulfil complex requirements of diverse market applications, including 3D printing technologies [3], planar and tubular architectures are the most commonly used [4,5]. Micro-Tubular Solid

Oxide Fuel Cells (mSOFCs) exhibit an excellent thermal shock and mechanical resistance, many orders of magnitude higher than that characteristic of planar ones [5,10–12]. Moreover, bearing in mind their very promising power density and especially almost instantaneous start-up, it is not surprising that they have been applied in the transport sector market [12–14]. Recently, they have been considered as the key element in the development of Auxiliary Power Units (APUs) for road trucks fed by liquid natural gas (LNG) or liquid petroleum gas (LPG) [15,16]. In order to be reliable, the designed APU should satisfy critical requirements: providing at least 100 W of power at operation temperatures around 700 °C with a maximum starting up time of 20min and especially showing a durability higher than 1000 h in continuous operation of 100 start-stop cycles. These specifications can be accomplished by using a stack of single micro-tubular SOFC cells with high thermal and mechanical stability [14,17]. Performance optimization through comprehension of the ageing mechanism of a single mSOFC is the main target to achieve the APU successful commercial use. Consequently, the definition of the degradation processes and their

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causes becomes a priority.

The determination of the SOFC degradation mechanism is very complex since requires long term studies. In this case, degradation issues are essentially related to the operating conditions: temperature, gas/fuel composition (impurities), current density and start-stop cycling. Temperature and current gradients, redox cycles, poisoning, leakages, etc. give rise to the chemical reactivity between the layers, chemical reaction with environment, reduction or oxidation. In consequence, the cation evolution, i.e. interdiffusion, segregation and coarsening, appears leading to irreversible morphological and chemical modifications that reduce the electrochemical paths and even to the critical failure of the cell.

Nowadays, literature data are mostly focused on the comprehension of the degradation mechanism of electrodes [17–21]. The decomposition of the perovskite structure into the constituting oxides and/or segregation of some cations to the grain boundaries and surfaces are the most common degradation mechanisms in the case of mixed electronic – ionic conductor (MIEC) cathodes like $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) or $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ (LSCF) [[18–20,22,23]]. The very reactive La or Sr elements can create carbonates, hydroxides or even more complex secondary phases especially in the case of open air cathode design. Another critical point concerning the cathode durability is related to its chemical reactivity with the electrolyte, usually yttria stabilized zirconia (YSZ) [24,25]. Diffusion of some elements – again mostly La and Sr, results in the formation of insulating phases such as SrZrO_3 or $\text{La}_2\text{Zr}_2\text{O}_7$. To avoid this reactivity during the fabrication and operation of the cell, a so-called barrier layer, mainly based on Gd-doped CeO_2 (GDC) or Sm-doped CeO_2 (SDC), is deposited between the cathode and electrolyte. Depending on the processing and sintering temperature reached, its efficiency is variable [26–31]. On the one hand, it helps to avoid secondary phase formation but, on the other hand, it can lead to the interaction between the barrier layer and YSZ giving rise to the formation of solid solutions with lower ionic conductivity [30–33]. Note that a detailed barrier layer characterization within planar cells can be found in an authors' previous article [31].

The evolution of the typical Ni-YSZ anode cermet is the most studied SOFC degradation issue, since it has been defined as the main process leading to the loss of the cell performance [17–20,34–41]. The mechanism behind this behaviour includes water formation in the anode as the driving force for Ni agglomeration and its reoxidation into a NiO through the formation of $\text{Ni}(\text{OH})_2$. These modifications lead to the Ni coarsening and can also provoke volume expansion. In consequence, loss of Ni percolation occurs and important microstructural changes give rise to the generation of cracks and even to the delamination between the anode and electrolyte.

Complementary to regular microstructural imaging and electrochemical analysis of degradation mechanisms usually proposed in the literature [17–20,34–42], Raman microspectroscopy is employed in this study as a non-destructive technique sensitive to local structural and chemical modifications occurring in long term tests. In order to understand the degradation mechanisms of micro-tubular SOFC cells, pristine anode supported LSCF/SDC/YSZ/Ni-YSZ tubes were first analyzed by Raman, SEM and EDX to be used as a reference. Based on these background results, the degradation and durability of four galvanostatically aged cells operated at different fuel utilization (FU) were discussed. As observed in previous works, FU appears as one of the most crucial parameters in the cell ageing processes [43–46]. The tubular configuration promotes the existence of operational gradients along the tube length, e.g. temperature gradients, FU or current density, revealing longitudinal heterogeneities in the degradation process [47]. With the goal of fully describing the system, in this work, a longitudinal analysis of the ageing mechanisms was carried out dividing the cell in three

different zones: inlet, center and outlet parts.

2. Experimental procedure

Anode supported micro-tubular solid oxide fuel cells with 5.5 mm of internal diameter and 9 cm length were prepared by high shear extrusion method as described elsewhere [12,14–17,46]. Fig. 1a presents the SEM micrograph of a new pristine cell and summarizes the composition and thickness of each characteristic layer. Four of these mSOFCs were previously aged in galvanostatic long term testing under different conditions [46]. After operation in the conditions listed in Table 1 (FU, time, current density, initial and final voltage and degradation rate), the different tubes were analyzed by micro-Raman scattering, SEM and EDX techniques. In order to analyse the longitudinal effects of the degradation, cross sections along each cell were carefully prepared.

Raman spectra were recorded in the backscattering geometry using a diffraction limited spatial resolution Raman micro-spectrometer Labram HR800 (Horiba, Jobin Yvon France) equipped with the high resolution back illuminated CCD detector cooled by Peltier effect till -80°C . Two excitation wavelengths 532 nm and 325 nm were used. Most of the measurements were performed using standard 532 nm Nd-YAG laser line; the 325 nm wavelength was applied in order to confirm/verify some spectral features. In order to enhance the lateral and spatial resolution, $100\times$ – N.A. = 0.9 objective was used in the case of 532 nm and an entrance slit was limited to 100 microns, maximum. Moreover, in the case of very thin barrier layers, confocal pinhole aperture was limited to 20 microns. In the case of the 325 nm excitation line, the UV adapted objective $40\times$ was applied in order to record the Raman spectra. The laser power on the sample was limited to 1–1.5 mW in order to avoid an undesirable heating effect of the layers that can be detrimental, especially in the case of black cathode material giving rise to the phase transformation under the laser [48]. The Raman spectra were recorded in a wide spectral range (100 – 1800 cm^{-1} typically or 100 – 4000 cm^{-1} in some specific cases) in order to detect the main spectral signature of different major phases as well as the eventual structural and chemical modifications related to the operating conditions (temperature, FU., electric field gradient, time), phase transformations, presence of 2nd phases or effect of oxidation/reduction. In order to determine/compare the Raman peak parameters (position, width, intensity) the Raman spectra were treated with the Labspec 6 as well as Origin software.

SEM-EDX microstructure analysis of every cell was performed using a Zeiss Auriga Scanning Electron Microscope equipped with the following detectors: secondary (SE), back-scattering (BSE) and InLens. For every characteristic part of each cell: inlet, center and outlet, a series of micrographs were recorded along the cross section in order to evaluate the microstructure and detect the evolution eventually present in different interfaces. In the case of the anode functional layer (AFL), low voltage ($<1\text{ kV}$) images were also recorded with InLens SEM detector to distinguish percolating and non-percolating Nickel pathways. Moreover, EDX analysis through maps and line profiles was performed over cross sections to deal with the element inter-diffusion through the interfaces.

3. Results

3.1. Characterization of reference pristine tubular mSOFCs

Fig. 1a presents the scheme of a single anode supported mSOFC used in this project: nickel-yttria-stabilized zirconia (Ni-YSZ) cermets act as anodes, lanthanum strontium cobalt ferrite (LSCF) act as MIEC cathodes whereas YSZ plays the role of an electrolyte. In order to avoid undesirable reaction between the YSZ and LSCF giving rise

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