



Multi-scale analysis of the diffusion barrier layer of gadolinia-doped ceria in a solid oxide fuel cell operated in a stack for 3000 h



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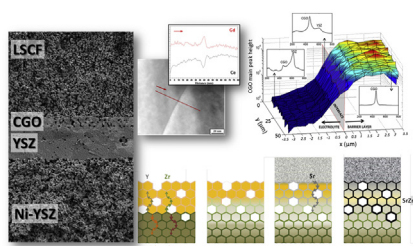
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HIGHLIGHTS

- Multi-scale analyses of CGO barrier layer in SOFCs operated in a stack for 3000 h.
- Cation diffusion at CGO barrier layer region was only caused by sintering process.
- No evidence of (Zr,Ce)O₂-based solid solution formation.
- Gd gradual doping loss and segregation at grain boundaries through CGO layer.
- CGO pores are preferential sites for nucleation and growth of SrZrO₃.

GRAPHICAL ABSTRACT



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ABSTRACT

The state-of-the-art materials for SOFCs are yttria-stabilized zirconia as electrolyte and lanthanum strontium cobalt ferrite as cathode. However, the formation of insulating phases between them requires the use of diffusion barriers, typically made of gadolinia doped ceria. The study of the stability of this layer during the fabrication and *in operando* is currently one of the major goals of the SOFC industry. In this work, the cation inter-diffusion at the cathode/barrier layer/electrolyte region is analysed for an anode-supported cell industrially fabricated by conventional techniques, assembled in a short-stack and tested under real operation conditions for 3000 h. A comprehensive study of this cell, and an equivalent non-operated one, is performed in order to understand the inter-diffusion mechanisms with possible effects on the final performance. The analyses evidence that the cation diffusion is occurring during the fabrication process. Despite the significant diffusion of Ce,Gd, Zr, Y and Sr cations, the formation of typically reported CGO-YSZ solid solution is not observed while the presence of isolated grains of SrZrO₃ is proved. All in all, this study presents new insights into the stability of the typically employed diffusion barriers for solid oxide cells that will guide future strategies to improve their performance and durability.

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1. Introduction

Solid oxide fuel cells (SOFCs) are efficient energy conversion devices that directly transform chemical energy of fuel into electricity [1]. The future of SOFCs depends on the development of efficient and robust materials capable to withstand long times at high temperature and typical harsh ambient conditions during operation. Current developments in SOFCs are focused on increasing the power density and minimizing degradation during operation. A number of factors, such as operation conditions, materials, design and environment promote different types of degradation processes that can have a significant influence on the cell performance [2,3]. A typical phenomenon related to the low performance and degradation of SOFCs is the reduction of the power output due to element diffusion and phase segregation in its different components. These processes can also substantially change the material composition near the interfaces. Inter-diffusion may occur during heat treatments for co-sintering of cell layers, but also during long term cell operation.

One of the main contributions to the poor performance and degradation comes from the cathode electrode. Several authors have evaluated the importance of cation diffusivities for surface segregation of Sr and thus for a major degradation mechanism of SOFC cathodes [4,5]. Currently, mixed ionic–electronic conductors (MIECs), such as lanthanum strontium cobalt iron oxide $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ (LSCF), are used as cathode due to their high catalytic activity, as well as good ionic and electronic conductivities at intermediate temperatures [6]. The reaction of LSCF with the YSZ electrolyte at high temperatures forming insulating secondary phases is a well-known phenomenon [7–9]. Strontium zirconate (SrZrO_3) and lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$) are generated, thus potentially forming ion blocking layers in critical regions such as the cathode–electrolyte interface. A side effect of this element diffusion is the formation of inert phases with low electrical conductivity like, Co_3O_4 at regions where Sr can be expelled from the LSCF structure [10–12]. A standard solution to avoid the crystallization of these phases is the introduction of a Gd or Sm-doped CeO_2 (CGO, SDC, respectively) layer between the cathode and the electrolyte, which acts as a barrier layer for the Sr diffusion [9,13,14].

The inter-diffusion barrier layers fabricated by conventional deposition techniques, like screen-printing or spraying-coating, generally present a wide thickness range of 4–10 μm [15]. Few exceptions, like the work of Van Berkel et al. [16] present thinner screen-printed ceria barrier layers (1.4 μm , in this case). The porosity of these deposited and sequentially sintered CGO layers may be in the range 20–30%, even after sintering at 1300 °C [17,18]. In addition, the ionic conductivities of the CGO barrier layers are lower than expected. This has been attributed to different factors, like inter-diffusion between CGO and YSZ, producing $\text{CGO}_x\text{:YSZ}_{(1-x)}$ solid solutions with high ionic resistances [19–21], the formation of resistive phases involving cathode species [9], and the appearance of the so-called Kirkendall voids, produced by the Ce diffusion into the YSZ [22].

Understanding the formation of the barrier layer region and its evolution along the operating lifetime is challenging due to the high complexity of the system and the number of processes that simultaneously take place and eventually interact. In the present work, a comprehensive multi-scale characterization of the CGO barrier layer and its interfaces has been carried out, combining different complementary analysis techniques at micro- and nano-scale levels. Representative samples have been used, comparing a non-operated cell with one coming from a cell operated in a stack under real conditions for 3000 h. The morphologic study carried out by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) is completed with the observation of

element distribution maps obtained by Energy Dispersive X-Ray Spectroscopy (EDX), Electron Probe Micro Analysis with Wavelength Dispersive X-Ray (EPMA-WDX), Secondary Ion Mass Spectroscopy (SIMS) and Electron Energy Loss Spectroscopy (EELS). Finally, micro-Raman Spectroscopy has provided complementary information about the presence of specific phases at a local level [23–26].

The final aim of this work is to give a broad multi-scale experimental basis that allows understanding the inter-diffusion phenomena taking place in the cathode/electrolyte barrier layer of SOFCs fabricated using industrially scalable techniques (i.e. tape casting and screen printing) and tested in a short stack under conditions close to real operation.

2. Experimental procedure

The degradation studies were performed on an anode supported cell from a stack with planar configuration. The fabrication of the system has been optimized for the maximization of the cell performance, using commercially viable production techniques [8,27–29]. The stack consists of six repeating units, composed by coated ferritic stainless steel interconnectors, cells and glass seals. The cells were supported on a 250 μm porous nickel-yttria-stabilized zirconia (Ni-YSZ) cermet anode with a dense YSZ electrolyte. Anode and electrolyte are produced by tape casting using water based suspensions and sintered at temperatures above 1400 °C. The rest of the components of the cell are screen printed on top of this supporting structure. $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) was deposited as a barrier layer between cathode and electrolyte to prevent the formation of poorly conducting secondary phases, being sintered at a temperature in the vicinity of 1200 °C. The cathode is a composite of a lanthanum strontium cobalt ferrite oxide ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$) and CGO. The cells were tested for 3000 h at 750 °C in a short-stack that included six repeating units. It was operated at 0.4 A cm^{-2} , with a fuel utilization of 80%. Dry H_2/N_2 fuel was used in the anodic compartment and air was introduced in the cathodic chamber.

The cross-section analysis of the cation diffusion across the cathode–interlayer–electrolyte was performed by Confocal Laser Raman Spectroscopy, Scanning Electron Microscopy and Electron Probe Micro Analysis with Wavelength Dispersive X-Ray (EPMA-WDX).

SIMS experiments were carried out using a Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) device from Ion ToF Company (ToF SIMS5). This technique uses a pulsed ion beam (here Bi^+) to remove both atoms and molecules from the sample surface (<4 monolayers). The secondary ions removed from the surface are then extracted and accelerated by an electrical field and their masses are then determined by measuring their time of flight over the analyser to reach the detector. A sub-micrometric in-plane spatial resolution is provided (c.a. 150 nm), being the in-depth resolution on the order of nanometres. In this study, an area of 1 μm^2 was averaged, using a focused 25 kV beam.

The Raman spectra were recorded using a Horiba Spectrometer HR800 (LabRAM Series, Horiba Jobin Yvon). The wavelength of the applied excitation line was 532 nm and 100 \times objective was used. In order to assess the possible formation of (Zr,Ce) O_2 -based solid solutions and the formation of secondary insulating phases 2D XY Raman mappings were performed on the cross section of the LSCF/CGO/YSZ interfaces. The mapping was recorded using the DXR xi Raman microspectrometer (Thermo Fisher). This spectrometer enables the high resolution (0.5 μm) mapping recorded on a large cross section area (21 lines were recorded, each composed of 87 pixel, leading to images formed by 1827 Raman spectra).

The microstructure of samples was examined by Scanning

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