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Degradation study by 3D reconstruction of a nickel–yttria stabilized zirconia cathode after high temperature steam electrolysis operation

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HIGHLIGHTS

- Microstructural evolution of Ni–YSZ cermet is analysed after steam electrolysis operation.
- Ni coarsening is quantified by 3D reconstructions.
- Reconstructions are obtained from synchrotron X-ray nano-tomography.
- Impact of Ni agglomeration on cell performances is evaluated through an in-house model.
- The cell voltage degradation due to Ni agglomeration is ≈1.3%/1000 h.

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ABSTRACT

Microstructural evolution of a Solid Oxide Electrolyser Cell (SOEC) Ni–YSZ cermet cathode is investigated using three dimensional electrode characterisations. 3D reconstructions are obtained on a reference and two long-term tested cells, which were maintained at −0.5 and −0.8 A cm^{-2} for 1000 h at 800 °C. During the long term tests, air was fed at the anode and a mixture of 10% H_2–90% H_2O was fed at the cathode. In this framework, reconstructions have been obtained from synchrotron X-ray nano-tomography technique. Microstructural properties extracted from the 3D reconstructions exhibit an evolution during the tests. Triple Phase Boundary length is decreasing from 10.49 ± 1.18 μm^{-2} for the reference cell to 6.18 ± 0.6 μm^{-2} for the long term tested cell at −0.8 A cm^{-2}. Evolutions of morphological parameters were introduced in an in-house multi-scale model to evaluate their impacts on the electrode degradation, and hence, on the global SOEC performance.

1. Introduction

High temperature steam electrolysis has a great potential for an efficient production of hydrogen. Indeed, this system produces hydrogen and oxygen from water vapour, with no greenhouse gas emissions. It is particularly attractive in a context of renewable energy for conversion and storage, e.g. when wind or solar energies are available. Nevertheless, the poor durability of this system is one of the main drawbacks of this technology. Indeed, Solid Oxide Electrolyser Cells (SOECs) performance currently decrease by few percent (about 2–5%) after 1000 h of operation [1,2], whereas an economic viability would be achieved for a degradation limited to few tenth of percent (<0.5%).

These degradations are mainly attributed to material deteriorations occurring in operation, such as electrodes microstructural evolutions or material chemical decomposition. Conversely to Solid Oxide Fuel Cells, few papers in literature have been dedicated to assess the SOEC stability over a long term of operation (>500 h). For e.g., Schefold et al. [1] have reported a 9000 h test carried out at $T = 780$ °C in SOEC galvanostatic conditions. A typical cathode supported cell was used for the experiment which was constituted of Yttria-Stabilised Zirconia (YSZ) for the electrolyte, Lanthanum Strontium-substituted Ferrite/Cobaltite (LSCF) for the anode and a nickel-YSZ cermet (Ni–YSZ) for the cathode. In that conditions, the authors have measured a mean voltage loss of 3.8% per 1000 h.

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Hauch et al. [2] have also reported long-term tests performed at 850 °C on Ni–YSZ cathode supported cells (YSZ for the electrolyte and a composite made of YSZ and Lanthanum Strontium-substituted Manganite (LSM) for the anode). They found an average cell voltage degradation rate of 2%/1000 h for a test of 1316 h. Even if all the mechanisms are not still fully understood, it seems that the main underlying process of degradation is mostly caused by atoms self-diffusion or inter-diffusion between the SOEC constituents. Indeed, at the considered high temperature of operation, those phenomena are rapid, and atoms are able to migrate through the interfaces, penetrate inside the materials, form secondary phases and modify the material functionality. The main degradation phenomena reported in literature are the followings:

(i) Nickel agglomeration in the cermet [2,3].
(ii) Oxygen electrode delamination [4–7].
(iii) Chromium poisoning of the oxygen electrode from the interconnection material [6].
(iv) Cations segregation, and phases precipitation in the different materials, such as a secondary phase formation between anode and electrolyte [8].
(v) Contamination (Ni, Cr, Si, Al …) of active sites [2,7,9]. Note that Cr can be released from the metallic interconnects, Si is liable to come from the glass seal material, while Al can originate from alumina addition for sintering aid during the cell manufacturing process.
(vi) Ionic conductivity loss of the electrolyte material because of the electro-reduction of the electrolyte [4,10,11].

In this context, it appears essential to quantify the actual morphological evolution of the classical cathode material used for SOEC, a cermet of nickel and yttria-stabilized zirconia (Ni–YSZ). It is worth noting that several 3D reconstructions of this electrode have been already reported in literature [12–21]. Nevertheless, among all these studies, very few have been dedicated to assess the three dimensional cermet microstructure change in operation [14,15,20,21]. For instance, Wilson et al. [14] and Nelson et al. [15] have compared the microstructure of a reference cell and a cell that was tested up to 1130 h in SOFC mode. They observed an agglomeration of the smallest Ni particles resulting in a significant Ni coarsening. It can be noticed that all the aforementioned articles have been dedicated to a Solid Oxide Fuel Cell (SOFC) purpose but, according to our best knowledge, no study has been yet devoted to the SOEC mode of operation.

In order to determine the extent of the degradation related to the Ni–YSZ electrode in electrolysis mode, microstructural evolution of the cathode functional layer is investigated using a 3D reconstruction technique, both on a reference and on long-term tested cells. In this study, 3D reconstructions have been obtained from synchrotron X-ray nano-holotomography, and then used to calculate/compute the microstructural parameters evolution upon operation. These properties have been introduced in an in-house micro-model [22] to determine their impact on the electrode behaviour. In order to estimate the influence of the microstructure degradation on the global cell polarisation curve, the local approach has been coupled to a home-made SOEC macro-model [23].

2. Experimental part

2.1. Samples

Commercial SOEC cathode supported cells, supplied by HC Starck producer, were used in this study. The materials, structure, and typical dimensions of the cell are illustrated in Fig. 1:

- The cathode consists of a thin (≈10 μm) functional layer deposited on a thick (500 μm) cathode current collector. A thin layer of pure Ni is deposited on the top of the current collector in order to improve the electrical contact with the metallic interconnect. As received, the functional layer and the current collector are composed of nickel oxide (NiO) and zirconia ZrO_2 stabilized with 8 (8YSZ) and 3 (3YSZ) mol.% of Y_2O_3, respectively, for the functional and the current collector layers. It can be noticed that 3YSZ is used for the support instead of 8YSZ in order to improve the mechanical robustness of the cell. Indeed, it is reminded that the 3YSZ bending strength is much higher than the characteristic strength of 8YSZ (*i.e.* 1300 MPa for 3YSZ *vs* 230 MPa for 8YSZ [24]).

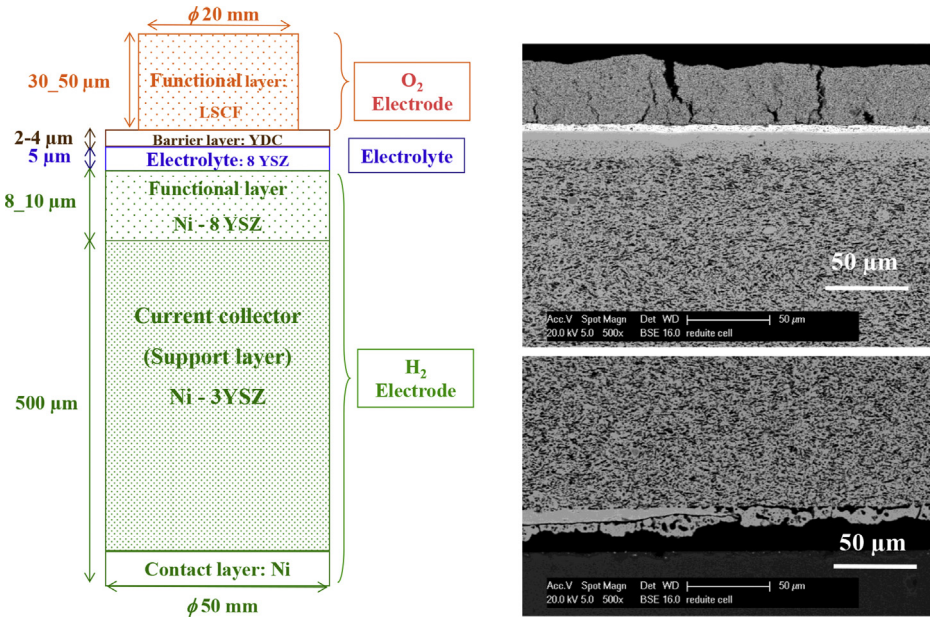

Fig. 1. Schematic representation of the cell structure. The global view of cell layers are illustrated by two polished cross section images obtained with a Scanning Electron Microscope (SEM) in Back Scattering Electron (BSE) mode (for the cell in its reduced state).