



# Impact of Nickel agglomeration on Solid Oxide Cell operated in fuel cell and electrolysis modes

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## HIGHLIGHTS

- Typical SOCs operated under fuel cell and electrolysis currents at 750 °C and 850 °C.
- Ni-YSZ cermets reconstructed by synchrotron X-ray holotomography.
- The inhibiting role of the YSZ backbone on Ni coarsening experimentally highlighted.
- Local Ni particle growth independent on polarization in SOFC or SOEC modes.
- Impact of Ni coarsening on cell performances computed for SOFC and SOEC modes.

## ARTICLE INFO

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## ABSTRACT

Long-term experiments have been carried out to investigate the impact of Nickel (Ni) coarsening on the performance of Solid Oxide Cell. Durability tests have been performed with H<sub>2</sub> electrode supported cells at 850 °C and 750 °C in fuel cell and electrolysis modes. Microstructural changes in the composite electrode of Nickel and Yttria Stabilized Zirconia (YSZ) have been characterized by synchrotron X-ray nanotomography. Analysis of the reconstructions have revealed that Ni coarsening induces a significant decrease of both the density of Triple Phase Boundary lengths (TPBLs) and the Ni/gas specific surface area. However, the contact surface between Ni and YSZ is not changed upon operation, meaning the Ni sintering is inhibited by the YSZ backbone. Moreover, the Ni coarsening rate is independent of the electrode polarization. The evolution of TPBLs in operation has been fitted by a phenomenological law implemented in an electrochemical model. Simulations have shown that microstructural changes in the H<sub>2</sub> electrode explain ~30% of the total degradation in fuel cell mode and ~25% in electrolysis mode at 850 °C after 1000–2000 h. Moreover, it has been highlighted that the temperature at which the degradation is estimated after the durability experiment plays a major role on the result.

## 1. Introduction

Solid Oxide Cells (SOCs), for either fuel cell (SOFC) or electrolysis (SOEC) operation, are being given a pronounced interest as they can offer high conversion efficiency due to their high operating temperature. Thanks to their reversibility, the same device can be alternatively used in fuel cell and steam electrolysis modes. Taking advantage of these characteristics, it has been proposed to couple the SOCs with intermittent renewable energy sources in order to match the fluctuations between the electricity demand and the production [1]. Besides, as part of the energy is supplied in the form of heat, the electrical demand required for the water splitting can be significantly reduced in SOEC mode [2].

The SOCs consist of two porous electrodes separated by a dense electrolyte. Typical materials for SOCs are Yttria-Stabilized Zirconia (YSZ) for the electrolyte, Ni-YSZ cermet for the H<sub>2</sub> electrode and Lanthanum Strontium Cobalt Ferrite (LSCF) for the O<sub>2</sub> electrode. In planar configuration, the cells are assembled with metallic interconnects to form a stack of high power density [3–5]. Nowadays, the SOCs durability is one of the main issues of the technology especially when operated in electrolysis mode. Indeed, the economic viability of the technology would be achieved for degradation limited to few tenth of percent (< 0.5%/kh). However, the degradation rates, which are in the range of ≈1%/kh for stacks operated in fuel cell mode, can be increased to ≈2–3%/kh for operation in electrolysis condition [6–9]. The loss in cell performances has been ascribed to various physical

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processes promoted by the high operating temperatures such as electrode poisoning, material instabilities, interdiffusion and reactivity [10–14]. Among all these phenomena, the microstructural evolution of the Ni-YSZ cermet is recognised to play a significant role in the global deterioration of SOCs performances [15–18].

The morphological change in the cermet microstructure is related to the Nickel phase coarsening that arises upon operation at high temperature [15]. The Ni particle growth results in the decrease of the density of Triple Phase Boundary lengths (TPBLs) where the electronic, ionic and gas phase meet [17,19–22]. As TPBLs are key parameters corresponding to the electro-active sites for the electrochemical reaction of charge transfer, it has been experimentally shown that the Ni agglomeration induces a substantial decrease of the electrode polarization resistance [16,23–26]. Therefore, many efforts have been paid to measure the growth of the Ni particle size as a function of the operating time on two-dimensional Scanning Electron Microscope (SEM) micrographs [15,19,25–27]. In order to quantify the loss in the density of TPBLs, some authors have also reconstructed aged electrodes by X-ray tomography [17,21] or by using a Focused Ion Beam combined with a SEM (FIB-SEM) [16,22,28,29]. The introduction in electrochemical models of the microstructural properties estimated on the 2D cross sections or measured on the 3D reconstructed volumes has allowed the quantification of the effect of Ni coarsening on the electrode and cell response [17,19,25].

The precise mechanisms responsible for the Ni microstructural change are not fully understood yet. Nevertheless, it is nowadays well established that two distinct underlying phenomena are involved in the Ni agglomeration:

- The first one is related to a kind of Ostwald ripening process based on the local sintering of two adjacent particles [27,30]. In this process, the main driving force would be the minimization of the Ni specific surface area with the growth of the biggest particles to the detriment of the smallest ones [31]. The mechanism, which involves a mass transfer at short-distance, could be controlled by (i) a solid-state diffusion of vacancies [30,31], (ii) a surface diffusion involving the transfer of Ni atoms or Ni<sub>2</sub>-OH species [30–35] or (iii) a transport in the gas phase by a local Ni vaporisation/condensation under Ni(OH)<sub>2</sub> volatile molecules [36,37]. The validity of this mechanism in the cermet has been demonstrated thanks to microstructural observations after operation, which have highlighted the local Ni reorganization with a shift of the Particle Size Distribution (PSD) toward bigger particles [15,17]. Besides, as expected for this process, it has been shown that the kinetic rate of the Ni particle growth decreases with increasing operating time [19,25]. Moreover, the YSZ backbone in contact with the Ni particle network is expected to interfere with the mechanism by lowering the sintering rates of the metallic phase [33,34]. However, this presumed inhibiting effect of the YSZ on the Ni agglomeration has not yet been experimentally proven.
- In parallel to the first process, observations of global compositional change within the electrode have been attributed to a mechanism based on a mass transfer at long-distance. In this case, after vaporisation into Ni(OH)<sub>2</sub> volatile molecules, Nickel could be transported into the gas phase either by diffusion in the cermet porosity or even by convection in the channel of gas distribution [17,27,33,36]. In contrast to the first mechanism, the kinetic rate of the Ni evaporation/deposition process should not slow down over time, and hence, could be predominant only for very long operating times [27]. Besides, it has been observed that the process tends to deplete the electrode/electrolyte interface with a displacement of Ni in the bulk part of the cermet [38–40]. It has been proposed by Mogensen et al. [38] that the mechanism could be promoted at high electrode polarization. However, the real extent of this mass transfer is still unclear. For example, Hagen et al. [39] and Mogensen et al. [38] have reported a massive Ni depletion whereas Rinaldi et al. [40]

have only observed a very slight relocation of Ni even after an operation of 10700 h. This apparent discrepancy points out that the Ni coarsening mechanisms must be strongly dependent on both the operating conditions and the cermet microstructure. Indeed, in contrast to Rinaldi et al. [40], the cells tested in Mogensen et al. [38] present a functionalization of the electrode with a fine microstructure at the interface with the electrolyte (i.e. a functional layer designed for the electrochemistry).

The operating temperature has been found to have a major role on the Ni agglomeration. Indeed, the Ni particle coarsening is based on a sintering process which is thermally activated [41,42]. Therefore, it has been shown that the Ni agglomeration is favoured when the temperature is increased [29,39]. However, this observation is apparently inconsistent with the measured electrochemical degradation rates that are found to decrease with increasing the temperature [39]. It has also been observed that the steam content in the gas stream accelerates the Ni agglomeration [27,29,33]. Indeed, the presence of water in the gas phase is liable to affect both mechanisms, by promoting the vaporisation of the Ni(OH)<sub>2</sub> gaseous molecules and the surface diffusion of the Ni hydroxide complex [27,33]. Finally, it is worth noting that most of the studies have been performed in fuel cell mode whereas very few have been dedicated to the electrolysis conditions [17,38]. No specific studies have been conducted to compare the effect of polarization in SOFC and SOEC modes on the Ni coarsening.

In this work, it is proposed to investigate the impact of the temperature and the SOFC/SOEC polarization on the Ni coarsening. For this purpose, a set of long term tests has been carried out in the two modes at different temperatures. 3D reconstructions of the cermet electrodes have been acquired by X-ray nanotomography in the bulk and at the electrode/electrolyte interface. After verification that, in our conditions, the Ni depletion at the electrolyte interface is limited and the change in Ni volume fraction in the bulk is negligible, the evolution of the cermet microstructural properties has been analyzed to study the mechanism of Ni particles growth based on a local sintering process. After identifying the parameters for a relevant law, the impact of Ni agglomeration on the cell response has also been modelled and discussed.

## 2. Experimental details

### 2.1. Materials and cell description

A H<sub>2</sub> electrode supported cells representative of the SOC technology have been used in this work. They have been produced by SOLIDpower® SpA. The cells exhibit a circular shape with an active area of 9 cm<sup>2</sup>. The electrolyte made of 8%mol Ytria Stabilized Zirconia (YSZ) is a dense and thin film of 5 μm. It is coated onto a 260 μm thick porous H<sub>2</sub> electrode substrate composed of Nickel and YSZ (Ni-YSZ) cermet. The O<sub>2</sub> electrode presents a multilayer structure which is deposited onto the electrolyte. The active part of the O<sub>2</sub> electrode is a porous bilayer constituted of a composite made of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF) and 10%mol Ceria doped Gadolinium Oxide (LSCF-CGO) (ca. 15 μm thick) associated to a pure LSCF layer (ca. 18 μm thick). In order to limit the chemical reactivity between LSCF and YSZ, a thin barrier layer of CGO (ca. 2–3 μm thick) is added between the electrolyte and the O<sub>2</sub> electrode. Finally, a 20 μm thick La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> (LSC) layer is coated on the top of the oxygen electrode to improve the current collection. The H<sub>2</sub> electrode and the electrolyte were manufactured by water based tape casting and co-sintered. Then, the barrier layer and the O<sub>2</sub> electrode were applied on the electrolyte by screen printing.

### 2.2. Electrochemical set-up and test conditions

Long-term durability tests have been performed with an in-house set-up already detailed in Ref. [43]. The anodic and cathodic gases are

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