Tracking Solid Oxide Cell Microstructure Evolution by High Resolution 3D Nano-Tomography

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Technical University of Denmark

Department of Energy Conversion and Storage

PhD Thesis

Tracking Solid Oxide Cell Microstructure Evolution by High Resolution 3D Nano-Tomography

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Supervisors: Jacob Ross Bowen, Peter Stanley Jørgensen, Erik Mejdal Lauridsen

November 7, 2017
Abstract

Solid oxide cells (SOCs) offer great prospects for the efficient and reversible conversion of chemical to electrical energy. Therefore, they are expected to play a key role in the renewable energy landscape. However, their limited lifetime under operating conditions hinders their widespread usage. The degradation processes are mainly attributed to morphological changes occurring within the electrodes microstructure. Therefore, precise tracking of 3D microstructural evolution during operation is considered crucial to understanding the complex relationship between microstructure and performance.

In this work, X-ray ptychographic tomography is applied to SOC materials, demonstrating unprecedented spatial resolution and data quality. The effect of a complete redox cycle on the same Ni-YSZ microstructure is visualized ex-situ in 3D, showing major rearrangement of the nickel network after reduction, the formation of cracks in the YSZ, and void formation in nickel oxide after oxidation.

Capitalizing on the high resolution of ptychography, the effect of nickel coarsening on the Ni-YSZ microstructure evolution is studied ex-situ in three dimensions, while the sample is repeatedly scanned and treated at high temperature in dry hydrogen. The analyses show the substantial evolution of the nickel and pore networks during the first 3 hours of treatment. The nickel coarsening leads to loss of nickel connectivity, a decrease in specific interface area and a decrease in total triple phase boundary density.
The *ex-situ* experiment on a redox cycle provides new insights on the nature of the redox processes occurring within a SOC fuel electrode. However, only the initial and final steps of the reactions can be analyzed. To gain information about the intermediate steps of the reduction and oxidation, in-situ holographic tomography is applied. Preliminary results show rapid kinetics for the two reactions. During oxidation, void formation in metallic particles is observed. During reduction, the nickel oxide particles first evolve to a nano-porous system of nickel crystallites and then coarsen towards dense nickel particles.
Resumé

Fastoxidceller (Solid Oxide Cells, SOC) er lovende teknologier til effektiv og reversibel omdannelse af kemisk energi til elektrisk energi. De forventes derfor at spille en nøglerolle i en fremtid der bygger på vedvarende energi. Deres begrænsede levetid under driftsbetingelser forhindrer derimod deres brede anvendelse. Nedbrydningsprocesserne i cellerne tilskrives hovedsageligt morfologiske forandringer i elektrodens mikrostruktur. Det er derfor vigtigt at kunne følge udviklingen af mikrostrukturen i 3D under drift for at forstå det komplekse forhold mellem mikrostruktur og ydeevne.

I dette arbejde anvendes X-ray ptychografisk tomografi på SOC materialer og der demonstreres en hidtil uset rumlig opløsning og datakvalitet. Effekten af en hel redox cyklus på den samme Ni-YSZ mikrostruktur visualiseres ex-situ i 3D. Dette viser en betydelig forandring af nikkelnetværket efter reduktion, dannelse af revner i YSZ netværket og dannelse af huller i nikkeloxiden efter oxidation.

Ex-situ-eksperimentet af en redox cyklus giver nye indblik i hvordan redox-processerne forløber i en SOC brænselseelektrode. Det er imidlertid kun de første og sidste trin i reaktionerne der analyseres. For at få information om de mellemliggende trin i reduktionen og oxidationen anvendes in-situ holografisk tomografi. Foreløbige resultater viser at de to reaktioner sker hurtigt. Under oxidationen observeres der dannelse af huller i metalliske partikler. Under reduktionen udvikler nikkeloxidpartiklerne sig først til et nano-porøst system af nikkel krystallitter og vokser derefter hen imod tætte nikkelpartikler.
Preface

This thesis is submitted in candidacy for the Ph.D. degree from the Technical University of Denmark (DTU). The work was carried out at the Department of Energy Conversion and Storage in the period from August 2014 to August 2017. The project was supervised by Senior Scientist Jacob Ross Bowen and co-supervised by Senior Scientist Peter Stanley Jørgensen and Erik Mejdal Lauridsen. Four months of the work were carried out through an external research stay at Northwestern University, Evanston, IL (USA) at the Peter W. Voorhees research group, Department of Materials Science and Engineering. This work was funded by ”the allianCe for ImaginNg of Energy MAterials” (CINEMA), DSF-grant no. 1305-00032B via ”The Danish Council for Strategic Research”.

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Chapter 1

Introduction

1.1 Motivations

Since the advent of the 2nd industrial revolution, electricity has mainly been produced by the combustion of fossil fuels in large generators. These large plants provide a constant electricity supply while, more flexible technologies such as hydropower and gas plants, provide additional power in time of high demand [1]. In 2016, 66 % of the global energy production was produced from fossil fuels while only less than 5 % came from solar or wind power. It is widely accepted that carbon emission from fossil fuels have a key impact on the ongoing climate change. Therefore, it is necessary to change the current methods of energy production in order to limit the global warming as stated in 2015 in the Paris Agreement [2].

Lowering greenhouse gas emissions involves the generation of a higher proportion of energy from renewables. As stated by the International Energy Agency (IEA), in order to meet the goals of the Paris agreement, solar and wind power should generate the 18 and 16 % of the global electricity by 2050 [3]. However, the grid should be prepared to accommodate an increasing proportion of electricity coming from intermittent renewable sources. In practice, it is crucial that electricity is supplied on demand and that the voltage and frequency of the grid remain within the quality standards. Energy storage will play an im-
important role in meeting these requirements. It is estimated that, for renewable sources such as wind or solar to reach the goals fixed by the Paris agreement, the capacity of storage connected (globally) to the grid should increase from 140 GW to 450 GW in 2050 [4, 5].

To date, many storage technologies are available on the market and they differ considerably in their operating principle. Briefly, they can be grouped as follow:

- **Electrochemical storage** which store electrical energy in chemical energy through electrochemical reactions.

- **Mechanical storage** which store potential mechanical energy such as pumped hydroelectric plants, flywheels or compressed air.

- **Electrical storage** which store electrical energy in devices such as supercapacitors or superconducting coils.

However, significant uncertainties remain around the costs, technical characteristics, and role of the different storage systems. In fact, most of the outlined technologies are immature and, despite many detailed reports on the topic [6, 7], there is a substantial lack of a comprehensive comparison of the different technologies.

One promising energy storage device is the solid oxide electrochemical cell (SOC). Even though most of the research so far focused on applying SOCs to generate power (fuel cells) from hydrogen or carbon-based fuels, SOCs can be operated reversibly [8]. Specifically, electrical energy can be supplied to the cell to drive an electrochemical reaction, which stores that energy as a form of fuel (electrolyses mode) and, subsequently, energy can be produced by the same reaction in reversed mode (fuel cell mode). In some sense, a reversible solid oxide cell can be considered as flow battery. However, while batteries use expensive metals (mostly Pb, Mn, Li, Co, Ni) to store energy in the electrodes,
SOCs have the advantage of storing energy in inexpensive fuels [9]. Reversible SOCs can operate using a wide variety of fuels (including hydrocarbons) which can be integrated with existing infrastructures. For example, co-electrolyses of both \(CO_2\) and \(H_2O\) can be performed to produce synthesis gas from which fuels such as gasoline or diesel can be obtained using well know catalytic processes [10, 11]. Alternatively, fuels can be used directly in the fuel electrode to produce electricity from the previously stored energy. The high operating temperatures of SOCs (from 500 \(^\circ\)C to 1,000 \(^\circ\)C) ensures high efficiency at high reaction rate. Current densities higher than 1 \(Acm^{-2}\) are easily obtained at efficiency close to 100\% [12].

However, maintaining this level of performance during long-term operation has been the main challenge for the widespread usage of SOC technology. Degradation in SOCs is characterized by a gradual decrease in performance, measured as the percentage of increased over-potential over a certain period of time [12, 13]. As will be clarified in the following sections, one of the main causes of the electrode degradation is the microstructural changes occurring during the cell operation. Understanding the complex phenomena involved in the microstructural evolution is considered critical for a more rational design of future electrodes.

### 1.2 Working principles of Solid Oxide Cells

Solid oxide cells (SOC) are electrochemical devices able to efficiently convert chemical energy to electrical energy and vice-versa. They differ from polymeric cells (PEM) considering that all the components are solid and their operating temperature ranges from 500 to 1000 \(^\circ\)C [14]. The solid state construction offers many advantages over the other conventional electrochemical cells such as fuel flexibility, efficiency and the use of non-noble materials in the electrodes.
In its simplest form, a solid oxide cell is made of two porous electrodes (anode and cathode) and a dense electrolyte placed in between the two. In SOC technology, the electrolyte is often an \( O^{2-} \) conductor. When the cell is operating in fuel cell mode, the working principle is shown in figure 1.1. Referring to the case of hydrogen used as fuel, the electrochemical reactions involve the oxidation of \( H_2 \) at the anode and the reduction of \( O_2 \) at the cathode with the following reactions:

\[
\begin{align*}
\text{anode:} & \quad H_2 + O^{2-} &\rightarrow H_2O + 2e^- , \\
\text{cathode:} & \quad \frac{1}{2}O_2 + 2e^- &\rightarrow O^{2-}, \\
\text{overall:} & \quad H_2 + \frac{1}{2}O_2 &\rightarrow H_2O.
\end{align*}
\] (1.1)

The formed \( O^{2-} \) ions diffuse from the cathode through the dense electrolyte and meet hydrogen ions to produce water as a product. During the hydrogen oxidation, electrons are formed and travel into an external circuit to produce power [14, 15, 11].

As all the electrochemical systems, SOC operation is governed by a number of physicochemical phenomena such as charge-transfer reactions, chemical reactions and transport of reactants and products in the electrodes [16, 17]. In thermodynamic conditions, the theoretical voltage for a single cell is given by the well known Nernst equation and, at open circuit voltage (OCV), is close to 1.1 V. When the cell is connected to an external circuit, the useful voltage is given by:

\[
V = E^0 - RI - \eta_a - \eta_b
\] (1.2)

where \( E^0 \) is the standard potential, \( RI \) is the ohmic loss in the cell and \( \eta_a \) and \( \eta_b \) are the anodic and cathodic polarizations respectively. These polarizations decrease the efficiency of the cell and are caused by a number of factors such as temperature, current density and, more importantly for the scope of this work,
1.3 Fuel electrode microstructure and overpotentials

The role of the fuel electrode is to facilitate the oxidation of the fuel, ensure the right electronic and ionic conductivity and allow the diffusion of the gas species (reactants and products) towards or away from the reactive sites. Furthermore, the high temperature and the reducing atmosphere in which the fuel electrode operates imposes strict restrictions on the materials selection. The most commonly used material for the fuel electrode is a porous ceramic-metal composite (cermet) of Ni and yttria-stabilized zirconia (YSZ). This material possesses a number of key features which make it an ideal electrode material for SOCs:

- Nickel exhibits excellent electrocatalytic properties in the oxidation of $H_2$
and presents high electrical conductivity ($\sigma \approx 10^4 S/cm$) at $1000 ^\circ C$ [18].

- The Ni-YSZ cermet is stable in reducing atmosphere and the two materials do not react over a wide range of temperature.
- Ni and YSZ have similar thermal expansion coefficient (TEC) [19]

In addition to the aforementioned points, the YSZ presents a framework for the dispersion of the nickel particles and acts as an inhibitor for nickel coarsening [20]. A typical Ni-YSZ microstructure is presented in figure 1.2 a) where the 3D rendering of a region close to the dense electrolyte is shown.

![Figure 1.2](image)

Figure 1.2: Typical solid oxide cell anode microstructure in 3D. (a) 3D microstructure rendering of a region containing the electrode-electrolyte interface. In (a) nickel is presented in red, the YSZ in gray and the pores are transparent. (b) Active triple phase boundary distribution in 3D for the volume presented in (a).

The Ni-YSZ is a composite material where the electrons are transported through the nickel, and oxygen ions trough the YSZ. The electrochemical reactions take place where the three phases (Ni, YSZ and pore) coexist. Such sites are referred as triple phase boundaries (TPB) and their number, location, and distribution within the electrode play a crucial role in the cell performance. Among the TPBs, only the sites percolated through all the three phases can be considered active. As an example, figure 1.2 (b) shows the distribution of the active triple
phase boundaries in the volume presented in 1.2 (a).

As expressed in equation 1.2, the fuel electrode is responsible for part of the cell overpotential. The anodic overpotential can be divided in three main contributions: activation polarization, ohmic polarization, and concentration polarization. The activation polarization is related to the ability of the electrode to oxidise the chemical compounds and it contributes to the polarization at low current density. The ohmic polarization is mainly caused by the electronic and ionic resistances and becomes predominant at intermediate cell currents. Finally, at high current density, the fuel is oxidized at a faster rate than the diffusion of reactants and product within the electrode causing the concentration polarization [14]. The study of the effect each polarization on the cell performance would require a detailed electrochemical characterization (e.g EIS) which is beyond the scope of this work. However, it is useful to briefly underline the impact of the microstructure on the electrode polarizations, and how 3D characterization techniques can represent a unique tool to complement electrochemical tests.

The length of active TPBs per unit volume (e.g TPB density) represents a key factor for the activation overpotential. A microstructure presenting high density of active TPBs will more likely present a lower activation overpotential and therefore, higher electrical efficiency [21]. Other factors influencing the activation overpotentials are phases surface area and tortuosity. The concentration polarization is linked with the transportation process of the species towards the reaction sites and the diffusion of reaction products out of the electrode. Therefore, the right connectivity of the pore phase is essential [22]. Furthermore, the quality of the pore pathways also affects the gas transport properties of the electrode. High pore tortuosity together with narrow pore channels will result in slower diffusion of the gas species contributing to the concentration polarization [23]. Similarly, tortuous nickel and YSZ networks will lead to low effective
electric and ionic conductivities increasing the electrode ohmic overpotential [24].

1.4 3D characterization of Ni-YSZ electrodes

The standard analysis to investigate SOC microstructure is electron microscopy. SEM analysis can give a good overview of the microstructure revealing the chemical composition of the constituent materials. 2D observations are often followed by image analysis in order to obtain quantitative information on the microstructure. In some cases, 3D parameters can be retrieved from 2D measurements using the stereological approach [25]. However, there are important microstructure parameters which cannot be computed in 2D. Among them, phase connectivity and phase tortuosity are the more obvious, since particles which appear isolated in 2D might be connected in three dimensions. Therefore, there is an intrinsic need for 3D characterizations of SOC microstructure.

In the pioneering work from Wilson et al, Focused Ion Beam - Scanning Electron Microscopy (FIB-SEM) was used to reconstruct a Ni-YSZ electrode of a solid oxide fuel cell in three dimensions [26]. In the FIB–SEM method, the ion beam is first used to mill a region of the electrode. Subsequently, thin sections are removed from the exposed surface and repeatedly imaged to yield a series of consecutive SEM images. A 3D reconstruction of the anode is obtained by stacking the 2D SEM images in 3D space. FIB-SEM tomography has been used to analyze the evolution of Ni-YSZ microstructure before and after annealing (in H$_2$) [27]. Using the same approach Cronin et al have analyzed the impact of the micro porosity evolution under annealing, linking this results with the increased polarization observed using impedance spectroscopy [28]. Finally, 3D reconstructions can be also used to optimize fabrication processes and sintering procedures [29]. FIB-SEM tomography is characterized by high resolution (\(\sim 20\) nm) and has the advantage of requiring trivial sample
preparation. However, the quality of FIB-SEM images can depend on several parameters such as detector position, the energy of the electron beam and the state of the surface. More importantly, the technique is destructive and doesn’t allow time-dependent studies [30].

X-ray nano-tomography is a relatively new technique which uses X-rays as the imaging probe. Lately, thanks to big improvements in X-rays optics and detector design, high-resolution images can be obtained using either synchrotron or lab-based sources. When operating in full field mode, the X-ray beam is focused by special X-ray optics to obtain a magnified image of the sample recorded by a high-resolution charge-coupled detector. From different projection at different angles, the 3D reconstruction is performed using reconstruction algorithms such as filtered back projection or algebraic methods [31, 32, 33, 34]. Izzo et al. demonstrated that X-ray nano-tomography can be used to reconstruct the complex microstructure of a Ni-YSZ electrode. In this preliminary work, a lab-source scanner has been used achieving a resolution of 42.7 nm. However, only the pore and the solid phase were successfully resolved while no contrast between the Ni and YSZ was achieved. In order to achieve the right contrast between all the phases, synchrotron radiation must be used [31].

X-ray Absorption Near Edge Spectroscopy (sometimes referred as XANES), is based on the rapid change in the absorption coefficient of materials in the proximity of the absorption edge. For example, in order to achieve the contrast between Ni and YSZ in Ni-YSZ anode materials, two tomograms are acquired above and below the nickel edge [34]. Subtracting the two datasets, a good segmentation can be obtained. Using this procedure Chen-Wiegart et al. realized a comprehensive 3D morphology analysis of a porous Ni-YSZ solid oxide fuel cell anode [35]. A volume of 3600 µm³ was resolved with structural data showing satisfactory statistical accuracy. Cronin et al. have used the NANO-TXM to reconstruct a Ni-YSZ/YSZ/LSM-YSZ microstructure imaging fuel electrode and
Four tomograms were performed tuning the energy of the beam across the Ni edge (8300 eV) and the Mn edge (6500 eV).

1.5 Objectives

In theory, SOCs look very attractive due to their versatility in terms of fuels, their efficiency and the relatively low cost of the constituent materials. However, for SOCs to become economically competitive, many challenges have to be addressed. Among them, long-term performance stability of the Ni-YSZ cermet is a critical aspect. Performance degradation is measured observing the percentage of decreased cell voltage (increased overpotentials) over a certain period of time. When using hydrogen as a fuel, degradation in Ni-YSZ electrode might occur through two major phenomena: redox cycling and nickel coarsening.

During SOCs life-time, they are expected to undergo several redox cycles. For example, if the fuel supply is interrupted due to leakages in the gas supply system, oxygen will permeate within the electrode oxidizing nickel in nickel oxide. A subsequent restoration of the normal reducing conditions will convert the NiO back to nickel. However, the original electrode microstructure is not generally recovered [36]. As will be clarified in the rest of this dissertation, the volume changes related to the redox process is detrimental for the electrode. Redox cycles lead to a major rearrangement of the nickel network, cause the formation of cracks in the YSZ network and the failure of the electrode-electrolyte interface.

When the fuel is constantly supplied to the electrode, the predominant microstructural change in the porous Ni-YSZ cermet is the nickel coarsening. Nickel coarsening is caused by the relatively low melting point of nickel (compared to the SOC operating temperatures) and the high specific surface area of oxygen electrode simultaneously [32].
nickel particles in the electrode [37]. Nickel coarsening decreases Ni/YSZ and Ni/pore interface areas and causes a considerable reduction in the TPB density leading to activation polarization losses. Furthermore, the nickel particles coalescence impacts on the overall connectivity of the network which causes fading in the electrode conductivity [38, 39].

In order to gain a deeper knowledge on the aforementioned degradation mechanisms, precise tracking of the 3D microstructure evolution of SOC materials under operation is crucial. The aim of this project is to investigate the effect these phenomena on SOC fuel electrodes in 3D, by means of X-ray nanotomography. The ultimate goal of this study is to lead to the development of future electrodes more robust to long-term degradation.

1.6 Outlines

The central chapters of this dissertation, cover the results of two \textit{ex-situ} experiments (redox cycle and nickel coarsening) and consist of one published paper and one ready for submission (\textit{In Manuscript}). The last part of the thesis provides the preliminary results of \textit{in-situ} holo-tomography studies obtained in a recent beamtime.

\textit{Chapter 2} presents a new sample preparation methods for \textit{ex-situ} ptychographic tomography, together with the development of a custom-made sample environment. Furthermore, the basic principle of ptychography and tomographic reconstruction are summarized. The chapter also introduces the segmentation method together with the data analysis involved in this work.

\textit{Chapter 3} presents the results of the first \textit{ex-situ} nano-tomography experiment performed on SOC microstructure during a redox cycle. Ptychography is demonstrated as a useful tool to investigate the evolution of Ni-YSZ electrodes.
Cracks formation in the YSZ, nickel final rearrangement and internal void formation in NiO particles are discussed in terms of global and local changes in the microstructure.

Chapter 4 presents the results of an ex-situ nickel coarsening experiment, where the sample is treated at high temperature in dry hydrogen. The 3D microstructure evolution is analyzed globally, performing accurate statistical analyses. The local effects of nickel coarsening are discussed in terms of formation of isolated particles, loss in Ni-Ni percolation and modification in the percolation of triple phase boundaries.

Chapter 5 presents the preliminary results of two in-situ experiments performed using holo-tomography. The basic principle of the technique is introduced together with the description of the sample environment. Preliminary results about an oxidation and reduction experiment are presented. These are discussed qualitatively in terms of reaction kinetics and microstructure evolution.

Chapter 6 summarizes the results presented in the thesis and the possibility of using the data acquired during this work for future nickel coarsening simulations.
Chapter 2

Experimental methods

The aim of this chapter is to provide a guide on the experimental procedure adopted to obtain the results presented in the following Chapter 3 and Chapter 4. The chapter describes the entire pipeline for acquisition and analysis of ex-situ ptychographic tomography data, showing the sample preparation procedure, the developing of the sample environment, and covering the methods for segmentation and data analysis.

2.1 Sample preparation

2.1.1 Challenges

Sample preparation for X-ray nanotomography is crucial for obtaining clear, accurate and high-quality 3D data. The sample should have a small cross section in order to allow enough X-ray transmission and limit the time of the acquisition. On the other hand, a statistically representative volume is required to accurately describe the microstructure [40]. In order to avoid artifacts during the tomographic reconstruction, the sample cross section should not vary during the rotation around the rotation axis. Therefore, ideally, the region to analyze should have a cylindrical shape.

The first examples of applying X-ray nano-CT for imaging SOFC electrodes were carried out using lab-based instruments, utilizing phase and absorption
In this case, from an anode-supported SOFC electrode, a small specimen including the dense electrolyte was mechanically removed. However, this sample preparation procedure leads to irreproducibility in sample shape (and volume) and expose the sample to microstructural local damage.

Later works on synchrotron-based nano-tomography used the focused ion beam (FIB) lift-out to produce sample of the required size and geometry. In this case, starting from the bulk material, the desired shape is milled out whilst removing enough material around the sample to allow the subsequent cutting. When this initial stage is complete, a tungsten needle is positioned close to the sample using a build-in micro-manipulator and micro Pt deposition. Finally, the sample is cut and positioned on an appropriate sample holder for the X-ray tomography. While the lift-out technique allows control over the size and the shape of the sample, it presents several disadvantages. For example, the Pt welding is risky and prone to failure during the preparation. Furthermore, Shearing et al. reported that the platinum welding could not withstand the high characteristic temperatures of SOC operation resulting in sample movement. The challenge in preparing samples for time-dependent studies at high temperature is the ability to create specimens large enough to be manually handled whilst, at the same time, present a region which meets the requirements for nano-tomography. Kennouche et al. recently reported a new sample preparation technique: the bulk material was first fragmented and a piece with a sharp tip was then selected. The latter was polished and milled using the focused ion beam in order to obtain a cylinder of 40 $\mu$m in diameter and 80 $\mu$m in height.

Inspired by this recent work, we developed a sample preparation technique which involves a hybrid approach between precision polishing and FIB-milling. The details of this new approach will be discussed in the following section.
2.1. Sample preparation for ex-situ X-ray nano-tomography

In this work, all the samples were prepared from a typical Ni-3YSZ (Yttria-Stabilized-Zirconia, mol. 3% $Y_2O_3$) anode supported half-SOC with a 15 $\mu m$ thick Ni-8YSZ hydrogen electrode and 10 $\mu m$ thick 8YSZ (Yttria-Stabilized-Zirconia, mol. 8% $Y_2O_3$) electrolyte where the Ni:YSZ volumetric ratio is 40/60%. Further details on the cell production can be found elsewhere [44]. The NiO-YSZ cermet was reduced for 1h at 850 $^\circ$C. From the bulk material, slices are carefully cut using a diamond saw from the reduced half-cell (~300 $\mu m$ in thickness). Afterwards, the slices are placed in hard wax to be mounted into the precision polishing machine *Multiprep*. Two configurations have been produced and the general polishing procedures are schematized in figure 2.1. The aim of the polishing procedure is to reduce the size of the sample in order to reduce the FIB milling time.

In order to facilitate the description, a system of coordinates is introduced in 2.1 (a) and (c). In *procedure 1*, the previously cut slice is oriented so that the z-axes is parallel to the direction of the cell thickness. The slice is first polished along the x-axes (figure 2.1 (a)) and finally along the y-axes (figure 2.1 b). Samples of 60x60 $\mu m$ and 300 $\mu m$ in length are produced. In this case, the cell thickness is limiting the dimensions of the final specimen. Samples of this dimensions, even if bigger than the ones produced by *lif-out*, are still difficult to be manually handled.

To overcome these limitations, a different geometry has been produced. In procedure 2 (figure 2.1 (c),(d)), the previously cut slice is mounted on the polishing machine with its long edge oriented with the z-axes. In this configuration, the slice is first polished along the y-axes. Since the cell thickness is not limiting the length of the specimen, 3 mm long samples can be polished down to a thickness of around 60 $\mu m$ (Figure 2.1 (c)). Subsequently, the specimen is polished along
CHAPTER 2. EXPERIMENTAL METHODS

Figure 2.1: Schematic procedures for the precision polishing.

Procedure 1

a) 

b) 

Procedure 2

c) 

d) 

the x-axes with a small angular offset able to form a truncated pyramid shape with a top square cross section of roughly 60x60 µm (2.1 (d)). Examples of results after polishing for both the configurations are shown in figure 2.2 (a) and (c).

Following procedure 2, the polished samples are big enough to be safely handled with tweezers and mounted manually on the sample holder.

For the ptychographic measurements performed in this work, the standard sample holder used at the X12SA (cSAXS, PSI) beamline has been used. The
2.1. SAMPLE PREPARATION

Figure 2.2: Final results of the sample preparation procedures. (a) sample after the precision polishing procedure 1 and (b) its final shape after FIB-milling. In (b), the top layer of the cylindrical pillar is the electrolyte. (c) top view of the sample after the precision polishing procedure 2 and (d) its final shape after FIB milling. In (d) the electrolyte is behind the porous electrode and is not visible in the presented micrograph.

cSAXS holder is specialized to accommodate samples produced by the lift-out technique and is not optimal for ex-situ studies at high temperature. Therefore, it was modified in order to accommodate the sample in its center of rotation and minimize sample tilting. The specimen was temporally mounted using super glue (Loctite 460, Loctite Corp., ONT) prior to being securely attached with platinum paste (CN38-019B Platinum Conductive Paste, Ferro). The entire procedure is carried out manually under an optical microscope to be within 100 μm from the beamline rotation axis. The super glue allows enough flexibility for fine adjustment of the sample position. Once the sample is centered, platinum paste is used to secure it for high-temperature treatment. Finally, FIB milling
(Zeiss, CrossBeam X1540) is used to produce the cylindrical pillars which are analyzed during ptychographic tomography. The dimension of the pillars varies from experiment to experiment. As examples, Figure 2.2 (b) and (d) shows two typical samples at the end of the FIB milling for the polishing procedure 1 (b) and 2 (d).

2.2 Sample Environment

X-ray tomography techniques are non-destructive, allowing dynamical observation of the morphological change of the same microstructure while it is operating. However, in-situ studies of SOC materials are challenging and not always possible given the present X-ray facilities. A step towards ambitious in-situ studies, is performing time-lapse ex-situ 3D observations of SOC electrodes after exposure to relevant conditions. In general, the sample is first analyzed in its pristine state. Subsequently, it is removed from the X-ray stage and treated at high temperature in controlled atmosphere conditions.

In summary, a suitable furnace for this scope should have the following characteristics:

- Reduced size to be easily transportable to the beamline.
• Reach temperatures characteristic for SOC operation (850-1000 °C).

• Provide the right atmosphere ($H_2$ and Air).

• Allows easy sample insertion and removal without risk of damaging the specimen.

In order to meet these requirements, a small custom-made made furnace has been developed for the scope (see Figure 2.3. A resistive heating element spirals around an alumina ($Al_2O_3$) tube to provide a uniform high-temperature environment. The alumina tube represents the heating chamber and is responsible for delivering gas to the sample. The tube is connected to an external gas supply through a *swagelock* connection. The gas flow is regulated before entering the heating chamber using a manual flowmeter. The temperature is checked inside the heating chamber by a thermocouple placed 5 mm from the sample. The latter is inserted into the furnace using a *sample carrier*. The *sample carrier* consists of a second alumina tube smaller than the heating chamber, modified in order to accommodate the cSAXS holder at one of its end.

The furnace is capable of reaching a maximum temperature of 890 °C with a maximum ramping rate of 10 °C/min. The temperature is controlled by a *Eurotherm* device within an error of ± 1 °C.

2.3 X-ray Ptychography

2.3.1 Basic principle

X-ray ptychography is a scanning-based realization of the family of coherent diffractive imaging (CDI) techniques. In particular, images of the sample are produced by combining a set of several far-field scattering patterns obtained with the same coherent, micrometer-sized X-ray probe at overlapping spots. In order to explain the working principle of ptychography, we refer to Figure 2.4.
Figure 2.4: Schematic diagram of a classic ptychographic setup. A coherent beam is directed to the sample and it can be described by a probe function $P(r)$. The beam travels across the object (sample) described by an object function $O(r)$. The probe is then transformed in the exit field $E(r)$ and, once it reaches the detector, it takes the form of its Fourier transform denoted with the function $D(r)$.

A coherent X-ray beam is sent to the object (sample) and, just before interacting with it, it can be described as a probe function $P(r)$. As the beam travels across the object (described by the function $O(r)$), the electric field of the probe is changed and, as it leaves the object, it can be described by a function $E(r)$:

$$P(r)O(r) = E(r) \quad (2.1)$$

The detector $D$, placed in the far-field region, will record the Fourier transform of the exit field so that:

$$D(r) = \mathcal{F}[E(r)] = \mathcal{F}[P(r)O(r)] \quad (2.2)$$

where $\mathcal{F}$ indicates the Fourier transform. Therefore, in order to retrieve the object function (and the probe), we can write:

$$O(r) = P(r)^{-1}\mathcal{F}^{-1}[D(r)] \quad (2.3)$$

where the symbol $\mathcal{F}^{-1}$ stands for the inverse Fourier transform. In order to
obtain a unique solution for the object function, constraints must be applied. In particular, we can impose that the intensity recorded at the detector, represent the square amplitude of the function $D(r)$. Therefore:

$$I(r) = |D(r)|^2 = (\mathcal{F}[P(r)O(r)])^2$$

(2.4)

The second constraint comes from the acquisition of overlapping measurements. As introduced before, in the ptychographic procedure, multiple overlapping measurements are used to cover the entire sample area. Therefore, regions of the sample are imaged multiple times with approximately the same probe, giving an over-determined object. It has been shown experimentally that the constraints are sufficient to converge towards a reasonable solution [45, 46, 47].

Two main algorithms have been proposed to solve the inverse problem and retrieve the object function from overlapping scattering patterns. The first one has been proposed by Rodenburg et al. [46] and it requires a known probe function. The second one, developed by Thibault et al. [45], does not require the knowledge of the probe a priori and therefore is more useful in practice. In the ptychographic studies presented in this work, the algorithm proposed by Thibault et al. has been used.

The underlying idea is to express the data as a point in Euclidian space and the two constraints as projections of that point. The optimal solution is obtained when the two constraints are fulfilled. Therefore, in other words, when the distance to the constraints is minimized [45]. In order to introduce the basic principle of the method, let us consider the set of all exit fields:

$$EE = \{E_1(r), E_2(r), ..., E_N(r)\}$$

(2.5)

The intensity constraint can be written as:
\[ \Pi_F(EE) : E_j \leftarrow E_j^F = \text{amplitude}(E_j) \]  

(2.6)

Where with \textit{amplitude}(E_j) we denote the substitution of the amplitude of the Fourier transform of \( E_j \) with \( \sqrt{I_j} \) (intensity recorded by the detector) and transforming back to the corrected field \( E_j^F \). Since the probe function \( P(r) \) is not known, the probe and the object function are found solving an optimization problem. In particular, we need to find \( P \) and \( O \) which minimize equation 2.7

\[ ||EE - EE^O||^2 = \sum_i \sum_r |E_j(r) - P(r - r_j)O(r)| \]  

(2.7)

The optimization problem can be solved using a suitable optimization method as, for example, the line minimization method proposed in [45]. Indicating now, \( P_{\text{min}} \) and \( O_{\text{min}} \) the functions which minimize equation 2.7, the overlap constraint can be written as:

\[ \Pi_O(EE) : E_j \rightarrow E_j^O = P_{\text{min}}(r - r_j)O_{\text{min}}(r) \]  

(2.8)

where the super and sub-script \textit{O} indicates the overlapping constraint. The iterative procedure can be written as:

\[ EE_{n+1} = EE_n + \Pi_F(2\Pi_O(EE) - EE) - \Pi_O(EE) \]  

(2.9)

In the iterative algorithm, convergence can be checked by measuring the distance between measured and calculated intensities or simply using the difference between consecutive iterations \( ||E_{n+1} - E_n|| \).

Processing all probe illuminations allows determining both object and probe simultaneously. However following this method, there will always be a different set of solutions \( P' \) and \( O' \) on which the algorithm can converge to. The existence of this new set of solutions depends on the distribution of \( r_j \). Therefore, in order to avoid such situation, Diederlof et al. [48] proposed the use of non-regular scattering pattern (e.g concentric circles, Fermat spiral) avoiding raster
2.3. X-RAY PTYCHOGRAPHY

scan artifacts.

2.3.2 Electron density

The presented algorithm allows obtaining ptychographic projections which can be assembled into a 3D dataset via tomographic reconstruction. From the projections, the 3D electron density distribution in the sample can be calculated. The complex refractive index of a given material can be expressed as:

\[ n = 1 - \delta - i\beta \]  

(2.10)

where \( \delta \) is the contribution of the phase while \( \beta \) is the absorption coefficient. Using ptychography, the 3D reconstruction of \( \delta(r) \) in the material can be retrieved. The \( \delta \) can be related to the electron density of materials using equation 2.11.

\[ \rho_e(r) = \frac{2\pi\delta(r)}{r_0\lambda^2} \]  

(2.11)

where \( \rho_e(r) \) is the electron density, \( r_0 \) is the classical atomic radius and \( \lambda \) is the wavelength of the incident radiation. Finally, the electron density can be converted to mass density following the relation:

\[ \rho_e = \rho_m \frac{N_a \sum_j a_j Z_j}{M} \]  

(2.12)

where \( N_a \) is the Avogadro’s number, \( M \) is the molar mass and \( a_j \) is the number of atoms having atomic number \( Z_j \). Therefore, ptychography has the advantage of being quantitative, allowing the identification of different phases within the sample at the nanometer scale [49].

2.3.3 X-ray computed tomography

3D tomographic reconstruction is a general technique which allows obtaining the 3D model of an object starting from a collection of 2D projections. There
are two ways of achieving this goal: analytic reconstruction [50, 51], and algebraic reconstruction [52]. The analytic reconstruction is the most widely used technique and, in this work, all the 3D reconstruction are based on the filtered back projection algorithm. In the filtered back projection algorithm, the object is assumed to be continuous and the method uses mathematical transformations between the object and its projections.

In order to understand how the analytic reconstruction works, we refer to the well known Beer-Lambert law for X-ray absorption. In this section, we will only refer to the parallel beam geometry while other extensions can be made using other forms of illumination such as cone beam or fan beam geometry [53]. Furthermore, only the 2D case is considered. The absorption coefficient for a single X-ray, \( \mu_r \) can be calculated dividing the object into multiple segments, each of length \( x \) characterized by their own absorption coefficient \( \mu_i \). The Beer-Lambert law for the system can be written as:

\[
I = I_0 e^{x \sum_i \mu_i} \tag{2.13}
\]

where \( I \) is the transmitted intensity and \( I_0 \) is the intensity of the incident beam. Therefore, the total absorption coefficient represents the linear combination of the single absorption coefficient \( \mu_r = \sum_i \mu_i \). During tomography, measurements are recorded for each detector pixel for multiple angles. When this operation is virtually done on a 2D object, the result is a typical pattern called a sinogram.

Knowing the continuous description of the 2D object \( f(x, y) \), the sinogram can be computed performing the line integral:

\[
g(s, \theta) = \int_{-\infty}^{\infty} f(s \cos \theta - u \sin \theta, s \sin \theta + u \cos \theta) du \tag{2.14}
\]

where \( g(s, \theta) \) represents the sinogram function in the \( s \) and \( \theta \) domain, \( s \) is pixel location relative to the center and \( \theta \) is the angle. Equation 2.14 is known as
the Radon transform of $f$.

In the tomographic reconstruction, we seek to reconstruct the object $f(x, y)$ knowing the function $g(s, \theta)$. Therefore, we need to find the inverse radon transform $R^{-1}$ so that:

$$R^{-1}(g(s, \theta)) = f(x, y)$$  \hspace{1cm} (2.15)

The Fourier slice theorem states that the Fourier transform $\mathcal{F}$ of a parallel beam projection, equals a slice of the 2D Fourier transform $\mathcal{F}_2$ of the object, described by the continuous function $f(x, y)$:

$$\mathcal{F}[g(s, \theta)] = \mathcal{F}_2[f](x, y) = F(t \cos \theta, t \sin \theta)$$  \hspace{1cm} (2.16)

where $t = 1/s$. Finally, the object $f(x, y)$ can be obtained using the inverse Fourier transform and applying a ramp filter:

$$f(x, y) = \int_0^{2\pi} (g * r)(\theta, x \cos \theta - y \sin \theta) d\theta$$  \hspace{1cm} (2.17)

where $r(s) = \frac{1}{2} \int_{-\infty}^{\infty} |t| \exp(i2\pi ts)$. Intuitively, the physical interpretation of the method is to take the projections $g$ for every angle $\theta$ and back-project them along their projection axes. The ramp filter $r$ acts as high-pass filter.

In the previous brief derivation, the object and the angle variations have been considered continuous. For further details about the discrete case, the reader can refer to [54, 55].

### 2.4 Segmentation

The acquisition of high-quality data is the first step in obtaining accurate 3D quantifications of the material microstructure. In order to obtain reliable measures of phase properties (e.g. surface areas, triple phase boundaries, connect-
ivity etc...) is necessary to assign to each voxel of the gray-scale data, its characteristic label. This process is referred as segmentation and it is a crucial step in the pipeline of the data analysis. Many factors can affect the quality of the segmentation such as the nature of the sample, contrast, signal-to-noise ratio and artifacts due to the reconstruction (e.g ring artifacts).

Figure 2.5: Segmentation procedure. (a) 2D histogram of the gray-scale data from a SOC fuel electrode, acquired via ptychographic tomography. In the figure, three threshold regions are identified. In (b), (c) and (d), the voxels identified by the outlined regions are highlighted with their respective color.

In very simple cases, where each phase can be directly linked to distinct levels of intensity in the image data, satisfactory results can be obtained by simply applying a basic threshold of the intensities. However, in materials characterized by complex microstructures, large overlaps between the intensity of different phases are usually occurring. Therefore, in such cases, simple thresholding does not yield accurate data segmentations. Different methods have been proposed
to accurately perform the segmentation of SOC microstructure both from FIB-SEM data to X-ray nano-tomography data [?, 57]. In this work, a simple 2D histogram is computed from the reconstructed volume, providing a distribution map of intensities gradients versus the intensity values of each individual voxel. An example of such a map is presented in figure 2.5.

In the image, three low gradient clusters are identified, signed with label Pore, YSZ and Ni. The low gradients of intensities are found in the internal phase regions. Contrarily, voxels with high gradients are located near the interfaces and form the characteristic arcs present in figure 2.5. Following this approach, the thresholding is done choosing a particular region (thresholding region) of the map and assigning all the voxels within that region to a particular phase. The choice of the thresholding region is done manually, visually inspecting the results applying a label mask as in Figure 2.5 (b),(c),(d).

At this stage, voxels which are not inside the thresholding regions are not assigned. These voxels are usually very close to the interfaces and therefore difficult to be labeled based on visual inspection. Therefore, the unknown voxels are assigned to their closest phase.

2.5 Data analysis

2.5.1 Surface area and TPB density

As explained in Chapter 1, solid oxide cell electrodes are complex composites materials where the distribution and interconnection of the constituent phases are critical for the electrochemical performance. The location of the triple phase boundaries determines where the electrochemical reaction takes place, and their number (density) affect the cell activation overpotential. Therefore, the precise identification of phase surface areas and triple phase boundary density is crucial in understanding the electrochemical performance of the cell.
In this work, in order to accurately obtain parameters such as TPB density and specific surface area, the algorithm developed by Joergensen et al. is used [58]. In particular, the method reconstructs all the two-phase interfaces in the structure as connected polygons. In this representation, each polygon shares edges and vertices with adjacent polygons. After constructing the data structure, the TPB lines are identified as the edges that are shared between the three polygons belonging to the three different phases (Ni, YSZ, and Pore). The details of the algorithm can be found in [58], while here only its main principles are reported.

Starting from the segmented data structure, a *signed function* is \( \phi \) introduced which, for every voxel, represent the distance between that voxel and the closest point present on the interface. The signed function will have positive values outside the interface and negative values inside the interface. With this representation, the interface is implicitly contained in the signed function as its 0 iso-level. The signed distance function is evaluated on a regular grid and is therefore discrete. Let us consider three phases which we denote with \( P_1 \), \( P_2 \) and \( P_3 \). Two signed function \( \phi_1 \) and \( \phi_2 \) are introduced and represent the implicit representation of \( P_1 \) and \( P_2 \). It is worth mentioning at this point that, a function \( \phi_3 \) is not needed since it can be derived by \( \phi_1 \) and \( \phi_2 \). From the implicit functions \( \phi_1 \) and \( \phi_2 \), a phase map is created where to each voxel location \( x \) is assigned a label \( L(x) \) which describes the phase to which it belongs.

Once the phase map is created, a simple polygonization scheme is applied which runs for every voxel of the phase map. Once the polygonization is performed, in order to achieve a sub-voxel accurate description of the interfaces, a vertex movement scheme is applied using the following procedure. For each vertex of the polygon, the value of the appropriate function \( \phi(x_v) \) and its gradient \( \nabla \phi(x_v) \) are computed. Subsequently, the new vertex position is found at \( x_{new} = x_v - \phi(x_v)\nabla \phi(x_v) \). Given a continuous signed distance function, this
movement scheme will move the vertex exactly onto the interface represented by the 0 iso-level of the signed distance function. After this step, the vertices from adjacent polygons are merged and neighborhood connection are stored for each polygon.

Using this mesh representation, it is straightforward to calculate both two-phase boundaries and TPB density. Area calculations are simply performed summing all the area of the polygons that separate two pairs of phases. The TPB edges are identified as the outline of the interface surface between $P_1$ and $P_2$. Finally, the TPB length can be calculated by summing the length of the edges that make up the TPB curves.

\subsection{2.5.2 TPB tortuosity and critical pathways}

The TPB tortuosity can be considered as a measure of how tortuous the pathways are which connect the TPB sites to a respective source or destination. In practice, the shortest distance between a TPB site and its source/destination is computed through a specific phase. Consequently, the Euclidian distance across the phase boundary is computed and the tortuosity value is obtained from the ratio of this two distances. By performing the same calculation on every TPB sites present in the volume, the distribution of TPB tortuosity is obtained.

The basis of the calculation is the possibility of computing the distance between two set of voxels denoted as source and destination. Following the procedure proposed by Jørgensen et al [59], the source is the set of voxels which is adjacent to the bottom edge of the considered volume, while the destination is represented by the voxels which belong to the phase of interest and participate to the TPB site. Thus, to calculate the TPB tortuosity, the distance from the source to every location within the phase of interest is calculated. Therefore, a distance map is computed through the phase which assign to every voxel its distance from the source. The distances from the TPB sites are obtained by
reading the value of the distance map at the TPB sites. Since the location of the TPB sites is known from the calculations presented in the previous section, this method allows computing only one distance map for each phase. The tortuosity at each TPB site is obtained as the distance through the phase network divided by the Euclidian direct distance. This calculation is performed for each of the three phases.

The TPB critical pathways can be seen as the thinnest section of the widest pathways which connects each TPB site through a particular phase. Following an alternative formulation, the TPB critical radius can be considered as the radius of the largest sphere which can pass through the network structure to reach a particular TPB site. In order to identify the critical pathway radius, the initial network is eroded in small steps, checking each time the percolation of a TPB site. Thus, the critical pathway radius is the one where the TPB site becomes non-percolated. Similar to the TPB tortuosity distribution, repeating this calculation for every TPB site in the volume allows obtaining a distribution of critical radii in the sample.

The TPB tortuosity and critical pathways distributions depend on the choice of the starting plane used as source in the calculation. Therefore, in this work, the calculation is repeated from all the 6 sides of the analyzed volume. In this way, possible anisotropies in the sample can be detected [59].

2.6 Conclusions

The aim of this chapter was to provide a guide on the experimental procedure adopted to obtain the results presented in the following Chapter 3 and Chapter 4.

The general pipeline for acquisition and analysis of ptychographic tomography
data has been summarized. A new sample preparation technique has been
developed in order to produce sample suitable for \textit{ex-situ} study at high tem-
perature. The combined use of precision mechanical polishing and FIB-milling
allows the production of samples which are feasible to be manually handled
and, at the same time, have a region which is optimal to be analyzed using
nano-tomography. A sample environment for \textit{ex-situ} tomography has been de-
veloped. In addition to providing the high temperatures characteristic of SOC
operation, the furnace is designed to be transportable and allow easy sample
insertion.

The basic principle of ptychography is briefly summarized together with the
principles of the filtered back projections algorithm.

Following in the pipeline, the segmentation procedure used in this work has
been explained. Due to the high contrast ensured by ptychography, a simple
segmentation method based on 2D thresholding has been implemented. The
method requires human interaction in choosing the thresholding regions, while
the unknown voxels are assigned later with a morphological operation.

The algorithms used to retrieve important microstructural parameters such as
surface areas, TPB density, TPB tortuosity and critical pathways have been
described. For the accurate measurements of surface areas and TPB density,
a sub-voxel accuracy procedure has been used. The approach describes the
segmented data as signed functions and applies a polygonization procedure to
describe the phases as meshes. Interface areas and TPB density are computed
simply adding face areas and vertices lengths of the polygon which describes
the phases.
Chapter 3

Tracking SOC Microstructural Evolution in a Redox Cycle by Ptychographic Nano-Tomography


Abstract

For solid oxide fuel and electrolysis cells, precise tracking of 3D microstructural change in the electrodes during operation is considered critical to understand the complex relationship between electrode microstructure and performance. Here, for the first time, we report a significant step towards this aim by visualizing a complete redox cycle in a solid oxide cell (SOC) electrode. The experiment demonstrates synchrotron-based ptychography as a method of imaging SOC electrodes, providing an unprecedented combination of 3D image quality and spatial resolution among non-destructive imaging techniques. Spatially registered 3D reconstructions of the same location in the electrode clearly show the evolution of the microstructure from the pristine state to the oxidized state.
and to the reduced state. A complete mechanical destruction of the zirconia backbone is observed via grain boundary fracture, the nickel and pore networks undergo major reorganization and the formation of internal voids is observed in the nickel-oxide particles after the oxidation. These observations are discussed in terms of reaction kinetics, electrode mechanical stress and the consequences of redox cycling on electrode performance.

3.1 Introduction

SOCs may undergo several redox-cycles during their lifetime. If fuel is supplied to the anode, the microstructure remains in its reduced state. However, if the fuel supply is interrupted, oxygen will oxidize the metallic nickel (Ni) in nickel oxide (NiO). Furthermore, oxidation can occur in conditions of high fuel utilization where the oxygen activity rises above the Ni and NiO equilibrium. When the reducing atmosphere is recovered, the newly formed NiO is reduced to nickel but, in many cases, the original microstructure is not recovered [14].

Redox cycle experiments on NiO/YSZ anodes (56 wt % NiO, 44 wt % of YSZ) at 1000 °C have shown a significant volume increase (3–9%) on re-oxidation [60]. Furthermore, higher oxidation temperatures yield to increased macroscopic strain leading to spontaneous mechanical failure [61]. However, in many reports, the rate of expansion under similar conditions differs, testifying the importance of the microstructure [62]. The water content in the oxidizing atmosphere is also expected to play a role in the oxidation rate, as reported in [63] where the macroscopic expansion increased from 0.68 % to 0.96 % when adding 6% of $H_2O$ to the dry air. Redox cycles have a strong impact on the electrical conductivity of the Ni-YSZ cermet. In some cases, an increase in conductivity was observed after the first redox cycle even though the conductivity decreased after multiple cycles [63]. Electrochemical impedance studies showed a decrease in the frequency of the peak corresponding to charge transfer resistance, sug-
suggesting an increase in the polarization due to the decrease in the active TPB density [60].

In order to understand the effect of oxidation on Ni-YSZ electrodes, FIB-SEM studies have been carried out on pure nickel particles. After oxidation, the particles presented a sponge-like structure with trapped porosity [64]. However, to the knowledge of the authors, only a few studies on real Ni-YSZ cermet have been performed. The non-destructive nature of X-ray tomography allows dynamic ex-situ or in-situ studies. The first steps in this direction are reported in [65] where nickel particle oxidation was studied using X-ray tomography. Only 2D projections were acquired and the nickel particles were isolated and not part of a composite electrode. Shearing et al [42] realized the first ex-situ oxidation tomography experiment in which a real SOFC electrode was successfully analyzed after several oxidation steps at different temperatures. However, in their work, only the effect of oxidation was examined and no reduction studies were performed.

In this chapter we describe the first application of ptychographic X-ray computed tomography (PXCT) on SOC electrodes and the first “ex-situ” redox cycling experiment in which the same microstructure is first analyzed in its pristine state and then successively oxidized and reduced.

### 3.2 Experimental methods

#### 3.2.1 Sample preparation

The sample was prepared from a typical Ni-3YSZ (Yttria-Stabilized-Zirconia, mol. 3% Y2O3) anode supported SOFC half-cell with a 15 µm thick Ni-8YSZ hydrogen electrode and 10 µm thick 8YSZ (Yttria-Stabilized-Zirconia, mol. 8%Y2O3, mol 8% Y2O3 ) electrolyte. The Ni:YSZ volumetric ratio is 40/60%. Following the preparation explained in chapter 2, a 3 mm long and 300 µm
wide slice was carefully cut using a diamond saw from the reduced half-cell (300 μm in thickness). The final shape of the sample has been produced using the procedure described in detail in Chapter 2. FIB milling was used to produce a cylindrical pillar: 17 μm in diameter and ca 15 μm in height. FIB milling enables positioning of the imaging volume close to the holder’s center of rotation and, more importantly, has the ability to place the electrolyte-electrode interface in the imaged volume.

3.2.2 Tomography procedure

The nano-tomography experiment was performed at the X12SA (cSAXS) beamline at the Swiss Light Source, Paul Scherrer Institut, Switzerland. The ptychography procedure was carried out at 7.2 keV. The scanning field of view acquired was around 24 by 15 μm with a scanning step of 1.0 μm. At each scanning point, a diffraction pattern was recorded 7.4 m downstream of the object using a Pilatus 2M detector with 172 x 172 pixel size and 0.1 s exposure time. Diffraction patterns with sizes of 400 x 400 pixels were used in the ptychographic reconstruction, giving an object pixel size of 18.4 nm. For each projection, one thousand iterations of difference map followed by 200 iterations of maximum likelihood refinement [66] were applied in the reconstruction. For each dataset, 500 projections over an angular range of 180 degrees were collected. Three-dimensional ptychographic computed tomograms [67] were obtained through fine alignment of the reconstructed 2D projections and filtered back projection. The sample was initially imaged in the pristine state and then subsequently in the fully oxidized and reduced states after each heat treatment to form a spatially coherent image of the electrode evolution (The diagram of the redox treatment is presented in Figure 3.1).

The oxidation and the subsequent reduction treatments were performed in the small tube furnace described in Chapter 2. The sample was treated at 850 ° with a flow rate of 5 l/h of either air or a gas mixture of 4% H2 in N2 respectively for the duration of the entire heating cycle. The heating time at maximum
3.2. EXPERIMENTAL METHODS

Figure 3.1: Diagram of the redox-acquisition procedure. The sample is first analyzed in its pristine state (red point), after three hours of oxidation (green point) and one hour of reduction (black point) at maximum temperature (850 °C).

Temperature was 3h for the oxidation and 1h for the reduction. The ramping rate was 10 °C /min for both heating and cooling.

3.2.3 Image analysis, segmentation, registration and microstructural quantification

Due to the excellent quality and the quantitative nature of the ptychographic image data, the raw volumes were easily segmented using the 2D (intensity vs. intensity gradient magnitude) histogram thresholding procedure (Chapter 2). Microstructural parameters such as surface areas and percolating triple phase boundary length were calculated as described in Chapter 2 and in [59].

The oxidized and reduced datasets were registered to the pristine dataset in 3D through a rigid transformation computed by the iterative closest point algorithm [68]. Only points sampled from the YSZ phase were used, allowing registration of the two datasets even under severe changes to the morphology.
and appearance of the Ni, NiO and pore phases. All the algorithms for segmentation and data analysis were written in-house using MATLAB.

3.3 Results

3.3.1 Image quality

The pristine Ni-YSZ anode microstructure studied in this work is presented in Figure 3.2. Figure 3.2 (a) shows an example of a cross-sectional image slice taken from the raw 3D data-set.

![Figure 3.2](image-url)

Figure 3.2: (a) Two-dimensional slice from the entire 3D volume of the pristine Ni-YSZ electrode (raw data). (b) Line profile indicated by the red line in (a) and (b) showing 50 nm resolution by the 10 %-90 % criteria. (c) Three-dimensional rendering of a region containing the electrode-electrolyte interface.

In the image, the bright phase is nickel, the gray phase YSZ and the pores and free space around the sample are dark. The image contains the electrode-electrolyte interface where the dense electrolyte is seen in the upper right part
of the slice. Figure 3.2 (b) shows an intensity profile plot corresponding to the red line indicated in 3.2 (a). Using the 10-90 % criteria [49], the 2D resolution is 50 nm while a 3D resolution of 55 nm was calculated from the entire volume using the Fourier shell correlation method[49]. The image in Figure 3.2 (a) shows no significant artifacts and a high signal-to-noise ratio, enabling reliable segmentation. Figure 3.2 (c) shows a 3D sub-volume rendering of the microstructure at the electrode-electrolyte interface.

3.3.2 Overall redox induced microstructural changes

The effect of the redox-cycle is summarized in Figure 3.3 in which slices of the spatially registered volumes are presented.

![Figure 3.3](image)

**Figure 3.3:** A slice through a sub-volume at identical locations in the electrode in the pristine (a), oxidized (b) and reduced (c) states. In (a) and (c) the pores are depicted in black, the YSZ in gray and the Ni in white. In (b) the brightest phase is NiO. The red arrows in (b) and (c) show the formation of cracks while the green circles in (b) highlight hollow NiO structures. The red rectangle in (a) and (c) indicate locations with a change in the morphology of the nickel phase after the redox cycle. The blue triangles in (a), (b) and (c) mark the same feature in the three different states illustrating the spatial alignment of the volumes.

Triangle markers are used to guide the eye to follow the same individual particles during the redox cycle. The original microstructure (Figure 3.3 (a)) is directly compared with the oxidized state (Figure 3.3 (b)) and the reduced state (Figure 3.3(c)). In Figure 3.3 (b) the brightest phase is now NiO and in Figure
3.3(c) the intensity of the phases is the same as in (a). Ptychography recovers the material’s electron density. The weak contrast in (b) between the solid phases is thus due to the similar electron density of NiO and YSZ. Examining the entire volume confirms that nickel was fully oxidized to nickel-oxide in the sample. The difference in unit cell volume between nickel (43.9 Å) and nickel oxide (72.93 Å$^3$) [69] leads to a considerable volume expansion, resulting in a reduction of total porosity of the sample as seen in Figure 3.3(b). The volume expansion also causes macroscopic deformation during oxidation and the induced stresses fracture the electrode YSZ backbone predominantly at the YSZ grain boundaries as illustrated by the red arrow in Figure 3.3 (b). The resulting microstructure after reduction is shown in Figure 3.3 (c). The presence of only three levels of intensity indicates that the NiO has been fully reduced to nickel. Comparing figure Figure 3.3 (a) and Figure 3.3 (c), it is evident that the original microstructure is not recovered and the morphology of nickel and pores change drastically.

For a microstructure statistical analysis, a sub-set of 12x12x12 $\mu$m$^3$ was extracted from the entire dataset. The quantitative analyses are summarized in Table 3.1.

Figure 3.4 shows the continuous particles size distribution (PSD) of the same volume in the pristine and reduced state . The present work compares microstructure parameters of the same location in the sample as it changes during the redox cycle. Therefore, the analysis is less prone to the issue of representative volume size in contrast to previous studies in which parameters from different samples are compared.

Based on Figure 3.3 and the statistical analysis, the following observations can be made:

i) nickel particles appear smaller and more numerous. The particles mean
3.3. RESULTS

<table>
<thead>
<tr>
<th></th>
<th>Pristine</th>
<th>Reduced</th>
<th>Relative difference [%]</th>
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<td>9.0</td>
</tr>
</tbody>
</table>

Table 3.1: Microstructure parameters for the sample in the pristine and reduced state

radius decrease from 350 nm in the pristine state to 200 nm in the reduced state and a significant shift in the continuous PSD towards smaller particles is observed. However, the fragmentation does not affect considerably the nickel connectivity which only decreases from 98 % to 94 % of the total nickel phase (3.1).

ii) Nickel particles have become detached from the YSZ and their shape has changed considerably (see the red square in (a) and (c)). The first observation is confirmed by the decrease of the Ni-YSZ interface area (41 %). Furthermore, together with the shift in PSD, the change in shape towards a more rounded and fragmented structure contributes to the increase of 91 % in total Ni interface area.

iii) Many fine cracks appear at YSZ grain boundaries (red arrows in Figure 3.3(b) and Figure 3.3(c)). However, because of their limited size, they could not be detected by the segmentation algorithm and they have limited effect of the YSZ connectivity and particle size distribution presented in Figure 3.4. Thus, an analysis of pore and YSZ tortuosity is of limited use as it would potentially carry significant uncertainty.
iv) The pore structure follows the same behavior of nickel, presenting a shift in the PSD from a mean radius of 350 nm in the pristine state to 100 nm after the redox cycle. Furthermore, the connectivity increases from 90 % to 99 % most likely due to the nickel fragmentation which opens new porosity.

3.3.3 Local effect of the redox cycle

Figure 3.5 shows the detailed evolution of the microstructure in a sub-volume representative of many observed locations. In the pristine state Figure 3.5 (a), a nickel particle (black) is surrounded by
3.3. RESULTS

Figure 3.5: 3D microstructure evolution of a 2.5x1.8 \( \mu m \) size region of the electrode. (a) Pristine, (b) oxidized and (c) reduced state. In the insets, the top two-dimensional slice from the same volume is shown in pristine (a), oxidized (b) and reduced (c) state. (d) a magnified and rotated view of the NiO particle presented in (b)

the YSZ structure (gray). In the oxidized state (Figure 3.5 (b)) the oxidized nickel particle (green) has expanded in volume and cracks can be observed in the YSZ. We observe that these cracks correspond to the location of grain boundaries (locations of high YSZ surface curvature) testifying the presence of intergranular fractures. Moreover, it is observed that the NiO particle protrudes into these cracks and the surface appears rough and fragmented. The presence of fine NiO particles presents an image segmentation challenge hence the absence of a statistical analysis of the oxidized state in Table 1. As shown in Figure 3.3 (b) (green circles) and in Figure 3.5 (d), we observe that several
nickel oxide particles are hollow. These voids can be observed to be completely surrounded by NiO by careful inspection of the surrounding volume. In the pristine state, the nickel particle has a well-defined polyhedral shape, dictated by the surrounding YSZ. In Figure 3.5 the subset volume after the complete redox cycle is presented. The reduced state shows that the nickel has evolved to a more rounded and fragmented structure. Furthermore, the nickel particle is almost completely detached from the YSZ. These structural changes to the Ni phase are observed in the entire sample and their effects can be seen by the decrease in the Ni-YSZ interface area and the increase in Ni-pore surface area (Table 3.1) from the pristine to the reduced state.

3.4 Discussion

3.4.1 Void formation in NiO particles

In this work, NiO particle void formation has been observed for the first time in three dimensions. Based on these new insights, we propose a mechanism referring to nickel particle oxidation kinetics drawing on our observations and reports of Ni oxidation in other systems. The mechanism is schematized in Figure 3.6.

Oxidation commences with a thin (several nm) surface oxide layer on Ni particles that nucleates and thickens by ion electro-migration (Cabrera-Mott) while the oxidation mechanism is limited by ion diffusion through the oxide (Wagner) [70]. At the temperature of interest for this work (850 °C), the dominant mass-transport process for NiO growth is the outward migration of Ni ions along NiO grain boundaries and dislocations in the NiO layer [70, 71] causing the oxide growth to proceed at the NiO-air interface. At the oxide-metal interface, Ni cations are supplied to the oxide, either entering lattice interstices or by filling cation vacancies and leave Ni vacancies in the metal at the oxide-metal interface. Such vacancy injection increases the total free energy until is energetically favorable to nucleate voids at the metal-oxide interface or in the proximity of
Figure 3.6: Nickel particles oxidation mechanism. Vacancies and Ni$^{2+}$ ions are injected at the Ni/NiO interface. The Ni$^{2+}$ ions migrate through the NiO layer and react at the NiO/air interface causing the oxide growth. Ni vacancies migrate from the interface to the particle core, resulting in the nucleation and growth of a central void

defects or impurities.

Such phenomenon has been described in more detail by Hales and Hill [72] where the oxidation of Ni rods with different surface-volume ratio has been studied. Void nucleation at the metal-oxide interface in the case of SOC electrodes would lead to failure of the metal-oxide interface generating separated concentric oxide shells. However, such situation is not observed here. Alternatively, in [72] the authors pointed out the possibility that, in presence of impurities, internal voids may nucleate and grow before scale-metal adhesion is lost, permitting continued oxidation and therefore leading to the formation of hollow structures. In this case, void formation by vacancy coalescence could lead to two void morphologies:

1. Finely dispersed voids in the NiO network
2. Coalescence to large voids.

The latter situation is in line with the observed morphology of the voids and it is likely the mechanism occurring in this case.

After the initial Ni particle oxidation the proposed mechanism can be briefly summarized: simultaneous outwards migration of $Ni^{2+}$ ions through NiO and injection of vacancies from Ni/NiO interface into Ni; oxide scale grows by outwards migration of NiO/air interface; continual injection of vacancies and the inward migration of the Ni/NiO interface into the shrinking Ni volume creates a driving force for vacancy migration to the Ni particle core, resulting in the nucleation and growth of a central particle void.

3.4.2 YSZ grain boundary cracking and NiO intergranular protrusions

After oxidation, cracks in the YSZ can be observed throughout the electrode as shown in Figure 3.3 and 3.7. During oxidation, the electrode experiences considerable volume expansion generating stress on the YSZ structure. From 2b and 4b, one can notice that such stress leads to the formation of cracks mainly located at the YSZ grain boundaries. This observation is in line with reports by Lawrie et al. [73], who described the tendency to change from transgranular fracture mode to intergranular mode when fully stabilized YSZ is tested at 950 °C. However, the results were obtained on dense samples applying the double cantilever mechanical test. Such situations are expected to generate quite different stress distribution within the material. The fact that we observed mainly intergranular fractures is in line with what was reported by Fouquet et al. [62] and can be explained considering two combined effects:

1. YSZ grain boundaries that intersect Ni-YSZ interfaces are observed to create sharply defined dihedral angles. Therefore, when Ni oxidizes and
expands, it acts as a local stress concentrator.

2. NiO protrusions into the YSZ grain boundary cracks act as a wedge producing further stress intensification.

The NiO protrusion formation is considered a direct consequence of the YSZ cracking. Once the crack is formed, new channels for the oxygen are produced and the oxide can grow within the crack itself.

### 3.4.3 Nickel rearrangement after reduction

From Figure 3.3 (c), it is evident that the original nickel microstructure is not recovered in agreement with previous reports [36]. During cell production, in order to achieve the starting microstructure presented in Figure 3.3 (a), a sintered cermet NiO-YSZ is reduced at high temperature. Reduction of NiO particles begins with an induction period for the nucleation of metallic clusters which then grow into crystallites [74]. The reduction reaction occurs at the interface between NiO and Ni and it is not controlled by Ni diffusion through the NiO layer (as in the case of oxidation) [75]. Therefore, during the initial NiO reduction, the reaction starts from the exposed surface of the NiO particles and proceeds towards the YSZ structure which acts as a template for the final
microstructure. In the case of a cracked YSZ backbone (Figure 3.3 (b)), hydrogen molecules can permeate the newly created channels. Thus, the reaction starts radially and proceeds inwards from the NiO particle surface leading to the structure presented in Figure 3.8.

![Figure 3.8: Nickel particle in Figure 3.4 before and after the redox cycle. (a) nickel particle before the redox cycle. (b) nickel particle after the redox cycle.](image)

Furthermore, once the reduction reaction is complete we speculate that, due to the presence of the observed voids, the Ni particles are free to shrink towards the center of the particle driven by the reduction of Ni-void interface energy producing dense nickel structures. The combined effect of a radial reaction front and the coalescence of the metallic crystallites within the internal voids lead to the nickel contraction away from the YSZ backbone.

Due to the spatial resolution limit, we cannot state if the hollow NiO particles have fractured due to volume expansion during oxidation. If this occurs, during reduction fractures would enable hydrogen access to the voids and thus NiO particle reduction may occur from the NiO particle exterior and interior surfaces leading to the Ni particle fragmentation observed in Figure 3.3 (c) and 3.5 (c).

Finally, due to NiO volume contraction on reduction and the corresponding increase in pore volume, Ni surfaces are now free to minimize the surface energy
eliminating sharp edges and minimizing the surface curvature. In our experiment, the reduction time was designed to ensure complete sample reduction and we do not have access to the time that reduction was completed. Therefore, the Ni microstructure most likely has had significant time for post-reduction rearrangement. Studies of the effect of annealing on Ni particle morphology are the topic of Chapter 4 and of future works.

3.4.4 The combined effects of voids, YSZ fracture and Ni particle rearrangement

The phenomena described in the previous sections have all an impact on the electrode performance. The YSZ cracking is detrimental for the electrode for two reasons:

1. the presence of cracks compromises the electrode mechanical properties.

2. the cracks reduce the ionic conductivity of the YSZ structure by reducing percolation and introducing constrictions in the remaining ionic conduction pathways.

The YSZ cracking is a direct effect of the nickel volume expansion of \( \sim 70 \% \) during oxidation due to the different molar volumes between Ni and NiO. However, in many cases as the one presented in Figure 3.5, the hollow oxide particles occupy a greater volume (volume expansion of 92\%) than the one expected based on theoretical calculation. This situation leads to further volume expansion and results in greater overall stress applied to the electrode contributing in the YSZ cracking.

Unlike the YSZ cracking, the nickel detachment is not necessarily detrimental for the electrode. The electrochemical reactions occur only at the triple phase boundaries (TPB) and the Ni-YSZ interface is not electrochemically active. On the other hand, the nickel fragmentation leads to a considerable increase
in the connected TPB density as reported in 3.1. However, it is unlikely that a microstructure like the one presented in Figure 3.3 (c) and 3.5 (c) is morphologically stable at high temperature since the Ni particles are expected to coarsen during the operation of the cell to reduce the Ni-pore surface area.

Since the nickel fragmentation leads to an increase of TPB density and pore connectivity, we conclude that YSZ fracture is the main mechanism of electrode degradation during a complete redox cycle.

The fact that a redox cycle leads to nickel particle fragmentation and increase in TPB density could be used in order to reset the effects of nickel coarsening and return electrodes back towards the optimal nickel particle size distribution. Nickel coarsening is considered a major phenomenon involved in the electrode degradation and leads to nickel particle agglomeration and migration away from the active layer [38]. Thus it is imagined that controlled periodic redox cycles, together with oxidation crack tolerant engineered YSZ microstructures, could be planned during cell lifetime to increase durability.

3.5 Conclusions

Spatially correlated microstructural evolution of a solid oxide cell electrode during a complete redox-cycle was observed using X-ray nano-tomography. For the first time, ptychography is demonstrated as a new tool for the study of SOC electrodes. Ptychographic X-ray nano-tomography allows detailed 3D microstructural characterization of Ni-YSZ SOC electrodes with high resolution, low noise, and unprecedented material phase contrast.

YSZ backbone failure during oxidation occurs predominantly by grain boundary fracture, as many YSZ grain boundaries are located at sites of stress concentration where Ni particles are in contact with YSZ. Furthermore, NiO particles
after oxidation present internal voids creating additional volume expansion and therefore mechanical stress during oxidation. Void formation is proposed to be due to vacancy annihilation in metallic nickel during the oxide growth.

After reduction, the electrode does not initially recover its original microstructure. The nickel particles are smaller, with smoother surfaces and are detached from the YSZ structure. The difference in the nickel morphology is a direct consequence of the oxidation. YSZ cracks act as new access channels for hydrogen and thus reduction proceeds radially from the surface towards the center of the particles. Furthermore, contraction towards the internal voids contributes to the nickel detachment from YSZ.

The redox cycle dramatically reduces Ni/YSZ interfacial area, increases the Ni/pore interfacial area and increases the triple phase boundary density. While the YSZ cracking must be avoided to preserve the electrode ionic conductivity and its mechanical integrity, the nickel fragmentation due to the redox cycle could potentially be exploited to reactivate the cell and postpone cell degradation.
Chapter 4

3D Observation of Nickel Coarsening in Solid Oxide Cells via High Resolution Ptychographic Nano-Tomography

This chapter is partially based on the paper: S. D. Angelis, P. S. Jørgensen, Esther H. R. Tsai, M. Holler, K. Kreka, and J. R. Bowen. 3D Observation of Nickel Coarsening in Solid Oxide Cells via High Resolution Ptychographic Nano-tomography. In Manuscript

Abstract

Nickel coarsening is considered as the main cause of solid oxide cell (SOC) performance degradation. Therefore, understanding the involved morphological changes in the fuel electrode is crucial for the widespread commercialization of SOC technology. In this chapter, we report the 3D observation of the microstructure evolution of a SOC fuel electrode analyzed in the pristine state and after 3 and 8 hours of annealing at 850°C in dry hydrogen. The analysis of the evolution of the same location of the electrode shows a substantial evolution of the nickel and pore network during the first 3 hours of treatment while only negligible changes are observed after 8 hours. The nickel coarsening yields to nickel loss of connectivity, reduced specific surface area and decrease total triple phase boundaries density. From the data, nickel coarsening is proven to be only
curvature driven. The changes in the electrode microstructure parameters are discussed in terms of local microstructural evolution.

4.1 Introduction

While nickel is an excellent electron conductor and exhibits high catalytic performance at high temperature, it undergoes severe microstructural changes during operation, which leads to degradation of the cell performance. Due to its relatively low melting point (compared to the SOC operating temperature) and high specific surface area, the system will tend to minimize its free energy through curvature minimization and particle agglomeration. Furthermore, the low wettability between Ni and YSZ will enhance the coarsening [76, 77].

In previous reports, Ni coarsening has been studied by SEM analysis [78] and more recently through FIB-SEM [27] and X-ray nano-tomography [33]. Theoretical studies on the Ni coarsening have been performed using a variety of techniques ranging from simple coarsening models [79] to 3D phase-field simulations [80]. However, in most of the previous studies, different samples were analyzed after treatment and then compared with similar reference specimens. Following this approach, only global statistical parameters such as triple phase boundaries length, surface areas, and particle size distributions can be used in the comparison and for models validation.

Kennouche et al. realized the first ex-situ Ni-YSZ annealing experiment where the same sample was successfully analyzed in its pristine state and after 24 and 48 hours of heat treatment at 1050 °C in 5 % H2/3 % H2O/95 % Ar [43]. This pioneering work shows that, at high annealing temperature, it is possible to achieve significant structural evolution on the time scale of a synchrotron beam time.

In this chapter, we capitalize on high-quality pytchographic imaging with the
aim to investigate the details of nickel microstructure evolution with high spatial resolution. This allows us to study the nickel coarsening during its early stages, at temperatures representative of Ni-YSZ electrode operation.

4.2 Experimental methods

4.2.1 Sample preparation

Following a similar procedure reported in chapter 3, the sample was prepared from a typical Ni-3YSZ (Yittria-Stabilized-Zirconia, mol. 3 %Y2O3) anode supported SOFC half-cell. From the reduced half-cell, a ∼3 mm long and 300 µm wide slice was carefully cut using a diamond cutting wheel (Minitom, Struers). The slice was precision polished with an angular offset to form a truncated asymmetric pyramidal sample of 60x60 µm at the top (see Chapter 2. FIB milling (Zeiss, CrossBeam X1540) was used to produce a cylindrical pillar of 14 µm in diameter and ∼15 µm in height using a 10 nA probe current ion beam.

4.2.2 Tomography procedure

The nano-tomography experiment was performed at the X12SA (cSAXS) beamline at the Swiss Light Source, Paul Scherrer Institut, Switzerland. The ptychography procedure was carried out at 7.2 keV with a scanning field of view or 19 by 11 µm. At each scanning point, a diffraction pattern was recorded 7.4 m downstream of the object using a Pilatus 2M detector with 172×172 µm pixel size at 0.1 s exposure time. Diffraction patterns with sizes of 400×400 pixels were used in the ptychographic reconstruction, giving an object pixel size of 18.4 nm. For each dataset, 500 projections over an angular range of 180° were collected. Three-dimensional ptychographic tomograms were obtained through fine alignment of the reconstructed 2D projections and filtered back projection [67].
The sample was initially imaged in the pristine state and then subsequently after additional annealing steps of 3 and 5 hours at 850 °C in a gas mixture of 4 % H2 and 96 % N2 for a total of 8 hours of exposure at maximum temperature. The treatments were conducted using the small custom-made tube furnace described in *Chapter 2* with a flow rate of 5 l/h. The ramping rate for each treatment was 10 °/min for both heating and cooling.

### 4.2.3 Segmentation, registration and microstructural quantification

The pristine dataset was first rotated in order to orient the electrolyte parallel to the x-axis. The remaining 2 volumes were then registered to the pristine datasets. A coarse transformation was determined manually followed by a 3D rigid transformation computed by the iterative closest point method [81] using points sampled only from the stable YSZ phase. The raw volumes were segmented using the 2D (intensity vs. intensity gradient magnitude) histogram thresholding procedure exposed in *Chapter 2*. Microstructural characterizations of particle sizes, interfaces, and pathway characteristics were calculated as described elsewhere [82, 58]. Furthermore, in order to obtain additional information on the quality of the phase networks, the TPB tortuosity and critical pathways were computed. TPB tortuosity and critical pathways are calculated as described in *Chapter 2* and [59]. All the algorithms for segmentation and data analysis were written in-house using MATLAB®.

### 4.3 Results

#### 4.3.1 Microstructural evolution and statistical analysis

Figure 4.1 visually summarizes the effect of the annealing on the microstructure where the same slice of the spatially registered volumes are presented. The original microstructure in its pristine state (Figure 4.1 (a)) is directly compared
with the one treated for 3 hours (Figure 4.1 (b)) and 8 hours (Figure 4.1 (c)) of total exposure at maximum temperature. In the tomographic slices, 3 different levels of gray are visible: black (air), gray (YSZ) and white (nickel). Nickel has a mass density of 8.908 $g/cm^3$. Taking the value of the electron density corresponding to the peak of the histogram for a volume of 9x9x6 $\mu^3$, we measured a mass density of 9.026 $g/cm^3$ in good agreement with the theoretical value.

Figure 4.1: Two-dimensional slices from a spatially registered sub-dataset at identical locations in the electrode in the pristine (a), annealed for 3 hours (b) and for 8 hours (c). Three different levels of grey are present: black (pore), grey (YSZ) and white (nickel). The green triangular markers indicate the same feature of the electrode to show the alignment of the datasets. The red arrows and blue circles indicate example locations where the effect of coarsening is visible. The color scale indicates the electron density.

From Figure 4.1, the three following qualitative observations can be made:

- The YSZ network does not detectably change.

- The nickel network appears to coarsen and sharp edges evolve towards more rounded surfaces after annealing (red arrows in Figure 4.1).

- From 3 hours to 8 hours of annealing, the electrode microstructure only undergoes minor changes. As an example, the shape of the particle indicated by the blue circles evolves considerably from the pristine to the 3 hours annealed state while only small rearrangement can be observed from the 3 to the 8 hours annealed states.
Table 4.1: Microstructure parameters for the sample in the pristine, three hours and 8 hours annealed state

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<td>YSZ phase fraction [-]</td>
<td>0.43</td>
<td>0.42</td>
<td>0.43</td>
</tr>
<tr>
<td>Pore phase fraction [-]</td>
<td>0.23</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>Connected Ni fraction [-]</td>
<td>0.96</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>Connected YSZ fraction [-]</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Connected Pore fraction [-]</td>
<td>0.90</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

For the microstructure statistical analysis, a sub-set of 9x9x6 \(\mu m^3\) was extracted from the entire spatially registered datasets. Microstructure parameters of the electrode in different states are reported in 4.1.

Note that the comparison is done on the same volume of the sample, making the analysis less prone to uncertainties due to representative volume size. Table 4.1 shows that from the pristine to the 8 hours annealed electrode, the YSZ and Pore surface areas remain unchanged while the total Ni interface area decreases from 1.6 to 1.3 \(\mu m^2/\mu m^3\). Furthermore, the Ni-YSZ interface area decrease of 20 % from the initial value while the Pore-YSZ interface increase of 10 %. Interestingly, while the total TPB density is reduced from 2.7 to 2.3 \(\mu m/\mu m^3\), the percolating TPB density decreased only from 2.0 to 1.9 \(\mu m/\mu m^3\) after 8 hours of annealing.

Figure 4.2 (a) shows the continuous cumulative particle size distribution (c-
PSD) of all three phases of the electrode in the pristine state, after 3 hours and 8 hours of annealing. From 4.2 (a), the YSZ continuous particle size distribution (c-PSD) in the different states is observed to be almost identical. The pore c-PSD presents a slightly higher fraction of pore regions with smaller radii. A bigger difference is observed for the nickel c-PSD, which presents a significantly coarser microstructure. In line with the observations from Figure 4.1, the particle size distribution shifts considerably towards larger structures from the pristine to the 3 hours annealed state while only evolving slightly after 8 hours of treatment. However, the data show that the trend is preserved and the nickel coarsening continues even if at a slower rate.

For the TPB tortuosity, the YSZ TPB tortuosity distributions are almost identical for all the three datasets, supporting what was observed for the cumulative PSD in Figure 4.2 (a). The pore network starts with 4 % of TPBs, which can be reached with a tortuosity between 1.1 and 1.2 in the pristine state to then evolve to a less tortuous network in the annealed states. A different behavior is observed for the nickel network, which presents a maximum of $\sim$7.5 % TPBs tortuosity around 1.2 to then decrease to only 6 % in the 3 and 8 hours annealed states. As for the c-PSD, the most significant change in TPB tortuosity is observed between the pristine and 3 hour annealed electrode, whereas an additional 5 hours of annealing results in almost insignificant change.

Figure 4.2 (c) and 4.2 (d) show the evolution of the critical pathways thickness for the electrode in the different states for nickel (4.2 (c)) and pores (4.2 (d)). For the sake of clarity, the curves for the not-evolving YSZ network are omitted. Figure 4.2 (c) shows that, while more TPBs are connected through the nickel pristine network, the distribution of critical pathways radii drops to zero more rapidly. Therefore, in the annealed states, the TPBs are connected through pathways with larger critical radii. Differently, the pore phase presents an opposite situation (Figure 4.2 (d)). The pore networks in the annealed states
connect a larger fraction of TPBs while they present smaller critical pathway radii. As observed for the PSD and TPB tortuosity, also the critical pathways analysis confirms that most of the microstructure evolution observed in this study occurs after only 3 hours of treatment.

Figure 4.2: Cumulative PSDs (a), TPB tortuosity (b) and critical pathways diameter (c),(d) distributions for the electrode in the pristine, 3 hours and 8 hours annealed state. In (a) and (b) all three phases are included. In (c) and (d) only the critical pathways distributions for nickel and pore respectively are shown.
4.4 Discussion

4.4.1 Nickel coarsening in a SOC electrode

Two main mechanisms for nickel coarsening have been proposed in the literature:

- Evaporation-deposition of Ni volatile compounds.

- Ni-Ni inter-diffusion which can occur either at the particles surface (surface diffusion) or through the bulk of the network (bulk diffusion) [80].

In order to identify the leading mechanism for this experiment, we investigate the evolution of the isolated nickel particles. Figure 4.3 shows a 3D rendering of the isolated nickel particles in the same volume used in the statistical analysis from the pristine (a) and after 3 hours of treatment (b).

In figure 4.3 (b), the orange particles are the new isolated nickel regions which become disconnected from the main network during coarsening. Since further annealing only produces very few new isolated particles in the 8 hours microstructure, to simplify the analysis, only the first two states of the electrode are shown.

The isolated particles represent a convenient system to assess the nature of nickel coarsening. Being disconnected from the main Ni network, changes in volume can only be due to nickel transport in other phases as in the case of nickel evaporation/deposition (through pores). Analysing all the isolated particles in the datasets, the volume of Ni in the different states remains constant within an error of 0.2 % and can be attributed to the limits of segmentation resolution. However, significant morphological evolution is observed from the pristine to the 3 hours annealed state.

Therefore, we can conclude that at the time scale and conditions of this experiment (850 °C in dry hydrogen), the leading phenomenon for the nickel
Figure 4.3: Evolution of nickel isolated particles in the pristine state (a) and after 3 hours of annealing (b). In (b), the orange particles are the newly formed isolated particles after annealing. (c) Magnified view of the highlighted particle in (a). (d) Magnified view of the same particle after annealing. In the insets, the mid two-dimensional slice from a 1.4x1.4x1.4 μm sub-volume containing the particle is shown in pristine (a) and 3 hours annealed state (b). The particle highlighted by the green circle is studied in Figure 4.4

coarsening is the Ni-Ni inter-diffusion. Such result is in agreement with the fact that the saturated partial pressure on Ni is negligible at this temperature [83].

As an example, Figure 4.3 (c) and 4.3 (d) show the evolution of one isolated nickel particle. The behavior of the latter seems to suggest a capillary driven phenomenon. The particle in the pristine state presents regions with high curvature, which have higher chemical potential than regions with lower curvature (Gibbs-Thomson effect). Thus, Ni atoms will diffuse from high curvature re-
gions towards regions with lower chemical potentials minimizing the system free energy. This mechanism leads to the nickel particle rearrangement observed in Figure 4.3 (d) where sharp edges are eliminated in favor of more rounded surfaces.

The isolated particles offer an ideal system to be compared with simulations. As the nickel particle is entirely enclosed in the volume of interest, simulations will be less dependent on the conditions applied to the volume boundaries. Furthermore, material parameters (difficult to obtain experimentally) such as Ni surface energy, Ni mobility, and Ni-YSZ surface energy can be estimated trying to match simulation results with experimental data using an iterative approach [84]. In this work, a phase-field model for nickel coarsening is proposed in the Future developments section in Chapter 6. More rigorous simulations and comparison with the presented datasets will the focus of future work.

4.4.2 Effect of the nickel coarsening on the nickel connectivity

Phase connectivity is one of the main requirements for a working electrode. The electrochemical reaction at the triple phase boundaries can only occur if the phase networks can provide a suitable pathway for electrons (nickel) ions (YSZ) and gas species (pore). The loss of Ni-Ni connections after cell operation has been reported as one of the main causes of cell degradation [37, 38, 39].

Referring to Figure 4.3, the following observation can be made:

- The isolated particles in the pristine state remain disconnected in the 3 hours annealed electrode (red particles in Figure 3a and 3b)
- Newly formed isolated nickel particles are observed after 3 hours of annealing.

The loss of nickel connectivity plays a role in the microstructural change observed in the statistical analysis. Comparing the pristine and the 3 hour an-
nealed electrode, Figure 4.2 (d) shows that a smaller fraction of TPBs is percolated in the 3 hour annealed nickel network. The disconnection of nickel particles causes a loss of TPB percolation (from 90 to 85 %) and closes some of the available pathways. Therefore, if the closed pathways were the shortest to reach a particular TPB site, this explains the increase in the TPB tortuosity reported in Figure 4.2 (d).

Nickel loss of connectivity can also explain the difference in the pore network. As a consequence of nickel disconnection, new pore channels are created increasing the pore overall connectivity. With the formation of new channels, new pathways are opened resulting in a bigger fraction of TPBs percolated through shorter pathways, leading to a decrease of pore TPBs tortuosity (Figure 4.2 (b)).

To investigate the causes of the nickel connectivity loss, the newly formed isolated particles in the 3 hour annealed microstructure are studied in terms of their original connection (in the pristine state) to the rest of the network.

Figure 4.4: Zoom in on the surrounding nickel network of the particle highlighted by the green circle in Figure 3. (a) Surrounding nickel network of the red particle in (b) in the pristine state. (b) The same region in the 3 hours annealed microstructure
As an example, Figure 4.4 shows a magnified view of the surrounding region of the particle highlighted in Figure 4.3 (b) (green circle). In Figure 4.4, the isolated particle is colored in red while the rest of the network is colored in green as it is connected to the rest of the nickel network outside the region shown in Figure 4.4. In the pristine state, the isolated particle in Figure 4.4 (b) was connected through only two narrow channels often referred as “bottlenecks” (magnified regions in Figure 4.4 (a)). The bottlenecks are regions of higher curvature and therefore Ni atoms tend to migrate out towards regions of lower chemical potential. This leads to the formation of two separated interfaces causing the loss of Ni-Ni connection.

The disappearance of the small bottlenecks represents one of the major effects of the nickel coarsening at this timescale. It is worth mentioning that, such phenomenon occurs in the entire nickel network and does not lead always to a loss in nickel percolation. Even if a small bottleneck disappears, two or more regions can still be connected through other available pathways. However, in that case, new pore channels are created and the phenomenon contributes to the decrease in TPB pore tortuosity previously discussed. The disappearance of bottlenecks is also in line with the critical nickel pathways radii distribution presented in Figure 4.2 (c). Particles which are connected only through small bottlenecks will become disconnected leading to the decrease in TPB percolation. Furthermore, the disappearance of narrow channels in the connected network leads to the shift towards bigger critical radii observed in 4.2 (c).

### 4.4.3 Effect of the nickel coarsening on the Triple Phase Boundaries

Table 4.1 shows that after 3 hours of annealing, the total TPB density decreases by 30 % from its original value. During the coarsening, in some regions of the electrode, nickel tend to become detached from the YSZ network (nickel dewetting) resulting in the decrease of Ni/YSZ interface area reported in Table 4.1. Therefore, the TPBs present in those regions disappear in the annealed
states. In previous reports [76, 77], the estimated contact angle between Nickel and YSZ has been estimated to be in between 110° and 120° testifying low wettability between the two materials. Thus, the system tends to create new Ni/Pore interfaces if the free energy is minimized.

Figure 4.5: Isolated TPBs in the pristine (a) and 3 hours annealed state. In (a) and (b), the pore, YSZ, and nickel disconnected TPBs are colored in blue, green and red respectively.

This phenomenon can be observed in the behavior of the region of the nickel network indicated by the red arrows in Figure 4.1. The bottom tip of the particle, originally connected to the YSZ, becomes detached in the annealed states.

Based on the decrease of total TPB density and the loss of nickel connectivity, it is reasonable to expect a considerable reduction of percolated TPB density. However, Table 4.1 shows only 10% reduction in percolated TPB density after 8 hours of annealing. In order to explain this observation, the isolated TPBs sites are identified and their evolution is tracked in the different states of the electrode. Recalling what exposed in Chapter 1, a TPB site is electrochemically active if it can be reached by all the three phases in the electrode, starting from a particular location (often one side of the volume of interest). Therefore, a TPB site is defined isolated if it cannot be reached starting from any side of
the volume. Here, for brevity, we define as pore disconnected TPBs the sites which are not reachable through the pore phase. The same definition is then applied to the YSZ and nickel phase.

Figure 4.5 shows the isolated TPBs in the pristine (a) and the 3 hours annealed state (b). A TPB site is not connected through a particular phase if it cannot be reached. In figure 4.5, the pore disconnected TPBs are labeled in blue while the YSZ and nickel disconnected TPBs are colored in green and red respectively.

Comparing figure 4.5 (a) and (b), one can notice that accordingly to the formation of new isolated nickel particles reported in figure 4.3 (b), new nickel disconnected TPBs appear in the annealed microstructure. Contrarily, the TPBs isolated through the pores almost disappear in the three hours treated electrode. Due to the improved connectivity of the pore network, previously isolated TPBs become percolated and electrochemically active. Therefore, even though the total TPB density decreases considerably, this effect is counterbalanced by the opening of newly available pore pathways. This phenomenon explains the small changes observed in the connected TPBs compared with the substantial decrease of total TPB density (4.1).

4.5 Conclusions

The 3D microstructural evolution of a solid oxide cell electrode while treated at high temperature in dry hydrogen was observed using X-ray ptychographic nano-tomography. The sample was first analyzed in the pristine state and subsequently after 3 and 8 hours of annealing. The high spatial resolution and data quality given by ptychography allowed the observation of small changes in the microstructure, occurring during the first instants of the nickel coarsening.

The statistical analysis, on the 3 spatially registered volumes, revealed that the
nickel coarsening causes a loss in nickel connectivity, nickel surface area, Ni-YSZ surface area and total TPB density. Furthermore, most of the morphological changes are observed during the first 3 hours of treatment suggesting that the phenomenon is faster during the first instants of thermal treatment.

The analysis of the evolution of isolated nickel particles shows that, at the conditions of this experiment, the nickel coarsening is mainly curvature driven and phenomena such as nickel evaporation-condensation can be excluded. The nickel coarsening causes the disappearance of narrow nickel bottlenecks which results in the formation of new isolated nickel particles. This process closes available pathways to the TPB sites, resulting in the increase of nickel TPB tortuosity and critical pathways radii. Differently, new channels for the pore phase are created leading to the improved connectivity of the pore network.

Finally, the study of the evolution of isolated TPBs shows that, the newly created pore channels after annealing results in the activation of many previously non-active TPBs. This phenomenon counterbalances the overall decrease of total TPB density due to the nickel particles coalescence.

The presented datasets can be used in future phase-field simulations in order to refine and validate existing models and compute materials parameters difficult to obtain experimentally.
Chapter 5

In-Situ Holo-Tomography on SOC Materials

5.1 Introduction

Thanks to its non-destructive nature, X-ray computed tomography (CT) can combine high spatial resolution with the possibility of performing time-resolved studies. However, to date, beam and sample stabilities, effective spatial resolution and long scan time have hindered the development of nanoscale in situ imaging (also referred to 4D imaging). In-situ observations are routinely achieved with micrometer spatial resolution. For example, 4D imaging studies have been performed for investigating failure mechanisms [85], to image the lithiation process in batteries [86], and solidification of colloidal suspensions [87].

However, in many applications, nanometer resolution is required. Furthermore, even though sometimes a given microstructure can be reconstructed with micrometer-scale resolution, the early stages of many phenomena (e.g. nucleation of phases, cracks propagation, solidification) requires examination at the nanoscale. When performing in-situ studies, a compromise must be made between two critical parameters: voxel size (which is strongly related to the spatial resolution) and the acquisition time required to fully obtain a 3D image [88]. During the years, there has been a gradual improvement in resolution and scan-
ning time, thanks to high-flux synchrotron radiation and the progress achieved in CMOS detectors development. However, Vilanova et al. reported that high spatial resolution and fast scan rate (order of minutes) have been difficult to achieve for in-situ studies [89].

Chapter 3 and 4 presented the results of two different ex-situ experiments where the sample is repeatedly scanned and removed from the X-ray stage to be treated in an external furnace. With this approach, although time-dependent studies can be performed by spatially registering the datasets, only a few points can be acquired. For example, the oxidation and reduction processes during the redox cycle presented in Chapter 3 were analyzed only comparing the initial and final steps of the reactions.

In this chapter, we report the preliminary results of two holo-tomographic in-situ experiments where the sample is scanned and subsequently treated in-line, when mounted on the X-ray stage.

5.2 X-ray Holo-tomography for SOC materials

X-ray holo-tomography is an imaging technique based on phase contrast which was originally developed for weakly absorbing objects. The method can also be useful in studying materials with phases which have similar absorption coefficients [90, 91]. In practice, a coherent X-ray beam is focused down by Kirkpatrick Baez (KB) multilayer mirrors to a focal plane P. Magnified images of the sample are recorded using the focused beam as a secondary X-ray source and placing the sample to a suitable distance from the focal plane. When using high X-ray energies and weakly absorbing materials, the radiographs are dominated by propagation based contrast which consists in interference fringes due to Fresnel diffraction [90]. Therefore, radiographs of this type cannot be used for standard tomographic reconstruction algorithms (e.g filtered back projec-
tion) and the phase must be retrieved.

Clothens et al. developed an approach to calculate the phase quantitatively [90]. With the aim of underlining the strength of method when performing in-situ studies, here we report its basic principle while the reader can refer to [90, 91] for more details on the technique. In its simplest form, holo-tomography consists in acquiring 4 data-sets at 4 sample-to-focus plane distances which we denote here as $D_1, D_2, D_3$ and $D_4$. Using these four data sets, the phase can be retrieved giving a single absorption-like projection corresponding to the first distance $D_1$. The phase is proportional to the projection of the refractive index decrement $\delta$ and can be used for standard tomographic reconstructions. The choice of 4 distances comes from the fact that, when a spatially coherent X-ray beam illuminates an object, some spatial frequencies are eliminated depending on the effective propagation distance.

Recalling what was already mentioned in Chapter 2, when a coherent X-ray beam interacts with matter, the latter affects both its amplitude and phase. This phenomenon can be described introducing the complex refractive index

$$n = 1 - \delta + i\beta$$  \hspace{1cm} (5.1)

where $\beta$ is related to the absorption coefficient $\mu$ with the relation $\mu = 4\pi\beta/\lambda$, with $\lambda$ the wavelength of the radiation. The absorption coefficient is proportional to $Z^{-4}$, with $Z$ being the atomic number of the material in which the beam propagates. Therefore, for light-weight material the ratio $\delta/\beta$ assumes high values and the sample behaves as a pure phase object.

In typical SOC materials, when working at 29 keV, the refractive index decrement $\delta$ is about only one order of magnitude larger than the absorption coefficient ($\sim 43$ times larger [92]). Therefore, the contribution of absorption cannot be neglected and the projections are a combination of pure phase images and
pure absorption images. In order to take into account the absorption, the phase map in the material is first estimated assuming a homogeneous ratio $\delta/\beta$. This rough estimation yields to a blurred version of the phase map which is subsequently improved iteratively using a non-linear least square optimization [92].

Holo-tomography has the advantage of being a full-field technique which allows acquiring projections in one single exposure. When compared to ptychography, holo-tomographic 3D images can be acquired in significantly less time. Furthermore, the high energy allows the use of bigger samples (easier to make and more statistically representative) and special sample environments for in-situ studies. The holo-tomographic experiments presented in this chapter have been carried out at the European Synchrotron Research Facility (ESRF) at the ID16B beamline.

5.2.1 Sample environment for high-temperature in-situ holo-tomography

The in-situ furnace used in this work was developed at ID16B (ESRF) and it is described in detail in [89]. Briefly, the furnace is based on a MHI FibHeat200-XRD microheater, where the original resistive coil has been replaced by a Nichrome to ensure higher temperature homogeneity. A cooling system has been implemented in order to efficiently dissipate the heat around the furnace, protecting the stage and the KB mirror from over-heating. A quartz chamber inside the furnace prevents the motion of the sample due to air convection. The temperature is measured using a thermocouple located in the heating chamber. The temperature recorded by this thermocouple is related to the sample temperature using the melting process of different alloys with eutectic composition. Since the melting point of these alloys is well known, the method allows accurate calibration without the use of additional thermocouples which might disturb the temperature field. Finally, the furnace temperature is controlled by a Eurotherm device with a precision of $\pm 1 \, ^\circ\text{C}$. 
The furnace is motorized on the x,y and z directions. The x and y movements are used to align the heater above the sample. The movement in z is used to position the furnace along the vertical axes, in order to place the sample inside the heating chamber and align the furnace with the X-ray beam. The furnace is mounted on the rotation stage and therefore it moves together with the sample during the holo-tomographic procedure.

5.3 Stop-and-go oxidation of a Ni-YSZ electrode

5.3.1 Sample preparation

The sample preparation for holo-tomographic studies follows the same procedure exposed in Chapter 2. For the oxidation experiment, the sample was prepared from a Ni-3YSZ (Yittria-Stabilized-Zirconia, mol. 3% Y2O3) anode supported SOFC half-cell with a 15 µm thick Ni-8YSZ hydrogen electrode and 10 µm thick 8YSZ (Yittria-Stabilized-Zirconia, mol. 8%Y2O3) electrolyte. A slice 3 mm long and 300 µm thick slice was carefully cut using the diamond saw and subsequently polished following Procedure 2 in Chapter 2. Thanks to the possibility of using larger samples compared with ptychography, the sample was not FIB-milled. After polishing, the specimen was mounted on a 4.5 mm long alumina rod of 1 mm of diameter (Friatec, AG). The rod was polished on one side to produce a flat surface on which accommodate the sample. The latter was then temporarily fixed using super glue and subsequently permanently attached with Pt paste for the high-temperature treatment.

5.3.2 Tomographic procedure

In this study, the holotomography has been performed based on tomography scans with 2998 projections collected over 360° for each distance $D_i$. The first
distance has been chosen in order to achieve a pixel size of 27 nm. Taking into account the use of a detector of 2048 x 2048 pixels, the field of view in the final image was 55x55 \( \mu m \). In the case of the oxidation experiment, the field of view was smaller than the sample size, for some angle projections. Therefore, a special padding scheme was applied and adapted to local tomography using the procedure described in [92]. The phase retrieval was carried out with in-house software (developed at ID16) using the GNU Octave programming environment and the public domain image analysis program ImageJ. Tomographic reconstruction using the filtered phase maps was performed using back-projection with the ESRF software PyHST. The acquisition time for each dataset was approximately 1 hour and 50 minutes.

From the previous \textit{ex-situ} redox experiment presented in \textit{Chapter 3}, we observed that the oxidation was complete after only 3 hours of treatment at 850 \( ^\circ \). Given an acquisition time of 1 hour and 50 minutes, the reaction kinetics is still too rapid to perform a pure \textit{in-situ} experiment. Therefore, a \textit{stop-and-go} procedure was adopted.

The sample is first analyzed in its pristine state. Subsequently, the furnace is positioned on the sample to have it inside the heating chamber. The specimen is then treated for an established period of time and the furnace is removed. When the heating step is completed, the sample is scanned again at room temperature and the procedure is repeated. During the experiment, the furnace is kept at the temperature of interest (850 \( ^\circ \)), in order to save the time spent in ramping up/down in temperature. The heating times chosen for this experiment are reported in the following table.
Although it was not possible to scan the sample while it was treated, the stop-and-go procedure allowed us to record many tomograms of the sample in many different oxidation states. Furthermore, following this procedure, the sample was scanned at the highest possible resolution, not compromising on the acquisition time.

However, this procedure could lead to non-representative phenomena in the microstructure evolution. For instance, cracks can be formed in the microstructure due to thermal shocks generated during the insertion or removal of the furnace.

### 5.3.3 Preliminary results

The aim of the present holo-tomographic experiment is to gain additional information on the intermediate steps of the oxidation process. The new information can be used to complement the results exposed in Chapter 3.

The effect of the oxidation is summarized in Figure 5.1 in which slices of vol-
Figure 5.1: A slice through a sub-volume at identical locations in the electrode in the pristine (a), after 30 s (b) 30 minutes (c) 150 minutes (d) of oxidation. In (a) the dark phase is metallic nickel, the gray phase the YSZ and the white phase represents the pores. In (b) The dark phase is metallic nickel while the gray phase is both NiO and YSZ. The green circles highlight some example locations where internal voids are formed in metallic nickel particles. In (c) and (d) the dark phase is nickel oxide. In the inset, a magnified view of the region marked by the red rectangle where the internal void and the contour of the NiO shell is highlighted.

Volumes after different oxidation time are presented. Differently to what reported in Chapter 3, the presented slices are not spatially registered. Furthermore, segmentation of the presented datasets is challenging and the simple 2D thresholding method presented in Chapter 2 cannot be applied. Therefore, here the comparison between different microstructures is done only qualitatively. For the sake of brevity, we only report here the states of the microstructure after 0, 30 seconds, 30 minutes and 150 minutes of total oxidation.
Figure 5.1 (a) shows the microstructure in its pristine state. Three different levels of intensities are present: black, gray, and white representing nickel, YSZ, and pores respectively. Figure 5.1 (b) shows the same location of the microstructure after 30 seconds of oxidation. Figure 5.1 (c) shows the microstructure after 30 min of oxidation while Figure 5.1 (d) shows the electrode after 150 minutes of oxidation. Based on Figure 5.1, the following observations can be made:

- Oxidation has occurred already after 30 seconds of treatment showing that the reaction kinetics is fast at 850 °C.
- Already after 30s, isolated internal voids can be detected in metallic nickel particles (green circles in Figure 5.1 (b)).
- The porosity level decreases during the oxidation.
- Internal voids in nickel oxide particles can be observed at the end of oxidation.

In Figure 5.1 (b), only three levels of intensity are detected. However, observing the morphological changes, it is reasonable to assume that partial oxidation has occurred. As an example, the location pointed by the red arrow shows that part of the original nickel particle disappears. Furthermore, the porosity present in Figure 5.1 decreases due to the expansion of the NiO upon oxidation. Therefore, we speculate that oxidation has already started and the newly formed NiO cannot be detected within our limit of resolution. It is important to state that more analysis and observations must be performed to confirm this statement.

In many locations of the electrode, isolated internal voids in metallic nickel can be observed (green circles in 5.1 (b)). Such observation is in line with what reported in Chapter 3. Recalling what exposed in Chapter 3, nickel oxidation proceeds by outwards migration of $Ni^{2+}$ from the core of the nickel particles towards the surface, forming a nickel oxide scale which grows at the NiO-Air
interface. During this process, vacancies, injected at the metal-oxide interface, diffuse towards the center of the particle, initiating the void formation [70, 71]. It is worth noticing that, following this mechanism, voids formation should occur during oxidation while metallic nickel is still present in the electrode. In the ex-situ experiment presented in Chapter 3, only the initial and final stage of oxidation were accessible for analysis. Therefore, this stop-and-go experiment allows us to gain new insight on the intermediate steps of the oxidation process, confirming the void formation mechanism previously proposed. Once again, more rigorous analyses must be performed to confirm this study.

Differently to what observed in Chapter 3, no evidence of cracks formation is detected. However, the cracks might be present but not detectable at this level of resolution.

In figure 5.1 (c) the electrode is completely oxidized testifying that the reaction is complete after 30 minutes of treatment. The level of porosity has decreased substantially due to the nickel expansion upon oxidation. In Figure 5.1 (d) the final dataset after 150 minutes of oxidation is presented. In the inset, a magnified view on a single NiO particle (highlighted by the red square in (d)) is shown. The green outline guides the reader to follow the contour of the nickel oxide particle. The inner green contour highlights the presence of the internal void discussed previously. More instances of nickel oxide particles have been detected in the dataset, however, further analysis must be done in order to confirm this preliminary observation.
5.4 Stop-and-go reduction of a SOC fuel electrode

5.4.1 Sample preparation

For the reduction experiment, the sample was prepared from a NiO-3YSZ anode supported half-cell with a ratio between NiO and YSZ of 40/60 %. After the polishing procedure 2 (Chapter 2), the sample was FIB-milled to form a square pillar of 30x40 \( \mu m \) (Figure 5.2 (c)) and subsequently attached to the alumina rod similarly to the procedure for the oxidation experiment (Figure 5.2 (b)).

![Figure 5.2: Sample preparation for the stop-and-go reduction experiment. (a) Overview of the sample mounted on the alumina rod inside the capillary. (b) Detailed view of the sample on top of the alumina rod. (c) SEM micrograph of the sample after the polishing procedure and FIB milling.](image)

In order to provide the reducing atmosphere, the sample was inserted into a quartz capillary tube. A 1.5 mm outer diameter capillary (Charles Supper, Natick, MA, USA) was chosen for its ability to withstand the high-temperature requirements (up to 1,730 \(^\circ\)C). The capillary has a nominal 10 \( \mu m \) wall thickness which ensures sufficient transmission signal.
In order to fill the capillary with the reducing atmosphere, the following procedure has been adopted. First, the capillary is inserted into the standard goniometer pin used at ID16B. The alumina rod (with the sample attached) is subsequently inserted from the bottom and temporarily fixed using super glue (Loctite). During this step, the rod is attached in a way to leave a free slot where the gasses can flush in/out of the capillary. The capillary is inserted in a glove-bag (Sigma Aldrich) which is inflated with a gas mixture of 5 % $H_2$ and 95 % $N_2$. In order to remove all the oxygen, the bag has been left partially open and the mixture has been flushed for 4 hours. Finally, the bag was closed and the capillary was sealed using UV glue as in Figure 5.2 (a).

5.4.2 Tomographic procedure

For the reduction experiment, the holo-tomographic procedure has been performed similarly to what reported for the oxidation experiment. 2998 projections were collected over $360^\circ$ for each distance, with a field of view of 55 x 55 $\mu$m. In this case, the sample was smaller than the field of view and the padding procedure was not applied. However, the presence of the capillary tube adds challenges in the tomographic reconstruction. The absorption of the capillary, even if minimal, cannot be simply neglected without generating artifacts in the reconstructed images. Therefore, reference images were taken above the sample (with the capillary in the field of view) and subsequently subtracted to the projections in the reconstruction procedure. The phase retrieval and the reconstruction were carried out as for the oxidation experiment. The acquisition time for each dataset was approximately 1 hour and 50 minutes.

As for the oxidation, the reduction kinetic is fast and therefore the same stop-and-go procedure was adopted.
5.4.3 Preliminary results

The effect of the reduction treatment is summarized in Figure 5.3 where two-dimensional slices of the sample in different reduction states are presented.

In figure 5.3 (a), the sample is in its unreduced state. The dark phase is the nickel oxide, the gray phase is the YSZ while the white phase is air (pore). Figure 5.3 (b) shows the evolution of the microstructure after 10 seconds of exposure at 850 °C. The reduction of NiO particles begins with an induction period for the nucleation of metallic clusters, which subsequently grow into nickel crystallites. Differently to the oxidation mechanism, the reduction occurs at the interface between NiO and the previously reduced porous Ni [74].

Interestingly, Figure 5.3 shows that the formation of metallic nickel occurs already after 10 seconds of thermal treatment, showing a very rapid reaction kinetic at this temperature. In Figure 5.3 (b), looking at the image intensities, it appears that all the nickel oxide has been converted to metallic nickel, suggesting a fast initial induction period. The metallic clusters appear to be organized in a sponge-like structure, where the previously dense NiO particles evolve towards a nano-porous system. Figure 5.3 (c) and (d) shows that, after 30 and 60 seconds of reduction, nickel clusters start to agglomerate to form a more ordered structure. Finally, in 5.3 (e) and (f) the agglomeration leads to the the final Ni-YSZ microstructure.

In 5.3 (e) and (f) we can observe that the final nickel agglomeration leads the nickel particle to agglomerate towards the YSZ backbone. Finally, comparing (a) and (f), more porosity is formed according to the contraction of NiO upon reduction. As for the oxidation experiment, more rigorous analyses must be performed to confirm these preliminary observations.
5.5 Conclusions and future perspectives

The microstructural evolution of a solid oxide cell electrode during oxidation and reduction was observed using X-ray holo-tomography. Holo-tomography, thanks to the ability to perform fast scans at high resolution is demonstrated to be a useful tool for time-dependent tomography studies of SOC electrodes.

The oxidation experiment reveals that at 850 °C, the reaction is rapid and partial oxidation occurs already after 30 seconds of treatment. The porosity in the sample decreases due to the expansion of nickel upon oxidation. Furthermore, the formation of internal voids in metallic nickel is observed, in line with the void formation mechanism proposed in Chapter 3. After 30 minutes, the oxidation is complete and nickel oxide shells are observed as result of the void formation mechanism.

The reduction experiment reveals that already after 10 seconds of treatment at 850 °C, the nickel oxide is converted in metallic nickel. The previously dense nickel oxide particles evolve towards a nano-porous system formed by metallic nickel clusters. These results demonstrate a fast induction period for the nickel reduction. Nickel crystallites proceed in the agglomeration, progressively eliminating the formed nano-porosity and evolving towards dense nickel particles. In the process, new porosity is formed according to the volume contraction of the NiO phase upon reduction. Furthermore, during the last steps of agglomeration, nickel particles tend to agglomerate towards the YSZ structure.

The two experiments reveal new insights on the oxidation and reduction mechanisms, highlighting the intermediate steps of the reactions. However, more work should be done in order to gain more rigorous information from the data. Firstly, the volumes must be spatially registered to directly compare the evolution of the same feature in the microstructure. A more advanced segmentation
method must be developed, in order to obtain quantitative information on the microstructure evolution (e.g., changes in surface areas, TPB density etc...) More importantly, the qualitative observation made in this chapter should be confirmed by a more accurate analysis of different locations of the electrode.
Figure 5.3: A slice through a sub-volume at identical locations in the electrode in the unreduced state (a), after 10 seconds, (b) 30 seconds (c), 60 seconds (d) 90 minutes (e), and 150 minutes (f) of reduction. In (a) the dark phase is nickel oxide (NiO), the gray phase is the YSZ and the white phase represents the pores. In (b),(c),(d),(e),(f) the dark phase is metallic nickel while the gray and the white phase represent the YSZ and the pores respectively.
Chapter 6

Conclusions

The aim of the project was to characterize the evolution of a SOC fuel electrode microstructure in three dimensions, in order to gain new insights on the most common degradation mechanisms for solid oxide cells. The ultimate goal of this study is to lead to the development of SOC electrodes less prone to degradation, with the aim of solving the long-term stability problems which hinder SOCs widespread commercialization.

For the first time, ptychographic tomography was applied to reconstruct the Ni-YSZ microstructure of a SOC fuel electrode showing unprecedented data quality. The redox mechanism was analyzed ex-situ, where the sample was first analyzed in its pristine state and subsequently after oxidation and reduction. Cracks in the YSZ were detected, mainly at grain boundaries which represent locations of stress intensification. In the oxidized state, NiO particles present internal voids which create a further expansion of the electrode upon oxidation, contributing to the YSZ fracture. Void formation is proposed to be due to vacancy annihilation in metallic nickel during the oxide growth. After reduction, the nickel network was observed to not recover its original microstructure. The nickel particles appear smaller and mostly detached from the YSZ. The difference in the nickel morphology is considered a direct consequence of the YSZ fracture since, the newly formed cracks, act as new channels for hydrogen. Thus the reduction proceeds radially from the surface towards the center of the
nickel particles. The redox cycle dramatically reduces Ni/YSZ interface area, increases the Ni/pore interfacial area and increases the triple phase boundary density. While the YSZ cracking must be avoided to preserve the electrode ionic conductivity and its mechanical integrity, the nickel fragmentation could potentially be exploited to postpone cell degradation.

To investigate the effect of nickel coarsening on the Ni-YSZ microstructure, the evolution of a solid oxide cell electrode while treated at high temperature in dry hydrogen was observed using X-ray ptychographic nano-tomography. The high spatial resolution allowed the observation of small changes in the microstructure, occurring during the first instants of the nickel coarsening. Most of the morphological changes are observed during the first 3 hours of treatment and this observation is confirmed by an accurate statistical analysis of the microstructure. The analysis of the evolution of isolated nickel particles shows that the nickel coarsening is mainly curvature driven. The nickel coarsening causes the formation of new isolated particles due to the disappearance of the narrow nickel bottlenecks. Finally, the study of the evolution of isolated TPBs shows that many previously non-active TPBs get connected after coarsening, due to the opening of new pore channels. This phenomenon counterbalances the overall decrease of total TPB density due to the nickel particles coalescence.

The ex-situ experiments allowed the investigation of the evolution of the same microstructure in great detail. However, due to the long scanning time required by ptychographic measurements, only the initial and the final step of the processes (reduction, oxidation, coarsening) were examined. To overcome this issue, X-ray holo-tomography was used. Compared to ptychography, X-ray holo-tomography is a full-field technique and has the ability to perform tomographic scans at high resolution using high energy beam. This ability has been exploited to investigate in-situ the intermediate steps of oxidation and reduction of a Ni-YSZ electrode. Preliminary results show that both the oxidation and
reduction are characterized by rapid kinetics. During oxidation, void formation in metallic nickel particles was already observed after 30 seconds of treatment. After 30 minutes, the microstructure appears fully oxidized and nickel-oxide hollow particles were detected. During reduction, already after 10 seconds of treatment at 850 °C, the nickel oxide appears to be fully reduced to metallic nickel. Dense NiO particles evolved towards a nano-porous system formed by metallic nickel clusters. Finally, the nickel crystallites gradually evolve towards dense nickel particles.

6.1 Future developments

6.1.1 Modelling of nickel coarsening

Modelling of nickel coarsening offers the advantage of allowing systematic analyses of coarsening effects on the SOC fuel electrode microstructure. Furthermore, it can be used as a tool to predict the long-term behavior of a particular structure, guiding the development of Ni-YSZ electrode more robust to long-term degradation.

However, most of the previous efforts are based on empirically fitted parameters or oversimplified microstructures [79]. With the development of FIB-SEM tomography and X-ray nano-tomography, real Ni-YSZ microstructures could be reconstructed and used as initial geometry in coarsening simulations. However, using FIB-SEM data or Post-mortem X-ray tomography studies [33], only statistical comparisons between simulated and experimental results can be made. The ex-situ experiment presented in Chapter 4 showed that the evolution of a Ni-YSZ microstructure, when treated at high temperature in dry hydrogen, can be tracked in 3D with a high level of resolution. These results can be used to allow a direct comparison between experimental and simulated data. From this direct comparison, more accurate models can be developed and material parameters such as Ni-Ni diffusion coefficient or Ni surface energy can be re-
Therefore, the developing of an accurate nickel coarsening model can be considered as a natural development from the tomographic studies performed in this work. The first steps in this direction are summarized in the following section.

6.1.2 Phase field modelling of nickel coarsening

Although the phenomenon of nickel coarsening can be described as a free-boundary problem, explicit tracking of the evolving phase boundaries is highly impracticable in three dimensions. Therefore a diffuse interface approach should be adopted in the framework of the phase-field modelling. The following derivation is based on [80].

If the nickel surface tension is assumed to be independent of crystal orientation, the entire system can be described by means of the Chan-Hillard equation:

\[ \frac{\partial \phi}{\partial t} = \nabla \cdot M(\phi) \nabla \mu \]  \hspace{1cm} (6.1)

Where the \( \phi(x, t) \) is the order parameter, \( M \) is the mobility function and \( \nabla \mu \) is the gradient of chemical potential. The order parameter is 1 in the bulk of nickel particles and 0 in the pores while it varies smoothly across the interface Ni-Pore. Let’s consider a free energy functional in the form:

\[ F = \int_V \left( \frac{\epsilon}{2} |\nabla \phi|^2 + f(\phi) \right) dV \]  \hspace{1cm} (6.2)

where the term \( f(\phi) \) is a generic double-well potential. The chemical potential \( \mu \) is defined by the variational derivative of \( F \) with respect the order parameter \( \phi \). Therefore:

\[ \mu = \frac{\delta F}{\delta \phi} = \frac{\partial f}{\partial \phi} - \epsilon^2 \nabla^2 \phi \]  \hspace{1cm} (6.3)

In order to account for the presence of the YSZ, following the derivation in [80], a domain parameter (DP) \( \psi \) is introduced. The DP is 0 in the YSZ bulk and
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1 elsewhere. In analogy with the order parameters, the DP varies smoothly across the YSZ interface. Multiplying equation 6.2 by $\psi$ and letting $\mathbf{J} = M\nabla\mu$ results:

$$\frac{\partial(\phi\psi)}{\partial t} = \psi \cdot \mathbf{J} = \nabla(\psi \mathbf{J}) - \mathbf{J} \cdot \nabla\psi$$ (6.4)

The no-flux boundary conditions should be applied to all internal boundaries ($\nabla\psi \neq 0$), therefore the last term of 6.4 becomes 0 giving:

$$\frac{\partial(\phi\psi)}{\partial t} = \nabla \cdot (\psi M \nabla\mu)$$ (6.5)

Taking advantage of the properties of $\psi$, the normal $\mathbf{n}$ to the YSZ surface can be expressed as a function of the derivative of $\psi$. Therefore:

$$\mathbf{n} = \frac{\nabla\psi}{|\nabla\psi|}$$ (6.6)

Assuming that the YSZ and nickel phase are immiscible and that $\phi = 1$ represents the bulk nickel phase, the contact angle $\theta$ at the triple phase boundaries can be expressed as the scalar product between the normals to $\phi$ and $\psi$:

$$\mathbf{n} \cdot \frac{\nabla\phi}{|\nabla\phi|} = \frac{\nabla\psi}{|\nabla\psi|} \cdot \frac{\nabla\phi}{|\nabla\phi|} = -\cos\theta$$ (6.7)

Using the planar solution of the thermodynamic equilibrium within the interface we can find that $|\nabla\phi| = \sqrt{2f}/\epsilon$, which can be substitute into equation 6.7, giving:

$$\nabla\psi \cdot \nabla\phi = -|\nabla\psi|\cos\theta\frac{\sqrt{2f}}{\epsilon}$$ (6.8)

This last term introduces a term related to the energy associated with the triple junctions, dictated by Young’s equation for a flat surface. Combining equation 6.7 with 6.4, the final evolution equation for $\phi$ with no-flux and contact angle boundary conditions is:

$$\frac{\partial(\phi\psi)}{\partial t} = \nabla \cdot \left\{ \psi M \nabla \left[ f_\phi - \frac{\epsilon^2}{\psi} \left( \nabla \cdot (\psi \nabla\phi) + \frac{|\nabla\psi|\sqrt{2f}}{\epsilon} \cos\theta \right) \right] \right\}$$ (6.9)
Where $\epsilon$ is the gradient energy coefficient, $\theta$ the contact angle and $f_{\phi}$ is the derivative of the double well potential to respect $\phi$. In equation 6.9, $M$ is the mobility function which can be either constant for bulk diffusivity or a function of $\phi$ in the case of surface diffusivity. In this last case, we can write $M$ as follow:

$$M(\phi, \psi) = \phi^2(1 - \phi^2)g(\psi)$$

(6.10)

where $g(\psi) = \psi^6(10\psi^2 - 15\psi + 6)$ is introduced to control the mobility near the triple phase boundaries [80].

This model can be used to simulate the nickel coarsening in a real Ni-YSZ electrode, considering the YSZ phase not evolving. Equation 6.9 is a partial differential equation which can be solved numerically using a finite difference scheme for the spatial derivatives and the forward-Euler integration for the time derivative. In order to test the behavior of the model when applied to a real Ni-YSZ microstructure, an in-house code was developed in C++, using the library for linear algebra Armadillo, http://arma.sourceforge.net.

Figure 6.1 shows the results of a simulation performed on a sub-volume obtained from the entire datasets presented in Chapter 4. From these preliminary results, two observations can be made:

i) During the simulation, the nickel network does not penetrate the YSZ structure, testifying that the no-flux boundary conditions are correctly implemented.

ii) Two regions of the nickel network originally connected through a narrow bottleneck get separated. This result is in agreement with what reported in Chapter 4 where, in the experimental data, the disappearance of Ni narrow bottlenecks during coarsening is observed to be the cause of Ni-Ni loss of percolation.
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Figure 6.1: Simulated evolution of the nickel network in a real SOC electrode. (a) Electrode in the pristine state, (b) after 2000 iterations, (c) after 5000 iterations and (d) after 9000 iterations. The white arrows indicate a region of the nickel network which gets disconnected during the simulation.

Based on this preliminary results, further studies are required to achieve a reliable model able to correctly predict the evolution of a Ni-YSZ electrode. In order to compare the simulated results with experimental data, the simulated time step (e.g. iteration) must be related to the real time of the thermal treatment. Therefore, an asymptotic analysis must be performed [80]. Furthermore, the first version of the code must be parallelized to reduce the computational time, allowing the simulation of more statistically representative volumes. Finally, an analytical way for comparing the experimental and simulated results must be developed.
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