Relationships Between 3D Topology and Reaction Kinetics in SOFC Electrodes

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RELATIONSHIPS BETWEEN 3D TOPOLOGY AND REACTION KINETICS IN SOFC ELECTRODES

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(Dr. sc. ETH Zurich)

presented by

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Abstract

Solid oxide fuel cells (SOFC) represent a promising and an attractive alternative energy technology, which combines high efficiency and fuel flexibility. Significant developments were made over the last few years, which enable to introduce this technology into the market. However, high costs of fabrication and manufacturing, and harsh operating conditions of SOFC systems challenge the economic viability for suppliers and end-users. One aspect of SOFC performance optimization is the investigation of microstructure-performance relationships, in order to establish criteria for new microstructure concepts of improved SOFC electrodes, with specific focus on mixed ionic electronic conducting materials (MIECs) such as LSC ((La,Sr)CoO₃) for cathodes and composite materials such as Ni-YSZ (yttria-stabilized zirconia) for anodes. A fundamental understanding of the underlying processes on a nano- to micro-scale is required for future improvements of the electrode performance. This requires an interdisciplinary approach involving: (a) materials synthesis and electrode fabrication, whereby the microstructure must be varied in a controlled way; (b) quantitative analysis of microstructure, whereby higher order topology such as tortuosity and connectivity requires 3D-information; and (c) experimental characterization of macroscopic properties with special focus on the electrochemical performance and its stability under operating conditions.

In this thesis, microstructure effects are investigated for two different types of SOFCs: (1) nanostructured LSC cathodes for micro-SOFC applications fabricated by thin film techniques such as spray pyrolysis; and (2) microstructured Ni-YSZ anodes for conventional SOFCs based on powder processing and screen printing.

In order to quantify the complex interplay between microstructure, intrinsic material properties, and electrochemical performance, physical models that link these properties are of great interest. For the LSC cathodes, the 1D Adler-Lane-Steele model is applied assuming that the surface exchange is the rate-determining step in the oxidation-reduction reaction (ORR). For the case of Ni-YSZ, a specific model
that describes the coupled transport of $O^{2-}$ and electrons with the corresponding charge transfer reactions at the TPB on a continuum level is used. This model uses results from 3D-analysis as microstructure input and it provides a quantitative description of different resistances, which originate from the limitations of charge transfer as well as ionic and electric transport within the anode.

The successful fabrication of thin nanoporous LSC and the detailed characterization of Ni-YSZ make it possible to perform fundamental research on the influence of microstructure on the oxygen reduction (cathode) and fuel oxidation (anode). Furthermore, the link between the fundamental understanding of microstructure-topology-performance relationships and degradation mechanisms serve as an effective avenue to improve optimized fabrication of SOFC electrodes and their operating conditions at the industrial scale.
Kurzfassung


In der vorliegenden Arbeit werden die mikrostrukturellen Effekte auf Nano- und Mikro-Stufe erforscht, die experimentell durch zwei verschiedene Typen von SOFC abgedeckt sind: (1) nanostrukturierte LSC-Kathoden für Mikro-SOFC Anwendungen, die mittels Dünnfilm-Techniken wie beispielsweise Sprüh-Pyrolyse
fabriziert werden; und (2) mikrostrukturierte Ni-YSZ-Anoden für konventionelle SOFC Anwendungen, die auf Pulververarbeitung und Siebdruck gründen.

Um das komplexe Wechselspiel zwischen Mikrostruktur, intrinsischen Materialeigenschaften und elektrochemischer Leistung zu quantifizieren, sind physikalische Modelle, die diese Eigenschaften verbinden, von grösstem Interesse. Für die LSC-Kathoden wird das 1D Adler-Lane-Steele Modell angewandt in der Annahme, dass die Austauschoberfläche der geschwindigkeitsbestimmende Schritt in der Sauerstoff reduzierenden Reaktion (oxygen reduction reaction; ORR) ist. Was Ni-YSZ betrifft, wird ein spezifisches Modell verwendet, das den Transport von O$_2^-$ und Elektroden sowie die entsprechenden Ladungstransfer-Reaktionen beschreibt und das eine quantitative Beschreibung verschiedener Widerstände liefert, die von Beschränkungen der Ladungstransfers wie auch vom ionischen und elektrischen Transport innerhalb der Anode herrühren.

Die erfolgreiche Herstellung dünner nanoporöser LSC und die detaillierte Charakterisierung von Ni-YSZ ermöglichen es, Grundlagenforschung zum Einfluss von Mikrostruktur auf die Sauerstoffreduktion (Kathode) und die Oxidation des Brennstoffes (Anode) zu betreiben. Ausserdem ist die Verbindung zwischen einerseits dem grundlegenden Verständnis von Zusammenhängen zwischen Mikrostruktur, Topologie und Leistung und andererseits Alterungs-Mechanismen eine wirkungsvolle Möglichkeit, die optimierte Herstellung von SOFC-Elektroden und deren industriellen Einsatzbedingungen zu verbessern.
I

Introduction and Outline
CHAPTER 1

1. General Introduction

In this fast-changing world, energy consumption has been dramatically increasing along with the transformations and improvements in technology, increase of world population and industrialization. The quest for environmentally friendly, reliable and sustainable energy sources is becoming a necessity. While the majority of the world’s energy need is currently fulfilled by combustion of fossil fuels, the associated environmental pollutants negatively impact the environment, thereby stirring great interest in alternative sources of energy such as solar, hydroelectric, wind, geothermal and bioenergy. These renewable energy sources can easily generate electricity but are subject to seasonal and irregular fluctuations in terms of availability [1]. Moreover, as an example in the transportation industry, which accounts for significant emissions, the renewable energy sources mentioned remain virtually impossible for direct utilization. This leads to the use of energy storage devices such as batteries, super-capacitors and flywheels. Although, these devices can address the issue of recurrent power from renewable energy sources, they are found not to be ideal for applications such as in transportation. An alternative concept, which is now seriously considered for storage of temporal excess energy, is power-to-gas (P2G) and gas-to-power (G2P), respectively. As a result, these challenges stimulated again the interest in fuel cells for decentralized G2P, and when used as electrolysis cells also for P2G.

1.1. Fuel Cells

The invention of fuel cells has been credited to Sir William Robert Grove in 1839 [2]. A milestone in the improvement of Grove’s work when the first technical fuel cell was built, was when Mond and Langer [3] presented their work in 1889 and referred to it as a new form of gas battery. After that time, efforts to understand and develop fuel cell technologies have been taken, and the fuel cell research and
development have come in waves depending on the popularity, effort and finances involved [1]. Fuel cells may be considered as a “factory” that takes fuel as an input and generates electricity as output [4]. Unlike combustion engines, fuel cells are devices that directly convert chemical fuels into electricity. Fuel cells operating on hydrogen as fuel represent a promising clean and efficient energy conversion and power generation for several applications. Furthermore, fuel cells together with the other renewable energy sources can be used to achieve a sustainable energy generation system. Figure 1.1 shows a comparison of the fuels cells against other technologies in terms of efficiency and power density.

Figure 1.1. (A) Conversion efficiencies of different systems for power generation as a function of nominal load [5], (B) Power density comparison of selected technologies [4]. (IC = Internal combustion)

There are different ways to classify the numerous types of fuel cells depending on the criteria used and these are often related to fuel cell operation and construction [1]. For example, fuel cells may be classified in terms of the electrolyte, ions transferred through the electrolyte, reactant types, temperature and pressure of operation, direct or indirect use of primary fuels, and primary or regenerative systems [1]. The more conventional one is the classification based on the type of electrolyte and these are the following [4]:
(1) Phosphoric acid fuel cell (PAFC)
(2) Polymer electrolyte fuel cell (PEFC)
(3) Alkaline fuel cell (AFC)
(4) Molten carbonate fuel cell (MCFC)
(5) Solid oxide fuel cell (SOFC)

These fuel cells operate under the same electrochemical principles but they are different in terms of the operating parameters, material considerations, system design, applications and performance. In the present study we are focusing on the investigation of SOFCs, which are also called high temperature FCs.

1.2. Solid Oxide Fuel Cells (SOFC)

Among all these fuel cell types, solid oxide fuel cells (SOFCs) which usually operate at 600 - 1000 °C offer the prospects of high efficiency, versatility, and cost-effective utilization of several types of fuels (e.g., hydrogen, coal gas, biomass, hydrocarbon fuels) with the potential to reach energy conversion efficiencies exceeding 60 % [5]. If heat is also harvested in so-called combined heat and power (CHP) systems, then conversion efficiencies as high as 95% can be reached. Aside these advantages, SOFCs are also favored for high-power, stationary applications and in the recent years have been extensively studied and even tested for distributed, mobile and auxiliary power unit applications such as micro-SOFCs [6,7].

The fundamental principles underlying the SOFC technology were originally proposed by Nernst [8-10] at the time when the technological interest in solid ion conductors first arose in connection with the development of electric lighting devices [11]. There are essentially three active components in SOFCs. These include the electrolyte, cathode, and anode as shown in Figure 1.2.
Oxide ions ($O^{2-}$) are produced by the reduction of oxygen ($O_2$) in the porous cathode. The oxide ions are transported from the cathode to the anode through a gas-tight electrolyte. The porous anode is then responsible for the fuel oxidation. Moreover, both anode and cathode must allow for the transport of electrons as well as gases (i.e., $O_2$ for the cathode; fuel as $H_2$ and exhaust-gas as $H_2O$-vapour for the anode). For the case where the fuel is hydrogen, the anode and cathode bulk half-cell reactions are given by:

\[
\text{Cathode: } \quad O_2 + 4e^- \rightarrow 2O^{2-} \quad (1.1)
\]
\[
\text{Anode: } \quad H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (1.2)
\]

And the overall cell reaction is given by:

\[
2H_2 + O_2 \rightarrow 2H_2O \quad (1.3)
\]

In general, the electrodes provide the electrochemically active sites and flow paths for the reactants, products and electrons. The electrolyte acts as an ion conductor and electron insulator, and as a barrier separating the reactants. The electrochemical potential between the cathode and the anode is the driving force of SOFC operation, which is described by the Nernst equation:
\[ E = E^0 + \frac{RT}{4F} \ln \left( \frac{p_{O_2}^c p_{H_2}^a}{p_{H_2O}^a} \right) \] (1.4) [11]

where \( E \) is the Nernst potential, also known as the open circuit voltage (OCV), \( p_{O_2}^c \) is the partial pressure of oxygen in the cathode gas, \( p_{H_2}^a \) and \( p_{H_2O}^a \) are the partial pressures of hydrogen and water in the anode gas, and \( R, F, \) and \( T \) are the universal gas constant, Faraday’s constant and absolute temperature, respectively.

### 1.3. Fuel Cell Electrochemical Performance

The electrochemical performance of fuel cells can be summarized using the current-voltage (i-V) curve as shown in Figure 1.3. The actual potential of fuel cells deviates from the ideal potential due to irreversible losses during the cell operation. These losses (also called overpotential, overvoltage or polarization, \( \eta \)) can be grouped into three types:

1. **Activation losses.** These losses originate from the lack of electrocatalysis [5] or from kinetic limitations towards the activation of the electrochemical reaction. Whenever the fuel and air are delivered to the electrodes, they must undergo an electrochemical reaction that involves charge transfer as a fundamental step [11]. Apart from operating conditions and fuel type, the activation losses mainly depend on the intrinsic properties of the electrode materials, as well as on the microstructure (e.g., density of active sites).

2. **Ohmic losses.** The electrochemical reactions involve ions and electrons, which must be transported from the generation sites to the consumption sites in order to achieve a balance of charges. These losses, which originate from the ionic (and electronic) transport either inside a material or across the phase boundaries, depend on intrinsic material properties (conductivity), microstructure (e.g., connectivity, tortuosity), operating temperature and fuel cell system design (e.g., electrolyte thickness). This is given by:
$\eta_{ohm} = (\rho_e l_e + \rho_c l_c + \rho_a l_a + R_{contact})i$ \hspace{1cm} (1.5) [11]

where $\rho_e$, $\rho_c$, and $\rho_a$ are the resistivities of the electrolyte, cathode, and anode, respectively, $l_e$, $l_c$, and $l_a$ are the thicknesses of the electrolyte, cathode, and anode, respectively, and $R_{contact}$ and $i$ are any other possible contact resistance and current density, respectively. In electrolyte-supported cells (ESC) a major source for ohmic losses is ion transport through the relatively thick electrolyte, while in anode-supported cells (ASC) it is transport of electrons through the thick anode layer. In both cell types the contact resistances become problematic after longer operation time due to contact degradation.

(3) Mass-transport losses. The reactants as well as the products must be delivered and removed at an acceptable rate. Otherwise, the build-up of product concentration can block the delivery of new reactants. Fuel cells with gas feed-electrodes at very high current densities are limited by the transport of reactants to the reaction sites [5]. Hence, the electrochemical performance may be limited by gas transport through the pore network of the electrodes. In general, the mass transport losses (also known as concentration polarization) are a function of several parameters given by:

$$\eta_{conc}^a, \eta_{conc}^c = f(D_{H_2-H_2O}, D_{O_2-N_2}, Pore\ Microstructure, Partial\ pressures, Current\ density) \hspace{1cm} (1.6) \ [11]$$

where $D_{H_2-H_2O}$ and $D_{O_2-N_2}$ are the binary H$_2$-H$_2$O and O$_2$-N$_2$ diffusivities.
Figure 1.3. Example of a current-voltage (i-V) curve representing the electrochemical performance of a fuel cell. Due to irreversible and unavoidable losses during the cell operation, the actual cell voltage is lower than the thermodynamically predicted cell voltage (ideal cell potential, OCV, horizontal line).

As shown in Figure 1.3 the origin of the main losses greatly depends on cell operation. Activation losses are dominant at low currents, ohmic losses at intermediate currents and mass transport losses (concentration polarization) at high current densities. Aside from the losses mentioned previously, one of the main limiting issues for commercial applications is the material degradation at high operating temperatures. The compatibility of the physical properties of the components such as thermal expansion and dimensional stability in reducing and oxidizing environment must be taken into consideration [5]. Chemical reactions between the component materials may also happen at high temperature, which may slow down or stop the electrochemical processes. Therefore, one aspect in designing and manufacturing SOFC systems is to decrease the operating temperatures (400 –
700 °C) as much as possible. Hence, an interesting strategy for increase of lifetime is to develop materials suitable for intermediate temperature applications (i.e., IT-SOFCs). This strategy is particularly interesting for micro-SOFCs with nanoporous thin film electrodes [7]. Also in anode-supported cells (ASCs) lowering the temperature is a valid strategy. For electrolyte-supported cells (ESCs), however, the reduction of temperature usually leads to relatively high ohmic resistances in the thick electrolyte. Therefore another durability strategy is necessary for ESCs, which materials and microstructures that are stable at high temperatures (750-1000°C). In the present study we investigate two types of electrodes: a) a nanoporous LSC thin film cathode, which is suitable for intermediate temperature applications, and b) a conventional Ni-YSZ anode, which is typically used in high temperature SOFCs. In these investigations we focus on microstructure property-relationships as well as on degradation issues due to limitations in physical and chemical stability.

An additional challenge for practical applications is to lower the production cost [12,13], thereby also making the SOFC economically competitive and commercially viable. These issues may be addressed by thinning down the solid electrolyte and by optimization of electrode microstructures. However, electrodes and electrolyte also become less catalytically active and less conductive at lower operating temperature thus lowering performance. Consequently, it is important to explore new possibilities in generating fuel cell components with optimized microstructures and effective material properties. Therefore, it is important to understand the underlying mechanism governing the redox cycling behavior of SOFCs in order to develop a knowledge-based optimization of their performance. A summary of SOFC components and materials investigated in literature is shown in Figure 1.4.

In general, the intrinsic conductivity as a function of operating temperature and potential for minimization of layer thickness govern the material considerations for the electrolyte. For the anode it is the compatibility of the materials system with fuels (i.e., stable and high electrochemical activity) and a small as possible
mismatch of thermal expansions that matter most. In addition to the electrochemical activity towards oxygen reduction, it is the compatibility with the electrolyte, which is the most crucial issue for the cathode [12].

**Figure 1.4.** A taxonomy of SOFC materials investigated in literature [12]. In this study we investigate LSC cathodes and Ni-O/YSZ anodes.
For the development of suitable electrodes with high performance and low degradation rates a large number of materials characteristics have to be considered. Thereby it is crucial to have efficient and reliable (reproducible) methods for fabrication, characterization and analysis. Consequently, the methodological challenges in the rational design of materials can be summarized as follows [13]:

(1) Well-designed cells for electrochemical measurements
(2) In-situ characterization techniques
(3) Prediction of intrinsic properties of materials
(4) Continuum modeling
(5) Quantification of microstructure effect

The above-mentioned challenges are only related to the materials design and do not include the SOFC system configurations. Already at this level, the involved methodological approach is characterized by a highly interdisciplinary nature addressing a wide spectrum of challenging scientific and technical issues [5].

1.4. General Approach and Methodology

This work aims to address some of the challenges in the SOFC research and development and to contribute further understanding and possible solutions to the field. In the first part, the perovskite material $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) is deposited by spray pyrolysis, a simple and cost-effective fabrication technique [15]. The successful fabrication of thin and nanoporous LSC makes it possible to perform investigations on the influence of microstructure on the oxygen reduction mechanism and on the kinetics in mixed conducting materials. Together with the availability of the necessary infrastructure to do microstructural imaging and analysis (sample preparation, SEM, TEM, FIB-SEM, BIB-SEM), methodologies for quantitative microstructure analysis of the electrodes were established in collaboration with the Scientific Center for Optical and Electron Microscopy.
(ScopeM) at ETH Zurich. Electrochemical performance of the LSC cathodes is measured by using the electrochemical impedance spectroscopy (EIS) facility at the Nonmetallic Inorganic Materials group at ETH Zurich. Further characterization of the LSC powders and films such as chemical composition, purity and crystallinity are analyzed through the collaboration with other research groups at ETHZ and Paul Scherrer Institute (PSI).

In the second part, the composite Ni-yttria-stabilized zirconia (YSZ), a state-of-the-art anode material is investigated to describe the influence of microstructure and redox cycling on the degradation and electrochemical performance. In collaboration with Hexis SA in Winterthur, Switzerland, the microstructures of three anodes of varying microstructure are analyzed before and after redox cycling. Morphological changes in the Ni and YSZ are investigated and quantified. An empirical relation between the transport-related parameters is obtained in a work [16] in collaboration with the Institute of Stochastics in Ulm, Germany. The associated equation is used to predict effective transport properties (i.e., ionic and electronic conductivities).

Two different physical models for MIEC and cermet anodes that simulate the complex interplay between charge transport and transfer reactions, which take into account material properties and microstructure effects are applied in order to understand the relationship between these parameters and the electrode performance. Insights from these methods can be used to determine physical quantities, which are not easily accessible through experiments. For example, ionic conductivities, surface exchange and diffusion coefficients, and the components of the ASR related to charge transport and charge transfer can be accessed or predicted.
1.5. Outline of the Thesis

This work involves two different materials for two different electrode applications. In part II (Chapters 2-4), the perovskite La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC) is investigated as cathode material for IT-SOFCs. In part III (Chapters 5-8), we consider the Ni-YSZ cermet as anode for HT-SOFC applications. In both cases the focus of investigation was on microstructure effects and material stability in order to improve performance and lifetime. The two materials are introduced in separate chapters. Chapter 2 provides an introduction to the perovskite materials. In particular, the properties of La$_{1-x}$Sr$_x$CoO$_{3-\delta}$, as well as the challenges presented in literature are discussed in relation to this work. Chapter 3 presents our published work on the investigation of the La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ deposited by spray pyrolysis entitled “Influence of strontium-rich pore-filling phase on the performance of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ thin-film cathodes” published in the Journal of Power Sources [17]. Chapter 4 provides insights and outlook on the applicability of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ and the influence of changing the layer thickness in the electrode performance. Moreover, additional data not presented in the paper published in Chapter 3 are also discussed in Chapter 4.

Chapter 5 introduces the Ni-YSZ cermet anodes. This introduction is adapted from the co-authored paper published in the Journal of Power Sources [18]. Chapter 6 is based on the published article in the journal Materials [19] and represents an extension of the previous study about microstructure effects and redox degradation in Ni-YSZ anodes. Thereby we focus on the relationship between microstructure and effective conductivities (ionic and electronic). Compared to the previous study [18], geodesic tortuosity instead of geometric tortuosity is used. An empirical equation from our previous work on virtual materials testing (VMT) [16] is used to predict effective conductivities based on the different transport-related microstructure parameters and the intrinsic conductivity. Chapter 7 presents the work on the same Ni-YSZ anodes but deals with the correlation between the electrochemical reaction sites at the triple phase boundary (TPB) and the
electrochemical performance ($R_{pol}$). Moreover, the influence of transport limitations on the charge transfer processes is also discussed. Chapter 8 uses the microstructure parameters obtained in Chapters 6 and 7 as input in a model that simulates coupled charge transport and charge transfer reactions. This model provides electrochemical performance for different anode microstructures and it allows to distinguish the associated ASR components from charge transport and transfer limitations. Chapter 7 has been accepted for publication [20]. A summary and the main conclusions of both parts (II: LSC cathodes and III: Ni-YSZ anodes) are given in Chapter 9.

Some portions of this work, which include papers published or submitted for publication are re-structured and re-formatted although the content is not significantly changed. Some portions may have been added or may have been removed when necessary. Co-authored published papers, which are relevant to achieve the goals of this thesis, as well as representative papers published as full papers or abstracts in the proceedings of conferences related to LSC [21-23] and Ni-YSZ [24-26] can be found in the Appendix section.
1.6. References


[22] O.M. Pecho, L. Holzer, Z. Yáng, T. Hocker, R.J. Flatt, J. Martynczuk, L.J. Gauckler, M. Prestat, Quantitative microstructure analysis and electrochemical activity of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ electrodes deposited by spray pyrolysis, MRS Fall Meeting, Boston, 2012.


LSC Cathodes for IT-SOFC Applications
2. Mixed Ionic-Electronic Conducting Cathode: \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3-\delta \)

2.1. Introduction

The mechanism of oxygen reduction reaction (ORR) in SOFC cathodes includes several reaction pathways, with steps of adsorption, dissociation, charge-transfer, and incorporation [1]. Reaction steps may simultaneously take place consecutively or in parallel, and one (or several of them) may be rate-determining. Therefore, understanding the relationship between intrinsic material properties, microstructure and the ORR mechanism is an important condition for performance optimization. Although the relationships between these parameters are not straightforward and they are discussed controversially, the following sections aim at summarizing some of the literature data that is relevant to the selection of appropriate cathodes. An overview of the crystal structure, transport properties and parameters of electrochemical kinetics, followed by typical electrochemical performance in terms of the area-specific resistance (ASR) are presented.

In the case of purely electronic conducting cathode, the electrochemical reaction is confined to the triple-phase boundary (TPB) between the cathode, electrolyte and gas phase. However, for the case where the electrodes exhibit mixed ionic-electronic conducting properties, the active sites are extended from the TPB to the cathode surface whereby more electrochemically active sites are available (Figure 2.1). Sr-substituted lanthanum cobaltite (\( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3-\delta \), LSC) is an example of mixed ionic-electronic conducting (MIEC) materials with perovskite structure.
Mixed conducting cathode: La$_{1-x}$Sr$_x$CoO$_{3-\delta}$

Figure 2.1. *Schematic representation of oxygen reduction mechanism in mixed ionic-electronic conducting (MIEC) cathode.*

Materials with perovskite structure have the general formula ABX$_3$. As shown in Figure 2.2, cations A and B are of 12-fold and 6-fold coordination, respectively and X is the anion bonded to both cations. In the case of lanthanum cobaltite and LSC, the La$^{3+}$ cation is coordinated by 12 O$^{2-}$ ions allowing close packing in an ideal cubic lattice [1]. The B-site is occupied by Co, which is coordinated by 6 O$^{2-}$ ions. Transport properties such as ionic and electronic conductivities as well as oxygen reduction mechanism depend greatly on the defects in the perovskite sub-lattice. It is generally assumed that the valence states of Sr, La and O are fixed (+2,+3,-2, respectively) while the Co valence state can vary between +2 and +4. As a result, the substitution of La$^{3+}$ by Sr$^{2+}$ requires the compensation of the effective negative charge to achieve electro-neutrality. This is done either by ionic compensation (formation of oxygen vacancies) or by increasing the valence state of Co (electronic compensation), which may compete with each other depending on the composition, oxygen partial pressure and temperature. Using the Kröger-Vink notation, this can be expressed as:

\[ 2[V_0^\cdot] + [Co_{Co}^\cdot] = [Sr_{La}^\cdot] + [Co_{Co}^\circ] \quad (1) \ [2] \]
Co$^{4+}_c$ and Co$^{2+}_c$ represent a hole and an electron localized on the B site (see Figure 2.2), respectively. The Sr$^{2+}$ substitution of La$^{3+}$ in the A site creates a fully ionized acceptor level (Sr$_{La}^-$) whose charge is compensated by the generation of holes (Co$^-_c$) and oxygen vacancies (V$_O^-$) [2]. For example, Prestat et al. [2,3] implemented this defect mechanism into an ORR model for MIEC cathodes (LSC/LSFC).

![Figure 2.2. Structure of perovskite materials with ABX$_3$ chemical formula.](image)

### 2.1.1. Oxygen Non-stoichiometry

Many of the interesting and useful properties of perovskite materials are attributed to the crystal structure and oxygen non-stoichiometry. Oxygen non-stoichiometry ($\delta$) refers to the number of oxygen atoms missing in the structure to reach electroneutrality in relation to the level of Sr substitution. These defects affect the rate of oxygen transport through these materials, which is also often reported as the complimentary process of vacancy diffusion. In this section we examine the factors affecting the number of these deficiencies. In the next section, we look at how the increased deficiencies generally penalize charge transport.

In general oxygen non-stoichiometry is influenced by temperature and by the oxygen partial pressure, thereby $\delta$ increases with increasing temperature and decreasing oxygen partial pressure (see Figures 2.3 and 2.4) [4, 5]. Figure 2.3a plots $3-\delta$ as a function of Sr substitution $x$ and the mean Co valence. As shown in
Figure 2.3a the oxygen non-stoichiometry increases with increasing Sr content at a fixed temperature [4,6]. Ionic compensation dominates at $0.2 \leq x \leq 0.5$ and the oxygen non-stoichiometry increases, which results in decreasing mean Co-valence. For $x < 0.2$, and $x \geq 0.5$ increasing $x$ results to increasing mean Co-valence. This means that Sr substitution does not change the number of oxygen vacancies so that the electronic compensation dominates. Additionally, it is generally observed that the oxidation state of such B cations, here Co, increases with increasing oxygen partial pressure in perovskite materials [7], independently of temperatures [8,9]. Figure 2.3b shows the direct relationship between $\delta$ and oxygen partial pressure at different Sr substitution $x$. Figure 2.4 shows the dependence of oxygen non-stoichiometry to both oxygen partial pressure and temperature. In summary, decreasing oxygen partial pressure and increasing temperature results to increasing oxygen non-stoichiometry, both of which generally decrease the oxygen diffusion and electrical conductivity as seen in the next section. Nonetheless, LSC with La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ stoichiometry shows the lower $\delta$ than LSC with La$_{0.4}$Sr$_{0.6}$CoO$_{3-\delta}$ at the same oxygen partial pressure and temperature.

**Figure 2.3.** a) Oxygen non-stoichiometry ($\delta$) as a function of Sr content (with corresponding Co-valence) at 800 °C and b) oxygen non-stoichiometry as a function of oxygen partial pressure for different $x$ at 800 °C [4]. Decreasing $pO_2$ and increasing Sr content results in increasing $\delta$ and decreasing Co-valence.
2.1.2. Transport Properties

MIEC materials, such as LSC, have sufficiently high electronic and ionic conductivities. Figure 2.5 shows the Arrhenius plots for different levels of La substitution [10]. Upon variation of the Sr content the electrical conductivity of LSC goes through a maximum that varies with temperature (as shown in Figs 2.3 and 2.4). At 600°C, which is the target application temperature of LSC cathodes in this work, the maximum electrical conductivity is achieved for LSC with $x=0.4$. This maximum is also observed by Petrov et al. [11] at temperatures between 100 °C to 700 °C. Moreover, as shown in Figure 2.6, the peak conductivity moves to higher Sr content with decreasing temperature from $x = 0.2$ ($T = 1000$ °C) to $x = 0.4$ ($T = 600$ °C). It should be noted that LSC with $x=0.4$ represents the standard composition considered in the subsequent study.
Mixed conducting cathode: La$_{1-x}$Sr$_x$CoO$_{3-\delta}$

Figure 2.5. Arrhenius plots of electrical conductivity as a function of temperature at different Sr-substitution levels [10]. 600°C is the target temperature for LSC applications in our investigation.

Figure 2.6. Electrical conductivity of LSC as a function of Sr content at different temperatures [10].
Figure 2.7 shows the relationship between the electrical conductivity and oxygen partial pressure \([12]\). In general, the electrical conductivity increases with decreasing temperature for a particular oxygen partial pressure. Moreover, while keeping the temperature constant, decreasing oxygen partial pressure results in a decreasing electrical conductivity. Looking back at the sets of data presented so far (Figures 2.5-2.7), these suggest that the electrical conductivity maximum observed at 600 °C in air for the \(\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}\) stoichiometry is related to the Co-valence minimum observed between \(x = 0.4\) and \(x = 0.5\) in Figure 2.3a.

![Graph showing electrical conductivity vs. oxygen partial pressure](image)

**Figure 2.7.** Electrical conductivity of \(\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}\) as a function of oxygen partial pressure in the temperature range of 400 - 900 °C (dry synthetic air) \([12]\).

Ionic conductivity of MIEC is generally three orders of magnitude lower than the electronic conductivity. For example, Teraoka et al. \([13]\) obtained an ionic conductivity less than 0.1 S/cm for \(\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}\) at 600 °C compared to the corresponding electrical conductivity which is typically around 1000 S/cm. Figure 8 shows the dependence of ionic conductivity on oxygen partial pressure at two different temperatures. Ionic conductivity is certainly influenced by oxygen non-stoichiometry, \(\delta\). This dependency changes at low oxygen partial pressures.
Mixed conducting cathode: $\text{La}_{1-x}\text{Sr}_{x}\text{CoO}_3-\delta$ (combined with high temperatures), where the ionic conductivity decreases when the vacancy concentration increases. This suggests that vacancy clustering may have a negative effect on the ionic mobility. Based on the results shown in Figure 2.4, Bucher [14] concluded that vacancy clustering is more easily formed at higher temperatures because of the higher oxygen non-stoichiometry formed at elevated temperatures. Consequently at intermediate temperature operation (i.e., 600 $^\circ$C), the effects of vacancy clustering are less important than at more elevated temperatures.

![Figure 2.8. Ionic conductivity as a function of oxygen partial pressure at two different temperatures [14] and as a function of oxygen nonstoichiometry [15].](image)

**2.1.3. Electrochemical Kinetics**

The capability of LSC or any other perovskite material to exchange oxygen is also related to the transport properties of the material. Hence, transport and transfer kinetics have to be considered in order to understand the ORR mechanism and associated performance. With respect to the oxygen transport it is important to note, that the ionic conductivity driven by the potential gradient is related to the diffusion of oxygen ion, which is driven by the concentration gradient. The relationship between ionic conductivity and diffusion coefficient is given by the Nernst-Einstein equation:
\[ D_i = \frac{\sigma_i}{c_i (e z_i)^2} k_b T \]  \hspace{1cm} (2)

where \( D_i \) is the diffusion coefficient of species \( i \), \( \sigma_i \) the conductivity, \( c_i \) the concentration, \( e \) is the elementary charge, \( z_i \) is the number of charges on the diffusing species, \( k_b \) the Boltzmann’s constant, and \( T \) the temperature. Hence the above described dependencies of ionic conductivity with vacancy concentration, Sr-substitution level, partial pressure and temperature can be related with \( D \) via the Nernst-Einstein equation. Frequently, it is the transport of vacancies instead of oxygen-ions, which is considered for quantitative descriptions, because numerically it is more sensitive and reliable to use the complementary species with the lower concentration.

Another kinetic parameter that influences the ORR mechanism and the associated cathode performance is the surface exchange coefficient, \( k \). Contrary to \( D \) that describes the rate of a bulk reaction, \( k \) describes the rate of a surface reaction. These two properties are often obtained from isotope exchange experiments or from electrical conductivity relaxation measurements [1].

Armstrong \textit{et al.} [1] extracted surface exchange coefficients for different perovskites using isothermal isotope exchange (IIE) (Figure 2.9) as a function of temperature. Pure electronic conductors such as Sr-doped LaMnO\(_3\) (LSM) have lower surface exchange rates as compared to MIEC such as LSC. Therefore, the results in Figure 2.9 imply the importance of ionic transport to the total ORR kinetics.
Mixed conducting cathode: $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3-\delta$

**Figure 2.9.** *Surface exchange coefficients of pure electronic conducting perovskites (LMO, LSM, LFO) and MIEC perovskites (LCO, LSF, LSCF, LSC) as a function of temperature* [1].

Figures 2.10 and 2.11 show a summary of $D$ and $k$ values for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3-\delta$ measured by Berenov et al. [16] as a function of temperature, oxygen partial pressure and Sr content. Figures 2.10a and 2.10b show that the logarithm of both $D$ and $k$ decreases linearly with the inverse of the absolute temperature showing that the bulk and surface reactions are thermally activated processes. This is quite challenging especially for applications in IT-SOFC that target low operating temperatures. For example in this work, the target temperature is 600 °C and the values of $D$ and $k$ at this temperature for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3-\delta$ stoichiometry are marked in Figure 2.10 (red line). For comparison, if we consider $D$ and $k$ values at higher temperature (e.g., 800 °C marked with a blue line, see Figure 2.10), a significant increase in diffusion and surface exchange can be achieved.

On the one hand, Figure 2.11a shows that $D$ inversely correlates with oxygen partial pressure. Diffusion is influenced by the vacancy concentration, which, in turn, is influenced by the oxygen partial pressure. On the other hand, the variation of $k$ with
oxygen partial pressure goes through a maximum as shown in Figure 2.11b. This can be explained by the vacancy concentration and surface coverage. At low oxygen partial pressure, k correlates well with the surface coverage, which increases with increasing oxygen partial pressure. At high partial pressure, surface coverage reaches saturation and at the same time vacancy concentration is relatively low so that the transfer of reduced oxygen into the bulk of LSC also becomes limited by ionic transport. These conditions lead to a decrease of k when further increasing oxygen partial pressure (i.e., above the k maximum).

**Figure 2.10.** Temperature dependence of oxygen diffusion coefficient and surface exchange coefficient in La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ [16]. The oxygen partial pressures used were A) 0.21 atm [16,17] and B) 0.023 atm [18].

Figure 2.12 shows the dependence of D and k on the Sr content. Both parameters correlate with Sr content, which influences the oxygen non-stoichiometry, $\delta$ (i.e., the oxygen vacancy concentration, also see Figure 2.3). Hence, D and k also depend on the oxygen vacancy concentration. For k, this holds if the surface coverage is not saturated (e.g., due to transport limitations, as shown in Figure 2.11 right). In the case of diffusion, this holds true if vacancy clustering does not hinder diffusion (as indicated in Figure 2.8, left). Therefore, not only the extent of oxygen non-
stoichiometry is important but also the concentration of mobile oxygen vacancies [19].

![Graph](image_url)

**Figure 2.11.** Effect of oxygen partial pressure on the oxygen diffusion and surface exchange coefficients in La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ at 600$^\circ$C [16].

![Graph](image_url)

**Figure 2.12.** Effect of Sr content on the oxygen diffusion and surface exchange coefficients in La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ at 600 $^\circ$C [16].

2.1.4. Chemical Inhomogeneities: Thermal Stability and Degradation of LSC

Electrode electrochemical performance at low operating temperature can be improved by optimizing either the microstructure or the intrinsic material properties
(or both). The former can be done by variation of the processing parameters during the fabrication or by utilizing different production routes to come up with different microstructures. The latter can be done by selecting different materials or by changing the composition. However, microstructure and material properties obtained during the fabrication tend to evolve during the cell operation. Fabrication parameters and operating conditions may trigger changes in microstructure and intrinsic properties, which can either, improve or degrade electrode performance as explained later in this section.

A non-desired segregation of cations has been reported for different perovskite systems [20-28] of different compositions and stoichiometries in bulk and thin films. In most cases, this is brought about by the dissolution or segregation of the mobile cation, which may form a separate phase during the cell operation especially at long annealing times. For example, the metal cations in LSC, especially Sr (A-site) and Co (B-site), may form oxides in the form of SrO and Co$_2$O$_4$. In most cases, Sr cations segregate toward the gas-exposed surface of the cathode [29-31].

As an example, Figure 2.13 shows the cation distribution along the electrode thickness from the surface to the bulk of La$_{0.6}$Sr$_{0.4}$CoO$_3$-$\delta$ prepared by pulsed laser deposition (PLD) at 450 °C and 650°C [29]. Usually sintering at higher temperatures helps to homogenize the materials, but an enrichment of Sr cations is observed at the surface of these electrodes even at higher temperatures (650 °C). After 3 days of annealing at 600 °C, the Sr/La and Sr/Co ratios at the surface show a further increase. This increase of Sr/La and Sr/Co ratios is accompanied by the degradation of electrode performance (Figure 2.14). As presented in these studies by Kubicek et al. [29] and Cai et al. [30], in general, for electrodes to have good electrochemical performance, the Sr/La and Sr/Co ratios must be kept low. Figure 2.14 shows the effect from etching of the surface-exposed region that was SrO- and Sr(OH)$_2$-rich (i.e., Sr/La and Sr/Co high). After etching, better performance is observed as shown in the drop of surface polarization resistance in Figure 2.14.
Consequently, it was suggested that the electrochemical activity depends on the initial surface composition and the microstructural and chemical transformations during operation. Moreover, this implies the negative impact on the electrode performance that originates from Sr segregation towards the LSC surface, which might be accompanied with the formation of secondary phases.

**Figure 2.13.** Secondary ion ratios from SIMS raw data. Sr:La ratio for LSC films prepared by PLD at 450 °C (a) and 650 °C (b) and Sr:Co ratio for the same films (c, d). An increase in both cation ratios is observable in the as-deposited films at 450 °C deposited and annealed (600 °C) films. For the thin films prepared at higher temperatures (right, 650 °C) the as-prepared and annealed (600 °C) samples show stongher increase of cation ratios, which indicates a Sr segregation towards the surface [29]. In all samples, the cation ratios can be reduced with chemical etching (HCl).
Figure 2.14. (a) Surface polarization resistance, $R_s$, of LSC deposited by PLD at 450°C and 650°C taken at 600°C in air and the likely mechanisms that govern the differences between the activity and stability of these cathode films. Illustrations 1–3 mark the critical points correlating the surface chemistry to the electrochemical activity, as explained in the text. The green box denotes LSC bulk with a stoichiometric cation content; the orange box denotes Sr enrichment in the perovskite structure close to the surface; the red boxes denote separated SrO-rich phases; and the blue boxes denote the particle free region with relatively reduced Sr content in LSC adjacent to the SrO-rich particles. (b) Surface polarization resistance $R_s$ of LSC_650°C and LSC_450°C measured at 600 °C in air before and after HCl etching. With etching the initial performance can be recovered. Overall, LSC_650°C degrades much faster than LSC_450°C (before and after etching) [30].
Mixed conducting cathode: \(\text{La}_{1-x}\text{Sr}_x\text{CoO}_3-\delta\)

In other studies with LSC it was reported that cobalt is segregating into the perovskite surface. For example, cobalt oxide precipitations were observed by Heel et al. [12] after heat-treatment of LSC at elevated temperature \(1350^\circ\text{C}\), which were not observed at lower temperatures. Transmission electron microscopy analysis of nanosized LSC deposited by metal organic deposition (MOD) and thermally treated at 700 °C revealed the presence of Co-rich precipitates in the surface, which were detected by applying energy dispersive X-ray and Debye electron diffraction in TEM but were not detected by XRD [32]. Dieterle et al. [33] also found \(\text{Co}_3\text{O}_4\) precipitates near the surface of MOD-derived LSC thin films even after calcination at 700 °C. This is attributed to the transport of Co-species upon evaporation of gaseous organics during the calcination process, taking into account that mobility of \(\text{Co}^{3+}\) dominates over the mobility of \(\text{La}^{3+}\) [34]. Contrary to the segregation of Sr into the surface, which stays over the long annealing times, it was found that chemical gradients after calcination are reduced and that the Co becomes more homogenously distributed with increasing annealing time and temperature. Moreover, despite the observed heterogeneities the thin films exhibit very good electrochemical performance \(T_{\text{calcination}}=700^\circ\text{C}, \ ASR_{\text{chem}} = 0.023 \ \Omega \ \text{cm}^2 \ \text{at} \ 600 ^\circ\text{C}\). Consequently, it was suggested that the high density of the nanoscaled \(\text{Co}_3\text{O}_4\) may be responsible for the strong enhancement of oxygen surface exchange. Moreover, Zhang et al. [31] and Baumann et al. [35] also detected Co segregation and showed that in general, high Co concentration in the LSC surface results in enhanced oxygen surface exchange. These findings also indicate that an under-stoichiometry on the A-site (La, Sr) may be beneficial for ORR kinetics.

The phase stability of \(\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta\) has been investigated previously by Morin et al. [36]. A narrow stability region has been found in terms of the A/B cation ratio, which is \(0.997<A/B<1.003\). This observation is extended for LSC with \(0.4 \leq x \leq 0.6\) stoichiometries. Moreover, the Co precipitation is dependent on the temperature and oxygen partial pressure and may either be present as CoO or \(\text{Co}_3\text{O}_4\).
An excess of B-site (Co) and an excess of A-site (La or Sr) may lead to cobalt oxide in combination with La- and Sr-rich phases, respectively. Moreover, in MOD-prepared LSC, SrO was detected at 600 °C and suggested that the SrO and Co$_3$O$_4$ may coexist with the LSC phase [32]. However, at higher temperatures, SrO reacts with LSC to form the Ruddlesden-Popper phase with (La$_x$Sr)$_2$CoO$_{4+\delta}$ stoichiometry. The work of Cizauskaite and Kareiva [37] on LaCoO$_3$ and LSC powders prepared by sol-gel method ($T_{\text{sinter}} = 1000^\circ\text{C}$ in air) also obtained secondary phases in the form of SrO, Co$_2$O$_3$, SrCO$_3$ and Co$_3$O$_4$, which were simultaneously present depending on the stoichiometry. Monophasic LaCoO$_3$ is obtained at 1000 °C while for LSC, single-phase perovskites were obtained between 900 °C and 1000 °C together with Co$_3$O$_4$ as an impurity.

Another form of secondary phase is the Ruddlesden-Popper phase (RPP), which has the K$_2$NiF$_4$-type structure with (La$_x$Sr)$_2$CoO$_{4+\delta}$ stoichiometry for Sr-substituted lanthanum cobaltite [38]. The RPP is known to be formed when the perovskite phase La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ is reduced and decomposed at high temperatures [36,39]. Using X-ray diffraction, Heel et al. [14] identified the presence of these phases upon powder production of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ via flame spray synthesis (FSS) whereby the dependence on the ratio of different solvents was investigated. Moreover, not only is the weight fraction of RPP dependent on the solvent ratio but also the LSC particle size. Dieterle et al. [33] also identified the formation of this RPP but emphasized the uncertainty of X-ray diffraction due to the overlap of reflections with those from other possibly co-existing phases.
Figure 2.15. Mechanism of enhanced oxygen incorporation at the hetero-interface of a) La$_{1-x}$Sr$_x$CoO$_{3-δ}$ and (La,Sr)$_2$CoO$_{4+δ}$, b) La$_{1-x}$Sr$_x$CoO$_{3-δ}$ and (La,Sr)$_2$CoO$_{4+δ}$ resulting from Sr-decoration [32], and c) SIMS images showing the intensity ratio of log $[^{18}\text{O}/^{16}\text{O}]$ at the surface and cross-section of La$_{1-x}$Sr$_x$CoO$_{3-δ}$/CGO [40].

Work of Sase et al. has also investigated the effects of the presence of the RPP phase [40,41]. Measurements using secondary ion mass spectrometry (SIMS) showed that the surface exchange along the hetero-interface between La$_{0.6}$Sr$_{0.4}$CoO$_{3-δ}$ and (La,Sr)$_2$CoO$_{4+δ}$ is faster than surface exchange only in La$_{1-x}$Sr$_x$CoO$_{3-δ}$ (Figure 2.15). Surface decoration by Sr-rich oxides also lead to the same hetero-interface as reported by Mutoro et al. [43]. The scheme in Figure 2.15 summarizes the mechanism of how the oxygen incorporation happens along the hetero-interface based on Hayd et al. [32] and Sase et al. [40]. A hypothetical model of surface exchange enhancement in surface-decorated perovskites is shown in Figure 16 [42].
Figure 2.16. Hypothetical model of surface exchange coefficient, $k^q$ enhancement considering $SrCO_3/SrO/Sr(OH)_2$ phases as insulating or blocking the oxygen reduction reaction (ORR). (a) Reaction active phase between LSC and $SrCO_3/SrO/Sr(OH)_2$ interfaces, (b) completely blocking $SrCO_3/SrO/Sr(OH)_2$, and (c) $Sr^{2+}$ dissolution in the outermost surface of LSC [42].

Figure 2.17 shows a summary of some related literature of surface exchange coefficients, $k$ of $La_{0.6}Sr_{0.4}CoO_3\delta$. The values can be sorted into two groups, whereby one group of materials benefits from the presence of hetero-interfaces (orange) and the other group is without hetero-interface enhancement (blue). The plot also illustrates that there is a wide range of $k$ values for each temperature, which can be obtained for LSC with different fabrication methods and oxygen partial pressures. In general, the chemical heterogeneities can hardly be prepared in a controlled way, and thus at this stage the application of hetero-interfaces is debatable. In contrast, nanoporous LSC with high surface area dominates the performance of controllable and homogeneous electrode materials that are suitable for low- to intermediate- temperature SOFC applications.
2.1.5. Electrochemical Performance

The electrochemical performance of fuel cell electrodes is often reported in terms of area specific resistance (ASR). It depends on the resistances of the fuel cell components (i.e., electrolyte and electrode), interfacial resistances and also on the fuel cell operation parameters. An overview of the area-specific resistances of pure and composite perovskite-based cathodes is shown in Figure 2.18. This data includes measurements from cathodes that were produced with different fabrication methods. Hence, the thickness and the microstructures of the cathodes vary significantly. It is observable that the values of ASR vary over a wide range also as a function of temperature. This wide range of ASR is due to the dependence on the processing and operational parameters, which leads to LSC with different compositions, (non-)stochiometries and microstructures. Form this plot it is obvious that it is realistic to reach an ASR of 0.1 Ω cm² at 600°C. Hence, porous LSC is a promising cathode for low- to intermediate-temperature SOFC applications.
The literature dealing with LSC presented above illustrates that transport properties and exchange kinetics are affected by numerous parameters, which can be influenced in many ways, e.g., by the processing method (e.g., spray pyrolysis and MOD), by operating conditions (e.g., oxygen partial pressure and temperature), and by the nature of the material itself (e.g., composition variations including different substitutions and (non-)stoichiometries. It should be noted, that the findings of this review are partly controversial, especially with respect to the interpretation of chemical heterogeneities and hetero-interfaces, which can obviously have a significant impact on the intrinsic materials properties of LSC. However, it is not only the intrinsic material properties that influence the kinetics of oxygen reduction reaction and the overall cathode performance. Microstructure also significantly affects the electrochemical kinetics. For example, the ionic transport is influenced by the tortuosity of the solid phase and the effective electrochemical kinetics is affected by the available active surface. The latter criterion is typically fulfilled with
Mixed conducting cathode: $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3 - \delta$

nanoporous structures.

For intermediate- to low-temperature applications, a good cathode material must fulfill criteria related to the intrinsic material properties, which may affect the reaction rates of different steps in the ORR mechanism (i.e., ionic and electronic transport, electrochemical kinetics). From the data presented above, it is clear that electronic conductivity is generally not the rate-limiting step. Therefore, the choice of material is more influenced by the ionic diffusivity and $k$. With $D$ and $k$ showing positive correlation with Sr content, the tendency is to use LSC with high $x$ values. However, one has to take into consideration the corresponding material stability at operating temperatures. For example, strong segregation of Sr is observed for LSC with high $x$. Consequently from the data shown, a good compromise between performance and stability is the use of LSC with La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ stoichiometry.

An additional criterion is the cost efficiency of the involved fabrication methods. Nanoporous layers of LSC with different compositions can be fabricated in a cheap and efficient way by using spray pyrolysis. Thus, in the following chapters, the results of processing and characterization of nanosized La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ by wet spray pyrolysis will be presented. In order to achieve a nanostructured layer the sintering temperature must not be too high in order to prevent coarsening. However, the material tends to form secondary phases at low sintering temperatures. The investigations thus also include the analysis of a strontium-rich secondary phase (SP) that can be found within the electrode pore network at lower sintering temperatures. Based on the analysis of FIB-SEM cross-sectional images and electrochemical modeling of MIECs, it is shown that upon decreasing the sintering temperature, the increase of electrochemical performance cannot be fully explained by the associated change of the microstructure (i.e., increase of surface area). Rather a large degree of the increased performance is assigned to the changes in intrinsic properties of the Sr-deficient LSC, such as exchange neutral flux density. The electrodes exhibit promising electrochemical performance with an ASR as low as
0.13 Ω cm² at 600°C in air. The approach in this work combines quantitative microstructural analysis and electrochemical modeling. Some of the methodological developments presented in this study may also be of general interest for microstructure investigations related to energy applications such as batteries, fuel cells, electrolyzers or photoelectrochemical cells.

2.3. References


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3. Influence of Strontium-rich Pore-filling Phase on the Performance of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ Thin-Film Cathodes*

3.1. Introduction

Solid oxide fuel cells (SOFC) are electrochemical devices that convert chemical energy directly into electrical energy (and heat) with high efficiency and fuel flexibility [1,2]. One of the major trends in SOFC research is to reduce the operating temperature from the ca. 800 °C of current industrial systems down to 600 °C (or lower) in order to slow down electrode degradation, decrease start-up times and reduce manufacturing and running costs [3]. To achieve this goal, novel materials exhibiting high activity towards oxygen reduction or fuel oxidation have to be developed and electrode microstructures have to be optimized in order to provide electrochemically active sites that favor fast reaction pathways.

Thin films (typically ≤ 1-2 µm) made significant contributions in the recent progresses towards operating temperature reduction. They have been used as electrodes of conventional SOFCs (for stationary applications) [4-6] and also constitute the main components of the emerging technology of miniaturized SOFCs integrated on silicon chips for delivering power to small portable electronics [7-13]. In order to facilitate access to future markets, cost-effective and upscalable deposition methods, such as spray pyrolysis [14], metal-organic deposition [4,15], aerosol-assisted CVD [16-19] and flame spray synthesis [20] are being developed.

* This chapter is based on the published article in the Journal of Power Sources: O. Pecho, L. Holzer, Z. Yáng, J. Martynczuk, T. Hocker, R. J. Flatt, M. Prestat, J. Power Sources 274 (2015) 295-303. (doi: 10.1016/j.jpowsour.2014.10.060) J. Martynczuk acquired and analyzed TEM data. Z. Yáng introduced and supported the deposition with spray pyrolysis. The author performed experiments, literature search and wrote the manuscript under the supervision and expertise of T. Hocker, R. J. Flatt, M. Prestat, and L. Holzer.
As far as SOFC cathodes are concerned, mixed ionic-electronic conductors (MIECs) form a popular class of materials for intermediate-temperature (~500-700 °C) applications. In MIECs, oxygen reduction takes place not only at the gas/electrode/electrolyte triple phase boundary (TPB), but may also expand into the bulk of the cathode material [2,21-24]. Among MIECs, the La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC) perovskite is seen as one of the most promising materials [4,6,7,15,20,25-29]. The overall oxygen reduction kinetics is believed to be limited by oxygen exchange at the perovskite/air interface. An enhancement of electrode activity can thus be achieved by using electrodes with small particle sizes and, to some extent, by increasing the thickness of the electrode in order to increase the number of sites for the oxygen exchange [4,30,31].

In order to improve SOFC cathodes, it is important to quantify the complex interplay between microstructure, intrinsic material properties and electrochemical performance. In this context, physical models that link all these entities are of great interest. One noticeable example is the 1D Adler-Lane-Steele model (ALS) [21,22]. For an electrode with a finite thickness $L$ (µm), the electrochemical impedance is given by:

$$Z_{chem} = R_{chem} \sqrt{\frac{1}{1+j\omega t_{chem}}} \tanh \frac{L}{\delta(\sqrt{1+j\omega t_{chem}})}$$ (3.1)

$$R_{chem} = \frac{RT}{2F^2} \sqrt{\frac{\tau}{(1-\epsilon)ac_pD_v\tau_0}}$$ (3.2)

$$t_{chem} = \frac{c_v(1-\epsilon)}{Aar_0}$$ (3.3)

with $Z_{chem}$ the non-charge-transfer impedance, $R_{chem}$ the characteristic resistance, $t_{chem}$ the characteristic time constant related to the thermodynamic, kinetic and intrinsic properties, $\omega$ the angular frequency (Hz), $\tau$ the MIEC tortuosity, $\epsilon$ the MIEC volume fraction, $a$ the pore wall specific surface area (µm$^{-1}$), $c_v$ the oxygen vacancy concentration (mol cm$^{-3}$), $D_v$ the oxygen vacancy diffusion coefficient
(cm² s⁻¹), \( r_0 \) exchange neutral flux density of oxygen through the LSC/air interface (mol cm⁻² s⁻¹), \( R \) the universal gas constant, \( T \) the temperature and \( F \) the Faraday's constant. This model is based on a continuum description of the electrode microstructure and the assumption that the charge transfer step at the MIEC/electrolyte interface is facile. It establishes a link between the intrinsic material properties \( (c_v, D_v, r_0) \), the microstructure parameters \( (\tau, \varepsilon, a) \) and electrode performance (ASR).

With the development of focused ion beam (FIB) technology and 3D image processing tools, there has been an increased research activity on SOFC microstructures in recent years. Investigations on electronic conducting catalysts, such as \( \text{La}_x\text{Sr}_{1-x}\text{MnO}_{3-\delta} \) (LSM) or Ni, in the form of single-phase or composite electrodes have been reported. Quantitative microstructure analyses have been performed to experimentally assess the TPB length as main parameter influencing the electrochemical activity [32-37]. Coarsening of Ni particles in anodes has also been the topic of several studies [38,39]. In contrast, fewer quantitative investigations have been reported on more complex systems such as MIEC. Recently FIB-tomography was used to evaluate the volume specific surface area, porosity and tortuosity of porous mixed-conducting single-phase \( \text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta} \) cathodes with micro-scaled [40-44] and nano-scaled structural features [4].

In this chapter, the influence of the microstructure on the intermediate-temperature (600 °C) oxygen reduction kinetics at nanostructured \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta} \) (LSC) thin films is reported. The LSC electrodes are prepared by cost-effective spray pyrolysis and exhibit a strontium-rich secondary phase besides LSC and pores. Different heat-treatments enable tuning the microstructures of the three-phase mixed-conducting layers. Focus is laid on the quantitative evaluation of the phase sizes as well as areas of the interfaces and surfaces so as to identify the effect on electrochemical performance of LSC, pores and secondary phase with particular emphasis on the
latter. Furthermore, the microstructural data is used as input for the electrochemical model described by Eqs. (3.1)-(3.3) in order to extract the intrinsic properties of the cathode materials ($r_0$).

3.2. Experimental

3.2.1 Deposition by Spray Pyrolysis

1-µm thick LSC films were deposited by wet spray pyrolysis [45,46]. A precursor solution was prepared by mixing appropriate amounts of lanthanum nitrate (La(NO$_3$)$_3$•6H$_2$O), strontium chloride (SrCl$_2$•6H$_2$O), and cobalt nitrate (Co(NO$_3$)$_2$•6H$_2$O) (all from Sigma-Aldrich, 99+%) into ethanol, diethyleneglycol monobutylether and PEG600 to form a solution of 0.04 M metal cation concentration. The flow rate of the precursor solution contained in a syringe and passing through a nozzle was fixed at 30 mL h$^{-1}$ with a deposition time of 90 min. The distance between the nozzle and the substrate was kept at 38 cm. Square-shaped LSC thin films were deposited at 340 °C onto heated 10 mol% gadolinium-doped ceria (GDC, Kerafol®) substrates (thickness 200 µm) with a 1 cm$^2$ shadow mask. To obtain different microstructures, the films were sintered at 600 °C·800 °C and 1000 °C (and labeled LSC600, LSC800 and LSC1000 respectively) for 4 h in air with both heating and cooling rates of 3 °C min$^{-1}$.

3.2.2. Microscopy Investigation

The morphology of the films was characterized by scanning electron microscopy (SEM) using an FEI Quanta 200 FEG for backscattered electron (BSE) and secondary electron (SE) imaging. For 2D analysis, cross-sections were prepared by using a broad ion beam (BIB) machine (IM4000, Hitachi). Milling parameters were 1.5 kV for accelerating voltage, 6 kV for discharge, 30° swing angle and 1-2 h milling time. In addition, focused ion beam (FIB)-SEM investigations were also
carried out using a Helios Nanolab 600i (FEI Europe, The Netherlands) with a through-the-lens detector (TLD) for imaging at 1.8 kV.

The chemical compositions of the different solid phases were analyzed with transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). TEM lamellae of LSC thin films were prepared using a FIB-SEM workstation (NVision 40 Crossbeam 1540XB, Carl Zeiss SMT, Germany). An FEI Tecnai F-30 (FEI, Eindhoven) TEM with an accelerating voltage of 300 kV and post-column CCD camera, and EDAX (silicon detector) detector was used to obtain EDX mappings in the scanning (STEM) mode with an electron-probe of about 2.5 nm in diameter. EDX mappings were taken in an energy range of 0-20 keV, with a dispersion of 5 eV/channel at 35 µs, a tilt angle of a $\alpha = 20^\circ$ towards the detector, and a dwell time of 500 ms. Nanodiffraction was done in STEM mode with a beam diameter of 0.8 nm on a line across the thin film cross-section to evaluate the amorphicity or crystallinity of the different phases. For the STEM imaging, a high angle annular dark field (HAADF) detector was used.

### 3.2.3 Quantitative Microstructure Analysis

Pore and solid networks were investigated based on the segmented images from BIB-SEM and FIB-SEM. For each phase, the volume fraction, specific surface area (and interface areas) as well as the phase size distribution were determined. The specific surface and interface areas within representative volumes ($\mu m^2 \mu m^{-3}$) were obtained by measuring the length of the perimeters (i.e., the boundary line of a phase) and of the interface lines (i.e., boundaries between two specific phases) and then normalizing to the size of the image window ($\mu m \mu m^{-2}$). This stereological relationship between lines in 2D and areas in 3D is valid when the 2D image captures a representative portion of the 3D microstructure [47], which was achieved here by averaging the analyses from several images of the same sample.
The phase size distributions and volume fractions were obtained by using the ‘continuous phase size distribution’ (c-PSD) method developed by Münch and Holzer [48]. The c-PSD measurement was based on the analysis of a distance map of the phase of interest derived from segmented FIB-SEM images. From the distance map, all identified domains were filled with spheres of decreasing specific radius. This yields a c-PSD curve that relates the size (volume) of the filled domains with the corresponding radius of the spheres. It must be reminded that the c-PSD method was applied to FIB-polished cross-sectional images, which do not capture grain boundaries and associated grains. Consequently, throughout this paper, the electrode microstructure is seen as a continuum and described using “particle” size (rather than grain size).

3.2.4. Electrochemical Characterization

Using a Solartron 1260 frequency response analyzer, electrochemical characterization was performed using LSC-GDC-LSC symmetrical cells (with 1 cm² electrode surface area). Measurements were obtained at equilibrium (with zero DC bias) and a voltage perturbation of 20 mV was applied over the frequency range from $10^6$ to $10^{-1}$ Hz. The impedance was measured in the temperature range from 400 °C to 600 °C in air. ZView 2.90 was used to analyze the impedance spectra. Current collection was ensured by placing the cells between two so-called “tripods”. Each tripod consisted of three platinum wires connected together at one end and provided a triangular mechanical support and electrical contact for the cell at the other end. Preliminary (unpublished) results showed that utilizing the tripods yields similar results in terms of low-frequency electrode impedance than the more conventional platinum paste that may modify the electrochemical LSC/air kinetics and partially clog the pore network at the top of the thin layers. It should be noted that tripod current collectors can only be considered for experiments with zero DC current (as in the present study) but not for investigations with current load.
3.3. Results

3.3.1. Qualitative Microstructure Analysis

Crack-free and amorphous thin films of LSC were obtained after deposition at 340 °C. Despite the differences in the thermal expansion coefficients (TECs) of the substrate (GDC) and the electrodes (LSC), no delamination and cracking occurred after sintering at various temperatures. Figure 3.1 shows the variation of microstructures with different sintering temperatures. At lower sintering temperature, finer particles are observed with horizontally elongated pores, which are homogeneously distributed over the entire film thickness. Higher sintering temperatures lead to coarsening of phases and to the formation of more isometric pore shapes. LSC and pores are more uniformly distributed in the films sintered at higher temperatures. Coarsening of LSC and pore sizes is found to be more significant from 800 °C to 1000 °C than from 600 °C to 800 °C.

As shown in Figure 3.1, a secondary phase is present in the pore network and more abundant at 600 °C. It is characterized by a gray scale level, which is intermediate between LSC (bright) and pores (black), and referred to as “secondary phase” (SP) throughout this paper. Upon increasing the sintering temperature, the amount of SP significantly decreases and disappears almost completely at 1000 °C. In LSC600, the SP fills a large portion of the pores and covers most of the surface of the LSC particles. In LSC800 there are more open pores and the SP does not entirely cover the surface of the LSC particles (in contrast to LSC600).

Furthermore, STEM-EDX analysis reveals that the SP is primarily composed of Sr and O and no traces of La and Co are observed (Figure 3.2). The presence of the SP indicates that a certain amount of Sr is not incorporated in the LSC phase. Consequently, in samples with abundant SP, the LSC phase is likely to be non-stoichiometric. Point EDX analysis qualitatively reveals that a significant amount of Sr is still in the LSC after sintering at 600 °C with a Sr to La ratio of ca. 0.3:0.7 (see Supplementary materials, Figure 3.S1). Within the accuracy limits of the EDX
method, the A-site understoichiometry of LSC is thus relatively small (0.1) compared to the nominal composition, even for samples with abundant SP (LSC600).

Figure 3.1. (Left) FIB-SEM cross-sectional micrographs of LSC layers sintered at different temperatures and (right) corresponding segmentation results with LSC (white), SP (gray) and pores (black).
Figure 3.2. (Left) STEM micrographs of a pore filled with SP. The orange square in the upper left picture marks the analyzed area; (Middle and right) Corresponding STEM-EDX maps of the La, Co, O and Sr elements.

Additionally, the non-uniform gray level in TEM and SEM images as well as the intensity variations in the elemental maps, document that the SP density varies locally. This is also shown in Figure 3.3 in which the material contrast varies within the SP phase. Finally, electron diffraction line-scan with STEM in Figure 3.4 evidences that, after sintering, the SP is amorphous while the LSC is crystalline (see Supplementary materials, Figure 3.S2). A detailed analysis of the crystallization of the LSC perovskite is beyond the scope of this manuscript and will be the topic of a forthcoming paper.
Figure 3.3. Typical FIB-SEM cross-sectional micrograph (taken with BSE detector) of a pore filled with SP exhibiting different gray levels (labeled SP1 and SP2).

Figure 3.4. Electron nanodiffraction line scan analysis of spray pyrolysis LSC thin films: (left) HAADF-STEM micrograph with representation of the line scan and diffraction pattern locations (1, 2, 3); (right) diffraction patterns of LSC, pore and SP. A full diffraction line scan movie is available in the supplementary materials (see Figure 3.S2).
3.3.2. Quantitative Microstructure Analysis

Image analysis is performed on segmented cross-sectional FIB-SEM and BIB-SEM micrographs similar to those presented in Figure 3.1 (right). The results of the quantification by c-PSD depend greatly on the quality of segmentation. The limited contrast between SP and LSC in the BSE images introduces an uncertainty for the segmentation and the subsequent quantification, which is estimated to be ± 10% of the measured values.

Figure 3.5 gathers the quantitative microstructural analysis in terms of phase volume fractions and radii. As summarized in Figure 3.5A, the volume fraction of LSC remains similar for all sintering temperatures with values between 60 and 70%. In addition the ratio of LSC to (SP + Pores) remains roughly constant (ca. 70:30) for all three sintering temperatures. However, the amount of SP decreases from 20% at 600 °C to 0% at 1000 °C. The decrease in the amount of SP is accompanied by an increase in porosity from 10% in LSC600 to more than 30% in LSC1000. With decreasing sintering temperature, the SP seems to grow at the expense of the pores rather than at the expense of the LSC. This is an indication that only a small portion of Sr is not incorporated from the LSC (in accordance with TEM-EDX results). Moreover, the relatively large volume of SP may be explained by a low density due to the presence of nanoporosity (which cannot be resolved by SEM).

Figure 3.5B summarizes the results of the average radii for each phase as a function of sintering temperature. The radii corresponding to 50% of the cumulative volume in the normalized plots (Figures 3.5D and 3.5F) are called $r_{50}$, and represent the average values for the particle or pore sizes. As shown in Figures 3.5D and 3.5F, the normalized phase size distributions of LSC phase and pores in LSC600 and LSC800 are very similar. In contrast, LSC1000 exhibits larger particle and pore sizes as well as wider phase size distributions. The $r_{50}$ values in LSC600 and LSC800 are similar and lie between 35 and 40 nm for LSC and between 25 and 30 nm for the pores. In contrast, a coarser microstructure is observed for LSC1000, with $r_{50}$ being ca. 95
Influence of Sr-rich pore-filling phase

nm for LSC and ca. 50 nm for the pores.

Figure 3.5. Quantitative microstructural analysis (c-PSD) of the LSC layers sintered at different temperatures. A: Phase volume fractions. B: Average radii ($r_{50}$). C, E: Non-normalized c-PSD curves of LSC and pores. D, F: Normalized c-PSD curves of LSC and Pores (i.e., phase volume is normalized to 100%). The $r_{50}$ values are obtained from normalized c-PSD.

From 2D-image processing, the specific surface areas, $S$, of each phase (Figure 3.6A) and the interface areas, $I$, (Figure 3.6B) between each couple of phases are obtained. Thereby, the specific surface area of the pores ($S_{\text{Pore, total}}$) is composed of the interface between pore and LSC ($I_{\text{Pore-LSC}}$) and the interface between pore and SP
(I_{\text{Pore-SP}}):

\[ S_{\text{Pore, total}} = I_{\text{Pore-SP}} + I_{\text{Pore-LSC}} \]  \hspace{1cm} (3.4)

In analogy, the specific surface area of LSC \( S_{\text{LSC, total}} \) is equivalent to the sum of the two interfaces:

\[ S_{\text{LSC, total}} = I_{\text{LSC-SP}} + I_{\text{Pore-LSC}} \]  \hspace{1cm} (3.5)

As illustrated in Figure 3.6A, the specific surface areas of LSC are similar \( i.e., 28 \pm 1 \, \mu\text{m} \, \mu\text{m}^{-2} \) for LSC600 and LSC800, but is much lower in LSC1000 \( i.e., <15 \, \mu\text{m} \, \mu\text{m}^{-2} \) due to the strong coarsening. The LSC-Pore interfaces exhibit a different trend, with a maximum at 800 °C. The increase of the LSC-Pore interface from 600 °C to 800 °C is attributed to the lower amount of SP, while the decrease of the LSC-Pore interface from 800 °C to 1000 °C is ascribed to the coarsening process.

**Figure 3.6.** Specific surface areas of LSC, SP and pores (A) and specific interface areas (B) as a function of sintering temperature.
3.3.3. Electrochemical Analysis

The electrochemical impedance spectroscopy (EIS) results are presented in Figure 3.7. Typical Nyquist plots are shown in Figure 3.7A. ASR values as low as 0.13-0.20 Ω cm² are measured at 600 °C in air for LSC600 and LSC800. As summarized in Figure 3.7B the ASR for LSC1000 is 10.1 Ω cm², 50 to 78 times higher than those of LSC600 and LSC800, respectively. As the commonly accepted ASR value for high-performance SOFC cathodes is 0.15 Ω cm² [49], LSC600 and LSC800 layers appear to be suitable as SOFC cathodes for intermediate temperature operation.

![Graphs showing impedance spectra and ASR versus sintering temperature.]

**Figure 3.7.** (A) Representative impedance spectra of LSC/GDC/LSC symmetrical cells measured at 600 °C in air. Only a small portion of the LSC1000 spectrum is shown due to its much higher impedance. (B) Effect of sintering temperature on the ASR.

3.4. Discussion

The presence of a secondary phase, which strongly depends on the sintering temperature influences both microstructure and intrinsic properties. However, the question is which of these two can explain the drastic increase in ASR with sintering temperature shown in Figure 3.7B. Therefore, the most important results describing the nature of SP (and LSC) and its influence on cathode performance are
summarized subsequently. A simple model linking the volume fraction and the nanoporosity of the SP to the strontium deficiency in LSC is also presented. Finally, by using the electrochemical and microstructural results, the ALS model is applied to extract intrinsic kinetics properties of LSC (exchange neutral flux density).

3.4.1. Properties of SP and its Influence on Cathode Performance

Figure 3.8 presents a correlation of cathode performance with the respective surface and interface areas. When decreasing the sintering temperatures from 1000 °C to 800 °C and 600 °C, the cathode performance (measured in units of $\text{ASR}^{-1}$) increases significantly. This behavior clearly correlates with the LSC total surface area. In contrast the pore-LSC interface goes through a maximum at 800 °C and does not correlate with $\text{ASR}^{-1}$. The SP fills a large portion of the LSC600 pores and covers most of the LSC800 surface. These results, combined with the good electrochemical performance of LSC600 and LSC800 strongly indicate that the SP is permeable to oxygen transport, and does not significantly hinder the electrochemical reaction.

TEM-EDX analysis also shows that the composition of LSC remains close to the nominal one ($\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$). The strontium deficiency in the LSC is relatively low ($ca.\ 0.1$) despite the relatively large volume fraction of SP. Furthermore, the amount of SP increases with decreasing sintering temperatures up to more than 20 vol.% in LSC600 whereas the volume of pores decreases significantly. Apparently, the SP grows at the expense of the porosity. In addition, the variable gray scale levels (in SEM) indicate that the SP has a low density and a heterogeneous structure. All these findings suggest the SP not only contains strontium and oxygen but is also nanoporous. A simple model based on quantitative microstructural and compositional analysis is proposed in the next section so as to estimate the nanopore volume fraction in the SP.
3.4.2. Relationship Between Strontium Deficiency and SP Nanoporosity

In the spray pyrolysis deposition process involving air, organic solvents and water (from the hydrated precursors), the strontium-rich SP might mainly be composed of SrO, SrCO$_3$ or Sr(OH)$_2$ in first approximation. The detailed analysis of the different reaction states during the formation of the LSC are not within the scope of this manuscript, but from similar systems (BSCF and BSFZ) it is known that the perovskite formation occurs over an intermediate carbonate formation [50]. It can be related to the strontium-deficiency of the LSC by the following reaction:

\[
(La(NO_3)_3 \cdot 6H_2O, SrCl_2 \cdot 6H_2O, Co(NO_3)_2 \cdot 6H_2O) + (O_2, H_2O, C) \rightarrow
La_{0.6}Sr_{0.4-x}CoO_{3.5} + x (SrO, SrCO_3, Sr(OH)_2)
\] (3.6)
whereby the A-site deficiency, $x$, is the part of strontium that is incorporated in the SP and not in the LSC perovskite. Taking into account information from microscopy analysis (i.e., volume fractions of LSC and SP), as well as nominal compositions and densities of LSC and possible Sr species (Table 3.1), one can link the SP nanoporosity volume to the strontium deficiency $x$.

The LSC molar volume, $V_{LSC}$, is defined by:

$$V_{LSC} = \frac{M_{LSC}}{\rho_{LSC}}$$  \hspace{1cm} (3.7)

with $M_{LSC}$ and $\rho_{LSC}$ being the molar mass and the density of the LSC phase, respectively. In first approximation, it is assumed that the $\rho_{LSC}$ is quasi-independent of $x$ and equals the density of the stoichiometric LSC (with $x = 0$ and $\delta = 0$). The SP is composed of the strontium-rich phase (Sr-P) and nanopores (np). The SP volume fraction is thus:

$$V_{SP} = V_{Sr-P} + V_{np}$$ \hspace{1cm} (3.8)

with $V_{Sr-P}$ and $V_{np}$ being the volume of the Sr-P and the nanopores created per mole of LSC synthesized during the spray process (Eq. (3.6)). In this simplified model, the Sr-P consists of one single phase and can be taken either as SrO, Sr(OH)$_2$ or SrCO$_3$. The corresponding $V_{Sr-P}$ can be expressed by:

$$V_{Sr-P} = x \frac{M_{Sr-P}}{\rho_{Sr-P}}$$ \hspace{1cm} (3.9)

with $M_{Sr-P}$ and $\rho_{Sr-P}$ being the molar mass and the density of the Sr-P, respectively.

It is assumed that the ratio $V_{LSC}/V_{SP}$ equals the ratio of the volume fractions ($V_{LSC,\,obs}$, $V_{SP,\,obs}$) obtained from microstructure analysis (Figure 3.5).

$$\frac{V_{LSC}}{V_{SP}} = \frac{V_{LSC,\,obs}}{V_{SP,\,obs}}$$ \hspace{1cm} (3.10)
By substituting Eqs. (3.7)-(3.9) into Eq. (3.10), $V_{np}$ can be obtained:

$$V_{np} = \frac{V_{SP,obs} * M_{LSC}}{V_{LSC,obs} * \rho_{LSC}} - \chi \frac{M_{Sr-p}}{\rho_{Sr-p}}$$  \hspace{1cm} (3.11)

The volume fraction of nanopores in the SP, $V_{np\%}$, is then given by:

$$V_{np\%} = \frac{V_{np}}{V_{np} + V_{Sr-p}} * 100$$  \hspace{1cm} (3.12)

With this simple approach, by using the densities and molar masses of LSC and Sr-rich SP, the amount of nanopores in SP as a function of $x$ can be obtained (Table 3.1). The calculations described above were only applied to LSC600 whose SP volume fraction is large enough to make the results reliable. The calculations show that the SP corresponding to $x = 0.1$ (obtained from point TEM-EDX analysis) has a nanoporosity that is higher than 60 vol.-%, regardless of the nature of the Sr-rich phase. By taking into account the limited reliability of the TEM-EDX measurement and enlarging the range of $x$ values from 0.04 to 0.2, all SP exhibit nanoporosity (from 29 to 93 vol.-%). These results are in good agreement with the findings reported in Section 3.2.

**Table 3.1.** Estimated volume fractions of solid and nanopores in the SP of LSC600 assuming that the Sr-rich phase is either SrO, Sr(OH)$_2$ or SrCO$_3$.  

<table>
<thead>
<tr>
<th>A-site occupancy</th>
<th>$x$</th>
<th>Volume SrO (%)</th>
<th>Volume nanopore (%)</th>
<th>Volume Sr(OH)$_2$ (%)</th>
<th>Volume nanopore (%)</th>
<th>Volume SrCO$_3$ (%)</th>
<th>Volume nanopore (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.6}$Sr$</em>{0.4-x}$CoO$_{3-\delta}$</td>
<td>0.2</td>
<td>37</td>
<td>63</td>
<td>61</td>
<td>39</td>
<td>71</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>18</td>
<td>82</td>
<td>30</td>
<td>70</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>7</td>
<td>93</td>
<td>12</td>
<td>88</td>
<td>14</td>
<td>86</td>
</tr>
</tbody>
</table>
3.4.3. Assessment of LSC Intrinsic Kinetics Properties

The formation of SP influences the microstructure as well as the intrinsic properties of LSC such as the exchange neutral flux density, $r_0$, which can be extracted from the ALS model, Eqs. (3.1) and (3.2). For MIEC cathodes, the utilization region for oxygen reduction is defined by Ref. [53]:

$$\delta = \sqrt{l_g \frac{D_o}{k_o}}$$  \hspace{1cm} (3.13)

where $l_g$ is the representative particle dimension in the MIEC electrode, and $D_o$ and $k_o$ are the diffusion and oxygen exchange coefficients, respectively. Using the values for $D_o$ (2.86 x 10^{-9} \text{ cm}^2 \text{ s}^{-1}) and $k_o$ (9.09 x 10^{-8} \text{ cm s}^{-1}) reported by Berenov et al. [54] for the stoichiometric La_{0.6}Sr_{0.4}CoO_3-δ at 600 °C and 0.227 bar, the utilization region is estimated to be ca. 4-6 μm for particle sizes in the range of 50 nm-100 nm.

Since the utilization region is greater than 1 μm, the whole thickness of the LSC electrodes in this study is electrochemically active. Consequently, Eq. (3.1) becomes [21]:

$$Z_{chem} = \frac{RT}{2F^2aLr_0(1+j\omega t_{chem})}$$  \hspace{1cm} (3.14)

The expression for ASR from Eq. (14) can be simplified [15,21] to:

$$ASR = \frac{RT}{4F^2aLr_0}$$  \hspace{1cm} (3.15)

This is the case where transport in the solid is fast and the entire surface of the cathode is utilized for oxygen exchange. By using Eq. (3.15), the values of exchange flux density, $r_0$, are assessed to be 5.3 x 10^{-8}, 5.0 x 10^{-8}, and 1.3 x 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1} for LSC600, LSC800, and LSC1000, respectively. When increasing the sintering temperature from 600 °C to 1000 °C, the ASR measured at 600 °C in air increases by a factor of 78. Correspondingly the LSC surface area
drops only by a factor of 2 whereas $r_0$ values change by a factor of 39. With these findings, it appears that, for the investigated system (i.e., 1 µm thick LSC thin films), changing the sintering temperature affects essentially the intrinsic kinetic properties of the LSC with no apparent detrimental effect of the SP on the electrochemical performance.

3.5. Conclusions

Nanostructured LSC thin-film electrodes have been successfully deposited by cost-effective spray pyrolysis. A secondary phase (SP) besides LSC and pores is found and identified to be nanoporous, amorphous, strontium- and oxygen-rich. The SP fills out a large portion of the pores if the LSC layers are heat-treated at 600 °C. Nonetheless, the latter exhibit low ASR values (0.13 Ω cm$^2$ at 600 °C in air) and are suitable as cathodes for SOFC operated at intermediate temperatures. In contrast, while the SP disappears at a sintering temperature of 1000 °C, the LSC electrodes show poor electrochemical performance.

By quantitatively analyzing the microstructure and applying the ALS model, it is evidenced that the significant ASR increase (by a factor of ca. 80) upon raising the sintering temperature from 600 °C to 1000 °C is barely due to the coarsening of the electrode (surface area changes only by a factor 2). Rather it is essentially ascribed to the change of exchange neutral flux density (by a factor of 39), an intrinsic property of the electrode material that can be linked to the degree of strontium deficiency in the LSC perovskite. However, these findings have to be seen as first steps towards a deeper understanding of the physical and chemical processes taking place. At this point of our research, it is not yet possible to single out the effect of the LSC and that of the SP on the electrochemical kinetics.

While strontium enrichment of the LSC surface has been already reported to be detrimental [55] or favorable [28] in the literature, it seems that strontium-rich
secondary phases do not negatively affect the oxygen reduction kinetics. The presence of the amorphous strontium-rich secondary phase at the interface with the LSC also suggests that there might be new ways to design highly active SOFC catalysts by tuning the crystallinity of the materials [25] and by developing heterostructures with higher complexity than the conventional one-phase electrodes [15,56].

3.6. References


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4. Influence of Film Thickness and CGO Buffer Layer on the Electrochemical Performance of Spray Pyrolysed LSC Cathodes*

4.1. Introduction

It was shown in Chapter 3 that LSC cathodes prepared by spray pyrolysis consist of nanosized particles with radii in the range between 35-40 nm for LSC sintered at 600 °C and 800 °C. It was also found that a secondary phase is formed besides LSC and pores, which fills out a large portion of the porous network. Despite the secondary phase formation, ASR values as low as 0.13 Ω cm² are obtained at 600 °C in air [1]. Therefore, spray pyrolyzed LSC is found suitable for intermediate temperatures applications.

Oxygen surface exchange at the perovskite/air interface has been shown to govern oxygen reduction reaction (ORR) kinetics. Consequently, at lower operating temperatures, the electrochemical performance can be improved by: (A) increasing the electrode layer thickness (i.e., higher surface area in total layer thickness) [2], and (B) by reducing the electrode particle size [3] (i.e., higher specific surface area per volume).

* The contents of this chapter is based on the research done in collaboration with several groups including the following: Z. Yáng¹, L. Holzer², J. Martynczuk³, P. Steiger¹, L. Meiler¹, P. Fuchs¹, T. Ryll¹, L. J. Gauckler¹, D. Stender⁴, C. Schneider⁴, J. Hwang⁵, J.-W. Son⁵, and M. Prestat¹.

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In this chapter, the influence of film thickness on the electrochemical performance is investigated. Moreover, the prospect of integration of the LSC into a full cell is also assessed.

The next sections also present the characterization of the as-deposited and sintered powders and films of LSC, which are not presented in the previous chapters. These include the thermogravimetric and differential scanning calorimetric analyses (TG-DSC), X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS) and the integration of LSC in full cells with and without gadolinium-doped ceria (CGO) buffer layer.

4.2. Experimental

In addition to variation of layer thickness, also composition of LSC and SP were further investigated. Specifically, thermogravimetric analysis (TGA), Rutherford backscattering spectrometry (RBS), and X-ray Diffraction (XRD) were employed.

4.2.1. Thermogravimetric Analysis-Differential Scanning Calorimetry (TGA-DSC)

The decomposition and crystallization processes of LSC powders are investigated by simultaneous thermal analyses using thermogravimetry (TG) and differential scanning calorimetry (DSC) (Netsch STA 449C). For this purpose powders are collected after spray pyrolysis at 340 °C (i.e., raw material before the calcination and sintering steps). The samples are heated to 900 °C at 3 K min⁻¹ and measured against empty Pt crucibles.
4.2.2. Rutherford Backscattering Spectrometry (RBS)

For the Rutherford backscattering spectrometry (RBS) [4], the samples were characterized at the ETH Laboratory of Ion Beam Physics. Measurements were performed using a 2 MeV $^4$He beam and a silicon PIN diode detector under 168°. The collected RBS data was analyzed using simulations by the RUMP code [5]. Characteristic X-ray spectra that were simultaneously taken during the RBS measurement showed no sign of contaminations above 1 at%.

4.2.3. X-ray Diffraction

The in-situ annealing X-ray diffraction was implemented using a D500 X-ray diffractometer (XRD) from Bruker-Siemens (Germany) with the high temperature attachment HTK10 from Anton Paar (Austria). The LSC samples were placed on the heating Pt stripe and fixed with ceramic glue. A thermocouple under the Pt stripe was used to measure the temperature and also to control the temperature during the measurements. As the sample surface may have a different temperature (usually lower) than measured by the thermocouple, a pyrometer was used in addition to determine the sample surface temperature. These XRD measurements were also performed in grazing incidence geometry with an omega angle of ca. 1°. For the in-situ XRD measurements during annealing of as-deposited LSC films, a temperature program was chosen, i.e., all heating ramps were set to a constant rate of ca. 3 °C/min and isothermal dwells were performed at 600 °C, 800 °C, and 1000 °C. As typical XRD scans take relatively long (ca. 30 min for 30° in 2θ) only one expected perovskite peak, (overlap of (110) and (104)) was chosen to observe during the heating ramps to strongly increase the time resolution of the measurements. The range was set to 31°-34° 2θ with a step size of 0.02° and 0.5 s per data point resulting in ca. 76 s per cycle. Only during the isothermal dwells larger ranges of 2θ (20°-65°) were measured to ensure the possibility of
comparisons to ex-situ measured XRD patterns. The largest uncertainties in these measurements originate from thermal gradients, which are displayed by the measured temperatures. Especially changes of the sample surface, which are expected, may influence the measurement. This was well observed during the isothermal dwell where e.g., the measured surface temperature dropped from 800 °C to 775 °C although the bulk temperature measured by the TC remained constant. Nevertheless, the reported measurements give insights on the crystallization kinetics which cannot be determined by other means and the measured temperatures are still correct within a range of +/-50 °C.

4.2.4. Symmetric Cell Preparation and Impedance Spectroscopy

The preparation of symmetrical cells follows the procedure published in previous work [1]. In summary, LSC film layers were deposited by spray pyrolysis at 340 °C on both sides of CGO tape substrate, which acts as an electrolyte. The LSC domains cover an area of ca. 1 cm². In order to achieve different film thicknesses, the time of deposition was varied between 20-450 minutes. Afterwards, the symmetrical cells were sintered at 600 °C, 800 °C, and 1000 °C for 4 h in air to obtain the perovskite phase and to vary the microstructure of LSC layers. A self-made platinum tripod contact was used in this work for the current collection besides the traditional platinum gauze contact with an area of 1.3×1.3 cm² (Alfa Aesar, A Johnson Matthey Company, 52 mesh woven from 0.1 mm diawire, 99.9% (metals basis), CAS # 7440-06-4, Stock # 10283, Lot # L11U017). For impedance spectroscopy a Solartron SI1260 was used. The symmetric cells were swept with an alternating voltage amplitude of 20 mV over the frequency spectrum from 10⁶ to 0.1 Hz.
4.2.5. Full Cell Fabrication and Cell Testing

The fabrication procedure summarized in this section was optimized in previous works [2,6-8]. Half cells (2 cm × 2 cm) made of a NiO-YSZ anode support and a ca. 6.5 µm-thick YSZ electrolyte were fabricated by a conventional powder process. Two types of cells were fabricated, with and without CGO buffer layer. For the cell with CGO buffer layer, a ca. 250 nm-thick CGO layer was deposited on the YSZ electrolyte by pulsed laser deposition (PLD) at a substrate temperature of 700 °C and an ambient oxygen pressure of 6.67 Pa, covering the entire surface of the YSZ. For the PLD, a KrF excimer laser (λ = 248 nm, COMPEX Pro 201F, Coherent) was used as an ablation source. The laser fluence (energy density) at the target surface was 3 J/cm² with a target-to-substrate distance of 5 cm.

For the cell testing, a custom-made button cell test set-up [2] using a ceramic-glass composite-based seal [9] was employed. Air and humidified H₂ (3% H₂O) were used as oxidant and fuel, respectively, and the flow rates of each side were kept at 200 sccm (standard cubic cm per min). The cell operation temperature was varied from 550 to 650 °C at intervals of 50 °C and impedance spectra and current-voltage-power (I-V-P) curves were obtained at each temperature using a Solartron impedance analyzer with an electrochemical interface (SI1260 and SI1287) at a frequency range from 10 MHz to 0.1 Hz.

4.3. Results and Discussion

DSC and TGA are used to understand the crystallization process of LSC powders collected after spray pyrolysis at 340 °C. Figure 4.1 shows the DSC-TGA curves. At T<200 °C, 2 wt.% mass loss was observed, which could be attributed to the water which was formed from the precursors. Between 200-500 °C, 28.5 wt.% mass loss is attributed to the decomposition of organic materials. At T>500 °C, 6 wt.% mass loss was observed. 4.5 wt.% of which corresponds to the small endothermic
peak at 550-720 °C in the DSC curve. Crystallization starts at 200 °C and full crystallization is reached at 500 °C with the evidence of 7 exothermic peaks in the DSC curve. However, a small endothermic peak at 600 °C is still present which relates to the 4.5wt% of mass loss at 550-720 °C. It is still unclear where this peak is coming from.

**Figure 4.1.** Thermal analysis of DSC and TG on the LSC precursor powders collected from as deposited thin films. Crystallization of LSC starts at 200 °C, and it is fully crystallized at 500 °C. 2 wt.% loss of water at T<200 °C, 28.5 wt.% loss of organics at 200-500 °C. 6 wt.% loss at T >500 °C, 4.5 wt.% loss at 550-720 °C corresponds to a small endothermic peak.

Rutherford Backscattering (RBS) was used to quantify the layer composition and to determine film thickness. In general, the results show that the ratio of the cations is very close to the target stoichiometry. The cation ratios were found to be 0.61 ± 0.02, 0.37 ± 0.06, and 1.02 ± 0.05 for the La, Sr and Co, respectively. Hence, the measured values are very close to the nominal target composition (La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$). For many samples the relative height of the film and substrate signals indicates the
possibility of significant oxygen deficiency in the films. However, the oxygen deficiency cannot be quantified due to high surface roughness and thickness range of the layers. Surface roughness increases from the film sintered at 600 °C and to 1000 °C. Film thicknesses can also be obtained from RBS measurements. As the RBS considers only the dense solid phase, porosity and defects are not included in the measured thicknesses. As a result, the values obtained by RBS are lower than the values obtained from SEM analyses of cross-sections. For example, a 1-µm thin LSC film has a measured film thickness of 0.54 µm in RBS. The representative RBS spectrum of La$_{0.6}$Sr$_{0.4}$CoO$_{3-δ}$ is shown in Figure 4.2.

Figure 4.3 presents the X-ray diffraction patterns of the as-deposited LSC cathode at 340 °C and the LSC cathodes sintered at 600, 800 and 1000 °C. Scan averaging was used to reduce the noise in the obtained XRD patterns. Amorphous LSC is evidenced in the as-deposited sample by the absence of any LSC diffraction peaks in Figure 4.3A. Only diffraction peaks from CGO substrate and Pt wires are detected. Figures (4.3B)-(4.3D) show LSC diffraction peaks with intensities increasing from 600 °C to 800 °C, and 1000 °C. Peaks marked by asterisks (*) in Figure 4.3 are unidentified phases, which may be impurities present in the LSC cathode. With higher sintering temperatures the relative height of unidentified peaks decreases whereas the LSC peaks increase. Assuming SP to be SrO, there are no peaks in the diffraction pattern corresponding to this oxide. Therefore, no relevant information about the SP can be deduced in the XRD analyses. However, considering SrO as amorphous, no diffraction peaks are expected to be observed.

The microstructures of the spray pyrolysed LSC with varying deposition time are shown in Figure 4.4. Variation of deposition time resulted in different LSC film thicknesses. The SEM images in Figure 4.4 also illustrate that variation of deposition time does not significantly influence the microstructure as shown by constant granularity in all samples. Hence, it is possible to vary the cathode layer thickness but keeping the same microstructure characteristics.
Influence of film thickness and CGO buffer layer

Figure 4.2. RBS spectra of 1-µm thin $La_{0.6}Sr_{0.4}CoO_3$ films deposited on CGO substrate after sintering for 4 h in air at three different temperatures (600, 800, and 1000 °C). The continuous line is a RUMP simulation [5]. The observed stoichiometries are close to the nominal compositions. The layer thickness corresponds to 0.54 µm assuming a density of 6.07 g cm$^{-3}$ [10] for LSC.

Figure 4.5 shows fractured LSC cross-sections after sintering at 600 °C, 800 °C and 1000 °C. The particle size is obviously increasing with sintering temperature. Elongated pore networks are also noticeable at lower sintering temperatures. No delamination of the layers from the CGO substrate is observed.
Figure 4.3. XRD patterns of LSC films measured at 20 °C (A) as deposited, and sintered at (B) 600 °C, (C) 800 °C, and (D) 1000 °C.

Figure 4.4. Cross-sections of LSC films deposited by spray pyrolysis. The thickness increases with deposition time.
Influence of film thickness and CGO buffer layer

Figure 4.5. SEM images of LSC films after sintering at 600 °C, 800 °C, and 1000 °C for 4 h in air. The particle and pore sizes increase with sintering temperature.

Figure 4.6 shows the results of ASR measurements as a function of film thickness for LSC cathodes sintered at 600, 800 and 1000 °C. ASR decreases with increasing thickness from 0.2 µm up to ca. 1 µm layers. This fits well with the traditional model of the electrochemical process for the cathode of SOFC [11]. The lowest ASR is 0.13 Ω cm² for a cell sintered at 600 °C and equipped with a 1 µm-thick LSC cathode. However, the ASR increases with a further increase of the thickness of the LSC layer from 1µm to 6 µm. This phenomenon does not fit to the traditional model anymore. Indeed, in this case, bulk diffusion seems to be the rate limiting parameter rather than surface exchange. A possible explanation is the transport of fuel in the pores (i.e., gas diffusion), which may be hindered due to the clogging by SP in the pores (Figure 4.7). Most probably at small thicknesses the mobility of gas species through the (nanoporous) SP is sufficient and thus gas diffusion in LSC600 and LSC800 only becomes limiting at higher thicknesses >2 µm. When gas diffusion is limited in thick layers, then the active zone moves away from the interface with the electrolyte. In this case also the transport distances for ions becomes longer and thus diffusion of oxygen ions may become limiting as well.

LSC1000 exhibits a different behavior, with an associated different rate limiting processes at high thicknesses. There is no minimum observed in the curve in Figure 4.6. Hence in LSC1000 surface exchange remains the limiting process over the entire thickness range as shown in Figure 4.7B. This different thickness-dependency

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of LSC1000 has two main reasons: (1) LSC1000 has a low exchange coefficient/low exchange current density (as shown in chapter 3). Therefore a high surface area is used to compensate the exchange limitation. However, LSC1000 has a very low specific surface area due to its coarse microstructure, so that a high thickness is necessary to provide sufficient surface sites, and (2) LSC1000 has no SP (i.e., no clogging), so that gas diffusion is not limiting also in relatively thick cathode layers of 10 µm or larger.

![Figure 4.6](chart.png)

**Figure 4.6.** ASR values measured at 600 °C for LSC|CGO|LSC symmetric cells sintered at 600 °C and 800 °C. With increasing thickness starting from ca. 200 nm the ASR values first decrease, then reach a minimum at ca. 2000 nm, and at even higher thickness the ASR increases again.
Figure 4.7. Hypothetical model of cathode activity, which explains the observed behavior in Figure 4.6. (A) For the LSC600 and LSC800: At lower thicknesses ($\leq 1$ µm), the whole cathode thickness is active towards oxygen reduction with minimal influence of charge transport. At higher thicknesses, the active zone is confined at the topmost layer of the cathode near the cathode-current collector interface. At some distance from this interface, the clogging of pores by the SP takes into effect. Thus at larger cathode thicknesses, limitations from charge transport dominate the cathode performance and $\text{ASR}_{\text{pol}}$ increases. (B) For LSC1000: The absence of SP makes the entire cathode surface of LSC active regardless of the thickness. Increasing the cathode thickness results to decreasing contribution of the electrochemical reaction to the ASR due to increasing available surface area. As the cathode layer becomes thicker, the contribution from charge transport also increases. However, up to ca. 6 µm the increase of transport resistance is not dominating.

When comparing our results to the performance of LSC-based cells reported in literature it is important to note that very often the thin films of LSC are prepared by more costly deposition techniques such as PLD. The results from our study document that the electrochemical performance of spray pyrolysed LSC is comparable to the performance range of dense and nanosized (20-70 nm size, 100-
200 nm layer thickness) PLD-deposited LSC [12,13]. LSC layers deposited by PLD at lower temperatures show better performance (450 °C, 470 °C) than samples deposited at higher temperatures (630 °C, 650 °C). At 600 °C, ASR values of 0.1 Ω cm$^2$ and 0.7 Ω cm$^2$ were obtained for LSC deposited at 450 °C and 650 °C by PLD, respectively [12]. Hence, they are in a similar range and they show the same temperature dependence as spray pyrolysed LSC.

The power densities of fuel cells with LSC cathodes sintered at 600 °C over anode-supported YSZ electrolyte buffer with and without CGO layers are shown in Figures 4.8A and 4.8B, respectively. The power densities are also comparable to PLD-fabricated LSC cathodes in the works of Noh et al. [2,6]. Unlike the PLD cathode, the presence of CGO buffer layer does not significantly influence the performance as shown in the comparable power densities observed for both cells with LSC sintered at 600 °C. It is reasonable to conclude that spray pyrolysed LSC cathodes are more resistant to chemical reaction than LSC cathodes deposited by PLD. Another possibility that may explain the high resistance obtained might come from the difference in the particle sizes obtained from these two different methods. Nonetheless, the comparable performance with and without CGO buffer layer demonstrates that there is no other interfacial issue, such as weak adhesion or massive delamination of the spray pyrolysed LSC. Therefore, the present results show the potential of spray pyrolysis as an effective and economical method of applying high-performance cathodes to YSZ-based SOFCs.

Comparable performance of cells with LSC heat-treated at 800 °C is observed as shown in Figure 4.8C with CGO buffer layer. This shows that the nanostructure obtained after annealing at 800 °C, like the nanostructure obtained at 600 °C is sufficient to provide reaction sites for reduction. However, as shown in Figure 4.8D, without a buffer layer, the electrochemical performance of the cell at 800 °C dropped from ca. 400 mW cm$^{-2}$ to ca. 150 mW cm$^{-2}$. This suggests that treatment at 800 °C results in LSC cathodes that are less resistant to chemical reaction with YSZ.
Consequently, without the CGO buffer layer, 800 °C sintering temperature for LSC is a too high temperature for applying the LSC cathodes by spray pyrolysis.

**Figure 4.8.** Power densities of cells with 1 µm-thick LSC layer annealed at 600 °C for 4 h in air (a) with CGO layer (b) without CGO layer. Power densities of cells with 1 µm-thick LSC layer annealed at 800 °C for 4 h in air (c) with CGO layer (d) without CGO layer.
4.4. Conclusions

This work primarily investigates the relationship between electrochemical performance (ASR) and the electrode layer thickness. For LSC sintered at 600 °C and 800 °C the following thickness dependency is observed: (1) ASR decreases with increasing film thickness up to ca. 1-2 µm and (2) then the ASR increases again with increasing film thickness (>2 µm to ca. 6 µm). The microstructure characteristics are not influenced by the film thickness (i.e., same granular texture throughout the layer). Decreasing ASR with increasing electrode thickness is attributed to higher surface area. This suggests that surface exchange plays a limiting influence in the electrode performance of thin LSC films. At higher thicknesses (i.e., >1-2 µm), transport limitations (gas diffusion, ionic diffusion) may take an active role, because due to pore clogging with SP only the top portion of the film ends up being active for the electrochemical reaction. In the case of LSC sintered at 1000 °C, ASR decreases continuously with increasing thickness. The minimum observed in the curves of the LSC600 and LSC800 is not observed in LSC1000 suggesting that the electrochemical performance is limited by surface exchange, and transport of gas and charges is not limiting up to the thickest electrode layer reached in this work.

In the prospect of the viability and applicability of spray pyrolysed LSC, this work shows that the LSC deposited by spray pyrolysis at 600 °C provides a comparable performance as LSC deposited by more expensive techniques such as PLD. Moreover, at lower operating temperature (i.e., 600 °C), LSC cathodes are chemically stable in vicinity to YSZ electrolytes. Hence, at or below 600 °C spray pyrolysed LSC can be applied without CGO buffer layer, which is much simpler and cheaper than cells with PLD based cathodes that require a buffer layer. However, the applicability and stability at long operating times are yet to be verified.
4.5. References


Influence of film thickness and CGO buffer layer
Ni-YSZ Anodes for HT-SOFC Applications
5. Ni-YSZ Cermet Anodes*

5.1. Introduction

Porous Ni-YSZ cermet is a standard anode material for high temperature solid oxide fuel cells (SOFC). The reaction mechanism of such composite anodes is shown in Figure 5.1. It includes a complex interplay of electrochemical reactions (oxidation of fuel at the triple phase boundary, TPB) with various transport processes (electronic conduction in nickel, ionic transport in yttria-stabilized zirconia (YSZ) and gas diffusion in the pores).

![Figure 5.1. Schematic representation of Ni-YSZ cermet anode and the mechanism of charge transport and charge transfer processes [1].](image)

* This introductory chapter on Ni-YSZ is adapted from the following co-authored article: L. Holzer, B. Iwanschitz, Th. Hocker, L. Keller, O. Pecho, G. Sartoris, Ph. Gasser, B. Muench, Redox cycling of Ni–YSZ anodes for solid oxide fuel cells: Influence of tortuosity, constriction and percolation factors on the effective transport properties, J. Power Sources 242 (2013) 179-194.(doi:10.1016/j.jpowsour.2013.05.047)
5.1.1. Charge Transport and Charge Transfer Processes

As described by Costamagna [2], the electrode working mechanism and associated performance can be simulated by coupling the transport processes (solved via Ohm’s law) with the electrochemical reactions (described by Butler-Volmer equation). A major challenge for such simulations is the incorporation of morphological features as for example the effects of variable grain sizes and variable compositions. A first approximation can be done using microstructure models that are based on idealized and simplified particle shapes. For example, Abbaspour and Kenney [3-5] presented numerical simulations of 3D-microstuctures in porous electrodes that consist of spherical particles (Ni and YSZ). They demonstrated that simulations with such simplified microstructures well describe the basic relationships between the TPB length and both anode composition (Ni/Ni+YSZ) and particle size. Under the assumption that the TPB length represents the active reaction sites, these numerical models in principle also capture the basic relationships between electrochemical activity and variable compositions or particle sizes. However, if one wants to simulate the electrode working mechanism and performance in a realistic way, all relevant properties, including the effective transport properties, have to be described accurately. In this context it is important to note that the effective transport properties cannot easily be deduced from models with simplified particle shapes. In reality, subtle changes e.g., in the dimensions of the bottlenecks can have a large impact on the effective transport properties, especially for compositions close to the percolation threshold. Therefore the morphological details, which are relevant for the transport properties, can only be captured in an accurate way by using high-resolution 3D-imaging techniques.
5.1.2. Tomography and Morphological Parameters

In this context the recent progress of serial sectioning with focused ion beam (FIB) technique opens new possibilities to study SOFC electrodes. For a review of FIB-tomography (method and applications), which is also called FIB-SEM serial sectioning, see Holzer and Cantoni [6]. Alternatively, the resolution of X-ray tomography has also improved considerably and it is now suitable for the study of some electrode microstructures. Both techniques, FIB- and X-ray tomography, were extensively used during the last few years for quantitative analysis of anode microstructures [7-16]. It is important to note that so far most of these 3D-studies on SOFC electrodes mainly intended to quantify electrochemical reaction sites and to distinguish between active and inactive TPBs. Only a limited number of studies focused on the relationships between morphological features and transport properties despite the obvious importance of this topic. In this context, two exceptional investigations from the group of prof. W. Chiu merit to be mentioned:

a) Grew et al. [17,18] studied the effect of 3D microstructures on the transport phenomena in the YSZ phase of cermet anodes with a lattice Boltzmann method, which provides information about localized resistive losses due to Joule heating. In addition, the 3D microstructures were characterized by phase size distributions, which are obtained with a ray-shooting method. The combination of both techniques opens the possibility to coherently examine the detailed geometry and the associated resistive loss, which finally results in resistive loss distributions (RLD). The RLD thus links the local resistive losses (Joule heating) with the associated local phase sizes in the microstructure. The RLD measurements document that transport losses mainly originate at locations with small phase sizes. These ‘high-loss locations’ can be interpreted as constrictions (so-called bottlenecks) in the percolating network of the conducting phase (in this case conduction of oxygen ions in YSZ were considered).
b) In more recent investigations, Nelson et al. [19,20] developed 1D- and 2D-models (electrochemical fin) to simulate the effect of varying cross-sections along the transport pathways (i.e., constrictions in YSZ). The models are capable of replicating experimentally observed electrode behavior such as the influence of electrode thickness on polarization resistance. Thereby varying cross-sections are described with a sintering quality parameter (SQ). In the modeling framework, a suite of dimensionless parameters (e.g., fin efficiency and base current) and performance metrics (transport resistivity / charge transfer resistivity) are established. From the correlation between dimensionless parameters and performance metrics, different transport regimes could be identified, which allows performance predictions for different types of microstructures and sintering quality (SQ).

In the above-mentioned investigations [17-20], constrictions and varying cross-sections are identified as important morphological features, which have a considerable influence on the transport properties. In these studies it was emphasized that, in order to establish a link between results from modeling and experimental results from laboratory samples, a method should be developed which allows measuring the constrictivity (i.e., a parameter that describes varying cross-sections and sintering quality) directly from realistic samples with complex disordered microstructures. Under this perspective, our own developments of 3D techniques become important. In a recent paper we have thoroughly described a methodology, which enables to quantify the constrictivity based on data from tomography [21]. In this recent work we have also described further methods for the quantification of additional morphological parameters which are relevant for the transport properties, such as the tortuosity and the percolation factor. Hence a 3D-toolbox was established, which enables describing the most important topological parameters that are relevant for the effective transport properties. The ultimate goal of these developments is the prediction of the effective transport properties entirely
based on 3D microstructure analysis (and intrinsic transport properties). For this purpose the quantitative relationships between topological parameters and effective transport properties have to be established empirically. A first empirical study in this direction was performed by Wiedenmann et al. [22], who applied those 3D methods in combination with impedance spectroscopy for the investigation of porous membranes in alkaline electrolysis cells. Thereby the overall impact of the microstructure on the effective ionic diffusivity is described by the so-called M-factor, where ‘M’ stands for microstructure.

5.1.3. Microstructure Factor, M

The M-factor is equivalent to the ratio of the effective ($\sigma_{\text{eff}}$) over the intrinsic transport properties ($\sigma_0$):

$$M = \frac{\sigma_{\text{eff}}}{\sigma_0} \quad (5.1)$$

The intrinsic properties ($\sigma_0$) characterize transport in a pure medium (e.g., diffusion in liquid electrolyte or electronic conductivity in pure nickel) without microstructure effect. Based on the experimental results it was shown that the effective transport properties could indeed be described with the M-factor, which itself is defined as the product of four distinct microstructure parameters, i.e., phase volume fraction ($\phi$), percolation factor ($P$), constriction factor ($\beta$) and inverse tortuosity ($1/\tau$):

$$M = \frac{(\phi P \beta)}{\tau} \quad (5.2)$$

In some publications (e.g., Clennell [23]) the effect of tortuosity on the transport properties is described as being proportional to $1/\tau^2$:

$$M = \frac{(\phi P \beta)}{\tau^2} \quad (5.3)$$

It must be emphasized that Equations 5.2 and 5.3 were formulated a long time ago based on theoretical and semi-empirical considerations. The relevant ‘historical
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literature’ goes back to Kozeny, 1927 [24], Carman, 1956 [25], Archie, 1942 [26], Clennell, 1997 [23], van Brakel and Heertjes, 1974 [27], and Petersen, 1958 [28]. A thorough discussion of these historical papers about microstructure effects on transport properties is beyond the scope of this chapter, but a summary thereof can be found in an earlier publication [21]. The synthesis that can be drawn from of the historical literature is the formulation of a hypothesis, which states that the effective transport properties can be predicted based on a set of volume-averaged topological parameters, which then leads to Equations 5.1-5.3. For many decades, however, it was impossible to quantify the volume-averaged parameters used in Equations 5.2 and 5.3 because no suitable techniques were available. However, the recent progress in 3D-imaging and 3D-image analysis now opens new possibilities. Today, all transport relevant parameters can be determined, for example with our 3D-toolbox. These techniques are described below in the methodology section, but more details can be found in the following original papers: Münch and Holzer [29], Keller et al. [30,31] and Holzer et al. [21].

5.1.4. Microstructure Degradation Upon Redox Cycling

In this PhD thesis, these 3D techniques are used to characterize microstructure degradation in a Ni-YSZ anode during redox cycling. More specifically in Chapter 6 we want to investigate how the effective transport properties in nickel, YSZ and pores are affected by redox cycling and how the measured performance drop relates to changes of the relevant morphological features (i.e., \( \phi, P, \beta, \) and \( \tau \)). In Chapter 7, we investigate the influence of TPB on the electrochemical performance and evaluate the relationship between the extent of loss of TPB and performance degradation upon redox cycling. Moreover, the limitations invoked by charge transport and transport-related parameters on TPB, and possible scenarios dealing with this complex interplay between processes are also discussed.
On a qualitative level, microstructure degradation in nickel cermets which is caused by redox cycling is well described *e.g.*, by Sarantaridis and Atkinson [32], Klemenso and Mogensen [33], Virkar *et al.* [34] and Fouquet *et al.* [35]. Their observations of the redox process in Ni based anodes can be summarized as follows:

The oxidation of nickel to form nickel oxide is associated with a volume increase of 70%. Due to the expansion of the nickel grains the entire material is 'swelling' on a macroscopic scale. The kinetics of the oxidation process is mainly controlled by the diffusion of nickel (outwards) and oxygen (inwards) through the oxidation layer. For temperatures that are typical for SOFC operation (600-1000°C), the nickel grains become fully oxidized within a relatively short time. For example at 800°C a 1 μm-thick NiO layer is formed within 4 minutes. During the re-reduction metallic nickel nuclei are first formed on the surface of the nickel oxide. Reduction leads to a volume decrease so that the surface of the metallic nickel grains remains accessible for the reducing gas and hence the kinetics of this process are controlled by surface reaction instead of diffusion. Subsequently the small nickel grains tend to minimize their surface energy due to the relatively high temperatures, which leads to the formation of larger nickel agglomerates. Thereby nickel is most probably mobilized as a (volatile) metal-hydroxide species, which re-precipitates at preferred locations in the microstructure. This Ni coarsening leads to degradation of electrical conductivity, loss of TPB and associated electrochemical activity.

Jeangros *et al.* [36] performed in-situ redox experiments with an environmental TEM. The TEM observations correlate well with their calculations based on density functional theory (DFT). The authors describe that the reduction process of NiO is triggered at the interface with YSZ, where oxygen ions from NiO migrate to the sites of oxygen vacancies in the neighboring YSZ-phase. Thereby nanovoids are formed at the NiO-YSZ interface. Also during the oxidation process pore formation is an important feature, which is observed at the interface between metallic Ni and the NiO layer. This phenomenon is explained by the outward diffusion of Ni.
On a grain scale the volume expansion caused by oxidation can be considered to be reversible during re-reduction. However on a microstructure scale the volume changes are not fully reversible due to expansive strain exerted to the ceramic backbone and to the associated formation of additional internal porosity (subsequently called pore-swelling). This leads to a macroscopic swelling upon repeated cycling, whereby also the network of the ceramic phase undergoes dilation and the distances between the rigid YSZ grains have to increase. Nevertheless, in literature the YSZ phase is generally considered as a rigid backbone, which ensures a certain mechanical stability to the cermet material. At this stage a quantitative description of redox induced microstructural changes in cermet anodes is largely missing. This is particularly true for the allegedly rigid YSZ backbone.

Hence, not only the microstructure degradation of the Ni-phase is poorly quantified [32]. Also the degradation of the YSZ phase is poorly understood. The ionic conductivity can be measured experimentally by dissolving the nickel phase from the cermet anode and then analyzing the remaining ceramic backbone. In this way, it was shown by Klemenso and Mogensen [33] that the ionic conductivity of YSZ significantly decreases during redox cycling. Under the traditional view that the ceramic phase represents a rigid backbone, which stabilizes the cermet material, the measured drop in ionic conductivity is somewhat surprising. Two explanations are possible: a) the properties of YSZ are changing without any degradation on the grain scale, but only due to a transformation from cubic to tetragonal crystallographic system. Alternatively, it was reported that the particle size of YSZ is changing due to the mobility of Zr species under SOFC operating conditions [16,37,38], which may explain the measured drop in ionic conductivity. In this study we will present quantitative descriptions, which document additional processes that are involved in the degradation mechanism of the YSZ phase. In any case, a change in ionic conductivity may significantly affect the overall
performance of the anode and therefore more detailed microstructural investigation is required to understand YSZ degradation upon redox cycling.

In the next chapter, quantitative microstructure analyses are performed for nickel-YSZ samples fabricated in a previous experimental investigation by Iwanschitz et al. [39]. The changes of first order parameters (i.e., volume fractions and size distributions) are documented for all three phases (nickel, YSZ and pores). This enables a quantitative description of nickel coarsening and pore swelling. Based on the 3D-data from FIB-tomography higher order topological parameters (i.e., constriction factor, tortuosity and percolation factor) are extracted. From these parameters the M-factors can be calculated according to an equation obtained from a previous work involving virtual materials testing (VMT) [40,41]. This equation has a similar form as Equation 5.2, and the effective transport properties can be predicted according to Equation 5.1. Following the work of Stenzel et al. [41], Equation 5.2 takes the form:

$$M = \frac{\phi_{eff}\beta^{0.36}}{\tau^{5.17}}$$  (5.4)

Effective conductivities can also be determined with numerical transport simulations and with input of 3D microstructures from tomography. For this purpose we are using a commercially available software package (GeoDict). The obtained simulated conductivities can then be compared with the predicted conductivities from the VMT-equation. In this way a thorough description of the transport relevant parameters can be obtained for all three phases in nickel-YSZ anodes. Furthermore it can be tested whether the M-factors obtained by image analysis (VMT-equation) and by direct numerical simulation are capable to predict the effective ionic and electrical conductivities of a cermet anode and their degradation upon redox cycling.
5.2. References


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Ni-YSZ cermet anodes


6. 3D Microstructure Effects in Ni-YSZ Anodes - Part I: Prediction of Effective Transport Properties and Optimization of Redox Stability*

6.1. Introduction

The electrochemical performance of Ni-YSZ anodes depends on the interplay between different transport processes and the electrochemical reactions at the triple phase boundary (TPB) (see Fig. 5.1, Chapter 5). The fuel oxidation at the TPB includes numerous intermediate steps [1], which can be summarized into the following net reaction:

$$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \quad (6.1)$$

The associated charge transport and charge transfer reactions provide specific contributions to the area specific resistance (ASR). The ASR contribution of each process depends on both, the relevant intrinsic property (e.g., intrinsic ionic conductivity of YSZ) and on the corresponding morphological characteristics (e.g., volume fraction and tortuosity of YSZ). The combination of intrinsic properties and microstructural characteristics results in an effective macro-property (e.g., effective ionic conductivity).

One way to improve the effective properties and the associated electrode performance is to tailor the microstructure. However, the optimization of electrode microstructures is challenging because of the complex interplay between the various

* This chapter is based on the published article in Materials: O. Pecho, O. Stenzel, B. Iwanschitz, P. Gasser, T. Hocker, R.J. Flatt, L. Holzer, Materials 8 (2015) 5554-5585. P. Gasser acquired FIB-tomography data. The samples were obtained from B. Iwanschitz, who also conducted the experimental conductivity measurements. Virtual Materials Testing performed by O. Stenzel, M. Neumann, and V. Schmidt provided an empirical equation that predicts transport-related properties, which was used to study microstructure effects on conductivity. The author analyzed and processed data, and wrote the manuscript under the supervision and expertise of M. Prestat, T. Hocker, R.J. Flatt, and L. Holzer.
processes taking place. The different properties cannot be manipulated independently from each other. In literature strong focus was laid specifically on the improvement of the electrochemical activity, which correlates with the TPB length (i.e., the number of electrochemically active sites). Therefore, the tendency is to develop finer-grained microstructures with higher TPB length [2]. Nevertheless, in order to ensure that the reaction from Equation (6.1) occurs throughout the anode, all three phases joining at the TBP must constitute a connected network. Thus, for a high anode performance the microstructure must be optimized also in terms of connectivity and effective transport properties of all three phases (Ni, YSZ, pores). In addition, it is not only the initial microstructure that is important for a successful application of the fuel cell technology. For example electrolyte supported SOFCs with open system configuration undergo several reduction-oxidation (redox) cycles, which often cause degradation of the microstructure and an associated loss of electrochemical performance. Hence, redox stability is an additional quality criterion for such SOFC anodes [3].

In order to study the influence of anode microstructure on the performance and redox stability, the relevant topological parameters must be quantified. For this purpose 3D image analysis is required to gain the necessary information on phase connectivity, tortuosity, constrictivity and active TPB length. Using focused-ion beam scanning electron microscopy (FIB-SEM) [4-11] and X-ray tomography [12- 17] it is possible to obtain 3D microstructure data, which can be used to quantitatively describe the anode topological characteristics. Moreover, information gained from 3D microstructure analysis can be used to design anode microstructures with improved effective properties and redox stability.

In principle, the controlled materials design includes two steps: 1.) Establishing experimental methods by which the topological parameters can be influenced in the fabrication process (e.g., deposition method, composition, powder fineness, sintering conditions) [18-24]; and 2.) Formulating relationships between
microstructure properties and effective material properties. In the past, the second relationship was not established on a quantitative level. However, recently this gap was filled by an approach using virtual materials design (VMT) [25]. Thereby a large number of virtual 3D microstructures were created by means of spatial stochastic simulations. The corresponding effective properties (i.e., conductivities) were then determined with numerical transport simulations. Using statistical analysis (i.e., error minimization) an empirical equation describing the relationship between topological parameters and effective transport property was obtained (see chapter 5, Equations (5.1) and (5.4)).

In Equation (5.4), $\Phi$ is the volume fraction of the transporting phase. $P$ is the percolation factor. $\Phi$ and $P$ together combine into $\Phi_{eff}$, which is the effective phase volume that contributes to transport. Constriction factor ($\beta$) introduced by Petersen [26] can be interpreted as the ratio between the average sizes of the bottlenecks and the bulges $(r_{\text{min}}/r_{\text{max}})^2$ [27], and describes the bottleneck effect [28-30]. Tortuosity ($\tau$) is a statistical expression for the windedness of transport pathways [31]. There are a few definitions of tortuosity. For example, the work with VMT [25] uses the so-called geometric tortuosity (with all transport pathways following a median axis skeleton), while another work [32] uses geodesic tortuosity (with shortest transport pathways through the voxel-space of a given phase). The exponential parameters $a$, $b$ and $c$ are determined empirically with the above-mentioned VMT approach and with statistical error minimization.

Whenever all the necessary topological parameters are known, the M-factor can be determined from Equation (5.4) and the effective transport property from Equation (5.1). One advantage of using such empirical relationships is the possibility to predict material properties that are difficult to access experimentally. For example in SOFC anodes, this approach opens new possibilities to gain information on the effective ionic conductivity in YSZ, which is usually not known or expensive to measure. More details on the methods to extract the required topological parameters.
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from tomographic data can be found in previous works [27,33,34]. The topological parameters are also described in the experimental section below.

In the present study we use the above-mentioned methods to quantify topology and to predict effective transport properties in order to investigate microstructure effects of Ni-YSZ anodes. A special focus is laid on degradation mechanism upon redox cycling and on the redox stability. Ni-YSZ anodes of varying microstructure coarseness (fine, medium, coarse) before and after redox cycling at 950°C are investigated. The microstructures of fresh anodes and the corresponding electric and ionic conductivities are compared to each other. Then the influence of redox cycling on anode properties is documented in order to unravel the degradation mechanisms.

We use the established empirical relationship between microstructure parameters and effective conductivity (resulting in $M_{\text{pred}}$) and apply the predictive model to different SOFC anode microstructures. Also in this work, we determine the M-factor by numerical simulation of conduction ($M_{\text{sim}}$), using the voxel-based tomography data as a structural input (with GeoDict software). The comparison of $M_{\text{sim}}$ and $M_{\text{pred}}$ can be considered as a validation of the empirical prediction approach.

So far the redox degradation was mainly described by qualitative observations (e.g., Ni agglomeration) or by measuring parameters, which cannot be linked directly to an effective property (e.g., average particle size). With the proposed approach where topological parameters are linked with conductivity on a quantitative level, the diagnosis of degradation effects becomes more specific. For example loss of conductivity can be directly related to change of bottleneck dimensions and associated constrictivity, or change of (average) length of transport pathway and associated geodesic tortuosity. As an outcome, the detailed analysis of microstructure parameters leads to a more differentiated interpretation of redox degradation. Finally, this knowledge leads to defining fabrication guidelines for improved redox stability of Ni-YSZ anodes.
6.2. Experimental

The procedures for fabrication and electrical characterization of Ni-YSZ anodes are described in great detail by Iwanschitz et al. [35,36]. The following Sections (6.2.1 and 6.2.2) represent a short summary of the experimental procedures, followed by a description of the applied imaging and image analysis techniques (Sections 6.2.3 and 6.2.4).

6.2.1. Anode Fabrication and Redox Cycling

Three different anodes with fine, medium, and coarse microstructures are produced by screen printing, oxidized sintering, and subsequent reduction. To vary the microstructure, three different powders (fine, medium, coarse) of 8YSZ (Mel Chemicals, purity >99%) are mixed always with the same powder of NiO (J.T. Baker, purity >99%) to form Terpineol-based slurries. The coarse powder is produced by calcination of the fine powder (Mel Chemicals). The particle size distributions of the raw NiO and YSZ powders measured using a Horiba LA-920 laser scattering analyzer can be found in the supplementary information (Table 6.S1). The ratio of the powders is chosen such that the solid volume fraction (Ni:YSZ) after reduction is 40:60. The Terpineol-based slurries are then screen-printed onto 3YSZ substrates (Nippon Shokubai, 140 µm) to give a 12 × 12 mm² cell dimension. The layer thickness of the fine, medium, and coarse anodes are 20, 25, and 26 µm, respectively. The anodes are sintered in air at 1350 °C for four hours after screen-printing. Subsequent reduction is performed at 950 °C.

Degradation experiments are done by exposing the anodes to eight redox cycles in a tube furnace at 950 °C. For each cycle, reoxidation is carried out for 30 min and the re-reduction is carried out by ramping H₂ flow for 5 min, with equilibration time of at least 30 min.
6.2.2. Electrical Conductivity Measurements

Four-point conductivity measurements are performed on $8.8 \times 21$ mm$^2$ samples cut from anode half-cells. The samples are placed in an alumina tube and contacted with Pt wire. The conductivity measurements are done at 950 °C with a gas flow of 200 mL/min using forming gas (5% H$_2$/95% N$_2$). The Nernst potential is kept constant at 1.1 V during the measurements and the gas is not humidified in order to exclude ill-controlled degradation effects from water during the redox cycling. Between each redox cycle, the alumina tube is flushed with N$_2$ for one hour and the anodes are oxidized in airflow of 100 mL/min.

6.2.3. Image Acquisition by FIB-Tomography and SEM

For microstructure analysis, polished cross-sections are prepared from the samples that were used for four-point conductivity measurements. The porous anodes are first impregnated with a low-viscosity resin and then polished on textile substrates with 1, 3, and 6 µm diamond suspensions. Focused ion beam (FIB)-SEM tomography is performed with a Helios Nanolab 600i (FEI) with Ga liquid metal ion source. FIB tomography includes a repetitive procedure of alternating ion sectioning and SEM imaging. The serial sectioning is done with an ion beam current of 2.5 nA and an accelerating voltage of 20 kV. For serial SEM imaging, good contrast settings are achieved with the so-called through-the-lens detector (TLD) at 2.0 kV accelerating voltage and 0.69 nA beam current.

6.2.4. Quantitative 3D Microstructure Analysis

FIB-tomography provides image stacks, which typically consist of 500 to 1000 two-dimensional (2D) images. Prior to the quantification of transport-relevant topological parameters the stacks have to be pre-processed. This procedure includes alignment (3D reconstruction), selecting a region of interest (cropping), noise
filtering, and segmentation (i.e., identifying Ni, YSZ, and pore phases). In our workflow we use Fiji [37], including some home-made plug-ins and Avizo (version 8.1.1) [38] software packages. Further details on image processing can be found in our previous study [27]. 3D reconstructions of the fine, medium, and coarse Ni-YSZ anodes before and after redox cycling are shown in Figure 6.1. The corresponding dimensions of the tomographic data are summarized in the supplementary information (Table 6.S2).

Particle and pore size distributions are determined by a method called continuous phase size distribution (c-PSD), which was developed by Münch and Holzer [34]. Contrary to conventional PSD methods, which are based on size statistics of discretized objects, c-PSD treats each phase as a continuum. A cumulative continuous size distribution is achieved by incrementally decreasing the size of spheres, which cover a particular phase volume and are completely contained in this volume. The radius corresponding to 50 vol % in the cumulative c-PSD curve ($r_{50,\text{max}}$) is considered a statistical measure for the average size of the phase. Hence, this so-called $r_{50,\text{max}}$ represents the average size of bulges in a percolating network of either a solid or pore phase.
Figure 6.1. 3D microstructures (FIB-tomography) of Ni-YSZ anodes with increasing coarseness from left to right. Top row is before and bottom row after redox cycling at 950°C. Pores (black), YSZ (gray) and Ni (white). Significant Ni agglomeration is visible in all samples after redox cycling.

Based on 3D information from tomography mercury intrusion porosimetry (MIP), a method that describes pore size distributions by pressure infiltration can be simulated. According to the so-called Washburn equation [39], the capillary radius is inversely proportional to the applied pressure. A cumulative MIP-PSD is thus obtained by linking the infiltrated volume with the corresponding pressure and capillary radius. It is currently well accepted that the MIP-PSD mainly captures the size of bottlenecks, which dominate the infiltration process [40]. Here we apply the method of Münch [41], which uses the same principle as the c-PSD analysis.
However, it adds the constraint that the incrementally added volume must be connected with the plane from where the infiltration starts. A cumulative MIP-PSD curve is thereby obtained by incrementally decreasing the sphere radius, which corresponds to increasing pressures in the experimental MIP analysis. The ‘inkbottle effect’ governs the measurement like in the experimental counterpart such that the dimensions of the bottlenecks limit the intrusion. Unlike the c-PSD, MIP-PSD measures the size of the bottlenecks \( r_{50,\text{min}} \) once the breakthrough pressure is passed. Both methods can be applied to describe size distributions of pores as well as solid phases.

The constriction factor \( (\beta) \) is given by the ratio of the cross-sectional areas of the bottlenecks to the bulges \( (A_{\text{min}}/A_{\text{max}}) \) and further simplification leads to the following relation:

\[
\beta = \left( \frac{\pi r_{\text{min}}^2}{\pi r_{\text{max}}^2} \right) = \left( \frac{r_{\text{min}}}{r_{\text{max}}} \right)^2 \quad (6.2)
\]

This concept was adapted to describe bottleneck effects in disordered microstructures (e.g., fuel cell anodes) [27]. For this purpose, the results from c-PSD \( (r_{50,\text{max}}) \) and MIP-PSD \( (r_{50,\text{min}}) \) are used to describe the average sizes of bulges and bottlenecks, respectively. By Equation (6.2) we obtain the constriction factor \( (\beta) \), which can be plugged into Equation (5.4). Tubes of constant radius have a constriction factor of 1, while in disordered microstructures of varying radii the values are \(<1\).

Geodesic tortuosity, \( \tau_{\text{geod}} \) (simply \( \tau \)) is defined as the ratio of geodesic distance \( (d_{\text{geod}}) \) and material thickness \( (l) \). In general, the geodesic distance can be interpreted as the shortest path length from one side of the material to the other side through the transporting material phase. For statistical accuracy, we consider the mean value of geodesic distances (shortest path lengths) for numerous starting points. More precisely, any pixel in the so-called in-plane, which belongs to the transporting phase, is considered a starting point for shortest path analysis. The shortest path
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Lengths are calculated using Dijkstra’s algorithm [42]. Therefore, the image is interpreted as a graph in which each voxel of the transporting phase is a node and all the nodes are connected whenever the corresponding voxels are connected with respect to the 26-neighborhood. Note that the geodesic tortuosity should not be mixed up with the geometric tortuosity. For the latter, Dijkstra’s algorithm is applied to a skeleton graph of the transporting phase. The two methods were compared in a recent study by Stenzel et al. [32] who concluded that the geometric definition overestimates the tortuosity, while the geodesic definition captures tortuosity with respect to the conductive transport processes more adequately.

6.2.5. Conductivities and M-Factor Simulation

Equations (5.2)-(5.4) describe a method to predict effective conductivities by using quantitative microstructure analysis and the M-factor ($M_{\text{pred}}$), respectively (see Equation (5.4)). As an alternative approach, the effective ionic and electrical conductivities are also assessed by numerical simulation using the software GeoDict (version 2014 Rev. March 2015) [43]. The mathematics involved in the simulation are extensively described by Wiegmann and Zemitis [44]. The simulations of electrical and ionic conductivities were done along x, y, and z directions, using the real tomographic data as input. It should be noted that for the case where the phase of interest takes an intrinsic conductivity value of 1, (while all other phases are set to 0), the obtained conductivities also represent the M-factor (i.e., $M_{\text{sim}}$). The results from the simulation ($M_{\text{sim}}$) are subsequently compared to the results from the predicted M-factor from the microstructure analysis ($M_{\text{pred}}$). The dimensions of the tomographic 3D data used in the simulations are summarized in Table 6.S3 in the supplementary information.
6.3. Results

6.3.1. Qualitative Description of Microstructures

The initial microstructures are strongly influenced by the sintering process and the initial reduction conditions. It is important to note that the morphological characteristics of Ni and the pores are influenced by the coarseness of the YSZ powder. During the anode fabrication only the starting particle size of the YSZ powder is varied (fine, medium, coarse) while the particle size of NiO is the same for all the samples.

The visual inspection of 3D reconstructed images in Figures 1 and 2D segmented images in Figure 6.2 show that upon sintering and reduction, the microstructures of Ni and pores are adapting to the microstructure of YSZ. This adaptation already starts during sintering in air (before reduction), where NiO changes its size according to the coarseness of the YSZ (not shown here). Hence, the anodes fabricated with coarser YSZ also exhibit coarser microstructures of Ni and pore phases. However, the inspection of 3D images also indicates that Ni and YSZ have different characteristics. YSZ appears to be more granular with distinct sinter necks, whereas Ni forms a more continuous network with a greater structural heterogeneity.

The microstructure degradation related to redox cycling can be observed in Figure 6.2 by comparing the top (before) and bottom rows (after redox). Significant Ni coarsening is observed after redox cycling. Ni tends to form agglomerated patches, which are particularly strong in the fine anode. In contrast, the microstructure of YSZ seems to withstand redox alterations. This is compatible with the interpretation of YSZ being the rigid backbone of Ni-based anodes. An additional aspect of redox degradation is the increase of intergranular porosity, which is again stronger in the fine anode. On a macroscopic scale, the increase of the pore volume fraction may result in an overall swelling. Consequently, the swelling will invoke a relative decrease of the solid volume fractions.
Figure 6.2. 2D-slices of segmented tomographs from all the Ni-YSZ samples investigated in this study. Three different YSZ powders (fine, medium, and coarse) were used for composite anode fabrication. In the initial microstructures (top row), Ni (white) and pores (black) follow the size of the YSZ (gray) starting particle size. Redox cycling (bottom row) leads to significant coarsening and agglomeration of Ni.

6.3.2. Electrical Conductivity Measurements

Figure 6.3 shows the evolution of electrical conductivities ($\sigma_{\text{eff}}$) during eight redox cycles at 950 °C [35]. The fine sample exhibits the greatest degradation of $\sigma_{\text{eff}}$, while the coarse sample even shows an improvement in $\sigma_{\text{eff}}$. Significant differences are measured for the initial values (zeroth) and for the first redox cycle. These initial differences are not well understood. They may be related to experimental issues such as contacting and/or to microstructure reorganization after reduction. In contrast, the linear trends from the first to the eighth cycle are interpreted as typical
redox behavior. Therefore, in the discussion, the values of $\sigma_{\text{eff}}$ after the first redox cycle are taken as the reference electrical conductivity ($\sigma_{\text{eff},\text{before}}$). The last redox cycle (eighth) is taken as the electrical conductivity after redox cycling ($\sigma_{\text{eff},\text{after}}$). The data set in Figure 6.3 will be compared to predicted transport properties, which are based on topological parameters obtained from 3D image analysis (see Equations (5.1) and (5.4)).

![Graph showing the evolution of electrical conductivities ($\sigma_{\text{eff}}$) of Ni-YSZ during exposure to 8 redox cycles at 950°C based on the work of Iwanschitz [35]. Linear trends of degradation are observed between the 1st and 8th cycles. $\sigma_{\text{eff}}$ of the fine anode is strongly degrading. In the medium-grained anode $\sigma_{\text{eff}}$ is slightly decreasing. In the coarse anode, $\sigma_{\text{eff}}$ is even improving. The differences in the initial values and in the curing behavior during the 1st cycle are not well understood.](image-url)

**Figure 6.3.** Evolution of electrical conductivities ($\sigma_{\text{eff}}$) of Ni-YSZ during exposure to 8 redox cycles at 950°C based on the work of Iwanschitz [35]. Linear trends of degradation are observed between the 1st and 8th cycles. $\sigma_{\text{eff}}$ of the fine anode is strongly degrading. In the medium-grained anode $\sigma_{\text{eff}}$ is slightly decreasing. In the coarse anode, $\sigma_{\text{eff}}$ is even improving. The differences in the initial values and in the curing behavior during the 1st cycle are not well understood.
6.3.3. Effective Volume Fractions ($\Phi_{\text{eff}}$, $\varepsilon_{\text{eff}}$) and Percolation ($P$)

In this and the subsequent sections (6.3.3-6.3.5), we present results from the quantitative 3D analysis with a strong focus on parameters that are relevant for the effective transport properties. The porosities ($\varepsilon_{\text{eff}}$) of the six investigated SOFC anodes are shown in Figure 6.4, and the ratios of the solid volume fractions ($\Phi_{\text{Ni}}/\Phi_{\text{YSZ}}$) are presented in Figure 6.5. Before exposure to redox cycling, the porosity increases from fine (25 vol %) to medium (36 vol %) to coarse (39 vol %). During redox cycling, the porosity increases in all three microstructures and is most pronounced in the sample with the fine microstructure (83 vol % increase) compared to medium and coarse samples (8 and 12 vol %).

![Figure 6.4. Porosity ($\varepsilon$) in Ni-YSZ anodes. In fresh samples, porosity increases from fine to coarse. After sintering the fine anode is relatively dense. Redox cycling then leads to a significant increase of porosity in the fine anode.](image)

The ratios $\Phi_{\text{Ni}}/\Phi_{\text{YSZ}}$ are similar for all six samples before and after redox cycling (40:60 vol%) as shown in Figure 6.5B. However, considerable differences occur with respect to the effective volume fraction ($\Phi_{\text{eff}}$), which is defined as the product of the total volume fraction ($\Phi$) multiplied by the percolation factor ($P$). The latter
parameter describes the fraction of a phase, which forms a connected network, and it can be obtained from the MIP-PSD analysis (Figure 6.5A). Before exposure to redox-cycling, the percolation factors are close to 1. The cumulated percolation factors for Ni, YSZ, and pores together comprise 0.991, 0.985, and 0.962 in fine, medium, and coarse microstructures, respectively. After redox cycling, the percolation factors of YSZ and Ni decrease. This change is particularly strong for YSZ in the coarse sample, where the percolation factor drops to 0.18. For the Ni phase the changes are largest in the fine sample, where the $P$ drops from 0.99 to 0.80 (compared to 0.90 in the coarse sample). In all samples the $P$ of pores remains close to 1 before and after redox cycling.

6.3.4. PSDs, Average Radii ($r_{50,\text{max}}, r_{50,\text{min}}$), and Constriction Factor ($\beta$)

The c-PSD and MIP-PSD curves for Ni in fine and coarse anodes are shown in the supplementary information (Figure 6.S1). The PSDs for medium-grained anodes are not shown for simplicity. The average radii ($r_{50,\text{max}}, r_{50,\text{min}}$) and associated constriction factors of Ni, YSZ, and the pores are summarized in Figures 6.6-6.8. The $r_{50,\text{max}}$ of Ni particles in fine, medium, and coarse anodes are 378, 540, and 636 nm (Figure 6.6a) and the average bottleneck sizes ($r_{50,\text{min}}$) are 204, 275, and 300 nm (Figure 6.6b). Although the bulges and bottlenecks increase from fine to coarse, the constriction factor ($\beta_{\text{Ni}}$) exhibits a slightly decreasing trend from 0.29 (fine) to 0.22 (coarse) (Figure 6.6c).

Upon redox cycling, the average size of Ni ($r_{50,\text{max}}$) increases from 378 nm (before) to 517 nm (Figure 6.6a). For medium and coarse microstructures, the c-PSDs and associated average Ni sizes ($r_{50,\text{max}}$) remain almost unchanged. In contrast, the Ni bottlenecks ($r_{50,\text{min}}$) in all the samples exhibit an increase upon redox cycling with the most significant change for coarse anodes (Figure 6.6b). Consequently, in the fine sample the constriction factor ($\beta_{\text{Ni}}$) decreases significantly from 0.29 to 0.18 (Figure 6.6c) mainly due to grain growth (increase of $r_{50,\text{max}}$). In the medium and
coarse samples $\beta_{\text{Ni}}$ increases to 0.34 and 0.37 due to the opening of the bottlenecks (Figure 7.S1B, increase of $r_{50,\text{min}}$) after redox exposure.

**Figure 6.5.** (A) Percolation factors ($P$) of the different phases and (B) solid volume fractions ($\Phi_{\text{eff}}$) in the 6 Ni-YSZ anodes. $P$ describes the interconnected portion of a phase. (A) After redox cycling the percolation factors of YSZ decrease significantly in the coarse anode. The percolation factors of Ni decrease only moderately (-10 to -20 %). (B) The ratio Ni:YSZ is similar in all six samples (40:60 vol%), however the effective volume fractions (interconnected portions) of YSZ and Ni show partially strong variations upon redox cycling due to changes of $P$ (e.g., YSZ coarse and Ni fine).
Figure 6.6. (a) Average sizes of bulges ($r_{50,\text{max}}$ from c-PSD), (b) bottlenecks ($r_{50,\text{min}}$ from MIP-PSD) and (c) constriction factors ($\beta_{Ni}$) for Ni in composite anodes, before (black) and after redox cycling (gray). The $\beta_{Ni}$ in the fine sample decreases due to the growth of bulges ($r_{50,\text{max}}$) while the $\beta_{Ni}$ in medium and coarse samples increase due to the widening of bottlenecks ($r_{50,\text{min}}$).
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Figure 6.7. (a) Average sizes of bulges ($r_{50,\text{max}}$), (b) bottlenecks ($r_{50,\text{min}}$) and (c) constriction factors ($\beta_{\text{YSZ}}$) of YSZ in composite anodes, before (black) and after redox cycling (gray). Upon redox cycling, the sizes of the bulges remain nearly constant while the bottlenecks are shrinking ($r_{50,\text{min}}$). Consequently, all the $\beta_{\text{YSZ}}$ decrease after redox cycling.
Figure 6.8. (a) Average sizes of bulges ($r_{50,\text{max}}$), (b) bottlenecks ($r_{50,\text{min}}$) and (c) constriction factors ($\beta_{\text{Pore}}$) for the pores in Ni-YSZ anodes, before (black) and after redox cycling (gray). For medium and coarse all parameters remain stable during redox cycling. In the fine sample the bottlenecks expand ($r_{50,\text{min}}$), which results in a higher $\beta_{\text{Pore}}$ after redox cycling.
As illustrated in Figure 6.7a, the YSZ phase exhibits the increasing size of the bulges from fine to coarse before redox cycling (i.e., 360, 557, and 981 nm for the fine, medium, and coarse samples, respectively). This is accompanied by decreasing average radii of the bottlenecks (195, 172, and 82 nm, Figure 6.7b). Consequently, the constriction factor (β_{YSZ}) before redox cycling decreases from 0.37 to 0.007 (fine to coarse). The ceramic phase is usually described as a rigid backbone in the composite anodes, which resists mechanical stress and morphological degradation. Nevertheless, for samples with a coarse microstructure, a significant decrease of 25% in the size of bulges is observed upon redox cycling (Figure 6.7a). In the fine and medium samples the changes in the size of the bulges (r_{50,max}) are small (-6% for fine and +4% for medium). In YSZ the bottleneck radii change considerably upon redox cycling. For example, in the coarse sample the initially small bottleneck radius (r_{50,min}) decreases again by 90%. However, in fine and medium samples the neck radii decrease strongly (Figure 6.7b).

The average sizes of bulges and bottlenecks in the porous network, as well as the corresponding constriction factors, are shown in Figure 6.8a-6.8c. In general, the size of the bulges and the bottlenecks of the pores increase as the initial microstructures become coarser. The biggest change in the pore structure upon redox cycling concerns the increase of the bottleneck radius in fine anodes (Figure 6.8b), which may be related to the qualitatively observed swelling. Before redox cycling, the constriction factor (β_{Pore}) in the fine sample is relatively low (0.25), compared to medium and coarse samples. After redox cycling the β_{Pore} is relatively large (0.5 ± 0.1) in all three samples.

### 6.3.5. Geodesic Tortuosities (τ)

The geodesic tortuosities of Ni, YSZ, and the pores are shown in Figure 6.9. In general, the geodesic tortuosities vary only in a narrow range between 1.0 and 1.5. Exceptionally high tortuosities are observed in the coarse samples for Ni (1.7 before
and 1.6 after redox) and for YSZ (before redox). Before redox cycling, the tortuosities of Ni and YSZ tend to increase from fine to coarse (Figure 6.9a,b). Upon redox cycling, the tortuosities of Ni and YSZ tend to increase in all samples except for YSZ in the coarse anode. However, the results for YSZ of the coarse sample must be questioned because the representative elementary volume (REV) may be larger than the image window. The REV for coarse YSZ is very large due to the significant loss of percolation upon redox cycling (see also Figure 6.5).

**Figure 6.9.** Mean geodesic tortuosity of (a) Ni, (b) YSZ, and (c) pores before (black) and after (gray) redox cycling. Note: Geodesic tortuosities are usually relatively low (i.e., <1.5) and represent the shortest pathways from A to B (in a predetermined direction) through the voxel-domain of a segmented phase.

In the initial state, the tortuosities in the pore structures (Figure 6.9c) increase from coarse to fine samples, which may be attributed to stronger densification of the fine anode upon sintering. After redox cycling, the tortuosities in the pores are generally low, which is due to the macroscopic swelling and associated opening of the pore
networks.

6.3.6. Simulation of Effective Transport Properties ($\sigma_{\text{eff}}$) and Microstructure Factors ($M_{\text{sim}}$)

Effective conductivities and the corresponding microstructure factors ($M_{\text{sim}}$) can be assessed by means of numerical simulations. In order to capture the microstructure effects in a realistic way, 3D information from tomography is used as geometric input. In this study, the transport simulations are performed with the commercial software GeoDict.

As shown in Figure 6.10b, the M-factors ($M_{\text{sim}}$) of YSZ in the fresh samples tend to decrease from fine to coarse. Hence, fine microstructures appear to be preferable. However, the M-factors of YSZ decrease strongly upon redox cycling, which leads to strong limitations for ionic conductivities. In the coarse microstructure this limitation is already present in the initial microstructure (before redox) due to the low sintering activity and strong constrictions at the bottlenecks.

![Graph showing M-factors of Ni and YSZ](image)

**Figure 6.10.** Simulated M-factors ($M_{\text{sim}}$) of (a) Ni and (b) YSZ before (black) and after (gray) redox cycling for fine, medium and coarse samples. Pristine samples exhibit a decreasing $M_{\text{sim}}$ from fine to coarse for Ni and YSZ. After exposure to redox cycling, the $M_{\text{sim}}$ of Ni in fine decreases while it improves in medium and coarse. $M_{\text{sim}}$ of YSZ in all samples decreases after redox cycling.
The trends observed for ionic conductivity in the simulation (i.e., decreasing M-factors from fine to coarse) are caused mainly by the reduction of bottleneck radii for coarser microstructures and by the associated reduction of constriction factors. These variations can be attributed to the inverse relationship between the particle size of YSZ and the corresponding sintering activities (i.e., coarser YSZ tends to have smaller bottlenecks). Apparently, in the coarse sample the necks are so weak that mechanical stresses from redox cycling even lead to a loss of connectivity between the YSZ particles (see Figure 6.5: drop of percolation factor) and to a reduction of the effective volume fraction. In the fine sample there is also an increase of tortuosity, which contributes to the significant reduction of the M-factor during redox cycling.

The M-factors ($M_{\text{sim}}$) of Ni vary in a relatively narrow range between 0.01 and 0.08 (Figure 6.10a). Before redox cycling, the M-factors of Ni decrease from fine to coarse. This result implies that in the fresh anode, fine microstructures are preferred due to the relatively high initial effective electrical conductivity. After redox cycling, the M-factor of Ni in the fine sample decreases, while the M-factors of medium and coarse samples increase. Overall, the simulated effective electrical conductivities in all investigated anodes are still relatively high, even after redox cycling, since they reach 1% to 8% of the intrinsic conductivity in bulk nickel. As mentioned above, since transport distances in thin anode layers are short, these effective electrical conductivities are not expected to impose significant limitations to the anode performance. However, as discussed later, the results for Ni in the medium and coarse microstructure have to be interpreted carefully, because the corresponding REV is very large, possibly even exceeding the thickness of the anode layer.
6.4. Discussion

This study focuses on three main points. (1) The first is the evaluation of the possibility to predict anode conductivities based on an empirical relation (Equation (5.4)) between the measured topological parameters and effective transport properties. The empirical equation was developed by means of virtual materials testing (i.e., analyzing virtual microstructures from a stochastic model). In this first part, the aim is to test whether this relationship also holds for real microstructures (i.e., porous Ni-YSZ anodes). (2) Next is the understanding of redox degradation mechanisms in Ni-YSZ anodes, with a special focus on effective transport properties. The knowledge of micro-macro relationships (Equation (5.4)) enables us to determine specific contributions to the degradation of conductivities, which originate from quantifiable changes of specific, transport-relevant topological parameters. This level of detail is novel and potentially sheds new light on degradation mechanisms. (3) The last point is to formulate fabrication guidelines and design concepts for improved redox-stable Ni-YSZ anodes. The mechanisms and degree of degradation are related to the initial microstructure (fine, medium, coarse). This information can be used to test new concepts for redox-stable anode microstructures with high electrical and ionic conductivities, which may be obtained by mixing powders with different levels of fineness.

6.4.1. Prediction of Effective Transport Properties

In the results section, we have presented topological parameters that are relevant for transport properties. In addition, the effective electrical and ionic conductivities were determined by numerical simulation ($M_{\text{sim}}$) using 3D microstructures as input. At this point we intend to predict the effective electrical conductivity based on the topological parameters using Equation (5.4). A plug-in of the topological parameters ($\Phi_{\text{eff}}, \beta, \tau$) obtained from 3D microstructure analysis into this equation gives the predicted M-factors ($M_{\text{pred}}$).
The prediction of effective transport properties and the corresponding electrochemical performance requires a clear definition of the topological parameters that are used for the prediction. For example, in literature, tortuosity factors are measured in several ways. Iwai et al. [45], Kishimoto et al. [46], and Ananyev et al. [47] used the random walk method, Wilson et al. [4], Izzo et al. [13], and Laurencin et al. [48] used the solution to the Laplace equation, Iwai et al. [45] and Grew et al. [14] used the Lattice Boltzmann method, while recent works of Boiguez-Muñoz et al. [49] and Brus et al. [50] used the modified Stefan-Maxwell model. The differences in the definition and implementation of these methods can be one source for the discrepancies between the predicted properties and the experimentally determined properties. A second problem is related to the representative elementary volume (REV), which may also affect the reliability of measured topological parameters. For example, the work of Kanno et al. [51] showed that when compared to other microstructural parameters such as volume fraction and surface, the tortuosity factor requires a larger sample volume for representative analysis [52]. A third problem for the prediction of effective properties based on topological parameters is the fact that, often, not all relevant microstructure effects are captured. Very often only tortuosity and effective volume are considered, whereas the bottleneck effect (i.e., constrictivity) is neglected. Despite these challenges, recent studies [49,52,53] show that it is possible to extend qualitative correlation between topological parameters and electrochemical performance to the simulation and prediction not only of effective transport properties but also of electrochemical performance.

While this work considers the microstructure influence on effective transport properties based on quantitative 3D analysis, other works in literature on porous media [54,55] base the transport-related parameters on a solution of transport equations involved to describe conductance [54] or permeability [52]. Similar to this work, effective volume fraction, tortuosity, and constrictivity are identified as the
three main parameters that describe the microstructure influence on effective transport properties.

A summary of the topological parameters for Ni and YSZ, as well as the predicted M-factors from Equation (5.4) are listed in Table 6.S4 in the supplementary information. As shown in Figure 6.11, the $M_{\text{pred}}$ of Ni and YSZ before redox cycling follows the same trends as $M_{\text{sim}}$ (Figure 6.10). The trends show the highest effective conductivities for the fine anode, which decrease to the coarse anode. Figures 6.11c and 6.11d also present the specific contributions of each topological parameter weighted by the exponents from the empirical Equation (5.4) ($\Phi_{\text{eff}}, \beta^{0.36}, \tau^{-5.17}$) and normalized against the values of the fine anode. The decrease of $M_{\text{pred}}$ for Ni from fine to coarse is highly influenced by changes of the tortuosity and effective volume fraction, while the decrease of $M_{\text{pred}}$ for YSZ is related to variations in constrictivity and tortuosity. The variation of constrictivity in YSZ is compatible with particle size-dependent sintering activity, which was discussed earlier (see Figure 6.7).

The correlations between $M_{\text{pred}}$ and $M_{\text{sim}}$ are shown in Figure 6.12. Before redox cycling, a strong correlation between $M_{\text{pred}}$ and $M_{\text{sim}}$ is observed (Figure 6.12a,b). This is a clear indication that the empirical relationship in Equation (5.4) is indeed able to predict the effective transport properties of real microstructures. However, for samples after redox cycling (Figure 6.12c,d) the correlation plot shows a more complex pattern. A good correlation between $M_{\text{pred}}$ and $M_{\text{sim}}$ is only obtained after redox cycling for YSZ (Figure 6.12d). However, for Ni, it is only for the fine anode as shown in Figure 6.12c. The data points of medium and coarse anodes plot at some distance away from the reference line. The reason for this mismatch is not clear. However, it can be suspected that it may be related to greater heterogeneity in the microstructure, which leads to larger REV, as it is shown in the following. If the REV becomes similar in size or larger than the sample, our analysis becomes flawed, which is suspected to be the case of the medium and coarse microstructure.
after redox cycling.

![Figure 6.11](image_url)

**Figure 6.11.** (a,b) Summary of $M_{\text{pred}}$ ($\approx M_{\text{sim}}$) and (c,d) topological parameters in pristine samples of fine, medium and coarse anodes. The $M$-factor of Ni is significantly affected by tortuosity, while the $M$-factor of YSZ is strongly affected by both, tortuosity and constrictivity.

The different degrees of heterogeneity and associated potential problems with the size of the REV are illustrated in Figs. 6.13 (fine anode) and 6.14 (medium and coarse). The figures show fluctuations of two topological parameters profiles through the anode layers. Figures 6.13a,b and 6.14a,b represent the effective volume fractions from stacked 2D analysis, whereby for each 2D image ($y$-$z$ plane) a connectivity check is performed with the inlet plane on the left ($x$-direction). If connectivity with the left side is lost completely, then the effective volume fraction drops to 0. Minor fluctuations of the volume fractions may arise when the size of
2D slices is not fully representative. Figures 6.13c,d and 6.14c,d show the fluctuations in tortuosity. Here each value at a specific distance \( x \) includes a complete 3D analysis (i.e., transport pathways from location \( x \) to the inlet plane are measured). Close to the inlet plane the pathways typically have straight connections, which results in tortuosity values close to 1. A plateau value is reached at larger distances, when the thickness is large enough to include a representative volume. The effective volume fractions of Ni and YSZ in the fine anode vary only in a limited range (Figure 6.13a,b). This indicates that connectivity issues are not important for this sample and even the single 2D images (15 x 25 µm\(^2\)) have (almost) a representative size. After redox the solid volume fractions are lower, because of macroscopic swelling and increase of porosity.

The tortuosities of Ni and YSZ (fine, before redox) approach plateau values, which again confirms that the 3D volume has a representative size (Figure 6.13c,d). After redox cycling the tortuosities are much higher and especially for Ni the fluctuations increase considerably, which indicates that the thickness of the 3D volume is at a lower limit for being representative. In summary the results in Figure 6.13 indicate that the analyses of fine anodes are reliable (i.e., representative), which is also confirmed by the good correlations in Figures 6.12a and 6.12b.

For the medium and coarse anode the fluctuations of volume fractions are higher (Figure 6.14a,b). In particular for coarse YSZ after redox cycling the effective volume fraction drops to 0 at a distance of \( ca. 7 \) µm, which is attributed to a loss of connectivity. However, the apparently complete loss of connectivity might be related to a limited size of the image window. Potentially some connected pathways may exist outside the image window. For tortuosity (coarse anode) the fluctuations are even higher. The curve for YSZ also ends at a distance of \( ca. 7 \) µm, which is again due to loss of connectivity (Fig. 6.14d). Overall, the coarse anode has a much larger REV that is not always captured in the image windows. Especially for the coarse anode after redox cycling the size of the tomographic data is smaller than the
REV, which may explain the mismatch between $M_{\text{pred}}$ and $M_{\text{sim}}$ in the correlation plot (Figure 6.12c,d). Similar problems are identified for the medium-grained anode after redox cycling.

**Figure 6.12.** Comparison between predicted ($M_{\text{pred}}$) and simulated ($M_{\text{sim}}$) microstructure factors of Ni and YSZ in pristine anodes (a, b) and after redox cycling (c,d). Before redox cycling, the data points lie close to the diagonal reference line (solid line), which confirms a strong correlation between the $M_{\text{pred}}$ and $M_{\text{sim}}$. (c) After redox cycling, the data points for the Ni fine anode lie close to reference line, whereas the data points of medium and coarse anodes are clearly off the diagonal reference line (weak correlation between the $M_{\text{pred}}$ and $M_{\text{sim}}$).
Figure 6.13. (a,b) Profiles of effective volume fraction ($\Phi_P = \Phi_{\text{eff}}$) and (c,d) geodesic tortuosity ($\tau$) in the fine anode as a function of the film thickness ($x$-direction). Note: Connectivity check is performed with the inlet plane on the left side (Distance 0). Connected volume fractions of Ni and YSZ in the fine sample vary in a narrow range. The effective (connected) volume fractions are slightly lower in samples after redox cycling, due to loss of percolation and swelling. Geodesic tortuosity lies between 1.1 and 1.35 before redox cycling, while higher (1.35 – 1.8) and more fluctuating tortuosities are observed after redox cycling.
Figure 6.14. (a,b) Profiles of connected volume fraction ($\Phi_P = \Phi_{eff}$) and (c,d) tortuosity ($\tau$) of Ni and YSZ in medium and coarse samples, respectively as a function of film thickness (x-direction). Connectivity check is performed with the inlet plane (left side). The fluctuating values for YSZ are attributed to significant loss of connectivity, which is particularly strong after redox cycling (Compare Fig. 6.5). Geodesic tortuosities are more fluctuating (values between 1-2.5) as compared to the fine sample.

In the context of concerns over the REV size, it must be emphasized that computational limitations are generally higher for the numerical simulation compared to the ones for topology analysis. Due to the limitation in memory and computing time, smaller sub-volumes are used as a structural input for numerical
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simulations with GeoDict. Figure 6.15 represents a correlation plot of the medium-grained anode, which highlights the problems related to different image window sizes used for simulation and image analysis. Before redox cycling, a reasonable correlation is obtained between $M_{\text{sim}}$ and $M_{\text{pred}}$ (Figure 12a,b), although the simulation is performed on the basis of a smaller 3D image window. Hence, even with the smaller image window, a representative analysis is obtained for pristine anodes. Upon redox cycling, the heterogeneity increases and, thus, the REV becomes larger. The corresponding data point represented by an open triangle (Figure 6.15a) is far away from the reference line. In this case the topology analysis is based on a larger image window (marked with “A” in Figure 6.15b) compared to the one for the numerical simulation (marked with “B”). The size dependence indicates that at least with the smaller window “B”, the REV is not reached. If both analyses are based on the same image window, then the correlation is still good (see data point marked with a star in Figure 6.15a). Hence, even if the image window is below REV (as it is in this case), a good correlation can be achieved. This finding can be considered as an additional confirmation that the empirical relationship (Equation (5.4)) is capable of reliably predicting the effective transport properties. On the other side, it must be noted that throughout this study, numerical simulations are performed on smaller image windows than the corresponding topology analyses. Good correlations of $M_{\text{sim}}$ and $M_{\text{pred}}$ (e.g., for all anodes before redox cycling) thus indicate that these analyses are based on a representative image window.
Figure 6.15. (Left) Comparison between $M_{\text{pred}}$ and $M_{\text{sim}}$ for Ni, illustrating the effect of varying image window size. The point represented by a star (*) is obtained if both $M_{\text{pred}}$ and $M_{\text{sim}}$ are obtained by analysis of the same image window (region B, right image). The data point marked with an open triangle ($\Delta$) is obtained if $M_{\text{pred}}$ is based on analysis of region A (right) while $M_{\text{sim}}$ was obtained from region B (right). Note: The image on the right is a 2D-cross section of a 3D image window. The larger image window (A, in 3D) exceeds the limits of conventional voxel based computations ($M_{\text{sim}}$) but can be used for topology analysis ($M_{\text{pred}}$).

6.4.2. Degradation Mechanism

Effective conductivities from the simulation ($M_{\text{sim}}$) and from the image analysis ($M_{\text{pred}}$) show a good correlation, provided REV is not too large with respect to the sampled image size. This is interpreted as a positive validation of the underlying empirical relationship (Equation (5.4)). However, both the simulation and image analysis basically use the same type of data from the tomography as input. A thorough validation should therefore be based on independent measurements. Hence, the experimental electrical conductivities presented in Figure 6.3 can be
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used for this.

Figure 6.16 shows a comparison of experimental data (open symbols) and $M_{\text{pred}}$ from the image analysis (filled symbols), and it shows how these properties degrade upon redox cycling. The experimental data are presented as relative conductivity, whereby for each data series the measured electrical conductivity after $n$ redox cycles is normalized by the measured conductivity after the first redox cycle for the considered series. As discussed earlier, the experimental data (Figure 6.3) shows linear trends between the first to eighth redox cycles, which is interpreted as a result from microstructure degradation. However, the initial values (zeroth) and the degradation during the first cycle also show strong irregularities for the three different anodes, which are speculated to result from experimental artifacts. The influence of these uncertainties can be suppressed by taking the value after the first cycle (instead of the zeroth) as a basis for normalization.

Normalized M-factors are based on tomographs from anodes after the zeroth and eighth cycle. In the tomographic data, the 3D microstructure after the first cycle was not obtained. Nonetheless, the comparison shows that the trends for degradation upon redox cycling are very similar for experimental conductivities and for the predicted M-factors. In both cases, the fine anodes show a high degradation rate, whereas degradation rates in the medium- and coarse-grained anodes are very low. For the coarse anode the experimental measurements even indicate a positive effect of redox cycling (i.e., increasing conductivities after redox exposure). In summary, the experimental results support the validity of the suggested empirical relationship (Equation (5.4)) to predict effective conductivity. Even though for some samples (e.g., coarse, after redox) the image size of the tomographs is at the lower REV limit, there is still a good correlation between predicted and experimentally measured degradation rates.
Figure 6.16. Relative experimental conductivities (open symbols) for fine, medium and coarse anodes and their evolution over 8 redox cycles at 950°C based on the work of Iwanschitz [35]. Relative experimental conductivity means that the measured conductivity after x cycles is normalized by the conductivity measured after the 1st cycle. The relative predicted conductivity (filled symbols) is based on the $M_{\text{pred}}$, with normalization by the initial values ($0^{th}$ cycle). Similar evolution curves are obtained by prediction and experiment.

In the following section, the modes of degradation after redox cycling are discussed separately for the fine and coarse samples. In Figures 6.17 and 6.18, the normalized M-factors and normalized topological parameters are used in order to illustrate details of microstructure degradation. Normalization in this case means plotting the ratios of values obtained after eight redox cycles over the values from pristine samples. The ratio of the microstructural parameter is elevated to the same power as in Equation (5.4) so that this ratio directly reflects the impact on the M-factor change.
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Figure 6.17. Redox degradation of the fine anode is described with normalized $M$-factors and topological parameters of Ni and YSZ. Normalization means building the ratio of values before over values after redox cycling. The degradation of the Ni $M$-factor is significantly affected by changes in volume fraction (i.e., percolation) and tortuosity, whereas the degradation of the YSZ $M$-factor is most significantly affected by changes in tortuosity. The exponents of the microstructural parameters are those from Equation (5.4), which allows to directly assessing the relative roles of these terms on the $M$-factors.

This reveals that in the fine sample, the degradation of the normalized $M$-factor of Ni is mainly due to changes of tortuosity and volume fraction. This is compatible with results in Figures 6.5 and 6.9 where a significant decrease in connectivity (effective volume fraction) and an increase in tortuosity are observed in the fine sample. For YSZ, the normalized $M$-factor of only 0.1 indicates a strong degradation. This is caused by significant changes in tortuosity, and to a lower degree, by changes in constrictivity. It is important to note that Ni agglomeration is a very evident feature in all Ni-based anodes. However, with respect to the
degradation of effective transport properties, our results for the fine anode indicate that the degradation rates are higher for YSZ (i.e., ionic conductivity) than for Ni (i.e., electrical conductivity). This is surprising, considering that a relatively high sintering activity in fine microstructures leads to relatively strong bottlenecks of YSZ. This example thus also illustrates that detailed quantitative analysis can provide counterintuitive results which contradict widespread interpretations of Ni agglomeration that are mainly based on qualitative observations that suffer from lack of detailed microstructural characterization and quantification.

![Graph showing redox degradation](image)

**Figure 6.18.** Illustration of redox degradation by normalized M-factors and topological parameters for Ni in the coarse anode (i.e., ratio of values before/after redox). Upon redox cycling the M-factor (Ni, coarse) and associated electrical conductivity do not degrade, since the effect of worsened tortuosity (normalized $\tau^{-5.17}<1$) is compensated by improved constrictivity (normalized $\beta^{0.36}>1$). The exponents of the microstructural parameters are those from Equation (5.4), which allows to directly assessing the relative roles of these terms on the M-factors.

For the coarse sample, the influence of the topological parameters on the degradation of $M_{\text{pred}}$ in Ni is shown in Figure 6.18. In general, the transport properties of Ni do not degrade during the eight redox cycles because the influence
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of a worsened tortuosity is compensated by improved constrictivity (i.e., wider bottlenecks). In addition, unlike for the fine anode, redox cycling did not involve remarkable loss of connectivity in the fine Ni network. For YSZ in coarse anodes, the redox cycling leads to significant degradation of the M-factor and the associated ionic conductivity. This is attributed to the substantial loss of connectivity (see Figure 6.5 and discussion of size-dependent sintering activity). This loss of connectivity also leads to a larger REV, which questions the reliability of the corresponding topological analyses of coarse YSZ after redox cycling.

Our interpretation of microstructural results leads to the postulation of different modes of Ni growth, depending on the coarseness of the initial microstructure. These modes are qualitatively illustrated in Figure 6.19. For the fine sample, Ni coarsening happens mainly along the bulges of the Ni network (indicated as red domains in Figure 6.19a). It is suggested that the smallest Ni particles from the initial microstructure have a relatively high mobility due to a high surface energy. Preferably, the mobile Ni becomes enriched at the pre-existing bulges in the Ni network and/or they may also form new isolated islands. This is also supported by the results for the fine anode in Figure 6.6, which show that the size of the Ni bulges ($r_{50,\text{max}}$) increases during redox cycling and the connectivity of Ni decreases at the same time. In addition, in the fine microstructure, YSZ and pores both form fine-structured networks which do not leave much space for unconstrained Ni coarsening. As a consequence, the reorganization of Ni also induces strain in the YSZ phase which is localized along the bottlenecks. This also leads to lower constrictivity in YSZ and to lower predicted ionic conductivity.

For coarse anode microstructures, the Ni growth is mainly localized along the bottlenecks (as indicated by red domains in Figure 6.19b). As shown in Figure 6.6, for coarser samples, the increase in constrictivity is mainly caused by an increase in bottleneck sizes. These results explain why the electrical conductivity and associated M-factors for Ni are more stable in coarse than in fine anodes. According
to experimental results, redox cycling may even lead to higher electrical conductivities, which may be attributed to the widening of bottlenecks.

![Diagram of Ni agglomeration and growth in Ni-YSZ anodes during redox cycling.](image)

**Figure 6.19.** Different modes of Ni agglomeration and growth in Ni-YSZ anodes during redox cycling. In the fine anode (a) where particles are more granular, Ni growth is mainly located around the Ni bulges. In the coarser anode (b) Ni forms irregularly shaped domains (not round particles), and growth is often located at the bottlenecks (i.e., at concavities with relatively high surface energy).

While Ni coarsening is an obvious feature of redox degradation, YSZ is also affected by the stress associated with the Ni agglomeration. For example, Figure 6.20 shows the splitting of YSZ particles invoked by the Ni growth. The strain is most probably concentrated along the sinter necks, which are weakest for the coarse anode. Consequently, the YSZ disintegrates and loses percolation.

In summary, the different modes of Ni agglomeration can be explained by the fact that the fine microstructure has a granular texture with numerous fine particles. The reduction of surface energy is achieved when Ni is redistributed from small particles to larger ones. In contrast, in the coarse microstructure, Ni forms a more continuous network with a sinusoidal surface morphology. The surface energy is minimized when mobile Ni moves into the concavities (i.e., bottlenecks).
3D visualization of YSZ (a), Ni (b), and Ni + YSZ (c) in coarse sample before (A) and after (B) redox cycling. Redox degradation invokes a splitting of YSZ particles and disintegration into numerous disconnected islands (a). Ni agglomeration leads to the formation of a less granular structure (b). Ni is partially overgrowing the small, disconnected YSZ islands (c).
6.4.3. Mixing Different Powders

The optimization of redox stability of Ni-YSZ has also been investigated by using various techniques such as the addition of Mg species [56], the infiltration of a polymeric NiO precursor into the YSZ skeleton [57], the dispersal of fine YSZ particles on the surface of NiO [58], and the lowering of the reoxidation temperature [59].

Based on the knowledge gained in this study, we suggest addressing the issue of redox degradation by combining the advantages of different microstructure fineness (see Table 6.1). According to this study, the fine anode has the highest initial electrical and predicted ionic conductivities. Moreover, it has the advantage of strong YSZ bottlenecks, which ensure relatively stable ionic conductivity (and, supposedly, high TPB). However, in terms of redox stability, the anode with coarse microstructure has distinct advantages, mainly because it has a higher initial porosity which leaves more space for the volume expansion upon oxidation. In the coarse anode, Ni undergoes a low loss of percolation and the mobilization of Ni even leads to wider bottlenecks, which have a positive effect on electrical conductivity. The disadvantage here is the relatively low sintering activity of YSZ. Consequently, for improved redox stability, we combine a 50:50 vol % ratio of fine and coarse, as well as fine and medium, powders of YSZ. This should lead to higher initial conductivities (from fine) and increase the redox stability of Ni (coarser pores) and of YSZ (fine particles as sinter help).

The relative electrical conductivities (Figure 6.21) show that in 50:50 mixtures the degradation behavior is mainly dominated by the properties of the fine powder and microstructure. The addition of medium and coarse powders seems to lower the degradation rate of the electrical conductivity but, obviously, the 50% fine is too high. For further optimization we thus suggest a lower amount of the fine powder (e.g., 10%). Such anode compositions should have better resistance to both ionic and electrical conductivity degradation.
Effective transport properties and redox stability

Table 6.1. Summary of degradation in Ni and YSZ upon redox cycling of fine and coarse anodes.

<table>
<thead>
<tr>
<th>State of degradation</th>
<th>FINE</th>
<th>YSZ</th>
<th>COARSE</th>
<th>YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before redox cycling</td>
<td>(+) High initial $e^-$ conductivity</td>
<td>(+) High initial ionic conductivity</td>
<td>(-) Low initial $e^-$ conductivity</td>
<td>(-) Low initial ionic conductivity</td>
</tr>
<tr>
<td>After redox cycling</td>
<td>(-) Strong coarsening, (-) Loss of percolation, (-) Increase of $\tau$</td>
<td>(+) Strong coarsening but, (+) Small increase of $\tau$</td>
<td>(-) Significant coarsening but, (+) Low loss of percolation, and (+) Low change of $\beta$ and $\tau$</td>
<td>(-) Weak bottlenecks due to low sinter activity, (-) High loss of percolation, (-) Strong change of $\beta$ and $\tau$</td>
</tr>
</tbody>
</table>

Figure 6.21. Relative conductivities of anodes fabricated with mixed powders (i.e., 50%/50% fine-medium and 50%/50% fine-coarse, respectively) compared to fine, medium and coarse. The 'mixed anodes' show a similar behavior as the fine anode, which indicates that the fraction of fine powders is too high.
It must be emphasized that in this study we focused on the effective transport properties. Therefore, a strong limitation is the lack of experimental measurements for ionic conductivity. Since the intrinsic conductivity of YSZ is much lower than the one of Ni, it follows that with respect to anode performance, the effective ionic conductivity is also more limiting than the electronic conductivity [60]. These investigations show that degradation of YSZ (i.e., reduction of M-factor) during the redox cycling can be even worse than the degradation of Ni. Significant loss of connectivity is observed for coarse YSZ, which hinders the distribution of ions throughout the anode layer. In principle, the properties of an anode do not have to be constant over the entire thickness. The functional layer close to the anode-electrolyte interface should have high electrochemical activity (TPB length) and high ionic conductivity. The anode regions at larger distances away from this interface serve as current collectors and, hence, they should have high electrical conductivity. This leads to the well-known concept of double-layered anodes [11,15,16]. A fine-grained anode is used as the functional layer (e.g., with 60 vol % YSZ vs. 40 vol % Ni) and the coarse-grained material is suitable to serve as a current collector (e.g., with 50 vol % YSZ vs. 50 vol % Ni). In this context, the addition of small amounts of fine YSZ (e.g., 5 vol %) to a generally coarse anode microstructure may lead to a current collector with stronger bottlenecks. However this latter hypothesis has not yet been tested.
6.5. Conclusions

In this study, we investigate the relationship between microstructure and effective transport properties in Ni-YSZ anodes and the corresponding degradation upon redox cycling. Our microstructure investigations reveal a complex pattern of different materials properties and degradation behaviors, which vary depending on the coarseness of the initial microstructure.

6.5.1. Comparison of Fine vs. Coarse Anodes: Before Redox Cycling

In the initial state, the fine anode has higher-predicted electrical and ionic conductivities compared to the coarse anode. The M-factors predicted from the topology analysis and from the numerical simulation are consistent with each other. These M-factors decrease from fine to coarse microstructures for both phases (Ni and YSZ). For Ni, the lower M-factor in the coarse anode is mainly related to a higher tortuosity and a lower effective volume fraction (due to low connectivity). For YSZ, the lower M-factor in the coarse anode can be attributed to a higher tortuosity and a lower constrictivity (small bottlenecks, low sinter activity).

6.5.2. Comparison of Ni in Fine vs. Coarse Anodes: After 8 Redox Cycles

Upon redox cycling at 950 °C, Ni coarsening and YSZ loss of percolation are the most obvious features of anode degradation, but the degree of degradation strongly depends on the initial particle size and on the fineness of the microstructure. The fine anode is affected by substantial Ni coarsening, which leads to a significant loss of percolation and increase of tortuosity. This microstructure degradation is compatible with the experimentally measured drop of electrical conductivity by ca. 50% over eight redox cycles. In the coarse microstructure Ni coarsening is also a prominent feature; however, due to larger pores, the spatial rearrangement of Ni is less harmful than in the fine anode. In the coarse anode, the loss of percolation as
well as the changes of tortuosity and constrictivity are relatively small. Moreover, this microstructure degradation is compatible with the experimental data, showing a stable evolution of the electrical conductivity over eight redox cycles.

6.5.3. Comparison of YSZ in Fine vs. Coarse Anodes: After 8 Redox Cycles

Redox cycling and the associated rearrangement of Ni exert stresses onto the rigid YSZ structure. In the fine sample, YSZ has stronger necks due to a higher sintering activity. Consequently, the fine YSZ remains relatively stable upon redox cycling. In contrast, the coarse YSZ has a lower mechanical stability due to weaker sinter necks. In coarse anodes, redox cycling leads to a significant loss of connectivity between the large YSZ grains despite the fact that the pores are more open and Ni has more room for volume expansion upon oxidation. The loss of connectivity also induces a strong increase of tortuosity. Together with a decrease in constrictivity, these three degradation phenomena (i.e., changes of percolation $P$, tortuosity $\tau$, and constrictivity $\beta$) lead to a significant drop of the YSZ M-factor and of the corresponding predicted ionic conductivity in the coarse anode.

Also, in this study, we followed a hypothesis that a mixture of fine- and coarse-grained (or medium-grained) particles would be beneficial to slow down the degradation of both phases (Ni and YSZ) and the associated drop of conductivities. The first experimental results in this direction indicate that mixtures with 50% fine and 50% coarse YSZ powders are not ideal. In the 50:50 (fine:coarse) mixtures the Ni coarsening and YSZ degradation appear to be dominated by the negative properties of fine particles and pores (i.e., strong Ni agglomeration and associated loss of electrical conductivity). Consequently, it is suggested that a smaller amount of fine YSZ may be sufficient to increase the stability of the sinter necks between larger YSZ particles. This improvement is important since, in general, ionic conductivity is a strongly limiting factor for high anode performances (i.e., distribution of $O^{2-}$ ions within the anode). In addition, relatively coarse pores are considered to be
beneficial in the sense that they represent buffer space during the expansion upon Ni oxidation to NiO, which is not available in the fine-grained anodes due to the higher density after sintering. The coarser pores may also be introduced with suitable pore formers. In conclusion, for future improvements of anode performance and redox stability, we propose a mixture of (<50%) fine and (>50%) coarse YSZ powders and the addition of relatively coarse pore formers. The optimum proportions of these components are yet to be defined.

Aside from the insights mentioned above, the following conclusions can be drawn with respect to the suitability of methods to study microstructure effects. In this study, the relationship between conductivity and microstructure was investigated in two ways: (1) by numerical simulation of conductivity and (2) by using an empirical relationship that allows the prediction of effective conductivities based on topological parameters from 3D analysis. With respect to numerical simulation it is important to note that, in the past, conventional FE (finite element) analysis was strongly limited by the number of structural elements (grid points). Therefore, it was necessary to transform the high-resolution tomographic data (voxels) into lower resolution meshes (cubic or tetragonal). However, recent progress of commercial simulation tools (e.g., GeoDict, Avizo) allows running simulations on voxel grids >500³ in a reasonable time. The option to perform computations directly on the voxel grid from tomography represents a considerable improvement. For the initial anode microstructures investigated in this study, this size is sufficient to describe the REV at a resolution that is high enough to capture the relevant details (e.g., small bottlenecks and connectivity). However, after redox cycling, the representative volume is clearly larger and the results obtained from the numerical simulation are not reliable. The second method (i.e., topological analysis) can handle larger data volumes and the limitations regarding REV are less severe. Nevertheless, for the coarse anode after redox cycling, the structures are very heterogeneous and the REV is strongly enlarged. This size could not be reached with either of the methods. For
this reason, the results for coarse anodes after redox cycling must be considered as qualitative and preliminary.

A further methodic aspect is the fact that transport simulations do not provide the specific topological parameters, which control the anode performance. 3D imaging and topological analyses are necessary to capture the complex picture of microstructure degradation and its relation with effective properties. In summary, since both methods provide complementary information, a combination of the two methods is considered as being ideal to study such microstructure effects.

6.6. References


Effective transport properties and redox stability

[37] http://fiji.sc/Fiji (accessed on 22 August 2015)

[38] http://www.fei.com/software/avizo3d/ (accessed on 22 August 2015)


6.7. Supplementary Information

Table 6.S1. Particle size distributions of the NiO (J.T. Baker) and YSZ (Mel Chemicals) raw powders measured with a Horiba LA-920 laser diffractometer.

<table>
<thead>
<tr>
<th>Raw Powder</th>
<th>$d_{10}$ (µm)</th>
<th>$d_{50}$ (µm)</th>
<th>$d_{90}$ (µm)</th>
<th>$d_{99}$ (µm)</th>
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<tr>
<td>NiO</td>
<td>0.34</td>
<td>0.62</td>
<td>2.02</td>
<td>3.18</td>
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<tr>
<td>8YSZ-fine</td>
<td>0.29</td>
<td>0.47</td>
<td>0.90</td>
<td>1.88</td>
</tr>
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<td>8YSZ-medium</td>
<td>1.09</td>
<td>3.33</td>
<td>6.42</td>
<td>9.88</td>
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<tr>
<td>8YSZ-coarse</td>
<td>6.01</td>
<td>10.19</td>
<td>15.82</td>
<td>22.50</td>
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</table>

Figure 6.S1. Representative c-PSD (solid lines) and MIP-PSD (dashed lines) before and after redox cycling. The c-PSD curves reflect the size of the bulges and the MIP-PSD curves reflect the size of the bottlenecks. (A) The shift in the c-PSD curve of Ni in fine sample after redox cycling illustrates the increase in the average size of the bulges while the MIP-PSD shows that the bottlenecks of the Ni hardly change. (B) In the coarse sample, the Ni bulges hardly changes and the bottlenecks expand after redox cycling.
Table 6.S2. Summary of image data for 3D quantitative microstructure analyses of Ni-YSZ anodes before and after redox cycling.

<table>
<thead>
<tr>
<th>State of Degradation</th>
<th>Anode Microstructure</th>
<th>Pixel Matrix</th>
<th>Nr of Slices</th>
<th>Pixel size (nm)</th>
<th>Slice thickness (nm)</th>
<th>Pixel matrix</th>
<th>Nr of slices</th>
<th>Total nr of voxels</th>
<th>Size of image window (µm)</th>
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<td>y</td>
<td>z</td>
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<td>19.53</td>
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<td>995</td>
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<td>951'052'846</td>
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<td>24.41</td>
<td>25.00</td>
<td>960</td>
<td>1'110</td>
<td>610</td>
<td>650'016'000</td>
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<tr>
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<td>Coarse</td>
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<td>29.14</td>
<td>30.00</td>
<td>744</td>
<td>1'417</td>
<td>456</td>
<td>480'737'088</td>
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<td>19.53</td>
<td>20.47</td>
<td>1'171</td>
<td>1'343</td>
<td>461</td>
<td>724'993'033</td>
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<td></td>
<td>Medium</td>
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<td>17.90</td>
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<td>919'542'246</td>
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<td>500</td>
<td>1'114'920'000</td>
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Table 6.S3. Summary of image data for 3D analyses of simulated M-factors ($M_{sim}$) on GeoDict.

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<th>Anode Microstructure</th>
<th>Pixel Matrix</th>
<th>Nr of Slices</th>
<th>Pixel size (nm)</th>
<th>Slice thickness (nm)</th>
<th>Pixel matrix</th>
<th>Nr of slices</th>
<th>Total nr of voxels</th>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>After redox</td>
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<td></td>
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166
<table>
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<tr>
<th>Ni</th>
<th>Before Redox Cycling</th>
<th>After Redox Cycling</th>
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<td></td>
<td>Fine</td>
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<tr>
<td>Φ</td>
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<td>P</td>
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<td>0.965</td>
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<td>0.317</td>
<td>0.241</td>
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<tr>
<td>$B$</td>
<td>0.275</td>
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<td>$M_{\text{pred}}$</td>
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<tr>
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<td>Φ</td>
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<tr>
<td>P</td>
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<td>$\tau$</td>
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<td>$M_{\text{pred}}$</td>
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<td>P</td>
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<td>0.998</td>
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<td>$\Phi_{\text{eff}} = \Phi \times P$</td>
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<tr>
<td>$\tau$</td>
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<td>1.110</td>
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<tr>
<td>$M_{\text{pred}}$</td>
<td>0.037</td>
<td>0.170</td>
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</table>
Effective transport properties and redox stability
7. 3D Microstructure Effects in Ni-YSZ Anodes - Part II: Influence of TPB Lengths on the Electrochemical Performance

7.1. Introduction

The aim of this chapter is to unravel the complex relationships among microstructure, anode performance and degradation behavior upon redox cycling, with a strong focus on the influence from variations in TPB density. The complexity of this topic is mainly due to the fact that the anode performance results from coupled transfer and transport processes. Thereby the charge transfer and the associated ionic and electronic current densities may spread over the anode in different ways, depending on the microstructure and materials properties. For example, if TPB and associated charge transfer kinetics are rate limiting then the electrochemical reaction tends to spread over a relatively thick active layer. In contrast, if the ionic conductivity is relatively low, then the active zone tends to be restricted in a narrow active layer close to the electrolyte-anode interface. Microstructure degradation usually leads to a decrease of both ionic transport as well as charge transfer properties. It is thus not easy to predict how microstructure degradation affects the distribution of current densities and electrochemical activity. The property, which degrades less strongly, usually has a dominating influence on current distribution and in this way it buffers the more severe decrease of the other property and its influence on the performance. Hence, knowledge about the

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distribution of current densities and electrochemical activity is a key to a profound understanding of the relationships between microstructure and anode performance.

Numerical modeling can be used to simulate coupled transport and transfer reactions in order to obtain profiles of current densities throughout the anode [1-3]. However in order to capture the influence of microstructure in a reliable way, the model requires input from detailed 3D-analysis. In our approach the 3D investigations of fine, medium and coarse grained anodes are split into a first part on topological parameters relevant for effective transport properties [4] and a second part on total and active triple phase boundary (TPB) lengths (this paper). This will be complemented with a follow-up study on numerical modeling.

In the first part [4] it was shown that the effective ionic and electronic conductivities are related to three main topological factors (i.e., effective volume fraction $\Phi_{\text{eff}}$, constrictivity $\beta$ and tortuosity $\tau$) of YSZ and Ni, respectively. Thereby it was also observed that degradation of fine and coarse anodes have very different characteristics:

The fine anode initially has a dense microstructure due to its relatively high sintering activity of the fine YSZ grains. The two main degradation features upon redox cycling are irreversible volume expansion and Ni agglomeration. For the Ni phase this degradation leads to a loss of effective volume fraction and increase of tortuosity. Consequently the electrical conductivity drops significantly. Also the ionic conductivity decreases in the fine anode, which is mainly due to a reduction of bottleneck dimensions in YSZ (i.e., decrease of constrictivity $\beta$). The ionic conductivities of fine, medium and coarse anodes are shown in Figure 7.1.

For the coarse anode the main degradation feature upon redox cycling is the loss of YSZ connectivity, which is attributed to weak bottlenecks associated with the low sintering activity of coarse YSZ grains. As shown in Figure 7.1, the ionic conductivity is already very low in the initial state due to the low constrictivity ($\beta$).
Redox cycling affects all three parameters ($\Phi_{\text{eff}}$, $\beta$, and $\tau$) of the coarse YSZ phase so that the ionic conductivity drops to almost 0 (S/m). In contrast, the electrical conductivity of the coarse anode does not degrade significantly upon redox cycling. In summary, the results in the first part provide a detailed description of the complex relationships between microstructure and effective conductivities. However this first part does not account for the influence of microstructure degradation on anode performance.

![Figure 7.1. Ionic conductivities in Ni-YSZ anodes as a function of microstructure coarseness. Conductivities ($\sigma_{\text{eff}}$) are predicted based on an empirical relationship using transport relevant topological parameters ($\sigma_{\text{eff}} = \sigma_0 \Phi_{\text{eff}}^{0.36} / \tau^{5.17}$) [5,6]. These parameters are obtained from 3D-analysis. $\sigma_0 =$ intrinsic ionic conductivity of YSZ ($\sigma_{0,\text{YSZ@950°C}} = 15.6$ S m$^{-1}$), $\Phi_{\text{eff}} =$ effective volume fraction, $\beta =$ constrictivity, $\tau =$ tortuosity.]

The chapter focuses mainly on the relationship between TPB and anode performance, thereby also taking into account the main findings on effective conductivity. In this context it should be noted that the investigated cells are electrolyte-supported (ESC). Because of the small anode layer thickness (20 mm)
used in ESC in combination with the high intrinsic conductivity of Ni ($\sigma_{0,Ni@950^\circ C} = 2.21 \times 10^6$ S m$^{-1}$), limitations from electrical conductivity can usually be neglected. Hence in our cells the performance is mainly controlled by charge transfer kinetics (including TPB) and effective ionic conductivity.

In literature, the TPB length is often directly correlated with the electrochemical performance [7,8]. A simplistic view of this correlation is an inverse relationship between the polarization resistance and the TPB length. This kind of correlation was observed for first generation anodes, which consist only of a single electronically conductive phase (e.g., Pt). For example, works of Virkar et al. on single-phase cathodes (i.e., patterned Pt [9] and Sr-doped LaMnO$_3$ (LSM) [10]) show that the area-specific resistance ($R_{pol}$, polarisation resistance) is inversely proportional to TPB length. The linear relationship between $1/R_{pol}$ and TPB is often also attributed to composite electrodes. However, in composite anodes ionic and electronic transport resistances usually also contribute to $R_{pol}$. The anode polarization thus contains two main contributions (in button cells) that are tightly coupled to each other:

$$R_{pol} = R_{trans} + R_{act} \quad (7.1)$$

where $R_{trans}$ is the resistance from transport of electrons and oxide ions in the anode and $R_{act}$ is the resistance related to the electrochemical charge transfer at the TPB. For anodes with a large contribution from $R_{trans}$, the simplistic relationship between $1/R_{pol}$ and TPB is no longer true.

In experimental studies using impedance spectroscopy the different contributions from transport and transfer are usually not easy to distinguish (see supplementary information, Figure 7.S1). However, it is well-understood that symmetrical semicircular curves indicate the absence of transport limitations (i.e., $R_{pol} = R_{act}$), whereas asymmetrical such as “teardrop” shapes may be the result of mixed
limitations from transport and activation, or complete domination by transport resistances [11,12].

In our work we use a finite element model (DC, macrohomogeneous) for coupled charge transport and transfer [2], which provides the distribution of current densities and electrochemical transfer rates throughout the anode layer. Based on these distribution profiles the two contributions \((R_{\text{trans}} + R_{\text{act}})\) contained in the polarization resistance can be described quantitatively. In the present paper we use the model to describe some basic scenarios that correspond with typical microstructure characteristics of the investigated anodes.

The TPB densities of the anodes investigated in this study are compared with numerous TPB values for Ni-YSZ materials available from literature [7,8,13-37] (see Figure 7.2, more details related to the compilation of TPB data from literature are given in the supplementary information, Table 7.S1). The TPB densities are plotted versus the volume of the analyzed data cube from tomography. It shows that most reported TPB densities are in the range of 1-4 mm\(^2\). The six data points for fine, medium and coarse anodes before and after redox cycling also fit into this 'normal' TPB-range (red crosses). The scatter (1-4 mm\(^2\)) is mainly attributed to true microstructure variations (i.e., different coarseness of the microstructures and different anode compositions). Some minor scatter may be also due to the fact that different image analysis techniques are used for TPB measurements (i.e., centroid method, volume expansion method, classical edge length). However, Figure 7.2 also illustrates that in some cases extraordinary high TPB values (>>5 µm\(^2\)) are reported. This is only the case, when the analyzed data volume decreases below 1000 µm\(^3\). It is indeed possible that some nanostructured materials do have much higher TPBs, which can be captured with small image windows at high resolution. But for most materials such high TPB-values are not realistic. It is thus probable that the high TPB values are due to the fact that the analyzed data cubes are smaller than the representative elementary volume (REV). In this context, Figure 7.2 also
documents that our own analyses are based on comparably large data cubes (6'000 - 12'000 µm³).

**Figure 7.2.** *TPB lengths in Ni-YSZ anodes as a function of volume analyzed from literature [7,8,13-37] (data table with references are given in the supplementary information, Table 7.S1).* Independent from the fabrication method, the TPB lengths increase significantly for some of the analyses that are taken on a very small volume (which is probably due to limitations of representativeness).

In this chapter, we are particularly interested in the quantitative correlation between the electrochemical performance and TPB lengths. Therefore, active and total TPB lengths need to be distinguished from each other. The active TPB lengths are obtained considering the connectivity in each of the three phases (*i.e.*, pores, Ni, and YSZ). The influence of redox cycling on the electrochemical performance and on the microstructure is established in order to unravel the degradation mechanisms. Furthermore, limitations to the transport of mobile species are discussed for three different microstructure scenarios. Thereby it is shown that the microstructure
limitations strongly influence the distribution of electrochemical activity and also of ionic and electronic current densities within the anode. Overall, for composite Ni-YSZ anodes the relationships between electrochemical performance and microstructure, which is not a simple function of the active TPB length can be rationalized through the complex interplay of charge transport and transfer processes, and the mechanistic scenarios proposed in this work.

7.2. Experimental

7.2.1. Anode Fabrication, Redox Cycling and Impedance Measurements

A detailed description of the anode fabrication, exposure to redox cycling and electrochemical impedance measurements can be found in the work of Iwanschitz et al. [38,39] and also in the previous chapter (section 6.2.1). The cells were characterized electrochemically without polarizing the cells during the experiments except during the current/potential measurements. The impedance curves were recorded at the beginning and after each cycle using a Zahner IM6 impedance analyzer in the frequency range between 20 mHz to 200 kHz with a 20 mV amplitude.

7.2.2. Determination of Triple Phase Boundary (TPB) Length

3D image stacks obtained by FIB-tomography (see Figure 6.1, Chapter 6) were pre-processed before the analysis of TPB. The pre-processing protocol includes image alignment, selection of the region of interest (ROI), noise filtration, and segmentation of the phases (i.e., pore, Ni, and YSZ). Fiji (http://fiji.sc/Fiji), including some in-house developed plug-ins and Avizo (http://www.fei.com/software/avizo3d/) software packages were used to execute the pre-processing protocol. Details on image processing can be found in our previous study [4,40]. The corresponding dimensions of the tomographic data (Number of
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Voxels in x, y, z / Voxel size / Cube dimensions) are summarized in the supplementary materials of Ref. [4].

The TPB analysis includes the following steps: After segmentation, each of the phases is indexed uniquely. For each voxel, the index values of the adjacent voxels are determined and examined. Thereby, if two different values are detected, the voxel is identified as a border voxel located at an interface. If there are three different values, the voxel is identified to be located at a triple phase boundary (TPB). Subsequently, a binary mask including the TPB voxels is created. Following the above evaluation scheme, the following parameters can be determined: (1) total number of pixels assigned to any TPB object, (2) total number of discrete TPB objects, (3) total number of 2 phase interfaces, and of pixels at each interface boundary. (4) The length of each TPB line is determined based on the skeletonization of TPB-voxels in each object. (5) Furthermore, active TPBs are distinguished from non-active TPBs using a connectivity check. At each TPB, the percolation of each phase towards each direction (i.e., to 6 directions in 3D) can be determined as the presence of an unbroken connection from the phase to the border. This feature is calculated by running region-growing processes from the examined borders. In active TPBs the connectivity check in each phase has to be positive for one specific direction (e.g., Ni has to be connected with the current collector side). An example output of the TPB analysis with connectivity checks, including a correction procedure for boundary truncation effects, is shown in the supplementary materials (Table 7.S2). Truncation effects at cube boundaries may introduce apparent interruptions of the percolating pathways. These truncation effects are suppressed by analyzing TPBs within a central sub-cube of reduced size, whereas the corresponding connectivity checks are performed within the total cube volume.
7.3. Results

Figure 3A shows the evolution of the polarization resistance \( R_{\text{pol}} \) of the fine, medium and coarse anodes upon redox cycling. The degradation of \( R_{\text{pol}} \) over 8 redox cycles is stronger in coarse and medium samples compared to the fine one, which is indicated by steeper slopes for medium and coarse anodes in Figure 3A. The initial \( R_{\text{pol}} (0^{\text{th}}) \) increases from fine to coarse. The change in \( R_{\text{pol}} \) is given by the difference between the 0\(^{\text{th}}\) and 8\(^{\text{th}}\) cycles (initial and final resistances), as shown in Figure 3B. The degradation of \( R_{\text{pol}} \) is similar for the medium and coarse anodes (ca. 0.120 \( \Omega \) \( \text{cm}^2 \)), while it is smaller for the fine anode (0.07 \( \Omega \) \( \text{cm}^2 \)).

![Figure 3A](image1)

**Figure 7.3.** (A) Evolution of polarization resistance \( R_{\text{pol}} \) of Ni-YSZ anodes during exposure to 8 redox cycles at 950 °C (adapted from Iwanschitz [38]). Degradation is stronger in medium and coarse samples compared to the fine anode. (B) Polarization resistance \( R_{\text{pol}} \) of the different Ni-YSZ anodes before (0\(^{\text{th}}\)) and after 8 redox cycles (8\(^{\text{th}}\)).

Figure 7.4 shows the TPB lines obtained from image analysis of Ni-YSZ tomographic data. There is a clear dependency of TPB density on the fineness of the initial microstructure. Moreover, Figure 7.4 also illustrates a reduction of TPB density due to redox cycling. It must be emphasized that these TPB lines are only active for electrochemical reactions if all three phases merging at the TPB are
connected to their base. For example YSZ has to be connected with the electrolyte (located on the left side of the cubes in Figure 7.4) in order to enable transport of oxygen ions from the electrolyte to the TPB. Similarly the pores must be connected with the gas channel and Ni with the current collector (both on the right side of the cubes in Figure 7.4).

![TPB lines](image)

**Figure 7.4.** *TPB lines (blue) determined from tomographic data for the fine and coarse anodes. Redox cycling obviously leads to a decrease of TPB density. Note: Some of the TPBs are not active, due to loss of phase connectivity in one of the transporting phases (not shown). Loss of connectivity is particularly strong for the YSZ phase in the coarse anode after redox cycling (bottom right). Total and active TPB lengths are given in Figure 7.5.*

Figures 7.5A and 7.5B show the TPB\(_{\text{total}}\) and the corresponding TPB\(_{\text{active}}\) for the different anodes before and after 8 redox cycles. In the initial microstructures
(Figure 7.5A), about 90% of TPB$_{\text{total}}$ in fine and medium is active, while it is lower for the coarse anode (73%). After redox cycling (Figure 7.5B), about 60% of the TPBs are still active in the fine anode, and 46% in the medium anode. However, only 9% remain active in the coarse anode. Hence, the effects from loss of connectivity upon redox cycling are much stronger in the coarse anode.

Upon redox cycling the decrease of TPB$_{\text{total}}$ in the medium and coarse samples are 41% and 39%, respectively, whereas for the fine anode the relative change is only 26% (Figure 7.5C). The drop of TPB$_{\text{active}}$ is significantly higher than the one measured for TPB$_{\text{total}}$ (Compare Figures 7.5C and 7.5D). TPB$_{\text{active}}$ decreases by ca. 50% in the fine anode, 70% in medium and 93% in the coarse anode.

Figure 7.5. Densities of total and active triple phase boundary lengths (TPB$_{\text{total}}$, TPB$_{\text{active}}$) for the different Ni-YSZ anodes before (A) and after (B) redox cycling. (C) TPB$_{\text{total}}$ before and after redox cycling. (D) TPB$_{\text{active}}$ before and after redox cycling.
The changes of TPB lengths presented in Figure 7.5 are related to some characteristic features of redox degradation, which are strongly dependent on the initial anode microstructure. Some of these characteristics (including volume fractions, connectivity, bottleneck dimensions, constrictivity and tortuosity) have been presented in a previous publication (see Ref. [4]). Here we briefly summarize the most important characteristics of the initial microstructures and of the associated redox degradation. Thereby we define the fine and the coarse anodes as 'end-members' with different degradation mechanisms.

The microstructure characteristics for the fine anode are illustrated in Figure 7.6. It shows 2D segmented images for the fine anode before and after redox cycling. The initial microstructure of the fine anode is relatively dense and has a porosity of 25 vol %. In the pristine sample the Ni phase (white) is homogeneously distributed. Repetitive redox cycling leads to irreversible volume expansion of the anode layer, so that the porosity increases to 47 vol %. After redox degradation Ni is concentrated in larger patches and also some isolated Ni particles exist. The coarsening and inhomogeneous redistribution of Ni results in a decrease of TPB\textsubscript{total}. Nevertheless, a significant portion of the Ni-phase is still connected (18 % of Ni) and forms a percolating network. Therefore the loss of TPB\textsubscript{active} in the fine anode is moderate (i.e., 40%).

In contrast to the fine anode, the initial microstructure of the coarse anode is characterized by a relatively high porosity of 39 vol %. The lower density compared to the fine anode is due to a lower sintering activity of the large YSZ particles. This low sintering activity also leads to relatively narrow bottlenecks and to a low constrictivity ($\beta$) for the coarse YSZ ($\beta_{\text{coarse}} = 0.01$ $\beta_{\text{fine}} = 0.37$). The difference in the initial microstructure (coarse vs fine) also leads to a different degradation behavior. First of all, Ni agglomeration is less severe in the coarse. This is illustrated by lower loss of percolation and also by lower decrease of electrical conductivity (In fact, the electrical conductivity in the coarse anode even increases...
during the first 8 redox cycles). The second important difference is the fact that connectivity of YSZ in the coarse anode is drastically reduced, which is visualized in Figure 7.7. At a distance of ca. 7 µm from the anode-electrolyte interface, the connected volume fraction of YSZ drops to 0. This loss of connectivity is attributed to strain localization at weak YSZ bottlenecks. Hence, although the Ni-degradation is less severe in the coarse compared to the fine anode, the influence of Ni-NiO transformation on the YSZ-connectivity appears to be much more detrimental in the coarse anode. Due to the breakdown of the YSZ-connectivity also the \( \text{TPB}_{\text{active}} \) is reduced by 93%. Assuming a direct correlation between \( \text{TPB}_{\text{active}} \) and \( R_{\text{pol}} \), significant performance degradation (>>100%) must be expected in the coarse anode. However, as shown in Figure 7.3, the anode still exhibits an acceptable performance (increase of \( R_{\text{pol}} \) by approximately 60%). These findings indicate that the complete loss of \( \text{TPB}_{\text{active}} \) does not necessarily lead to an anode failure. Possible explanations for such controversial observations shall be discussed below.

**Figure 7.6.** Microstructures of the fine anode before (left) and after redox cycling (right). After redox cycling, Ni forms larger particles and some isolated islands, which results in a loss of \( \text{TPB}_{\text{total}} \) and \( \text{TPB}_{\text{active}} \).
Figure 7.7. (Left) Profiles of connected volume fractions of YSZ in the coarse anode as a function of the distance to the electrolyte-anode interface (x-direction). After redox cycling, complete loss of percolation is observed at ca. 7 µm. (Right) 3D reconstructed image of YSZ showing the connected particles (red) confined to a region near the electrolyte-anode interface.

7.4. Discussion

The results can be summarized by three main points: (1) The initial microstructure and the associated TPB lengths inversely correlate with $R_{\text{pol}}$. Finer microstructures with higher TPB exhibit lower $R_{\text{pol}}$, as shown in Figure 7.8. (2) Such a correlation also exists for the samples that were exposed to redox cycling, in the sense that the decrease in anode performance scales with the decrease in TPB length. Thereby, the coarser the initial microstructures the higher are the degradation rates of both TPB and $R_{\text{pol}}$. (3) However, TPB and anode polarization ($R_{\text{pol}}$) are linked in a complex way, which cannot be directly expressed in a simple, linear relationship. The third point contradicts the frequent interpretation that $R_{\text{pol}}$ can be easily related to TPB
length. This simplistic interpretation neglects the interplay of charge transfer reactions with the various charge transport processes (see Figure 5.1, Chapter 5).

Figure 7.8 represents a comparison of polarization resistances with (A) TPB_{total}, (B) TPB_{active} length, and (C) the effective ionic conductivity (YSZ). (Note: effective ionic conductivities are taken from a previous paper dealing with transport properties in the same Ni-YSZ anodes. See Ref. [4]). We define the so-called degradation ratio (\( \Delta R_{pol}/\Delta x \)), where x is TPB_{total}, TPB_{active} or the effective ionic conductivity. This ratio (shown in Figure 7.8D) represents the sensitivity of \( R_{pol} \) with respect to changes of TPB and conductivity, respectively. The decrease in TPB (both total and active) upon redox cycling is accompanied by the increase in \( R_{pol} \) as shown in the degradation ratios (Figures 7.8A and 7.8B, blue and red arrows). However this ratio is different for fine, medium and coarse samples. It is worth to note that the degradation ratio for ionic conductivity (Figure 7.8C) show a similar behavior as for TPB, with shallow slopes for the fine and steeper slopes for the coarser sample. Despite the strong degradation of ionic conductivity and TPB_{active} in the fine anode, the degradation of \( R_{pol} \) is not very severe in this sample. In contrast, medium and coarse anodes show a strong increase of \( R_{pol} \).

Overall, Figure 7.8 documents that \( R_{pol} \) and TPB do not follow a simple linear relationship, otherwise the data points in Figure 7.8A and 7.8B would plot on straight lines and the degradation ratios would be equal for fine, medium and coarse. The changing values of the degradation ratios indicate that there is no simple and linear micro-macro-relationship (\( \Delta R_{pol}/\Delta TPB \)), neither for TPB_{total} nor for TPB_{active}.

The data points for the coarse anode in Figure 7.8 require particular attention. As mentioned earlier the TPB_{active} drops to almost 0 upon redox cycling (see Figure 7.8B). In addition, the effective ionic conductivity is very low already in the pristine state due to narrow bottlenecks and it drops to 0 upon redox cycling due to loss of
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percolation. The question arises, why low TPB$_{\text{active}}$ combined with a breakdown of phase network for ionic conduction does not lead to a complete failure of the anode.

**Figure 7.8.** Polarization resistance ($R_{\text{pol}}$) versus (A) TPB$_{\text{total}}$ and (B) TPB$_{\text{active}}$ before and after redox cycling. Degradation ratios (indicated by arrows) include a $y$-component for the changes in polarization resistance ($R_{\text{pol}}$) and an $x$-component for changes of TPB. The slopes of the degradation are shown as bar plot (D). It documents that the influence of $\Delta$TPB on $\Delta R_{\text{pol}}$ does not follow a constant slope. The degradation ratios $\Delta R_{\text{pol}}/\Delta$TPB increase from fine to coarse. (C) The relationship between $R_{\text{pol}}$ and effective ionic conductivity shows a similar pattern of degradation ratios with steeper slopes for coarser microstructures.
In order to answer this question, one would have to consider the distribution of ionic and electronic current densities throughout the anode, together with the associated electrochemical transfer activity. In electrochemical impedance measurements, the electrode contributions of transport processes and electrochemical reactions to the overall polarization usually cannot be easily distinguished from each other and are often reported as a single value ($R_{pol}$). This corresponds to the width of the corresponding arc in the Nyquist plot. From numerical simulation, however, it is well understood that the anode resistance ($R_{pol}$) results from a complex interplay between charge transport (ions, electrons, gas) as well as from charge transfer. Rüger et al. [1] for example has presented current density profiles through the anode for different microstructures. These profiles nicely document how current densities and associated electrochemical activities are distributed depending on the effective conductivities and on the TPB densities.

Since these coupled phenomena are hardly distinguishable by EIS measurements, we consider mechanistic scenarios with different limiting processes in order to explain the observed non-linear relationships between $R_{pol}$ and TPB. For this purpose we use a macro-homogeneous 1D finite-element model (FEM) to simulate the anode reaction mechanism. Ionic and electronic transport processes are described by ohm's law and charge transfer at the TPB is described with the Butler-Volmer equation (see Refs. [2,3]). This model takes into account microstructure characteristics of the anode due to the input of effective ionic and electric conductivities, as well as TPB from separate microstructure analyses. A detailed description of the model as well as a detailed discussion of simulation results will be presented in a follow-up paper. Here we summarize in a simplistic way some simulation results for basic scenarios that help to explain the observed non-ideal relationship between TPB and $R_{pol}$ in Ni-YSZ anodes.

We distinguish the following three anode scenarios that are discussed on a qualitative level: (1) no transport limitation of mobile species, neither ionic nor
electric; (2) limitation of ionic transport \( \text{i.e., low ionic conductivity} \); and (3) extreme limitation of ion transport and reduction of TPB_{active} due to complete loss of YSZ connectivity. Scenario 1 represents an idealized anode. Scenario 2 is comparable with the degradation phenomena observed in the fine anode, whereas scenario 3 corresponds with the degradation phenomena observed in the coarse anode.

For all scenarios we apply a constant voltage drop over the anode and consider the corresponding current \( j \) profiles depending on TPB lengths and ionic conductivity. In any case the total charge current density is constant: \( j_{\text{total},x} = j_{\text{ion},x} + j_{\text{elec},x} \). The current distribution profiles for the first case are shown in Figure 7.9A. For scenario 1 there is no transport limitation. Therefore the entire anode is being used for the charge-transfer reaction. The slope \( (\Delta j_{\text{ion}}/\Delta x) \) is constant, which signifies constant electrochemical activity throughout the entire anode. The decrease of TPB length (as indicated with red color in Figure 7.9), still assuming no transport limitation, leads to changes in total current density \( (j_{\text{total},x}) \) and electrochemical activity, as indicated by a shallower slope \( (\Delta j/\Delta x) \). It must however be emphasized that this simplified scenario is not realistic. Indeed, in our anodes relatively strong transport limitations arise from the rather low intrinsic ionic conductivity of the ceramic phase \( \sigma_{0,\text{YSZ} \, 950^\circ C} = 15.6 \, \text{S m}^{-1} \). These limitations are enhanced by microstructure effects, which lead to effective ionic conductivities in the range 0.02-2.7 S m\(^{-1}\), as documented in a previous study [4]. In contrast, intrinsic electric conductivity of Ni is much higher \( \sigma_{0,\text{Ni} \, 950^\circ C} = 2.21 \times 10^6 \, \text{S m}^{-1} \), so that electric transport limitations can usually be neglected for thin anodes in electrolyte-supported cells.
Figure 7.9. Schematic representation of current density distributions for three different anode scenarios, where $j_{\text{ion}}$ decreases and $j_{\text{elec}}$ increases from left to right ($j_{\text{tot}}=\text{constant}$): (A) Idealized scenario where no limitation on transport of mobile species exists. The whole anode acts as an active layer with constant electrochemical activity. (B) Anode scenario with limitations for ionic transport. This leads to a concentration of charge transfer reactions in the active layer and associated inhomogeneous distribution of current densities. This scenario is representative for most Ni-YSZ anodes, including Ni-coarsening as observed in the fine anode. (C) Anode scenario with low ionic conductivity including a complete loss of percolation for YSZ in domain II. This scenario is representative for the coarse anode before and after redox cycling. ($j =$ current density, $\Delta V =$ voltage drop)
The second scenario is more realistic since it takes into account the influence of ionic transport resistance. As shown in Figure 7.9B, the system optimizes the distribution of transport and transfer reactions in order to minimize energy losses. In this second scenario (compared to the first one without transport limitations), the transport distances of ions are reduced and the electrochemical activity is concentrated within a limited zone called the active layer. The slope ($\Delta j/\Delta x$) also becomes steeper as the active layer moves closer to the electrolyte-anode interface and deviates from linearity, in contrast to the simplified scenario in Figure 7.9A. Consequently, the charge-transfer activity is highest near the electrolyte-anode interface. Similar current density profiles are reported e.g., in the modeling work of Rüger et al. [1].

Upon degradation the TPB\textsubscript{active} decreases, which leads to a drop of the total current density (at constant cell voltage). Such a scenario corresponds with the case 'fine anode degradation' in Figures 7.5 and 7.6. The TBP degradation also leads to a shallower slope ($\Delta j/\Delta x$), as illustrated by the red curve in Figure 7.9B. This implies lower electrochemical activity and as a result, the active layer is again spread (change in thickness of active layer) to compensate for the loss of TPB. Hence, qualitatively two opposing effects are identified from degradation: ionic transport limitations have the tendency to decrease the active layer thickness (shorter transport distances), whereas loss of TPB leads to an increase of active layer thickness (increase of absolute TPB-number). Usually the redox degradation affects both, transport properties as well as TPB-lengths. Thereby, the thickness-change of the active layer upon degradation cannot easily be predicted. This thickness and its change upon degradation can only be determined with a suitable model describing coupled transport and charge transfer processes, which also takes into account the relevant microstructure characteristics and effective properties of the anode.

Figure 7.9C shows the current distribution profiles for an anode where loss of YSZ connectivity is present. This setting is observed in the coarse anode after redox
cycling, which is also illustrated in Figure 7.7. At some distance away from the electrolyte-anode interface the loss of YSZ leads to a drop of TPB_{active} to zero. These distant regions are electrochemically dead (domain II in Figure 7.9C). However, close to the electrolyte-anode interface (domain I in Figure 7.9C) where ionic transport distances are short, the loss of percolation (at longer transport distances) has no detrimental effect so that the electrochemical activity is linked mainly with TPB_{total} (i.e., effective TPB_{active} at short distances \( \approx TPB_{total} \)). This phenomenon is called 'short-range effect'. It means that close to the interface the influence of microstructure cannot be explained by volume averaged parameters such as TPB, constrictivity (\( \beta \)), tortuosity (\( \tau \)), and effective conductivity (\( \sigma_{eff,io} \)). When transport distances are shorter than the size of the representative elementary volume (REV), then volume averaged microstructure characteristics and associated effective properties are not relevant for the reaction kinetics. Hence in the active layer close the interface the microstructure limitations are overestimated if they are described by volume averaged parameters (TPB, \( \beta \), \( \tau \), \( \sigma_{eff} \)). Some important microstructure limitations, which are due to tortuous pathways, narrow bottlenecks and loss of connectivity (and active TPB), require transport distances similar as the REV-dimensions, in order to become relevant. Consequently, in order to capture microstructure effects reliably in a macro-homogeneous model, one has to take into account this so-called short-range effect. This is of particular importance for electrode scenarios with a narrow active layer.

The postulation of a short-range effect provides an explanation for the complex pattern in the measurements as discussed earlier for the coarse Ni-YSZ anode after redox cycling. As shown in Figure 7.5, TPB_{active} in the coarse anode decreases from 0.8 to 0.06 \( \mu \text{m}^2 \) (i.e., by 93%). Hence, with a simplistic view on TPB-performance relationships it would be expected that this anode should exhibit a very low electrochemical performance. Nevertheless, although a significant increase of \( R_{pol} \) is measured (from 0.18 to 0.30 \( \Omega \text{ cm}^2 \)), this increase is much lower than expected
based on the measured changes in TPB_{active}. The short-range effect thus provides an explanation, in the sense that ΔR_{pol} does not correlate with ΔTPB_{active}, because loss of percolation in YSZ is only relevant at longer transport distances.

In contrast to TPB, R_{pol} is not a volume average property but it is the result of coupled transport and transfer processes that lead to uneven distributions of current densities throughout the anode. In particular, as shown in the third scenario, limitations due to loss of percolation are compensated by the concentration of the electrochemical activity in a narrow active layer close to the electrolyte, where (almost) all TPBs are active due to short transport distances for oxygen ions. Consequently it is assumed that the effective TPB activity changes across the anode layer - from the short distances, where all TPBs are active, to longer distances, where electrochemical activity correlates with TPB_{active}. The more limiting the TPB_{active} at long distances, the stronger will be the concentration of electrochemical activity close to the electrolyte-anode interface. But a complete loss of TPB_{active} (as a volume averaged microstructure characteristic) does not necessarily lead to anode failure. Nor does a loss of effective ionic conductivity.

7.5. Conclusions

We compared microstructure-performance relationships of fine, medium and coarse Ni-YSZ anodes. The initial performance (i.e., R_{pol}) of the fine anode is better, due to a higher density of TPB length and due to a higher ionic conductivity. Also after redox cycling the fine anode has the better performance, since both the loss of TPB and the drop of ionic conductivity are lower compared to the coarser anodes.

In literature, the electrochemical performance (i.e., R_{pol}) of Ni-YSZ anodes is often directly linked with the length of active TPBs. The variation of R_{pol} for different microstructures upon redox cycling clearly shows the influence of the TPB density (i.e., inverse relationship). However, contrary to the simplistic view of a linear
relationship between $R_{pol}$ and TPB, the results of this work suggest a more complex correlation between these two parameters in composite anodes. $R_{pol}$ is influenced also by charge transport, and especially the contributions from ionic transport limitations on the anode performance may be a reason for the observed deviation from linearity.

We identify two main scenarios that are suitable for a qualitative description of microstructure-performance relationship upon degradation of Ni-YSZ anodes. 'Scenario 2' represents the degradation behavior of the fine and medium grained anodes. They are dominated by Ni coarsening, which leads to a reduction of TPB lengths. In addition, the microstructure degradation also leads to a drop of ionic conductivity due to changes in tortuosity and constrictivity (bottleneck effect). Both degradation phenomena (reductions of TPB$_{active}$ and ionic conductivity) may have opposite effects on the distribution of current densities and active layer thicknesses. Hence, the relationship between $R_{pol}$ and TPB in these anodes deviates from simple linearity because it depends on a complex interplay between charge transfer, charge transport and associated current distributions across the anode layer.

In scenario 3, which is compatible with degradation phenomena observed in the coarse anode, the loss of YSZ percolation leads to a complete loss of active TPB and breakdown of effective ionic conductivity in the anode layer. However, the anode remains electrochemically active because charge transfer gets localized near the anode-electrolyte interface. This case also illustrates some limitations of conventional approaches used to establish quantitative microstructure-property relationships. Hereby the macroscopic electrode behavior is dominated by a process, which takes place in a thin active layer close to the interface. In this case the microstructure influence cannot be described by volume-averaged parameters such as TPB, since the representative volume for TPB analysis is much larger than the thickness of the active layer. We call this phenomenon a 'short range effect', meaning that the structure-performance relationships must be considered in a thin
layer close to the interface (i.e., in a domain smaller than the representative volume). This is particularly important when connectivity issues are considered. The short-range effect is a further important reason why there is no simple linear relationship between $R_{\text{pol}}$ and $\text{TPB}_{\text{active}}$.

As an outlook, the microstructure parameters related to the charge-transport ($\phi, \beta, \tau$) and charge-transfer (TPB) processes can be used as an input for numerical simulations of the anode reaction mechanism. In to predict reliably the distribution of current densities and electrochemical activity as well as to quantify the different contributions from transfer and transport on the polarization resistance it is also necessary to consider the short-range effect. Such insights obtained from the quantification of microstructure effects in combination with modeling do not only give an in-depth understanding and a more differentiated interpretation of composite anode degradation, but may also be useful in the conceptualization of new anode designs and microstructure optimization.

7.6. References


Influence of TPB lengths


[27] Z. Jiao, N. Shikazono, N. Kasagi, Quantitative Characterization of SOFC


[34] J. Joos, M. Ender, I. Rotscholl, N.H. Menzler, E. Ivers-Tiffée, Quantification of double-layer Ni/YSZ fuel cell anodes from focused ion beam tomography data, J. Power Sources 246 (2014) 819-830.


### 7.7. Supplementary Information

**Table 7.S1.** Summary of TPB lengths determined by several groups available in literature.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Pub. Year</th>
<th>Method</th>
<th>TPB (µm µm⁻³)</th>
<th>Volume under study (µm³)</th>
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Influence of TPB lengths
Figure 7.1. Representative impedance curves for the fine, medium, and coarse samples before redox cycling. The contributions to the polarization resistance are not easy to distinguish by simple inspection of the impedance arcs.
Table 7. S2. An example output from the TPB analysis described in the experimental section.

Table 7. S2 shows an example of the output sheet from the TPB analysis. The results include the number of discrete TPB lines, and the corresponding number of voxels and associated length (in metric units). Each TPB line is described by its center of gravity (COG) where the TPB is located in 3D space (in x, y and z coordinates). The connectivity of each phase in each TPB object is checked with respect to the 6 faces of the cube. For our anodes with 3 phases (Ni, YSZ, Pores) multiplied by 6 directions this results in 18 characteristic connectivity checks. This method can also be used to analyze the TPB within a sub-region in the total volume, in order to suppress effects from boundary truncation. Specific criteria (i.e., start and end of the sub-region with the corresponding connectivity criteria in x, y and z-directions) can be introduced. To identify active TPBs in anodes the connectivity criteria have to consider three specific contacts: with the electrolyte (YSZ), with the current collector (Ni) and with the gas channel (pores). The total TPB length is then evaluated from the total cube volume (without any connectivity check), whereas the active TPB lengths are determined using the specific connectivity check for TPBs in the reduced volume.
8. 3D Microstructure Effects in Ni-YSZ Anodes - Part III: Numerical Simulation of Charge Transport and Charge Transfer Processes

8.1. Introduction

In this study we investigate microstructure effects by using a steady-state continuum model for Ni-YSZ anodes, which describes the transport of $\text{O}^{2-}$ and electrons and the corresponding charge transfer reactions at the TPB following the descriptions from Costamagna et al. [1]. This model was developed previously at ZHAW [2]. Here it is adapted for more detailed simulation of microstructure effects, including the short-range effects that were introduced in chapter 7.

The presented anode model characterizes processes on a continuum level, whereby the influence of microstructure is based on two types of volume-averaged parameters: 1) effective conductivities $\sigma_{io}$ and $\sigma_{el}$ for transport (see Chapter 6), and b) active reaction sites $A_{TPB}$ ($\text{TPB}_{\text{active}}$ in Chapter 7). These volume-averaged parameters are obtained from detailed microstructure analysis, which is described in the previous chapters. The continuum model then provides a quantitative description of different resistances, which can originate from limitations of charge transfer as well as from limiting ionic and electric transport within the anode. Since it is combined with a detailed 3D-microstructure analysis, the different ASR components can be related to specific topological features of the anode (i.e., the mentioned volume averaged parameters). The simulations thus provide additional insight into the complex microstructure-performance relationships. It must be

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* This chapter is based on a paper in preparation for submission: Thomas Hocker¹, Omar M. Pecho¹², Boris Iwanschitz³, Robert J. Flatt², Lorenz Holzer¹

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emphasized that the ASR components related to transport and transfer obtained with this anode model are not congruent with the ohmic and polarization resistances directly obtained from impedance spectra as width of a specific arc in the Nyquist plot. We will discuss these differences after the presentations of a) the traditional view of a ‘global characterization’ for entire cells and b) the specific anode model.

8.1.1. Global Characterization of Cell Resistance and Electrode Polarization

In button cell experiments with an abundant supply of hydrogen fuel, the current-voltage relationship defines an almost perfectly straight line with negative slope, \( i.e., \)

\[
U(j) = U_{OCV} - ASR_{tot} j \quad (8.1)
\]

where \( U_{OCV} \) is the voltage when \( j = 0 \). The total area-specific resistance, \( ASR_{tot} \), can be written as

\[
ASR_{tot} = ASR_{gas} + ASR_{ohm} + ASR_{pol} \quad (8.2)
\]

\( ASR_{gas} \) is related to the concentration-dependence of the Nernst equation. With increasing electrical current, more hydrogen will be converted into water and this will cause a drop in the (local) Nernst potential. However, for rather small current densities and an abundant supply of hydrogen fuel, \( ASR_{gas} \) is usually negligible for button-cell experiments of electrolyte supported cells (ESC). \( ASR_{ohm} \) contains all ohmic losses within the cell, with the electrolyte resistivity \( ASR_{ely} = d_{ely}/\sigma_{ely} \) being by far its largest contribution in the case of ESCs[1]. \( d_{ely} \) is the thickness and \( \sigma_{ely} \) is the ionic conductivity of the electrolyte. \( ASR_{pol} \) is associated with losses that
originate from limitations in the charge-transfer processes taking place at the electrochemically active domains within the electrodes, both in anode and cathode. We assume that \( ASR_{pol} \) can be obtained either by solving the following equation:

\[
ASR_{pol} = \frac{u_{OCV} - u(j)}{j} - ASR_{gas} - ASR_{ohm} \tag{8.3}
\]

where all properties on the right-hand side can be assessed experimentally [3], or alternatively, \( ASR_{pol} \) itself can be obtained experimentally from electrochemical impedance spectroscopy (EIS) (see e.g., results of \( R_{pol} \) for Ni-YSZ anodes in chapter 7) [4].

### 8.1.2. Local Charge Transfer and Transport in a Continuum Model Approach

In contrast to the global characteristics of the entire cell, we formulate a model that describes charge transfer and charge transport only within the anode. In Ni-YSZ anodes charge transport takes place in the ionic conducting phase (YSZ, denoted with the subscript “\( io \)”) and in the electronic conduction phase (nickel, denoted with the subscript “\( el \)”). The local form of Ohm’s law describes charge transport in both phases by drift in the presence of an electrical field:

\[
\vec{i}_{el} = -\sigma_{el} \nabla \phi_{el} \tag{8.4}
\]

\[
\vec{i}_{io} = -\sigma_{io} \nabla \phi_{io} \tag{8.5}
\]

Here \( \vec{i} \) is the ionic or electric current density in A m\(^{-2}\), \( \sigma \) the ionic or electronic conductivity in S m\(^{-1}\), \( \nabla \) is the Nabla operator and \( \Phi \) is the ionic or electric potential in V.
The conservation-equation of ionic and electric charges is given by the Gauss-Green-theorem:

$$\text{div } \vec{i} = p$$  \hspace{1cm} (8.6)

which states that the divergence of the local charge-flux is a consequence of charge-sources or –sinks, denoted as $p$ (given in charges per s m$^3$) [5]. The combination of Eqs. (8.4), (8.5) and (8.6) gives:

$$-\text{div} (\sigma_{el} \nabla \phi_{el}) = p_{el} \quad -\text{div} (\sigma_{io} \nabla \phi_{io}) = p_{io}$$  \hspace{1cm} (8.7)

Due to the symmetry of sink and source one gets $p_{el} = -p_{io}$. In our model we consider only charge transport perpendicular to the anode layer \((i.e., \text{no \ in-plane transport, only through plane})\). In this case Eq. (8.7) simplifies to

$$-\sigma_{el} \frac{d^2 \phi_{el}}{dx^2} = -p_{io} \quad -\sigma_{io} \frac{d^2 \phi_{io}}{dx^2} = p_{io}$$  \hspace{1cm} (8.8)

To proceed further, Costamagna \textit{et al.} \[1\] introduced the potential $U_{loc}$ as the difference between the local ionic and electronic potentials,

$$U_{loc} = \phi_{io} - \phi_{el}$$  \hspace{1cm} (8.9)

Based on Eq. (8.9), the local overpotential $\eta_{loc} > 0$ can then be written as

$$\eta_{loc} = U_{loc}^{eq} - U_{loc} = (\phi_{io}^{eq} - \phi_{el}^{eq}) - (\phi_{io} - \phi_{el})$$  \hspace{1cm} (8.10)
where \( U_{loc}^{eq} \) is the potential difference under equilibrium, \( i.e. \), under open circuit voltage conditions [6]. Rearranging Eq. (8.10) (\( i.e. \), \( \eta_{loc} - U_{loc}^{eq} = -(\phi_{io} - \phi_{el}) \)) and combination with Eq. (8.8) gives

\[
\frac{d^2 \eta_{loc}}{dx^2} - \frac{d^2 U_{loc}^{eq}}{dx^2} = p_{io} (\sigma_{io}^{-1} + \sigma_{el}^{-1}) \tag{8.11}
\]

We then characterize the charge-transfer reaction at the TPB by the Butler-Volmer equation

\[
p_{io} = A_{TPB} i_n = A_{TPB} i_0 \left[ \exp \left( \frac{\alpha_a F}{RT} \eta \right) - \exp \left( - \frac{\alpha_c F}{RT} \eta \right) \right] \tag{8.12}
\]

where \( \alpha_a \) and \( \alpha_c \) represent the transfer-coefficients for the reduction and the oxidation steps, respectively. In theory \( \alpha_a + \alpha_c = 1 \). We use \( \alpha_a = \alpha_c = 0.5 \). At relatively low overpotentials it is justified to use the linearized form of the Butler-Volmer equation

\[
p_{io} = A_{TPB} \frac{i_0 F}{RT} \eta_{loc} \tag{8.13}
\]

In Eqs. (8.12) and (8.13), \( A_{TPB} \) is the so-called triple-phase boundary, which represents the location with electrochemically active sites. \( R \) is the universal gas constant and \( F \) is the Faraday constant. Depending on the topological consideration, this location is either defined as the length of the TPB-line (\( m \cdot m^{-3} \)) or as the specific interface area per volume (\( m^2 \cdot m^{-3} \)), such as the contact area between ion- and electron-conducting phases. Furthermore \( i_0 \) is the current-exchange density, \( i.e. \), the
forward and backward charge-transfer rate at equilibrium conditions. \( i_0 \) represents the "ability" of the electrode to perform electrochemical charge transfer. \( i_0 \) depends on the details of the microscopic charge transfer process (that is usually assumed to be a combination of adsorption, dissociation, surface diffusion and redox reaction steps).

In Eqs. (8.12) and (8.13), one can introduce an effective current-exchange density \( (i_{\text{eff}}) \) that determines the electrochemical activity of the electrode. \( i_{\text{eff}} \) is the product of the intrinsic materials property \( i_o \) and the microstructure property \( A_{\text{TPB}} \) with units of \( \text{A/m}^3 \). Depending on the topological consideration of \( A_{\text{TPB}} \) either as a line (\( \text{m/m}^3 \)) or as an active area (\( \text{m}^2/\text{m}^3 \)), the units of current-exchange density \( i_o \) are either \( \text{A/m}^2 \) or \( \text{A/m}^3 \). In our model \( i_o \) is the only parameter, which can neither be assessed experimentally nor is it known reliably from literature. Hence, \( i_o \) is the only parameter that is used to fit the model with experimental ASR measurements. Ideally, for a specific temperature \( (i.e., \text{for } 950^\circ\text{C}) \) all simulations can then be performed with the same value for \( i_o \).

For the special case where \( U_{\text{loc}}^{\text{eq}} \) is constant, the combination of Eqs. (8.11) and (8.13) becomes

\[
\frac{d^2 \eta_{\text{loc}}}{dx^2} = (\sigma_{\text{to}}^{-1} + \sigma_{\text{et}}^{-1}) A_{\text{TPB}} \frac{i_0 F}{RT} \eta_{\text{loc}}
\]  

(8.14)

This equation is also described (as Eq. 2d) in Costamagna et al. [1]. The boundary conditions are defined for the outer surface of the electrode (at the current collector) as being located at \( x = 0 \), whereas the electrode-electrolyte interface is at \( x = a \) (where \( a \) is the electrode thickness). Then, the conditions
\[ x = 0 : \quad i_{io} = -\sigma_{io} \frac{d\phi_{io}}{dx} = 0 \quad \text{and} \quad i_{el} = -\sigma_{el} \frac{d\phi_{el}}{dx} = i_{tot} \]

\[ x = a : \quad i_{io} = -\sigma_{io} \frac{d\phi_{io}}{dx} = i_{tot} \quad \text{and} \quad i_{el} = -\sigma_{el} \frac{d\phi_{el}}{dx} = 0 \quad (8.15) \]

hold, which state that the electron-flux at the outer surface equals the ion-flux at the electrode-electrolyte interface. In terms of \( \eta_{loc} \), the boundary conditions become

\[
\left. \frac{d\eta_{loc}}{dx} \right|_{x=0} = -\frac{i_{tot}}{\sigma_{el}}, \quad \left. \frac{d\eta_{loc}}{dx} \right|_{x=a} = \frac{i_{tot}}{\sigma_{io}} \quad (8.16)
\]

Eq. (8.16) indicates that the gradient of the local overpotential approaches 0 at the electrode surface, since the electronic conductivity \( \sigma_{el} \) of nickel is relatively high. Alternatively, since the ionic conductivity \( \sigma_{io} \) is rather low, this means that the gradient of the local overpotential and the associated electrochemical activity are relatively high at the interface between electrode and electrolyte.

To solve Eq. (8.14) in combination with Eq. (8.16), it is convenient to introduce the following dimensionless variables for the overpotential \( \eta_{loc} \) and the space-coordinate \( x \):

\[
\hat{\eta} = \frac{\eta_{loc}}{U_{eq}} = \frac{U}{U_{eq}} - 1, \quad U_{eq} = \text{const.}, \quad \hat{x} = \frac{x}{a}, \quad 0 \leq \hat{x} \leq 1 \quad (8.17)
\]

Here, \( a \) represents the thickness of the anode. Insertion of Eq. (8.17) into Eqs. (8.14) and (8.16) then results in

\[
\frac{d^2\hat{\eta}}{d\hat{x}^2} = \Gamma^2 \hat{\eta}, \quad \left. \frac{d\hat{\eta}}{d\hat{x}} \right|_{\hat{x}=0} = -\Theta_{el}, \quad \left. \frac{d\hat{\eta}}{d\hat{x}} \right|_{\hat{x}=1} = -\Theta_{io} \quad (8.18)
\]
where

$$\Gamma^2 \equiv (\sigma_{io}^{-1} + \sigma_{el}^{-1}) a^2 A_{TPB} \frac{i_0 F}{RT}, \quad \Theta_{el} \equiv \frac{a i_{tot}}{\sigma_{el} U_{eq}}, \quad \Theta_{io} \equiv \frac{a i_{tot}}{\sigma_{io} U_{eq}} \quad (8.19)$$

have been used. Once $\dot{\eta}$ has been obtained, the electric and ionic current densities follow from the conditions

$$\frac{d \dot{\eta}}{d \bar{x}} = \frac{a}{U_{eq}} \left( \frac{i_{io}}{\sigma_{io}} - \frac{i_{el}}{\sigma_{el}} \right) \quad (8.20a) \quad i_{io} + i_{el} = i_{tot} = \text{const} \quad (8.20b)$$

resulting in

$$i_{el} = \frac{\sigma_{el} (a i_{tot} - \sigma_{io} U_{eq} \frac{d \dot{\eta}}{d \bar{x}})}{a (\sigma_{el} + \sigma_{io})} \quad (8.21a) \quad i_{io} = \frac{\sigma_{io} (a i_{tot} - \sigma_{el} U_{eq} \frac{d \dot{\eta}}{d \bar{x}})}{a (\sigma_{el} + \sigma_{io})} \quad (8.21b)$$

According to Costamagna [1], the total anode resistance $\text{ASR}_{an}$ can be obtained by considering the potential difference at both sides of the anode as follows

$$\text{ASR}_{an} = \frac{U_{tot}}{i_{tot}} = \frac{\phi_{el}|_{x=0} - \phi_{io}|_{x=a} - U_{eq}}{i_{tot}} \quad (8.22)$$

where

$$\phi_{el}|_{x=0} - \phi_{io}|_{x=a} = U_{eq} (1 + \dot{\eta}|_{\bar{x}=0}) + \frac{a}{\sigma_{io}} \int_{0}^{1} i_{io} d \bar{x}. \quad (8.23)$$

Hence

$$\text{ASR}_{an} = \frac{1}{i_{tot}} \left[ U_{eq} \dot{\eta}|_{\bar{x}=0} + \frac{a}{\sigma_{io}} \int_{0}^{1} i_{io} d \bar{x} \right]. \quad (8.24)$$

Insertion of Eq. (21b) into Eq. (8.24) then gives

$$\text{ASR}_{an} = \frac{1}{i_{tot}} \left[ U_{eq} \dot{\eta}|_{\bar{x}=0} + \frac{a i_{tot} - \sigma_{el} U_{eq} (\dot{\eta}|_{\bar{x}=1} - \dot{\eta}|_{\bar{x}=0})}{(\sigma_{el} + \sigma_{io})} \right]. \quad (8.25)$$
The total anode resistance $ASR_{an}$ can be subdivided into components that are related to either transport or to electrochemical transfer reactions. The activation polarization ($ASR_{act}$), which results from electrochemical losses at the TPB, is obtained by application of the linearized Butler-Volmer equation (see Eq. (8.13)) as follows:

$$ASR_{act} = \frac{1}{a \sigma_{TPB} i_0} \frac{RT}{F}$$  (8.26)

Hence the activation polarization is entirely dependent on intrinsic materials properties (i.e., exchange current density $i_o$), on anode thickness ($a$) and on microstructure ($A_{TPB}$). The resistance related to both, electric or ionic transport within the anode is then obtained from:

$$ASR_{transport} = ASR_{an} - ASR_{act}$$  (8.27)

Alternatively the $ASR_{transport}$ can be obtained by integration of the local currents, and in this way contributions from ionic and electric charge transport can be distinguished from each other:

$$ASR_{i_{o, \text{transp}}} = \frac{1}{a \sigma_{i_o}} \int_0^a (a - x) \frac{j_{i_o(x)}}{j_{i_o(a)}} \, dx$$  (8.28)

$$ASR_{e_{\text{transp}}} = \frac{2}{a \sigma_{\text{ele}}} \int_0^a (a - x) \frac{j_{e_{\text{ele}}(x)}}{j_{e_{\text{ele}}(0)}} \, dx$$  (8.29)

$$ASR_{\text{transp}} = ASR_{e_{\text{transp}}} + ASR_{i_{o, \text{transp}}}$$  (8.30)
As mentioned earlier, there is a considerable potential for confusion when speaking about the different components of ASR. It is important to note that the ASR terms used either for charge transfer or for charge transport resistances are not the same in the above described anode model (Eqs. (8.4)-(8.30)) as in the global cell characterization (Eqs. (8.1)-(8.3)). The global characterization is strongly related to experimental investigations, e.g., with impedance spectroscopy. Thereby $ASR_{ohm}$ and $ASR_{pol}$ can be obtained directly from the width of the respective arc in the Nyquist plot. In the ideal case $ASR_{pol}$ from anode and from cathode can be distinguished from separate semi-circles. The $ASR_{pol}$ from each electrode is then generally attributed to transfer processes at the corresponding TPBs. Nevertheless, teardrop-shaped spectra are often observed in the Nyquist plot, and it is well understood that in composite and mixed conducting electrodes this teardrop shape is the result of overlapping transport and transfer limitations in the electrode (as discussed e.g., for LSC cathodes by Adler [7]). Hence, in global cell characterization with impedance spectroscopy the transport limitations within the electrodes are part of the $ASR_{pol}$ and they are usually not contained in the $ASR_{ohm}$.

In contrast to the global cell characterization obtained from the high-frequency intercept in the Nyquist plot (in the absence of any physically sound impedance models), with the anode model we can distinguish between the different components that contribute to the total anode resistance ($ASR_{an}$). In order to emphasize this difference we use different terms for these components. Hence the $ASR_{transp}$ represents the limitations from transport in the anode, which is contained within the often observed teardrop-shaped arc and therefore also in the $ASR_{pol}$ of the global characterization, but it is not included in the $ASR_{ohm}$ of the global characterization as extracted from the high-frequency unit of the impedance spectra. Furthermore the $ASR_{act}$ in our anode model explicitly only describes the limitations from TPB charge transfer as given by the linearized Butler-Volmer equation. It
follows that total anode resistance in the anode model corresponds to the 
polarization resistance of the anode in the global characterization:

\[
ASR_{\text{pol}} = ASR_{\text{an}} = ASR_{\text{el-transp}} + ASR_{\text{io-transp}} + ASR_{\text{act}} \quad (8.31)
\]

Whereas \(ASR_{\text{pol}}\) is accessible with EIS, the different ASR components on the right 
side of Eq. (8.31) can be obtained with the presented steady-state anode model. It 
must be noted that in this work, gas diffusion limitation is neglected. This can be 
justified by a high gas diffusivity at 950 °C (operating temperature) and by 
relatively short transport distances in electrolyte supported cells (ESC usually has 
anode thicknesses <30 µm) [8].

8.2. FE-Simulation of ASR with Input from Microstructure Effects

In Chapter 6, we discussed the issue with the representative elementary volume 
(REV), which is larger than the FIB-cube acquired for microstructure analysis of 
the coarse anode. Hence, the reliability of transport-related microstructure 
parameters obtained from 3D image analysis is questionable in this case. 
Consequently, in this chapter, only the fine and medium samples are used to 
simulate the total anode resistance and its contributions.

The equations described in the previous section are implemented in SESES, an 
in-house software developed at the ICP-ZHAW for FE-modeling. The simulations 
are done in 1D whereby the input of microstructure properties is defined as the 
profiles across the anode layer (i.e., spatial variations of microstructure parameters 
are taken into account). The microstructure input in the simulations related to 
transport (ionic and electronic conductivities) and electrochemical reaction (TPB) is
summarized in Table 8.1. The spatial dependency of these microstructure input is shown in Figure 8.1.

![Figure 8.1](image)

**Figure 8.1.** (A) Schematic representation of the spatial dependency of the transport-related properties and the microstructure input parameters used in the simulations. (B) Total and active TPB profiles along the electrode layer thickness of the fine anode.

It is important to identify which factors govern charge transport or charge transfer processes in the simulations. For the electronic and ionic conductivities two parameters labeled $f_1$ and $f_0$ are defined depending on the location of the interface (see Figure 8.1). At the electrolyte-anode interface, the ionic conductivity (blue line, Figure 8.1A) is significantly affected by the effective volume fraction of the YSZ phase ($f_1$). As the transport moves away from this interface, other parameters start to affect the ionic conductivity (*e.g.*, constrictivity and tortuosity). The effect of theses changes reaches a certain distance where the electronic conductivity reaches a plateau ($f_0$). At this point, the ionic conductivity is governed by the microstructure factor (M-factor, $M_{\text{pred}}$ in Chapter 6). The same is the case for the Ni. The electronic conductivity is governed by the Ni effective volume fraction from the current collector-anode interface ($f_0$). As the electrons move away from this interface, other
microstructure properties start to take effect and a plateau is reached (M-factor, $f_i$). These parameters are summarized in Table 8.1.

Another important aspect of the simulation is the incorporation of the short-range effect (SRE) that was postulated in Chapter 7. Close to the anode-electrolyte and anode-current collector interface where ionic and electronic transport distances are short, the loss of percolation at longer transport distances has no effect so that the electrochemical activity is linked with the total TPB. Therefore for the spatial dependency of the charge transfer at the TPB near the YSZ electrolyte is defined as $P_2/P_3$, where $P_2$ is the product of the percolation factors of Ni and pore, and $P_3$ is the product of the percolation factors of all the three phases (pore, Ni, and YSZ). Moreover, the short-range effect is assumed to be influenced by a factor of $6r_{50}$ of the phase (Ni or YSZ) from the anode-electrolyte and the anode-current collector interfaces.

Figure 8.1B shows the cumulative total and active TPB profiles along the anode thickness in the fine anode. The continuously increasing TPB profile signifies the presence of TPB throughout the electrode layer. Moreover, the difference between the total and the active TPB in the case of the fine anode is small, thereby the degradation upon redox cycling does not significantly induce loss of TPB.
Simulation of charge transport and charge transfer

Table 8.1. Summary of microstructure parameters used in the simulation of ASR_{an}. \( M_{\text{pred}} \) is obtained using Eq. 4 in Chapter 6.

<table>
<thead>
<tr>
<th>Ni</th>
<th>Before redox cycling</th>
<th>After redox cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FINE</td>
<td>MEDIUM</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>0.322</td>
<td>0.25</td>
</tr>
<tr>
<td>( P )</td>
<td>0.985</td>
<td>0.965</td>
</tr>
<tr>
<td>( f_0: \Phi_{\text{eff}} = \Phi \times P )</td>
<td>0.317</td>
<td>0.241</td>
</tr>
<tr>
<td>( f_1: M_{\text{pred}} )</td>
<td>0.071</td>
<td>0.033</td>
</tr>
<tr>
<td>( r_{50} ) (nm)</td>
<td>378.1</td>
<td>540.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>YSZ</th>
<th>FINE</th>
<th>MEDIUM</th>
<th>FINE</th>
<th>MEDIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Phi )</td>
<td>0.421</td>
<td>0.388</td>
<td>0.312</td>
<td>0.376</td>
</tr>
<tr>
<td>( P )</td>
<td>0.999</td>
<td>0.986</td>
<td>0.961</td>
<td>0.869</td>
</tr>
<tr>
<td>( f_1: \Phi_{\text{eff}} = \Phi \times P )</td>
<td>0.421</td>
<td>0.383</td>
<td>0.3</td>
<td>0.327</td>
</tr>
<tr>
<td>( f_0: M_{\text{pred}} )</td>
<td>0.173</td>
<td>0.071</td>
<td>0.02</td>
<td>0.022</td>
</tr>
<tr>
<td>( r_{50} ) (nm)</td>
<td>306.1</td>
<td>557.4</td>
<td>288.0</td>
<td>577.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pore</th>
<th>FINE</th>
<th>MEDIUM</th>
<th>FINE</th>
<th>MEDIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P )</td>
<td>0.988</td>
<td>0.998</td>
<td>0.999</td>
<td>0.998</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TPB</th>
<th>FINE</th>
<th>MEDIUM</th>
<th>FINE</th>
<th>MEDIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>active (µm ( \mu \text{m}^3 ))</td>
<td>2.371</td>
<td>1.801</td>
<td>1.185</td>
<td>0.547</td>
</tr>
</tbody>
</table>

8.2.1. Determination of Exchange Current Density (\( i_0 \))

FE-simulations with input of microstructure properties of fine and medium anodes are performed in order to determine the exchange current density, which is then used for further sensitivity analysis of other model parameters. For four samples (fine and medium grained anodes, both before and after redox cycling) FE-simulations are performed at varying \( i_0 \). In Figure 8.2, the resulting \( ASR_{an} \) from FE simulation (curves) is plotted together with the experimentally measured ASR (horizontal lines). The x-value of the intercept between simulated and measured ASR is considered as characteristic \( i_0 \) (and shown as dashed vertical lines in Figures 8.2A and 8.2B), which will be used for further simulations. Before redox cycling, the \( i_0 \) of fine and medium anodes are 249.9 and 247.3 A m\(^{-2}\), respectively. After redox cycling, these values increased to 559.8 and 498.3 A m\(^{-2}\) for the fine and medium anodes, respectively.
Figure 8.2. Total ASR determined from FE-simulation with varying exchange current density \(i_0\) for the fine and medium anodes before (A) and after redox cycling (B). Characteristic values of \(i_0\) are determined from the intercept between simulated and measured ASR. Before redox cycling the characteristic \(i_0\) is ca. 250 A m\(^{-2}\) and after redox cycling \(i_0\) is ca. 530 A m\(^{-2}\), respectively.

8.2.2. Determination of ASR Components

The different ASR components for charge transport and transfer within the anode can be calculated with the anode model. Figure 8.3 shows the ASR components and values as a function of electrode thickness for the Ni-YSZ anode with fine microstructure. Whenever the anode is too thin (\(i.e., <5\) - 10 \(\mu\)m), the total anode ASR \(ASR_{an}\) is extremely high. This is the region in the curve of \(ASR_{an}\) that is dominated by the activation ASR \(ASR_{act}\). This also implies that in thin anodes the total amount of electrochemically active sites is limiting. For thicker anodes \(i.e., >5\) - 10 \(\mu\)m), the total amount of electrochemically active sites increases and the contribution from \(ASR_{act}\) decreases. However, larger anode thicknesses result in an increase of contribution from the transport of ions \(ASR_{io\text{-transp}}\). In the example in Figure 8.3, above a ‘critical thickness’ of ca. 20 - 30 \(\mu\)m the ASR-total reaches a plateau and does not change anymore with further increase in thickness. This is due
to the incremental increase of \( \text{ASR}_{\text{io-transp}} \) that compensates the incremental decrease in \( \text{ASR}_{\text{act}} \). Therefore, the optimum thickness can be defined as the point where \( \text{ASR}_{\text{an}} \) reaches a plateau, which is close to the thickness of the experimentally investigated anode (19.5 \( \mu \text{m} \) for the fine anode).

**Figure 8.3.** \textit{ASR components determined from FE-simulation for a Ni-YSZ anode with fine microstructure. At lower thicknesses, the \( \text{ASR}_{\text{an}} \) is dominated by charge transfer (\( \text{ASR}_{\text{act}} \)) while ionic transport (\( \text{ASR}_{\text{io-transp}} \)) dominates at higher thicknesses. (expt=experimental)}

Figure 8.3 also shows the ASR component from the electronic transport (\( \text{ASR}_{\text{el-transp}} \)), which is very low (\textit{i.e.}, \(< 0.01 \text{ m}\Omega \text{ cm}^2\)) in this case. This contribution becomes important in the case where percolation in the network of Ni gets lost due to extreme Ni coarsening. Moreover, both limitations (for electric conductivity and gas diffusivity) become more significant in anode-supported cells (ASC) with much higher thicknesses [6].
Figure 8.4 shows the thickness dependency of $ASR_{an}$ and its sub-components for the fine and medium grained samples before redox cycling. The differences are due to microstructure effects. As discussed in Chapters 6 and 7, the fine anode has a higher TPB and a higher ionic conductivity.

The $ASR_{an}$ curves (Figure 8.4A) show two different regions: (1) a steep region dominated by the $ASR_{act}$ and (2) the region where it starts to reach a plateau. With increasing coarseness and decreasing TPB lengths, the first region is shifted to higher thicknesses (see also Figure 8.4B $ASR_{act}$ curves). As a result, the thickness of the active layer in the fine anode is smaller than in the medium anode. The second region as mentioned previously in Figure 8.3 is dominated by contributions from ion transport (i.e., $ASR_{io-transp}$). This contribution increases when the electrode becomes thicker and reaches a plateau. This plateau has a higher $ASR_{an}$ and higher $ASR_{io-transp}$ in the medium anode compared to the fine anode (see Figures 8.4A and 8.4C). The higher plateau values in the medium grained anode results from two different microstructure effects: a) in coarser samples the transport distances for ions are larger due to limitations in TPB (i.e., increased thickness of active layer, see discussion in chapter 7), and b) in coarser microstructures the effective ionic conductivity is lower due to narrow bottlenecks associated with lower sintering activity of coarse YSZ (see discussion in chapter 6).

For both anodes, the transition between the transfer- and transport-dominated regions (in Figure 8.4A) represents the critical thickness, above which the $ASR_{an}$ hardly changes (i.e., 20-25 µm for fine and 25-30 µm for coarse anodes).
Figure 8.4. Influence of the initial microstructure (medium and fine grained anodes) and of electrode thickness on the ASR components. (A) \( \text{ASR}_{\text{an}} \), (B) \( \text{ASR}_{\text{act}} \), and (C) \( \text{ASR}_{\text{transp}} \).

Figure 8.5 shows the impact of microstructure degradation upon redox cycling on different ASR components in the fine (A) and in the medium anodes (B). In the fine anode (Figure 8.5A), \( \text{ASR}_{\text{act}} \) remains nearly unchanged, although the TPB is significantly lower after redox cycling. Obviously, a potential increase of \( \text{ASR}_{\text{act}} \) resulting from TPB-loss is compensated due to lower current densities \( (j) \), which decreases the \( \text{ASR}_{\text{act}} \). In contrast to \( \text{ASR}_{\text{act}} \), the component from transport of ions \( (\text{ASR}_{\text{io-transp}}) \) increases significantly, which is mainly attributed to a decrease of ionic conductivity upon redox cycling associated with changes of tortuosity and
constrictivity in YSZ (see chapter 6). Consequently the $ASR_{an}$ increases significantly upon redox cycling, but the critical thickness of the active anode layer remains similar ($i.e.$, 20-25 µm) for both samples (fine, before and after redox cycling).

**Figure 8.5.** Influence of redox cycling on the ASR components determined by FE-simulation for Ni-YSZ anodes with fine (A) and medium (B) microstructures. In both anodes $ASR_{an}$ and $ASR_{io-transp}$ increase upon redox cycling. In the fine anode the component from charge transfer ($ASR_{act}$) does not change significantly whereas in the medium sample it increases upon redox cycling.

In the medium grained anode, redox cycling leads to stronger microstructure degradation, with significant drop of TPB and ionic conductivity. Figure 8.5B shows the resulting changes of the ASR components, which are all increasing upon redox cycling. However, again the critical thickness ($i.e.$, 25-30 µm), above which $ASR_{an}$ defines a plateau, does not change due to redox exposure. For all four samples the contribution from electric transport ($ASR_{el-transp}$) is less than 0.01 mΩ cm$^2$ and therefore the $ASR_{transp} \cong ASR_{io-transp}$. 
8.3 Conclusions and Outlook

This work shows that the use of 3D image analysis to provide microstructure input parameters for steady-state continuum model provides a better understanding of the complex interplay between the charge transport and charge transfer processes in Ni-YSZ anodes. Microstructure parameters are quantified and incorporated into the model that delivers different contributions to the total electrode ASR that cannot be directly identified from experimental measurements, such as impedance spectroscopy. Upon thickness variation of the anode layers two 'regions' are observed. For thin Ni-YSZ anodes, the ASR is dominated by charge transfer (i.e., $ASR_{act}$), which correlates with the number of electrochemically active sites (TPB). Above a certain critical thickness, the $ASR_{an}$ approaches a plateau. For thick anodes in this plateau region, the $ASR_{an}$ is dominated by contributions from ionic transport ($ASR_{io-transp}$).

Outlook: The present study shows that the model is capable to reproduce experimental data with a single fitting parameter (i.e., $i_0$) under the condition that the microstructure can be described reliably. Detailed insight was gained about the influence of microstructure on the effective conductivity (chapter 6) and on the charge transfer (chapter 7). In addition, also the influence of redox degradation on microstructure parameters was described quantitatively. All these information can be used for the optimization of anode microstructures in order to achieve higher performance and lower degradation rates. For the optimization powders of different grain size can be mixed and the volumetric phase compositions (e.g., higher porosity) can be adapted.

In the future such parametric studies can be performed using stochastic models, which provide virtual (but realistic) 3D microstructures. The numerical model presented in this chapter can then be used to evaluate microstructure-property relationships for these virtual microstructures.

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8.4. References


Conclusions
9. General Conclusions and Outlook

9.1. Spray Pyrolysed La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC) Cathodes for IT-SOFC Applications

Spray pyrolysis was successfully used to fabricate nanostructured LSC thin-film electrodes. In literature, the surface exchange reaction is considered to be the rate-limiting step for oxygen reduction in LSC cathodes. Consequently, for this study, the hypothesis was that increasing the surface area would improve the cathode performance. Cathodes with different specific and total surface areas were produced by varying the sintering temperatures and the layer thicknesses. In the samples sintered at 600 °C and 800 °C, a secondary phase (SP) besides LSC and pores is found and identified to be nanoporous, amorphous, strontium- and oxygen-rich. Although, the secondary phase fills out a large portion of the pores, it seems that it does not hinder gas transport in the pores significantly, nor does it negatively impact the oxygen reduction kinetics. ASR values as low as 0.13 $\Omega$ cm$^2$ at 600 °C in air are obtained, thereby making the LSC sintered at low temperature (e.g., 600 °C) suitable as cathodes for SOFC operated at intermediate temperatures.

9.1.1. Microstructure Analysis and ALS Model

Sintering at 1000 °C gives a phase pure material with nominal composition of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$. At lower sintering temperatures (600 °C and 800 °C) the formation of the Sr-rich secondary phase results in an LSC composition with A-site understoichiometry. In addition, the electro-chemically active LSC-pore interfaces are covered with the Sr-rich secondary phase (at 800 °C) and/or the pores are filled with the secondary phase (600 °C). Despite these non-desired phenomena related to secondary phase formation, the ASR of the cathode sintered at 600 °C performs 78 times better than the phase pure cathode sintered at 1000 °C.
Quantitative microstructure analysis and the application of a physical model (Adler-Lane-Steele, ALS), show that the significant ASR increase (factor of 78) upon raising the sintering temperature from 600 °C to 1000 °C can only to a small extent be attributed to the change in surface area (only by a factor of 2) associated with coarsening of the electrode at higher temperatures. It is attributed to the changes in exchange neutral flux density (factor of 39) determined from the ALS model, with input from EIS-measurements and microstructure analysis. This intrinsic material property of LSC is attributed to the above-mentioned Sr deficiency that increases from 1000 °C to 600 °C with the amount of Sr-rich secondary phase. It is one of the main findings of this part of the study, that Sr deficiency is beneficial for the oxygen reduction kinetics.

### 9.1.2. Influence of Electrode Layer Thickness

The above results refer to cathodes with a thickness of 1 µm. The influence of film thickness on the electrochemical performance was also investigated. Film thicknesses were varied in the range of 200 nm - 7 µm, by changing the deposition time during the spray pyrolysis. For films sintered at 600 °C and 800 °C, the ASR shows a minimum between 1-2 µm cathode thickness. Below 1 µm, decreasing ASR with increasing thickness is attributed to the total surface area available for surface exchange reaction, while an increase of ASR at higher thicknesses is attributed to the fact that gas diffusion and charge transport may become limiting. For cathodes sintered at 1000 °C the ASR is much higher, and it does not show a minimum at 1-2 µm thickness. Instead the lowest ASR is measured for the largest thickness (ca. 7 µm). The different behaviors are attributed to the presence or absence of secondary phase, which limits gas diffusion at larger cathode thicknesses.

In order to better understand the gas permeability of the secondary phase the
measured volume fraction of the secondary phase was compared with the amount of strontium oxide (SrO) that can form upon non-incorporation of Sr into the LSC perovskite lattice. These calculations take into account the density of SrO, the LSC non-stoichiometry measured by TEM-EDX, the volumetric ratio of pore, LSC and secondary phase from 3D-analysis and the nominal (i.e., bulk) composition of the sample. From TEM-EDX it is known that approximately 25% of the Sr are not incorporated in LSC but are instead used for the amorphous Sr-oxide phase. However, the calculations also show that this amount of Sr is by far not enough to produce such large amounts of secondary phase. It is also observed in TEM and FIB-SEM that the secondary phase must have a significantly lower density than LSC or than normal SrO. This leads to conclude that the secondary phase itself is a highly porous amorphous material with a 'gel-like' structure. The calculations indicate a nonoporosity of up to 80 vol %.

The postulation of a nanoporous secondary phase that is permeable to gas diffusion is compatible with the measured performances for the cathodes sintered at 600 and 800 °C. For cathode thicknesses of 1-2 µm minimal ASR values are observed, because the nanoporous secondary phase is hardly affecting gas diffusion, nor does it reduce surface exchange. At higher thicknesses the secondary phase, which fills the pores, also leads to limitations for gas diffusion so that the electrochemical reaction takes place at larger distance from the cathode-electrolyte interface. Thus the transport distances through the secondary phase (for gas) and through the LSC (for oxygen ions) increase. This explains the observed increase in ASR for larger cathode thicknesses (e.g., 7 µm). In contrast, for the phase pure cathode sintered at 1000 °C such transport limitations do not exist and the electrochemically active zone is supposed to be close to the electrolyte interface.
9.1.3. Outlook: Materials Design and Applicability of LSC

In general, these findings have to be considered as preliminary steps towards a deeper understanding of the physical and chemical processes governing the performance of LSC cathodes. In literature, fuel cells with LSC cathodes are often reported to undergo Sr segregation during operation. However, the Sr non-incorporation observed in this work results from the fabrication using spray pyrolysis. The results indicate that the presence of SP has a positive effect, either directly (because of high exchange current density) or indirectly (because it leads to a beneficial Sr deficiency of LSC). At this point, it is not yet possible to precisely single out the effects of the SP on the electrochemical kinetics of LSC cathodes. Nonetheless, the presence of a secondary phase suggests that there might be new ways to design highly active SOFC catalysts by tuning material properties such as Sr deficiency, crystallinity or by deliberate addition of other phases to come up with multi-phase electrodes. Therefore, it is proposed here to produce understoichiometric LSC by spray pyrolysis and to investigate their performance and properties.

One important aspect addressed by this thesis is also to assess the viability and applicability of spray pyrolysed LSC. A performance, which is similar as LSC fabricated by more costly deposition techniques such as PLD could be achieved. Moreover, also the chemical stability is comparable in spray pyrolysed LSC with and without the CGO buffer layer.
9.2. Ni-YSZ Cermet Anodes for HT-SOFC Applications

The electrochemical performance of cermet anodes such as Ni-YSZ is influenced by the complex interplay between (1) transport of mobile species and (2) electrochemical reaction at the triple phase boundary (TPB). These processes depend on the microstructure and on intrinsic material properties. Moreover, redox cycling often results in inevitable degradation not just of microstructure but also of electrochemical performance. In the present investigation fine, medium and coarse-grained anodes are exposed to 8 redox cycles at 950 °C. The microstructure characteristics of anodes before and after redox cycling are quantified based on FIB-tomography and detailed topological analysis. The results from 3D analysis are used as input to a finite element model in order to simulate microstructure influence on the anode performance. This work reveals a complex pattern of different degradation behaviors, which vary depending on the coarseness of the initial microstructure.

9.2.1. Influence of the Initial Microstructure

The initial characteristic properties of the anodes trigger the degradation behavior during redox cycling. The fine anode is found to be relatively dense (low porosity) due to the high sintering activity of the fine YSZ. This leads to a more constrained space for the Ni-NiO transition upon redox cycling. In contrast, the coarse anode exhibits low sintering activity, which leads to the smaller (and weaker) YSZ bottlenecks. In the initial state, higher electrical and ionic conductivities are obtained for the fine anode compared to the coarse anode. The total TPB as well as the active TPB also decrease from fine to coarse. Consequently, the polarization resistance \( R_{pol} \) increases from fine to coarse anode microstructures, due to a decrease of both, TPB lengths and effective conductivities.
9.2.2. Degradation After Redox Cycling

Microstructure degradation of Ni-YSZ anodes upon redox cycling includes three main phenomena: a) Ni coarsening and associated changes of electrical conductivity, b) YSZ loss of percolation and associated changes of ionic conductivity and c) Loss of TPB and associated change in electrochemical activity.

a) Ni coarsening strongly depends on the fineness of the microstructure. The fine anode, which is also denser (i.e., lower porosity), exhibits substantial Ni coarsening and this observation correlates well with the drop of electrical conductivity measured experimentally. Ni coarsening is less harmful in the coarse anode, where the electrical conductivity over 8 redox cycles is even improving slightly. Obviously, the extent of Ni-degradation is also influenced by the available porosity, which may serve as expansion space to compensate redox induced volume changes.

b) The rearrangement of Ni during the redox cycling exerts stresses onto the rigid YSZ backbone. The mechanical stability of the ceramic backbone depends on the strength of the bottlenecks. Although the Ni-degradation is stronger in the fine anode (as stated above), the YSZ backbone remains relatively stable in the fine sample, which is due to stronger YSZ bottlenecks associated with higher sintering activity. Weaker sinter necks in the coarser anodes results in lower mechanical stability, which then leads to significant loss of connectivity in the YSZ network. YSZ degradation leads to a drop of the effective ionic conductivity upon redox cycling. In the fine anode the decrease of ionic conductivity is mainly due to a reduction of bottleneck dimensions. However, the loss of YSZ percolation in the coarse anode has a much stronger influence on the ionic conductivity, which drops to almost zero (S m\(^{-1}\)).

c) Ni coarsening and YSZ loss of percolation also influence the TPB. The total and active TPB lengths decreased in all samples after redox cycling. The loss of TPB in the fine sample is dominated by the coarsening of Ni, while the loss of TPB in the
coarse sample is dominated by the loss of YSZ percolation. For the anodes before redox cycling, the performance (1/ASR) correlates well with the active TPB that decreases from fine to coarse. However, after redox cycling, TPB-performance relationships are more complex. Particularly in the coarse anode the active TPB drops by 93% upon redox cycling, whereas the corresponding performance decrease is much less pronounced.

9.2.3. Differentiated Interpretation of Degradation

The details obtained in the microstructure analysis and the relationships established on a quantitative level make it possible to precisely identify the topological parameters involved in a certain degradation behavior. For the fine anode the main degradation is associated with Ni-coarsening and for the coarse anode it is related to YSZ loss of percolation. More precisely, degradation of Ni in the fine anode leads to a lower M-factor, which is mainly related to a higher tortuosity and a lower effective volume fraction, the latter being the result of macroscopic volume changes (anode swelling). For YSZ in the coarse anode, a very low M-factor is measured already for the initial microstructure, which can be attributed to a relatively high tortuosity and a low constrictivity (small bottlenecks, low sinter activity). Upon redox cycling the M-factor for YSZ in the coarse anode further decreases significantly due to a loss of percolation and associated increase of tortuosity. The loss of YSZ percolation is also the main reason for the above-mentioned loss of active TPB in the coarse anode. Hence, combining 3D imaging, topological analyses and electrical/electrochemical characterization, it is possible to capture the complex picture of microstructure degradation and its relation with effective properties.
9.2.4. Outlook: Anode Design Concept and Improvement of Material Properties

It was shown that the electrochemical performance of cermet anodes such as Ni-YSZ is influenced not only by the TPB. Charge transport, especially ionic transport may also limit the electrochemical process and the anode performance. Consequently, insights gained in this work show the importance not only of optimizing the cermet anode microstructure properties in relation to the TPB but also considering the transport-related microstructure properties. For example, on the one hand, it was shown in this work that coarse Ni-YSZ has very good stability of the Ni-phase and that electrical conductivity even increases after redox cycling. This suggests the possibility to use coarse Ni-YSZ as a current collector layer. On the other hand, fine Ni-YSZ with its high TPB length is a suitable material for an active (functional) anode layer with enhanced electrochemical reactivity. Furthermore, in the fine anode the YSZ-backbone has a high mechanical stability (strong sinter necks), which helps to preserve the relatively high ionic conductivity. Consequently, these results support the concept of double-layered anodes where the fine anode acts as the functional layer and the coarse anode is used as the current collector layer.

As an outlook the properties of these bi-layer components can be further improved by the following measures: (1) adapting the fabrication procedure to increase the porosity of the fine anode (e.g., addition of pore formers) and (2) addition of fine YSZ in the coarse anode to improve YSZ sinter necks (i.e., fine YSZ as sintering aid).

The first measure (for improving the fine anode) supposedly increases the redox stability, since the low porosity appears to be a major factor for the severe spatial redistribution of Ni (agglomeration) upon redox cycling. As shown in the coarse anode, the volume expansion can be prevented with a higher porosity. This will then also reduce the loss of TPB in the fine material.
The second measure (for improving the coarse anode) was already tested with a ratio of 50% fine and 50% coarse YSZ powder. It turned out that 50% of fine powder is too much, since the resulting properties are very similar to the fine anode (i.e., low density due to high sinter activity). Hence, it is proposed here to use 3 to 10% of fine YSZ. Thereby the fine YSZ should act as a sintering aid that improves the sinter necks between the coarse YSZ particles. However, the coarse YSZ should still be the dominant ceramic component (>90%), so that the main properties of the microstructure resemble those of the coarse anode. In this way a material is obtained that undergoes low volume expansion (due to high initial porosity), low Ni-agglomeration and low degradation of electrical conductivity (as observed for the coarse anode), but with much improved stability of the YSZ backbone due to stronger sinter necks.
9.3. Methods

It was observed in Chapter 3 that the spray pyrolysed LSC sintered at low temperatures (600 °C, 800 °C) is not a phase pure material. Hence, it is not the most suitable material if one wants to investigate microstructure effects systematically. In fact, using a simple model (Adler-Lane-Steele, ALS) it was found that the presence of a secondary phase more significantly affects the electrochemical performance than the corresponding changes in microstructure (i.e., increase of surface area at lower sintering temperatures). These observations from the cathode investigation directed our efforts to investigate microstructure effects systematically in Ni-YSZ. This material is more stable with respect to intrinsic property (i.e., no secondary phases) as compared to the spray pyrolysed LSC. Moreover, the microstructures are easy to vary systematically.

9.3.1. Effective Material Properties and Microstructure Effects

The relationship between conductivity and 3D microstructure was investigated in two ways: (1) by numerical simulation of conduction using the tomography data as direct input and (2) by using an empirical relationship that allows prediction of effective conductivities based on topological parameters from 3D analysis.

Recent progress of commercial simulation tools (e.g., GeoDict, Avizo) allows running numerical simulations of transport on voxel grids >500³ in a reasonable time. Moreover, a considerable improvement is the possibility to perform computations directly on the voxel grid from tomography (i.e., no error introduced from mesh-generation and associated data reduction). The second method (predictions based on topological parameters) can handle larger data volumes and the limitations regarding representative elementary volume (REV) are less severe. The issue on REV is encountered in the coarser anodes after redox cycling due to increased heterogeneity. At this stage it is not realistic to run the numerical
simulations on the complete data volume from FIB-tomography (data cubes with edge lengths of 1000 - 2000 voxels). Hence, a combination of these two methods is ideal to study microstructure effects as they provide complementary possibilities and information. Moreover, it is possible with these methods to access physical properties, which are difficult and costly to measure in actual experiments. In particular, the ionic conductivity can usually not be measured under anode operating conditions. Here, 3D-analysis combined with numerical transport simulation as well as with topology-based predictions open new possibilities to access the required materials properties.

In terms of the TPB, a rather complex correlation between $R_{\text{pol}}$ and TPB is documented in this study. Several scenarios are discussed to explain the observed non-linear relationships between $R_{\text{pol}}$ and TPB. These scenarios include limitations from both, charge transfer as well as charge transport, and they describe their effects on the current density profiles across the anode layer. Furthermore the scenarios show that the $R_{\text{pol}}$ must be understood as a result from the interplay between transport and transfer processes and from the resulting current distributions. Nevertheless, the successful determination of TPB lengths (total and active) through the method described in Chapter 7 makes it possible to correlate TPB and the features of microstructure degradation during the redox cycling.

9.3.2. Modeling of Coupled Phenomena

Preliminary results in Chapter 8 show that numerical models that incorporate microstructure effects, which are quantitatively described by 3D image analysis, provide an improved understanding of the complex interplay between the charge transport and charge transfer processes in Ni-YSZ anodes. The ASR components related to transfer and transport are distinguished which enables to identify the limiting processes for the electrochemical anode performance. Results show that for
lower thicknesses, the ASR is dominated by the amount of TPB. For coarse and for degraded microstructure the activation ASR is high due to lower TPB lengths. For higher anode thicknesses, although the amount of available TPB increases, transport distances for ions become longer and therefore the decrease in activation ASR is compensated by the increase of ASR related to ion transport.

Moreover, the limitations of the bulk effective properties and volume averaged microstructure parameters in relation to the representative elementary volume (REV) can also be addressed using the FE-model. In particular, if the active (functional) layer thickness of the anode is smaller than the REV, the anode performance is no longer controlled by the bulk effective properties. This problem is accounted for in the FE-model when the properties close to the anode-electrolyte and anode-current collector are corrected accordingly, which is described as the short-range effect (SRE).

9.3.3. Outlook: Towards Virtual Microstructure Design of SOFC Electrodes

Numerical modeling used to simulate electrochemical performance, in combination with modern methods for topological analysis and prediction of effective properties, opens new possibilities for virtual materials design, e.g., by performing parametric studies on the influence of microstructure on the electrochemical performance. Using microstructure input for different scenarios of fabrication (e.g., variation of powder fineness, variation of sintering temperature) the numerical model is able to predict the corresponding anode performance. This information can then be used for systematic microstructure optimization. In a similar way, using microstructure input for different scenarios of degradation (e.g., redox cycling at specific operating conditions), the model can be used to find optimized microstructures with enhanced material stability (i.e., durability).
In this concept, the microstructure input can be obtained either from real materials (i.e., from 3D-analysis, as it is demonstrated in this study). Alternatively, the input may also be obtained from virtual microstructure modeling. Using input from real materials suffers from the drawback that the number of datasets and associated microstructure variations are usually limited to a few samples. If virtual microstructures are created based on spatial stochastic simulation a large parametric range can be covered more easily. However, in this case the challenge is to vary the microstructure in a realistic way. At this stage, more effort is required for realistic variation of virtual microstructures so that they are capable to fit with real microstructures that originate either from changes of the fabrication parameters (e.g., different powder fineness, different sintering temperatures etc.) or from changes due to degradation during the operation (e.g., redox cycling at a specific temperature). The matching of stochastic models with reality is the main methodological gap, which needs to be closed in the future in order to create reliable input for numerical simulation in an efficient way. All other techniques (i.e., numerical model to simulate electrode reaction mechanism, 3D-imaging and topological analysis, relationship of topology with effective properties, experimental methods (EIS) for validation) that are required for a virtual design of SOFC electrodes are nowadays available, as demonstrated in the present study.
Conclusions and outlook
10. Appendix

This section presents the co-authored papers published in peer-reviewed journals, which are related and contributed significantly in realizing the objectives of this work. Moreover, the proceedings of conferences, which are related to the works in parts II and III are also included in this section as full papers or abstracts. These papers are included in this thesis for completeness of information but do not necessarily have a significantly different content.
10.1. Co-authored Publications

10.1.1. Redox cycling of Ni-YSZ anodes for solid oxide fuel cells: Influence of tortuosity, constriction and percolation factors on the effective transport properties

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Abstract

A methodology based on FIB-tomography and image analysis (IA) is proposed which allows quantification of all relevant morphological features that are necessary to predict effective transport properties in porous SOFC electrodes. These morphological features are constrictivity, tortuosity, percolation factor and phase volume fraction. An M-factor can then be calculated which represents the ratio of effective over intrinsic conductivities. The methodology is used to describe effects of microstructure degradation in Ni-YSZ anodes which are caused by redox cycling at 950 °C. The so calculated M-factors predict that because of redox cycling the effective electronic conductivity of nickel decreases from 3 to 1.2% which is mainly due to changes of percolation and constriction factors. Based on these results the effective electrical conductivity of nickel is predicted to be 685 S/cm before redox and 243 S/cm after 8 redox cycles. The predictions fit well with the experimental measurements that reveal 600 S/cm before and 200 S/cm after redox cycling at 950 °C. For YSZ the M-factors obtained with 3D-analysis predict that the degradation causes a drop of the effective ionic conductivity from 7 to 0.6%, which is due to a change of the bottleneck dimensions. This finding contradicts the frequent interpretation of YSZ as a ‘rigid backbone’ that is not affected by microstructure degradation. Finally, the effective bulk gas diffusivity in-creases from 2 to 11% due to an increase of porosity associated with swelling of the anode.

* This paper has been published in the Journal of Power Sources. (L. Holzer, B. Iwanschitz, Th. Hocker, L. Keller, O. Pecho, G. Sartoris, Ph. Gasser, B. Muench, J. Power Sources 242 (2013) 179-194.)
10.1.2. Quantitative Relationships Between Microstructure and Effective Transport Properties Based on Virtual Materials Testing†

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Abstract

The microstructure influence on conductive transport processes is described in terms of volume fraction $\varepsilon$, tortuosity $\tau$, and constrictivity $\beta$. Virtual microstructures with different parameter constellations are produced using methods from stochastic geometry. Effective conductivities $\sigma_{\text{eff}}$ are obtained from solving the diffusion equation in a finite element model. In this way, a large database is generated which is used to test expressions describing different micro–macro relationships such as Archie’s law, tortuosity, and constrictivity equations. It turns out that the constrictivity equation has the highest accuracy indicating that all three parameters ($\varepsilon$, $\beta$, $\tau$) are necessary to capture the microstructure influence correctly. The predictive capability of the constrictivity equation is improved by introducing modifications of it and using error minimization, which leads to the following expression: $\sigma_{\text{eff}} = \sigma_0 \left(2.03\varepsilon^{1.57}\beta^{0.72}/\tau^2\right)$ with intrinsic conductivity $\sigma_0$. The equation is important for future studies in, for example, batteries, fuel cells, and for transport processes in porous materials.

† This paper has been published in the AIChE Journal. (G. Gaiselmann, M. Neumann¹, V. Schmidt, O. Pecho, T. Hocker, L. Holzer, AIChE J. 60 (6) (2014) 1983-1999.)
10.1.3. Predicting Effective Conductivities Based on Geometric Microstructure Characteristics

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Abstract

Empirical relationships between effective conductivities in porous and composite materials and their geometric characteristics such as volume fraction $\varepsilon$, tortuosity $\tau$ and constrictivity $\beta$ are established. For this purpose, 43 virtually generated 3D microstructures with varying geometric characteristics are considered. Effective conductivities $\sigma_{\text{eff}}$ are determined by numerical transport simulations. Using error-minimization the following relationships have been established: 

\[ \sigma_{\text{eff}} = \sigma_0 \varepsilon^{1.15} \beta^{0.37} / \tau_{\text{geod}}^{0.39} \]  

and 

\[ \sigma_{\text{eff}} = \sigma_0 \varepsilon^{0.36} / \tau_{\text{geod}}^{5.17} \]  

(simplified formula) with intrinsic conductivity $\sigma_0$, geodesic tortuosity $\tau_{\text{geod}}$ and relative prediction errors of 19\% and 18\%, respectively. We critically analyze the methodologies used to determine tortuosity and constrictivity. Comparing geometric tortuosity and geodesic tortuosity, our results indicate that geometric tortuosity has a tendency to overestimate the windedness of transport paths. Analyzing various definitions of constrictivity, we find that the established definition describes the effect of bottlenecks well. In summary, the established relationships are important for a purposeful optimization of materials with specific transport properties, such as porous electrodes in fuel cells and batteries.
10.2. Conference Papers

10.2.1. Microstructural and electrochemical characterization of thin La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ cathodes deposited by spray pyrolysis§

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Abstract

Mixed ionic-electronic conducting La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC) has recently drawn much attention as one of the most active materials for intermediate temperature SOFC cathodes. The electrochemical kinetics is believed to be limited by oxygen incorporation at the perovskite/air interface. Hence improvement of the cathode performance can be achieved by increasing the number of sites for oxygen exchange. This is realized either by making the electrode thicker and/or by producing nanosized LSC grains.

Spray pyrolysis (SP) constitutes a cost-effective alternative technique to vacuum-based deposition techniques, such as pulsed laser deposition (PLD) and sputtering, to produce such nanocrystalline components for thin films SOFC and micro-SOFC. Its versatility in terms of processing parameters (e.g., deposition temperature, precursor concentration, flow rate …) enables to fabricate a large variety of electrodes with various microstructures, grain sizes and pore sizes.

In this work, nanoporous La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ cathodes are sprayed on yttria-stabilized zirconia (YSZ) and gadolinium-doped ceria (GDC) electrolyte substrates. As-deposited layers are amorphous. The desired perovskite phase, electrical conductivity and porosity develop upon annealing at ca. 500-600°C. Grain and pore size from 10 to 50 nm can be obtained by adjusting the heat-treatment of the as-deposited layers. Power density data of anode-supported SOFC shows that SP-LSC and PLD-LSC cathodes yield similar electrochemical performance in the 450-650 °C range. This contribution will also present quantitative microstructure analyses of annealed electrodes (such as specific surface area, constrictivity and tortuosity, using continuous phase size distribution), area-specific resistance values of LSC/GDC (or YSZ)/ LSC symmetrical cells as well as results on the SP-LSC/YSZ chemical compatibility and the need of a GDC interlayer.

§ This work has been presented at the 10th European Fuel Cell Forum. (O. Pecho, M. Prestat, Z. Yáng, J. Hwang, J.W. Son, L. Holzer, T. Hocker, J. Martynczuk, L.J. Gauckler, Microstructural and electrochemical characterization of thin La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ cathodes deposited by spray pyrolysis. In Chapter 13, Proceedings of the 10th Eur. Fuel Cell Forum, Lucerne, Switzerland, June 26-29, 2012, Eds. F. Lefebvre-Joud et al., pp. 61-67.)
Appendix

10.2.2. Quantitative microstructure analysis and electrochemical activity of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ electrodes deposited by spray pyrolysis

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Abstract

Mixed ionic-electronic conducting La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC) is one of the state-of-the-art cathode materials for thin film and miniaturized SOFC [1] operated at intermediate temperatures. The electrochemical kinetics is believed to be limited by oxygen incorporation at the perovskite/air interface. Hence, for porous electrodes, increasing the number of sites for oxygen exchange either by making the electrode thicker or by producing nanosized LSC grains can improve the cathode performance.

In this work, nanoporous LSC cathodes are deposited by spray pyrolysis onto gadolinium-doped ceria (GDC) electrolyte substrates. The as-deposited films are dense and amorphous. Different porous microstructures are produced by changing the heat-treatment, 600°C and 800°C for 4 hours in air in this study. XRD and DSC analyses reveal that the layers are crystalline after heat treatment.

The electrode microstructure is analyzed using focus-ion beam nanotomography, continuous phase size distribution (c-PSD) and mercury intrusion porosimetry PSD (MIP-PSD)[2]. The latter methods, based on the analysis of 2D-micrographs and 3D-reconstructions allow for the determination of the phase sizes, volume fractions, surface areas and percolation levels of the various phases present in the annealed films.

The area specific resistance (ASR) of symmetrical LSC/GDC/LSC cell is measured in air between 400 and 600°C by impedance spectroscopy. The 800°C annealed LSC layers, with an average grain size ($r_{50}$) of ca. 30 nm show higher electrochemical performance than those annealed at 600°C ($r_{50} = 12$ nm), ca. 0.12 Ωcm$^2$ and 0.35 Ωcm$^2$, respectively. This is attributed to an improved percolation level of pores (ca. 100% vs. 60%) making more LSC surface available for oxygen exchange.

The principle of c-PSD and MIP-PSD will be described. More results on the relationships between microstructural features (such as percolation factor, constrictivity, and tortuosity) and oxygen reduction activity will be reported.


** This work has been presented at the Materials Research Society, Fall Meeting (November 25-30, 2012) in Boston, USA.
10.2.3. Effects of sintering temperature on composition, microstructure and electrochemical performance of spray pyrolysed LSC thin film cathodes††

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Abstract

Thin nanoporous LSC (La$_{0.6}$Sr$_{0.4}$CoO$_3$-$\delta$) cathodes are deposited by spray pyrolysis onto gadolinium-doped ceria (GDC) electrolyte substrates, followed by sintering at 600°C, 800°C, and 1000°C. The investigation includes quantitative microstructure analysis, electrochemical characterization and application of Adler-Lane-Steele (ALS) model in order to extract intrinsic material properties and to explain the effects of variation in sintering temperature. A secondary gray phase (SGP) is detected, which consists of Sr and O and has a contrast in backscatter imaging intermediate between the pores and the LSC. SGP fills 66% of the mesopores in LSC sintered at 600 °C. With increasing sintering temperature the amount of SGP decreases until it disappears at 1000 °C. In this investigation we intend to understand the effect of SGP formation. For this purpose the influence of microstructural changes (i.e., active surface area) and variation of intrinsic material properties (exchange flux density) associated with SGP formation need to be quantified.

The area specific resistance (ASR) of symmetrical LSC/GDC/LSC cells is measured between 400 and 600°C by impedance spectroscopy. ASR values as low as 0.13 Ω cm$^2$ are obtained for samples sintered at 600°C, and 80 times higher for samples sintered at 1000 °C. These results indicate that the SGP is not blocking gas diffusion of O$_2$ in the pores and therefore surface oxygen reduction reaction may take place over the entire LSC surface. Hence at low sintering temperatures a high specific surface area is obtained and the results indicate that formation of SGP does not bring a negative effect neither on the oxygen transport in 1-µm thin electrodes, nor on the oxygen reduction kinetics of LSC. An inverse correlation between the measured ASR values and the LSC-surface is obtained. The exchange neutral flux density, $r_0$, is calculated using the ALS model, which results in $r_0$-values in the range between $10^{-8}$ (600°C) and $10^{-9}$ mol/cm$^2$/s (1000°C). Considering the formation of a secondary SrO-phase in a mass-balance for the entire sample also leads to the conclusion that there must be an increase of A-site deficiency and oxygen vacancies in LSC. In summary, it can be concluded that the variation of the ASR between LSC sintered at 600°C and 1000 °C is more strongly related to the difference in intrinsic material property, ($r_0$ varies by a factor of 40) than the difference in surface area, ($a$ varies by a factor of 2). For a controlled optimization of cathode performance it is necessary to consider all these different aspects (non-stoichiometric compositions, microstructure, secondary phase formation, intrinsic properties, sintering temperature).

Introduction

Over the last several years, the development of solid oxide fuel cells (SOFC) progresses towards lower operating temperature, which encompasses both conventional and miniaturized SOFC applications [1-8]. Lowering the operating temperature has the benefits of slower rate of SOFC components degradation and reduced start-up time. Consequently, electrodes must be optimized to meet these demands. Microstructure must be designed to increase the number electrochemically active sites. Materials that exhibit high activity towards oxygen reduction are also desired especially at relatively low operating temperatures.

The electrochemical performance of cathodes is affected by two coupled phenomena: transport of mobile species (gas, ions and electrons) and oxygen reduction reaction at the surface. The overall kinetics of oxygen reduction is generally described as being limited by surface exchange at the electrode/air interface. Electrode activity can therefore be enhanced by using electrodes with mixed ionic-electronic conducting (MIEC) properties such as LSC [1,2,9-11], which can extend the reaction from the triple phase boundary at the electrolyte-electrode interface into the porous cathode layer. Moreover, utilization of thin film cathodes has attracted attention due to increased thermo-mechanical stability and reduced grain size due to the nanostructure.

In this work, thin LSC electrodes are deposited by wet spray pyrolysis. Microstructure characterization is done by scanning electron microscopy (SEM) and FIB-nanotomography. Local chemical compositions are analysed with TEM-EDX. The electrochemical performance is evaluated in terms of area specific resistance (ASR, symmetrical cells) obtained from impedance measurements. Moreover, the ASR and the specific surface area from image analysis are used as input in the ALS model to evaluate the neutral flux density, \( r_0 \).

Experimental

The precursor solution consisted of \( \text{La(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \), \( \text{SrCl}_2\cdot6\text{H}_2\text{O} \), \( \text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (metal concentration 0.4 mol L\(^{-1}\)), which was dissolved in a mixture of 32 vol% ethanol, 63 vol% diethylene glycol monobutyl ether (DGME) and 5 vol% polyethyleneglycol (PEG600). The solutions were sprayed onto gadolinia-doped ceria (GDC, \( \text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_1.95 \), Kerafol\({}^\text{®} \), 0.20 mm thick) tapes heated at 340°C with the set-up schematically described in Figure 1. The resulting LSC films were sintered at three different temperatures: 600 °C, 800 °C and 1000 °C for 4 hours in air. Focused ion beam – scanning electron microscope (FIB-SEM, Helios Nanolab 600i) was used for quantitative and qualitative characterization of the microstructures. Quantification of the phase sizes was done by continuous phase distribution (c-PSD, [12]) using in-house plugins for Fiji software and applying them to 2D-images from FIB-SEM. Specific surface and interface area was determined by measuring the corresponding phase perimeters from segmented 2D-images. Spot analysis and compositional mapping were done with TEM-EDX.
Symmetrical cells (LSC/GDC/LSC) were used to evaluate the ASR of the films measured by impedance spectroscopy. Measurements were done between 400-600 °C in steps of 50 °C in air. For the electrochemical measurements, a Solartron impedance analyser (SI1260) and a Solartron potentiostat (SI1287) were utilized.

**Results**

The as-deposited amorphous films crystallized after sintering at the different temperatures and no delamination of cathode film was observed after sintering. At lower sintering temperature, the phases are smaller with elongated pores randomly distributed over the entire film thickness. As the sintering temperature increases, the phases become more isometric with significant coarsening especially between 800°C and 1000°C. However, single-phased LSC was not obtained. A secondary phase (SP), with contrast in backscatter imaging intermediate between the pores and LSC is observed (Figure 2). Quantitative microstructure analysis reveals that the amount of secondary phase is temperature-dependent. Significant volume fraction of the secondary phase was determined for the samples sintered at 600°C. The secondary phase is filling the pores and covering the LSC surface. This fraction decreases at 800 °C and disappears at 1000°C.
Figure 2. LSC obtained after sintering at 600°C. The secondary phase fills the pores and covers the surface of LSC.

Lowering the sintering temperature resulted to smaller phase sizes. Consequently, due to the smaller LSC phase size, the LSC surface area at 600°C is greater than at 1000°C. The ASR of LSC/GDC/LSC symmetrical cells were measured in air. The ASR values increased by a factor of 78 with higher ASR for samples sintered at 1000°C (Table 1). The relatively good ASR of the LSC cathode sintered at 600°C indicates that the approach of lowering the sintering temperature (phase size) is appropriate. However, the good electrochemical performance cannot be solely explained by the improvement in the microstructure (since the secondary phase is filling the pores). For a better understanding of the microstructure-property relationship in these samples the intrinsic properties of the secondary phase must be investigated. TEM-EDX analyses indicate that the secondary phase is composed of Sr and O. Under consideration of a mass balance for the entire sample, it must be assumed that LSC has a modified (non-)stoichiometry with associated Sr-deficiency on the A-site.

In order to evaluate semi-quantitatively the extent of Sr-deficiency in LSC we perform some mass balance calculations. For these calculations, we assume that the secondary phase is made of SrO, and that the specific volume of LSC does not change although a fraction of the Sr is not fully incorporated into the LSC lattice (only the stoichiometry changes). Using the molecular mass, density and amount of Sr not incorporated (given by x in La_{0.6}Sr_{0.4-x}CoO_{3-δ}), the volume of the crystalline SrO-phase corresponding to a certain A-site deficiency can be calculated. Furthermore, we can then compare this calculated volume fraction for a crystalline SrO-phase with the measured volume fraction obtained by image analysis for the secondary phase. The results from mass balance calculation show that even at the maximum amount of Sr-deficiency (x=0.4, i.e., all Sr in the secondary phase), there would not be enough volume of a crystalline SrO-phase to occupy the whole volume of the secondary phase (from image analysis). This indicates that the bulk density of the observed secondary phase is much lower than the density of the crystalline SrO-phase.

For the series of samples sintered at different temperatures, it was found that the total surface area of LSC inversely correlates with the ASR. This indicates that the total surface area of LSC is electrochemically active, and hence the secondary phase, which fills the pores in the better performing samples (600°C), must be permeable to gas. The mass balance calculations as well as the backscatter contrast indicate that the density of the secondary phase is very low, most probably due to finely dispersed nanoporosity. This may explain why the secondary phase has a high permeability for oxygen-diffusion. The distribution of secondary phase in the sample sintered at 600°C is shown in Fig. 3, based on 3D-images from FIB-tomography. The simulation shown in Fig. 3 (D) was performed under the assumption that the secondary phase is a dense material, which leads to an apparent disconnection of the pores from the cathode surface. Oxygen can only diffuse into the sample if the secondary phase is permeable.
As mentioned, the formation of the secondary phase affects not just the microstructure but also the non-stoichiometry and associated intrinsic material property. As summarized in Table 1, the difference (factor of 78) between the ASRs of the LSC cathodes sintered at 600 °C and 1000 °C cannot be solely explained by microstructure (because the surface area varies only by a factor of 2). For our thin films the simplified version of the Adler-Lane-Steele model is applicable, since the whole layer thickness is electrochemically active (i.e., the calculated utilization region is greater than 1 µm). The neutral flux density, \( r_0 \), can then be resolved by substituting the values of the surface area obtained from image analysis and the ASR obtained from EIS measurements into equation 1.

\[
\text{ASR} = \frac{RT}{4F^2} \frac{1}{aLr_0(a_f + a_b)}
\]

The results summarized in Table 1 show, that the neutral flux density (\( r_0 \)), which is a kinetic material property of the materials, changes by factor of 39 from LSC cathodes sintered at 600 °C to 1000 °C. This indicates that the understoichiometry and Sr-deficiency is beneficial to the electrochemical performance of LSC.

Table 1. Summary of quantitative microstructural and electrochemical characterization of 1-µm thin film LSC cathodes

<table>
<thead>
<tr>
<th>( T_{\text{sinter}} )</th>
<th>600 °C</th>
<th>factor</th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSC total surface area (( \mu \text{m}^2 ))</td>
<td>28.9</td>
<td>2</td>
<td>14.3</td>
</tr>
<tr>
<td>ASR (Ω•cm²)</td>
<td>0.13</td>
<td>78</td>
<td>10.1</td>
</tr>
<tr>
<td>SGP volume fraction (%)</td>
<td>20.7</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Non-stoichiometry</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Intrinsic property, ( r_0 ) (mol/cm²/s)</td>
<td>5.20•10⁻⁸</td>
<td>39</td>
<td>1.35•10⁻⁹</td>
</tr>
</tbody>
</table>
Conclusion

This work has successfully demonstrated that lowering the post-deposition sintering temperature results to lower phase sizes in the cathode nanostructures. Consequently, the available surface also increases thereby enhancing the electrochemical kinetics. However, as a consequence of lowering the sintering temperature some of the Sr is not incorporated into the LSC lattice. As a result, a secondary phase composed of Sr and O is observed in backscatter imaging. The inverse correlation between the total LSC specific surface and ASR measurements indicates that the secondary phase is not blocking gas diffusion. Furthermore, mass balance calculations indicate that the secondary phase is not a dense SrO-phase, but contains a high fraction of nanoporosity, making it permeable for oxygen diffusion. The amount of secondary phase is also linked with the A-site deficiency in LSC, which brings changes in the intrinsic material property of the LSC. In particular, the neutral flux density resolved from ALS model shows that $r_0$ increases with decreasing sintering temperature and associated A-site deficiency. These results show that lowering the sintering temperature is beneficial for both the microstructure and the intrinsic material property, whereby the latter is dominating the enhanced electrochemical properties in LSC sintered at 600°C.

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10.2.4. Microstructure-Performance Relationships in Ni-YSZ Anodes: Quantitative Microstructure Characterization and FE-Simulation

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Abstract
The electrochemical performance of SOFC electrodes is greatly influenced by the microstructure and intrinsic material properties. The complex interplay between various transport processes (e.g., ionic and electronic transport) and electrochemical processes (e.g., fuel oxidation) depends on the corresponding transport-relevant parameters (i.e., tortuosity, constrictivity, percolation level, volume fraction) and active reaction sites (i.e., Triple phase boundary, TPB). Quantification of the relevant microstructure parameters is necessary to fully describe microstructure characteristics. Over the last years, state-of-the-art high-resolution tomographic techniques made it possible to quantitatively describe microstructure parameters and consequently, to analyze and to understand microstructure-performance relationships. However, in order to understand this mechanistically, models that simulate electrode reaction mechanism and incorporate these microstructure parameters in simulations must be developed. In this work, a relationship between the transport-relevant parameters determined recently is used to quantitatively describe the extent of microstructure effects in effective transport properties of the electrodes (i.e., effective conductivities). Insights on the effects of microstructure degradation on the electrochemical performance are also provided. The description and analysis of the TPB are also presented, in which changes are also correlated with loss of electrochemical performance. A model that incorporates the relevant microstructure parameters is used to simulate the complex anode reaction mechanism to evaluate the different components of the area specific resistance (i.e., ASR-transport, ASR-activation). Insights on the limitations in charge transport affecting electrochemical performance due to microstructure effects are all presented. The simulated ASRs are compared with experimental data obtained from impedance measurements (EIS). The results of this work give a deeper understanding on the complex relationship between microstructure parameters, material properties and electrode performance.

\textsuperscript{"‡‡} This work has been presented at the Materials Research Society, Fall Meeting (November 30-December 5, 2014) in Boston, USA.
10.2.5. Microstructure effects in Ni-YSZ anodes: 3D-analysis, FE-simulation and experimental correlation

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Abstract
Fuel cell electrode performance is affected by various electrochemical processes and transport phenomena that depend on the microstructure characteristics and intrinsic material properties. An elaborate quantification of microstructure parameters is necessary to quantitatively describe microstructure-performance relationships and a model that incorporates microstructure effects to simulate complex anode reaction mechanisms. Quantification of the relevant microstructure parameters such as particle size, size distributions, triple phase boundaries (TPBs), interfaces, surfaces, tortuosity and constrictivity are important to describe microstructure profiles. Furthermore, results from the incorporation of these microstructure parameters into models that simulate electrode reaction mechanisms can be used to evaluate their influence on the electrode performance. In this work, microstructure effects in composite Ni-YSZ anodes are investigated. Insights about the influence of microstructure degradation on the effective ionic and electronic conductivities, charge transfer reactions, and electrode performance are provided. Changes in the microstructure parameters such as the TPBs are correlated with the loss of the anode performance. Moreover, a model capable of simulating complex anode reaction mechanism is used to evaluate the specific components (ionic and electronic transport, electrochemistry and charge transfer) of the area specific resistance (ASR). The results are compared with the experimental data obtained from electrochemical impedance spectroscopy (EIS) and conductivity measurements. The results give further insights and understanding on microstructure-performance relationships in degradation mechanisms in fuel cell electrodes.

\textsuperscript{\textcopyright}\hspace{1em} This work has been presented at the 11\textsuperscript{th} Symposium on Fuel Cell and Battery Modeling and Experimental Validation – ModVal 11 (March 17-19, 2014) in Winterthur, Switzerland.
10.2.6. Improved redox-stability of Ni-YSZ anodes based on 3D microstructure and experimental analyses

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Abstract

The electrode performance (polarization resistance, $R_{pol}$) in solid oxide fuel cells (SOFC) is influenced by the interplay between the different electrochemical (activation, $R_{act}$) and transport processes ($R_{trans}$) that depend on the intrinsic material property and also on the electrode microstructure. In order to capture microstructure effects, the evolution of electrical conductivity and polarization resistance of varying Ni-YSZ anodes (fine, medium, coarse) over 8 redox cycles are measured (Fig. 1), and correlated with transport-relevant microstructure parameters and triple phase boundary (TPB).

![Figure 1](image)

**Figure 1.** (Left) Evolution of the relative conductivities and (right) the inverse of polarization resistance of Ni-YSZ anodes. The relative TPB before ($0^{th}$) and after ($8^{th}$) redox cycling is also shown (right).

The detailed image analysis results to a complex phenomenological pattern of microstructure-performance correlation upon redox degradation. Coarsening of Ni, loss of percolation of YSZ and loss of TPB are determined to be the dominant effects of redox cycling. The initial microstructure is also shown to influence performance and degradation behavior. Fine anode exhibits high TPB and high initial electrical conductivity but the fine anode microstructure also leads to a severe degradation of Ni, whereas the coarser anode have strong degradation of YSZ (weak YSZ sinter necks), which leads to severe degradation of TPB. Based on these findings, new fabrication guidelines for improved redox stability of Ni-YSZ anodes can be proposed. Initial results from mixtures of fine and coarse YSZ powder show that addition of <50% fine will be beneficial for the electrical conductivity, while addition of >50% fine will be beneficial for the TPB ($R_{act}$). Consequently, fine >50% with the addition of pore former may lead to a compromise between the optimization of these two processes.

*** This work has been presented at the 12th International Conference on Materials Chemistry (July 20-23, 2015) in York, United Kingdom.
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[20] O.M. Pecho, M. Prestat, Z. Yáng, L. Holzer, T. Hocker, J. Martynczuk, L.J. Gauckler, Quantitative microstructure analysis and electrochemical characterization of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ electrodes deposited by spray pyrolysis, CFN Summer School on Nano-Energy, Bad Herrenalb, Germany, September 14-17, 2012. [Poster]

[21] O.M. Pecho, M. Prestat, Z. Yáng, J. Hwang, J.W. Son, L. Holzer, T. Hocker, J. Martynczuk, L.J. Gauckler, Microstructural and electrochemical characterization of thin La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ cathodes deposited by spray pyrolysis, 10$^{th}$ European Fuel Cell Forum, Lucerne, Switzerland, June 26-29, 2012. [Poster]


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