Design and Development of Atmospheric Plasma Sprayed Ceramic Anodes for Solid Oxide Fuel Cells Operating Under High Fuel Utilization Conditions

by

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A thesis submitted in conformity with the requirements

for the degree of Master of Applied Science

Graduate Department of Mechanical and Industrial Engineering

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2012

Abstract

High fuel utilization SOFCs could eliminate emissions from systems that include afterburners and potentially be suitable for carbon sequestration, while producing electricity more efficiently. Current fuel utilization operating points are typically chosen at approximately 85% for Ni-cermet anodes because higher fuel utilization frequently results in the formation of nickel oxide and reduces drastically the performance of the SOFC. In this work the feasibility of an in-plane graded anode architecture with a transition from a material with high catalytic activity to materials more stable under high fuel utilization conditions was evaluated through a steady-state SOFC finite element model. Thereafter, plasma spraying of solution precursor feedstock (SPPS) and suspension feedstock (SPS) was used to fabricate ceramic coatings that could potentially be used as SOFC anodes for high fuel utilization conditions. Microstructural, electrical and electrochemical properties of LST, LSBT and LSFCr coatings with additions of carbon black pore former were investigated.
Acknowledgments

I am mostly grateful to my supervisor Olivera Kesler, for her unconditional support, guidance and encouragement, both professionally and personally. Sinceramente gracias Olivera por entenderme tan bien y por enseñarme continuamente a creer en mis capacidades.

I would like to thank all my fellow graduate students who helped me make this project possible, especially Joel Kuhn for his remarkable work designing and building the test stations used in this project, Jeff Harris and Mark Cuglietta for being so generous with their time, Michael Marr for developing the electrolytes and Craig Metcalfe for all the coffee and insights given during this project.

Many thanks to Mr. Tiegang Li for assisting me in the spraying of my coatings. I also express my gratitude to Kerry Kirton for all the help during the long plasma spray sessions and for making me feel that I was not alone in this boat.

I would like to give my very special thanks to my parents for everything that they have given me, all their love and support throughout these two years, despite the distance.

Finally, I gratefully acknowledge the financial support from Carbon Management Canada and Solid Oxide Fuel Cells Canada Strategic Research Network.
“Remember when atmospheric contaminants were romantically called stardust?”

Lane Olinghouse.
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Chapter 1
Introduction

1.1 Introduction

SOFCs are electrochemical devices that can convert chemical energy of a wide variety of fuels into electrical energy, with low pollution and high efficiency. Since SOFCs do not have to convert chemical energy into mechanical energy and heat they are not subject to Carnot efficiencies. A further reason that makes SOFCs an environmentally compatible device is their capability to convert fuels into electricity, water, and carbon dioxide without involving combustion. As a consequence, most of the pollutants produced during combustion can be avoided.

Fuel cells operate electrochemically similarly to a battery. However, in SOFCs, fuels are continuously fed into the cell. The basic structure of an SOFC includes an electrolyte, two electrodes (anode and cathode) and an external circuit or interconnects (as shown in figure 1).

Figure 1. Schematic of an SOFC.
The progress achieved by this technology in the last few years has resulted in excellent performances and the ability to use hydrocarbons as a fuel. E. Tang et al. reported a single cell power density of 1.4 W/cm$^2$ at 750 °C in humidified H$_2$ at 0.7 V and 75 % fuel utilization [1]. However, SOFCs are not completely developed in relevant operating conditions, such as high fuel utilizations [2]. Under such operating condition, SOFCs have poor performance compared to the idealized low fuel utilization condition, and the durability of the cells or stacks is low because of degradation mechanisms such as cracking in the electrolyte caused by volume expansions produced by the formation of nickel oxide.

There is interest in operating SOFCs at higher fuel utilization conditions, mainly because it increases the efficiency of the overall system. Likewise, there is increasing attention to the potential application of high fuel utilization SOFCs in the carbon dioxide capture and sequestration process. Additionally, high fuel utilization is preferred because the burning of the fuel coming from the exhaust of the cell is a common practice that reduces the environmental advantage of the technology.

Currently, the fuel utilization operating point is chosen at approximately 85% for Ni-cermet anodes [3]. A higher fuel utilization can result in the formation of nickel oxide or can reduce drastically the performance of the SOFC.

One path to increase the fuel utilization involves the optimization of the anode materials to minimize degradation and other negative effects when the cell operates under such conditions. In the present work, the major challenges faced in the design of SOFCs for operation under high fuel utilization conditions are discussed. Atmospheric plasma spray processing technique is used in this work for manufacturing SOFC anode materials due to the remarkable flexibility of this process to combine electrode materials that otherwise would not be compatible for simultaneous fabrication using the standard ceramic processing methods.

1.2 Motivation and objectives of the thesis

The motivation of this thesis was to study the feasibility of in-plane graded anode architectures with a transition of materials along the fuel flow path as a possible solution to increase the fuel utilization achievable by SOFCs. The first objective was to increase the understanding of the
electrical behaviour of an in-plane segmented anode with different materials along the fuel channel. This goal was achieved by finite element simulations of the SOFC architecture proposed. After a general understanding of the electrical behaviour of that architecture, work began on developing potential materials to be placed towards the outlet of the cell. Atmospheric plasma spraying of liquid feedstocks was used as the manufacturing process for fabricating the materials due to its ability to synthesize (SPPS) and fabricate (SPPS, SPS) fully-consolidated coatings of various materials in a single manufacturing step. Fabrication of ceramic materials suitable for conditions of high fuel utilization by plasma spraying will be the initial step towards the fabrication of in-plane graded anodes with a transition from a material with high nickel content for catalytic activity to anode compositions that are stable in slightly more oxidizing conditions such as those created near the anode exhaust outlet in conditions of high fuel utilization. An anode able to operate under high fuel utilization conditions will increase considerably the efficiency of the system. Moreover, high fuel utilization SOFCs operating with natural gas as a fuel could produce a very high purity CO₂ stream potentially suitable for CO₂ capture and sequestration applications.

1.3 Description of chapters

This work has been divided into seven chapters. Chapter one consists of an introduction to the thesis motivation and objectives. Chapter two consists of background information on SOFCs, focusing on information about fuel cells and plasma spray technology that is most relevant to the understanding and direction of this study. Chapter three details the procedure used to carry out the SOFC finite element simulations, laboratory experiments including feedstock preparation and plasma spray methodology, and feedstock and coating characterization techniques used. Chapter four presents a detailed explanation of the simulation studies performed to evaluate the electrical performance of an in-plane graded anode architecture and its respective results. Chapter five describes the initial plasma spray coating development work, including screening experiments to determine plasma spray parameters suitable to deposit ceramic materials, initial evaluations of the relative deposition efficiencies, microstructure characterization, and phase and composition analysis. Chapter six continues with coating development work and describes the detailed characterization of SPPS LST and LSBT and SPS LSFCr, and discusses their potential as
ceramic anode materials. Results including SEM, XRD, EDS, porosity, and conductivity measurement results are presented. Additionally, the electrochemical performance of each anode material is evaluated by impedance measurements on symmetrical cells. Finally, chapter seven presents the overall conclusions and gives specific recommendations for future work.
1.4 References


2.1 SOFC components and operation

SOFCs convert chemical energy of fuels directly into electrical energy via three solid electrochemically active layers: two porous electrodes separated by a dense electrolyte. Generally, the fuel is supplied continuously to the anode electrode, where it is oxidized. At the cathode electrode, oxygen from the air obtains electrons from the external circuit, and it is reduced to oxygen ions. Finally, oxygen ions travel through the electrolyte and reach the anode, where they oxidize the fuel, forming water and producing heat and electrons that travel to an external circuit or interconnect and produce usable electricity. In addition, carbon dioxide is produced when the fuel involves hydrocarbons (as showed previously in figure 1). SOFCs are able to use hydrocarbons as fuels, both by internal reforming and direct oxidation. The reactions at the anode when direct oxidation of hydrocarbons is involved are expressed in equations 1-3.

\[
\begin{align*}
\text{CH}_4 + 4\text{O}^{2-} & \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + 8\text{e}^- \\
\text{H}_2 + \text{O}^{2-} & \rightarrow \text{H}_2\text{O} + 2\text{e}^- \\
\text{CO} + \text{O}^{2-} & \rightarrow \text{CO}_2 + 2\text{e}^- 
\end{align*}
\]

The steam reforming and water gas shift reactions are presented in equations 4 and 5, respectively.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow 3\text{H}_2 + \text{CO} \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]
The reaction at the cathode is shown in equation 6.

\[
\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}
\]  
(6)

Direct oxidation of hydrocarbons may be preferred over internal reforming because it offers improved conversion efficiency.

2.1.1 Component Requirements

The SOFC components should meet key requirements, discussed here [1].

- **Catalytic activity**

The main function of the SOFC anode is to provide reaction sites for the electrochemical oxidation of the fuel. In order to achieve good performance, the anode must have sufficient catalytic activity for this reaction. Depending on the fuel used, the anode should be tolerant to certain levels of contaminants, such as sulphur. Similarly, the main function of the cathode is to provide reaction sites for the electrochemical reduction of the oxidant. Therefore, the cathode should have sufficient catalytic activity for this reaction.

- **Stability**

The anode must be chemically, morphologically, and dimensionally stable in the fuel environment. The anode material must be stable not only at the fuel inlet conditions, but also in the more oxidizing conditions of the fuel outlet. In the same way, the cathode must be chemically, morphologically and dimensionally stable in the oxidant environment, while the electrolyte must be able to withstand the dual atmosphere.

Both the cathode and the anode should preserve the desired microstructure during long term operation; significant microstructure changes can cause cell degradation and poor performance.
• **Conductivity**

SOFC electrodes must be electronic conductors in the respective environments at the operating temperatures. Furthermore, in order to increase the reaction sites and lower the polarization resistance, an ionically conductive phase is generally included in both the anode and the cathode [1]. The electrochemical reactions within a composite electrode made of a purely ionic and a purely electronic material can occur only where three phases meet: the electron conductor, ion conductor, and reactant gas. All such locations are termed three-phase boundaries (TPBs). In order for the electrochemical half cell reaction to occur, each phase must be connected from the reaction site to the source of the transported species. Specifically, there must be an electron conduction path to the current collector (interconnect), an oxygen ion conduction path to the electrolyte, and a gas diffusion path to the air channel in the cathode or fuel channel in the anode [2]. In the case of mixed ionic-electronic conducting oxides (MIEC), the active zones where the electrochemical reactions can occur are extended to any position of interface between the MIEC material and the gas phase [3]. The electrolyte must possess high ionic conductivity in the dual atmosphere to minimize ohmic losses and it must also have negligible electronic conductivity to prevent electrons from flowing through it.

• **Compatibility**

The electrodes and electrolyte must be chemically compatible at the operating temperatures and also at the fabrication temperatures to avoid undesired interdiffusion and unwanted phase formation.

• **Thermal expansion**

All the components of the SOFC must have similar thermal expansion coefficients to avoid cracking or delamination during fabrication or operation. Additionally, the coefficient of thermal expansion of the anode must be stable despite changes in the partial pressure of oxygen during operation.
• Porosity

The electrodes must have sufficient porosity to allow gas transport to the reaction sites. The electrolyte should be dense or have no connected porosity to prevent gas cross leakage.

2.2 The ideal performance of the SOFC

The maximum electrical work that can be obtained in an SOFC operating at a constant temperature and pressure is given by the change in Gibbs free energy ($\Delta G$) of the electrochemical reaction [4].

The ideal cell potential is given in equation 7,

$$E = -\frac{\Delta G}{nF} \quad (7),$$

where $n$ is the number of electrons participating in the reaction per molecule of reactant, and $F$ is the Faraday’s constant.

The Gibbs free energy change is given in equation 8,

$$\Delta G = \Delta H - T\Delta S \quad (8),$$

where $\Delta H$ is the enthalpy change, $\Delta S$ is the entropy change, and $T$ is the absolute temperature. The total thermal energy available is $\Delta H$. The available free energy is equal to the enthalpy change minus the $T\Delta S$ term, which represents the unavailable energy resulting from the entropy change within the system.

For the general cell reaction:

$$\alpha A + \beta B \rightarrow cC + \delta D \quad (9),$$

the Gibbs free energy change of the reaction can be expressed by the equation:
\[ \Delta G = \Delta G^\circ + RT \ln \frac{f_i^E f_i^B}{f_i^A f_i^C} \]  

where \( \Delta G^\circ \) is the Gibbs free energy change of the reaction at the standard state pressure (1 atm) and at the temperature \( T \). \( R \) is the ideal gas constant, and \( f_i \) is the fugacity of the species \( i \). Substituting (7) in (10) and approximating the fugacity as the partial pressure of the gases gives the general form of the Nernst Equation:

\[ E = E^\circ + \frac{RT}{nF} \ln \frac{\Pi_{\text{reactant partial pressure}}}{\Pi_{\text{product partial pressure}}} \]  

The Nernst potential \( E \) gives the ideal open circuit cell potential. This potential is the maximum voltage achievable for the cell.

### 2.3 Electrochemical efficiency of the SOFC

The electrochemical efficiency of an SOFC is governed by three factors: the thermodynamic efficiency, the voltage efficiency, and the fuel utilization or current efficiency [1]:

#### 2.3.1 The thermodynamic efficiency

The thermodynamic efficiency is defined as the maximum useful energy produced relative to the change in enthalpy [4].

\[ \varepsilon_T = \frac{\Delta G}{\Delta H} = 1 - \frac{T \Delta S}{\Delta H} \]  

Because SOFCs convert chemical energy directly into electrical energy, they are able to reach efficiencies higher than the Carnot maximum efficiency. Conventionally, chemical energy is converted to heat, then to mechanical energy, and finally to electrical energy. In SOFCs, the \( \Delta G \) of the reaction is potentially available as useful electrical energy [4].
2.3.2 The voltage efficiency

In an operating SOFC, the cell voltage experiences losses that depend on numerous factors including the material of the cells, composition of the fuels, current density, and conditions such as temperature and pressure. The voltage efficiency is defined as the ratio of the operating cell voltage under load, $E_{\text{ope}}$, and the open circuit voltage $E_{\text{ocv}}$ [1]:

$$\varepsilon_V = \frac{E_{\text{ope}}}{E_{\text{ocv}}} \quad (13)$$

The difference between the operating voltage and the open circuit voltage is the result of losses commonly called polarization, overpotential, or overvoltage. Note that the ideal voltage can differ from the open circuit voltage in situations with side reactions, short circuiting, or leakage through the electrolyte or seals of the cell. The three main polarization mechanisms studied in fuel cells are: charge transfer or activation polarization, diffusion or concentration polarization, and ohmic or resistance polarization [1].

The total polarization $\eta$ of the cell is the sum of each contribution of the different losses:

$$\eta = \eta_A + \eta_D + \eta_R \quad (14)$$

- **Charge transfer or activation polarization $\eta_A$**

Charge transfer or activation polarization results from the energy barrier of the electrochemical reaction that needs to be overcome, also called activation energy. It is the result of the sluggish electrode kinetics of surface electrochemical reactions such as adsorption of reactant onto the surface of the electrode or electron transfer.

The governing equation for the activation polarization when charge transfer at the electrode-electrolyte interface is the rate-limiting step is the Butler Volmer equation [5]:
where $\alpha_1$ and $\alpha_2$ are the reduction and oxidation transfer coefficients, respectively. $R$, $T$, $\Delta V_{\text{act}}$ and $i_0$ represent the ideal gas constant, the absolute temperature, the losses due to activation or charge transfer, and the equilibrium exchange current density, respectively. $i_0$ is a function of the cell material composition and microstructure and temperature, as described in the expression:

$$i_0 = A e^{-G_{\text{act}}/RT} \quad (16)$$

where $A$ is a pre exponential term that is a function of the reactant and product partial pressures, and $G_{\text{act}}$ is the activation energy for the electrochemical charge transfer reaction.

Since the full Butler-Volmer (BV) equation has implicitly the activation voltage losses, D.A. Noren et al. [5] summarized and clarified the most common approximations as follows:

When the activation loss is large ($\Delta V > 200\text{mV}$), the first exponential term in the BV equation has a much larger magnitude than the second. If the second exponential term is neglected, the resulting equation is the Tafel equation (high field approximation). This equation is valid when $i/i_0 > 4$ and takes the form of equation 17.

$$\Delta V_{\text{act}} \approx \frac{RT}{\alpha_1 F} \ln \left( \frac{i}{i_0} \right) \quad (17)$$

If the exponential terms in the one-step single electron transfer process BV equation are expanded in a power series, and the higher-order non-linear terms are neglected, the resulting equation is the low field approximation (sometimes called the linear current potential equation). This equation is valid when $i/i_0 < 1$ and takes the form of equation 18.

$$\Delta V_{\text{act}} \approx \frac{RT}{F} \left( \frac{i}{i_0} \right) \quad (18)$$
Finally, the hyperbolic sine approximation comes from the observation that the shape of the corresponding $\Delta V_{\text{act}}$ versus current curve is similar to a hyperbolic sine function; $\alpha_1$ and $\alpha_2$ are assumed to be equal, and the activation loss can be obtained using equation 19.

$$
\Delta_{\text{act}} = \frac{RT}{\alpha_1 i_F} \sinh^{-1} \left( \frac{i}{2i_0} \right) \quad (19)
$$

Activation losses were commonly neglected in previous SOFC models [5]. One reason behind this simplification was the rapid chemical kinetics for the past generation SOFCs operating at temperatures of approximately 1000°C, which tend to have lower activation losses than cells operating at lower temperatures (e.g. 600-800°C). Another reason was the dominating ohmic losses with greater magnitudes than the activation losses at typical current densities. These assumptions were valid for the older tubular geometries, which were originally designed to operate at high temperatures and had relatively long current paths. Modern stacks are being designed to operate below 800°C and utilize planar geometries with very short conduction paths. All the above results in activation polarization losses close in magnitude to or even greater than the concentration or ohmic loss mechanisms.

- **Diffusion or concentration polarization $\eta_D$**

This type of overpotential occurs when finite mass transport rates limit the supply of fresh reactant and the evacuation of products. In SOFCs, gas diffusion processes control mass transfer. Losses related to mass transport are significant during conditions such as high current densities or low fuel and air concentrations. For gas-phase fuel cells with large pores, Fick’s first law of diffusion governs the rate of mass transport to an electrode [4]:

$$
i = \frac{n F D (C_B - C_s)}{\delta} \quad (20),
$$

where $D$ is the diffusion coefficient of the reacting species, $C_B$ is its bulk concentration at the gas channels, $C_s$ is its surface concentration at the reaction sites, and $\delta$ is the diffusion distance. The
limiting current \((i_L)\) occurs when \(C_s=0\), and it is determined by the maximum rate at which a reactant can be supplied to the electrode.

\[
i_L = \frac{nFD CB}{\delta} \quad (21)
\]

The diffusion or concentration polarization can be expressed as equation 22 [1].

\[
\eta_{conc} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_L} \right) \quad (22)
\]

- **Resistance or ohmic polarization \(\eta_\Omega\)**

Ohmic polarization is due to the resistance of the cell materials to the conduction of ions through the electrolyte, and to the conduction of electrons through the electrodes. Contact resistance between the cell components also influences the overall ohmic polarization. The ohmic polarization is governed by Ohm’s law and can be expressed as shown in equation 23 [4].

\[
\eta_\Omega = i.R \quad (23)
\]

where \(R\) is the sum of the area-specific resistances (resistances of a unit area) mentioned above and \(i\) is the current density passing through the cell.

\[
R = R_{ionic} + R_{electronic} + R_{contact} \quad (24)
\]

2.3.3 Fuel utilization or current efficiency

Fuel utilization has to be taken into account because the voltage efficiency must be multiplied by the fuel utilization to obtain the net cell efficiency; as a consequence, fuel utilization directly impacts the efficiency of the system. In existing fuel cell technologies, the fuel is not completely utilized, in contrast with most heat engine systems.
To better understand this point, Bertoldi [6] proposed an example. If a fuel cell operates with pure hydrogen at a given cell potential ($E_{\text{ope}}$), the electrical efficiency ($\varepsilon_{el}$) can be expressed according to equation 25 [4].

$$\varepsilon_{el, \text{LHV}} = \frac{U_f E_{\text{ope}}}{1.25} \quad (25)$$

where the subscript LHV refers to the lower heating value for hydrogen oxidation in standard conditions, $U_f$ is the fuel utilization, and 1.25 is an approximation of the ideal standard potential at 298K for a fuel cell in which $H_2$ and $O_2$ react. A more accurate number is 1.229 volts with liquid water product, or 1.18 volts with gaseous water product. This value is the oxidation potential of $H_2$. The difference between 1.229 volts and 1.18 volts represents the voltage corresponding to the Gibbs free energy change of vaporization of water at standard conditions [4]. Using equation 25, electrical efficiencies of 14%, 28% and 42% are calculated for a fuel cell operating at 0.7 V with a $U_f$ of 25%, 50%, and 75%, respectively.

Fuel utilization ($U_f$) refers to the ratio of the spent fuel flow and the inlet fuel flow, as expressed in equation 26 [7],

$$U_f = 1 - \frac{m_f^{\text{Fo}}}{m_f^{\text{Fi}}} \quad (26)$$

where $m_f^{\text{Fo}}$ is the fuel mass flow at the outlet of the anode and $m_f^{\text{Fi}}$ is the fuel mass flow at the inlet of the anode. Such a definition is most useful when a single fuel species, i.e. hydrogen, is present. In the case of fuel mixtures such as reformate or hydrocarbon fuels that can internally reform to mixtures of hydrogen and carbon monoxide, other definitions of fuel utilization can be used that are based on moles of fuel utilized rather than mass, or more usefully, current produced from the fuel divided by the amount of current that could potentially have been produced from the fuel if all of it had been oxidized. For a single fuel species such as hydrogen, these ratios (mass of fuel, moles of fuel, or electrons released from the fuel) are equivalent, so the definition in equation 26 is used in this thesis. For this work it is assumed that only fuel supply affects the reactant utilization efficiency of the fuel cell, and that oxidant flow is not limited.
2.4 Application fields for SOFCs

2.4.1 Stationary applications

Different applications have been studied as possible fields for SOFCs. Jong-Ho Wee [8] made a broad analysis of the opportunity of different types of fuel cells to have leadership in diverse applications. Stationary applications have been identified as the field in which SOFCs can have the greatest impact. Specifically, distributed generation (DG) seems to be the best target for SOFCs. The high temperatures of operation of the SOFCs allow the use of conventional natural gas (NG) for on-site reforming or direct oxidation and the possibility of combined heat and power generating units. SOFCs can be effectively operated in distributed generation systems. Some examples of this application may be universities, hospitals, breweries, water treatment facilities, communication centers, grid support, and manufacturing [8].

Hybrid systems have been widely studied in order to enhance the efficiency of SOFC systems [9-15]; they can include gas turbines, steam turbines, or a combination of both types of turbines. SOFC hybrid systems have been reported to achieve electrical efficiencies of approximately 70% [8]; they allow the unspent fuel at the exhaust of the fuel cell to be combusted, using it to produce additional electricity through heat engines. It is important to highlight that in the case of large fuel cell power systems with bottoming cycles, low utilizations of fuel by the fuel cell stack can be practical because this condition improves the performance of the cell and produces more accessible heat [4]. However, combustion represents an environmental threat that should not be overlooked.

Atmospheric pollution is a worldwide concern; particulate matter resulting from incomplete hydrocarbon combustion, and nitric oxide (NO) and nitrogen dioxide (NO₂) resulting from oxidation of nitrogen during high-temperature combustion processes with air are recognized as very harmful species for the atmosphere and human health. They are released constantly into the atmosphere by activities involving combustion of fossil and biomass fuels. This alarming reality brings out the need of processing hydrocarbons in a more environmentally responsible way, and SOFCs have been identified as a potential technology to achieve this goal.
2.4.2 SOFC applications for CO₂ capture and sequestration

Concern about CO₂ emissions has motivated a lot of work on solutions, as well as new technologies to solve this environmental problem. Additionally to energy production efficiency improvements, and the implementation of cleaner ways to produce energy, CO₂ capture and storage have also been recognized as necessary. SOFCs are a power generation technology recognized as suitable for CO₂ capture and storage. This capability can be achieved without affecting noticeably the efficiency of the system. One special advantage of the SOFC technology is that the fuel is not combined with the oxidant stream. As a consequence, CO₂ is not diluted with nitrogen [16].

SOFCs with natural gas as a fuel with CO₂ capture were classified into three groups by J.W Dijkstra et al. [16]. The first group consists of pre-fuel cell CO₂ capture, which separates the CO₂ from the main stream of converted syngas before the fuel is delivered to the cell; then the H₂ is fed to the SOFC anode. The second group consists of post-fuel cell CO₂ capture. The post-fuel cell treatment gives a CO₂ stream; the remaining stream consists of H₂ and, depending on the type of treatment, also CO, CO₂, and other components. Finally, in the third group, or post-fuel cell oxidation group, the anode off-gas has a high CO₂ content, but also contains H₂O, CO and H₂. The water can easily be removed by conventional techniques; and there are various options for oxidizing all the H₂ and CO from the SOFC. E.g. oxidizing with pure oxygen; using an oxygen conducting membrane reactor placed after the SOFC, or using multiple SOFC stacks in series.

Using multiple SOFC stacks in series allows the reaching of high fuel utilizations and conversion of almost all the fuel to CO₂ and H₂O. This approach allows an exhaust stream of CO₂ without the need of further treatment. However, extremely high fuel utilization can lead to differences in the flow to the cells within the fuel cell stack, or areas with no fuel at the end of the flow channel, exposing the cell to irreversible damage, as will be discussed later in this work. However, Taniuchi et al. [17] reported a 99.98 % fuel utilization SOFCs/gas turbine combined cycle for CO₂ recovery. They installed high fuel utilization SOFCs stacks in the downstream stages of conventional stacks, as shown in figure 2.
The outlet gas of the initial SOFC stack is partially recirculated, and the remaining fuel is fed to the high fuel utilization SOFC stack. Since the power density drops with the decreasing Nernst potential in the high fuel utilization stack, the average power density is reduced gradually along with the fuel concentration. The high fuel utilization SOFCs are divided into multiple stages (four in the example shown) and the cell voltage is gradually decreased to equalize the current. The voltage, current density, and temperature distribution for a four stage system studied in [17] are shown in figures (3-6). They aimed for nearly 100% reaction of the remaining fuel.

Figure 2. Structural diagram of a normal and high fuel utilization SOFC [17].

Figure 3. Potential, current density, and temperature distributions in the flow direction in a high fuel utilization SOFC (first stage). Reproduced with permission from [17][A].
Figure 4. Potential, current density and temperature distributions in the flow direction in a high fuel utilization SOFC (second stage). Reproduced with permission from [17][A].

Figure 5. Potential, current density and temperature distributions in the flow direction in a high fuel utilization SOFC (third stage). Reproduced with permission from [17][A].
The fuel flowing out of the high fuel utilization SOFCs in [17] was subjected to regenerative heat exchange via an external reformer; H₂O was condensed and separated while compression was applied to obtain liquid CO₂ at concentrations of 99.95%. The exhaust air was subjected to regenerative heat exchange, expanded to atmospheric pressure at the gas turbine (GT), and then was subjected to another regenerative heat exchanger before being exhausted to the atmosphere. This approach increased the overall power generation efficiency by approximately 10% compared to a conventional SOFC/GT cycle where the exhaust fuel is burned and the CO₂ is recovered by an amine process.

It is important to notice from figures 4-6 the high overpotentials and the drops in the power that the cells experience when working at high fuel utilization. It can be emphasized that the average current density decreased from 0.11 to 0.0036 A/cm² and the cell voltage decreases from 0.60 to 0.28 V as the utilization increased across the stages of the system studied in [17].

2.5 Performance with high FU

According to Bertoldi et al. [6] real fuel cell systems should be able to operate at fuel utilizations higher than 75% to guarantee sufficient electrical efficiency. This group also
supports the idea that, if low fuel utilization is used, the unreacted fuel has to be burned in order to increase the efficiency of the system. As discussed above, this procedure decreases the low emission advantage of the fuel cell technology.

If SOFCs could operate at close to 100% fuel utilization, emissions from the combustion process could be eliminated, and the exhaust gases from the complete energy process would be cleaner and even more suitable for carbon sequestration. However, this is an ambitious objective, since operating the cell at too-high fuel utilization conditions causes a number of performance problems. Changes in the concentration of the fuel flow across the flow path are rapidly manifested in the cell open circuit voltage because changes in the partial pressures of reactants directly influence the Nernst potential (equation 11). Moreover, changes in the concentration of the fuel also have an effect on the concentration and activation polarization of the fuel cell. In addition, conditions of high fuel utilization are strongly favourable to the formation of nickel oxide from the nickel typically used in the anodes, which can lead to irreversible damage of the cell.

2.5.1 Impact of fuel utilization on the Nernst Voltage

As the utilization of the fuel rises, the partial pressures of the reactants drop. In other words, the concentrations of the reactants at the exit of the cell are lower than at the entrance. This change in fuel concentration between the inlet and the outlet of the fuel path leads to a Nernst correction that reduces the open circuit voltage locally at the outlet of the cell, often by as much as 250 mV. Since the electrode materials are generally very conductive, the cell voltage cannot be higher than the lowest local potential of the cell; consequently, the cell voltage adjusts to the Nernst potential at the exhaust of the anode and cathode chambers.

S Aruliah et al. [18] observed the influence of fuel utilization on the Nernst voltage of their electrolyte- and cathode-supported cells. They tested various cells for more than 1600 hours and registered a decrease in cell power density when fuel utilization was increased to more than 80%. They attributed the decrease in power density primarily to the decrease in the Nernst voltage from the change in fuel composition because the
internal cell resistance increased only 8% as the fuel utilization was increased from 40% to 80%.

P. Metzger et al. [19] studied the characteristics of a Ni – YSZ SOFC with a measurement system that allowed the local characterization of the cell in 16 different points. The cell was situated in a metallic housing that was subdivided into 16 galvanically isolated segments. The test was performed on electrolyte supported cells (ESC) and anode supported cells (ASC) operating in counter flow conditions of the air and fuel streams, with hydrogen as a fuel in concentrations of 2 to 10% and N₂ as a supplementary gas at the anode. During the tests, current density distribution, voltage drops, temperature distributions, impedance spectra, and gas concentrations were measured at 16 points across the cell.

When the system was operated at H₂ contents above 25%, the power density distribution remained uniform, as shown in figure 7 (a). When higher fuel utilization was applied, significant gradients in the power density were observed, resulting from both the variations in voltage and current density across the cell. At a hydrogen concentration of 10%, the fuel utilization already reached nearly 80% at the fuel outlet. However, the power densities varied only by about 20%. With even lower hydrogen contents, the fuel utilization reached levels of nearly 100% or even above 100%, and power densities varied by approximately 90%. Utilizations above 100% are impossible to achieve, but in this study fuel utilization was calculated from the average current density of the segments, assuming that the gas distribution among the 16 segments was uniform, and that every segment line was fed with the same amount of gas, with an identical residence time. To verify the calculated levels of the fuel utilization, they were compared with the values measured with the gas chromatograph at 2%, 10% and 50% hydrogen content shown in figure 7 (b). The graph exhibits good agreement between the measured and the calculated values.

The differences in power densities are large in the cases with less than 10% hydrogen content. The authors highlighted this result, focusing on segments 8 and 5 at 2% hydrogen content. Segment 8 at the fuel exit only reaches a value of 8.8 mW/cm²,
compared to 87.1 mW/cm$^2$ at segment 5. In contrast, the differences in the power density at hydrogen contents higher than 20% are about 10% or less, and therefore barely evident.

Figure 7. (a) Locally resolved power density distribution (filled bars) and fuel utilization (filled symbols) for different hydrogen concentrations of the electrolyte supported cell (ESC). (b) Comparison of calculated (filled symbols) and measured hydrogen concentration (open symbols) by gas chromatography for a segment row in the ESC. Average cell voltage: 0.6 V, operating temperature: 800°C. Fuel flow: 0.025 standard liters per minute (SLPM)/cm$^2$ H$_2$+N$_2$+3%H$_2$O, oxide gas flow: 0.08 SLPM/cm$^2$ air, 73.96 cm$^2$ active area, fuel is entering from the left side at segment 5.

Reproduced with permission from[19][B].
Figure 8. Voltage distribution in the ESC at different hydrogen concentrations, average cell voltage: 0.6 V, operating temperature: 800 °C, anode gas flow: 0.025 SLPM/cm² H₂+N₂+3%H₂O, cathode gas flow: 0.08 SLPM/cm² air, 73.96 cm²; (a) 2% H₂, (b) 5% H₂, (c) 10% H₂, (d) 20% H₂, (e) 50%H₂, (f) 100% H₂, counter flow. Reproduced with permission from[19][B].
The effect of changing gas concentration along the flow path on the voltage distribution is evident in figure 8. Particularly, figures 8(a) and (f) are contrasting. They correspond to hydrogen levels of 2% and 100%, respectively. At 2% hydrogen content, the cell voltage shows a maximum variation of approximately 0.3 V, with the lowest voltages at the exit being approximately 0.45V and the equilibrium voltage being 0.738V at 800°C.

It is important to highlight these differences in voltage distribution; in the case of high fuel utilization, low voltages are usually associated with relatively high oxygen pressures at the anode. This condition is favourable for the oxidation of the nickel and could be detrimental for the cell.

SOFCs can operate using fuels containing hydrogen, carbon monoxide, and diluents found in a typical coal syngas mixture. Burnette et al. [20] tested electrolyte supported solid oxide fuel cells, with a composite GDC, Ni, and YSZ anode, operating using different fuel flow compositions to determine the changes in power densities. The goal of the study was to determine the changes in SOFC performance when removing a significant portion of hydrogen from a chosen syngas mixture for its use in other fuel cell types that might be favoured in some applications, such as PEM (Polymer Electrolyte Membrane) in transportation applications. Table 1 shows the flow rates used in the experiment. The results showed the expected drop in the theoretical potential due to the reduced hydrogen content of HDS. Even without taking into account activation and concentration losses, there will still be a drop in the performance of the cell when removing hydrogen for other purposes. Figure 9 shows representative characteristic curves for the three fuels tested at 820°C. There is a clear offset in the potentials when fuels are changed.
Table 1. Experiment Flow Rates. Reproduced with permission from[20][C].

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Component</th>
<th>Flow rate (ml/min)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>humidified hydrogen</td>
<td>H₂</td>
<td>351.09</td>
<td>83.8</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>67.87</td>
<td>16.2</td>
</tr>
<tr>
<td>syngas</td>
<td>H₂</td>
<td>139.65</td>
<td>24.9</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>90.86</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>211.44</td>
<td>37.7</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>86.37</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>32.53</td>
<td>6.8</td>
</tr>
<tr>
<td>HDS</td>
<td>H₂</td>
<td>87.16</td>
<td>14.22</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>133.41</td>
<td>18.50</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>263.91</td>
<td>43.06</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>167.81</td>
<td>17.59</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>40.60</td>
<td>6.03</td>
</tr>
</tbody>
</table>

Figure 9. Representative characteristic curves for various fuels at 820°C. Reproduced with permission from[20][C].

In general, high fuel utilization is desired, especially in smaller systems, because the required fuel and oxidant flow is minimized, reducing fuel costs and increasing the efficiency of the system. However, too-high fuel utilization could result in significant voltage drops. As a consequence, the selection of the operating point of fuel utilization is a trade-off between fuel consumption and cell performance.

2.5.2 Impact of fuel utilization on activation losses

As mentioned before, activation voltage losses are no longer negligible for new generation planar SOFCs having temperatures of operation lower than or equal to 800°C. Activation losses in present-day planar cells are comparable to or larger than diffusion and ohmic losses. In the case
of high fuel utilization, activation losses are also affected because reactant concentrations play a role in the kinetics of the reaction; as a consequence, too low concentrations or depletion of fuel considerably increase the activation losses.

A.A. Kulikovsky [21] developed a model for anode performance of a planar SOFC and studied the anode activation polarization, taking into account the hydrogen consumption along the channel. The dependence of the anode activation polarization on hydrogen utilization was studied in the low current and high current regimes. The “low current case” and “high current case” were defined as cell current density being lower than the critical current density (i<ic) and higher than the critical current density (i > ic), respectively; details of how ic was determined are found in [21]. The results of that study showed that increases in the hydrogen fuel utilization shift the polarization curve as a whole over the entire operating current range. Specifically, values above 80 % fuel utilization (U_f) dramatically increased the activation polarization. Figure 10 shows the voltage loss for the (U_f) range in the high current density regime.

![Graph showing voltage loss due to finite hydrogen utilization](image)

**Figure 10. Voltage activation loss due to finite hydrogen utilization in the high current regime.** When utilization is above 80%, the voltage loss dramatically grows. Reproduced with permission from [21][D].

Similarly, Paola Costamagna et al. [22] evaluated a model for a planar circular SOFC stack under conditions of high fuel utilization. In particular, the expression of the anodic polarization as a function of H_2 and H_2O concentration was considered, because of the relevance that it has
for high fuel utilization conditions. In the literature there are various models developed previously for the activation anodic polarization; in their study, Costamagna et al. carefully analyzed contradicting models proposed by Yamamura et al. and Mogensen et al. for the anodic exchange current density term used in the Butler-Volmer equation (specifically the term A used in equation 16). The model proposed by Yamamura et al. supports the expression represented in equation 27,

\[ I_o = \gamma_{anode} \left( \frac{p_{H_2}}{p_{ref}} \right) \left( \frac{p_{H_2O}}{p_{ref}} \right)^{-0.5} e^{-\frac{G_{act,anode}}{RT}} \]  (27)

where \( \gamma \) is a coefficient, \( p \) represents the partial pressure of the gases, \( R \) and \( T \) have their common values, and \( G_{act} \) is the activation energy. In this model the resulting polarization resistance is inversely proportional to the partial pressure of the reactant and directly proportional to the partial pressure of the reaction product raised to the \( \frac{1}{2} \) power. The model proposed by Mogensen et al. is, in the other hand, an example that does not follow the stoichiometry of the electrochemical reaction:

\[ I_o = \gamma_{anode} \left( \frac{p_{H_2}}{p_{ref}} \right) \left( \frac{p_{H_2O}}{p_{ref}} \right) e^{-\frac{G_{act,anode}}{RT}} \]  (28)

The results for the I-V curves are shown in figure 11 for the two model predictions for anodic activation polarization as a function of the fuel gas composition. The curves behave almost linearly up to a fuel utilization of approximately 80%. After 80%, the increases of the slope magnitudes are visible, suggesting an increase in activation and concentration effects on the anode side. The difference between equations 27 and 28 is not relevant at low \( U_f \), but then becomes significant for high \( U_f \) values. However, the trend is similar in both cases, making the qualitative observation still suitable.
Figure 11. Characteristic curves at low and high fuel utilization, calculated on the basis of two alternative models of anodic polarization. Hydrogen inlet flow is the varying parameter. Reproduced with permission from [22][E].

For activation polarization, 80% fuel utilization appears to be a threshold in the behaviour of the cell; based on these studies [21, 22], above that fuel consumption value, the activation losses experience a strong increase.

The activation losses are an important factor to accurately predict the voltage-current relationship in the new generation of SOFCs; the Butler–Volmer equation or an appropriate approximation should be carefully implemented when modeling SOFCs to accurately predict these losses. It is no longer reasonable to neglect or undervalue activation losses when building models for SOFCs operating at temperatures below 800°C [5].

2.5.3 Impact of fuel utilization on the Electrochemical Impedance of the cell

Electrochemical impedance spectroscopy is a useful tool to identify the contribution from a specific physical process to the total cell impedance. However, in some cases it can be ambiguous to prove the connection between physical processes and impedance features [23]. The
impedance of an SOFC includes contributions from various processes and there is some discrepancy in the literature that has led to different interpretations of the impedance related to gas transport phenomena.

Concentration losses were briefly mentioned above as a factor affecting the voltage efficiency of the cell. In SOFCs, gas species must be transported from the gas flow channel through the porous electrode to the triple phase boundary to meet the oxygen ions. The transport of species must be consistent with the net current flowing through the cell adjusted for the charge and mass balance at steady state condition. Products formed should be transported away from the reaction sites to the fuel stream. The physical ‘resistance’ to the transport of gaseous species is reflected as an electrical voltage loss [18] and it is commonly referred to as gas transport loss. Voltage losses caused by gas transport depend on various parameters, including the anode microstructure and thickness, the test set-up geometry, and the gas flow rate. Additionally, with the consumption of the fuel along the flow channel, the downstream part of the cell is notably influenced by lower fuel concentrations [24].

The spectra of an SOFC were analyzed by M. Mogensen et al. [25]. Three arcs corresponding to the anode impedance were reported: (i) a high-frequency arc that was attributed to charge transfer between YSZ and Ni and diffusion of charged species to the triple phase boundary, (ii) a mid-frequency arc that was attributed to gas diffusion, and (iii) a low-frequency arc related to gas conversion. The latter impedance is exclusively significant in conditions of high fuel utilization.

When conditions allow both gas diffusion impedance and gas conversion impedance to show in the impedance spectra (usually at high fuel utilizations and when testing is done with a reference electrode in a different atmosphere than the anode), the gas diffusion impedance appears as an intermediate frequency feature. Gas diffusion impedance is mainly affected by cermet thickness and microstructural properties [23]. Consequently, it practically vanishes when ideal porous transport is present.

The gas conversion impedance has been described by M. Mogensen et al. [26] as a process with a high time constant related to a variation in Nernst potential vs. a stable reference electrode, caused by the passage of current at a finite fuel flow rate. Consequently, this contribution is only
observed when characterizing anodes in cells with a reference electrode in another well-buffered (high partial pressure of oxygen) atmosphere. In other words, the gas conversion impedance is caused by the weak convection transport in the gas flow channel, and has no relation to the anode performance itself, but it is a function of the setup geometry and the gas flow rate [27].

Gas conversion impedance is especially significant in conditions of high fuel utilization because changes in concentrations along the gas flow channel are relevant. The fuel is consumed almost completely along the flow channel. As a consequence, the part of the cell that is closest to the exhaust experiences extremely low concentrations or even depletion of the fuel, impacting drastically on the impedance in question.

The term gas conversion impedance was first introduced by Primdahl and Mogensen, who aimed in their study [27] to draw attention to the presence of the gas conversion impedance, quantify its nature, and highlight how it is dependent on the measurement set-up. In order to achieve these objectives, they designed an experiment with two different test set-ups. The first setup, shown in figure 12, includes a 3 electrode set-up and provides a reference atmosphere and a sealed cylindrical anode compartment for exposing the anode to a reducing fuel gas. The reference electrode works as a cathode and it is placed in air (reference gas). The second setup is shown in figure 13 and it is a symmetric cell with two identical anodes on each side, in 1 atmosphere. Gas flow rates in the range of 10 to 200 SCCM were applied and impedance spectroscopy was conducted. The results showed that the impedance spectrum of the 2 atmosphere setup contains one more arc than the spectrum of the 1 atmosphere setup, as shown in figure 14.
To further explain this difference, they represented this extra arc with an equivalent circuit. They found that this extra arc, located at low frequencies, had a dependence on gas flow rates. Varying the molar fraction of water, $X_{H_2O}$, at a constant flow rate, with $X_H$ values of 0.5 or 0.97 to 1.00 (the balance being nitrogen), revealed a significant variation in the low frequency arc. The parameters $R$ (resistance) and $C$ (capacitance) corresponding to this arc varied as a function of $X_{H_2O}$. In particular, $C$ appeared very high at high water contents. It was assumed that this bulk process could be gas conversion in the volume over the anode. To further examine this assumption, a continuously stirred tank reactor (CSTR) model was proposed, and the gas conversion impedance was derived quantitatively for small AC perturbations and for steady-state
DC conditions. With this model, the predictions of the measurable parameters R and C in a set-up were compared to the actual measurements and showed good agreement over the investigated range.

Figure 14. Impedance spectra obtained on nominally identical anodes in a 1 atmosphere setup (Δ) and in a 2 atmosphere setup (○). Measurements in 97% H₂ + 3% H₂O at 1000°C at OCV. The spectra are corrected for anode area and series resistance for presentation purpose. Nine impedance points per frequency decade. Reproduced with permission from [27][F].

The evaluation concluded that gas conversion impedance was an effect of the passage of current in an electrode in a finite flow rate and it is not detectable when the reference electrode is positioned in the same gas as the tested electrode.

Similarly, Bin Liu et al. [24] analysed the impedance spectra of a cell measured under different cathode and anode flow rates at 900°C, shown in figures 15 and 16, respectively. When increasing the cathode flow rate, the low frequency arc at ~0.016 Hz shrinks and its peak frequency shifts to the higher frequency. This lower frequency arc is incorporated into the higher-frequency impedance arc at ~0.63 Hz and finally disappears as the cathode gas flow rate exceeds 321 mL/min. When the anode flow rate is increased, the low frequency arc at ~0.025 Hz gradually decreases and then reaches a constant value as the anode gas flow rate exceeds 290.3 mL/min. Bin Liu et al. [24] came to the conclusion that both insufficient anode and cathode gas flow rates can result in gas conversion impedance. They also observed that gas conversion
impedance appears at frequencies of less than 0.1 Hz, and its magnitude strongly depends on the gas flow rates and could be effectively suppressed by increasing them.

Figure 15. Impedance spectra measured under different cathode gas flow rates at 900°C. The anode gas flow rate is kept at 435 mL/min. Reproduced with permission from [24][G].

Figure 16. Impedance spectra measured under different anode gas flow rates at 900°C. The cathode gas flow rate is kept at 1268 mL/min. Reproduced with permission from [24][G].

Tohru Kato et al. have also studied the gas conversion impedance extensively [28 - 30]. They carried out measurements [29] of the cell impedance under conditions of high fuel utilization and
varied gas flow rate. Figure 17 shows the impedance spectra measured while changing the load current at the standard flow rate and figure 18 shows the cell impedance measured while changing the flow rates at the standard load current.

![Impedance spectra at a fixed flow rate (H₂: 170 ml/min) at 1018K with the fuel utilization parameter (load current): (a) 4.1% (1.0 A); (b) 23.3% (5.67 A); (c) 46.5% (11.35 A); (d) 69.8% (17.0 A); (e) 80.0% (19.5 A). Symbols indicate experimental and (—) fitting results. Reproduced with permission from [29][H].]

The presence of a large semi-circle corresponding to the low frequency range (between 0.13 and 0.4 Hz) that changes with fuel utilization and flow rates can be observed. The low frequency semi-circle increases with the increase of fuel utilization and with the reduction of H₂ flow rate, as expected. This impedance feature is dominant under high utilization power generation conditions and shows agreement with their simulation. The high and intermediate frequency semi-circles, which they suggest represent the electrode reaction and the finite-length diffusion, respectively, were relatively small compared with the gas conversion impedance. Unfortunately, they did not have any reasonable explanation for the change in the ohmic resistance throughout their measurements. According to the simulation, the resistance at a sufficiently high frequency was not supposed to be affected by the current distribution or by the fuel utilization. One potentially explanation may be partial oxidation of the nickel in the anode, as discussed in the following section.
Figure 18. Impedance spectra at a fixed load current (17.0 A) at 1018K with the parameter of H₂ flow rate: (a) 170 ml/min; (b) 235 ml/min; (c) 395 ml/min. Symbols indicate experimental and (—) fitting. Reproduced with permission from [29][H].

As observed above, the gas conversion impedance can be the dominant contribution to the spectra in cases where changes in gas concentrations are significant.

### 2.5.4 High fuel utilization and anode oxidation

High fuel utilization conditions result in a high concentration of steam in the anode, especially near the exhaust of the cell; this circumstance favours the oxidation of the anode, causing degradation problems. The fuel utilization is commonly chosen at 85% with Ni-cermet anodes; a higher fuel utilization would result in significant formation of nickel oxide, which decreases the catalytic activity for the hydrogen oxidation.

Anode oxidation is an issue that emerges from conditions of high fuel utilization, especially when metals, such as nickel, are present. Ni-YSZ anodes are vulnerable to oxidation in the anode atmosphere when an excess of steam and depletion of fuel is present.

Ni/YSZ is the state of the art material used for SOFC anodes. Nickel is an electronic conductor and has good catalytic activity for both steam reforming of methane and for the direct oxidation of hydrogen and of hydrocarbons. The YSZ functions as an ionic conductor for the electrode, provides good thermal expansion match with the electrolyte, and suppresses sintering of nickel
[31]. But, on the flip side, Ni-YSZ anodes suffer degradation when they are exposed to reduction and oxidation cycles. Even though NiO can be reduced back to Ni, redox cycling causes irreversible structural changes in the anode that lead to mechanical damage and even complete failure [32].

Anode microstructure changes upon reduction and oxidation were studied by Jurgen Malzbender et al. [33]. Figures 19 a-c show micrographs taken before reduction and after re-oxidation of the anode. Ni/NiO particles are the dark ones in these figures, and the light matrix is YSZ. Shrinkage in the material can be observed when NiO particles are converted to Ni. After re-oxidation, the anode structure is different compared to the structure prior to oxidation; particles have more porosity compared with the initial anode, and there is an increase in the total volume. The increase in volume is between 3 and 9% [34]. These changes have been attributed to sintering of nickel particles and redistribution of the Ni metal phase [35], and they lead to compressive stresses in the anode and tensile stresses in the electrolyte.

In general, the electrolyte can experience small and large cracks (as shown in figure 20), and the cell can experience bending and warping [33].

![Fracture cross-section of half cell. Same cell location with a) oxidised, b) reduced, and c) re-oxidised anode. Reproduced with permission from [33][I].](image-url)
Figure 20. Microstructure changes and cracks in the electrolyte. a) Initial co-fired state b) reduced C) re-oxidized d) re-reduced and e) re-reoxidized. Reproduced with permission from [32][J].

Effects of redox cycling on SOFC performance

Performance changes of the SOFC after its exposure to redox cycling can be visible in the open circuit voltage (OCV), polarization resistance, and ohmic resistance behaviour.

Waldbillig et al. [36] observed a slightly decreased OCV after long redox cycles (4 and 6 h). They suggested that this result was indicative of some electrolyte fracture or to the loss of electrical conductivity, e.g. disconnection between Ni/NiO particles. Also supporting this idea, M. Cassidy et al. [34] observed in their study that the OCV before shut down of the anode was much higher than after it was allowed to re-oxidize.

Polarization of the cell is also affected by redox cycling; this change was measured by D. Fouquet et al. [35] by impedance spectroscopy. An increase in the polarization resistance of approximately 18% was reported after the third redox cycle. They suggested that this change can be attributed to the formation of cracks within the bulk sample, which disrupt current paths and reduce the active TBP length.

Similarly, Bin Liu et al. [37] monitored the ohmic resistance in redox conditions using EIS and measured the OCV of cells tested. The ohmic resistance curves showed that anode re-oxidation could be largely divided into three stages: one stage in which the ohmic resistance increases very slowly, the second stage in which a sharp increase of ohmic resistance occurs, and the last stage
in which the ohmic resistance slightly decreases with the oxidation process. They explain these results by suggesting that in the first stage, oxidation may have started to occur, but still without impact on the Ni-Ni electronic conduction network; in the second stage, the nickel electrical conduction network is completely destroyed, and in the final stage, they suggest formation of a new conduction network from interconnections of NiO particles. Another possible justification of the decrease of ohmic resistance mentioned by Bin Liu et al. could be the deposition of highly conductive materials such as silver on some cracks formed in the YSZ film (they used silver mesh current collectors).

The redox problem can be affected by factors such as the temperature at which oxidation happens and microstructure. Taking these factors into account can help in solving or lessening the redox issue. Modification of the microstructure is one of the approaches that can help improve the redox stability. There are some contradicting opinions on this topic: Malzbender et al. [32] suggested that higher porosity should be beneficial for redox tolerance of substrate and anode. On the other hand, Fouquet et al. [35] found that initially smaller NiO particles and a finer microstructure were advantageous for redox stability. Finally, D. Waldbilling et al. [38] supported the Malzbender et al. [32] opinion, and found that a coarser structure was stable, while a finer structure tended to crack. They suggested that this observation was indicative that a coarser structure does not experience noticeable volume changes. The reason may be that the coarser structure has sufficient porosity to absorb the volume change upon oxidation, in contrast to the finest structure, which shows significant volume changes [38]. Variations in the microstructure have been investigated by several different groups [39, 40]; even though this solution does not solve the problem completely, it can be a partial solution to the redox problem.

Temperature also has a strong influence on the redox cycling behaviour. Tests of electrochemical performance showed that redox cycling at lower temperatures (650°C) causes less damage to the cell than redox cycling at high temperatures (850°C). Higher temperatures allow higher oxidation rates, and causes larger volume expansions that lead to severe damage [32]. This result is particularly relevant in the case of anode supported cells, which are able to operate at lower temperatures.
Nickel diffusion through the growing nickel oxide layer appears to be the rate determining step for re-oxidation in the porous Ni/YSZ, according to Bin Liu et al. [37]. Since diffusion is temperature dependent, lower temperatures slow the oxidation of Ni. Based on the temperature influence on the redox rate, Vedasri et al. [41] suggested, for cells containing thick anode layers (1.1 mm), cooling down the system during air exposure. The cooling rate should be rapid enough to ensure that the Ni particles near the AFL and the electrolyte are not fully oxidized (3°C/min), while also being sufficiently slow to avoid damage from thermal shock.

Pedro Nehter [42] presented a high fuel utilization SOFC cycle model with special focus on the formation of NiO, system efficiency, and required cell area. That study included a system with high efficiency and high fuel utilization, focusing on the avoidance of formation of nickel oxide and determination of the required cell area at a fixed system power of 1 MW. Simulation models including the SOFC, methane reformer, and other system components were developed. The cycle operates a secondary SOFC stack to further utilize the residual fuel from the core SOFC stack. This approach was possible because the exhaust from the first stack was condensed to decrease the water fraction. A system efficiency of 60% and a fuel utilization of 97% were simulated.

That study considered that the oxidation of nickel could occur due to the reaction with H₂O and CO. They suggested that if the oxidation of hydrogen and carbon monoxide reach the equilibrium condition, the oxygen activity can be calculated by one of those reactions. Additionally, it was assumed that at OCV, conditions for the formation of NiO can be estimated by the equilibrium activity of the oxygen resulting from the H₂O-H₂ ratio of the gaseous phase. The formation of nickel oxide was estimated by comparing the anodic potential with the oxygen activity governed by equilibrium of the Ni-NiO system. To avoid the formation of nickel oxide at electrochemical equilibrium conditions, it was assumed that the oxygen activity given by the hydrogen oxidation had to be lower than the oxygen activity of the nickel oxidation. The equilibrium oxygen activities for both reactions were calculated by empirical equations detailed in [42].

Figure 21 shows a tendency for the nickel oxidation in the grey area, the potential equivalent of the hydrogen oxidation as the dashed lines, and the anode potential as the full lines, as a function of temperature and $pH_2/pH_2O$ ratio. The formation of nickel oxide thermodynamically occurs at
oxygen pressures higher than $5.9 \times 10^{-11}$ bar (1000°C). This partial pressure is equal to an anode potential of $-603$ mV versus air (1 bar, 1000°C). The anode potential is chosen lower than $-800$ mV in the Neher study [42] to avoid nickel oxide formation. This value is reached at a $pH_2/pH_2O$ ratio of 0.15 (fuel utilization = 85%) and at a temperature of 1000°C. This is particularly important at the gas outlet of the anode, where high fuel utilizations lead to high partial pressures of steam. The influence of the activation and diffusion overpotential on the anode potential is comparably small in this range of temperature and fuel utilization. The activation overpotential increases with lower temperatures and the diffusion overpotential increases mainly with lower $pH_2/pH_2O$ ratios.

![Figure 21. Anode potential (H₂–H₂O) vs. air (1 bar). Reproduced with permission from [42][K].](image)

In the study in [42], the anodes of a second SOFC stack were supplied by the anode exhaust of the first SOFC stack after it passed through a regenerative heat exchanger and a condenser where its $pH_2/pH_2O$ ratio was increased to 0.46, allowing further fuel utilization without the formation of nickel oxide. The overall fuel utilization was thus increased to 97%. An additional advantage of this configuration is that the final exhaust stream has a CO₂ mass fraction of 92%, which could be interesting for CO₂ sequestration applications.
Redox cycling is an issue that has a significant effect on the cell performance and lifetime, and remains as one of the key challenges for commercialization of SOFCs. In order to alleviate this problem, the use of metal in the anode could be reduced, and investigations of new materials for substituting Ni-YSZ anodes should continue. Redox stability is a desired attribute of an anode material in order to permit conditions of high fuel utilization, which may be linked to high oxygen concentrations, without irreversible loss of structural coherence and electrochemical functionality [16].

2.6 Alternative anode materials

Additionally to the discussed disadvantages of the state of the art Ni-YSZ anodes under high fuel utilization conditions, the low tolerance of Ni-YSZ anodes for carbon deposition and their susceptibility to poisoning by sulfur contents as low as 2ppm H$_2$S at 1273 K [31,43] have motivated extended research on alternative anode materials due to the increasing interest in the direct use of available hydrocarbons as fuels.

Different types of oxides have been investigated as potential alternative anode materials. Since Ni is an excellent catalyst for both direct oxidation and steam reforming of hydrocarbons, it has been a challenging assignment to find a competitive alternative material. Tolerance to carbon deposition, sulfur poisoning, and high fuel utilization conditions are desired. To the present, only a few reports have presented alternative materials that meet all the requirements of an anode electrode, and further research is under development to optimize these materials and to better understand their behaviour under long term operation.

A variety of oxides are under investigation, as single phase anodes or composites, to better meet the requirements of good ionic and electronic conductivity. In the context of direct utilization of available hydrocarbon fuels by SOFCs, materials with mixed ionic and electronic conductivity may be preferred. The mixed conductivity extends the active zones where electrochemical reactions can occur to any position of interfaces between the mixed conducting material and the gas phase [31].

The materials of most interest have been doped and undoped ceria, transition metal perovskites, fluorite related structures, and tungsten bronze anode materials [31, 44]. Among them,
Perovskites have attracted considerable interest. The perovskite-type oxide has the general formula ABO$_3$, in which A and B are cations with a total charge of +6. The A cations (such as La, Sr, Ca, and Pb) are large and reside on the larger spaces in the 12-fold oxygen coordinated sites. The B cations (such as Ti, Cr, Ni, Fe, Co, and Zr) occupy the smaller octahedral sites (six-fold coordination). Full or partial substitution of the A or B cations with cations of different valence is possible. When the overall valence of the A-site and B-site cations adds up to less than 6, the missing charge is made up by introducing vacancies in the oxygen sub-lattice \cite{31, 45}. Different combinations present the possibility of enhancing the performance using cations of complementary functionality, and could increase the electrical conductivity of the perovskites.

Shanwen Tao et al. \cite{46} found that perovskite structures with two different B-site ions, based on Cr and one or more other transition elements, forming compositions such as (La,Sr)Cr$_{1-x}$M$_x$O$_{3.5}$ (where M could be elements such as Mn, Fe, V, Co or Cu) \cite{47} have good redox resistance and can achieve very good performance, overcoming the restrictions of current Ni-YSZ anode materials.

(La$_{0.75}$Sr$_{0.25}$)Cr$_{0.5}$Mn$_{0.5}$O$_3$ was demonstrated to be an efficient redox stable anode and cathode by Bastidas et al. \cite{48}. They tested a symmetrical cell using LSCM electrodes both anode and cathode sides of a 200 µm thick YSZ electrolyte. The cell performance at 900°C with wet H$_2$ showed a maximum power density of 300 mW/cm$^2$. With methane as fuel, a maximum power density of 230 mW/cm$^2$ was achieved. This approach can reduce costs in terms of simplifying the manufacturing process, since both electrodes involve the same materials. Even though LSCM performance is still lower than the performance obtained with Ni-YSZ cermets (at least 1.4 W/cm$^2$ at 750°C has been reported with Ni-YSZ cermets working with wet H$_2$ \cite{49}), the fact that LSCM is a stable anode material under redox conditions makes this material a prospective solution to the redox problem.

Strontium titanates (SrTiO$_3$) are highly attractive because of their desirable thermal and chemical stability and MIEC behaviour at low oxygen partial pressures. Materials based on SrTiO$_3$ have been investigated extensively by A-site or B-site doping as SOFC anode materials, with an emphasis on the electrical properties \cite{50}. Marina et al. \cite{51} studied the properties of La$_x$Sr$_{1-x}$TiO$_3$ where x=0.1, 0.2, 0.3, 0.35, and 0.4, in relation to their potential use as SOFC
anode materials, with an emphasis on the redox cycling of these compositions. The initial electrical conductivity of La$_x$Sr$_{1-x}$TiO$_3$ was found to be strongly dependent on the partial pressure of oxygen ($pO_2$) during sample sintering. The samples sintered in air exhibited an electrical conductivity in the range of 1 to 16 S/cm, and the samples sintered in hydrogen showed conductivities of 80 – 360 S/cm under experimental conditions typical for SOFC anode operation. While the electrical conductivity of the samples sintered in air was completely reversible after redox cycling at 1000 °C, that of the specimens sintered in hydrogen decreased irreversibly after the oxidation to values similar to the samples sintered in air. After further redox cycles, the values of the conductivity of the samples sintered in hydrogen dropped to values even lower than those of the samples sintered in air. It is believed that the cause of this effect was microcracks found after cooling and inspection. The oxidation kinetics of LST were reported to be slow. Moreover, LST sintered on YSZ was found to be dimensionally and chemically stable when subjected to redox cycling [51].

Moreover, the electrocatalytic properties of LST anodes were studied on YSZ electrolyte supported cells containing a lanthanum strontium manganite (LSM) cathode. Typical I-V curves and power densities obtained are shown in figures 22 and 23. The initial performance with a La$_{0.4}$Sr$_{0.6}$TiO$_3$ anode was fairly good, and 340 mA/cm$^2$ was drawn from the cell. However, the performance rapidly degraded over the test period. After 1 hour, the performance decreased severely. Figure 23 shows the comparison with a standard 40 mol % Ni – 60 mol % YSZ anode. Similar behaviours were observed with all of the compositions fabricated [51]. The decrease in the activation energy and the increase in the conductivity at lower $pO_2$ for most of the cases and compositions of LST studied could be explained by Ti$^{4+}$ being reduced to Ti$^{3+}$. The more reducing the conditions, the more Ti$^{3+}$ is present in the sample, which leads to an enhancement of the electronic conductivity, as explained by Canales-Vazquez et al. [52].
Figure 22. I-V curves of a cell with a La$_{0.35}$Sr$_{0.65}$TiO$_3$ anode obtained in 97% H$_2$+3% H$_2$O at 990 °C before and after a full redox cycle. Reproduced with permission from [51][L].

![I-V curves of a cell with a La$_{0.35}$Sr$_{0.65}$TiO$_3$ anode](image)

Figure 23. Initial (1) and steady state (2, 3) performances of cells with 160 µm YSZ electrolytes, LSM cathodes, and La$_{0.4}$Sr$_{0.6}$TiO$_3$ (1, 2) or Ni–YSZ (3) anodes. T = 1000 °C. Fuel gas was 97% H$_2$+3%H$_2$O, air was on the cathode side. Flow rates were 200 cm$^3$/min. Reproduced with permission from [51][L].

![Initial (1) and steady state (2, 3) performances of cells](image)

Similarly, Hashimoto et al. [53] studied the electrical properties of Sr$_{1-x}$La$_x$TiO$_{3+\delta}$ prepared in air, focusing on the compositions where x=0.1 and 0.3. The values of the conductivity under different partial pressures of oxygen and temperatures are shown in figure 24. They found that the conductivity of the x=0.1 solid solution was strongly dependent on the pO$_2$ and temperature,
while the x=0.3 solid solution showed a very low dependence of the conductivity on temperature and pO₂. Their hypothesis to explain this observation is the possibility of point defect clustering and/or Ruddlesden–Popper phase formation in highly La-doped SrTiO₃ specimens that blocked the rapid diffusion of oxygen and the electronic conduction between titanium ions.

Canales-Vazquez et al. [52] performed electrical characterization and initial cell tests of the n=6 member (La₂Sr₄Ti₆O₁₉₋₅) of the La₂Srₙ₋₂TiₙO₃n₋₅ family. A pronounced dependence of the conductivity on the oxygen partial pressure was found. The activation energy calculated from the corresponding Arrhenius plots (shown in figure 25) revealed the same tendency, and it decreased as the pO₂ decreased, from 1.3eV for the sample measured in air to 0.3 eV for the sample measured in dry argon. In that study, a metallic behaviour was found, with conductivity dropping at higher temperatures, presenting a discrepancy with the previous studies mentioned, where semiconducting behaviour was observed. It is believed by the authors that this discrepancy is the consequence of using longer times under reducing atmospheres in their study. The polarization resistance and fuel cell performance are shown in figures 26 and 27. The Rₚ decreased with increasing temperature, and it was also sensitive to hydrogen concentration. A polarization resistance of 2.97 Ω.cm² was obtained at 900 °C in wet H₂. The polarization resistance in wet CH₄ was almost 3 times higher than in wet H₂, suggesting that this composition of LST by itself is not a suitable anode material for direct methane cells. The fuel cell performance with an LSM cathode was limited by the anode polarization, and a maximum power density of 76 mW/cm² was obtained in wet H₂ at a potential of 0.47 V. Possibly with modifications of the composition of the anode to include a better ionic conductor material and improvements in the microstructure, LST can be a potential anode material for SOFCs.
Figure 24. Conductivities of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3 \pm \delta$ sintered in air: (a) $x = 0.1$ and (b) $x = 0.3$; $9\%$ \(\text{H}_2/\text{N}_2\): \(\text{PO}_2 = 10^{-13}\) Pa at 1273 K. Reproduced with permission from [53][M].

Figure 25. Arrhenius plots for $\text{La}_2\text{Sr}_4\text{Ti}_6\text{O}_{19.8}$ in air, wet Ar, and dry Ar. Reproduced with permission from [52][N].
Figure 26. Impedance measurements obtained at OCV and 850 °C in 4.9% H₂ + 2.3% H₂O + 92.8% Ar (∇), at 900 °C in 97% CH₄ + 3% H₂O (□), 4.9% H₂ + 2.3% H₂O + 92.8% Ar (O) and 97% H₂ + 3% H₂O (Δ), respectively. Rp = 8.93 Ω.cm² (CH₄), 4.56 Ω.cm² (5% H₂), 2.97 Ω.cm² (H₂) at 900 °C, 6.59 Ω.cm² (5% H₂) at 850 °C. Reproduced with permission from [52][N].

Figure 27. Fuel cell performance using La₂Sr₄Ti₆O₁₉₋₄ as anode and La₀.8Sr₀.2MnO₃ as cathode. (a) 97% H₂ + 3% H₂O at 850 °C; (b) 97% H₂ + 3% H₂O at 900 °C and (c) 97% CH₄ + 3% H₂O at 900 °C. Note: current densities at 600 mV are 75, 119, 30 mA/cm² for (a), (b) and (c), respectively. Maximum power densities are 50 mW/cm² at 0.45 V, 76 mW/cm² at 0.47 V, and 21 mW/cm² at 0.45V for (a), (b) and (c), respectively. Reproduced with permission from [52][N].
Vincent et al. [54] studied the performance of LST as an anode with different levels of barium doping (La_{0.4}Sr_{0.6-x}Ba_{x}TiO_3, where 0\leq x\leq 0.2). Partial substitution of Sr by Ba in LST to form LSBT did not appear to affect the chemical stability, except that reduction of LST was more dependent on temperature than in LSBT. In pure dry H_2 at 900°C, Ba doping remarkably increased the performance of the cell; however, a negative effect was observed at lower temperatures (results shown in figure 28 A). In the presence of dry methane, the performances of all of the compositions were very poor. As a consequence, it is difficult to determine if there was a relevant difference in the performance with the presence of Ba doping (figure 28 B). In the presence of dry methane with 5000 ppm of hydrogen sulfide, the maximum power density increased to values approximately 20 times higher than when the fuel was pure CH_4 (figure 28 C). These results remained unexplained. The presence of Ba doping in the case of CH_4 and H_2S enhanced the performance in some compositions and decreased it in others. In the presence of dry hydrogen and 5000 ppm of hydrogen sulfide, the performance was also enhanced, and the dependence on the temperature was more significant than for CH_4 and H_2S (figure 28 D). LST and LSBT were found to be active for conversion of H_2 and CH_4, and when 0.5% H_2S was added, the performance increased significantly. However, the influence of Ba did not have a consistent trend.

**Figure 28.** Maximum power densities obtained as a function of anode feed: a, H_2; b, CH_4; c, CH_4 + 0.5% H_2S; d, H_2 + 0.5% H_2S. Reproduced with permission from [54][O].
Danilovic et al. [55] studied the performance of a series of perovskites having the chemical formula La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$X$_{0.5}$O$_{3-\delta}$ (where X=Ti, Mn, Fe, or Co, and occupies the B site), as SOFC anodes. The study focused on the conversion of H$_2$, CH$_4$, and CH$_4$/0.5% H$_2$S. All the compositions were sufficiently conductive for the anode requirements. Results are shown in figure 29. However, LSCCo was not stable under reducing conditions, and there was a large thermal expansion mismatch with the YSZ electrolyte. The addition of ionic phase Ce$_{0.9}$Gd$_{0.1}$O$_2$ (GDC) enhanced the performance of all the compositions compared to the corresponding LSCX alone and stabilized LSCCo sufficiently to enable its use as anode catalyst. In general, the fuel cell performance using each of the LSCX materials was highest using H$_2$ fuel and lower using CH$_4$. When the fuel was 0.5% H$_2$S/CH$_4$, the performance was considerably greater than that in CH$_4$ alone, and close to that when using H$_2$. The authors suspect that the addition of H$_2$S changed either or both of the reaction mechanisms and the surface state. Figure 30 shows a summary of the performance of the different compositions at 850°C. The highest performance obtained was 250 mW/cm$^2$ using a fuel cell with the configuration LSCFe-GDC/YSZ (0.3mm)/Pt at 850°C.

![Figure 29. Conductivity comparison for (a) LSCTi, (b) LSCMn, (c) LSCFe, and (d) LSCCo in air (solid symbols) and humidified 5% H$_2$ (open symbols). Reproduced with permission from [55][P].](image-url)
Figure 30. Summary of influence of GDC on performances at 850°C. Reproduced with permission from [55][P].

LSFCr perovkite has been of great interest recently due to its good performance as an SOFC anode catalyst [55-60]. Haag et al. [60] tested the oxide composition LaSr$_2$Fe$_2$CrO$_{9.8}$ (LSFC) and Gd$_{0.1}$Ce$_{0.9}$O$_{2-δ}$ (GDC) on a La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-δ}$ (LSGM) GDC electrolyte. GDC was included in the anode to provide high ionic conductive pathways in the anode. Figure 31 (a) and (b) shows the performance. This result demonstrates that the composite LSFCr-GDC is a promising SOFC anode. Power densities of 300-360 mW/cm$^2$ and anode polarization resistances of 0.2-0.25 Ω.cm$^2$ were measured at 750-800 °C. Additional work needs to be done to determine the fuel flexibility of this anode and the optimal composition by varying the LSFeCr:GDC ratio.

Key progress in anode development for SOFCs has been achieved in the last decade. The crucial characteristics of the next generation of anodes include redox stability and carbon tolerance for enhanced stability under operation with hydrocarbon fuels. Generally, different requirements are met by different materials and compositions. As a result, more work needs to be done in order to identify optimal combinations with complementary functionalities, and there is also a need to evaluate the long term performance of these new generation anodes.
2.7 Processing techniques

Fabrication techniques depend greatly on SOFC designs and applications. Feasibility, costs, repeatability, and the possibility of mass production are usually factors to consider in the selection of a manufacturing process. In this section, traditional SOFC production methods and plasma spray manufacturing processes are reviewed.

2.7.1 Traditional SOFC production methods

Fabrication techniques for SOFC components depend on the cell design. The selection criteria should consider cost, viability for mass production and automation, repeatability, and precision [4,7]. The traditional wet ceramic methods of SOFC fabrication use well established
manufacturing techniques that require between 1 and 4 firing steps, each taking approximately 24 hours to complete at temperatures of up to 1400°C [61]. Such high temperature conditions limit the rates of production. Additionally, with these traditional methods, the different components of the SOFC should be chemically stable at the fabrication temperatures, limiting the possibility of using some high performing materials that are not compatible at these temperatures with the rest of the components.

In the case of planar SOFC architecture, anode supports are widely used because they improve the electrical performance of the cell in comparison with the electrolyte supported architecture. The commonly used technique for fabricating an anode substrate is tape casting. In a typical tape casting process, a slurry is poured into a reservoir behind a doctor blade, and the carrier to be cast upon is set in motion, as shown in figure 32. The wet film of slip passes into a drying chamber, and the solvents are evaporated from the surface, leaving a dry tape on the carrier surface. The slurry or slip is typically prepared by dispersing the anode material (a mixture of YSZ and NiO) in solvents, binders, plasticizers, and wetting agents. The in situ reduction of NiO to Ni adds desired porosity for anode gas diffusion. A green (un-fired) electrolyte substrate can also be made by tape casting followed by sintering at high temperature into a dense ceramic [62].

The mechanical support of the cell usually ranges between 100μm and 1 mm. In the case of electrolyte-supported cells or anode-supported cells, the fabrication of the thin electrodes is dominated by screen printing, with thicknesses between 40 and 60 μm.

Figure 32. Schematic of tape-casting process. Redrawn from[62].
In screen printing, the formulation of the ink, the printing material, is analogous to that of the tape casting slip. The technique uses a mesh to support an ink blocking guide. The attached guide forms open areas of mesh that transfer the ink that is pressed through the mesh as an image onto a substrate. It is a fairly simple method for depositing a layer of ceramic slurry; screen printing steps are typically followed by sintering steps to consolidate the deposited slurry layer. Electrolytes are typically fired at high temperatures of approximately 1400°C, while screen-printed electrodes are fired at temperatures ranging from 900°C to 1200°C [62].

2.7.2 Plasma spraying technology

While SOFC technology has significant potential, there are barriers preventing its widespread adoption and commercialization at the present. One main concern is the economics of existing manufacturing techniques at early scale production due to the multiple fabrication steps for each of the cell layers, and the compatibility of high temperature firing steps with low-cost metallic support structures [63].

Plasma spraying is a well-established manufacturing technique commonly used in the aerospace and power-generation industries for thermal barrier coatings of gas turbine blades, vanes, combustor cans, and turbine shrouds. The plasma spray process features injection of coating materials (such as metals, ceramics and polymers) into a high velocity ionized gas stream (plasma). During the very short residence time the material is melted and propelled towards a substrate, where it solidifies and builds up a solid coating [62]. The materials are deposited in a molten or semi-molten state, and the plasma may reach temperatures above 10000 K [61]. The two principal variations of plasma spraying atmospheres are air plasma spraying and vacuum plasma spraying, where air and vacuum refer to the conditions under which the process is carried out. There are several plasma spray parameters that have an effect on the quality and properties of the coatings produced. The most relevant include electrode current, plasma gas flow rate, plasma gas composition, feedstock flow rate, feedstock size distribution, and standoff distance [63].

Plasma spray processing has been identified as having the potential to overcome some of the limitations of conventional manufacturing processes for fabrication of SOFCs, especially due to
the high speed of the process and the possibility of eliminating the need for sintering [63]. One of the most important drivers to develop PS SOFCs is to increase cell production rates and manufacturability. The current state of the art wet ceramic processing method may have up to 10 separate unit operations, involving a number of different pieces of equipment, which is likely to make automation difficult and to be costly [61]. The use of plasma spray processing also opens the possibility of supporting the cell mechanically on a metal substrate (for example, stainless steel). Metallic substrates can potentially reduce costs further by enabling the use of thinner active layers. Additionally, metal supports are more robust and can be more rapidly thermally cycled to the cell operating temperature than cermet or ceramic support layers [63].

Another advantage of the plasma spray process is the expansion of the number of materials that can be used due to the elimination of the high temperature firing steps. The maximum temperatures experienced by the cell for extending times are the operating temperatures, much lower than the sintering temperatures, avoiding unwanted formation of secondary phases by the chemical interaction of different components or extensive oxidation or sintering of metal supports [61].

Conventional PS set-ups typically use powder feedstock that has particle sizes in the range of 25-150 μm. This kind of feedstock presents some challenges for the desired cell properties because they produce relatively coarse microstructures, with low active area. However, suspension plasma spraying (SPS) of suspended micro- and nano-size powders in liquid, or solution precursor plasma spraying (SPPS), have been explored more recently in order to fabricate coatings with significantly finer microstructures and enhanced active area [61, 64, 65, 66]. Liquid feedstock has the advantage of facilitating the use of finer feedstock particle sizes, in the case of SPS, or of atomically-mixed precursor feedstock in the case of SPPS, both of which have the potential to produce electrodes with finer structures without subsequent sintering. Moreover, SPPS is a simple, single-step and rapid technique for both synthesizing and depositing materials. The preparation of the feedstock is easier in SPPS because there is no need for powder feedstock preparation such as agglomeration by spray drying nor for dispersion of powders in suspension [64].
Another challenge when fabricating SOFC active layers by the atmospheric plasma spraying manufacturing process is the low porosity typical of the nature of the process. Generally porosity on the order of 5 to 15% is created by the superposition of splats. This value is too low for the electrodes, which usually require approximately 30-40% porosity, and too high for gas tight electrolytes. Work has been done determining the optimum spray parameters for fabricating electrolytes in order to significantly increase the density of the layer. Similarly, the addition of pore former in the initial feedstock in order to increase the porosity of the electrode layers has been investigated [67, 68].

Once these technical challenges are overcome, plasma spray technology may allow better control over the composition and the microstructure of the functional layers and significant improvement on the electrochemical performance and the mechanical resistance of the cells. Moreover, the rapid deposition rate and the elimination of high temperature firing operations represent an important opportunity to lower the equipment and labour costs and simplify the process of manufacturing SOFCs in order to make this technology more feasible for mass production and bring it closer to the commercialization stage.
2.8 References


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Chapter 3
Procedure

3.1 Introduction

This study explores the possibility of architecture modifications of the traditional SOFC design to allow a more complete conversion of the fuel to CO$_2$ and water, while producing electricity more efficiently. This novel approach involves the option of an in-plane graded anode architecture with a transition from a material with high catalytic activity to materials that are more stable in oxidizing conditions.

The first step was modeling of this architecture to evaluate the feasibility of the approach. The electrochemical behavior of different in-plane graded or segmented anodes was analysed by the finite element method. Once the feasibility of this anode architecture was assessed with the electrochemical model, work began on fabricating anode materials suitable for conditions of high fuel utilization. Plasma spraying of solution precursor feedstock (SPPS) and suspension feedstock (SPS) was chosen as the fabrication technique due to the ability to synthesize (SPPS) and fabricate (SPPS, SPS) fully-consolidated coatings of various materials in a single manufacturing step.

3.2 Modeling

An SOFC electrochemical finite element model was previously developed by Gazzarri, J et al. [1-3]. This model was adapted to evaluate an-in-planed graded anode architecture. The main changes compared to the original model were the geometry, the influence of the concentration of the reactants and products on the performance of the cell, and the assumptions made for the electrical properties of the anode materials. In this section we do not focus on deriving the equations that describe the model, since a full description can be found in [1-8]. However, a detailed description of the modifications mentioned is given.

3.2.1 General description and assumptions of the SOFC model

In the original model the main physical processes that are considered are charge and mass balance within the cell. Hydrogen and water are the only species considered in the anode and
oxygen diffuses through nitrogen at the cathode at constant partial pressure. Binary diffusion is therefore assumed to be the dominant mass transfer process within the electrodes. The electrochemical reactions modeled at the anode and cathodes are represented in equations 28 and 29, respectively.

\[ H_2 \text{ (anode)} + O^{2-} \rightarrow H_2O \text{ (anode)} + 2e^- \] (28)

\[ \frac{1}{2} O_2 \text{ (cathode)} + 2e^- \rightarrow O^{2-} \] (29)

The generic equation for the transport of species is represented in equation 30.

\[ \frac{\partial x}{\partial t} = - \nabla \cdot N_{x} + Q_{x} \] (30)

This fundamental equation states that, within an elemental volume, the time variation in the amount of quantity \( x \) equals the negative divergence of its flux, \( N_{x} \), plus the rate of production or consumption of \( x \), \( Q_{x} \). This general equation takes the form of charge or mass conservation equations to solve for electric potential and concentrations throughout the cell components, respectively. For example, if \( x \) represents ionic or electronic charge per unit volume (Coul/m\(^3\)), \( N_{x} \) will represent a current density (A/m\(^2\)), and \( Q_{x} \) will take the form of a Faradaic current source or sink (A/m\(^3\)). In this case, the fundamental variable to be solved is the electric potential, and the accumulation term on the left hand side will describe the charge of an interfacial double layer, given by a time change in potential. The current density is proportional to the gradient in electric potential using Ohm’s law, using an effective conductivity as the proportionality constant [1].

Charge and mass conservation equations were used to solve for electric potential and reactant and product concentrations throughout the cell components, respectively. For details on the complete set of equations used in the model for steady-state charge balance and steady-state mass balance, readers are suggested to refer to [2].
**Steady-State Charge Balance**

From the general form of the charge balance equation for an elemental volume within a porous electrode, assuming a Butler-Volmer relationship between overpotential and Faradaic current density, and modifying it to include mass transport effects, the equation 31 was used for the DC electronic potential at the anode.

\[
-k_{\text{ELE,ANO}} \nabla^2 \Phi_{\text{ELE}} = -S_{\text{ANO}} i_{0,\text{ANO}} \left[ \frac{c_{\text{H}_2}}{c^0_{\text{H}_2}} \exp\left( \frac{\alpha_{\text{ANO,ANO}} F}{R_g T} \eta_{\text{ANO}} \right) - \frac{c_{\text{H}_2O}}{c^0_{\text{H}_2O}} \exp\left( -\frac{\alpha_{\text{ANO,CAT}} F}{R_g T} \eta_{\text{ANO}} \right) \right]
\]  

(31)

where \( k \) represents the effective conductivity [S/m], \( \Phi \) denotes potential [V], \( S \) is the active surface area [m\(^2\)], \( i_o \) represents the exchange current density [A/m\(^2\)], \( C^0_{\text{H}_2} \) and \( C^0_{\text{H}_2O} \) are the reference hydrogen and steam concentrations [mol/m\(^3\)] (at the channel), \( C_{\text{H}_2} \) and \( C_{\text{H}_2O} \) are the local concentrations [mol/m\(^3\)] (at the reaction sites), \( \alpha \) represents the charge transfer coefficient for the reaction, with the first sub-index indicating the electrode, and the second sub-index indicating the anodic or cathodic direction. \( F \) is the Faraday’s constant [A.s/mol], \( R_g \) represents the universal gas constant [J/mol.K], \( T \) is the absolute temperature [K], and \( \eta \) is represents the overpotential [V].

In a similar way, the electronic charge balance equation at the cathode, and the ionic charge balance at the anode and at the cathode were obtained.

**Steady-State Mass Balance**

Analogously, using Fick’s law of diffusion, the mass balance equation used at the anode is expressed in equation 32.

\[
-D_{\text{H}_2,H_2O} \nabla^2 c_{\text{H}_2} = -\frac{S_{\text{ANO}} i_{0,\text{ANO}}}{2F} \left[ \frac{c_{\text{H}_2}}{c^0_{\text{H}_2}} \exp\left( \frac{\alpha_{\text{ANO,ANO}} F}{R_g T} \eta_{\text{ANO}} \right) - \frac{c_{\text{H}_2O}}{c^0_{\text{H}_2O}} \exp\left( -\frac{\alpha_{\text{ANO,CAT}} F}{R_g T} \eta_{\text{ANO}} \right) \right]
\]  

(32)

The mass balance equation for the cathode was obtained similarly.
The geometry of the model is restricted to two dimensions: an in-plane direction and the thickness direction of the cell configuration. In addition, the system is assumed to be isothermal, and no internal reforming is considered.

### 3.2.2 Modifications to the concentrations of the gas species

The formulation for porous electrodes used in this model was first described by Newman and Tobias [4], and states that the local overpotential equals the potential difference between the electronic and ionic phases. In a full-cell model, one of the reference potentials can be arbitrarily set to zero (the anode reference potential, in this model), and the other reference potential must be equal to the open-circuit potential of the system [2], as shown in equation 33.

\[ \eta = \varphi_{\text{ele}} - \varphi_{\text{ion}} - \varphi_{\text{ref}} \]  

(33)

The open circuit potential is calculated from the Nernst equation (11). In the original model, it was set constant, because the changes in the concentrations of the reactants and products along the fuel channel were not considered. Changes in the partial pressures of the reactants and products directly affect the Nernst potential and consequently the local overpotential. In this work, the concentration of hydrogen and steam were set as variables dependent on the distance along the fuel channel. Linear and step functions were considered as input parameters for the partial pressures of the gases along the fuel channel, as will be described in more detail in chapter 4.

Similarly, if the concentration of gases along the channel is changing, a proportional variation in the electrochemical production or consumption will occur. Changes in the concentration affect the current production, as the steady state charge balance equation is solved simultaneously with the mass transfer equation, and the driving force for reactant transport within a porous electrode is the concentration gradient between the electrode/channel and the electrode/electrolyte boundaries (concentration terms in equations 31 and 32).
3.2.3 Geometric modifications

![Diagram of a 10 cm cell without interconnects with 5 partitions in the anode and cathode electrodes.](image1)

**Figure 33.** Geometry of a 10 cm cell without interconnects with 5 partitions in the anode and cathode electrodes.

The architecture of the cell was modified compared to the previous model in order to evaluate the electrochemical behaviour of an in-plane segmented anode, and the effect of the concentration changes of the gases along the fuel flow path. This approach allows the simulation of an SOFC with a ceramic material towards the outlet of the cell that could be sufficiently tolerant to oxidation conditions but still conductive and catalytic enough to maintain a good performance.

![Diagram of a 4 cm cell with interconnects, with 4 partitions each of the anode and cathode along the cell length.](image2)

**Figure 34.** Geometry of a 4 cm cell with interconnects, with 4 partitions each of the anode and cathode along the cell length.
A two-dimensional geometry was adopted for most of the cases studied. In this work, the length direction of the cell will be referred to as the X-axis (horizontal axis) or flow direction, and the thickness direction of the cell will be referred to as the Y-axis (vertical axis). Geometries with 1, 4, 5, and 10 cm length were evaluated. The thickness of the cell without interconnects was approximately 100 μm. When included, the interconnects were 3 mm thick each, if not otherwise detailed. The anode electrode was segmented in 2, 4, or 5 different sections, to evaluate the performance of the cell with 50, 25, and 20% of the anode having properties of a ceramic material, a candidate for high fuel utilization conditions. Figure 33 shows the geometry of a 10 cm cell without interconnects (not to scale). The anode and cathode are segmented in 5 parts.

Additionally, interconnects were included in the simulation to evaluate their influence on the current and voltage distribution when segmented anodes were used. Finally, isolated electrical connections were also evaluated. Figure 34 shows a 4 cm cell with interconnects. The anode and cathode are segmented in 4 parts along the X direction and the cathode is a bi-layer electrode.

3.2.4 Model parameters

This section focuses in the procedures used to obtain the general parameters used in the model. Details on the exact parameters used in each simulation are given in chapter 4.

For SOFC systems, many important parameters are difficult to measure independently. Some parameters, like tortuosity, exchange current density, and charge transfer coefficients, were approximated to values available in the current literature. For that reason, in order to validate the model, experimental results presented by P. Metzger et al. [5] at the German Aerospace Center (DLR) were simulated. That study focused on the characteristics along the flow path of the SOFC with different concentrations of fuel. The geometry of the DLR cell was replicated and some of the kinetics parameters of the model were better fitted to match the DLR results. More details of this assessment simulation are given in chapter 4.

Electrical conductivity

Bulk ionic and electronic conductivity of common SOFC materials are well known and the values were taken from the literature. However, most of the ceramic candidates for operation
under high fuel utilization conditions are still under development, and there is some inconsistency in the literature regarding the conductivity values. Most of these materials are ionic and electronic conducting ceramics with electrical properties that vary considerably with small changes in composition and synthesis techniques.

The main objective of the modelling section of this study was to investigate the feasibility of such a segmented architecture. Therefore, in order to reduce variability, only LSCM with the conductivity values reported in [6] was simulated as the alternative material to be the electronic conductor placed close to the outlet of the anode, where the more oxidizing conditions will exist.

The effective conductivity value $\sigma_{\text{eff}}$ of the porous electrode much be corrected for the presence of the non-conducting phases (solid and pore). The method used in this study is the same selected by [3] and described in [7], approximating the probability of percolation with the volume fraction of the corresponding phase [8]. This correlation is represented in equation 34. (For more information about the correction factors used in this model and other similar approaches the reader can refer to [3]).

$$\sigma_{\text{eff}}^k = (1 - \varepsilon) x_k P(x_k) \sigma_{\text{bulk}}^k$$  \hspace{1cm} (34)

where $P(x_k)$ indicates the probability of percolation of the phase of interest, $k$, $x_k$ is the mole fraction of the conductive phase $k$, and $\varepsilon$ is the porosity.

**Diffusion Parameters**

For the gas species diffusion through the porous media, the effective diffusivity was calculated from the correlation presented in equation 35 [9], where $\tau$ is the tortuosity of the pore phase, and the value of tortuosity selected was 3 [2, 10].

$$D_{\text{eff}} = \frac{\varepsilon}{\tau} D_{\text{bulk}}$$  \hspace{1cm} (35)
In the present simulation, for some of the cases studied, the hydrogen bulk diffusivity included the consideration of a three component gas including nitrogen in the anode mixture of gases. This allowed hydrogen to be diluted in nitrogen when evaluating the cell performance to simulate low concentration conditions. The diffusion coefficient calculation was done by extending the Stefan-Maxwell equations for a binary system to a multi-component gas system [11]. The diffusion coefficient of hydrogen in the mixture \(D_{(H_2-m)}\) was set as a variable depending on the hydrogen, nitrogen and steam partial pressures, the diffusivity coefficient of hydrogen in steam \(D_{H_2-W}\), and the diffusivity coefficient of hydrogen in nitrogen \(D_{N_2-H_2}\), as represented in equation 36. An analogous calculation was made for the steam diffusivity coefficient in the mixture. The final fuel diffusivity depends on both the reactant and product ability to diffuse within the mixture. Consequently, the hydrogen bulk diffusivity coefficient was considered as an average of the hydrogen and steam diffusivity coefficients with respect to the mixture, as expressed in equation 37.

\[
D_{(H_2-m)} = \frac{1-p_{H_2}^0}{\frac{p_{H_2}^0}{D_{H_2-W}} + \frac{p_{N_2}^0}{D_{N_2-H_2}}} \quad (36)
\]

where \(p_{N_2}^0\) is the nitrogen partial pressure.

\[
D^b H_2 = \frac{D_{(H_2-m)} + D_{(W-m)}}{2} \quad (37)
\]

**Electrochemical Parameters**

The electrochemical reactions that occur at the SOFC electrodes depend on several parameters that remain largely unknown, mainly because of measurement limitations due to the nature and the scale of the physical processes involved. Factors like exchange current density, charge transfer coefficients, and electro-active surface area are necessary from the modeling point of
view to determine the rate at which the reactions occur. In the present model, first approximations of the values of such electrochemical parameters were made based on a literature survey, and later, the approximations were enhanced by fitting the model with the experimental results from [5], as is discussed in detail in chapter 4. When suitable, some electrochemical parameters were preserved from the original model [1-3], and others were adapted according to the new materials and temperatures of operation.

Charge transfer coefficients were taken from published results on single electrode studies at the modeled temperatures. Surface areas were estimated based on TPB length and width values published by Metcalfe et al. [12] and Jiang et al. [13], respectively. The Metcalfe et al. study [12] calculates the TPB length in a sintered composite electrode as a function of the mean particle diameter, total porosity, and electrode composition. In the present model, a particle size between 0.1 and 1 micron were used as assumptions, in combination with the porosity and composition parameters corresponding to each simulation (parameter values can be found in chapter 4). Within this possible range of values for TPB length, a final fit was made to match experimental results reported in [5]. TPB width is the distance from the geometrical TPB line over which electrochemical activity occurs, and it depends on factors such as surface diffusivity of adsorbed species and ionic conductivity of ionized species on and in the ionic conducting phase in the electrode, temperature, and polarization state of electrodes [13-15]. A TPB width value of 0.20 μm was used in this study, which is a value estimated by Zhang and Wang [13] in an SOFC with an LSM cathode and YSZ electrolyte by electrochemical impedance spectroscopy and atomic force microscopy.

The exchange current density for Ni-YSZ and LSM- YSZ were taken from the previous model. Gazzarri, J. et al. [2] matched the results to fit published polarization resistance values in impedance spectroscopy performed on single electrode experiments. Co, Xia, and Birss [16] showed the calculation of exchange current density using impedance data in a similar way, for an LSM-YSZ composite cathode, demonstrating the validity of that approach independently of the assumed reaction mechanism [3]. The exchange current densities for Ni-GDC, LSCM, and LSM were calculated in this work from reported polarization curves of Ni-GDC, LSCM and LSM electrodes. A Tafel approximation was made to calculate the exchange current density of the
sample anode electrode. TPB length was estimated as described previously [12] with the reported particle sizes of the materials used to fabricate the ionic and electronic phases. TPB width was set constant to $0.2\mu m$ [13]. With the calculated surface area and the reported geometry of the electrodes, the electrochemical exchange current density was calculated from equation 38. Details of the values and references used can be found in chapter 4.

\[
\frac{i_{o,sp}}{t_S} = i_{o,elec}
\] (38)

where $i_{o,sp}$ is the volumetric exchange current density of the electrode, $t_S$ and $S_v$ are the thickness and electrochemically active surface area of the electrode, respectively, and $i_{o,elec}$ is the local electrochemical current density at the reaction site used in the present model.

### 3.3 Coating fabrication

#### 3.3.1 Atmospheric plasma spray system

For the fabrication of the coatings presented in this project, an atmospheric plasma spray system with an Axial III Series 600 Plasma Torch (Northwest Mettech Corp., North Vancouver, BC) was used (as shown in figure 35). The main components of the system that participate in the fabrication of plasma sprayed coatings are the torch, the suspension/solution delivery system, the substrate holder, and the robot that manipulates the torch. Each of these components is controlled by a computer with a user interface. Additionally, the system requires other key components, such as power supplies, gas supplies, a water chiller, and mass flow controllers.

The Axial III Series 600 Plasma Torch has three anodes and three cathodes, with an axial feeding system that injects the feedstock between the three electrodes in the same direction as the plasma jet flow. Axial injection represents an advantage compared to the common radial injection systems mainly because the feedstock is fed directly into the core of the plasma jet, offering better control over the feedstock trajectory and a more complete treatment of the particles. This set-up facilitates the use of liquid feedstocks containing micron-scale or sub-micron particles that would otherwise have difficulty to penetrate the plasma plume with radial injection.
Additionally, the deposition efficiency and quality of the coatings are less sensitive to particle size distribution and injection conditions, facilitating the manufacturing of composite electrodes by using mixed feedstock [17].

![Suspension or solution feed tube (axial)](image)

**Figure 35. Axial III Series 600 Plasma Torch (Northwest Mettech Corp., North Vancouver, BC).**

The system can use up to three different plasma gasses. For this study, argon, nitrogen and hydrogen were used. The torch spray parameters that can be controlled through the main computer include plasma gas composition, plasma gas flow rate, and electrode current. Variations of these parameters can lead to different plasma jet conditions and power outputs of up to 150 kW. Additionally, the torch nozzle can be changed manually. There are 5 different nozzle sizes available. Nozzle size influences the torch power, the residence time of the feedstock in the plasma, and the velocity of the plasma jet. In this study, nozzle sizes of 5/16” and 3/8” were used. The front of the torch and nozzle are shown in figure 36.

The solution/suspension delivery system allows single or dual delivery of suspensions or solutions to the torch. The system consists of two separate feeding lines. Each feedstock flow rate can be controlled independently by changing the speed of the respective pump. Mass flow rate can be measured directly by flow meters included in the system. Once the feedstocks are transported to the torch, they pass through a single or dual syringe tube that is placed in the
center of the torch and injects the feedstock directly behind the torch convergence. Nitrogen atomizing gas is used to ensure better injection of the feedstock into the plasma jet.

![Image](image_url)

**Figure 36. Front of the torch with 3/8” diameter nozzle installed.**

The torch trajectory is manipulated by a robot that is programmable through an auxiliary computer. Parameters for the torch runs such as number of passes, number of steps, robot speed, and X and Y movements are managed through the computer interface. The sample holder is a metal structure; substrates are clamped between masks that are bolted to the holder, with spring-loaded thermocouples contacting the substrates in the back that are used for temperature measurement. The sample holder allows heating and cooling of the substrates from the back with air jets controlled with feedback from the thermocouple temperature measurements. The system is controlled by a computer with which the temperature for pre-heating and cooling can be set through the user interface.

### 3.3.2 Feedstock preparation

In the present study, both suspension and solution feedstocks were used. These feedstocks have the advantage of resulting in considerably finer microstructures compared to more conventional powder feedstocks, enhancing the active area of the electrodes. Additionally, carbon black in aqueous suspension was used as a pore former to improve the microstructure of the electrodes.

#### 3.3.2.1 SPPS

Solution precursor plasma spraying (SPPS) has been studied recently in order to fabricate coatings with fine microstructure. The preparation of the feedstock is considerably easier in SPPS compared to powder or suspension feedstock because there is no need for powder
feedstock preparation or studies of suspension stability. SPPS allows synthesis of the material in-flight and deposition of the material in a single step.

- **LST**

The targeted composition for LST anodes was $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_{3+\delta}$, due to the literature reporting this percentage of La doping being more stable under oxidizing conditions than LST with higher proportions of La doping, and more conductive than lower values of La doping (refer to chapter 2 for more details).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Chemical Formula</th>
<th>Amount [mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium (IV) Isopropoxide*</td>
<td>$\text{C}<em>{12}\text{H}</em>{28}\text{O}_4\text{Ti}$</td>
<td>0.1/0.99</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>$\text{C}_2\text{H}_6\text{O}_2$</td>
<td>1.5</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>$\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$</td>
<td>0.5</td>
</tr>
<tr>
<td>Deionised Water</td>
<td>$\text{H}_2\text{O}$</td>
<td>2.88</td>
</tr>
<tr>
<td>Lanthanum Nitrate Hexahydrate*</td>
<td>$\text{La(NO}_3\text{)}_3\cdot\text{6H}_2\text{O}$</td>
<td>0.03/0.92</td>
</tr>
<tr>
<td>Strontium Nitrate*</td>
<td>$\text{Sr(NO}_3\text{)}_2$</td>
<td>0.07/0.8</td>
</tr>
</tbody>
</table>

*S* adjusted to account for losses in the plasma jet

Solutions were prepared with an adjusted proportion of precursor to account for the deposition efficiencies of each of the materials in the plasma jet. The final molar contents and constituents are listed in table 2. These molar values are specific to the plasma spray conditions given in table 29. It should be noted that for different plasma spray conditions, the deposition efficiencies of the materials may be different.

To prepare the solution, first the deionized water was mixed with the citric acid, stirred and heated to 70°C for approximately 20 minutes, or until clear, and then cooled down to room temperature. Separately, the titanium isopropoxide was slowly added to the ethylene glycol at room temperature. Immediately, the citric acid solution was added rapidly. After this step, the solution became cloudy with some precipitates, and it was stirred for approximately 8 hours until
cleared. Finally, the nitrates of lanthanum and strontium were added. The solution was stirred for an additional 8 hours until cleared.

- **LSBT**

The targeted composition for LSBT was La\textsubscript{0.3}Sr\textsubscript{0.55}Ba\textsubscript{0.15}TiO\textsubscript{3+δ}, as reported by Vincent et al. [18]. The solution was prepared the same way as the LST solution, and the additional barium nitrate was added as the last step. The molar contents and constituents are listed in table 3. In contrast to the LST solution, the LSBT solution never cleared completely.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Chemical Formula</th>
<th>Amount [mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium (IV) Isopropoxide*</td>
<td>C\textsubscript{12}H\textsubscript{28}O\textsubscript{4}Ti</td>
<td>0.1/0.95</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>C\textsubscript{2}H\textsubscript{6}O\textsubscript{2}</td>
<td>1.5</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>C\textsubscript{6}H\textsubscript{8}O\textsubscript{7} - H\textsubscript{2}O</td>
<td>0.5</td>
</tr>
<tr>
<td>Water</td>
<td>H\textsubscript{2}O</td>
<td>2.88</td>
</tr>
<tr>
<td>Lanthanum Nitrate Hexahydrate*</td>
<td>La(NO\textsubscript{3})\textsubscript{3} - 6H\textsubscript{2}O</td>
<td>0.03/0.94</td>
</tr>
<tr>
<td>Strontium Nitrate*</td>
<td>Sr(NO\textsubscript{3})\textsubscript{2}</td>
<td>0.055/0.83</td>
</tr>
<tr>
<td>Barium Nitrate*</td>
<td>Ba(NO\textsubscript{3})\textsubscript{2}</td>
<td>0.015/0.35</td>
</tr>
</tbody>
</table>

*adjusted to account for losses in the plasma jet

### 3.3.2.2 SPS

Suspension plasma spraying allows the possibility of fabricating coatings with slightly coarser microstructure than SPPS, but still finer microstructure than from dry powder feedstock. The average particle size of suspended powders is usually less than 10 μm. In some particular conditions, SPS coatings are preferred over SPPS coatings because they lead to coatings with less roughness than SPPS. As will be discussed in chapter 6, under some plasma spray conditions, some solution precursor feedstocks do not have enough momentum within the plasma jet to make it to the substrate; consequently, uneven coatings with column formations are fabricated. A detailed study of this phenomenon can be found in [19].
- **LFSCr**

The targeted composition of LSFCr selected was \( \text{La}_{0.30}\text{Sr}_{0.70}\text{Fe}_{0.70}\text{Cr}_{0.30}\text{O}_{3.5} \). This composition was reported by Haag et al. [20] to be stable down to a \( p_{O_2} \) of 10^{-20} atm at 800°C, at which point a spinel phase formed. The phase separation was also shown to be completely reversible with an increase in the partial pressure of oxygen and re-oxidation of the material. The powder was synthesized by traditional solid state reaction. Initial powders of \( \text{La}_2\text{O}_3 \), \( \text{SrCO}_3 \), \( \text{Fe}_2\text{O}_3 \), and \( \text{Cr}_2\text{O}_3 \) were first dried and then weighed in the correct cation proportions. Powders were ground under ethanol for 24 hours and then fired at 1250°C for 4 hours to form the solution solutions. XRD was done to the powder to verify the formation of a single phase perovskite structure. The resulting powder was further ground to reduce agglomerates.

A water suspension of LSFCr with 0.75 wt.% of polyethyleneimine (PEI) relative to the solid mass and a concentration of 3 vol.% was prepared. These values of concentration and dispersant were taken as guidelines from Arevalo-Quintero et al. [21], where they studied the stability of YSZ and SDC suspensions for plasma spray applications. The LSFCr suspension was placed into an ultrasonic agitator for approximately 3 hours before each coating fabrication. Particle sizes were measured.

- **Carbon Black**

Carbon black was used as pore former to improve the microstructure of the SPPS and SPS coatings. A stability study of different carbon black suspensions was made to determine the best amount of dispersant and concentration of the pore former suspension. Viscosity and settling time were the primary conditions studied because of their importance for the feeding system. A water suspension with 3 vol.% of carbon black with 0.5 wt.% of PEI relative to the solid mass was selected. The suspension was placed into an ultrasonic agitator for approximately 3 hours before each coating fabrication. The carbon black suspension was fed simultaneously with the LST, LSBT, or LSFCr feedstock through a dual syringe tube.
YSZ

Two different $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ suspensions were prepared, one with a concentration of 3 vol.% of YSZ and 0.75 wt.% of PEI relative to the solid mass, as described in [21]. The second had a concentration of 2 vol.% of YSZ, 3 vol.% of carbon black, and 0.75 wt.% of PEI relative to the solid mass of YSZ (no additional dispersant was needed to suspend the carbon black). The first suspension was used for the fabrication of the electrolytes, and the second was delivered simultaneously with the LSFCr suspension to introduce porosity and a purely ionically conducting phase in the anode coatings to potentially reduce the polarization resistance.

3.3.3 Plasma spray conditions

LST, LSBT, LFSCr and LFSCr-YSZ coatings were fabricated to characterize the microstructure, electrical properties, and deposition efficiency. Additionally, symmetrical cells with identical electrode materials and YSZ electrolytes were fabricated for electrochemical testing. Electrolyte fabrication is described elsewhere [22]. The range of spray conditions used in this study for fabrication of the electrodes is presented in table 4.

<table>
<thead>
<tr>
<th>Plasma Spray Condition</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standoff Distance [mm]</td>
<td>50-70</td>
</tr>
<tr>
<td>Nozzle Size [in]</td>
<td>1, 2 3/8, 5/16</td>
</tr>
<tr>
<td>Atomizing gas flow rate [slpm]</td>
<td>10-25</td>
</tr>
<tr>
<td>Plasma gas flow rate [slpm]</td>
<td>150-225</td>
</tr>
<tr>
<td>A2 [%] in the plasma gas composition</td>
<td>25-55</td>
</tr>
<tr>
<td>N2 [%] in the plasma gas composition</td>
<td>40-80</td>
</tr>
<tr>
<td>H2 [%] in the plasma gas composition</td>
<td>0-5</td>
</tr>
<tr>
<td>Current [A]</td>
<td>570-750</td>
</tr>
<tr>
<td>Torch power [kW]</td>
<td>70-142</td>
</tr>
</tbody>
</table>

The substrates used were dense or porous 430 stainless steel disks with a geometrical area of 5.10 cm$^2$ and thickness of 0.16 cm. Substrates were preheated in the sample holder to a temperature of 300°C prior to plasma spraying and cooled down to approximately the same temperature during plasma spraying.
3.4 Feedstock and coating characterization techniques

3.4.1 Viscosity measurements

The viscosity of the carbon black suspension was measured using a Thermo Scientific viscometer model Haake Viscotester 7 Plus (Thermo Fisher Scientific Process Instruments), in order to investigate the effect of the PEI and the concentration of carbon black on the viscosity of the suspension.

3.4.2 Particle size measurements

Particle size measurements of the powders in suspension were carried out by laser light scattering using a Mastersizer 2000 instrument (Malvern Instruments, Worcestershire, UK). Samples were tested in water using a Hydro 2000 S sample dispersion unit. Particle size distribution was used as a guideline to determine the length of the ultrasonic treatment needed by the suspensions. Ultrasonic treatment helped to break the agglomerates that can cause clogging of the plasma spray delivery system or imperfections in the coatings.

3.4.3 Coating preparation for SEM

The samples were mounted in epoxy (Epo Heat Epoxy Resin and Epo Heat Epoxy Hardener, Buehler). Samples were cut to expose cross sections of the coatings, mounted in epoxy again, and polished for analysis by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).

3.4.4 XRD

X-Ray Diffraction (XRD) was used to determine the phases present in the powders used for suspension preparation, and in the sprayed coatings. A Philips PW 1830 generator (40 kV, 40 mA) was used. The common scan program used was $20^\circ \leq 2\Theta \leq 70^\circ$, with $0.02^\circ$ step size and 2 seconds per step.

3.4.5 SEM

A JEOL Scanning Electron Microscope model JSM-661 OLV and a Hitachi Analytical TableTop Microscope TM3000 were used to characterize the coatings during development. The secondary
electron detector was used to observe microstructure, and a backscattered electron detector was used to differentiate phases present in the coating. Elemental maps and spot analyses by Energy Dispersive X-ray Spectroscopy (EDS) were performed with a model X-Max from Oxford Instruments (installed in the JEOL microscope) and with a model BrukerQuantax 70 (installed in the Hitachi microscope) to evaluate the composition of the coatings.

3.4.6 Image analysis

Image analysis using Clemex Vision (Clemex technologies, Guimond, QC, Canada) was performed on SEM images to determine porosity. High contrast and low brightness images taken with a low acceleration voltage (5 kV) were used for the porosity identification. Even though these SEM conditions are not suitable for microstructure analysis, they are more accurate for determining the porosity at the surface plane of the coatings. As first described in [23], a lower porosity limit was determined by setting the threshold of the grayscale of the image such that only the darker areas will be identified as porous, without including any solid phase. A higher porosity limit was determined by selecting the threshold of the grayscale of the image such that it included all the dark areas and some apparent solid phase that was darker than the rest of the surface, suggesting that it could be porosity of less depth than the darker areas. The lower limit will underestimate the porosity because some porosity with less depth will not be selected. In contrast, the upper limit will potentially overestimate the porosity. These two values of porosity were calculated and an average was taken as the best estimate of porosity.

3.4.7 Calculation of the deposition efficiency

The deposition efficiency of the coatings was estimated by measuring the weight gain of the substrates after spraying, and calculating the ratio of the weight gain of the substrate to the expected material delivered to the substrate during the spray run. The expected material delivered to the substrate during the spray run was calculated using the torch speed, the substrate area, and the pattern of the robot program. With the area of the substrate, the distance between each stripe of the robot program, and the torch speed, the time that the torch is over the substrate was calculated using (39), where $t$ is the time the torch is over the substrate per pass, $A_s$ is the area of the substrate, $V_r$ is the velocity of the torch robot, and $d_s$ is the distance between stripes...
of the torch robot program. This time was multiplied by the flow rate of solid (SPS) or the cation mass expected (SPPS) and the number of torch passes in front of the substrate (40).

\[ t = \frac{A_s}{V_r s} \] (39)

\[ Me = Fr \times t \times N \] (40)

where \( Me \) is the expected flow rate of solid (SPS) or of cation mass (SPPS) sprayed over the substrate area, \( Fr \) is the flow rate of the solution or suspension, and \( N \) is the number of passes of the torch. In the case of suspension spraying, the total mass of material expected in the coating was calculated from \( Me \) and the corresponding concentration of the powder in the suspension. In the case of solution spraying, the actual mass of material expected in the coating was calculated from \( Me \), the molar concentration of the precursors in the solution, and the assumption that they resulted in the synthesis of the targeted composition. Even though this approach for calculating the deposition efficiency has some simplifications regarding the area that the plasma plume is spraying, and the acceleration and deceleration of the robot, it was considered sufficient to evaluate the relative deposition efficiency between different plasma spray conditions, since the same simplifications applied to all of the coatings sprayed, and previous accelerometer measurements had indicated that the torch velocity was approximately constant in the location where the substrates were mounted for plasma spraying.

3.4.8 Conductivity measurements

Coatings were fabricated on dense, sand blasted 430 stainless steel supports with an area of 5.10 cm\(^2\) and thickness of 0.16 cm. Conductivity measurements were performed in button cell test stations fabricated in-house. Gold meshes were used as current collectors. Each sample was connected to a potentiostat (Solartron Analytical 1470E) using a four wire configuration. Current versus potential curves were measured across the coating and substrate. The resistance across the coating, substrate, and contacts was calculated by equation 41 according to ohm’s law, where \( Rt \) is the total resistance, \( V \) is the voltage applied, and \( I \) is the electrical current measured.
The resistance of the substrate and contacts was measured independently under the same conditions, and this value was subtracted from the overall resistance, assuming a series resistor combination (equation 42), where \( R_s \) represents the resistance of the substrate, \( R_e \) represents the resistance of the electrode or coating, and \( R_c \) represents the contact resistance.

\[
R_t = \frac{V}{I} \quad (41)
\]

\[
R_t = R_s + R_e + R_c \quad (42)
\]

The resistivity \( (\rho) \) of the coating was calculated using equation 43.

\[
\rho = \frac{R_e \times A_c}{t e} \quad (43),
\]

where \( A_c \) is the contact area and \( t e \) is the thickness of the coating. The thickness of the coating was calculated with image analysis. Five different micrographs were taken along the cross section, and 5 measurements of thickness were made in each micrograph, aided by the SEM software package. The value of the thickness of the coating used for the calculations was the average of these 25 measurements. The contact area was assumed to be the area of the smaller contact mesh. Finally, conductivity \( (\sigma) \) of the coatings was calculated from equation 44 in \( H_2, N_2, \) and air atmospheres at 650°C, 700°C, and 750 °C. Fuel and air flow rates were set at 200 sccm.

\[
\sigma = \frac{1}{\rho} \quad (44)
\]

3.4.9 Electrochemical testing

Electrochemical testing was conducted to characterize the anode materials. Symmetrical cells with an active area of 1.00 cm\(^2\) were fabricated on porous 430 stainless steel (SS) substrates. The cells consist of two plasma sprayed anodes separated by a YSZ electrolyte, as shown in figure 37. A symmetrical cell approach is used in the place of a full cell test during the initial
development of the anode materials in order to distinguish the anode effect from the cathode effect in the impedance spectra. Electrolyte development and fabrication is described elsewhere [22]. Tests were performed in button cell test stations fabricated in-house. The samples were held in air at 650°C for 4 hours before testing in order to remove the pore former introduced during the fabrication process. The necessary heat treatment to burn out the carbon black was previously determined by thermo-gravimetric analysis. Gold meshes were used as current collectors. The cells were connected to a potentiostat (Solartron Analytical 1470E) using a four wire configuration. A frequency response analyzer (Solartron Analytical 1260 or 1455) was used to perform Electrochemical Impedance Spectroscopy (EIS). The frequency range used was from 0.0001 Hz to 1000000 Hz, with a voltage perturbation amplitude of 20 mV. The measured impedance spectra were used to calculate the polarization resistance of the electrodes. No inductance corrections were made. EIS was performed in H₂, N₂, H₂ and N₂ mixtures, and air atmospheres at temperatures ranging from 650°C to 750°C. Degradation studies were performed by measuring the polarization resistance over several days of operation. Fuel and air flow rates were set at 200 sccm.

![Figure 37 Schematic of the symmetrical button cell on SS support.](image-url)
3.5 References


Chapter 4
Modeling of an SOFC

4.1 Introduction

High fuel utilization is desired in SOFC systems because the required fuel flow is minimized, reducing fuel costs. Additionally, practices such as after burning of the excess fuel are avoided, keeping the environmental advantage of the technology. However, as mentioned in section 2.5, conditions of high fuel utilization affect the performance of the cell. Changes in the concentrations of the gases are reflected in the open circuit voltage, activation losses, and gas transport losses.

The present model was used to study the electrochemical performance of an SOFC when changes in the concentrations of reactants exist. Additionally, the feasibility of an in-plane graded anode architecture with a transition of materials along the fuel flow path was evaluated.

4.2 Concentrations of species and variations in the Nernst potential.

In the first phase of the study, the influence of concentration changes of the species along the fuel flow channel was evaluated. Two simulations were made to compare the cell performance. A first simulation was made with constant concentration of the species along the fuel flow channel, and a second simulation was made with drastic changes in the concentration of the fuel along the fuel flow channel in order to mimic fuel depletion. The parameters used in both cases are presented in tables 5-10. Prescribed potential boundary conditions for the steady state equations are only required for the electronic potential along the current collecting lines, at the outside boundary of the cathode and at the outside boundary of the anode:

\[ \phi_{ELE|cathode\ current\ collector} = V_{cell} \]

\[ \phi_{ELE|anode\ current\ collector} = 0 \]
where $V_{\text{cell}}$ is the operating voltage of the cell.

Table 5. Operating parameters used in the reference case with no variations in the species concentrations along the fuel flow channel.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Range of values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>1173</td>
<td>K</td>
</tr>
<tr>
<td>Operating point</td>
<td>$V_{\text{cell}}$</td>
<td>0.7</td>
<td>V</td>
</tr>
<tr>
<td>Anode channel hydrogen partial pressure</td>
<td>$pH_{2}^{0}$</td>
<td>0.97</td>
<td>atm</td>
</tr>
<tr>
<td>Anode channel water partial pressure</td>
<td>$pH_{2}O^{0}$</td>
<td>0.03</td>
<td>atm</td>
</tr>
<tr>
<td>Cathode channel oxygen partial pressure</td>
<td>$pO_{2}^{0}$</td>
<td>0.21</td>
<td>atm</td>
</tr>
</tbody>
</table>

Table 6. Operating parameters used in the case with variations in the species concentrations along the fuel flow channel.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Range of values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>1123</td>
<td>K</td>
</tr>
<tr>
<td>Operating point</td>
<td>$V_{\text{cell}}$</td>
<td>0.7</td>
<td>V</td>
</tr>
<tr>
<td>Anode channel hydrogen partial pressure</td>
<td>$pH_{2}^{0}$</td>
<td>(-80.X+0.9)/m</td>
<td>atm</td>
</tr>
<tr>
<td>Anode channel water partial pressure</td>
<td>$pH_{2}O^{0}$</td>
<td>1- $pH_{2}^{0}$</td>
<td>atm</td>
</tr>
<tr>
<td>Cathode channel oxygen partial pressure</td>
<td>$pO_{2}^{0}$</td>
<td>0.21</td>
<td>atm</td>
</tr>
</tbody>
</table>
Table 7. Electrical and physical properties of the components of the cell used for the case of comparison between constant and varying Nernst potential.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte ionic conductivity @ 1123 K</td>
<td>$K_{ION,ELY}$</td>
<td>4.07</td>
<td>S/m</td>
<td>[1,2,3]</td>
</tr>
<tr>
<td>Ni bulk electronic conductivity @ 1123 K</td>
<td>$K^b_{ELE,ANO}$</td>
<td>$1.94 \times 10^6$</td>
<td>S/m</td>
<td>[3,4]</td>
</tr>
<tr>
<td>LSM bulk electronic conductivity @ 1123 K</td>
<td>$K^b_{ELE,CAT}$</td>
<td>$2.66 \times 10^4$</td>
<td>S/m</td>
<td>[3]</td>
</tr>
<tr>
<td>Anode porosity volume fraction</td>
<td>$\varepsilon_{ANO}$</td>
<td>0.4</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Cathode porosity volume fraction</td>
<td>$\varepsilon_{CAT}$</td>
<td>0.4</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Anode electronically conductive phase solid volume fraction *</td>
<td>$X_{ELE,ANO}$</td>
<td>0.4</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Cathode electronically conductive phase solid volume fraction *</td>
<td>$X_{ELE,CAT}$</td>
<td>0.5</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Anode ionically conductive phase solid volume fraction *</td>
<td>$X_{ION,ANO}$</td>
<td>0.6</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Cathode ionically conductive phase solid volume fraction *</td>
<td>$X_{ION,CAT}$</td>
<td>0.5</td>
<td></td>
<td>[3]</td>
</tr>
</tbody>
</table>

*Based on total solid phase.

Table 8. Electrochemical parameters used for the case of comparison between constant and varying Nernst potential.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode charge transfer coefficient, anodic direction</td>
<td>$\alpha_{AA}$</td>
<td>1.2</td>
<td></td>
<td>[3,6]</td>
</tr>
<tr>
<td>Anode charge transfer coefficient, cathodic direction</td>
<td>$\alpha_{AC}$</td>
<td>0.8</td>
<td></td>
<td>[3,6]</td>
</tr>
<tr>
<td>Cathode charge transfer coefficient, anodic direction</td>
<td>$\alpha_{CA}$</td>
<td>1.5</td>
<td></td>
<td>[2,3,7]</td>
</tr>
<tr>
<td>Cathode charge transfer coefficient, cathodic direction</td>
<td>$\alpha_{CC}$</td>
<td>0.5</td>
<td></td>
<td>[2,3,7]</td>
</tr>
<tr>
<td>Anode and cathode active surface area</td>
<td>$S_{ANO, S_{CAT}}$</td>
<td>$1e6$</td>
<td>1/m</td>
<td>[3,8]</td>
</tr>
<tr>
<td>Anode exchange current density *</td>
<td>$i_{o,ANO}$</td>
<td>25</td>
<td>A/m^2</td>
<td>[3]</td>
</tr>
<tr>
<td>Cathode exchange current density *</td>
<td>$i_{o,CAT}$</td>
<td>50</td>
<td>A/m^2</td>
<td>[3,9]</td>
</tr>
</tbody>
</table>

*fitted to reproduce empirical impedance results. For details the reader is advised to refer to [3].
Table 9. Gas diffusion properties used for the case of comparison between constant and varying Nernst potential.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>units</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen bulk diffusivity @ 1123</td>
<td>(D_b^{H_2})</td>
<td>(8.94 \times 10^{-4})</td>
<td>(m^2/sec)</td>
<td>[3,5]</td>
</tr>
<tr>
<td>Oxygen bulk diffusivity in (O_2^- N_2) @ 1123</td>
<td>(D_b^{O_2})</td>
<td>(2.34 \times 10^{-4})</td>
<td>(m^2/sec)</td>
<td>[3,5]</td>
</tr>
<tr>
<td>Hydrogen effective diffusivity @ 1123</td>
<td>(D_{H_2})</td>
<td>(1.19 \times 10^{-4})</td>
<td>(m^2/sec)</td>
<td>[3]</td>
</tr>
<tr>
<td>Oxygen effective diffusivity in (O_2^- N_2) @ 1123</td>
<td>(D_{O_2})</td>
<td>(3.12 \times 10^{-4})</td>
<td>(m^2/sec)</td>
<td>[3]</td>
</tr>
</tbody>
</table>

Table 10. Geometric parameters used for the case of comparison between constant and varying Nernst potential.

<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
<th>Size</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte thickness</td>
<td>(t_{ely})</td>
<td>15</td>
<td>(\mu m)</td>
</tr>
<tr>
<td>Anode thickness</td>
<td>(t_{ano})</td>
<td>40</td>
<td>(\mu m)</td>
</tr>
<tr>
<td>Cathode thickness</td>
<td>(t_{cat})</td>
<td>40</td>
<td>(\mu m)</td>
</tr>
<tr>
<td>Cell length</td>
<td>(L)</td>
<td>1</td>
<td>(cm)</td>
</tr>
</tbody>
</table>

For the case with variations in the concentrations along the fuel flow channel, changes in the partial pressures of the reactants and products were considered significant and included in the evaluation of the open circuit voltage of the cell, as described in section 3.2.2. Consequently, the part of the cell that was located towards the fuel path exhaust experienced lower fuel concentrations. In order to simulate the depletion of the fuel along the fuel flow path, the concentration changes were represented by reducing the concentration of the fuel (\(H_2\)) and proportionally increasing the concentration of steam. The partial pressure of the fuel was defined as a linear function depending on the length of the cell (as shown in table 6), with the balance being steam. Figure 38 shows the representation of the partial pressure of hydrogen simulated along the channel.
Figure 38. Partial pressure of hydrogen along the fuel flow channel for the case including variations in the species concentrations.

The boundary conditions for hydrogen and oxygen concentrations are prescribed concentrations at the boundaries between the electrodes and channels, and no-flux everywhere else:

\[ C_{H_2} = c^0 H_2 \text{ at the channel/anode boundary} \]

\[ \nabla C_{H_2} \cdot \overrightarrow{n} = 0 \text{ everywhere else on the anode side} \]

\[ C_{O_2} = c^0 O_2 \text{ at the channel/cathode boundary} \]

\[ \nabla C_{O_2} \cdot \overrightarrow{n} = 0 \text{ everywhere else on the cathode side} \]

where \( \overrightarrow{n} \) is the unit vector normal to each boundary. \( c^0 H_2 \) is the concentration of hydrogen, calculated from the pH\( ^0 \) as expressed in equation 44.

\[ c^0 H_2 = \frac{p_{H_2} \cdot 101300}{R \cdot T} \text{ [mol m}^{-3} \text{]} \quad (44) \]
It is calculated in an analogous way for the cases of oxygen and steam.

Changes in the partial pressures of the reactants and products directly affected the Nernst potential and, consequently, the electrical current density distribution across the electrodes. The focus of the model was on the concentration of the species involved in the anode electrode; it was assumed that the cell was exposed to air at the cathode side and that the oxidant consumption did not influence the fuel utilization calculation.

Figure 39 shows the comparison between the concentration of the species for the reference case, where the hydrogen partial pressure is considered constant along the fuel channel, and the case where the hydrogen partial pressure is varied as represented in figure 38.

**Figure 39.** Concentrations of the species. Left case with no variations in the species concentrations along the fuel flow channel. Right case with variations in the species concentrations along the fuel flow channel. Fuel flows from left to right in the anode channel (bottom) and oxidant flows from right to left in the cathode channel (top).

Similarly, figure 40 shows the electronic current density distribution for both cases. The results showed that the maximum current density produced by the cell is lower for the case where the partial pressure of hydrogen is decreasing towards the outlet. This result demonstrates the expected proportional drop in the current production towards the outlet of the anode, where the smaller concentration gradient between the electrode/channel and the electrode/electrolyte boundaries and the local lower open circuit voltage dictate the lower performance.
The average current density produced by the cell with no fuel concentration gradients was 4264 A/m$^2$, and 2457 A/m$^2$ for the case with variations in the concentrations. This value represents a 42% decrease in the current density when the partial pressure of hydrogen is depleting linearly towards the outlet of the cell as represented in figure 38.

### 4.3 Fitting parameters to experimental results

In order to validate the model, experimental results presented by P. Metzger et al. [10] at the German Aerospace Center (DLR) were simulated. This study focused on the characteristics along the flow path of the SOFC with different concentrations of fuel. The objective of this validation was to make realistic assumptions about the distribution of the current, voltage, and fuel consumption in different segments of the cell and to fit critical kinetic parameters such as exchange current density and active surface area of the electrodes to the experimental data.

The geometry of the DLR cell consisted of an electrolyte supported cell with a Ni-GDC anode, a double layer 8YSZ/LSM-LSM cathode and a 3YSZ electrolyte. The cell was square shaped with an area of 100 cm$^2$, integrated in a metallic housing subdivided into 16 galvanically isolated segments on both sides, as shown in figures 41 and 42. This subdivided geometry resulted in an
active area of 73.96 cm². The hydrogen content in the fuel gas supplied to the cell was varied between 2% and 100%, with the supplementary gas being nitrogen. The measuring system allowed the determination of the current density/voltage characteristics, impedance, and temperature data over the complete cell and the 16 distinct segments. Additionally, auxiliary voltage probes were integrated in the middle of 4 of the 16 segments along the flow path at the cathode side. These voltage probes were isolated from the metallic segments and are in direct contact with the cathode surface, allowing the measurement of the over-voltages related to the cathodic contact resistance. To determine the balance of the anode gases, capillary tubes were integrated in the middle of the segments at the anode side. The sample gas composition was determined by gas chromatography. For more details on the experimental setup the reader is advised to refer to [10].

Individual 2 cm length segments corresponding to the second row of the DLR cell were simulated (segments 5, 6, 7, and 8 in figure 42). Figure 43 shows the geometry of one segment and table 11 shows the values of the geometrical parameters used. The charge transfer coefficients of the materials and the electrical conductivity were selected from a literature survey as described in chapter 3; they are shown in tables 12 and 13. An initial electrochemically active area and exchange current density range of values were also estimated from the literature as described in section 3.2.4. Parameters, values, and references used are summarized in table 14. The voltages reported by DLR for the second row of segments of the cell (refer to figure 8 in

Figure 41. The segmented cell approach of DLR for SOFCs. Schematic representation of the metallic housing, which is segmented on both sides. Reproduced with permission from [10][B].
chapter 2) were used as the boundary conditions for the electronic current density in the model. Different values for electrochemically active area and exchange current density parameters within the range shown in table 14 were evaluated. The best fit of these parameters was obtained by comparing the results from the electronic current density produced by the model at each segment at the different fuel concentrations (2, 5, 10, 20, 50 and 100 % H₂ with N₂ as the balance) with the experimental values of current density reported by DLR. DLR current density values were calculated from the power densities reported (shown in figure 7 in chapter 2) and the voltages corresponding to each segment (shown in figure 8 in chapter 2). DLR voltages and current density values for the case with 50 % hydrogen concentration can be found in table 15. The final values selected for active surface area and exchange current density are reported in table 16. The different operating conditions evaluated are shown in table 17 and the gas diffusion properties can be found in table 18. All the parameters were kept constant for the rest of the simulations unless otherwise noted.

Figure 42. Voltage distribution of the DLR cell, with the positions of the segments shown.

Reproduced with permission from [10][B].
Figure 43. Geometry of one segment.

Table 11. Geometric parameters of one segment used for the case of fitting parameters.

<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
<th>Size range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte thickness</td>
<td>$t_{el}$</td>
<td>90</td>
<td>μm</td>
</tr>
<tr>
<td>Anode Thickness</td>
<td>$t_{ano}$</td>
<td>45</td>
<td>μm</td>
</tr>
<tr>
<td>Cathode Thickness</td>
<td>$t_{cat}$</td>
<td>40</td>
<td>μm</td>
</tr>
<tr>
<td>Cell length</td>
<td>L</td>
<td>2</td>
<td>cm</td>
</tr>
</tbody>
</table>

Table 12. Charge transfer coefficients used for the case of fitting parameters.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode charge transfer coefficient, anodic direction</td>
<td>$\alpha_{AA}$</td>
<td>1.2</td>
<td></td>
<td>[3,6]</td>
</tr>
<tr>
<td>Anode charge transfer coefficient, cathodic direction</td>
<td>$\alpha_{Ac}$</td>
<td>0.8</td>
<td></td>
<td>[3,6]</td>
</tr>
<tr>
<td>Cathode charge transfer coefficient, anodic direction</td>
<td>$\alpha_{ca}$</td>
<td>1.5</td>
<td></td>
<td>[2,3,7]</td>
</tr>
<tr>
<td>Cathode charge transfer coefficient, cathodic direction</td>
<td>$\alpha_{cc}$</td>
<td>0.5</td>
<td></td>
<td>[2,3,7]</td>
</tr>
</tbody>
</table>
Table 13. Electrical and physical properties of the components of the cell used for the case of fitting parameters.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 YSZ ionic conductivity @ 1073 K</td>
<td>$K_{ION,ELY}$</td>
<td>3.93</td>
<td>S/m</td>
<td>[3]</td>
</tr>
<tr>
<td>3 YSZ ionic conductivity @ 1073 K</td>
<td>$K_{ION,ELY}$</td>
<td>1.86</td>
<td>S/m</td>
<td>[11]</td>
</tr>
<tr>
<td>Ni bulk electronic conductivity @ 1073 K</td>
<td>$K^{b}_{ELE,ANO}$</td>
<td>$2.04 \times 10^6$</td>
<td>S/m</td>
<td>[3,4]</td>
</tr>
<tr>
<td>LSM bulk electronic conductivity @ 1073 K</td>
<td>$K^{b}_{ELE,CAT}$</td>
<td>11730</td>
<td>S/m</td>
<td>[12]</td>
</tr>
<tr>
<td>GDC ionic conductivity @ 1073 K</td>
<td>$K_{ION,ANO}$</td>
<td>9.31</td>
<td>S/m</td>
<td>[13]</td>
</tr>
<tr>
<td>Anode porosity volume fraction</td>
<td>$\varepsilon_{ANO}$</td>
<td>0.5</td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>Cathode porosity volume fraction</td>
<td>$\varepsilon_{CAT}$</td>
<td>0.5</td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>Anode electronically conductive phase solid volume fraction *</td>
<td>$X_{ELE,ANO}$</td>
<td>0.4</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Cathode electronically conductive phase solid volume fraction *</td>
<td>$X_{ELE,CAT}$</td>
<td>0.5</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Anode ionically conductive phase solid volume fraction *</td>
<td>$X_{ION,ANO}$</td>
<td>0.6</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Cathode ionically conductive phase solid volume fraction *</td>
<td>$X_{ION,CAT}$</td>
<td>0.5</td>
<td></td>
<td>[3]</td>
</tr>
</tbody>
</table>

*Based on total solid phase.

Table 14. Exchange current density and active surface area range of values used for the case of fitting parameters.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample anode max active surface area (particle size 0.25 μm)</td>
<td>$S_v,ano$</td>
<td>$7.5 \times 10^6$</td>
<td>1/m</td>
<td>[14]</td>
</tr>
<tr>
<td>Sample anode min active surface area (particle size 2 μm)</td>
<td>$S_v,ano$</td>
<td>$2 \times 10^5$</td>
<td>1/m</td>
<td>[14]</td>
</tr>
<tr>
<td>Sample anode max active surface area (particle size 0.5 μm)</td>
<td>$S_v,cat$</td>
<td>$8 \times 10^6$</td>
<td>1/m</td>
<td>[14]</td>
</tr>
<tr>
<td>Sample anode min active surface area (particle size 1 μm)</td>
<td>$S_v,cat$</td>
<td>$2 \times 10^5$</td>
<td>1/m</td>
<td>[14]</td>
</tr>
<tr>
<td>Min anode exchange current density *</td>
<td>$i_{o,ano}$</td>
<td>6</td>
<td>A/m²</td>
<td>Figure 2 from [15]</td>
</tr>
<tr>
<td>Max anode exchange current density *</td>
<td>$i_{o,ano}$</td>
<td>217</td>
<td>A/m²</td>
<td>Figure 2 from [15]</td>
</tr>
<tr>
<td>Min cathode exchange current density *</td>
<td>$i_{o,cat}$</td>
<td>19</td>
<td>A/m²</td>
<td>Figure 8 and table 1 from [16]</td>
</tr>
<tr>
<td>Min cathode exchange current density *</td>
<td>$i_{o,cat}$</td>
<td>76</td>
<td>A/m²</td>
<td>Figure 8 and table 1 from [16]</td>
</tr>
</tbody>
</table>

*Calculated from overpotential curves using equation 38 (details can be found in section 3.2.4).
Table 15. Voltage and current density corresponding to segments 5-8 of the 50% H₂ case, calculated from [10].

<table>
<thead>
<tr>
<th>Segment</th>
<th>Current density [A/m²]</th>
<th>Voltage [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Segment 5</td>
<td>3852.00</td>
<td>0.623</td>
</tr>
<tr>
<td>Segment 6</td>
<td>3744.00</td>
<td>0.633</td>
</tr>
<tr>
<td>Segment 7</td>
<td>3720.00</td>
<td>0.621</td>
</tr>
<tr>
<td>Segment 8</td>
<td>3650.00</td>
<td>0.608</td>
</tr>
</tbody>
</table>

Table 16. Selected parameters for active surface area and exchange current density.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode and cathode active surface area</td>
<td>S_ano , S_cat</td>
<td>3.6x10^6</td>
<td>1/m</td>
<td>[14] and this work fitting to [10] results</td>
</tr>
<tr>
<td>Anode exchange current density *</td>
<td>io, ano</td>
<td>40</td>
<td>A/m²</td>
<td>[15] and this work fitting to [10] results</td>
</tr>
<tr>
<td>Cathode exchange current density *</td>
<td>io, cat</td>
<td>19</td>
<td>A/m²</td>
<td>[16] and this work fitting to [10] results</td>
</tr>
</tbody>
</table>

Table 17. Range of operating parameters used during the fitting simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Range of values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>T</td>
<td>1073</td>
<td>K</td>
</tr>
<tr>
<td>Operating point</td>
<td>Vcell</td>
<td>0.471-0.726</td>
<td>V</td>
</tr>
<tr>
<td>Anode channel hydrogen partial pressure</td>
<td>pH₂^0</td>
<td>0.0194-0.97</td>
<td>atm</td>
</tr>
<tr>
<td>Anode channel water partial pressure</td>
<td>pH₂O^0</td>
<td>0.03-0.17</td>
<td>atm</td>
</tr>
<tr>
<td>Cathode channel oxygen partial pressure</td>
<td>pO₂^0</td>
<td>0.21</td>
<td>atm</td>
</tr>
</tbody>
</table>
Very good agreement was obtained between the current density produced by the DLR cell and the model, especially in the region from 100% concentration to 10% concentration of H2, as shown in figure 44. However, even with the best fit of parameters found, the model started to differ from the experimental results when very low concentrations of hydrogen were reached. It can be noticed from the figure 44 that the modeled cell had a higher performance compared with the experimental cell when extremely high fuel utilizations were reached. One reason could be that the present model assumes charge transport as the rate limiting process. In particular, at very low concentrations of H2, diffusion losses may dominate, and the present model may not accurately represent those conditions, resulting in slightly better performance than the experimental cell.
Figure 44. Comparison of the current density produced by the fitted model and the DLR cells for each concentration case.

4.4 Anode segmentation

After the model was validated using the individual cell segments, it was used to evaluate the option of anode segmentation. The objective was to determine if it was possible to support a voltage difference across the in-plane length of the anode. The influence of the segmented architecture on the voltage distribution was studied through the electrical behaviour of 4 connected segments corresponding to the second row of the DLR cell (shown in figure 45). Since the current densities are equal to the negative gradients of the potential times the corresponding conductivities, for example: $\tilde{i}_{ELE} = -k_{ELE} \nabla \phi_{ELE}$, the 4 different values for current density production reported by DLR (in A/m², corresponding to the segments 5, 6, 7, and 8, shown in table 15 for the 50% H₂ case) that would exist in the case of fuel consumption along the channel, were used as Neumann boundary conditions for the electronic potential, to evaluate the voltage distribution and the performance of the cell. Geometric parameters are shown in table 19.

Figures 45-48 show the results for the case with 50% hydrogen concentration. A voltage gradient of 23 mV across the length of the cathode and 0.5 mV across the length of the anode was obtained. Voltage gradients with no unpredictable performance drops or drastic changes in current distribution were observed in all of the fuel concentration cases evaluated (2, 5, 10, 20, 50, and 100 % H₂ with N₂ as the balance). This operating condition could simulate the case
where the cell is operating under a constant current drawn (for example, the average of the 4 segments), and the voltage is free to vary within a small range.

**Table 19. Geometric parameters used for the anode segmentation case.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
<th>Size range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte thickness</td>
<td>$t_{ely}$</td>
<td>90</td>
<td>µm</td>
</tr>
<tr>
<td>Anode Thickness</td>
<td>$t_{ano}$</td>
<td>45</td>
<td>µm</td>
</tr>
<tr>
<td>Cathode Thickness</td>
<td>$t_{cat}$</td>
<td>40</td>
<td>µm</td>
</tr>
<tr>
<td>Cell length</td>
<td>$L$</td>
<td>8</td>
<td>cm</td>
</tr>
<tr>
<td>Number of anode segments of equal size</td>
<td>$N_s$</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

![Electronic Potential](image)

**Figure 45.** Electronic potential obtained for the case of 50% H$_2$ concentration and anode segmentation.
Figure 46. Electronic potential obtained at the anode and cathode boundaries. Case of 50% \( \text{H}_2 \) concentration and anode segmentation.

Figure 47. Electronic and ionic current density distributions obtained in the Y direction. Case of 50% \( \text{H}_2 \) concentration and anode segmentation.
Figure 48. Electronic current density obtained in the Y direction at the boundary of the anode and cathode. Case of 50% H\textsubscript{2} concentration and anode segmentation.

In order to further evaluate the voltage distribution of the SOFC with a segmented anode, the cell was modeled as 4 anode and cathode segments electrically isolated and supported on an electrolyte (shown in figure 49). Table 20 shows the geometric parameters used in this case. Similarly to the previous case, the 4 different values for current density produced in the experimental results reported by DLR (in A/m\textsuperscript{2}, corresponding to the segments 5, 6, 7, and 8) were used as Neumann boundary conditions for the electronic potential. Figures 49-51 show the results for the case with 50% hydrogen concentration. The voltage gradients observed across the different isolated segments were larger than in the case where the electrodes are electrically connected. Voltage gradients of 58 mV across the anode and 78 mV across the cathode were observed. Voltage gradients with no unpredictable performance drops or drastic changes in current distribution were observed in all of the fuel concentration cases evaluated (2, 5, 10, 20, 50, and 100 % H\textsubscript{2} with N\textsubscript{2} as the balance).
Table 20. Geometric parameters for the segmented anode electrically isolated case.

<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
<th>Size range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte thickness</td>
<td>( t_{\text{ely}} )</td>
<td>90</td>
<td>( \mu \text{m} )</td>
</tr>
<tr>
<td>Anode Thickness</td>
<td>( t_{\text{ano}} )</td>
<td>45</td>
<td>( \mu \text{m} )</td>
</tr>
<tr>
<td>Cathode Thickness</td>
<td>( t_{\text{cat}} )</td>
<td>40</td>
<td>( \mu \text{m} )</td>
</tr>
<tr>
<td>Cell length</td>
<td>( L )</td>
<td>10</td>
<td>cm</td>
</tr>
<tr>
<td>Number of segments of equal size</td>
<td>( N_s )</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Spacing between segments</td>
<td>( S_g )</td>
<td>6.6</td>
<td>mm</td>
</tr>
</tbody>
</table>

Figure 49. Electronic potential obtained for the case of 50% \( \text{H}_2 \) concentration and when the segmented anode is electrically isolated.
Figure 50. Electronic potentials obtained at the anode and cathode boundaries. Case of 50% H₂ concentration and when the segmented anode is electrically isolated.

Figure 51. Electronic and ionic current density distributions obtained in the Y direction. Case of 50% H₂ concentration and when the segmented anode is electrically isolated.

The results for both approaches, of connected and isolated segments, suggested that the anode segmented architecture is potentially feasible, since no abnormal behaviours or unpredictable voltage losses were observed when the voltage and current distributions changed along the fuel path, due to fuel consumption.

4.5 Interconnects

Interconnects were also integrated into the model in order to evaluate their influence on the performance of the cell with the presence of fuel consumption. The geometric parameters used
are shown in table 21. The electronic conductivity used for the stainless steel interconnects was $8 \times 10^5$ S/m [3]. A constant voltage of 0.62 V was set as the boundary condition. The concentration of the fuel was varied in a step function as shown in figure 52, from 90 % to 10 % H$_2$, with steam being the balance. Since the voltage was set as the boundary condition, in this case the voltage was forced to equalize by the moment it reached the IC boundary. However, there were local gradients of voltages at the electrode/IC boundary, as shown in figure 54, that equalized towards the boundary.

Table 21. Geometric parameters for the case with rectangular channel interconnects.

<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
<th>Size range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte thickness</td>
<td>$t_{ely}$</td>
<td>90</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Anode Thickness</td>
<td>$t_{ano}$</td>
<td>45</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Cathode Thickness</td>
<td>$t_{cat}$</td>
<td>40</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Interconnect Channel Height</td>
<td>$ich$</td>
<td>0.5</td>
<td>cm</td>
</tr>
<tr>
<td>Interconnect Landing Width (interior)</td>
<td>$ilw_c$</td>
<td>0.25</td>
<td>cm</td>
</tr>
<tr>
<td>Interconnect Landing Width (edge)</td>
<td>$ilw_e$</td>
<td>0.125</td>
<td>cm</td>
</tr>
<tr>
<td>Interconnect Channel Width</td>
<td>$icw$</td>
<td>0.25</td>
<td>cm</td>
</tr>
<tr>
<td>Interconnect Solid Height</td>
<td>$ish$</td>
<td>0.5</td>
<td>cm</td>
</tr>
<tr>
<td>Interconnect Number of Landings</td>
<td>$inl$</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Cell length</td>
<td>L</td>
<td>4</td>
<td>cm</td>
</tr>
<tr>
<td>Number of anode segments of equal size</td>
<td>$Ns$</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
Figure 52. Partial pressure of hydrogen along the fuel flow channel used for the case including variations in the species concentrations and interconnects.

Figure 53. Electronic potential obtained for the case with interconnects.
Figure 54. Local gradients of voltages obtained at the electrode/IC boundary.

The electrical current density distributions are shown in figure 55. The current density produced by the cell with ICs was 2016 A/m$^2$; this value is approximately 80 % of the current density produced by the same cell without ICs (not shown). The main reason for the lower performance is that the interconnect landings reduce the size of the flow channel exposed to the fuel, and the diffusion of the species through the electrodes limited the performance in the areas under the landings. The observed gradients in the voltage distribution were smaller compared to the case without ICs; the ICs provided a highly conductive surface to better equalize the voltages across the length of the cell.
Figure 55. Electronic and ionic current density distributions in the Y direction obtained for the case with interconnects.

Figure 56. Electronic current density in the Y direction at the boundary of the anode and cathode obtained for the case with interconnects.

The current density distribution at both boundaries of the interconnects are shown in figure 56. It can be noted that the surface of the interconnects above the fuel channel is poorly utilized. Localized high density of current can cause higher temperatures in that area and contribute to the degradation of the cell. For that reason, ICs with round channels were also evaluated; they demonstrated a better distribution of the current density than the rectangular channel interconnects. The geometric parameters are shown in table 22.
Table 22. Geometric parameters for the case with circular channel interconnects.

<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
<th>Size range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte thickness</td>
<td>$t_{ely}$</td>
<td>90</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Anode Thickness</td>
<td>$t_{ano}$</td>
<td>45</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Cathode Thickness</td>
<td>$t_{cat}$</td>
<td>40</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Interconnect Channel Radius</td>
<td>icr</td>
<td>0.25</td>
<td>mm</td>
</tr>
<tr>
<td>Interconnect Landing Width (interio)</td>
<td>ilw$_i$</td>
<td>0.5</td>
<td>mm</td>
</tr>
<tr>
<td>Interconnect Landing Width (edge)</td>
<td>ilw$_e$</td>
<td>0.25</td>
<td>mm</td>
</tr>
<tr>
<td>Interconnect Solid Height</td>
<td>ish</td>
<td>0.6</td>
<td>mm</td>
</tr>
<tr>
<td>Interconnect Number of Landings</td>
<td>inl</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Cell length</td>
<td>L</td>
<td>2</td>
<td>mm</td>
</tr>
<tr>
<td>Number of anode segments of equal size</td>
<td>Ns</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 57. Electronic current density distribution obtained in the Y direction for the case with circular channel interconnects.

The IC surface was better utilized with the round channel geometry, as can be observed in figure 57. Interconnects with round channels could be beneficial in reducing localized higher temperatures due to regions with high localized current density in the rectangular interconnect channels.
4.6 In-plane gradient of anode materials

In order to evaluate the electrical behaviour of the cell when there is an in-plane gradient of the anode materials along the fuel channel, the case in which the anode has a different material near the outlet of the cell was evaluated. An anode with high nickel content at the inlet of the fuel channel and a material more stable in oxidizing conditions, such as an electronically conducting ceramic, for the final section is desired to allow higher fuel utilization by the cell.

The cell was modeled with an in-plane graded anode consisting of $\frac{3}{4}$ of the anode being Ni-GDC and $\frac{1}{4}$ of the anode being LSCM-GDC, as shown in figure 58. The geometric and operational parameters are shown in tables 23 and 24. The Ni-GDC section was modelled with the kinetic parameters obtained from the experimentally correlated model (tables 12, 13 and 16). The electrical conductivity, physical characteristics, and charge transfer coefficients of the LSCM section were selected from a literature survey; they are shown in tables 25 and 26. The exchange current density was also estimated from the literature, as described in section 3.2.4. Parameters, values, and references used are summarized in table 26. Average current density values corresponding to the DLR experimental results, as described for the previous cases, were applied as the BCs for the Ni-GDC region. For the LSCM-GDC region, V-I curves from the literature were used to obtain a suitable value. The current density values for boundary conditions and the corresponding references for the case of 50 % H$_2$ are shown in table 27.
Figure 58. Electronic potential of the in-plane segmented anode with a transition of materials from Ni to LSCM.

Table 23. Geometric parameters used for the case of the in-plane segmented anode with a transition of materials from Ni to LSCM.

<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
<th>Size range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte thickness</td>
<td>$t_{ely}$</td>
<td>90</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Anode Thickness</td>
<td>$t_{ano}$</td>
<td>45</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Cathode Thickness</td>
<td>$t_{cat}$</td>
<td>40</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Cell length</td>
<td>L</td>
<td>8</td>
<td>cm</td>
</tr>
</tbody>
</table>

Table 24. Operating parameters used for the case of the in-plane segmented anode with a transition of materials from Ni to LSCM.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Range of values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>1073</td>
<td>K</td>
</tr>
<tr>
<td>Anode channel hydrogen partial pressure</td>
<td>$pH_2^0$</td>
<td>0.485</td>
<td>atm</td>
</tr>
<tr>
<td>Anode channel water partial pressure</td>
<td>$pH_2O^0$</td>
<td>0.03</td>
<td>atm</td>
</tr>
<tr>
<td>Cathode channel oxygen partial pressure</td>
<td>$pO_2^0$</td>
<td>0.21</td>
<td>atm</td>
</tr>
</tbody>
</table>
Table 25. Electrical and physical properties of the LSCM-GDC segment.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCM bulk electronic conductivity @ 1073 K</td>
<td>$\kappa_{\text{ELE,ANO2}}^b$</td>
<td>100</td>
<td>S/m</td>
<td>[18]</td>
</tr>
<tr>
<td>GDC ionic conductivity @ 1073 K</td>
<td>$\kappa_{\text{ION,ANO}}$</td>
<td>9.31</td>
<td>S/m</td>
<td>[13]</td>
</tr>
<tr>
<td>LSCM- GDC anode porosity volume fraction</td>
<td>$\varepsilon_{\text{ANO2}}$</td>
<td>0.5</td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>LSCM- GDC anode electronically conductive phase solid volume fraction in final anode segment*</td>
<td>$X_{\text{ELE,ANO2}}^*$</td>
<td>0.4</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>LSCM- GDC anode ionically conductive phase solid volume fraction in final anode segment*</td>
<td>$X_{\text{ION,ANO2}}^*$</td>
<td>0.6</td>
<td></td>
<td>[3]</td>
</tr>
</tbody>
</table>

*Based on total solid phase.

Table 26. Electrochemical properties of the LSCM-GDC segment.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCM- GDC anode charge transfer coefficient, anodic direction</td>
<td>$\alpha_{\text{AA2}}$</td>
<td>0.2</td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>LSCM- GDC anode charge transfer coefficient, cathodic direction</td>
<td>$\alpha_{\text{AC2}}$</td>
<td>0.2</td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>LSCM-GDC anode exchange current density</td>
<td>$i_{o,\text{ano2}}$</td>
<td>6.6</td>
<td>A/m$^2$</td>
<td>[19]</td>
</tr>
<tr>
<td>Sample anode active surface area (Particle size 0.1 μm)</td>
<td>$S_{\text{ano}}$</td>
<td>$3.2 \times 10^6$</td>
<td>1/m</td>
<td>[14] and this work</td>
</tr>
</tbody>
</table>

Table 27. Average current density values used as boundary conditions.

<table>
<thead>
<tr>
<th>Segment</th>
<th>Current density [A/m$^2$]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Segment 5</td>
<td>3852.00</td>
<td>[10]</td>
</tr>
<tr>
<td>Segment 6</td>
<td>3744.00</td>
<td>[10]</td>
</tr>
<tr>
<td>Segment 7</td>
<td>3720.00</td>
<td>[10]</td>
</tr>
<tr>
<td>Segment 8</td>
<td>1800</td>
<td>[20,21]</td>
</tr>
</tbody>
</table>

The voltage distribution was evaluated. An electronic voltage gradient of approximately 100 mV was observed across the anode length and of approximately 16 mV across the cathode. The voltages at the anode and cathode boundaries are shown in figure 59. Similarly to the previous case, the overall behaviour of the cell was stable and no unpredictable performance drops were observed due to the electrical mismatch of the two materials comprising the anode.
Figure 59. Electronic potential gradients at the anode and cathode boundaries obtained for the case of the in-plane segmented anode with a transition of materials from Ni to LSCM.

Figure 60. Electronic and ionic current density distributions obtained in the Y direction for the case of the in-plane segmented anode with a transition of materials from Ni to LSCM.
Figure 61. Electronic current densities at the boundaries of the anode and cathode obtained for the case of the in-plane segmented anode with a transition of materials from Ni to LSCM.

The electronic and ionic current density distributions across both electrodes are shown in figure 60. The electronic current densities at the cathode and anode boundaries are shown in figure 61. The LSCM-GDC anode was able to perform connected to the Ni-GDC anode with no unpredictable losses in the performance, and producing the expected current density of 1800 A/m² with no harmful voltage drops.
4.7 References


[18] Kharton, V. Tsipis, E. Marozau, I. Viskup, A. Frade, J. Irvine, J. (2006). Mixed conductivity and electrochemical behavior of \((\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}\). Solid State Ionics, 178, 101-113.

[19] Deleebeeck, L. Birss, V. (2009). Investigation of Sr-doped and Sr-free \(\text{LaMn}_{1.2}\text{Cr}_{0.8}\text{O}_{3.5}\) Perovskites as Sulfur Tolerant SOFC Anodes. ECS Transactions, 25 (2), 2231-2239.


Chapter 5
Early coating development

5.1 Solution Precursor Plasma Spray (SPPS) LST and LSBT coatings

With the goal of identifying plasma spray parameters to fabricate a single phase LST coating, a wide range of spray conditions was tested. The relationships between the spraying parameters and the final coating microstructures and properties were studied. Phase analysis by XRD, microstructural analysis by SEM, compositional analysis by EDS, and calculations of the deposition efficiencies of the materials sprayed with the different conditions tested were performed. Solution precursor plasma spraying has the useful ability to both synthesize the materials in the plasma deposit them on the substrate to create a coating. Therefore, in the case of LST and LSBT, it was important not only to obtain high deposition efficiency and good microstructure, but also to ensure that the final coating had the desired phase and composition.

The initial screening parameters covered a range of plasma power conditions from 86 to 105 kW. The plasma power was controlled by the amount of nitrogen and argon in the mixture of plasma gases, for a total plasma gas flow rate of 200 SLPM. Variations from 40% nitrogen content to 70% nitrogen content were tested (balance Ar). Additionally, the standoff distance was varied from 50 mm to 70 mm. The rest of the parameters were kept constant, and no hydrogen was used in the plasma gas mixtures. The current across each pair of torch electrodes was set to 200 A, the torch nozzle diameter was 3/8”, the atomizing gas flow rate was 20 SLPM, and the solution feed rate was approximately 40 g/min.

During these screening tests, most of the plasma gas mixtures and standoff distances tested produced coatings with XRD patterns that exhibited a single phase perovskite structure, as shown in figure 62. The additional peak presented in the XRD pattern at 44° corresponds to the main peak of the stainless steel substrate. However, for some cases, small traces of not fully formed material (possibly La₂O₃) were observed close to the main perovskite peak, between 2θ=30° and 32°.
The deposition efficiencies for this set of conditions were in general very low, with the highest being approximately 33% when the highest content of nitrogen was used. Therefore, one hypothesis to explain the low deposition efficiency was that the plasma energy was too low for the synthesis and deposition of this particular material.

In order to explore higher plasma powers, plasmas with 80% nitrogen were used to fabricate coatings with current values between 200 and 250 A per pair of electrodes. These conditions resulted in torch power values between 112 and 134 kW. Standoff distances between 60 and 90 mm were investigated in order to explore longer residence times of the particles in the plasma. The XRD patterns showed considerable amounts of decomposition for most of the conditions with 80% nitrogen content. Therefore, this amount of nitrogen was avoided for the rest of the experiments.

The wide range of plasma powers initially explored did not result in any satisfactory deposition efficiencies. It was believed that the low concentration of the solution (0.73 mol/L) was a possible reason for these results. Therefore, the solution concentration was increased to its
saturation limit, reducing the amount of citric acid and water by half (for the original recipe, see chapter 3, table 7). The solution concentration was increased to 0.9 mol/L.

The new solution concentration was tested and, simultaneously, the feedstock flow rate was increased to approximately 60 g/min. The current was set constant to 225 A per pair of electrodes, plasma gas mixtures with 70% nitrogen, 0 or 5% hydrogen, and balance argon were used for these experiments. The plasma gas flow rate was set to 200 SLPM. The atomizing gas flow rate was kept constant at 20 SLPM, and the standoff distance ranged from 50 mm to 100 mm. Nozzle sizes used were 3/8” and 1/2”. Significantly higher deposition efficiencies were obtained with standoff distances ranging from 50 to 70 mm with both nozzles, as shown in figure 63.

Figure 63. Deposition efficiency versus standoff distance of LST coatings.
The XRD analysis showed a single phase perovskite structure with no traces of impurities for all of the coatings produced at standoff distances between 50 and 70 mm, as shown in figure 64. The microstructural analysis revealed good adhesion of the coating to the substrate. However, substantial dense areas, as shown in figure 65, and high roughness of the coatings suggested the need for further optimization.

The compositions were analysed by EDS and a deficiency of strontium was found compared to the targeted composition. Similarly, a relative excess of titanium and lanthanum were present in the coatings; possibly because of the low melting temperature of strontium compared to lanthanum and titanium, leading to a higher extent of evaporation of the strontium in the plasma.

In order to achieve the desired composition of the final coatings, the initial solution composition was adjusted according to the individual deposition efficiencies of each material. The relative deposition efficiencies were 60%, 118%, and 122% for strontium, titanium, and lanthanum, respectively, compared to the total deposition efficiency of all of the cations.
Figure 65. Microstructure of LST coating fabricated with a plasma containing 70% nitrogen and 0% hydrogen at a 70 mm SD and with a ½” Nozzle.

The adjusted recipe to achieve the targeted composition resulted in coatings with the right composition, and the XRD patterns of those coatings showed only small traces of an impurity phase between $2\theta = 30^\circ$ and $32^\circ$.

**Carbon Black Suspension Development**

In order to further optimize the microstructure of the coatings, carbon black suspension was added as a pore former. Three suspensions of carbon black in water were selected for stability studies in order to determine the optimal concentration. Stability of the suspensions is crucial to avoid the formation of clogs in the suspension delivery system.

**Table 28. Settling time of carbon black water suspension**

<table>
<thead>
<tr>
<th>Concentration of Suspension (Vol. %)</th>
<th>Settling time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No dispersant</td>
</tr>
<tr>
<td>3</td>
<td>Started settling after a few minutes</td>
</tr>
<tr>
<td>5</td>
<td>Started settling after a few minutes</td>
</tr>
<tr>
<td>10</td>
<td>Started settling after a few minutes</td>
</tr>
</tbody>
</table>

Initial concentrations of 3, 5, and 10 % volume of carbon black in water were evaluated. The stability of the suspension was not good, as settling started a few minutes after stirring was stopped for all three concentrations. In order to delay the onset of settling of the suspensions, 0.5 wt. % of PEI relative to the solid mass was added to the water before the carbon black powder.
Particle size distributions, results of the viscosity measurements, and settling time study results are shown in figure 66, figure 67, and table 28, respectively.

**Figure 66.** Carbon black (CB) suspension particle size distributions with and without PEI dispersant addition.

**Figure 67.** Carbon black suspension viscosity as a function of concentration with and without PEI.

The carbon black suspension with 3 vol.% of carbon black and 0.5 wt.% of PEI relative to the solid mass was selected based on the stability study results.
The carbon black suspension was delivered simultaneously with the LST solution in a separate feed line with dual syringe tubes at the ends of the lines. The carbon black suspension flow rate was set to approximate values of 20 g/min, 38 g/min, and 56 g/min to observe the resulting differences in microstructure. The LST flow rate was approximately 60 g/min for all three cases. The arc current was varied between 225 and 250 A per electrode. The standoff distance was 50 mm for each of the cases. Carbon black suspension was dual fed successfully and introduced significant porosity to the coatings, improving the microstructure. Unfortunately, the pore former addition tended to lower the deposition efficiency values significantly, as can be observed in figure 68. Figure 69 shows the microstructure obtained with the lowest load of carbon black (feed mass ratio LST/CB = 4.3, current = 250 A/electrode pair). Figure 70 shows the microstructure obtained with the highest load of carbon black (feed mass ratio LST/CB= 1.5, current = 225 A/electrode pair). In all of the coatings, higher current values led to higher plasma energies and lower porosity. A possible explanation is that the percentage of carbon black that survived the plasma was lower for higher plasma energies, or that the extent of melting of the LST phase was higher, leading to lower intrinsic porosity. An LST/CB feed mass ratio of approximately 2.6 was selected as providing the optimum amount of porosity (in the range of 35 to 40%) to ensure a good balance between deposition efficiency and microstructure. More details about the porosity measurements are provided in chapter 6. In general, the coatings were not uniform, and rougher than acceptable for fuel cell electrodes due to the need to subsequently deposit the other fuel cell layers.

![Graph](image)

**Figure 68.** Influence of the pore former suspension addition on the deposition efficiency (DE) of the LST solution. Average of 2 data points per symbol. Error bars are within symbol width.
Figure 69. Microstructure obtained with the lowest load of carbon black (feed mass ratio LST/CB = 4.3, current 250 A/electrode pair).

Figure 70. Microstructure obtained with the highest load of carbon black (ratio LST/CB feed mass ratio = 1.5, current = 225 A/electrode pair).

As mentioned in chapter 3, the high roughness of the coatings was attributed to a low momentum of the droplets within the plasma. Therefore, for the next set of experiments, the torch nozzle with 5/16” diameter was tested to investigate the effects of using a higher velocity of the plasma jet. Due to limitations of the torch power compatible with this particular nozzle, some of the conditions were adjusted to obtain a final power below 100 kW. The current was set to 190 A/electrode pair, the nitrogen plasma gas content was lowered to 40%, and the standoff distance was kept between 50 and 60 mm. 5% hydrogen gas was used for the plasma gas mixture. The rest of the parameters were kept constant. For this set of conditions, the quality of the coatings increased significantly. Figure 71 shows the microstructure of a coating with LST/CB feed mass ratio =4.3 and figure 72 shows the microstructure of a coating with LST/CB feed mass ratio...
=2.6. However, the EDS showed a composition with a relative excess of strontium and deficiency of lanthanum and titanium. Additionally, the XRD patterns showed a considerable amount of impurity phases. It was believed that the reason for these results was the different ratios of the individual deposition efficiencies of the materials in the solution for this nozzle size and plasma condition compared to those previously investigated.

![Microstructure](image)

**Figure 71.** Microstructure of a coating with LST/CB feed mass ratio = 4.3, 5/16" nozzle diameter, and 60 mm SD.

![Microstructure](image)

**Figure 72.** Microstructure of a coating with LST/CB feed mass ratio = 2.6, 5/16" nozzle diameter, and 60 mm SD.

The deposition efficiency for the materials was adjusted accordingly for the new conditions, and a single phase material was obtained with the right composition, as shown in figures 73-75.

In order to further improve the roughness of the coatings, a set of experiments were carried out varying the plasma gas flow rate and the atomizing gas flow rate. The plasma gas flow rate was varied from 150 slpm to 225 slpm, and the results showed that higher plasma gas flow rates led
to better adhesion of the coatings and less roughness. Figure 76 shows a coating sprayed with 150 slpm plasma gas flow rate, and figure 77 shows a coating sprayed with 225 slpm plasma gas flow rate. The deposition efficiency was also higher for the coating fabricated with a higher plasma gas flow rate.

**Figure 73.** Atomic fraction deviation of titanium from the targeted composition.

**Figure 74.** Atomic fraction deviation of lanthanum from the targeted composition.
Figure 75. Atomic fraction deviation of strontium from the targeted composition.

Figure 76. LST coating sprayed with 150 slpm plasma gas.

Figure 77. LST coating sprayed with 225 slpm plasma gas.
In another screening study, the atomizing gas flow rate was varied from 10 to 25 slpm of nitrogen. The results showed that lower atomizing gas flow rates resulted in smoother coatings. Figure 78 shows a coating sprayed with 25 slpm of atomizing gas flow, and figure 79 shows a coating sprayed with 10 slpm of atomizing gas flow.

**Figure 78.** LST coating sprayed with 25 slpm of nitrogen as atomizing gas.

Figure 79. LST coating sprayed with 10 slpm of nitrogen as atomizing gas

Based on these preliminary results, the range of parameters was narrowed down to produce the best coatings obtainable. For LSBT, the same conditions that produced good LST coatings were used successfully. Deposition efficiency, adhesion to the substrate, material composition, phase composition, and microstructure were the factors determining the selection of the final parameters, shown in table 29. A detailed description of the properties of the optimized coatings is presented in chapter 6.
Table 29. Plasma spray conditions used for the fabrication of SPPS LST and LSBT

<table>
<thead>
<tr>
<th>Plasma Spray Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standoff distance [mm]</td>
<td>60</td>
</tr>
<tr>
<td>Nozzle diameter [in]</td>
<td>5/16</td>
</tr>
<tr>
<td>Atomizing gas flow rate [slpm]</td>
<td>10</td>
</tr>
<tr>
<td>Plasma gas flow rate [slpm]</td>
<td>225</td>
</tr>
<tr>
<td>Ar composition in the plasma gas [%]</td>
<td>55</td>
</tr>
<tr>
<td>N$_2$ composition in the plasma gas [%]</td>
<td>40</td>
</tr>
<tr>
<td>H$_2$ composition in the plasma gas [%]</td>
<td>5</td>
</tr>
<tr>
<td>Current [A/electrode pair]</td>
<td>190</td>
</tr>
<tr>
<td>Power [kW]</td>
<td>100</td>
</tr>
</tbody>
</table>

5.2 Suspension Plasma Spray (SPS) LSFCr coatings

The initial conditions used to develop SPS LSFCr coatings were 3/8” nozzle diameter, 15 slpm of nitrogen atomizing gas, 220 A of current per pair of electrodes, 60 mm standoff distance, 200 slpm of plasma gas, and a gas mixture of 60% nitrogen and 0 or 5% hydrogen balanced with argon. The flow rate was 60 g/min of suspension. These conditions led to plasma powers between 105 and 108 kW. The suspension concentration was 3 vol. % and the particle size distribution is shown in figure 80. Both gas mixtures, with and without hydrogen, produced highly dense coatings with very little porosity and a high degree of melting, as shown in figure 81. Also, many cracks were observed across the coating, possibly because of the high density of the ceramic coating and its thermal expansion mismatch with the substrate, leading to a higher susceptibility to thermal shock during the fabrication process compared to more porous coatings with lower resulting elastic moduli. The deposition efficiency of these coatings was approximately 70%.
In order to increase the porosity, the same carbon black suspension used for the LST and LSBT coatings was delivered simultaneously in a separate line with the LSFCr suspension using a dual syringe tube. With the addition of the pore former, the deposition efficiency did not decrease, possibly because for this particular case, a large LSFCr/CB feed mass ratio of 4.7 was used. The microstructure of the coatings was improved significantly; however, the porosity was not sufficient, and there was still some degree of cracking. Figure 82 shows the microstructure of a coating fabricated with an LFSCr suspension feed rate of approximately 60 g/min and a carbon black suspension feed rate of approximately 30 g/min.
EDS analysis revealed a deficiency of chromium in the initial coatings compared to the targeted composition. The deposition efficiency of individual materials was taken into account, and the initial oxide proportions were adjusted to account for the loss for subsequent coating fabrication. Possible reasons for this loss could be the evaporation of chromium in the plasma jet or in the furnace during solid state synthesis of the powders.

The results of the initial coating development work were used to identify optimal fabrication conditions (shown on table 30) for further studies of coating microstructures, properties, and performance, which are presented in chapter 6.

**Figure 82. Microstructure of an LSFCr coating fabricated with an LSFC/CB mass feed ratio of 4.7.**

**Table 30. Plasma spray conditions used for the fabrication of SPS LSFCr**

<table>
<thead>
<tr>
<th>Plasma Spray Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standoff distance [mm]</td>
<td>60</td>
</tr>
<tr>
<td>Nozzle diameter [in]</td>
<td>3/8</td>
</tr>
<tr>
<td>Atomizing gas flow rate [slpm]</td>
<td>10</td>
</tr>
<tr>
<td>Plasma gas flow rate [slpm]</td>
<td>200</td>
</tr>
<tr>
<td>Ar composition in the plasma gas [%]</td>
<td>40</td>
</tr>
<tr>
<td>$N_2$ composition in the plasma gas [%]</td>
<td>60</td>
</tr>
<tr>
<td>$H_2$ composition in the plasma gas [%]</td>
<td>0</td>
</tr>
<tr>
<td>Current [A/electrode pair]</td>
<td>220</td>
</tr>
<tr>
<td>Power [kW]</td>
<td>100</td>
</tr>
</tbody>
</table>
Chapter 6
Characterization of plasma sprayed anodes: results and discussion

6.1 Introduction
After the identification of suitable parameters to deposit the various anode materials successfully, further characterization was performed. Phase analysis by XRD, microstructural analysis by SEM, compositional analysis by EDS, porosity determination by image analysis, and conductivity measurements were performed on the sprayed coatings. Symmetrical cells were fabricated on porous stainless steel substrates and impedance measurements were conducted to characterize the performance of the ceramic materials as potential anodes for SOFCs.

6.2 LST
6.2.1 LST Coatings
SPPS LST coatings were deposited with the plasma spray conditions shown in table 29, an LST solution flow rate of 38 g/min, and a solution concentration of 1.12 mol/L. The composition targeted was La$_{0.3}$Sr$_{0.7}$TiO$_3$$\pm$$\delta$. Carbon black suspension was used as a pore former at a flow rate of 38g/min. An LST/CB mass feed ratio of 1.66 was used.

- XRD

Figure 83 shows the XRD pattern of an as-sprayed LST coating. The main peak of the perovskite structure is shown. No presence of unwanted phases was observed (the primary peaks of the most common impurity phases occur in the 30-32° range, where no non-perovskite peaks were found).
Figure 83. XRD pattern of an LST as-sprayed coating.

- SEM

Cross section SEM images of typical LST coatings produced with the conditions shown in table 29 are shown in figures 84-86. The deposition efficiency was approximately 65% for each of the coatings. The average thickness of the coatings shown was 55 μm. The ceramic material was well mixed with the pore former. The coatings were relatively uniform and provided good coverage of and contact with the substrates, following their roughness features closely and with good adhesion. Large porosity was found, possibly caused by the formation of columnar structures, as shown in figures 85 and 86. In some areas of the substrate surface, it can be observed that the coating bridged some irregularities, which can be beneficial in the case of porous substrates, reducing the irregularities propagated to subsequent layers. No visible cracks were found in the coatings.
Porosity

As described in section 3.4.6, high contrast and low brightness SEM images taken with a low acceleration voltage (5 kV) were used for the porosity determination. Figure 87 shows the typical porosity obtained in the LST coatings characterized. The coating shown was fabricated with an LST/CB feed mass ratio of 2.66. The porosity identified in the LST coatings was
characteristically fine, with some areas of larger porosity possibly caused by the formation of tower-type structures.

![SEM image of LST coating](image.jpg)

**Figure 87.** High contrast and low brightness SEM image of an LST coating taken with 5kV of accelerating voltage for porosity identification.

Figures 88 and 89 show an example of the process used to determine the lower and upper porosity limits, respectively. The blue regions represent the areas of the images that were identified as porosity by the image analysis software once the gray scale threshold to be used in the identification process was set by the user. It can be observed in figure 88 that some dark areas were not filled with blue. The lower threshold of porosity may underestimate the porosity that is closest to the surface because the difference in the gray scale between the porosity with shallow depth and the surface is ambiguous; these pores are not taken into account in this lower-bound estimate selected to avoid identifying any solid regions as pores. Figure 89 shows the upper threshold of porosity selected. In this case, the threshold was set so that all of the darker areas visible in the original image were identified by the software as porosity. The upper threshold may overestimate the porosity because some solid phase could be considered porosity as well.
Figure 88. Lower threshold of porosity selected for porosity determination of an LST coating.

Figure 89. Upper threshold of porosity selected for porosity determination of an LST coating.

For the coating shown, the lower threshold resulted in a porosity estimate of 32% and the upper threshold resulted in a porosity estimate of 43%. The average of these two values was calculated as the porosity and the range of values used for the error estimate, resulting in an estimated porosity of 38±6%.

Analogous analyses were made of coatings with different LST/CB mass feed ratios. The results are shown in table 31. The variability of three different coatings sprayed with the conditions in table 29 and a LST/CB mass feed ratio of 1.66 showed a standard deviation of 4% porosity. This
value is lower than the error introduced by the selection of the lower and higher thresholds of porosity.

Table 31. Porosities of coatings fabricated with various LST/CB mass feed ratios.

<table>
<thead>
<tr>
<th>LST/CB mass feed ratio</th>
<th>Porosity [%]</th>
<th>error [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.41</td>
<td>44</td>
<td>8</td>
</tr>
<tr>
<td>1.66</td>
<td>44</td>
<td>7</td>
</tr>
<tr>
<td>1.8</td>
<td>42</td>
<td>6</td>
</tr>
<tr>
<td>2.66</td>
<td>38</td>
<td>6</td>
</tr>
</tbody>
</table>

• EDS

Figures 90, 91 and 92 show the results of the EDS analysis for coatings with LST/CB feed mass ratios of 1.41 and 2.6, when the LST solution recipe was adjusted for a targeted LST/CB mass ratio of 2.6. It can be observed that the atomic fraction deviation from the target of the three elements varies with the LST/CB mass feed ratio. The LST solution composition shown in table 2 was re-adjusted to use an LST/CB feed mass ratio of 1.66, because this LST/CB mass ratio was considered to produce the coating with the best microstructure. For an LST/CB feed mass ratio of 1.66, the relative deposition efficiencies were 92%, 80% and 99% for lanthanum, strontium and titanium, respectively, relative to the overall deposition efficiency of all of the cations in the solution. It should be noted that these values apply only for the plasma spray conditions listed in table 29; different plasma spray conditions will also influence the relative deposition efficiencies of each element.
Figure 90. Deviation from the lanthanum targeted atomic fraction calculated by EDS in LST coatings fabricated using the plasma spray conditions in table 29.

Figure 91. Deviation from the strontium targeted atomic fraction calculated by EDS in LST coatings fabricated using the plasma spray conditions in table 29.
Figure 92. Deviation from the titanium targeted atomic fraction calculated by EDS in LST coatings fabricated using the plasma spray conditions in table 29.

- **Conductivity**

Conductivity measurements of the LST coating shown in figures 93 and 94 were performed. The LST/CB feed mass ratio of the coating was 1.44. An average thickness of 60 μm was measured and 44% porosity was assumed based on the analyses performed on identically-made coatings shown in table 31.

Figure 95 shows the results of the conductivity measurements in pure hydrogen at temperatures ranging between 650°C and 800 °C. The reduction kinetics of the as-sprayed LST coatings were found to be particularly slow. Within the first 72 hours of testing, the conductivity was still increasing, regardless of whether the temperature was increased or decreased over this time period. After 96 hours, the atmosphere was switched to nitrogen and then subsequently to air, as shown in figure 96, in order to oxidize the pore former present in the coating. The conductivity decreased slowly from a value of 2.15 S/cm in hydrogen to 0.005 S/cm in air. After approximately 200 hours of testing, the atmosphere was switched back to nitrogen and the coating conductivity increased to a value of 0.024 S/cm in nitrogen at 750°C. After the first exposure to air, the coating exhibited an increase in conductivity with increasing temperature in both nitrogen and hydrogen. Figure 97 shows the conductivity of the coating when it was...
exposed to hydrogen for the second time. The conductivity was still increasing after 10 hours in hydrogen, showing values of approximately 0.63 S/cm.

Figure 93. LST coating used for conductivity measurements, at 500x magnification.

Figure 94. LST coating used for conductivity measurements, at 100x magnification.

Figure 95. Conductivity measurements made on an LST coating in a pure hydrogen atmosphere.
Figure 96. Conductivity measurements made on an LST coating in N\textsubscript{2} and air atmospheres.

Figure 97. LST coating conductivity in H\textsubscript{2}
6.2.2  LST Symmetrical cells

Electrochemical testing was conducted to characterize the LST as an anode material. Symmetrical cells were fabricated on porous stainless steel substrates as described in section 3.4.9.

- Impedance measurements

A cell was heated to 650°C at a rate of 2°C/min in air and dwelled for 4 hours in order to burn the carbon black in the anode layers. The atmosphere was then changed to nitrogen, followed by 4% hydrogen and 96% nitrogen, and the cell was then ramped at the same rate to 750°C. Figure 98 shows impedance spectra of an LST symmetrical cell after dwelling for 72 hours in 4% hydrogen and after dwelling for 48 hours in 100% hydrogen. Both anodes were sprayed with identical conditions.

![Figure 98. Impedance spectra of an LST symmetrical cell in H2.](image-url)
Figure 99. Close-up of the high-frequency intercept of the impedance spectra shown in figure 98.

- **SEM**

Cross sectional images of the tested symmetrical cell are shown in figures 100 and 101. The electrodes as well as the electrolyte had a thickness of approximately 50 μm. The first anode layer was able to fill most of the deep pores of the substrate. The three cell layers were well adhered to each other and the first anode layer was strongly adhered to the metal support. The electrolyte was able to bridge the areas were the first anode layer was uneven due to surface roughness; even though bridging the roughness created some large pores, short circuits between the two anodes were not observed in the examined cross section. The electrolyte contained some vertical cracks, possibly because caused by thermal shock during fabrication. Most of the vertical cracks propagated through the second anode layer. It can be observed that the electrolyte contains some porosity.
6.2.3 Discussion of LST results

Relatively uniform coatings of single phase LST with the targeted composition and porosity in the range of 32-52% were fabricated. However, additional microstructural development should be performed in order to further reduce the roughness of the coating. Tower-type structures were observed in the coatings, increasing the surface roughness and generating large voids throughout the coatings. VanEvery et al.[1] studied column formation in SPS coatings with nanometer-sized particle feedstock. Their hypothesis of the formation mechanism producing these defects suggested that the plasma drag forces could dominate the droplet inertia and re-direct the droplet velocity from normal to along to the substrate surface. Consequently, droplets impact preferentially on asperities. Initially, deposits formed on substrate asperities grow both laterally and vertically. During this time, the lateral growth of taller deposits may overcome shorter deposits. Among the remaining deposits of similar heights, the increase in drag forces generated by the decrease in spacing separating these structures reduces the plasma flowing between them. This process eventually causes the lateral growth to stop, leaving an inter-deposit gap and generating deposits that grow to become columnar structures separated by linear porosity bands [1]. This hypothesis seems to explain the large porosity observed in some areas of the LST coating shown in 86. The observation that the tower-type formation shown in figure 86 was located on top of a substrate asperity also coincides with this hypothesis. Additionally, this unique tower-type microstructure has been reported to produce coating surfaces with...
cauliflower-like formations [1,2]. Figure 102 shows the surface of an LST coating produced with 15 slpm of nitrogen atomizing gas. Cauliflower-shaped structures similar to the ones reported in [1,2] can be observed. Even though the final conditions used for the deposition of LST produced more uniform coatings, further microstructural development should be done in order to fully eliminate the presence of these rough surface features.

![Figure 102. Surface of an LST coating showing cauliflower-shaped structures.](image)

The EDS compositional analysis revealed that higher amounts of pore former tend to increase the extent of evaporation of strontium in the plasma, lowering its relative deposition efficiency. One possible explanation can be the extra enthalpy carried in the plasma due to the presence of higher amounts of a combusting material such as carbon. However, there was not a clear trend that allowed further conclusions to be made.

LST coatings fabricated by SPPS had reasonable electronic conductivities under reducing atmospheres. The low conductivities in nitrogen and air suggested that they are not potential candidates for use as an electronic conductor under highly oxidizing atmospheres. However, theoretical calculations of the equilibrium partial pressures of oxygen in the anode when extremely high fuel utilizations are reached suggest that for the most critical case, where the partial pressure of hydrogen reaches 0.01 atm with the balance being steam at 750°C (99% fuel utilization), the equilibrium partial pressure of oxygen would still be only $2.78 \times 10^{-16}$ atm. This partial pressure of oxygen is sufficient to oxidize nickel metal present in an anode based on the Ellingham diagram for the $\text{Ni} + \frac{1}{2} \text{O}_2 \rightarrow \text{NiO}$ reaction. However, this condition may still be sufficiently reducing for the LST coating to be an adequate electronic conductor. Based on the
high frequency intercepts of the impedance spectra shown in figure 99, the LST coating was still moderately conductive in a 4% hydrogen atmosphere. The series resistance decrease when the hydrogen in the atmosphere was varied from 4% to 100% was only 0.24 $\Omega \cdot \text{cm}^2$, suggesting that the decrease in the conductivity of the electrodes was not as large for the case of 4% hydrogen as it was for the conductivity measurements made in nitrogen or air. Furthermore, the nitrogen used for this study had approximately 1ppm of impurities according to the supplier’s specification. Assuming that the impurity in bottled nitrogen consists primarily of oxygen remaining from the air distillation process, a fuel cell test performed in 99% hydrogen and 1% nitrogen would be expected to expose the anode material to an oxygen partial pressure of $1 \times 10^{-8}$ atm. This condition is more oxidising than that theoretically expected at the anode exhaust (2.78$x10^{-16}$ atm) when 99% fuel utilization is reached at 750°C, with 99% steam and 1% hydrogen in the anode exhaust stream.

The conductivity of LST in all of the atmospheres tested was generally lower than the range of values reported in the literature [3,4]. A possible reason was the microstructural characteristics of the coating used for the conductivity measurements. The coating tested had a high surface roughness, and consequently, the actual contact area with the current collector may have been smaller than the planar geometrical area used in the conductivity calculations. Additionally, the tower-type formations may have reduced the connectivity of the solid phase in the horizontal direction of the coating, limiting the access of the current to only those parts of the coating in direct contact with the current collector mesh.

The impedance measurements suggested that the pure SPPS LST fabricated in this study was not a good catalyst of the hydrogen oxidation reaction. A high polarization resistance of approximately 93$\Omega \cdot \text{cm}^2$ at 750°C in pure H$_2$ was calculated. However, it was shown to be a potential electronic conductor in slightly oxidizing conditions. Further work remains to be done in order to improve the performance of SPPS LST. Additions of an ionically conducting phase and possibly of small amounts of a more catalytically active material to enhance the performance could be explored.
6.3 LSBT

6.3.1 LSBT Coatings

SPPS LSBT coatings were deposited with the plasma spray conditions shown in table 29 and an LSBT solution flow rate of 42 g/min with a concentration of 1.08 mol/L. The composition targeted was La$_{0.3}$Sr$_{0.55}$Ba$_{0.15}$TiO$_3$$_{3+\delta}$. Carbon black suspension was used as a pore former at a flow rate of 39 g/min. The LSBT/CB feed mass ratio used was 1.84.

- XRD

Figure 103 shows an XRD pattern of an as-sprayed LSBT coating. The main peak of the perovskite structure is shown. No evidence of the presence of unwanted phases was observed in the 30-32° range where the main impurity peak is normally found for La$_2$O$_3$, the most common phase impurity in plasma sprayed La-containing perovskites.

![XRD pattern of an LSBT as-sprayed coating.](image)

- SEM

Cross section SEM images of typical LSBT coatings produced with the conditions shown in table 29 are shown in figures 104-106. The deposition efficiency was approximately 55 % for each coating. The average thickness of these coatings was 47μm. The ceramic material was well mixed with the pore former. The coatings were well-adhered and followed the roughness features of the substrate. There was some bridging of the irregularities of the substrate, which can be
beneficial in the case of porous substrates, reducing the irregularities propagated to subsequent layers. Some small horizontal cracks were found along with some larger inter-splat porosity.

![Image](image1.png)

**Figure 104. Typical LSBT coating, magnification 2500x.**

![Image](image2.png)

**Figure 105. Typical LSBT coating, magnification 250x.**

![Image](image3.png)

**Figure 106. Typical LSBT coating, magnification 1000x.**

- **EDS**

Figures 107-110 show the results of the EDS analysis for coatings with LSBT/CB mass feed ratios of 1.86 and 2.34, when the LST solution composition for a targeted LSBT/CB mass ratio of 1.8 was used. It can be observed that the atomic fraction deviation from the target of the four
elements (La, Sr, Ba and Ti) varies with the LSBT/CB mass feed ratio. For the two LSBT/CB mass ratios tested, the barium deposition efficiency was lower than expected. The recipe shown in table 3 was readjusted to use an LSBT/CB mass feed ratio of 1.86, because it was considered the coating with the best microstructure obtained. For an LSBT/CB mass ratio of 1.86, the relative deposition efficiencies were 94%, 83%, 35%, and 95% for lanthanum, strontium, barium, and titanium respectively, relative to the overall cation deposition efficiency in the solution. It should be noted that these values apply only for the plasma spray conditions listed in table 29; different plasma spray conditions will also influence the relative deposition efficiencies of each element.

![La Deviation](image)

**Figure 107. Deviation from the lanthanum targeted atomic fraction calculated by EDS in an LSBT coating.**

![Sr Deviation](image)

**Figure 108. Deviation from the strontium targeted atomic fraction calculated by EDS in an LSBT coating.**
Figure 109. Deviation from the barium targeted atomic fraction calculated by EDS in the LSBT coating.

Figure 110. Deviation from the titanium targeted atomic fraction calculated by EDS in the LSBT coating.

6.3.2 LSBT Symmetrical cells

Electrochemical testing was conducted to characterize LSBT coatings as anode materials. Symmetrical cells were fabricated on porous stainless steel substrates as described in section 3.4.9.

- Impedance measurements

An LSBT/YSZ/LSBT symmetrical cell was heated to 650°C at a rate of 2°C/min in air and dwelled for 4 hours in order to burn out the carbon black in the anode layers. Nitrogen was then introduced and the air flow stopped, followed by the introduction of 4% hydrogen in nitrogen.
The cell was then ramped at the same rate to 750°C. Figure 111 shows an impedance spectrum of an LSBT symmetrical cell after dwelling for 24 hours in 99% hydrogen. Both anodes were sprayed with identical conditions.

**Figure 111.** Impedance measurements made on an LSBT symmetrical cell in a H₂ atmosphere.

**Figure 112.** Close-up view of the high frequency intercept of the impedance spectrum of an LSBT symmetrical cell in a H₂ atmosphere.
SEM

Cross sections of the tested symmetrical cell are shown in figures 113 and 114. The electrodes as well as the electrolyte had a thickness of approximately 50 μm. The first anode layer was able to fill most of the deep pores of the substrate. The three layers were well adhered to each other and the first anode layer was also strongly adhered to the metal support. The electrolyte was able to bridge the areas where the first anode layer was uneven due to tower-type formations, and no short circuits between the two anodes were observed in the examined cross section. The electrolyte had slightly fewer vertical cracks than the LST symmetrical cell, and it also contained small pores.

![Figure 113. LSBT symmetrical cell, magnification 250x.](image1)

![Figure 114. LST symmetrical cell, magnification 800x.](image2)

6.3.3 Discussion of LSBT results

Relatively uniform coatings of single phase LSBT were produced successfully by SPPS. More optimization of the feedstock composition needs to be done in order to obtain the targeted amount of barium doping. The LSBT coating was very similar in its microstructural characteristics to the LST coating. A large amount of tower-type formations can be observed in the LSBT coating (e.g. see figure 113). Additionally, considerable concentrated porosity aligned in the horizontal direction (parallel to the plane of the coating) was observed. A possible reason could be particles that were not directly in the center of the plasma jet, leading to a lower extent of heating and melting, and causing additional porosity between the splats deposited by each
pass of the torch, in addition to the usual inter-splat porosity within each individual torch pass. Further microstructural development should be performed in order to improve the uniformity of the LSBT coatings and to reduce the inter-splat separation observed in the regions of aligned porosity, which can be detrimental for the performance and the conductivity of the electrode, reducing the area of reaction sites and the conductivity and percolation of the solid phase.

The impedance measurements shown in figures 111 and 112 of the cell shown in figures 113 and 114 suggested that SPPS LSBT is more catalytic towards the hydrogen oxidation reaction than SPPS LST. The polarization resistance was estimated to be approximately 60 Ω.cm². Addition of an ioniically conducting phase and possibly of small amounts of a more catalytic material could enhance the performance significantly. The high frequency intercept was 1.6 Ω.cm² in 99% hydrogen, compared to 1.17 Ω.cm² in 100% hydrogen for LST. Since the electrolyte was sprayed simultaneously with the LST symmetrical cell and the LSBT electrodes were approximately 8 μm thinner than the LST electrodes, this difference in the series resistance suggests that the LSBT may be somewhat less conductive than LST.

6.4 LSFCr

6.4.1 LSFCr Coatings

SPS LSFCr coatings were deposited with the plasma spray conditions shown in table 30, with a suspension flow rate of 66 g/min and a concentration of 3 vol. %. The composition targeted was \( \text{La}_{0.30}\text{Sr}_{0.70}\text{Fe}_{0.70}\text{Cr}_{0.30}\text{O}_{3-\delta} \). Carbon black suspension was used as a pore former at a flow rate of 30 g/min. The LSFCr/CB mass feed ratio used was 6.16.

- **XRD**

Figure 115 shows an XRD spectrum of an as-sprayed LSFCr coating. No presence of unwanted phases was observed.
• EDS

Figures 116-119 show the results of the EDS analysis for coatings with no carbon black and with an LSFCr/CB mass feed ratio of 6.16, when the recipe used contained the targeted stoichiometry. It can be observed that the atomic fraction deviation from the target values of the four elements varies with the LSFCr/CB mass feed ratio. The amount of carbon black included in the coating was small; therefore, the changes in atomic fraction obtained were small for the different mass feed ratios. For both cases, the chromium deposition efficiency was lower than expected.
Figure 117. Deviation from the strontium targeted atomic fraction calculated by EDS in the LSFCr coating.

Figure 118. Deviation from the iron targeted atomic fraction calculated by EDS in the LSFCr coating.
**Figure 119. Deviation from the chromium targeted atomic fraction calculated by EDS in the LSFCr coating.**

- **SEM**

Cross section SEM images of typical LSFCr coating produced with conditions shown in table 30 are shown in figures 120-122. The deposition efficiency was approximately 50%. The average thickness of the coating shown in the figures 120-122 was 72μm. The coating was fairly dense with the presence of large clumps. The coating was strongly adhered and it followed the contour of the substrate. Small vertical and horizontal cracks were found throughout the coating, possibly because of thermal shock during fabrication.

![Cr Deviation Chart](image1)

![SEM Image](image2)

**Figure 120. LSFCr coating showing cone-shaped defects.**
Figure 121. Typical LSFCr coating, magnification 250x

Figure 122. Typical LSFCr coating, magnification 100x

- Porosity

Figure 123 shows a micrograph used to determine the porosity obtained with an LSFCr/CB mass feed ratio of 6.16. Figures 124 and 125 show the selections of the lower and upper porosity limits, respectively. The color blue represents the porosity and the color red represents the solid. For this case, the low threshold resulted in a porosity estimate of 22% and the high threshold resulted in a porosity estimate of 27%. The average of these two values was calculated, resulting in an estimated porosity of 25±3%.

Figure 123. LSFCr image for porosity identification
Conductivity measurements of the LSFCr coating shown in figures 120-122 were performed. The LST/CB mass feed ratio used to fabricate the coating was 6.16. An average thickness of 72 μm and porosity of 25% were determined using image analysis.

The coating was first heated in air from room temperature to 650°C for 4 hours to burn out the carbon black contained in the coating. Figure 126 shows the result of the conductivity measurements in air at temperatures ranging between 650°C and 800°C. After 70 hours, the atmosphere was switched to nitrogen. The conductivity rapidly decreased from 0.18 S/cm to 0.008 S/cm. Similarly, low values of conductivity were measured during exposure to 4% and 100% hydrogen. After 126 hours of testing, the atmosphere was switched back to air, and the conductivity in the temperature range from 650°C to 750°C increased to slightly higher values than the first time that the sample was exposed to air. When the sample was exposed to nitrogen followed by 4% hydrogen for the second time, the conductivity decreased again to values on the order of 0.003 S/cm. The conductivity showed an increase in the conductivity with increased temperature in all of the atmospheres except for the last exposure to 100% hydrogen, in which
the conductivity did not show any dependence with temperature and was unstable, ranging from values of approximately 0.004 S/cm to 0.003 S/cm.

![LSFCr Conductivity](image)

**Figure 126. Conductivity measurements made on an LSFCr coating in H₂, N₂, and air atmospheres, after oxidation.**

6.4.2 LSFCr Symmetrical cells

Electrochemical testing was conducted to characterize the LSFCr as an anode material. Symmetrical cells were fabricated on porous stainless steel substrates as described in section 3.4.9.

- **Impedance measurements**

The cell was heated to 650°C at a rate of 2°C/min in air and dwelled for 4 hours in order to burn out the carbon black in the anode layers. Nitrogen was then introduced and the air flow stopped, followed by the introduction of 4% hydrogen in a balance nitrogen atmosphere. The cell was then ramped at the same rate to 750°C. Figure 127 shows impedance spectra of an LSFCr symmetrical cell after dwelling for 24 hours in 4% hydrogen and after dwelling for 24 hours (red) and 48 hours (green) in 100% hydrogen. Both anodes were sprayed with identical conditions.
Impedance measurements were also made in air at 650°C and 750°C to evaluate the performance of LSFCr as a cathode. Figure 128 shows the impedance of the cell after the burning of the pore former step at 650°C (blue), at 750°C in air after 72 hours of exposure to hydrogen (green), and lastly, at 650°C after 24 hours of exposure to air (red).
• SEM

Cross section images of the tested LSFCr symmetrical cell are shown in figures 129 and 130. The electrodes and the electrolyte had a thickness of approximately 72 and 40 μm, respectively. The first anode layer was able to fill the deep pores of the substrate and it was strongly adhered to the metal support. Severe vertical cracking was found starting at the first anode layer and propagating all the way to the surface of the cell, likely due to thermal shock during fabrication resulting from the low thermal conductivity of the ceramic layers and high heat impulses into the coating. The porosity of the layers was approximately 25%. Cone shaped defects were observed along the surface of the cell.

Figure 129. LSFCr symmetrical cell, magnification 100x.

Figure 130. LSFCr symmetrical cell, magnification 500x.

6.4.3 Discussion of LSFCr results

Relatively uniform SPS coatings of single phase LSFCr with porosity in the range of 22-27% were fabricated. Formation of large cone-shaped clumps was observed, as shown in figure 120. The formation mechanism for these defects is believed to be different than that of the surface roughness features in the LST and LSBT coatings, since the feedstock suspension had a particle size distribution with a d(0.5) of 4.752 μm, as shown in figure 131. With this particle size distribution, it is highly feasible that the droplets in the plasma jet had sufficient inertia to reach the substrate without being carried laterally by the plasma gas impacting the substrate.
In the case of the LSFCr coatings, splashing is believed to be the cause of the cone-shaped large clumps observed in the coating. Ondrej Racek [5] studied the splashing phenomenon. The hypothesis of the formation mechanism of these defects suggests that droplets or fragments of splashed or fractured particles are responsible for the effect. Since the trajectories of the splashed particles are more parallel to the substrate than the trajectories of larger incoming droplets, they are deposited primarily on surfaces inclined to the substrate plane, such as the sides of a substrate protrusion. Microstructural analysis of the rough coatings revealed that the speckles corresponding to splashed droplets often originated at a substrate protrusion and grew in size progressively with coating deposition, forming an approximately conical volume of aligned porosity. Analysis of different spray conditions and the corresponding microstructures obtained indicated that under certain conditions, usually when spray parameters associated with higher particle velocities are used, there is a stronger tendency of the droplets to splash when impacting the substrate surface [5].

![Particle Size Distribution](image)

**Figure 131. Particle size distribution of the LSFCr suspension.**

The high level of melting of the splats observed in the LSFCr coating, due to the high torch power and plasma enthalpy used, may have favoured conditions for the splashing phenomenon. Longer standoff distances and plasma spray condition that lower the particle velocity have been recognized to reduce the splashing effect [5]. Additional microstructural development of LSFCr coatings taking into account this consideration could be performed in order to reduce these types of defects. Larger amounts of pore former could also be included in order to further increase the porosity of the LSFCr coatings.

Regarding the compositional analysis of LSFCr coatings, similarly to the case of LST, the addition of carbon black significantly boosted the evaporation of strontium in the plasma,
lowering the atomic fraction of Sr by approximately 0.05. For all of the fabrication conditions tested, the chromium deposition efficiency was lower than expected. Since the LSFCr suspension was made from powder fabricated in house by solid state reaction synthesis, further investigations should be done in order to determine if the change in the composition occurred during the synthesis process or during the plasma spray process. It is possible that chromium, may become deficient due to volatilization during either sintering or during plasma.

SPS LSFCr showed a maximum conductivity of 0.18 S/cm at 800°C in air. This value is lower than the desired value for an electronic conductor material for the anode. In hydrogen, the conductivity decreased to values as low as 0.008 S/cm. The measured conductivity of the LSFCr coating was lower than the conductivity values reported in the literature of approximately 6.5 S/cm at 750°C for both air and hydrogen atmospheres. One possible explanation could be the different composition obtained after the loss of chromium and strontium that may have affected the properties and the stability of the material. There, further adjustment to the synthesis process is needed to compensate for the Cr and Sr losses.

Impedance measurements of SPS LSFCr coatings suggested that LSFCr alone is not catalytic towards hydrogen oxidation. This result contrasts with data from the literature that suggested LSFCr as a mixed ionic and electronic conductor with good catalytic activity to the hydrogen oxidation reaction [5,6]. However, the impedance measurements carried out under air atmospheres suggested excellent catalytic activity for the cathode reaction and with an apparently reversible performance after exposure to hydrogen. Similarly, the conductivity measurements demonstrated that the conductivity in air was completely reversible after reduction. It has been previously reported that a reversible phase change occurs during hydrogen exposure, as observed by Jacob Haag et al.[8]. In that study, they found that La_{0.30}Sr_{0.70}Fe_{0.70}Cr_{0.30}O_{3-δ} perovskite was stable down to a pO_2 of 10^{-20} atm at 800°C, at which point a spinel phase formed and further reduction led to the formation of Fe metal. They also observed that the phase separation of La_{0.30}Sr_{0.70}Fe_{0.70}Cr_{0.30}O_{3-δ} was completely reversible with an increase in the partial oxygen pressure and re-oxidation of the material [8]. However, XRD performed after the symmetrical cell test in this study revealed the presence of decomposition of LSFCr even after its re-oxidation, as shown in figure 132. In the case of the SPS LSFCr composition obtained in this study, even though the conductivity and polarization resistance
results suggested that the properties of the coating were reversible after its exposure to hydrogen, the phase change that occurred did not appear to be fully reversible.

Further compositional and porosity optimization should be done in order to determine if SPS LSFCr is a potential anode material for high fuel utilization conditions.

Figure 132. XRD pattern of an LSFCr symmetrical cell after electrochemical testing.
6.5 References


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Chapter 7
Conclusions

7.1 Conclusions and future work

SOFCs able to operate under high fuel utilization conditions are desirable because they would allow emissions from common afterburners to be eliminated, and the exhaust gases from the complete energy conversion process would be cleaner, and potentially suitable for carbon sequestration. Moreover, a more complete conversion of the fuel to CO\textsubscript{2} and water will produce electricity more efficiently.

This study used a finite element SOFC model to evaluate the electrochemical behaviour of an in-plane graded anode architecture with a transition in the direction of the fuel flow path from Ni-GDC to LSCM-GDC, the latter being a material more stable in oxidizing conditions. The results suggested that anode segmentation and transition of materials with different electrical properties was potentially feasible, since no abnormal behaviours or unpredictable voltage losses were observed when the voltage and current distribution changed along the fuel path as a consequence of high levels of fuel consumption.

A previous model was modified to incorporate the segmented anode geometry and varying concentrations of reactants along the flow channels. The modified model was then validated and input parameters further modified by comparison with experimental results presented by P Metzger et al. [1] at the German Aerospace Center (DLR). Excellent agreement of the electronic current density produced was obtained between the modeled and the experimental cell in the range of 10\% to 100\% mole fraction of hydrogen in the fuel channel. Small deviations in the results were found at extremely low concentrations of hydrogen, possibly because of diffusion limitations dominating the performance of the experimental cell, in contrast to the model, which assumes that charge transfer is the rate limiting process.

Further improvements were made to the model, including considerations of variations of the Nernst potential as a function of the partial pressure of the fuel, and the inclusion of a function for a three-component gas diffusion coefficient for the anode channel that depends on the partial pressure of the fuel. Further geometric modifications and inclusion of interconnects were also completed.
Once the feasibility of this anode architecture was assessed with the electrochemical model, work began on fabricating anode materials suitable for use in conditions of high fuel utilization, by atmospheric plasma spraying of liquid feedstocks.

Initial screening experiments were designed to improve the understanding of the relationship between the different plasma spray parameters and the coating microstructures and compositions. The effect of plasma gas compositions, torch power, nozzle size, feedstock flow rate, solution concentration, atomizing gas flow rate, and standoff distance on the deposition efficiency, composition, phases, and microstructure of LST, LSBT and LSFCr coatings was investigated.

Furthermore, studies on the influence of additions of carbon black as a pore former on the final microstructure and deposition efficiency of LST coatings were performed. With the best spray conditions found, carbon black pore former was able to successfully introduce porosity in the range of 38-44% with only small decreases in the deposition efficiencies of the coatings.

EDS analysis was performed for LST, LSBT, and LSFCr coatings, and it was found that the relative deposition efficiencies of the different elements were dependent on the mass ratio of the ceramic material and the pore former. Optimization of the initial recipes in order to account for the losses was performed.

Microstructural analysis revealed relatively uniform coatings for the three materials developed, with the presence of certain surface roughness features. The surface roughness observed in the SPPS LST and LSBT coatings was characteristic of tower-type formations. The mechanism of formation of those features was believed to be the low momentum of the solution droplets in the plasma jet, causing the droplets to be carried away laterally by the plasma when reaching the substrate and depositing on top of nearby asperities. On the other hand, the surface roughness found in the SPS LSFCr coating was cone shaped and more characteristic of the splashing phenomenon. It was assumed that the mechanism of formation of those features was high power plasma spray conditions that increased the velocity of the particles and lowered their viscosity, increasing the susceptibility of the melted droplets to splashing. Fragmented splashed or fractured particles were believed to be responsible for the effect that led to the cone-shaped formations.
Conductivity measurements were performed on the three materials developed. LST showed a maximum conductivity of 2.15 S/cm in hydrogen at 650°C. LSFCr showed a maximum conductivity of 0.18 S/cm in air at 800°C.

Impedance measurements were carried out for the three materials developed. Results did not show good catalytic activity towards the hydrogen oxidation reaction with any of the as-sprayed coatings, although LSFCr showed good catalytic activity towards oxygen reduction in air.

The most important work recommended to be performed in the near future is the evaluation of the conductivity and electrochemical behavior of these three materials in conditions more comparable to those that would exist in a high fuel utilization SOFC. For example, high steam/hydrogen ratios and high polarization losses in the case of electrochemical testing. The results obtained in the conductivity and electrochemical evaluation in this work may not accurately represent the conditions that would exist in a real high fuel utilization cell. For example, LSFCr showed very little catalytic activity towards the hydrogen oxidation reaction, but it has been reported as unstable when strongly reducing conditions exist [2]. Intermediate atmospheres could ensure stability of the structure of LSFCr and consequently improved performance. Similarly, LST was shown to have a low electronic conductivity in air, but it is not yet understood how it would behave under intermediate P_{O2} atmospheres.

Additionally, inclusion of ionically conductive phases can be explored for the materials developed in this work to improve the electrochemical performance. Most anode materials, even highly catalytic ones such as nickel, are used in composite anodes together with an ionically conductive phase to increase the electrochemically active surface area at the three-phase boundaries. This approach will need to be used with the synthesized anode perovskite materials studied in this work as well.

Additional compositional development could be done in LST, LSBT, and LSFCr coatings to better to replicate the compositions reported in the literature and to compare the properties of sprayed coatings with those of sintered samples. For example, Cheng-Xin Li et al. [3] obtained results that showed that the electrical conductivity of plasma-sprayed LSCo coatings was lower than that of sintered bulk material with the same composition, and that the dependence of electrical conductivity of plasma-sprayed LSCo on temperature was also different from that of sintered materials. Similar observations were reported in [4]. Moreover, Chao Zhang et al. [5]
found anisotropy of the electrical conductivity, and attributed it to the phases of different properties in the composite coating and to the APS coating structure characteristics. For the same LSM/YSZ specimen, they measured that the electrical conductivity perpendicular to the plane was less than one-tenth of that in the plane.

Finally, the ultimate objective of this work is to fabricate a cell with an in-plane graded anode architecture suitable for high fuel utilization conditions. Once the individual materials for each segment of the anode are successfully developed and evaluated in the respective conditions, work needs to be done to adjust the plasma spray process to fabricate larger area (possibly 5 cm x 5 cm) square cells to be able to produce prototypes of this new architecture concept.

7.2 Contributions

Original research contributions of this thesis include:

- Modifications of an existent SOFC model to include variations in the Nernst potential corresponding to changes in the concentrations of the fuel along the fuel flow channel, and the consideration of a three-component gas in the hydrogen bulk diffusivity in order to allow dilution of hydrogen in nitrogen.

- Validation of a modified SOFC finite element model by fitting results with an experimental cell tested by DLR.

- Demonstration of the feasibility of an in-plane graded architecture for SOFC anodes through simulations made with the validated SOFC finite element model.

- Use of atmospheric axial injection SPPS to produce single phase porous LST and LSBT coatings and symmetrical cells.

- Use of atmospheric axial injection SPS to produce single phase porous LSFCr coatings and symmetrical cells.
7.3 References


