Computational Fluid Dynamics Analysis on Transport Phenomena in Solid Oxide Electrochemical Cells

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Al mirall no hi ha cap imatge del teu enigma

Salvador Espriu
Abstract

The thesis comprises an analysis of the heat transfer phenomenon in solid oxide fuel cells (SOFCs) and a description of various transport phenomena in a solid oxide electrolysis cell. Both devices are encompassed under the solid oxide electrochemical cell concept. Moreover, a CFD model of an SOEC was developed to study the behavior of the cell under different conditions of operating and structural parameters.

In the first part, the different heat sources that take place within an operating SOFC have been described together with the regions where they are located with special attention on their relationship with the chemical and electrochemical reactions that occur in an SOFC. The kinetics of the internal reforming reactions and of the electrochemical reactions are believed to be one of the main issues for improving the SOFC performance. A literature study on the different kinetic expressions based on the overall reaction schemes for methane steam reforming reaction in Ni-YSZ catalysts on SOFC anodes has been performed revealing the difficult comparison between the reported reaction rate expressions due to different experimental conditions. Furthermore, from a CFD analysis on a 2D planar SOFC, it is found that the main heat source contributor of the cell is the heat generation due to the electrochemical reactions followed by the heat consumption by the steam reforming reaction.

In the second part, various transport processes in SOECs are described. Besides, a FVM based CFD model was developed and applied for a cathode-supported planar SOEC operating in cross-flow configuration arrangement. The behavior, in terms of current density, temperature distribution and the hydrogen production in an SOEC, has been investigated for different cases, such as varied operating voltages, the reduced porosity of the porous materials, the presence of hydrogen at the inlet of the cathode channel and in parallel-flow configuration. The predicted results show that higher current densities are obtained for higher operating voltages being the anodic current density higher than the cathodic one. However, no significant difference was observed when decreasing the porosity of the cell nor when hydrogen was present at the inlet of the cathode channel. Yet, the parallel-flow configuration yields lower current density values although they remain in the same order of magnitude as those from the cross-flow arrangement. The temperature simulation reveals various profiles depending on the operating voltage emphasizing the three thermal operating modes of an SOEC: endothermic, thermo-neutral and exothermic. A decrease in the porosity leads to higher temperature values in the cell due to an increase in the joule heating. The presence of hydrogen in the water channel inlet also gives higher temperature values. Per contra, the parallel-flow arrangement reveals a temperature decrease along the flow direction although operating in exothermic mode. Higher hydrogen molar fractions at the outlet of the cathode channel were obtained with higher operating voltages due to the higher current densities generated and the exothermic operating mode. However, no difference was observed when reducing the porosity value. The hydrogen fueled cell yields lower hydrogen production and so does the parallel-flow arrangement due to the lower current densities revealed.
List of publications


Nomenclature

\( A \)  Pre-exponential factor, \([A \cdot m^{-2}]\)
\( A_v \)  Active surface area-to-volume ratio, \([m^2 \cdot m^{-3}]\)
\( c_p \)  Specific heat at constant pressure, \([J \cdot kg^{-1} \cdot K^{-1}]\)
\( D_m \)  Mass diffusion coefficient, \([m^2 \cdot s^{-1}]\)
\( D_T \)  Thermal diffusion coefficient, \([kg \cdot m^{-1} \cdot s^{-1}]\)
\( E_A \)  Activation Energy, \([kJ \cdot mol^{-1}]\)
\( E^0 \)  Nernst potential, [V]
\( F \)  Faraday constant, \([C \cdot mol^{-1}]\)
\( G \)  Gibbs free energy, \([kJ \cdot mol^{-1}]\)
\( H \)  Enthalpy, \([kJ \cdot mol^{-1}]\)
\( h \)  Heat transfer coefficient, \([W \cdot m^{-2} \cdot K^{-1}]\)
\( h_v \)  Volumetric heat transfer coefficient, \([W \cdot m^{-3} \cdot K^{-1}]\)
\( i \)  Current density, \([A \cdot m^{-2}]\)
\( i_0 \)  Exchange current density, \([A \cdot m^{-2}]\)
\( J \)  Mass diffusion flux, \([kg \cdot m^{-2} \cdot s^{-1}]\)
\( j \)  Volumetric current density, \([A \cdot m^{-3}]\)
\( K \)  Permeability, \([m^2]\)
\( K_{eq} \)  Equilibrium constant, dimensionless
\( k \)  Thermal conductivity, \([W \cdot m^{-1} \cdot K^{-1}]\)
\( k_i \)  Reaction rate constant, \([mol \cdot m^{-3} \cdot Pa^{-2} \cdot s^{-1}]\)
\( M_i \)  Molar mass of species \( i \), \([kg \cdot mol^{-1}]\)
\( N \)  Number of species \( i \) in the gas mixture, dimensionless
\( n_e \)  Number of electrons transferred per reaction, dimensionless
\( P \)  Pressure, [bar]
\( P_i \)  Partial pressure, [bar] or [Pa]
\( Q \)  Heat source or flow, \([W \cdot m^{-3}]\)
\( R \)  Ideal gas constant, \([J \cdot mol^{-1} \cdot K^{-1}]\)
\( r \)  Reaction rate, mainly \([mol \cdot m^{-2} \cdot s^{-1}]\)
\( S \)  Entropy, \([kJ \cdot mol^{-1} \cdot K^{-1}]\)
\( S_d \)  Source term for momentum conservation equation, \([W \cdot m^{-3}]\)
\( S_m \)  Source term for the mass conservation equation, \([kg \cdot m^{-3} \cdot s^{-1}]\)
\( S_T \)  Source term for the energy conservation equation, \([W \cdot m^{-3}]\)
\( S_\Phi \)  Source term for charge transfer equation, \([A \cdot m^{-3}]\)
\( T \)  Temperature, [K]
\( t \)  Time, [s]
\( U \)  Velocity vector, \([m \cdot s^{-1}]\)
\( V \)  Voltage, [V]
\( v \)  Diffusion volume, \([cm^3 \cdot mol^{-1}]\)
\( Y_i \)  Molar fraction of species \( i \), dimensionless

Greek letters

\( \alpha \)  Reduction/oxidation transfer coefficient, dimensionless
\( \beta \)  Symmetry factor, dimensionless
\( \varepsilon \) Porosity of the porous material, dimensionless
\( \eta \) Polarizations, [V]
\( \mu \) Dynamic viscosity, [Pa \cdot s]
\( \rho \) Density, [kg \cdot m^{-3}]
\( \sigma \) Electric conductivity, [S \cdot m^{-1}]
\( \Phi \) Potential, [V]

**Subscripts & superscripts**

- \( \text{act} \) Activation
- \( \text{an} \) Anode
- \( \text{b} \) Bulk
- \( \text{cat} \) Cathode
- \( \text{conc} \) Concentration
- \( \text{eff} \) Effective
- \( \text{g} \) Gas phase
- \( \text{i} \) Gas species \( i \)
- \( \text{j} \) Gas species \( j \)
- \( \text{por} \) Porous phase
- \( \text{s} \) Solid phase
- \( \text{0} \) Standard conditions
- \( \Omega \) Ohmic

**Abbreviations**

- CFD Computational fluid dynamics
- ER Electrochemical reaction
- FVM Finite volume method
- HTE High-temperature electrolysis
- IT Intermediate temperature
- LSM Strontium-doped lanthanum manganite
- LT Low temperature
- MSR Methane steam reforming
- OCV Open circuit voltage
- PEMFC Proton exchange membrane fuel cell
- SIMPLE Semi-implicit method for pressure-linked equations
- SOEC Solid oxide electrolysis cell
- SOFC Solid oxide fuel cell
- S/C Steam-to-carbon ratio
- TPB Triple-phase boundary
- WGS Water-gas shift
- YSZ Yttria-stabilized zirconia
### Chemical species & compounds

<table>
<thead>
<tr>
<th>Chemical Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>Cerium (IV) oxide</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Methane</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Cu</td>
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<td>e$^-$</td>
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<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>O$_2$</td>
<td>Oxygen</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>Oxide ion</td>
</tr>
</tbody>
</table>
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Chapter 1

Introduction

One of the most common questions humans ask, meaning by humans: friends, family members and such, after some time without communication or just by simple interest or education, apart from the typical How are you?, is What are you doing right now? What are you working with? and here starts my headache.

My first response is I work with fuel and electrolysis cells followed with nearly no pause with the question Do you know what they are? Almost everybody, without need of a survey, stare back at me with a crooked grin on their faces. Well, I guess you have heard about the cars than run on hydrogen rather than gas... I pronounce with a big smile, as a technique to make the words fuel cell and electrolysis cell a bit more friendly to the public. At this point, some faces start to illuminate and sparkling eyes lead nodding heads followed by a relieve in my face. But the conversation never ends up here. It does not because I know, as a fuel and electrolysis cell supporter, that I should go a bit further, promote and divulgate the cells despite the big effort it requires. Moreover, at this point, people get interested into the topic and more questions arise: But how do they really work? How do you produce the hydrogen to fuel the car? Why cannot we buy cars like that yet as we have heard about these fuel cells for some time now? Can they be used for something else than in cars?, etc.

After two years dealing with the same questions I still cannot say that scientists and engineers, researchers throughout the world, can explain the complex world of fuel and electrolysis cells without leaving no stone unturned. Fuel and electrolysis cells are very complex devices which present many advantages compared to conventional power generation devices or fuels based on carbon based compounds, or in other words, petroleum related. Whether we like it or not, and despite the fact that some countries and organizations are really betting for green or renewable energies, the world still relies on oil. Hopefully, some time soon, roles will change.

As a simply definition, fuel cells can be understood as a device that is able to convert, by chemical reactions, the energy in a fuel to electrical energy without the need of any mechanical process. The main fuel is hydrogen although other fuels
1. Introduction

can be used. Nevertheless, if other fuels are used, chemical reactions convert these fuels into hydrogen, leaving hydrogen as the fuel that can be directly fed into the fuel cell. Different types of fuel cell exist according to the operating temperatures and materials used in the cells. As mentioned, hydrogen is the star fuel of fuel cells and thus, one of the big headaches is the availability of hydrogen. Sticking into the green world concept, electrolysis, or obtaining hydrogen from water after applying an electrical current to break water molecules, seems to be a concept directly related to fuel cells. And it is. Still, electricity is required for the electrolysis of water and to be consistent in terms of environmental friendliness, we do not want to use electricity that comes from the combustion of some gas-derived fuel if we want to obtain hydrogen so that our cars can run without emitting pollutant gases, the electric current must be generated from other renewable energies. Solar energy, wind power, hydropower or other resources can provide the required electricity for the electrolysis of water while the available high temperature heat waste from industry can be used if the electrolysis is performed at high temperatures.

Solid oxide fuel cells operate at high temperatures and have many different applications. Moreover, if they operate in reverse mode, they are known as solid oxide electrolysis cells. In this case, obtention of hydrogen takes place from the electrolysis of water steam at around 800 °C. The work presented in the thesis is based on these two devices and hopes to provide a bit of light to the remaining dark sides of solid oxide electrochemical cells.

1.1 Research Objectives

The objectives of the research carried out are to study the different elements that contribute to the heat transfer phenomenon in a solid oxide fuel cell, with special emphasis to the effects of chemical and electrochemical reactions, and develop a numerical model on the macroscale level of a solid oxide electrolysis cell to analyze the transport processes that take place in the device.

More specifically, the aims are:

- Analyze the heat transfer phenomenon in a solid oxide fuel cell (SOFC) device. Determine which elements contribute to this phenomenon and where they are located in the cell. Estimate the contribution of each element on a 2D macro-scale SOFC model.

- Determine the relationship between the chemical and electrochemical reactions in an SOFC and the effects on the heat transfer phenomenon. Provide different solutions to optimize the reforming reactions with special attention to the reaction kinetics.

- Develop a 3D macro-scale model for a planar cathode-supported solid oxide electrolysis cell (SOEC) to investigate the transport processes associated to the electrochemical reactions that take place in the device. Study the effect of different operating voltages and fuel concentrations on the transport phenomena and overall cell performance.
To this end, a complete macro-scale 3D model considering all the transport processes that occur in a SOEC was developed whereas a deep analysis on the heat transfer phenomenon was performed on an SOFC.

1.2 Methodology

In order to analyze the different transport phenomena and chemical reactions for a whole unit cell device, an SOFC or an SOEC, there is a need for computational or numerical models in which the different transport phenomena are coupled.

An analysis of the heat transfer phenomenon was performed on an SOFC unit. The effects of the electrochemical and the chemical reactions were considered together with the different polarizations or voltage losses that take place in an SOFC. Furthermore, a numerical study was performed to evaluate the contributions from each heat source element in the cell. The study was performed based on a 2D computational fluid dynamics (CFD) model developed in COMSOL Multiphysics, by the finite element method (FEM), for an anode-supported SOFC operating under co-flow conditions and fueled with pre-reformed natural gas. The unit cell is represented by a cathode, an anode and an electrolyte and surrounded by the interconnects. Air and fuel channels were also considered. Momentum, mass and heat transport together with the chemical and electrochemical reactions were solved together.

A macro-scale CFD model was further developed in ANSYS FLUENT, based on the finite volume method (FVM). The model was applied for a cathode-supported 3D planar SOEC. The unit cell in the model consists of an anode, a cathode, an electrolyte and two interconnects. It contains also a fuel or water channel and an air channel. Momentum, heat, mass and charge transfer coupled with the electrochemical reactions were simulated and solved simultaneously. Different operating voltages as well as different fuel compositions were implemented to study the effects on the transport processes and the cell performance. The effect of different flow configurations, cross-flow and co-flow, was also evaluated.

1.3 Thesis Outline

In Chapter 2, a general description of solid oxide fuel cells and solid oxide electrolysis cells is provided. A brief summary of different modeling methods as well as a concise literature review on both cell devices are included. A detailed analysis on the heat transfer phenomenon in SOFCs is carried out in Chapter 3 with special remark on the different sources that contribute to this transport phenomenon. Chapter 4 presents the different transport phenomena that take place in an SOEC and their governing equations. The SOEC macro-scale model used for the work is presented and described in Chapter 5. In Chapter 6, the results of the SOEC macro-scale model are presented and discussed. Finally, Chapter 7 presents the conclusions drawn from the results obtained and ideas for future work are proposed as well.
Chapter 2

Introduction to Solid Oxide Electrochemical Cells

A brief description of solid oxide fuel cells and of solid oxide electrolysis cells is presented in the chapter. Similarities and differences between the two cells are highlighted. A short introduction into computational modeling is given for both types of cells followed by a precise review of existing models.

2.1 Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) are high-temperature electrochemical devices which convert chemical energy of fuels into electrical energy in an environmental friendly and efficient manner. For this reason and due to the depletion of fossil fuels, SOFCs are regarded as promising candidates for energy conversion and thus, for being able to obtain electrical power for our society in an environmental friendly way.

The invention of solid oxide fuel cells (SOFC) is not as recent as one can think of. In fact, the principle behind fuel cells dates from the 19th century [1]. Despite almost two centuries have passed, they are still nowadays not being commercialized in large scales. Many reasons can be given to the non-commercialization of SOFCs in large scales but the lack of sufficient knowledge of some phenomena that take place in an SOFC may be the key to the slow development of this technology. Other factors that can contribute to the moderate development can be the low market demand, the high cost, the small number of available commercial systems and the lack of successful designs.

Solid oxide fuel cells consist of two porous electrodes (an anode and a cathode) separated by a dense electrolyte and connected into an electrically conducting circuit, see Fig. 2.1. Moreover, gas channels appearing in interconnects contribute to the unit cell. Interconnects are used for the electrical connections between the adjacent cells in a stack, i.e. a group of cells.
2.1 Solid Oxide Fuel Cells

Figure 2.1: Schematic image of an SOFC with some details on surface chemistry.

Oxygen or air is supplied into the channel on the cathode side whereas the fuel (hydrogen, methane, methanol, etc.) is supplied into the fuel channel on the anode side. Oxygen molecules diffuse through the cathodic diffusion layer, the porous cathode, to the cathodic triple-phase boundaries (TPBs). The cathodic TPBs, also known as the cathodic active layer, is where the reduction of oxygen to oxide ions ($O^{2-}$) takes place. The electrons required are supplied by the oxidation of the fuel in the anodic active layer. The fuel molecules diffuse through the porous anode supporting structure, also known as the anode diffusion layer, to the anodic triple phase boundaries. If another fuel rather than hydrogen is supplied, reformation of the fuel, as further described, takes place in this porous region. Hydrogen molecules diffuse to the anodic TPBs where they are oxidized to water when reacting with the oxide ions that have diffused through the electrolyte from the cathodic TPBs.

SOFC electrodes consist of three-phase composites (an ion conducting, an electron conducting and a gas phase) creating a porous microstructure in order to allow the transport of ions, electrons and gases at the same time within the electrodes. It is widely assumed that the electrochemical reactions take place at the percolated TPBs where the ionic and the electronic pathways meet together with the gas phase. Electrode performance is determined by several factors but two of the primary factors are the abundance of TPBs and the transport properties of the mentioned phases and thus, the electrode microstructure is a key for improving the fuel cell performance. Porous composite structures have been developed to increase the length of TPBs in the electrodes. Nevertheless, the length of the TPB alone is not enough for characterizing an electrode as transport phenomena through the gas phase are also important. Due to the degree of complexity of the interactions between these and in order to be able to improve the cell performance, a deep understanding of the electrode microstructure is required in quantitative terms [2].

Electrochemical reactions are those chemical reactions that occur at sites where electrons, ions and chemical species coexist simultaneously. In SOFCs, these sites are known as triple-phase boundaries and one can differentiate the anodic TPBs,
located in the anode close to the electrolyte and the cathodic TPBs, located in the cell’s cathode.

The general electrochemical reaction of an SOFC is the oxidation of hydrogen, which is the driving force of the energy conversion in an SOFC device, and can be written as follows:

\[
H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)
\]  

(2.1)

This general electrochemical reaction consists of two semi-reactions that take place in the different electrodes of the fuel cell. The oxidation of hydrogen, Eq. (2.2), takes place in the TPBs of the anodic active layer while the reduction of oxygen, Eq. (2.3), occurs in the TPBs of the cathodic active layer.

\[
H_2(g) + O^{2-} \rightleftharpoons H_2O(g) + 2e^-
\]  

(2.2)

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

(2.3)

Despite the two semi-reactions that allow one to describe the general electrochemical reaction in the corresponding electrode, not much detail is given about the reaction mechanisms that constitute this reaction. It is not a matter of interest if a simulation at cell length scale is desired but, if numerical simulation at smaller scales, like pore scale, the reaction mechanisms, and thus, the different surface compounds that act as reactants and products at the same time, are of big interest.

Different existing reaction mechanisms try to describe the electrochemical phenomena taking place in the anode and in the cathode of the fuel cell without a clear consensus on which is the most accurate one. Thus, different surface compounds are suggested under different assumptions stating that nothing is clear in this field when going down into details of the reaction mechanisms. However, the general reaction can always be used but if the performance of SOFCs must be improved, the understanding of the reaction mechanism for this reaction is the key to success. Yet, the electrochemical reactions are not the only chemical reactions that take place at the electrodes of the fuel cells. The other main group of reactions are the reforming reactions. Both of these types of reactions; the electrochemical and the reforming reactions, are known as surface reactions because both take place at the surface of the electrodes, mainly at the anode, and thus the active surface is very important.

One of the main characteristics of SOFCs is that they are operating at high temperatures. The fact that these cells initially operated at temperatures around 1000 °C is due to the material of the electrolyte used, yttria-stabilized zirconia (YSZ). This is a ceramic material which becomes conductive to oxygen ions at certain temperatures and non-conductive to electrons as well as the anode and cathode materials. Thus, electrochemical reactions can take place at the electrodes without the need of expensive catalysts. In fact, the anode material (usually Ni-YSZ) is catalytic itself for both the internal reforming and electrochemical reactions that take place while strontium-doped lanthanum manganite (LSM) is the the
common material for the cathodic electrode. The limited range of the available materials to operate at high temperatures is one of the major limitations to mass production of SOFCs due to the material cost and thermal management issues. Nevertheless, long starting time is required for high temperature SOFCs and thermal control becomes difficult despite the high thermal efficiency and long-term stability. In order to be able to mass produce SOFCs, a substantial reduction in the system cost (cell and stack production processes) is required. One way to reduce the costs is by reducing the material costs and increase the durability of the cells. This can be done by reducing the operating temperature to an intermediate temperature, 600-800 °C (IT-SOFC), or even lower than 600 °C, (LT-SOFC). When the temperature decreases, the overall performance is reduced because the electrolyte resistance increases and the reactions at the electrode become weaker [3, 4]. Another benefit of operating at lower temperatures is the availability of other materials, apart from Ni-YSZ and LSM, that can be used to reduce the cell cost like for example, ceria-carbonate composites and ceria-lanthanum oxide composites to produce ionic doped ceria and lanthanum gallate electrolytes [5]. A brief discussion is presented further in the thesis. However, it is not just a matter of decreasing the operating temperature as other phenomena must be taken into account as well. As well known, the kinetics of the chemical reactions that take place in SOFCs are temperature dependent and this is also a matter of concern.

When comparing SOFCs to other current fuel cell types, for example, proton exchange membrane fuel cells (PEMFCs), SOFCs present a number of attractive features. SOFCs are fuel flexible, which means that different fuels apart from pure hydrogen can be used due to the tolerance of carbon monoxide CO, being a fuel as well. Then, short-chain hydrocarbons like methane or ethanol among others can be supplied as fuel to SOFCs. Long-chain hydrocarbons can lead to carbon deposition if no previous treatment is done. Moreover, all components are at solid state (there are no liquid electrolytes like for example in alkaline fuel cells), there are no water management issues, which is the main headache for PEMFCs, and the high quality waste heat produced at a high temperature by SOFCs can be utilized effectively for either combined heat and power or for use in hybrid systems together with gas turbines.

If SOFCs use another fuel than hydrogen, e.g. methane, methanol, ethanol and others, this fuel needs to undergo reformation of the fuel as it cannot be directly used in the fuel cell. By reforming the fuel, hydrogen and carbon monoxide are produced which can now be directly supplied as fuel. This reforming process can be done internally or externally but due to the high operating temperatures of SOFCs, internal reforming is beneficial which results in less equipment required. One of the most common fuels used is methane and thus, the general reaction that describes the methane steam reforming (MSR) reaction is the following:

$$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$$  \hspace{1cm} (2.4)

The MSR reaction takes place in the anode of the fuel cell. Nevertheless, the MSR reaction is not the only reaction that constitutes the reforming of the fuel. The
2. Introduction to Solid Oxide Electrochemical Cells

MSR reaction is accompanied by the water-gas shift (WGS) reaction. The WGS reaction describes how carbon monoxide reacts in presence of water as below:

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (2.5)

Both reactions are written in the general form where only the initial reactants and final products are shown. However, these reactions take place in different steps where different surface compounds form and react at the same time. This different reaction steps and surface compounds are described in the reaction mechanisms as previously mentioned. The most common reaction mechanism for the reforming of methane is the one described by Hecht et al. [6] and Janardhanan et al. [7]. This mechanism consists of 42 irreversible or 21 reversible reactions.

The steam reforming reaction is a widely studied reaction mechanism for catalytic reactors but not for SOFCs. Although one may think of quite similar systems, there are important differences that explain why steam reforming is not perfectly known and defined for an SOFC. The main differences are the different support material used, the catalyst structure, operating pressures and moreover, one must take into account that charge transfer takes place in an SOFC but not in a catalytic reactor.

As with the reforming reactions, the general electrochemical reaction can be expressed through different reaction steps that constitute a reaction mechanism as previously described. However, the degree of uncertainty in the reaction paths is much higher for the electrochemical one. In fact, the electrochemical reactions and related transport phenomena are one of the least understood aspects of fuel cell performance.

2.2 Solid Oxide Electrolysis Cells

Hydrogen is believed to be a promising fuel for a better utilization of renewable energy sources apart from being known as an ideal energy carrier. For example, devices such as fuel cells can convert hydrogen into electricity in an environmentally friendly and efficient way as previously mentioned. Due to the increasing interest of hydrogen as a fuel, industry and governmental institutions are putting more effort to develop hydrogen-related technologies [8]. Although nowadays the main hydrogen source is by hydrocarbon reforming, hydrogen can also be obtained through green energy procedures such as water splitting (electrolysis, photolysis or thermochemical water splitting), from biomass, etc. [9-12]. At present, water electrolysis is the most viable process for hydrogen production at large scales and consists of splitting water into hydrogen and oxygen by applying electrical energy [9]. The total energy required for electrolysis increases slightly with temperature while the required electrical energy decreases. Thus, high-temperature electrolysis might be a really interesting process to consider when waste heat from other processes is available [8, 9]. In fact, electrolyzer cells can use the waste heat from industry and the electricity obtained from solar cells or wind turbines. Moreover, there is growing interest in integrating electrolysis cells together with nuclear energy to improve the hydrogen production efficiency [13, 14].
High-temperature electrolysis (HTE) of water takes place at high temperatures (700-1000 °C) and its technology is based on the high-temperature fuel cells, especially solid oxide fuel cells (SOFCs). Thus, one of the most typical devices for HTE is the solid oxide electrolysis cell (SOEC).

SOECs are usually understood as SOFCs operating in reversed mode. In fact, some devices can operate in both ways. Due to the similarity, an SOEC consists of the same components as a fuel cell: fuel and air channels, a cathode, an anode and an electrolyte. The components' materials are also usually the same: nickel-yttria stabilized zirconia (Ni-YSZ) cermet for the steam/hydrogen electrode, YSZ for the electrolyte and strontium-doped lanthanum manganite (LSM) for the oxygen-side electrode. However, it seems that the transport characteristics in SOECs differ considerably from SOFCs, especially those related to kinetic models, and thus, results from SOFCs cannot be directly applied to SOECs, emphasizing the significant need for SOEC modeling as a limited amount of research has been done in this field [15].

Steam is fed into the electrolysis cell where water splitting takes place giving hydrogen and oxygen as products, as shown in Eq. (2.6). Although hydrogen is the most important product obtained, oxygen should be considered as a co-product instead of a by-product as it is a valuable commodity which can be sold for other applications.

\[
H_2O(g) \leftrightarrow H_2(g) + \frac{1}{2}O_2(g) \tag{2.6}
\]

Water vapor is fed into the fuel channel on the cathode side. The water molecules diffuse through the porous cathode structure (the cathode diffusion layer in Fig. 2.2) to the triple phase boundaries (TPBs) at the cathode-electrolyte interface (the cathode active layer layer in Fig. 2.2) where they react with the electrons supplied by an external source to produce hydrogen gas and oxide ions, Eq. 2.7. The oxide ions are transported through the electrolyte to the TPBs at the anode-electrolyte interface (the anode active layer layer in Fig. 2.2) where the oxide ions are oxidized to oxygen gas, as shown in Eq. 2.8. The oxygen gas molecules produced diffuse back through the porous anode (the anode diffusion layer in Fig. 2.2) to the air channel. Note here the difference between the two devices, although the reactions are the same, they take place in opposite ways and at opposite electrodes.

\[
H_2O(g) + 2e^- \leftrightarrow H_2(g) + O^{2-} \tag{2.7}
\]
2. Introduction to Solid Oxide Electrochemical Cells

\[ \text{O}^{2-} \rightleftharpoons \frac{1}{2} \text{O}_{2(\text{g})} + 2 \text{e}^- \]  

(2.8)

2.3 SOFC and SOEC Modeling

Current research in both SOFCs and SOECs is oriented towards solving a certain number of problems like, for example, those material related arising from the high operating temperatures, mechanical and thermal stability of the cells and stacks, those related to the different types of available fuels in case of SOFCs or those associated with the electrochemical reactions: mechanisms, surface species, etc. among others. Different possibilities exist to solve these problems among which experimental measurement and numerical modeling are the strongest ones. However, due to the small dimensions of the cells and the high operating temperatures, which lead to very demanding and expensive experiments due to the materials and instruments required, leaves numerical modeling as a powerful method for solving the existing problems. Different levels of modeling have been performed by researchers depending on the scientific targets and objectives.

Available numerical approaches exist depending on the purpose of the research, each with its advantages and disadvantages. The ability to choose an adequate method relies on the clear understanding of the processes to model in terms of physical phenomena, the different parameters involved as well as the dimensions and the computational capability. In general, the computational capability is still increasing which leads to more possibilities for more detailed modeling at smaller scales and more complex problems [16]. As known, the modeling of fuel cells and electrolysis cells involves complex geometrical structures, which are important to implement the electrochemical reactions at micro- and nano-scale, which in turn, also add a high degree of difficulty due to the limited information known on the reaction mechanisms. Yet, numerical approaches require experimental data in order to validate the simulated models. Obtaining experimental data under realistic conditions for these devices is as straightforward as one can imagine, especially at micro- and nano-scale.

SOFCs and SOECs are known to be complex devices as different transport phenomena take place at the same time and these are interconnected. In terms of numerical modeling, this is known as multiphysics modeling and it has become increasingly trendy for both devices. Multiphysics models consider the interaction and coupling between several physical phenomena. Another prominent modeling is multiscale modeling which consists of connecting a specific process at different time- and length scales. Different length scales define the multiscale model: macro-, micro-, meso- and nano- although the divisions between the different scales is not stated clearly in literature.

A rough division of numerical models considering multiphysics and multiscale concepts consists of continuum models, discrete models and molecular dynamics based models.

Some continuum models are also known as homogeneous models because homogeneity is assumed throughout the porous structure at macroscale. Besides, several
models are based on the assumption that the porous structure is isotropic and can be described by effective and volume-averaged parameters. Examples of these parameters are porosity, tortuosity and surface area to volume ratio which are known to have a significant influence on the cell performance [17]. The effective properties of the porous electrodes are usually estimated based on the statistical properties of random packed systems of binary spherical particles. By this approach, a detailed macroscale prediction of the electrochemical reactions in the porous electrodes is possible while taking also into account the important microstructural properties of the porous electrodes as the percolation behavior and the coordination number [18]. Examples of continuum models are the conventional computational fluid dynamics (CFD) methods and the macroscopic porous-electrode methods.

Discrete models represent another group of numerical methods for describing the electrodes’ microstructure. These models simulate the electrode structure as randomly packed spheres of various particle types [2, 19, 20]. This is the main difference against the continuum models. While continuum models treat the porous structure as homogeneous or that the structure is simply connected, discrete models define the microstructure as a group of different spherical particles randomly packed. Thus, discrete models are suitable for smaller length scales than continuum models. By these models, microscopic transport phenomena in SOFCs or SOECs can be modeled in a three-dimensional randomly packed structure composed of ionic, electronic particles and the voids (gas phase). Examples of discrete models are the Lattice Boltzmann method and the Monte Carlo method.

Molecular dynamics is a computer simulation of physical movements of atoms and molecules based on statistical mechanics. The atoms and molecules are allowed to interact for a period of time, giving a view of the motion of the molecules and atoms. Usually, the atoms and molecules’ trajectories are determined by solving the Newton’s equation of motion for a system of interacting particles, where forces between the particles and potential energy are defined by molecular mechanics force fields. Molecular dynamics models are then suitable for microscopic scale [nm] as the discrete models but the main difference between these two is that molecular dynamics models are not involved in any assumption regarding the electrode structure as it is based on the physical movements of the molecules and atoms while discrete models assume a randomized structure of spherical particles.

2.3.1 Previous studies for SOFCs and SOECs

Studies regarding the different numerical models previously described have been reported in the literature. A huge variety of numerical models at different scales and multiphysics can be found for SOFCs while a limited amount is reported for SOECs. A brief discussion is presented for SOFCs while a more extended one is presented for SOECs as the modeling part of the thesis is based on this type of cells.
2. Introduction to Solid Oxide Electrochemical Cells

Solid oxide fuel cells

Solid oxide fuel cells have been and are an important area of research and thus, a wide number of computational methods have been reported, from macroscale to nanoscale. A very short description of few available models for SOFCs are presented.

A micro-/macro-scale model was developed by Sohn et al. [21] with special emphasis on the operating potential and the current density on counter- and co-flow configurations. Although counter-flow configuration claimed better performance, co-flow configuration showed a better current density configuration. Moreover, Sohn et al. showed the capabilities of modeling electrochemistry, as well as heat and mass transfer in SOFCs at micro-/macro-scale with less computational cost compared to full CFD calculations. A detailed 3D model of an anode-supported SOFC was presented by Yakabe et al. [22]. Special attention is given to the flow distribution inside the cell in order to obtain the distributions of the polarizations, the open circuit voltage as well as the species concentrations. Counter- and co-flow configurations have also been compared by Janardhanan and Deutschmann during internal methane reforming for mass and heat transport [23]. Reforming of methane and the possibility of using other fuels have also been an important issue in SOFCs.

Different groups have reported different possible reactions for the methane steam reforming reaction among which the one from Hecht et al. [6] and Janardhanan and Deutschmann [7] are the most known ones. Other groups like Xu and Froment [24], Blaylock et al. [25] and Wei and Iglesia [26] have presented other possible reaction mechanisms for other reaction conditions and catalyst materials.

A wide variety of numerical methods have also been reported to study the effect of different operating parameters when considering some transport phenomena. For example, Ni et al. [27] examined the effect on the polarizations by different graded anode structures.

The reconstruction of the microstructure of the cell is also a relevant research topic from the multiscale and the multiphysics modeling point of view. Different groups have reported different computational models that simulate the anode structure at different scales in order to be able to understand and implement the electrochemical reactions and the transport phenomena at such small length scales. For example, Cai et al. [19] generated an anode microstructure by the Monte Carlo method while Nishida and Itoh [20] applied the particle element method, based on the Newton’s equation of motion, to compute the 3D anodic microstructure.

Solid oxide electrolysis cells

Although solid oxide electrolysis cells are not brand-new devices, a considerable less amount of research has been carried out compared to solid oxide fuel cells up to date. This applies to all areas of research of SOECs but due to the similarities with SOFCs, some research topics can be shared, i.e., those related to material properties. However, when modeling, the differences between the two cells become more noticeable and thus, special effort is needed.
Several models can be found in the literature from different research groups. Most of the models reported until nowadays are based on 1D mathematical models or 1D/2D computational fluid dynamics (CFD) simulations on a unit cell or a stack of planar SOECs. Some models selected from the literature are briefly discussed in the following lines.

The first 3D model was reported by Hawkes et al. [28] and O’Brien et al. [14, 29, 30]. Hawkes et al. have presented 3D CFD cell stack models by using the commercial software ANSYS FLUENT. All their models include mass, momentum, energy and species conservation equations. The electrochemical reactions are implemented as well. The geometry of the electrolyte is simplified by treating the electrolyte as a 2D component, resulting in a zero thickness electrolyte. All their cells operate under cross-flow conditions. Moreover, this research group from the Idaho National Laboratory has also performed some experimental measurements on cell stacks to verify the models. Together with the Argonne National Laboratory, as they share the same geometric cell, they have performed parametric studies on the operating conditions: operating voltage effects on the distributions of gas compositions, current density and temperature distribution of an SOEC stack among others. A comparison between cross- and parallel-flow has also been performed and discussed. The CFD simulations performed by Argonne National Laboratory were conducted by using Star-CD [31].

Ni has also developed a couple of CFD models of SOECs. The effects of the inlet velocity as well as the electrode porosity were studied under different operating potentials for a 2D model operating under parallel-flow configuration. The governing equations for momentum, mass, heat and species were discretized by the Finite Volume Method (FVM) and solved by an in-house code [8]. Furthermore, Ni has also simulated a 2D model of an SOEC for the co-electrolysis of carbon dioxide and water operating also in parallel-flow. The effects of the operating temperature as well as the inlet gas composition and the cell operating potential have been studied [32]. A mathematical model of the coupled transport phenomenon (mass transfer only) and electrochemical reactions at micro-scale level has also been developed by Ni et al. to study the effect of the gas transport on the concentration polarizations [33]. Co-electrolysis of carbon dioxide and water is one of the latest research areas in SOECs as this device can be used for carbon dioxide adsorption.

Other one-dimensional mathematical models can be found in the literature. Udagawa et al. [34–36] developed a mathematical model considering the electrochemical reactions, mass and heat transfer for a cathode-supported planar SOEC stack for steady and unsteady state. The effects of the current densities, the temperature under exothermic and endothermic operations as well as the air flow on the stack temperature were studied. With the same mathematical model developed by Udagawa et al., Cai et al. [37] evaluated the effects of temperature, average current density, steam molar fraction as well as steam utilization among other parameters on the stack performance.

Regarding CFD simulations, 2D models are the most reported ones in the literature. Grondin et al. [38] conducted a simulation of a single circular SOEC considering charge, mass and heat transfer. The authors pointed out that the mechanism of water steam reduction on Ni-YSZ is not clearly identified for YSZ. Moreover, they
showed that the temperature distribution depends on the gas feeding configuration under the three thermal operating modes (endothermal, exothermal and thermo neutral) of SOECs. Jin and Xue [39] developed a more complete 2D planar SOEC model considering the coupled processes of charge balance, electrochemical reaction kinetics, mass, momentum and energy balances to perform an analysis of the SOEC performance due to the size and position of delaminations at the electrode/electrolyte interface. Validation was carried out through an in-house cell. Another example is the in-house model developed by Laurencin et al. [40] considering the electrochemical reactions, heat and mass transfer. The effects of the cell polarization, the geometrical and operation parameters as well as the radiative heat losses were studied for an SOEC stack.

As previously mentioned, 2D models are the common ones found in the literature for CFD SOEC modeling. Although Hawkes et al. were the first ones to model a solid oxide electrolysis stack in 3D, not many similar models have been reported so far. Boëdec developed a new 3D cell stack design based on metallic seals using ANSYS FLUENT. Calculations were focused on the evaluation of the contact resistance under operation as it appears to be a critical issue for the electrode performance. The results obtained from the numerical calculations were compared to experimental results.

Despite the limited number of complete CFD models available, considering both 2D and 3D, one of the current trends in the SOEC field is to consider the electrolysis of carbon dioxide; probably due to environmental considerations. Yet, some research groups have reported the electrolysis of carbon dioxide in SOECs alone or the co-electrolysis of water and carbon dioxide to obtain hydrogen and carbon monoxide, respectively. Zhang et al. [41] have conducted an analytical thermal-electrical model of an SOEC to study the electrochemical characteristics of these devices for carbon dioxide reduction. Xie and Xue [42] reported a more complete model consisting of a 2D button cell system for syngas production, which means that the co-electrolysis of water and carbon dioxide takes place. The mathematical model, which considers mass, momentum and energy conservation together with charge transfer and a detailed surface chemistry, is solved using COMSOL Multiphysics. The gas species distribution, the distribution of the adsorbed species within the hydrogen electrode, the operating temperature, the operating voltage as well as the supplied gas composition have been evaluated. Shi et al. [43] and Li et al. [44] presented a one-dimensional elementary reaction model of an SOEC considering elementary heterogeneous reactions, electrochemistry kinetics, the electrode microstructure as well as mass and charge transfer. The main difference between these two groups is that Shi et al. only consider carbon dioxide while Li et al. take into account water as well. The effects of different operating conditions are studied for both cases.

Even though solid oxide electrolysis cells are similar to solid oxide fuel cells, the results obtained from fuel cells cannot be directly applied to electrolysis cells mainly due to the electrochemical reactions. Electrochemical reactions are one of the least understood phenomena in SOFCs and this uncertainty is also present in SOECs. Furthermore, other transport phenomena take place at the same time in the cell and coupling of the different phenomena results in a very complex device. In order to understand how all the different transport phenomena are coupled,
how the electrochemical reactions take place and by which reaction mechanism, which operating parameters affect the performance of the cell or to simplify, how does the electrolysis cell operate in detail, computational simulations are of great interest. Although some groups have performed CFD simulations, more extensive studies should be done in this field. 3D models can provide accurate results of the performance of the cell while decreasing the need for expensive experimental tests. Besides, special effort on the water electrolysis, and also on the carbon dioxide electrolysis, must be done in order to understand the complicated electrochemical reactions and at the same time, obtain more accurate models. Experiments are very important as they also serve to verify the computational models.
Chapter 3

Heat Transfer in SOFCs

Heat transfer analysis is one of the major parts of the thesis. In this chapter, an analysis of this transport phenomenon in a solid oxide fuel cell is described considering the effects of the reforming reactions, the electrochemical reactions and the different polarizations that take place. Besides, a comparison of the different heat transfer processes in a cell is carried to evaluate the contribution of each source in a CFD SOFC model.

3.1 Heat Transfer Phenomena within an SOFC

Solid oxide fuel cells consist of two porous electrodes (an anode and a cathode) separated by a dense electrolyte and connected into an electrically conducting circuit (interconnect), see Fig. 2.1. The electrodes must present a large number of reaction sites for the electrochemical reactions to have a great number of paths for ion and electron conduction and an appropriate porosity for oxygen, hydrogen and the formed water migration. The required properties for the electrolyte are somehow similar to those required for the electrodes but present some variations. The electrolyte must present a high ionic conductivity, high density, long-term high temperature performance stability and high long-term reliability which means high strength and high durability [45].

Heat transfer within the whole SOFC unit cell consists of convection and conduction. Convection occurs between the flowing gas and the solid surfaces while conduction takes place in the solid and in the porous parts. Moreover, thermal radiation also takes place within the electrode-electrolyte structure, from the stack to the surrounding environment and surface to surface radiation in the air and fuel channels. Nevertheless, considering radiation in the model adds a higher degree of complexity to the governing equations and previous studies have demonstrated that conductive heat transfer dominates among radiation for a SOFC [46]. Heat
generation or consumption is also present due to different sources but, especially, as a result of the chemical (MSR and WGS) and electrochemical reactions. The different heat sources will be further described. The energy balance equation is used to calculate the temperature distribution for the solid phase in the porous electrodes [21, 47]:

$$\rho_s c_{p,s} \frac{\partial T_s}{\partial t} = \nabla \cdot (k_s \nabla T_s) + Q_s \quad (3.1)$$

where $\rho_s$, $c_{p,s}$ and $k_s$ are the density, the specific heat and the thermal conductivity of the solid phase, respectively. $Q_s$ is the heat transfer between the gas and the solid phases and the heat generation due to the ohmic polarizations and the internal reforming reactions.

The temperature for the gas phase in the porous electrodes (also valid for the air and fuel channels) is governed by [21, 47]:

$$\rho_g c_{p,g} \frac{\partial T_g}{\partial t} + \nabla \cdot (\rho_g c_{p,g} \mathbf{u} T_g) = \nabla \cdot (k_g \nabla T_g) + Q_g \quad (3.2)$$

where $k_g$ is the gas thermal conductivity, $\rho_g$ the gas density, $c_{p,g}$ the gas specific heat and $\mathbf{u}$ is the velocity vector. $Q_g$ is the heat transfer between the gas and the solid phases which is calculated as follows:

$$Q_g = -Q_s = h_v (T_g - T_s) = A v h_{s,\text{g,por}} (T_g - T_s) \quad (3.3)$$

where $A v$ is the active surface area-to-volume ratio [m$^{-1}$] and the subscript $s$ refers to solid, $g$ to gas and por to porous. If no heat generation nor consumption is present in the solid and in the fluid phase, then:

$$Q_s = Q_g = 0 \quad (3.4)$$

All previous equations are based on the local temperature non-equilibrium (LTNE) approach where the temperature from the gas and solid phases in the electrodes are assumed not to be locally the same. Nevertheless, in the current study, the local temperature equilibrium (LTE) approach is used [48]. For the LTE approach, the heat governing equation is defined as in Eq. (3.5) and as Eq. (3.6) for pure heat conduction in the electrolyte and interconnects [48].

$$\nabla \cdot (\rho_g c_{p,g} \mathbf{u} T) = \nabla \cdot (k_{eff} \nabla T) + Q \quad (3.5)$$

$$\nabla \cdot (-k_s \nabla T_s) = Q_s \quad (3.6)$$

where $k_{eff}$ is effective value of the thermal conductivity and calculated as:

$$k_{eff} = \varepsilon k_g + (1 - \varepsilon) k_s \quad (3.7)$$
where $\varepsilon$ is the porosity of the material.

There are different mechanisms of heat generation or consumption taking place in an SOFC. Basically, the major heat sources within an SOFC are due to the electrochemical and chemical reactions as aforementioned. Thus, knowledge about these sources is of interest as it can provide information for evaluation of the overall performance, possible thermal stresses, etc. The mentioned heat sources will be described in the following sections.

### 3.2 Effects of Methane Steam Reforming and Water-Gas Shift Reactions in Anode Supports

SOFCs using methane as fuel need to undergo a reforming process of the fuel as methane cannot be directly used because of its very slow electrochemical reaction rate and also due to carbon deposition in the anode. Thus, by reforming methane, carbon monoxide and hydrogen are produced which can now be directly used as fuel in an SOFC. The reforming process can be done internally or externally but SOFCs present the possibility to have internal reforming reaction of methane due to the high operating temperatures. The methane steam reforming (MSR) reaction, Eq. (2.4), is a highly endothermic reaction ($\Delta H_{\text{MSR},1273K} = 227.6 \text{ kJ} \cdot \text{mol}^{-1}$) and thus, introduces a high sink of heat into the cell components involved in the process [49]. The steam reforming reaction of methane takes place in the anode of the fuel cell as it requires the Ni particles to act as catalysts of the reaction. Thus, the MSR reaction strictly takes place at the Ni particles’ surface.

As the MSR reaction is endothermic, the heat absorbed or consumed by the reaction in $W \cdot m^{-3}$ can be determined by the reaction rate and the enthalpy change of the reaction. Different expressions for the reaction rate $r$ can be found in Table 3.1.

\[
Q_{\text{MSR}} = r_{\text{MSR}} \Delta H_{\text{MSR}} A_v^{an} \tag{3.8}
\]

where $r_{\text{MSR}}$ is the reaction rate for the methane steam reforming reaction $[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]$, $\Delta H_{\text{MSR}}$ the enthalpy change of the reaction $[\text{kJ} \cdot \text{mol}^{-1}]$ and $A_v^{an}$ is the active surface area-to-volume ratio of the anode $[\text{m}^{-1}]$.

Anyhow, the reformation of methane is accompanied by the water-gas shift (WGS) reaction, Eq. (2.5). The WGS reaction is slightly exothermic ($\Delta H_{\text{WGS},1273K} = -31.8 \text{ kJ} \cdot \text{mol}^{-1}$) and it is usually assumed to be in equilibrium as it is a much faster reaction than the MSR reaction [49–53].

The heat generated by the WGS reaction $[W \cdot m^{-3}]$ can be expressed as follows.

\[
Q_{\text{WGS}} = r_{\text{WGS}} \Delta H_{\text{WGS}} A_v^{an} \tag{3.9}
\]

where $r_{\text{WGS}}$ is the reaction rate for the water gas shift reaction $[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]$ and $\Delta H_{\text{WGS}}$ the enthalpy change of the reaction $[\text{kJ} \cdot \text{mol}^{-1}]$. 
3.2 Effects of Methane Steam Reforming and Water-Gas Shift Reactions in Anode Supports

The equilibrium WGS reaction rate can be modeled as [52],

\[ r_{\text{WGS}} = k_{\text{WGS}} P_{\text{CO}} \left( 1 - \frac{P_{\text{CO}_2} P_{\text{H}_2}}{K_{e,q,\text{WGS}} P_{\text{CO}} P_{\text{H}_2} O} \right) \]  

(3.10)

\[ K_{e,q,\text{WGS}} = \exp \left( \frac{4276}{T} - 3.961 \right) \]  

(3.11)

where \( k_{\text{WGS}} \) is the reaction rate constant and can be calculated according to Haberman and Young [52] and \( K_{e,q,\text{WGS}} \) is the equilibrium constant for the WGS reaction.

3.2.1 Chemical reactions: heat transfer effects

One of the major concerns for SOFC technology at the temperatures used nowadays is that the methane steam reforming reaction rate is much faster than the electrochemical reaction rate. This fact can be explained by the high nickel (Ni) content which is necessary for the electric conductivity and offers a high number of catalytic sites. The methane steam reforming reaction (Eq. (2.4)) is a highly endothermic reaction (\( \Delta H_{\text{MSR}} = 206 \text{ kJ} \cdot \text{mol}^{-1} \)) and thus, consumes energy while the electrochemical reactions produce energy as they are exothermic.

If the steam reforming reaction is faster than the electrochemical reaction, there will be a cooling effect at the inlet of the cell and heating at the outlet resulting in a large temperature gradient in the cell. This temperature gradient can cause thermal stresses as well as reduced efficiency [54]. The MSR reaction takes place in the anode support layer of the fuel cell while the electrochemical reactions take place at the three-phase boundaries in the reaction active region or functional layer, see Fig. 2.1.

The steam reforming reaction rate needs to be reduced in order to decrease the existing temperature gradients and thus, improve the cell performance. To do so, detailed knowledge of the steam reforming kinetics is required. At present, steam reforming reaction on Ni based catalysts has been widely studied for catalytic reactors because of their industrial importance. However, few studies have been performed for SOFC.

The goal for optimizing the internal reforming reactions for an SOFC is to reduce the reaction rate of the steam reforming reaction while maintaining a high electronic conductivity and a high reactivity for the electrochemical reaction. Yet, high reforming reaction rates are still required compared to the electrochemical reaction rates. To reduce the reforming reaction rate, different solutions have been presented [54, 55]:

- Lowering the temperature. The general trend is to lower the operating temperature as MSR has a high activation energy (depending on the mechanism 63.3 – 228 kJ · mol\(^{-1}\), Table 3.1) and the reaction rate decreases rapidly with reducing temperature. The present lower temperature limit for efficient operation is between 650 – 700°C (IT–SOFC) [54, 55] although the
current trend is to even decrease it more to 300 – 600°C (LT–SOFC) by using ceria-based composites as electrolyte [56]. Such low temperatures, close to 300 °C, are too low for internal reforming reactions and thus, external reforming is required. The major limitation for decreasing the operating temperature is the ionic conductivity in the electrolyte and thus, the materials used. Different kinetic expressions for the MSR reaction over Ni/YSZ anodes have been reported and are shown in Table 3.1. The different expressions shown seem to vary significantly most probably due to different experimental conditions. Moreover, two types of kinetic expressions are often used: power law expressions derived from data fitting from experimental conditions and general Langmuir-Hinshelwood expressions. Furthermore, it was intended to have the same units for the reaction rate in order to be able to compare the different expressions with more precision but the lack of information and the ambiguities with units add difficulty in this task stating that more work needs to be done in this field. Although no activation energy \( (E_A) \) value is shown in expression 5, the stated \( E_A \) value is calculated experimentally by Bebelis et al. [57].

- Reducing the fuel concentration. The fuel concentration can be decreased by recirculating part of the anode exhaust gas [55].

- Modification of the Ni/YSZ anode or design of other anode materials to decrease the MSR activity. Possibility exists to replace some Ni in the anode by copper (Cu) or using Cu/CeO\(_2\)/YSZ among others. The replacement of some Ni particles by Cu seems to be a promising option as it reduces the reforming rate without a significant reduction in the electrochemical reduction. However, more work needs to be done in this field [54, 55].

- Increase the particle size. For the same amount of Ni particles, the surface area decreases for larger Ni particles and thus, there are less active sites. Moreover, if the particle size in the active region also increases, the TPBs, where electrochemical reactions take place, decrease as well. This means that the Ni particle size also influences the electrical conductivity: when the particle size increases, the electrical conductivity decreases [58]. So, increasing the particle size to decrease the MSR rate may reduce the cell performance [54]. However, a better alternative is to use functionally graded particle size electrodes. By this way, a large TPB reaction area near the anode-electrolyte can be obtained while avoiding high diffusion losses by using large particles at the electrodes, away from the active region [27, 59].
Table 3.1: Steam reforming reaction kinetics reported for Ni/YSZ SOFC anode/anode-supports.

<table>
<thead>
<tr>
<th>No.</th>
<th>Expression r</th>
<th>[r]</th>
<th>E_A [kJ·mol⁻¹]</th>
<th>T [°C]</th>
<th>k₀, kₜ, k⁻, kₜ⁺</th>
<th>S/C&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>k₀P&lt;sub&gt;CH₄&lt;/sub&gt; exp&lt;sup&gt;(−E_a¹000/RTₚ)&lt;/sup&gt;</td>
<td>mol m⁻²a⁻¹</td>
<td>82</td>
<td>700–940</td>
<td>4274 [mol m⁻²a⁻¹bar⁻¹]</td>
<td>2.6–8</td>
<td>[60]</td>
</tr>
<tr>
<td>2</td>
<td>k₀P&lt;sub&gt;CH₄&lt;/sub&gt;P&lt;sub&gt;H₂O&lt;/sub&gt; exp&lt;sup&gt;(−E_a¹000/RTₚ)&lt;/sup&gt;</td>
<td>mol m⁻²a⁻¹</td>
<td>205</td>
<td>600–700</td>
<td>30.8 · 10¹⁰ [mol m⁻²a⁻¹bar⁻¹]</td>
<td>2–3.5</td>
<td>[61]</td>
</tr>
<tr>
<td>3</td>
<td>k₀P&lt;sub&gt;CH₄&lt;/sub&gt;P&lt;sup&gt;0.85&lt;/sup&gt;H₂O&lt;sup&gt;−0.35&lt;/sup&gt; exp&lt;sup&gt;(−E_a¹000/RTₚ)&lt;/sup&gt;</td>
<td>mol m⁻²a⁻¹</td>
<td>95</td>
<td>850–900</td>
<td>8542 [mol m⁻²a⁻¹bar⁻¹]</td>
<td>1.5–2.5</td>
<td>[62]</td>
</tr>
<tr>
<td>4</td>
<td>k₀P&lt;sub&gt;CH₄&lt;/sub&gt;P&lt;sup&gt;−1.2&lt;/sup&gt;H₂O&lt;sup&gt;exp&lt;/sup&gt; (E_a¹000/RTₚ)</td>
<td>mol m⁻²a⁻¹</td>
<td>191</td>
<td>-</td>
<td>1.01 · 10¹³ [mol m⁻²a⁻¹bar⁻¹]</td>
<td>-</td>
<td>[63]</td>
</tr>
<tr>
<td>5</td>
<td>kₜ⁺P&lt;sub&gt;CH₄&lt;/sub&gt; (1 - kₜ⁺)&lt;sub&gt;Kₜ&lt;/sub&gt;P&lt;sub&gt;H₂O&lt;/sub&gt; exp&lt;sup&gt;(−E_a¹000/RTₚ)&lt;/sup&gt;</td>
<td>mol s⁻¹</td>
<td>228</td>
<td>800–900</td>
<td>kₜ⁺&lt;sub&gt;1073K&lt;/sub&gt; = 0.26 · 10⁻⁶ [mol [kPa]⁻¹]</td>
<td>0–2</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>kₜ⁺&lt;sub&gt;1073K&lt;/sub&gt; = 3.44 · 10⁻⁶ [mol [kPa]⁻¹]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>k₀P&lt;sub&gt;CH₄&lt;/sub&gt; (1 - Pₐ₀P&lt;sup&gt;−1&lt;/sup&gt;ₐ₀P&lt;sub&gt;H₂O&lt;/sub&gt; exp&lt;sup&gt;(−E_a¹000/RTₚ)&lt;/sup&gt;)</td>
<td>mol m⁻²a⁻¹</td>
<td>63.3</td>
<td>650–950</td>
<td>k₀ = 498 [mol m⁻²a⁻¹bar⁻¹]</td>
<td>2</td>
<td>[64]</td>
</tr>
<tr>
<td>7</td>
<td>kₜ⁺P&lt;sub&gt;CH₄&lt;/sub&gt;P&lt;sub&gt;H₂O&lt;/sub&gt;P&lt;sub&gt;H₂O&lt;/sub&gt; exp&lt;sup&gt;(−E_a¹000/RTₚ)&lt;/sup&gt;</td>
<td>mol m⁻²a⁻¹</td>
<td>-</td>
<td>700–1000</td>
<td>[65]</td>
<td>3–7</td>
<td>[66]</td>
</tr>
<tr>
<td>8</td>
<td>kₜ⁺P&lt;sub&gt;CH₄&lt;/sub&gt;P&lt;sub&gt;H₂O&lt;/sub&gt; – kₜ−P&lt;sub&gt;CO&lt;/sub&gt;P&lt;sup&gt;3&lt;/sup&gt;ₐ₀P&lt;sub&gt;H₂O&lt;/sub&gt;</td>
<td>mol m⁻²a⁻¹</td>
<td>-</td>
<td>700–950</td>
<td>kₜ⁺&lt;sub&gt;1073K&lt;/sub&gt; = 2.3 · 10⁻⁸ [mol [kPa]⁻¹]</td>
<td>3</td>
<td>[50, 67]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>kₜ⁻&lt;sub&gt;1073K&lt;/sub&gt; = 1.4 · 10⁻²⁰ [mol [kPa]⁻¹]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>288.52P&lt;sub&gt;CH₄&lt;/sub&gt;P&lt;sub&gt;H₂O&lt;/sub&gt; exp&lt;sup&gt;(−1/10⁰00/RTₚ)&lt;/sup&gt;</td>
<td>mol m⁻²a⁻¹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[68]</td>
</tr>
</tbody>
</table>

<sup>a</sup>S/C is the steam-to-carbon ratio

<sup>b</sup>kₜ⁺ = kₜ⁺<sub>1073K</sub>
One of the main goals in the fuel cell research is to decrease the material cost in order to be able to mass produce SOFCs. As seen, the current trend in SOFC development is to decrease the operating temperature. By lowering the operating temperature, other phenomena that take place within the SOFC are also affected. Therefore, the relationship between the chemical and electrochemical reactions with temperature is more than obvious. For this reason, considering heat transfer when performing a numerical simulation of an SOFC is of great interest.

3.3 Effects of Electrochemical Reactions in Electrode Active Regions

The oxidation of hydrogen in the anode is the driving reaction of the energy conversion in an SOFC device. This process can be written as a general reaction as shown in Eq. (2.1).

Nevertheless, this general electrochemical reaction consists of two semi-reactions that take place in different parts of the fuel cell. The reduction of oxygen, Eq. (2.3), takes place in the active layer of the triple-phase boundaries of the cathode while the oxidation of hydrogen, Eq. (2.2), takes place at the anodic TPBs.

However, another electrochemical reaction takes place in the anodic TPBs if carbon monoxide is present and taken into account. This reaction is the oxidation of carbon monoxide to carbon dioxide which is of special interest when considering the carbon monoxide as a reactant as well. Note that carbon monoxide also reacts with water in the WGS reaction and a strong coupling between the WGS reaction and the electrochemical reactions occurs.

\[
\text{CO} + \text{O}^2- \leftrightarrow \text{CO}_2 + 2e^- \quad (3.12)
\]

As mentioned previously, the global electrochemical reaction for hydrogen is highly exothermic \((\Delta H_{1273K} = -250 \text{ kJ} \cdot \text{mol}^{-1})\) but only a part can be converted into electric work. The maximum work that can be obtained is given by the Gibbs free energy \((\Delta G)\).

\[
\Delta G_{ER} = \Delta H_{ER} - T\Delta S_{ER} \quad (3.13)
\]

where the subscript \(ER\) refers to electrochemical reaction and the term \((-T\Delta S_{ER})\) is the heat related entropy change due to the electrochemical reaction.

Despite the fact that most global models assume that the heat associated with the general electrochemical reaction is assigned to the anodic TPBs, this heat is generated at the two different electrodes and in different amounts. Therefore, a detailed model should take into account the entropy changes for each semi-reaction and thus, calculate the heat generation due to the electrochemical reactions for each electrode as follows. However, one must consider the reaction sites and thus, the
23 3.3 Effects of Electrochemical Reactions in Electrode Active Regions

released heat per unit volume \([W \cdot m^{-3}]\), by considering TPBs reaction area, can be calculated as follows [49].

\[
Q_{ER}^{an,cat} = \frac{i_{an,cat}^2}{2F} \left( -T \Delta S_{ER}^{an,cat} \right) A \nu_{an,cat} 
\]  

(3.14)

where \(i_{an,cat}^\) is the local current density for the anode or the cathode. Moreover, Fischer et al. [49] showed that the heat released or absorbed by the semi-reactions are the most important sources or sinks of heat in the fuel cell.

The local current density presents different expressions for the cathode and for the anode. Besides, it is calculated separately for hydrogen and carbon monoxide at the anode TPBs according to an approach developed by Suwanwarangkul et al. [69]. This approach assumes that the rate of carbon monoxide oxidation reaction is 2.5 times lower than for the hydrogen oxidation reaction, i.e., \(i_{an}^H_2 = 2.5i_{an}^CO\) because the carbon monoxide oxidation presents a much higher activation overpotential than for the hydrogen oxidation reaction for the same current density [70]. Note that the partial pressure terms for this electrochemical reaction approach are frequently neglected within the open literature.

\[
i_{cat} = 0.25 \cdot 10^{10} \exp \left( \frac{-130000}{RT} \right) \frac{RT}{P_{O_2}} \exp \left( \frac{-2F\eta_{act}^{cat}}{RT} \right) - \exp \left( \frac{2F\eta_{act}^{cat}}{RT} \right) \right]
\]  

(3.15)

\[
i_{an}^{H_2} = 2.1 \cdot 10^{11} \exp \left( \frac{-120000}{RT} \right) \frac{RT}{P_{H_2}^{0.266}} \exp \left( \frac{2F\eta_{act,H_2}^{an}}{RT} \right) - \exp \left( \frac{-F\eta_{act,H_2}^{an}}{RT} \right) \right]
\]  

(3.16)

\[
i_{an}^{CO} = 0.84 \cdot 10^{11} \exp \left( \frac{-120000}{RT} \right) \frac{RT}{P_{CO_2}^{0.266}} \exp \left( \frac{2F\eta_{act,CO}^{an}}{RT} \right) - \exp \left( \frac{-F\eta_{act,CO}^{an}}{RT} \right) \right]
\]  

(3.17)

where \(K_{eq}\) is the temperature dependent equilibrium constant for the electrochemical reactions of hydrogen and carbon monoxide, respectively.

The two electrochemical fuels, hydrogen and carbon monoxide, are treated as two resistances in parallel. Thus, the total local current density for the anode is calculated as the sum of the hydrogen and carbon monoxide anodic current densities.

\[
i_{an} = i_{H_2}^{an} + i_{CO}^{an}
\]  

(3.18)
Moreover, the actual cell voltage for this case is related to the open circuit voltage (OCV), also known as Nernst potential \( (E_0^0) \) \cite{71}, and to the different polarizations as follows \cite{72}.

\[
V = E_{\text{H}_2/\text{H}_2O}^0 - \eta_{\text{act, H}_2/\text{H}_2O} - \eta_{\text{conc, H}_2/\text{H}_2O} - \sum \eta_\Omega \\
= E_{\text{CO}/\text{CO}_2}^0 - \eta_{\text{act, CO}/\text{CO}_2} - \eta_{\text{conc, CO}/\text{CO}_2} - \sum \eta_\Omega 
\]

\[ (3.19) \]

\[
E_{\text{H}_2/\text{H}_2O}^0 = 1.253 - 2.4516 \cdot 10^{-4}T - \ln \frac{RT}{2F} \left( \frac{P_{\text{H}_2O}}{P_{\text{H}_2}P_{\text{O}_2}^{0.5}} \right) 
\]

\[ (3.20) \]

\[
E_{\text{CO}/\text{CO}_2}^0 = 1.467 - 4.527 \cdot 10^{-4}T - \ln \frac{RT}{2F} \left( \frac{P_{\text{CO}_2}}{P_{\text{CO}}P_{\text{O}_2}^{0.5}} \right) 
\]

\[ (3.21) \]

where \( \eta_{\text{act}} \) are the activation polarizations, \( \eta_{\text{conc}} \) the concentration polarizations and \( \eta_\Omega \) are the ohmic polarizations.

![Figure 3.1: Fuel cell voltage as a function of the current density.](image)

In Fig. 3.1, the operating voltage of the fuel cell as a function of the current density is presented. The effects from the different polarizations in the cell voltage are remarked and thus, the deviation from the operating cell voltage.

3.4 Effects of Polarizations in the SOFC

3.4.1 Concentration polarizations by mass transfer

Concentration polarizations are those potential losses associated with the variation of concentration of the critical species due to mass transfer processes. There are
basically two main sources due to mass transport: transport of reactants and products through the electrodes and diffusion between the bulk flows and cell surfaces. Thus, concentration polarizations are highly dependent on the diffusion length, the pore volume percentage of the components as well as the gases involved [73]. Therefore, these concentration polarizations give a surplus heat at the anodic and cathodic reaction sites which can be calculated as follows [W·m⁻³] [49].

\[ Q_{\text{conc}}^{\text{an,cat}} = i^{\text{an,cat}} \eta^{\text{an,cat}}_{\text{conc}} A v^{\text{an,cat}} \] (3.22)

The concentration polarizations used are specified from [74] and are calculated separately for the cathode and the carbon monoxide and hydrogen in the anode. However, the concentration polarizations for the carbon monoxide are shown below.

\[ \eta^{\text{an}}_{\text{conc}, \text{CO}} = \frac{RT}{\eta^{\text{an}}_{\text{e}} F} \ln \left( \frac{P_{\text{CO}_2,\text{TPB}} P_{\text{CO},b}}{P_{\text{CO},\text{TPB}} P_{\text{CO}_2,b}} \right) \] (3.23)

where \( n_e \) is the number of electrons involved, \( P_{\lambda,\text{TPB}} \) the partial pressure of gas component \( i \) at the TPB and \( P_{i,b} \) is the partial pressure of component \( i \) at the interface between the electrode and the gas channel.

### 3.4.2 Activation polarizations by electrochemical reactions

Activation polarizations can be considered as the extra potential needed in order to overcome the activation energy (\( E_A \)) or energy barrier of the rate-determining step to a value that the reaction proceeds at a desired rate [48, 49, 73]. The heat generated by these irreversible polarizations is released at the anodic and cathodic catalyst particle surfaces in the active regions. Thus, the heat source will be [W·m⁻³] [49].

\[ Q_{\text{act}}^{\text{an,cat}} = i^{\text{an,cat}} \eta^{\text{an,cat}}_{\text{act}} A v^{\text{an,cat}} \] (3.24)

The local current densities can be obtained through Eq. (3.17) and Eq. (3.15).

### 3.4.3 Ohmic polarizations by charge transfer

Ohmic polarizations are due to the joule heating effect or, in other words, they are due to the resistance to ion transfer through the electrolyte, electron transfer through the electrodes and current collectors and also by the contact resistance between the different cell components. Thus, they are characteristic for the solid parts of the fuel cell and they lead to a release of heat which can be determined by the local current density and the material conductivity (\( \sigma \)) [48, 49, 73].

\[ Q_{\Omega} = \frac{1}{\sigma} i^2 \] (3.25)

where \( Q_{\Omega} \) is the local heat source [W·m⁻³].
3.5 Comparison of Heat Sources

A comparison of the different forms that contribute to heat generation or consumption within SOFCs is carried out to study the contribution of each source to the total heat generation of the cell. The contributions obtained are estimated for the model used by Andersson et al. [75] in which reforming reactions take place through the whole anode operating at 30% pre-reformed natural gas as fuel. The electric conductivities ($\sigma$) used can be found in [48].

The different types of heat generation or consumption within SOFCs previously described are summarized in Table 3.2. Moreover, the percentage contributed by each one in absolute values is shown in the last column. The sum of all contributions adds up to 100%. The locations where the different mechanisms occur are also shown.

The results show that the main contribution to heat generation or consumption is by the electrochemical reactions. It must be pointed out that this is the net contribution from both semi-reactions. A more accurate approach would have been to consider the two semi-reactions as independent as they take place at different electrodes, one being endothermic and the other, exothermic. Nevertheless, electrochemical reactions are still the main contributors. The second most important heat contribution is the one due to the methane steam reforming reaction, which introduces a heat sink to the SOFC as it is a strong endothermic reaction. Thus, as electrochemical and reforming reactions are the main contributors, it is reasonable that the major concerns of the current technology are that the methane steam reforming reaction is much faster than the electrochemical reaction and the need of lowering the methane steam reforming reaction rate. Activation polarizations are quite significant as they are directly related to the chemical reactions. The contributions from the WGS reaction and the ohmic polarizations are quite similar while the contribution from the concentration polarizations is less than 1%.

Table 3.2: Heat transfer mechanisms and their relative contribution to the total heat in SOFCs.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Location</th>
<th>Expression</th>
<th>Relative (%) contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSR reaction</td>
<td>anodic active layer</td>
<td>$r_{\text{MSR}} \Delta H_{\text{MSR}} A_e^{n=m}$</td>
<td>27</td>
</tr>
<tr>
<td>WGS reaction</td>
<td>anodic active layer</td>
<td>$r_{\text{WGS}} \Delta H_{\text{WGS}} A_e^{n=m}$</td>
<td>6</td>
</tr>
<tr>
<td>Electrochemical reaction</td>
<td>electrodes’ TPBs</td>
<td>$i \frac{F}{2} (T \Delta S_{\text{ER}}) A_e^{n,m}$</td>
<td>47</td>
</tr>
<tr>
<td>Concentration pol. a</td>
<td>electrodes’ reaction sites</td>
<td>$i \eta_{\text{conc},\text{ent}} A_e^{n,m}$</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Activation pol. a</td>
<td>electrodes’ reaction sites</td>
<td>$i \eta_{\text{act},\text{ent}} A_e^{n,m}$</td>
<td>16</td>
</tr>
<tr>
<td>Ohmic pol. a</td>
<td>solid cell components</td>
<td>$i \sigma$</td>
<td>3</td>
</tr>
</tbody>
</table>

*a polarizations

These results can be extrapolated to solid oxide electrolysis cells although the contribution percentage values would be slightly different as no reforming reactions (MSR and WGS) take place. Yet, the electrochemical reactions would still be the predominant source.
Chapter 4

Governing Equations for Transport Phenomena in SOECs

The success of a good and reliable computational fluid dynamics (CFD) simulation relies on how well the computational domain as well as the numerical model reflect the physical processes of the system. In this chapter, the most important transport phenomena involved in solid oxide electrolysis cells (SOECs) are presented.

An SOEC, likewise SOFCs, is a complete device as many different transport phenomena occur simultaneously and are strongly coupled. Mass diffusion through porous layers, mass convection in the gas channels, heat generation or consumption as a function of the operating voltage and transport of ions and electrons are some of the phenomena that occur in an SOEC. When modeling, it is thus essential to connect the different transport processes to achieve a closer performance to reality. In the following sections, the main transport processes are briefly described. It must be stated that steady state and laminar flow conditions are assumed.

4.1 Momentum Transfer

Momentum transport is directly related to the mass transfer phenomena, especially in an SOEC. Momentum transfer takes place in the operating fluid, a gas phase in this case, in the porous electrodes (the diffusion layers and the TPBs in the anode and cathode) and in the gas channels.

Momentum transfer is based on a gradient of the momentum as a driving force and thus, momentum should be conserved. The momentum conservation equations are known as the Navier-Stokes equations, named after the French mathematician L.M.H. Navier and the English mechanician Sir G.G. Stokes [76].

\[ \nabla \cdot (\rho \mathbf{U} \mathbf{U}) = -\nabla P + \nabla \cdot (\mu \nabla \mathbf{U}) + S_d \]  (4.1)
where $\mathbf{U}$ is the velocity vector, $P$ the pressure and $\mu$ the dynamic viscosity of the gas mixture. $S_d$ is the momentum source term.

For the gas channels, the source term is zero, see Eq. (4.2), and thus, the Navier-Stokes equation remains in its initial form. However, in the diffusion layers and in the TPBs, the source term from Eq. (4.3) must be considered. When Eq. (4.3) is taken into account, the resulting equation is known as the Darcy equation for the porous structures.

\begin{equation}
S_d = 0 \quad (4.2)
\end{equation}

\begin{equation}
S_d = -\frac{\mu}{K} \mathbf{U} \quad (4.3)
\end{equation}

where $K$ is the permeability.

### 4.2 Heat Transfer

If the momentum conservation equation is required, the energy conservation equation is at least as important in an SOEC. The famous conservation of the energy principle, also known as the first law of thermodynamics, states that the energy cannot be created nor destroyed during a process, just transformed [77].

An SOEC is a complex device in terms of heat transfer. Different heat transfer mechanisms dominate at the different cell components like for SOFCs. Furthermore, heat generation or consumption is also present and is function of the operating voltage. Heat transfer within an SOEC consists of conduction, convection and radiation. The different heat transfer mechanisms for an SOEC are the same, and occur at the same cell components, as in an SOFC, see Chapter 3. Radiation has been neglected in the simulated model to avoid a high degree of complexity. This assumption is valid as single cell is modeled which is located in the middle of a fuel cell stack. Otherwise, radiation effects are stronger and can be considered, although resulting in a higher calculation time. Besides, a previous study demonstrated that radiative heat transfer inside the cell could be neglected ahead of conductive heat transfer in an SOFC [46]. Examples of other models where radiation effects are neglected can be found in the literature [8, 38]. Nevertheless, the effects of radiation can be considered for future studies.

As mentioned previously, heat generation or consumption within an SOEC is bonded to the operating voltage of the cell. The net heat flux of the cell is negative at low current densities, where the endothermic heat requirement from the electrochemical reactions dominates. The net heat flux is zero at the thermal neutral voltage and then becomes positive as Ohmic heating prevails. Ohmic heating is due to electric resistance of the transport of ions and electrons and cell irreversibilities. Activation and concentration polarizations are also included [28].
As energy must be conserved throughout the whole computational domain, the energy conservation equation must be applied.

\[ \nabla \cdot (\rho c_p U T) = \nabla \cdot (k \nabla T) + S_T \]

(4.4)

where \( c_p \) is the specific heat at constant pressure, \( T \) the temperature and \( k \) is the thermal conductivity of the material. \( S_T \) is the thermal source term which takes into account the electrochemical reactions, the ohmic and the activation polarizations. Concentration polarizations are not taken into account as their contribution is very small compared to the other polarizations as shown in Table 3.2.

The thermal source term, \( S_T \), only takes into account Ohmic heating at the diffusion layers, electrolyte and interconnects, Eq. (4.5). For the TPBs, Eq. (4.6), should be applied. For the gas channels, \( S_T = 0 \).

\[ S_T = \frac{j^2}{\sigma} \]

(4.5)

\[ S_T = \frac{j^2}{\sigma} + j \left( \eta_{\text{act}} + \frac{T \Delta S}{2F} \right) \]

(4.6)

where \( j \) is the volumetric current density \([\text{A} \cdot \text{m}^{-3}]\), \( \sigma \) the material electric conductivity, \( F \) the Faraday constant, \( \Delta S \) the entropy change for the reaction and \( \eta_{\text{act}} \) are the activation polarizations.

### 4.3 Mass Transfer

When a fluid mixture contains two or more components, a concentration gradient exists. The natural tendency for each component is to flow in such a direction in order to minimize the concentration gradient and reach the ideal equilibrium state. This process is what is the so-called as mass transfer [78].

An SOEC is a high-temperature (800°C) operating device and thus, the fluid is in gas phase. Moreover, due to such high temperatures, the anodic and cathodic gases are always far from the critical conditions and hence, the ideal gas law can be applied [79]. Gas flows through the gas channels by convection and diffuses through the porous electrodes to the electrode-electrolyte interface, where the electrochemical reactions take place. The electrodes consist of porous material with graded porosity and are finest at the electrode-electrolyte interface.

As mass must be conserved throughout the whole computational domain, the mass conservation equation is applied. Eq. (4.7) is also called the continuity equation.

\[ \nabla \cdot (\rho U) = S_m \]

(4.7)

where \( \rho \) is the fluid density, \( U \) the velocity vector and \( S_m \) is the source term due to the electrochemical reactions. This source term has different values in the different
regions of the electrolysis cell. Eq. (4.8) applies to all regions except the triple phase boundary (TPB) domains where Eq. (4.9) should be considered.

\[ S_m = 0 \]  
\[ (4.8) \]

\[ S_m = \sum_i S_{m,i} \]  
\[ (4.9) \]

\( S_{m,i} \) is the contribution of each species due to the electrochemical reactions. The source term for each species related to the electrochemical reactions is defined as follows. For all regions except from the TPBs, Eq. (4.10) applies. For the TPBs, Eq. (4.11) should be considered to take into account the rate of generation or consumption of the species due to the specified reactions.

\[ S_{m,i} = 0 \]  
\[ (4.10) \]

\[ S_{m,i} = \frac{j}{n_e F} M_i \]  
\[ (4.11) \]

where \( M_i \) the molar mass of species \( i \), \( n_e \) is the number of electrons transferred per molecule of hydrogen produced and \( j \) is the volumetric current density. For a system where oxide ions (\( O^{2-} \)) are transported through the electrolyte, \( n_e = 2 \) [30].

The continuity equation, Eq. (4.7), is the global mass conservation equation but, within a mixture, a species balance equation for \((N-1)\) components is also required. This equation is known as the species transfer equation, Eq. (4.12). Four different species are modeled for the SOEC described in the work. Then, the species conservation equations have to be solved for three of them. The species to be considered are hydrogen and water vapor for the cathode side and oxygen and nitrogen for the anode side. Nitrogen is an inert gas acting as a carrier gas for the produced oxygen.

\[ \nabla \cdot (\rho Y_i) = -\nabla \cdot J_i + S_{m,i} \]  
\[ (4.12) \]

where \( Y_i \) is the molar fraction of species \( i \), \( J_i \) the mass diffusion flux of species \( i \) and \( S_{m,i} \) is the source term due to electrochemical reaction for species \( i \). Gas diffusion is influenced by the electrochemical reaction at the solid surfaces of the TPB. The mass is diffusion complex, especially within this region [18]. The mass diffusion flux \( J_i \) in Eq. (4.12) can be calculated by Fick’s law, Eq. (4.13).

\[ J_i = -\rho D_{m,i}^{eff} \nabla Y_i - D_{T,i} \frac{\nabla T}{T} \]  
\[ (4.13) \]

where \( D_{m,i}^{eff} \) is the effective mass diffusion coefficient of component \( i \) in the gas mixture and \( D_{T,i} \) is the thermal diffusion coefficient of component \( i \) in the gas mixture as well.
The effective value of the mass diffusion coefficient is taken into account by considering the effects of tortuosity in the porous media and thus, expressing the reduction from the bulk diffusion [80]. Several methods are available in literature to consider the reduction effects. However, Eq. (4.14) is the method considered in the model.

\[ D_{m,i}^{\text{eff}} = \varepsilon^{1.5} D_{m,i} \]  

(4.14)

where \( \varepsilon \) is the average porosity and \( D_{m,i} \) is the mass bulk diffusion coefficient which can be calculated as follows:

\[ D_{m,i} = \frac{1 - Y_i}{\sum_{j=1,j\neq i}^{N} \left( \frac{Y_i Y_j}{D_{ij}} \right)} \]  

(4.15)

where \( D_{ij} \) is the binary diffusion coefficient which can be evaluated by the kinetic theory of gases applying the Chapman-Enskog theory [81], Eq. (4.16).

\[ D_{ij} = D_{ji} = 3.198 \cdot 10^{-8} T^{1.75} P \left( \frac{1}{M_i} - \frac{1}{M_j} \right)^{1/2} \]  

(4.16)

where \( T \) is the temperature, \( P \) the pressure, \( v_i \) the diffusion volume of component \( i \) and \( M_i \) the molecular weight of the gas component \( i \). The same procedure is applied to gas component \( j \).

Fick’s law is the simplest diffusion model and it is only valid for a binary mixture, for a multicomponent mixture with invariable composition, dilute mixtures or when the mass diffusion coefficient is independent of composition. As an SOEC operates under a mixture of four different gas species with variable composition, the Stefan-Maxwell equations should be used.

By the assumption that for ideal gases the Maxwell diffusion coefficients can be approximated by the binary diffusion coefficients, the external force is assumed equal on all species and neglecting pressure diffusion, the Stefan-Maxwell equations can be written as [82]:

\[ \sum_{j=1,j\neq i}^{N} \frac{Y_i Y_j}{D_{ij}} \left( \frac{J_i}{\rho_i} - \frac{J_j}{\rho_j} \right) = \nabla Y_i - \frac{\nabla T}{T} \sum_{j=1,j\neq i}^{N} \frac{Y_i Y_j}{D_{ij}} \left( \frac{D_{T,j}}{\rho_j} - \frac{D_{T,i}}{\rho_i} \right) \]  

(4.17)

4.4 Charge Transfer

The electrochemical reactions, reduction of water to hydrogen and oxidation of oxygen ions to oxygen, take place at the TPBs. Reduction occurs at the cathodic TPBs while oxidation takes place at the anodic TPBs. The electrolyte is the component which is placed between the anodic and the cathodic TPBs and has
two main functions regarding transport. The first one is the transport of oxygen ions through the electrolyte (from the cathodic TPBs to the anodic ones). The second, prevent the electrons crossing over from the anode to the cathode. The flow of ions through the electrolyte is balanced with the flow of electrons through the external circuit. The transport of ions and electrons is described by the current conservation equation, Eq. (4.18), and Ohm’s law, Eq. (4.19) [16, 21, 33, 83].

\[
\int_{\text{anode}} j_{\text{an}} \, dV = \int_{\text{cathode}} j_{\text{cat}} \, dV
\]  

(4.18)

\[-\nabla \cdot (\sigma \nabla \Phi) = S_{\Phi}
\]  

(4.19)

where \(\sigma\) is the ionic or electronic conductivity, \(\Phi\) the ionic or electronic potential, \(S_{\Phi}\) the related source term and \(j\) is the volumetric current density [A·m\(^{-3}\)]. For all components except for the TPBs, Eq. (4.20) applies while for the TPBs, the source term is the one stated in Eq. (4.21).

\[S_{\Phi} = 0\]

(4.20)

\[S_{\Phi} = j\]

(4.21)

The current density is calculated by the Butler-Volmer equation which is the expression for the activation polarizations at each electrode (TPB)-electrolyte interface. Accordingly, the equation is applied separately at the anode and at the cathode. The general Butler-Volmer equation is [84, 85]:

\[i = i_0 \left[ \exp \left( \alpha_1 \frac{F\eta_{\text{act}}}{RT} \right) - \exp \left( -\alpha_2 \frac{F\eta_{\text{act}}}{RT} \right) \right]\]

(4.22)

where \(R\) is the ideal gas constant, \(\eta_{\text{act}}\) is the activation polarization and \(i_0\) is the exchange current density which depends strongly on the the cell materials, construction and temperature. The equilibrium exchange current density is typically calculated by an Arrhenius type expression:

\[i_0 = A \exp \left( -E_A/RT \right)\]

(4.23)

where \(A\) is the pre-exponential term and is function of the cell temperature as well as the reactant and product partial pressures [53, 84, 86–88]. \(E_A\) is the activation energy of the reduction or oxidation reaction depending on the electrode. \(\alpha_1\) and \(\alpha_2\) are the reduction and oxidation transfer coefficients governed by the electron transfer process at the TPBs. The two semi-reactions that take place at the anode and at the cathode are well known and understood. However, the intermediate steps and the exact reaction mechanisms are difficult to identify and not well known for an SOEC. More work has been done in this field for SOFCs but more effort must be done for both types of cells. If the reaction mechanisms were known, the transfer
coefficients could be easily obtained as stated in [84, 85]. Yet, a simplification is usually made for these cells which is to assume each reaction as a single-step and single-electron transfer process. The simplified Butler-Volmer equation results in:

\[ i = i_0 \left[ \exp \left( (1 - \beta) \frac{F}{RT} \eta_{\text{act}} \right) - \exp \left( -\beta \frac{F}{RT} \eta_{\text{act}} \right) \right] \]  

(4.24)

where \( \beta \) is the symmetry factor and is related to the rate of electrochemical transformation. To simplify, the symmetry factor is assumed to be 0.5 for these devices [84, 89].

The Butler-Volmer equation can be applied to both SOECs and SOFCs. One must just consider that although the semi-reactions are the same, they are reversed and take place at opposite sides. Thus, the values obtained are not the same. Yet, the symmetry factor is the same for both devices.

![Figure 4.1: Electrolysis cell voltage as a function of the current density.](image)

For an SOEC, as for an SOFC, the actual cell voltage is also related to the open circuit voltage and to the different polarizations that occur in the device. However, some important differences exist between the two devices being the major one that the operating cell voltage is lower than the OCV for an SOFC and the opposite, higher operating voltage than OCV, for an SOEC. This fact can be observed when comparing the different voltage as a function of the current density curves for both devices, Fig. 4.1 and Fig. 3.1. In Fig. 4.1, the electrolysis cell voltage as a function of the current density is shown. Note that the current density is treated in absolute values. Fig. 3.1 was previously presented in Chapter 3. Yet, the relationship between the operating circuit voltage and the different polarizations is as follows and can be also compared to Eq. 3.19.

\[ V = E_{H_2O/H_2}^0 + \eta_{\text{act},H_2O/H_2} + \eta_{\text{conc},H_2O/H_2} + \sum \eta\Omega \]  

(4.25)
\[ E_{\text{H}_2\text{O}/\text{H}_2}^0 = 1.253 - 2.4516 \cdot 10^{-4} T + \ln \frac{RT}{2F} \left[ \frac{P_{\text{H}_2} P_{\text{O}_2}^{0.5}}{P_{\text{H}_2\text{O}}} \right] \] (4.26)

where \( \eta_{\text{act}} \) are the activation polarizations, \( \eta_{\text{conc}} \) the concentration polarizations and \( \eta_{\Omega} \) are the ohmic polarizations.
Chapter 5

SOEC: Studied Cases & Boundary Conditions

This chapter contains the description of the configuration and domain for the electrolysis cell used for simulations and the studies performed in this work as well as the solution methods employed.

5.1 Solid Oxide Electrolysis Cell Geometry & Parameters

The simulated electrolysis cell is a three-dimensional single planar cell operating in cross-flow mode, i.e., the steam and hydrogen channel flow direction is perpendicular to the oxygen channel flow direction. Cross-flow configuration has been set due to the ease of separating the product streams from each other, especially in a stack. However, if achievable in practice, parallel flow yields lower temperature gradients, which increases the durability of the cell. Nevertheless, the difference between cross- and parallel-flow becomes significant at higher operating voltages and current densities [31].

A sketch of the geometry to be modeled is presented in Fig. 5.1. Please note that the sketch is not to scale. The modeling domain consists of two gas channels: one for the steam and hydrogen at the cathode side and another one for the oxygen. A single channel for each electrode side is chosen to simplify the computational domain although future models will include the effect of multiple smaller channels for each electrode. Connected to each channel, the diffusion layer is located where the transport of the reactants from the gas channel to the triple-phase boundary (TPB) layer occurs. The next component is the TPB layer where the different electrochemical reactions take place; reduction of steam to hydrogen at the cathodic TPB and the oxidation of oxide ions to oxygen at the anodic one. The component which separates the two TPBs is the electrolyte layer, through which the oxide ions
are transported but not the electrons. Interconnects for both side are also taken into account.

In Table 5.1, the different parameters used in the simulations and the dimensions of the various components of the cell are stated. The parameters used in the study are based on the typical values found in the literature, especially from the models developed by Hawkes et al. [28] and O’Brien et al. [14, 29, 30].

Table 5.1: Parameters used in simulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature</td>
<td>1073</td>
<td>K</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>1</td>
<td>bar</td>
</tr>
<tr>
<td>Length and width</td>
<td>0.2</td>
<td>m</td>
</tr>
<tr>
<td>Cathode diffusion layer thickness</td>
<td>$5 \cdot 10^{-4}$</td>
<td>m</td>
</tr>
<tr>
<td>Cathode TPB layer thickness</td>
<td>$1 \cdot 10^{-5}$</td>
<td>m</td>
</tr>
<tr>
<td>Electrolyte thickness</td>
<td>$1 \cdot 10^{-4}$</td>
<td>m</td>
</tr>
<tr>
<td>Anode TPB layer thickness</td>
<td>$1 \cdot 10^{-5}$</td>
<td>m</td>
</tr>
<tr>
<td>Anode diffusion layer thickness</td>
<td>$5 \cdot 10^{-5}$</td>
<td>m</td>
</tr>
<tr>
<td>Gas channel height</td>
<td>$1 \cdot 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>Gas channel width</td>
<td>0.1</td>
<td>m</td>
</tr>
<tr>
<td>Open circuit voltage (OCV)</td>
<td>0.84</td>
<td>V</td>
</tr>
<tr>
<td>Cathode exchange current density</td>
<td>7500</td>
<td>A·m$^{-2}$</td>
</tr>
<tr>
<td>Anode exchange current density</td>
<td>2000</td>
<td>A·m$^{-2}$</td>
</tr>
<tr>
<td>Active surface area-to-volume ratio in TPBs</td>
<td>$2 \cdot 10^{5}$</td>
<td>m$^{-1}$</td>
</tr>
</tbody>
</table>
5.2 Parameter Study

A parameter study has been performed to investigate the effects of different operating conditions and a porous structure property on the cell performance. The effects of the operating voltage, porosity and fuel inlet composition have been studied on the temperature distribution in the cell, on the current density and on the hydrogen molar fraction as they are good indicators of the solid oxide electrolysis cell performance.

Four different operating voltages have been considered to investigate the behavior of the electrolysis in the endothermic, exothermic and thermo-neutral operation modes under the assumption that the anodic and cathodic diffusion layers and the cathodic and anodic TPB layers have the same porosity. The porosity value, assumed constant throughout all the porous regions, is 0.5. Despite being a high value for the anodic and cathodic active regions, it allows to obtain a reasonable approximation and it is very close to the usual porosity range for these materials. Yet, the effect of porosity on the cell performance is studied. Moreover, for all four cases, water has been assumed to be the only inlet component for the water channel and nitrogen for the air channel. All the different set-ups for the different cases have been summarized in Table 5.2. The four operating voltages are: 1.1 V, 1.2867 V, 1.3 V and 1.5 V. The voltage 1.1 V (case No. 1 in Table 5.2) corresponds to operating under endothermic conditions, 1.2867 V (case No. 2) is the thermo-neutral voltage at 800 °C, 1.3 V and 1.5 V correspond to voltages at the exothermic region (cases No. 3 and 6 in Table 5.2). The voltage 1.3 V has been chosen for the base case.

The effect of the porosity has been studied by comparing the base case (case No. 3 in Table 5.2) with case No. 5. Case No. 5 presents different porosity values for the diffusion and the active layers being the diffusion layers more porous than the TPB regions. Contrarily, the same porosity was assumed throughout the porous structure for the base case. Moreover, the porosity values in case no. 5 are lower than that in the base case, which can predict some effects from the electrochemical reactions point of view.

Hydrogen can be desirable at the inlet of the cathode to avoid the degradation of the Ni catalyst in the Ni-YSZ cathode due to oxidation [31]. The influence of hydrogen excess has been evaluated in case No. 4 where the molar fraction of hydrogen at the water or cathode channel inlet has been increased from 0 in the base case to 10% in case No. 4.

Despite that cross-flow configuration of the flow paths has been the conventional scheme for SOECs, and also for SOFCs, due to simplicity for separating the product streams in a cell stack [31], a parallel-, co-flow configuration has also been considered to study the effects of this flow configuration in the cell performance. The results from the parallel-flow configuration, case No. 6 in Table 5.2, are compared to those from the base case, case No. 3.
5.3 Boundary & Initial Conditions

When performing a CFD simulation, as well as in other simulation methods, a set of boundary conditions is required to complete the system of equations. Different boundary conditions are required for the different transport phenomena modeled and these can either be a fixed value or a fixed flux of the variable at a specific boundary. The selected calculation domain represents one repeat unit cell, surrounded by other cells similar to each other.

The major boundary conditions applied in the SOEC computational model are specified in Table 5.3. The operating voltage (V) and the inlet molar fractions for the water channel species, water and hydrogen, are specified in Table 5.2 according to the different simulation cases.

5.4 Solution Methods

The simulations have been performed by using the commercial software ANSYS FLUENT together with the add-on module Fuel Cell and Electrolysis Module. ANSYS FLUENT is based on the finite volume method (FVM) for representing and evaluating the partial differential equations.
The semi-implicit method for pressure-linked equations (SIMPLE) has been used for the pressure-velocity coupling. The first-order upwind discretization scheme has been used for the convection term of all the equations except for pressure where the standard scheme has been used. A first-order discretization scheme was required to achieve converge in the model. For the diffusive fluxes, the Green-Gauss cell based method has been applied.

Moreover, all the residuals have been set to $10^{-4}$ except for the energy equation, which has been set to $10^{-7}$. A stabilization method based on the F-cycle with the bi-conjugate gradient stabilized method (BCGSTAB) has been chosen for the species and the potential equations to avoid convergence problems. Pressure is stabilized by the V-cycle while the other governing equations are set with the flexible cycle [80].

### 5.5 Grid Independence Study

A hexahedral mesh type arrangement has been used in order to perform the CFD calculations on the SOEC. A mesh independence study was performed on three different mesh sizes. A coarse mesh of 198744 nodes and 270343 elements, a finer mesh of 584808 nodes and 716074 elements and the finest mesh which consists of 1497840 nodes and 1731190 elements. The results from the mesh dependence study show that although the current density distribution is almost invariable with the mesh size, the temperature distribution is not independent. Thus, the finest mesh, despite the higher computational cost involved, was used for all the cases studied in the thesis. Moreover, this mesh presents good quality parameters: a maximum value of the equiangle skewness of 0.029 and very good orthogonal quality values in the 0.999-1 range. It must be pointed out that this is a graded mesh where the anodic and the cathodic TPBs are more finely meshed as these are the regions where the electrochemical reactions occur, see Fig. 5.2.

In the future work, more mesh independence tests will be performed on finer meshes to guarantee a complete mesh independence from the different operating parameters involved in the electrolysis cell.

![Figure 5.2: Detail of the mesh at the electrolyte, TPB regions and anode diffusion layer.](image)
5. Validation Analysis

If possible, validation of the results from a computational model is necessary. The CFD model was validated by comparing temperature values as a function of the cell potential to the data from the literature. Figure 5.3 shows the minimum and maximum cell temperature values for different operating voltages compared to the average cell values reported by Yildiz et al. [31].

As it can be seen in Fig. 5.3, the results obtained from the current CFD model show very good agreement with the ones divulged by Yildiz et al. for the temperature values. Nevertheless, it should be pointed out that validation of the CFD model presents a high degree of difficulty due to different cell size (larger than ones found in the literature), the cross-flow configuration applied (most models reported in literature employed a parallel-flow arrangement) and the different operating and structural parameters. For example, the model reported by Yildiz et al. [31] corresponds to a 64 cm² cell active area operating in cross-flow arrangement at 800 °C and 1 atm. Moreover, no hydrogen is considered in the water channel inlet but a nitrogen mass fraction of 0.5 is considered for the air channel. Radiation effects have also been neglected. Despite the differences between the models, the average temperature as a function of the operating voltage verifies a good agreement, at least for this parameter.

Experimental data is required for a better validation of the SOEC model and for the physical and material properties which are currently from the literature.
The chapter starts with a presentation of the results from the base case. Afterwards, results from the parametric study are presented and discussed. Note that the values of the current densities are all presented in absolute values as negative current density values are proper of an SOEC.

6.1 Base Case

The base case, as previously described in Chapter 5, operates at a voltage of 1.3 V in cross-flow configuration. A porosity of 0.5 is assumed for all the porous structures: the anodic and cathodic diffusion layers and the anodic and cathodic active layers. Water is assumed to be the only inlet component of the fuel stream at the water channel inlet. Nitrogen is also the only component for the air channel inlet. The results from the base case are presented as follows.

6.1.1 Current density distribution

The current density distributions at the active layers of the anode and the cathode have been presented in Fig. 6.1. The images correspond to the surface between the active layer and the diffusion layer. The highest values of the current density are identified in four regions under the respective channel close to the side interconnects (the so-called channel ribs) while the lowest values are found in the center region of the cell. This can be explained by higher electron concentration in the solid regions. Electrons are supplied by an external source (electricity) at the interconnect bottom wall. Electrons diffuse from the interconnect to the active layers through the metal (Ni) material in the porous region. The shortest path for those electrons distributed at the interconnects on top of the channel, see Fig. 5.1, is to diffuse to the channel walls to continue their pathway to the reaction sites, increasing the concentration of this species in this area and thus, the current density. Besides, a
higher current density is found at the anode TPBs, Fig. 6.1a, than in the cathode TPBs, Fig. 6.1b, in terms of the maximum current density. It could be due to the fact that the cathode diffusion layer is much thicker than the anodic one making the electron transfer pathway strongly dominated in this side which results in a larger area of electron concentration due to the larger diffusion electron pathway and thus, the current density is lower at this side of the electrolysis cell. Anyway, the maximum values for the current density of the two electrodes are in the same order of magnitude.

![Figure 6.1: Current density in [A · m⁻²] at the electrodes' active layers for base case condition.](image)

### 6.1.2 Temperature distribution

The temperature distributions at the active layers surfaces, the interface between the diffusion layers and the active layers, have been presented in Fig. 6.2. Furthermore, the temperature profiles at the gas channels are shown in Fig. 6.3 and in Fig. 6.4.

If the temperature profiles at the active surfaces are compared, Fig. 6.2a and Fig. 6.2b, almost no difference is observed. The same temperature ranges are present for both sides but a stronger effect from the electrochemical reactions is observed at the cathode active layer, especially in the regions closest to the inlet of the water channel. The inlet temperature for both gas channels is set to 1073 K as a boundary condition and, from Fig. 6.2, it can be seen that at the active layer, close to the water channel inlet side, a lower temperature than the inlet specified value is present. The temperature drop observed is due to the endothermic semi-reaction that takes place in the cathode reaction sites (the reduction of water) which occurs very close to the channel inlet. A temperature increase is observed downstream of the water channel because of the effects from the exothermic semi-reaction from the anode side and possible charge transfer related ohmic heating. The highest temperature values are found in the intersections of the two channels, being the downstream regions larger than the upstream ones. This can probably be explained by the diffusion of the gas streams from the gas channels to the active layers plus the effects from the electrochemical reactions. Due to the similarity between the
two figures, for the next cases, the cathodic active layer is presented unless different temperature profiles are observed in opposite sides of the electrolyte.

![Figure 6.2: Temperature distribution in [K] at the electrodes’ active layers for base case condition.](image)

Figure 6.3 and Fig. 6.4, present the temperature distribution for the gas phase in the SOEC. The temperature distribution for the air channel cross-sections along the main flow direction is presented in Fig. 6.3 The profiles shown correspond to z=0.19 m (very close to the inlet of the channel), z=0.15 m, z=0.1 m, z=0.05 m and z=0.01 m (just before the outlet). Note that the profiles are presented with a different view angle compared to Fig. 6.2 and Fig. 6.1 in order to have a better display of the different profiles. A general temperature increase is observed throughout the channel in the flow direction with the highest value corresponding to the center of the cell. The areas with higher temperature in z=0.1 m (the center of the cell and the third profile from the left) are the same regions where the maximum temperature values where observed in the active layers’ surfaces in Fig. 6.2.

![Figure 6.3: Temperature distribution in [K] along the flow direction in the air channel for base case condition.](image)

Figure 6.4 displays the temperature profiles for the water channel cross-section along the flow direction. The different profiles shown correspond to x=0.01 m (by the channel inlet), x=0.05 m, x=0.1 m, x=0.15 m and x=0.19 m (very close to
the channel outlet). At $x=0.01$ m, the first profile from the left, the effects from the reduction of water semi-reaction where the cooling effect at the bottom of the channel is clearly distinguished. It must be pointed out that the cooling effect from the electrochemical semi-reaction of water is only 0.4K. The highest temperatures of the gas phase are also found at the middle of the channel, at $x=0.1$ m, which corresponds to the middle of the cell and presents the same type of distribution as in the air channel, Fig. 6.3. Higher temperature values are observed in the air channel rather than in the water channel due to the exothermic semi-reaction in the anodic part of the cell. Moreover, the total temperature distribution of the cell is consistent with operating under exothermic conditions, i.e., temperatures are higher than the inlet temperature despite the cooling effect, as the operating voltage is above the thermo-neutral voltage at the operating temperature of 800 °C(1.2867 V).

Figure 6.4: Temperature distribution in [K] along the flow direction in the water channel for base case condition.

6.1.3 Hydrogen production

The last parameter evaluated to study the performance of an SOEC operating on cross-flow configuration is the production of hydrogen. The production of hydrogen can be evaluated by the molar fraction of this species. Although other species are also present in the cell, hydrogen is the target product and for this reason, only the distribution of the molar fraction of hydrogen is analyzed and discussed.

The molar fraction distribution of hydrogen in the water channel is presented in Fig. 6.5. The profiles shown correspond to the same channel positions as for the temperature distribution in this channel, that is $x=0.01$ m, $x=0.05$ m, $x=0.1$ m, $x=0.15$ m and $x=0.19$ m. The molar fraction distribution in the water channel is useful for obtaining the total hydrogen produced but, for a more detailed distribution of this species, i.e., in the reaction sites and other regions like the active and diffusion layers, should be considered.

An increase in the molar fraction in the flow direction can be observed in Fig. 6.5 as expected. Higher molar fractions are found in the regions close to the channel walls, associated with those areas where the current density is also higher. Furthermore,
the effects of mass diffusion inside the channel can also be observed when moving in
the flow direction, from left to right in Fig. 6.5, as the concentration of hydrogen in
the channel increases due to the electrochemical reaction occurring at in the TPBs.
At the outlet of the SOEC, an average hydrogen molar fraction of 0.58 is achieved.

**Figure 6.5:** Hydrogen molar fraction along the flow direction in the water channel for base case condition.

### 6.2 Parameter Study

The results of the parameter study are presented below for the different cases outlined in Table 5.2. First, the results from the effect of the different operating voltages on the current density, on the temperature and on the hydrogen molar fraction are discussed. Afterwards, the results considering the effects from the change in porosity and the fuel inlet composition are presented. Finally, a comparison between the cross-flow configuration and the parallel-flow is given.

#### 6.2.1 Variation of the operating voltage

Four different voltages have been tested to evaluate the effects on the parameters previously mentioned. The characteristics of the different cases simulated are described in Table 5.2. The results from voltage operated at 1.1 V, 1.2867 V, 1.3 V and 1.5 correspond to cases No. 1, 2, 3 and 5 in Table 5.2. Note that the case No. 3 corresponds to the base case, a voltage very close to the thermo-neutral value at the operating temperature of 800 °C (1.2867 V), but operating under exothermic mode.

The first parameter discussed is the current density followed by the temperature distribution and finally, the hydrogen production in the cell.
Current density distribution

Figure 6.6 shows the current densities at the anode active layer surface, the same interface described beforehand for the base case, for the four different operating voltages. Note that the same scale has been considered for the four different cases and thus, the profile in Fig. 6.6a, is not as clear as the other three. Anyhow, a similar trend of the current density distribution is observed for the four cases presented. With increasing voltage, higher current densities (maximum values) are achieved and larger areas of higher current density values are observed as well. This is due to higher electron concentration at the solid regions and the diffusion mechanism of electrons from the solid interconnects to the porous layers and then to the reaction sites.

![Figure 6.6: Current density in \( [\text{A} \cdot \text{m}^{-2}] \) at the anode active layer for different operating voltages.](image)

The current density distribution at the cathode active layer surface for the different operating voltages are shown in Fig. 6.7. For this side, the results follow the same trend as in the anode. That is, for higher operating voltages, higher current densities are achieved, being the highest values those areas close to the interface with the cannels’ walls. Moreover, the maximum values of the current density for the cathode side are smaller than those obtained at the anodic site, Fig. 6.6, following the same trend as discussed in the base case. Yet, the same distribution trend of the current
density is observed for the four cases. The same scale for the current density has been used in this figure as well for easier comparison.

![Current density distribution](image)

**Figure 6.7:** Current density in $[\text{A} \cdot \text{m}^{-2}]$ at the cathode active layer for different operating voltages.

**Temperature distribution**

The temperature profile at the cathode active layer is presented in Fig. 6.8. Aforementioned in the base case, the temperature profile at the anode side is omitted due its similarity and thus, being of no significance.

In comparison with the current density distribution at different voltages where not much difference was observed as in Fig. 6.6 and Fig. 6.7, the temperature profiles shown in Fig. 6.8 present noticeable differences at first sight.

First of all, different temperature scales have been used to highlight the differences between the different cases although Fig. 6.8b and Fig. 6.8c share the same scale due to the proximity in voltage values. In the same line, a clear distinction between the different cases can be made, the temperature profiles are similar for the 1.2867 V and 1.3 V but differ from the 1.1 V and 1.5V cases despite presenting some similarities between them.

Figure 6.8a presents the temperature distribution for 1.1 V which corresponds to a voltage below the thermo-neutral value and thus, the SOEC operates under the
endothermic condition. Operating at the endothermic mode means that the electric energy is lower than the enthalpy change of reaction and heat must be supplied in order to maintain the electrochemical reaction as it is endothermic and thus, consumes heat. The results obtained for 1.1 V are consistent with the endothermic mode requirements. From Fig. 6.8a a decrease in the temperature value is observed throughout the cell in the flow direction being highest at the region closest to the water channel inlet. As the reaction proceeds in the cell, a temperature drop is observed which, if heat was supplied, the temperature could be maintained constant. Moreover, note that the temperature values are lower than the gas inlet temperature, 1073 K. This temperature drop is due to the strong effect of the electrochemical reaction when operating at the endothermic mode.

The temperature distribution profile obtained from the exothermic operating mode corresponds to the SOEC operating at 1.5 V, Fig. 6.8d, as it is a higher voltage than the thermo-neutral one. Contrarily to the endothermic mode, the electric ohmic resistances are predominant against the the enthalpy change of reaction in the exothermic mode and in order to maintain the same temperature, heat should be removed from the device. From Fig. 6.8d, an increase in the temperature values can be observed when moving downstream from the two channels, in a similar distribution as for the endothermic case, Fig. 6.8a and the values presented are also higher than the inlet temperature values for the gas flows due to the predominance of electric resistances.

These two profiles in Fig. 6.8a and Fig. 6.8d are similar to those presented by the Argonne National Laboratory [31] despite the different operating voltages.

However, the temperature profiles shown in Fig. 6.8b and in Fig. 6.8c, are considerably different to the ones discussed previously. Figure 6.8c corresponds to the 1.3 V which is the base case. Although the operating voltage 1.3 V is higher than the thermo-neutral value, but really close, which can explain why the temperature distributions are very similar. The thermo-neutral voltage, 1.2867 V at 800 °C, is that point where the generated joule heat due to ohmic resistances in the cell and the heat consumption for the electrochemical reaction are the same. Thus, no heat must be supplied or removed to maintain the temperature constant. Figure 6.8b, which corresponds to the thermo-neutral voltage, verifies this condition as the temperature difference is very small compared to the values obtained at 1.1 V and 1.5 V. The same happens for the 1.3 V case, Fig. 6.8c. Nevertheless, the temperature values are higher at 1.3V than at the thermo-neutral voltage which can indicate a slight effect from the joule heating due to operating at a voltage higher than the thermo-neutral one.

The temperature profiles at different positions along the flow direction for the air channel are presented in Fig. 6.9. The positions are the same as those previously defined for the base case. Reasonable profiles are obtained for the different operating voltages for the gas phase in the air channel. The same temperature scales as those used for the the temperature distribution at the cathode active layer are used. Figure 6.9a shows the temperature profiles for the 1.1 V. Higher temperatures are found at the lower parts of the channel, close to the interconnect and the upstream influence area while lower temperature values are confined to the downstream parts being consistent with the temperature profile at the cathode interface at
6.2 Parameter Study

Figure 6.8: Temperature in [K] at the cathode active layer for different operating voltages.

this voltage, Fig. 6.8a. The same applies to the temperature profiles for 1.3 V but with opposite temperature distributions. Lower temperature values are found in the upstream region and close to the interconnect while higher values are found in the related downstream regions. For the thermo-neutral voltage case and the base case, Fig. 6.9b and Fig. 6.9c, similar profiles are obtained like for the temperature distribution at the cathode active surface being the values for 1.3 V higher than for the thermo-neutral voltage (1.2867 V).

Similar to that for the air channel, the temperature distribution in the water channel is also shown for different positions along the flow direction in Fig. 6.10. Again, the position of the different profiles obtained are the same as those described for the base case. Moreover, the same temperature scale has been used as for the temperature distributions at the cathode active layer and at the gas channel. The temperature profiles shown are really similar to those presented for the air channel, Fig. 6.9, but with opposite temperature variation. The higher temperature values are found in the upper regions of the channel (close to the interconnect), at the left positions of the channel due to the flow effect, upstream region. Moreover, the temperatures are also consistent with the operating modes. In Fig. 6.10a the temperature decreases and it is lower than the inlet condition due to the strong effect from the endothermic electrochemical reaction. In this case, the strong effect from the reaction is clearly observed at the profile close to the inlet, the first plot from the left. Figure 6.10d shows how the temperature increases when operating at the exothermic mode while
Fig. 6.9: Temperature in [K] at the air channel for different operating voltages.

Fig. 6.10b and Fig. 6.10c present small temperature variations across the channels being the values higher for the 1.3 V case. The profiles obtained from the water channel are consistent with those previously discussed.

**Hydrogen production**

The hydrogen molar fraction profiles obtained for the different operating voltages at different positions along the flow direction are shown in Fig. 6.11. The same scale for the molar fraction has been kept for easier comparison. The positions for the different profiles are the same as for all the previous profiles shown for the water channel: x=0.01 m, x=0.05 m, x=0.1 m, x=0.15 m and x=0.19 m.

As expected, the highest molar fraction, $Y_{H_2} = 0.81$ is obtained at the highest voltage operation, 1.5 V, see Fig. 6.11. Lower values are obtained for the 1.3 V, $Y_{H_2} = 0.58$, for the 1.287 V, $Y_{H_2} = 0.55$, being the lowest one obtained for the case corresponding to the 1.1 V, $Y_{H_2} = 0.51$. This leads to emphasize the strong relationship between the operating voltage and the hydrogen molar fraction produced. However, other parameters affect this relation. When operating in the exothermic mode, which means operating at high voltages, high current densities can be obtained leading to larger hydrogen molar fractions when compared to lower operating voltages. Considerably higher current density values are obtained at the higher voltage for the cathodic and anodic sides than for the cases at or close the
6.2 Parameter Study

Figure 6.10: Temperature in [K] at the water channel for different operating voltages.

thermo-neutral voltage or operating at the endothermic mode, see Fig. 6.6 and Fig. 6.7. Thus, depending on the operating mode: exothermic, thermo-neutral or endothermic, higher or lower values of the current density are achieved affecting the hydrogen production in an SOEC device. No significant difference between the profiles for the different cross-sections along the flow direction is observed, regarding the different values of the molar fraction, under the effect of different operating voltages.

6.2.2 Effect of the porosity

An SOEC with graded porosity in the cell thickness direction has been tested to investigate the effects of porosity on the distribution of the current density, temperature and hydrogen production of the electrolysis cell. The results obtained from the electrolysis cell with graded porosity are compared with those from the base case. The base case presents a porosity of 0.5 throughout all porous domains while the graded cell has a diffusion layer of porosity 0.4 and an active layer of porosity 0.27. The characteristics of the two cases simulated and compared are described in Table 5.2. The results from the graded porosity cell correspond to case No. 5 and the base case is case No. 3 as already stated.
First, the effect on the current density is discussed. Second, the temperature distribution is presented and finally, the hydrogen production of the cell is considered.

Current density distribution

The distribution of the current density at the anodic and cathodic active layer surface is presented in Fig. 6.15.

When comparing the current density distributions at the anode for both cases, Fig. 6.1a and Fig. 6.12a, and at the cathode, Fig. 6.1b and Fig. 6.12b, no significant difference from a variation of the porosity is observed. The same profiles are obtained with the same maximum values indicating that a decrease in the porosity of the porous materials of the cell, when switching from the base case to case No.5, does not have any effect on the current density distribution at the active layer surfaces of the SOEC modeled.
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Figure 6.12: Current density in \( \text{A} \cdot \text{m}^{-2} \) at the electrodes’ active layers for a different porosity value.

Temperature distribution

Figure 6.13 shows the temperature distribution at the cathode active layer surface. The temperature distributions at the water and air channels are not presented in this case as they are similar to the ones presented for the base case in Fig. 6.3 and Fig. 6.4.

Although the temperature profiles obtained at the cathode active layer surface are very similar for both cases as shown in Fig. 6.2 and Fig. 6.13, note that different temperature scales have been used in order to emphasize the different temperature gradients across the cell. Figure 6.13, which corresponds to the graded porous structure, case No. 5, presents higher temperature values than those presented for the base case in Fig. 6.2. When the porosity value of the porous materials of the electrolysis cell is decreased and the other parameters are kept the same, the proportion of solid material for the charge flow in the cell increases leading to higher joule heating due to the ohmic resistances and thus, higher temperatures are achieved in the cell when compared to a the base case with higher porosity values. However, the temperature differences across the cell are almost the same for both cases, 4 K.

Hydrogen production

The hydrogen molar fraction profiles at different cross-sections along the flow direction obtained for the two different cases of the porosity study are shown in Fig. 6.14. The positions of the profiles are the same as the ones defined in the previous studies. Analogous to the current density distributions, as previously discussed, almost no significant change is perceptible between the two cases, when Fig. 6.14 is compared with Fig. 6.5. The maximum average hydrogen molar fraction achieved for the base case, Fig. 6.5, is 0.58 while for case No.5, is 0.576. A variation in the porosity of the material does not affect the production of hydrogen of the electrolysis cell. This can be explained by the fact that although a decrease in the porosity of the material leads to more available solid surfaces for the electrochemical
reaction to occur, if the active area-to-volume ration is kept constant, the available sites for reaction are the same and thus, no variation in the hydrogen production is expected.

6.2.3 Effect of fuel composition

The influence of excess hydrogen at the cathode inlet on the current density, temperature distribution and hydrogen production has been studied and compared with the base case aforementioned. The presence of excess hydrogen is an interesting parameter to investigate as it can be desirable for avoiding oxidation degradation related issues of the catalyst material in the cell. An SOEC with a hydrogen molar fraction at the cathode inlet, which corresponds to case No. 4 in Table 5.2, has been compared to the base case, case No. 3, where water is assumed to be the only species at the cathode channel inlet. The characteristics of the two mentioned cases can be found in Table 5.2.
The results presented for this study follow the same order of discussion as the results already conferred.

**Current density distribution**

Figure 6.15 presents the different current density distribution profiles, at the anodic and cathodic active layer surfaces. Very similar current density values are achieved at the anode side, Fig. 6.1a and Fig. 6.15a. The same trend can be observed at the cathode side, Fig. 6.1b and Fig. 6.15b. An excess of hydrogen in the cathode inlet leads to increasing the cell potential at a required current density, mainly due to an increase in the open circuit voltage based on the presence of hydrogen [31]. However, no increase in the current density is observed in this case.

![Current density profiles](image)

**Figure 6.15:** Current density in \([\text{A} \cdot \text{m}^{-2}]\) comparison at the respective active layers for a different fuel inlet composition.

**Temperature distribution**

The temperature profile for the hydrogen fuel cell obtained is shown in Fig. 6.16 together with the one from the base case. Note that despite the temperature distributions are very similar and correspond to a voltage very close to the thermoneutral value, different temperature scales are used to highlight the difference between the two cases studied. The temperature values obtained for case No. 4, Fig. 6.16 are higher than those obtained for the base case, Fig. 6.2. These higher values can be due to higher electrical requirement for the presence of hydrogen in the cell.

**Hydrogen production**

Figure 6.17 presents the hydrogen molar fraction profiles at different positions along the flow direction. The positions of the profiles are the same as the ones specified in the previous studies. Despite the fact that the plots in Fig. 6.5 and Fig. 6.17 present the same molar fraction scale, one must take into account that the hydrogen production is different for each case. The hydrogen production at the outlet of the
Figure 6.16: Temperature distribution in [K] at the cathode active layer for a different fuel inlet composition.

cell can be measured as the difference in the hydrogen molar fractions between the inlet and the outlet of the cell. All previous cases studied did not consider any hydrogen so the hydrogen production could be directly obtained from the hydrogen molar fraction at the outlet of the cathode channel, i.e., the base case presented,

Figure 6.17: Hydrogen molar fraction at the water channel for a different fuel inlet composition.

6.2.4 Effect of flow configuration

An SOEC operating in parallel-flow arrangement has been simulated to investigate the effects of the flow configuration on the current density, temperature and hydrogen production of the electrolysis cell. The results obtained from the parallel-flow configuration are compared with those from the base case, which operates in cross-flow mode. The parallel-flow configuration case corresponds to case No. 6 in Table 5.2. More specification details about the cases compared can be found in Table 5.2.
The parallel-flow case operates in co-flow mode, i.e., the cathodic and the anodic channel inlets are specified at the same side of the cell located at $z=0.2$ m.

The results obtained are presented in the same order as the ones for the previous studies. First, the current density distribution is presented. Then, the temperature distribution at different cell locations is discussed and last, the hydrogen production in the cathode is considered.

### Current density distribution

The current density distribution at the anode and cathode active layers are shown in Fig. 6.18. The anode current density distribution is presented in Fig. 6.18a while the cathodic one in Fig. 6.18b. Not like in the base case, Fig. 6.1, the highest values of the current density are identified at the continuous regions corresponding to the interface between the respective channel and the side interconnects. Moreover, the anode side also presents higher current density values than the cathode side, note here the different scales for the current density have been used due to the big differences in the order of magnitude between the two electrodes. Yet, a similar distribution profile is obtained for both sides. In general, the maximum current density values for the parallel-flow configuration are slightly lower than those obtained for the cross-flow configuration, but still the values remain in the same order of magnitude. Thus, no remarkable effects are observed from switching from cross- to parallel-flow configuration on the current density values although different values are obtained, in terms of the maximum current densities.

![Figure 6.18: Current density in $[\text{A} \cdot \text{m}^{-2}]$ at the electrodes’ active layer for parallel-flow condition.](image)

### Temperature distribution

Figure 6.19 shows the predicted temperature profile when operating in parallel-flow configuration. Only the temperature at the cathode active layer surface is presented as the same profile is obtained for the respective surface at the anode side. A large temperature gradient is observed in the parallel-flow case when compared to the cross-flow operating one in Fig. 6.2. Moreover, the temperature decreases along
the flow direction and lower values than the inlet temperature are observed. These results contradict the general definition of the exothermic operating mode where the temperature should increase in the cell along the flow direction due to joule heating by the ohmic resistances. It can be possible that when operating in parallel-flow configuration, the diffusion pathway for the reaction species is shorter and thus, the electrochemical reactions become much stronger and predominate at voltages near the thermo-neutral value. Nevertheless, different operating voltages should be applied for further study on this phenomenon observed for the parallel flow configuration.

Figure 6.19: Temperature distribution in [K] at the cathode active layer for parallel-flow condition.

The temperature profiles for different cross-sections along the flow direction are presented as follows. Due to the parallel flow configuration, the location of the profiles are the same for the air channel, Fig. 6.20, and the water channel, Fig. 6.21. The cross-sections selected are located at \( z = 0.19 \) m (very close to the channel inlet), \( z = 0.15 \) m, \( z = 0.1 \) m, \( z = 0.05 \) m and \( z = 0.01 \) m (by the channel outlet).

Figure 6.20: Temperature distribution in [K] at the air channel for parallel-flow condition.

The temperature distribution profiles obtained for both gas channels are consistent with the one at the cathodic active layer presented in Fig. 6.19. Temperatures decrease along the flow direction presenting higher values close to the interface between the channel and the porous diffusion layer. The profiles obtained are
different than those for the cross-flow case, Fig. 6.3 and Fig. 6.4, due to the different flow configuration.

**Hydrogen production**

Last but not least, the hydrogen molar fraction profile for the different cross-sections along the flow direction for the water channel are presented in Fig. 6.22. The different cross-sections showed correspond to the same locations defined for the temperatures at the water and air channels. The same scale for the hydrogen molar fraction has been used as in the base case, Fig. 6.5, for easier comparison.

The main finding is that a lower average hydrogen molar fraction at the water channel outlet is achieved, $Y_{H_2} = 0.50$ when operating in parallel-flow than when operating in cross-flow configuration, $Y_{H_2} = 0.58$. An explanation to this drop in the hydrogen molar fraction is the lower current densities obtained for the parallel-flow configuration.
The work presented in the thesis can be divided into two main parts. The first part is based on the analysis of the heat transfer phenomenon in an SOFC. The second part describes various transport phenomena in an SOEC as well as the CFD model developed and the results obtained for the SOEC. The main conclusions for both parts are presented as follows.

The research done lately in the fuel cell field has allowed a decrease in the operating temperature of SOFCs. This has resulted in a big gain for SOFCs as internal reforming of natural gas is still possible, but cheaper materials can be used for the cells and also higher stability of the overall fuel cell stack. This is indeed an important path for improving SOFC performance to increase the future potential market.

Special attention has been given to the kinetics of the internal reforming reactions as it is believed to be one of the main issues for improving the SOFC operation and performance. Different kinetic expressions based on the overall reaction schemes have been found in the literature for the methane steam reforming reaction in Ni-YSZ catalysts on SOFC anodes. However, these expressions differ ones from others making comparison difficult as the conditions they are derived from are also different. Moreover, the different heat sources that take place within an operating SOFC have been described, together with the regions at which they are located as well as their relationship with the chemical and electrochemical reactions in an SOFC. From the CFD analysis, it is found that the heat originated or consumed due to the electrochemical reactions at the two active regions of the electrodes is the main contributor followed by the steam reforming reaction related heat consumption.

The physics and the transport processes in SOECs, as well as for SOFCs, can be described at different length and time scales. A FVM based CFD model was developed for a cathode-supported planar SOEC operating in cross-flow configuration mode. The model was implemented in ANSYS FLUENT together with the add-on Fuel Cell and Electrolysis Module for the analysis of three different parameters under different operating conditions. The behavior of the current
density, the temperature distribution and the hydrogen production in an SOEC have been investigated under different operating and structural parameters.

First, the results for the base case selected for the study have been presented. Higher current densities are observed in the anode active layer than in the cathodic one as the cathode diffusion layer is much thicker than the anodic one making the electron transfer pathway strongly dominated in this side. Besides, the highest current density values are identified in four regions close to the channels' ribs while the lowest values are located in the center of the cell due to higher concentration of electrons at the ribs. The temperature profiles at the electrodes' active layers, water and gas channels show a temperature drop close to the water channel inlet due to the endothermic reaction while higher temperature values are found close to the outlet because of possible charge transfer related ohmic heating. A hydrogen molar fraction of 0.58 was obtained for this case.

Second, four different operating voltages have been applied to evaluate their effect on the aforementioned parameters. With higher operating voltages, higher current densities are obtained. Similar current density profiles are obtained for all four cases following the same trend described for the base case. However, the temperature distribution profiles present noticeable differences. A temperature decrease is observed throughout the cell in the flow direction being highest at the region closest to the channel inlet for the 1.1 V case due to operating in the endothermic mode. On the other hand, for the 1.5 V, a temperature increase is observed in the cell along the flow direction due to operating in the exothermic region where joule heating from the electric resistances predominate among the electrochemical reactions. The 1.2867 V (thermo-neutral voltage) and 1.3 V cases present similar temperature profiles due to being very close operating voltages. Moreover, the temperature difference in the cell is the lowest. A higher hydrogen molar fraction is obtained with a higher operating voltage although the effects from the current density as well as the thermal operation modes should be taken into account.

Third, the effect of the variation of the porosity of the porous electrodes was investigated. A cell with graded porosity in the thickness direction of the cell, $\varepsilon_{\text{TPBs}} = 0.27$ and $\varepsilon_{\text{diffusion}} = 0.4$, was evaluated and the predicted results were compared to the base case, $\varepsilon_{\text{electrode}} = 0.5$. Almost no effect of a decrease in the porosity values on the current density and hydrogen molar fraction is revealed. Per contra, higher temperature values were obtained than for the base case due to higher joule heating because the proportion of solid material for the charge flow is increased when the porosity is lowered.

Forth, the effect from the fuel inlet composition has been evaluated by increasing the molar fraction of hydrogen from 0 in the base case to 0.10. Although the presence of hydrogen at the cathode channel inlet leads to higher cell voltage at a required current density, no variation of the current density distribution was observed in comparison with the base case. Similar temperature profiles are obtained for the hydrogen fueled cell despite higher temperature values are achieved. The presence of hydrogen at the cathode channel inlet leads to a lower hydrogen molar fraction of hydrogen produced from the electrolysis, $Y_{H_2} = 0.53$, in comparison to the $Y_{H_2} = 0.58$ obtained in the base case.
Fifth, a parallel-flow arrangement has been simulated to investigate the effects of the flow configuration in the SOEC. Not like in the base case, the highest values of the current density are identified at the continuous regions corresponding to the interface between the respective channel and the side interconnects. However, the anode side presents higher current density values than the cathodic side as in the cross-flow base case. Yet, the parallel-flow arrangement presents lower current density values than the cross-flow case although they remain in the same order of magnitude. A large temperature difference is observed due to the parallel-flow configuration. The temperature decreases along the flow direction at an exothermic operation mode probably due to a strong effect of the endothermic electrochemical reaction in this flow arrangement. A lower hydrogen molar fraction is obtained, $Y_{H_2} = 0.5$, because of the lower current densities obtained in the parallel-flow configuration.

Finally, the parametric studies performed allow to obtain a general idea of the behavior of the SOEC performance when some cell parameters are modified. However, more studies are required, especially for the porosity, fuel inlet composition and parallel-flow configuration in order to obtain necessary results for better understanding the relations between SOEC operating and design parameters. Yet, the SOEC cell used in the study presents a very large projected area with wide gas channels. Thus, in the future work, a cell will be modeled with multiple and smaller channels on both electrodes.

Furthermore, a part from considering a cell with graded porosity in the thickness direction of the cell due to more resemblance with reality, a more detailed electrochemical model is likely to be implemented to capture the electrode microscopic structures and the materials’ properties.

Last but not least, experimental data is required for the validation of the SOEC model and for the physical and material properties, which are currently from the literature.
Bibliography


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