Analysis and Simulation of an Anode Supported Solid Oxide Fuel Cell Single Channel for Operation with Biosyngas and Methane

M.Sc. Thesis

by

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TU Delft

December 2011
‘Analysis and Simulation of an Anode Supported Solid Oxide Fuel Cell Single Channel for Operation with Biosyngas and Methane’

Thesis, submitted in partial fulfillment of the requirements for the degree of Master of Science in Sustainable Energy Technology (M.Sc. SET), Report nr: 2484

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Abstract

Mathematical modeling together with simulation is an essential tool for the design and optimization of solid oxide fuel cells (SOFCs). The present work aims to investigate the development of an anode-supported intermediate temperature direct internal reforming planar solid oxide fuel single channel model, under co-flow operation. The corrugated bipolar plates serve as gas channels and current collector above the active area of the cell. The direct internal reforming reaction of methane, water-gas shift reaction of carbon monoxide and the electrochemical reaction of hydrogen are taken into account. In order to obtain convincing results, simulations were made for operation with biosyngas, methane, and a mixture containing methane and pre-reformed methane. The goal was to investigate whether the operation of the fuel cell is safe (avoid carbon deposition and oxidation of Ni contained in the anode) and how the performance can be enhanced. The performance of the cell can be improved by manipulating the methane steam reforming reaction. The modeling results show the current density distributions and temperature change profiles in the channel and gas concentrations profiles along the channel. Furthermore, the temperature gradients inside the channel are investigated. Detailed comparisons about the gas concentrations, current density distributions and temperature change profiles between these three simulation models are illustrated and discussed in details. These predicted simulation results could provide useful information and constructive suggestions to future experiments.
Acknowledgement

First of all, I would like to thank my supervisor, Dr. ir. P.V. Aravind for giving me the opportunity to work on the challenging field of solid oxide fuel cells, and for his guidance throughout the completion of this M.Sc. Thesis. I would also like to thank the other two members of the reviewing committee Professor A.H.M Verkooijen and Dr. ir. M.J.B.M. Pourquie for honouring me by accepting to be in the evaluating committee of this work. I am also thankful to my daily supervisor, PhD candidate Liyuan Fan for her valuable help, co-operation and guidance during my effort.

Special thanks to Michalis Abatzis, Michalis Seiragakis, Dimitris Michailidis, Dimitris Deligiannis, Marilena Kyriakou, Aris Goulas, Nikos Avgirinos and all the new friends I made during my two-year stay in the Netherlands, for their company and happy moments we had. I feel the need to express my thanks to Michalis Seiragakis, Giannis Dafnomilis and Faidra Filipidou for their hospitality during the last two months of my stay in the Netherlands. I would also like to recognize the warm welcome from my fellow-students Jip, Sander, Gerrard and Hans working in the same office in the Process and Energy Department building. Credit to all football fans for joining our online football radio show ‘The Fans Coffeeshop’ (aka ‘Το Coffeeshop των Φιλάθλων’) for their discussions and debates around football and tactics every Sunday night.

I would also like to express my thanks and appreciation to Olga Souridi for her positive attitude, encouragement and support she offered me.

Finally I would like to point out the assistance and support that my parents Dimitris and Georgia Dimitriou and my brother Panos have offered me. My gratitude is the minimum reciprocation for their contribution to my efforts.

Themis Dimitriou

Delft-December 2011
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Chapter 1: Introduction

1.1 World energy scenarios and need for renewable technologies

Modern societies continue to rely largely on fossil fuels to preserve economic growth and today's standard of living. However, for the first time, physical limits of the Earth are met in our encounter with finite resources of oil and natural gas and its impact of greenhouse gas emissions onto the global climate. The global primary energy consumption is expected to rise by 40% until 2030. This is interpreted as an annual increase by 1.5% till 2030. The energy related carbon dioxide emissions are expected to be 40 Gt by year 2030, that is a rise by 45% compared to current CO$_2$ emissions [1]. The energy future being created is unsustainable. If this situation continues, the energy supply to meet the needs of the world economy over the next 25 years is too vulnerable to failure arising from under-investment, environmental catastrophe or sudden supply interruption. Never before has accurate accounting of mankind's energy dependency been more pertinent to developing public policies for a sustainable development of societies, both in the industrial world and the emerging economies. In order to reduce the dependency on fossil fuels the following actions are required:

1) Development of technologies that will improve the efficiency of present day energy consumption systems, thus leading to reduced emissions.
   - Clean fossil fuels (e.g. natural gas)
   - Advanced power plant technologies
   - Combined cycles and cogeneration of heat and power.

2) Development of technologies producing energy from renewable sources:
   - Hydropower
   - Geothermal
   - Solar
   - Wind
   - Biomass

1.2 Biomass and methane as energy sources

1.2.1 Energy from biomass

Biomass is a term used to define the organic material coming from vegetation, wastes or other biological sources. It is the combination of the energy from the sun with the absorbed carbon dioxide from the atmosphere during photosynthesis. Biomass is considered to be a renewable energy resource, because during its production the amount of CO$_2$ emitted, is the same as the CO$_2$ absorbed during its life. Biomass as a renewable source can help to deal with the climate change issue, and help maintain a balance in ecosystems. This means that use of biomass
will not contribute to greenhouse gases emission [2]. Biomass can directly replace fossil fuels as it can be used in solid, liquid or gaseous form. Additionally there is valorization of waste streams (agricultural, municipal). However, there are also disadvantages such as low energy density compared to oil, competition with food, environmental concerns and emissions during seeding, growing, harvesting and processing.

Some types of biomass from crop residues can be seen in Table 1.1. Biomass is used in many applications as a solid material in the form of pellets or briquettes. However this is not the case in most applications. It is preferable to convert biomass to liquid or gaseous energy carriers, offering more advantages in handling and applications. The most usual processes to convert biomass are thermo-chemical conversion processes (gasification, combustion, liquefaction) or biological conversion processes (digestion, fermentation) [3].

The world derives about 10 % of its energy from biomass. In developing countries biomass is the most important energy source, accounting for about 35 % of the total. In the largest developing countries, China and India, biomass accounts for 19 % and 42 % of the primary energy supply mix [1]. Although most biomass is used in traditional ways (as fuel for households and small industries) and not necessarily in a sustainable manner, modern industrial-scale biomass applications have increasingly become commercially available. The annual global primary production of bio-matter totals 4500 EJ (220 billion dry tons). The theoretically harvestable bio-energy potential is estimated to be 2900 EJ, of which 270 EJ could be considered technically available on a sustainable basis [5].

<table>
<thead>
<tr>
<th>Crop residue</th>
<th>HHV (MJ/kg)</th>
<th>Crop residue</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk</td>
<td>12.9-14.9</td>
<td>Vineyard prunings</td>
<td>16.81</td>
</tr>
<tr>
<td>Rice straw</td>
<td>16.3</td>
<td>Corn cobs</td>
<td>18.02</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>17.5</td>
<td>Sugar beet leaves</td>
<td>17.72</td>
</tr>
<tr>
<td>Barley straw</td>
<td>17.1-18.2</td>
<td>Rice straw</td>
<td>12.16</td>
</tr>
<tr>
<td>Olive tree prunings</td>
<td>18.86</td>
<td>Peach tree prunings</td>
<td>18.86</td>
</tr>
<tr>
<td>Cotton stalks</td>
<td>15.81</td>
<td>Almond tree prunings</td>
<td>18.43</td>
</tr>
<tr>
<td>Durum wheat straw</td>
<td>17.92</td>
<td>Oats straw</td>
<td>18.11</td>
</tr>
<tr>
<td>Corn stalks</td>
<td>17.82</td>
<td>Sunflower straw</td>
<td>20/83</td>
</tr>
<tr>
<td>Soft wheat straw</td>
<td>17.92</td>
<td>Cherry tree prunings</td>
<td>21.78</td>
</tr>
</tbody>
</table>

**Table 1.1:** Higher heating value (HHV) of various crop residues [4].

Biomass has the perspective to become a renewable energy source and be used by a wide range of small and large-scale power production technologies [6]. However, large-scale bioenergy plants have to face logistical problems associated with the collection of the required residual biomass fuel, different fuel provision or large economic risk. Apart from this, large Combined Heat and Power (CHP) plants can’t take full advantage of co-generation economics, due to complex cooperation of the different stakeholders involved: biomass fuel producers, electricity and heat consumers etc. In order to deal with these issues, high efficiency small-scale biomass CHP units could be developed to provide a solution. These systems can be based on gasification integrated with high temperature solid oxide fuel cells (SOFC) and they could be scaled down to meeting the demands of only one household [7,8]. SOFCs can also be used for large-scale power plants. When a SOFC fed with biosyngas is coupled with a gas turbine (GT), efficiencies as high as 50% can be achieved [11].
1.2.2 Techniques for biomass processing
In considering methods for extracting energy from biomass, the processes can be ordered by complexity as followed:

- Direct combustion of raw biomass
- Combustion after relatively simple physical processing, such as: sorting, grinding, compressing and/or air-drying
- Thermochemical processing to upgrade the biofuel, such as: pyrolysis, gasification and liquefaction
- Biological processing such as anaerobic digestion and fermentation leading to a useful gaseous or liquid fuel

1.2.3 Energy from methane

Natural gas is the combustible gas that occurs in porous rocks in the earth’s crust. It is found with or close to crude oil reserves, but may also occur alone in separate reservoirs. Most commonly, it forms a gas cap trapped between liquid petroleum and an impervious rock layer (cap rock) in a petroleum reservoir. If the pressure is high enough, the gas will be intimately mixed with or dissolved in the crude petroleum. Chemically, natural gas comprises a mixture of hydrocarbons of low boiling point.

Methane is the component usually present in the greatest concentration (75-95%), with smaller amounts of ethane, propane, and so on. In addition to hydrocarbons, natural gas contains various quantities of nitrogen, carbon dioxide, and traces of other gases such as helium (often present in commercially recoverable quantities). Sulphur is also present to a greater or lesser extent, mostly in the form of hydrogen sulphide. The overall composition varies according to the source of the natural gas, and there are also seasonal variations [1,9,10].

Methane is important for electricity generation by burning it as a fuel in a gas turbine or a steam boiler. Compared to other hydrocarbon fuels burning methane produces less carbon dioxide for each unit of heat released. Apart from generation of electricity, in certain cities methane (usually called natural gas) is piped into homes for domestic heating and cooking. Methane in the form of compresses natural gas can be used as a vehicle fuel [1,9,10]. According to the IEA World Energy Outlook [1], methane will play a key role in the energy section worldwide whatever the policy landscape. Methane can be used as a fuel for CHP in SOFC-GT systems with total efficiency around 80%.

1.3 Fuel Cells

1.3.1 Introduction to fuel cells

Fuel cells are electrochemical devices that convert chemical energy in fuels and an oxidant into electrical energy directly, promising power generation with high efficiency and low environmental impact. In a typical fuel cell, gaseous fuels are fed to the anode and gaseous oxidants are fed to the cathode. The anode and cathode are made from porous materials provided with electro catalysts and are separated by electrolytes which conduct ions. The electrolyte allows only the flow of ions, but blocks the flow of electrons. The electrochemical reaction causes a flow of ions from the anode/cathode through the electrolyte to the cathode/anode. The electrons that are released at the electrode/electrolyte interphase cause an external current [9,10].
Because the intermediate steps of producing heat and mechanical work typical of most conventional power generation methods are avoided, fuel cells are not limited by thermodynamic limitations of heat engines such as the Carnot efficiency. What actually happens is that the fuel cell, prevents the direct irreversible combustion of fuel. In addition, because combustion is avoided, fuel cells produce power with minimal pollutant emissions. However, unlike batteries the reductant and oxidant in fuel cells must be continuously replenished to allow continuous operation.

The most important design features in a fuel cell are:

- The electrolyte substance.
- The fuel used.
- The anode catalyst.
- The cathode catalyst.

Most fuel cell power systems comprise a number of components:

- Unit cells, in which the electrochemical reactions take place.
- Stacks, in which individual cells are modularly combined by electrically connecting the cells in parallel or in series to form units with the desired output capacity.
- Sealing, which prevents mixing of fuel and oxidant and mixing of reactants with the environment. In addition to this, sealing provides mechanical bonding of components and electrical insulation between stack components.
- Balance of plant, which comprises components that provide fuel and oxidant conditioning, thermal management, and electric power conditioning.

1.3.2 Different types of fuel cells

Polymer Electrolyte Membrane Fuel Cell (PEMFC/SPFC)

The electrolyte in this polymer electrolyte membrane fuel cell (or solid polymer fuel cell) is an ion exchange membrane (usually fluorinated sulfonic acid polymer known as nafion). Typically, carbon electrodes with platinum electro-catalyst are used for both anode and cathode, with either carbon or metal interconnects. Hydrogen is fed to the anode side of the fuel cell where the hydrogen atoms release electrons and become protons. The electrons travel through the external circuit from anode to cathode generating electric current. The operating temperature is typically around 40 to 120 °C. A H₂-rich gas with minimal amount of CO is used. The anode can be poisoned by sulfur species, halogens or low levels of CO. Thus, extensive fuel processing is required. Although significant development of PEMFC for stationary applications has taken place, many developers focus on automotive and portable applications. PEMFCs have high power density and can vary their output quickly to meet variations in power demand. They are reported to have electrical efficiencies up to 50% when running with hydrogen as fuel [9,10].

Direct Methanol Fuel Cells (DMFC)

The direct methanol fuel cells are similar to the PEMFC, in that they both use nafion as the electrolyte. However, in the DMFC the anode catalyst itself accelerates the reaction to obtain hydrogen from the liquid fuel (methanol), and thus no fuel reformer is required. This type of fuel cell typically operates at temperatures between 20-90 °C. Higher efficiencies could be achieved at
higher temperatures, but the use of nafion sets a restriction. In addition, nafion shows a large cross over of methanol, which is a disadvantage. Electrical efficiencies of about 40% are expected with this type of fuel cell [9,10,11].

**Alkaline Fuel Cells (AFC)**

Alkaline fuel cells use aqueous potassium hydroxide (KOH) as the electrolyte. Their operating temperature is up to 65-220 °C. The electrolyte is retained in a matrix (usually asbestos), and a wide range of electro-catalysts can be used (Ni, Ag, metal oxides, spinels, and noble metals). Hydrogen is considered as the preferred fuel for AFCs. CO is a poison, and even the small amount of CO₂ in air must be considered a potential poison for the alkaline cell. CO₂ will react with the KOH (potassium hydroxide) to form K₂CO₃, thus altering the electrolyte. Electrical efficiency of this type of fuel cell is around 50-60% percent with hydrogen [9,10].

**Phosphoric Acid Fuel Cell (PAFC)**

Phosphoric acid is used as the electrolyte in this fuel cell, typically operating at a temperature range between 150 and 220 °C. At lower temperatures, phosphoric acid is a poor ionic conductor, and CO poisoning of the Pt electro-catalyst in the anode becomes severe. The matrix most commonly used to retain the acid is silicon carbide, and the electro-catalyst in both electrodes is Pt. With hydrogen as fuel, the fuel cell electrical efficiency is around 40 percent [9,10].

**Molten-carbonate Fuel Cells (MCFC)**

Molten-carbonate fuel cells have a molten mixture of alkali metal carbonates as electrolyte carrying oxygen from cathode to anode in the form of carbonate ions and fuel oxidation takes place at the anode. They have high operating temperature around 650 °C. This high operation temperature offers MCFCs the advantage that they can be combined in CHP power production installations. Molten-carbonate fuel cells have been operated with hydrogen, carbon monoxide, natural gas, propane, and coal gasification products. Carbonate fuel cells for stationary applications have been successfully demonstrated. A major problem with MCFC is the corrosion due to molten carbonate electrolyte. MCFCs are reported to have electrical efficiencies up to 60% when running with hydrogen. [9,10].

**Solid-Oxide Fuel Cells (SOFC)**

Solid-oxide fuel cells (SOFCs) are fuel flexible. They have an oxide ion conducting solid electrolyte and the fuel oxidation takes place at the anode. They can be used in industrial and large-scale central electricity generating stations. Auxiliary power units with SOFCs are another expected application. A SOFC usually uses a gas-tight ceramic material, at high operating temperatures of 600-1000 °C. SOFCs are reported to have electrical efficiencies up to 60% with hydrogen as fuel. They have the advantages that they can operate with carbonaceous fuels too and also offer a possibility of combining Solid oxide fuel cell-gas turbine systems (SOFC-GT systems). SOFC-GT systems operating on fuels such as hydrogen and methane are expected to have electrical efficiencies of the order of 60-80%. SOFC systems can make an important contribution to the energy conservation industry because decentralized cogeneration in smaller systems is an important element in the efficient utilization of fossil fuels and biogenic fuels. Of all potential technologies for small cogeneration plants, SOFC fuel cell systems offer the highest efficiency, highest end-user benefit/cost ratio and the lowest pollutant emissions. [9,10].
### Table 1.2: Summary of major differences of the fuel cell types [10].

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>PEMFC/SPFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrated polymeric ion exchange membranes</td>
<td></td>
<td>Mobilized or Immobilized KOH in asbestos matrix</td>
<td>Immobilized Liquid Phosphoric Acid in SiC</td>
<td>Immobilized Liquid Molten Carbonate in LiAlO₂</td>
<td>Perovskites (Ceramics)</td>
</tr>
<tr>
<td>Electrodess</td>
<td>Carbon</td>
<td>Transition metals</td>
<td>Carbon</td>
<td>Nickel and Nickel Oxide</td>
<td>Perovskite and perovskite / metal cermet</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Electrode material</td>
<td>Electrode material</td>
</tr>
<tr>
<td>Interconnect</td>
<td>Carbon or metal</td>
<td>Metal</td>
<td>Graphite</td>
<td>Stainless steel or Nickel</td>
<td>Nickel, ceramic, or steel</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>40-80 °C</td>
<td>65°C – 220 °C</td>
<td>205 °C</td>
<td>650 °C</td>
<td>600-1000 °C</td>
</tr>
<tr>
<td>Charge carrier</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>CO₂⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>External reformer for HC fuels</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No. Only for some fuels</td>
<td>No. Only for some fuels and cell designs</td>
</tr>
<tr>
<td>External shift conversion of CO to hydrogen</td>
<td>Yes, plus CO trace removal</td>
<td>Yes, plus purification to remove CO and CO₂</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Prime cell components</td>
<td>Carbon-based</td>
<td>Carbon-based</td>
<td>Graphite-based</td>
<td>Stainless-based</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Product water Management</td>
<td>Evaporative</td>
<td>Evaporative</td>
<td>Evaporative</td>
<td>Gaseous Product</td>
<td>Gaseous Product</td>
</tr>
</tbody>
</table>

#### 1.3.3 Fueling SOFCs

SOFCs operating at high temperatures apart from high efficiency present flexibility concerning the fuel used and can also provide heat for gas or steam turbine electricity generation or for CHP installations. SOFCs produce heat and electricity by electrochemically oxidizing H₂ and CO. The benefits of using SOFCs include the possibility of operation using natural gas, NH₃, LPG, biosyngas or coal gases. For low temperature fuel cells hydrogen is produced by reforming hydrocarbons in an external steam reformer. In SOFCs because of the high operating temperature and the Ni containing anode, hydrocarbons can be internally reformed. One of the most commonly used hydrocarbons in SOFCs is CH₄. One of the advantages of internal steam reforming is that part of the heat generated in the cell by electrochemical reactions, and ohmic heating is directly used for the endothermic reforming reaction [10]. With the current SOFC technology, the internal steam reforming is much faster than the electrochemical reactions, which means that the temperature gradients are actually larger than for SOFC’s running on pure hydrogen [12,13]. By gradually removing heat and producing hydrogen through the cell, the
temperature and concentration gradients can be decreased which could significantly improve its performance [12,13]. The reforming reactions for CH₄ are:

\[
\begin{align*}
CH_4 + H_2O &\rightarrow CO + 3H_2 & \Delta H_{298}^0 &= 206 \text{ kJ/mol} \quad (1.1) \\
CO + H_2O &\rightarrow CO_2 + H_2 & \Delta H_{298}^0 &= -41 \text{ kJ/mol} \quad (1.2)
\end{align*}
\]

Equation (1.1) is called the methane steam reforming reaction (MSR) and equation (1.2) is the associated water gas shift reaction (WGS).

One of the major issues for internal steam reforming at the temperatures used in SOFCs today is that the reforming reaction is much faster than the electrochemical reactions. This is mainly due to the high Ni content, which is required for electric conductivity, but also offers a high number of catalytic sites. Steam reforming consumes heat and the electrochemical reactions produce heat and since the steam reforming is fastest, the result is cooling at the fuel inlet and heating at the fuel outlet. This introduces large temperature gradients, resulting in thermal stress and lower efficiency [12,13]. The goal for optimizing internal steam reforming is to lower the reaction rate of steam reforming, while maintaining high electric conductivity and high reactivity of the electrochemical reactions. The general tendency of today’s SOFC research is to lower the operating temperature and since the steam reforming reaction has a high activation energy (58–228 kJ/mol), the reaction rate decreases rapidly with temperature [13].

In situ microscopy studies reported by Sehested [14,15] show that step sites on the Ni catalyst particles are the most active nucleation sites for both carbon formation and steam reforming. This is backed up by density functional theory calculations [16,17] and is in line with the observation that potassium, sulfur and gold reduce carbon formation by blocking these step sites [18, 19, 20,21-23]. Blocking the step sites also significantly reduces the steam reforming rate, which makes this method one of the most promising ones for reducing carbon deposition in SOFCs with internal steam reforming.

The size of nickel particles in the anode support will influence the steam reforming rate because larger particles give a smaller surface area for the same nickel content and thereby less active sites for catalysis. Sulfur adsorption in the anode has a much stronger impact on the steam reforming rate than it does on the electrochemical processes [13] and hence, slowing down the reforming rate by controlled sulfur poisoning is an interesting technological possibility [13]. Alkali poisoning is a promising method for fine tuning of catalytic activity in SOFCs [13,19]. Replacing some of the nickel in the anode with copper reduces the steam reforming rate with a factor 4-20 without significant reduction in electrochemical performance [27].

1.4 Motivation and scope of this work

1.4.1 Motivation

Given the actual energetic context, and in particular the aspects concerning production, storage and distribution infrastructures of hydrogen, the use of other fuels based on hydrocarbons sounds interesting to be considered. Natural gas, biogas, waste fuels, bio-ethanol or other sources are interesting candidates for clean and cheap operation of SOFCs. The fundamental ability of SOFC systems to adapt to a variety of fossil and biogenic fuels (biogas, ‘biomass-to-liquid’ fuels) offers the ideal opportunity to build up an energy economy based on
locally available biomass resources. Such a system could be useful in remote places where grid connection is difficult or unavailable. The integration of biomass gasification and solid oxide fuel cells (SOFCs) could be such a solution for the production of heat and electricity. A system like this could also help households to reduce their energy bill and also make people aware of the need and the advantages of ‘going green’.

However, the development of SOFC is still facing some challenging problems, such as proven longer life time, a lower net cost and an elevated performance, towards its large-scale commercialization and profitability. In order to achieve these, a more detailed understanding of the internal processes and an accurate prediction of operating parameters inside the fuel cell are required. The SOFC’s high operating temperature makes the experimental investigation and measurement of these parameters costly and difficult, therefore mathematical modeling becomes an important tool. Compared with experimental investigations, mathematical modeling is an economic and useful tool to predict the SOFC performance, to perform parametric analysis, to better understand SOFC mechanisms, as well as to achieve design optimization.

1.4.2 Goals

In this study, a three-dimensional thermo-fluid model coupled with electrochemical reaction for an anode-supported planar SOFC has been developed to investigate the internal processes and temperature distribution within a single cell unit for the design proposed by the Energy research Center of the Netherlands (ECN) [28] in cooperation with TU Delft. The SOFC developed is for operation with natural gas. In this work, operation with bio-syngas is evaluated. The electrochemical reactions, heat and mass transfer phenomena between the solid and gas phases have all been included in the cell model. The conservation equations of the thermo-fluid model are solved, by using the commercial CFD (computational fluid dynamics) software ANSYS FLUENT [29]. The coupled electrochemical processes are simulated by external user-defined subroutines (UDFs), written in C++ programming language. The electrochemical model utilizes an empirical equation for the cell resistance with experimentally determined values of the different parameters for calculating the electrochemical parameters. The variation of gaseous species concentrations, distribution of current density and temperature profile, etc., over the cell unit are presented and discussed. Furthermore, the effects of thermal radiation are investigated by comparison between the cases with and without radiation heat transfer.

Different compositions of fuel streams will lead to changes in SOFC operation, such as the differences in gas distribution, current densities, heat production, temperature gradients etc, and maybe safety issues for the fuel cells. All these differences mentioned above would bring in new challenges to the materials and the structures for SOFCs. The object is to investigate the complete cell using the models developed and make comparisons for the cell performance when fed with hydrogen, methane and different bio-syngas compositions, come up with suggestions for efficient and ideal SOFC operation conditions when fed with different fuels and investigate safety issues under different working conditions.

In order to clarify the goals of this work, the following questions have to be answered

- Is operation with bio-syngas safe for the SOFC (Ni oxidation, carbon deposition)?
- Is operation with methane safe for the SOFC (Ni oxidation, carbon deposition)?
- What is the impact of different fuel compositions on SOFC performance?
- What is the impact of the steam reforming reaction of methane on the SOFC performance for operation with bio-syngas and methane?
- What constructive suggestions can be made for further development of SOFCs?
Abbreviations
AFC  Alkaline Fuel Cell
CFD  Computational fluid dynamics
CHP  Combined Heat and Power
DMFC  Direct Methanol Fuel Cell
ECN  Energy research Center of the Netherlands
GT  Gas Turbine
HHV  Higher heating value
LPG  Liquefied petroleum gas
MCFC  Molten-carbonate Fuel Cell
MSR  Methane steam reforming
PAFC  Phosphoric Acid Fuel Cell
PEMFC  Polymer Electrolyte Membrane Fuel Cell
SOFC  Solid oxide fuel cells
SPFC  Solid Polymer Fuel Cell
WGS  Water gas shift reaction

References:
Chapter 2: SOFCs and Biomass Gasification

2.1 Introduction

SOFCs operating at high temperatures apart from high efficiency present flexibility concerning the fuel used and can also provide heat for gas or steam turbine electricity generation or for CHP installations. There is a tendency for developing and investigating the viability of decentralized energy production systems. It could be a way of effectively using sustainable energy on a small scale to build a system, which could provide a considerable number of houses with heating and electricity. SOFC systems can make an important contribution to the energy conservation industry because decentralized cogeneration in smaller systems is an important element in the efficient utilization of fossil fuels and biogenic fuels. Decentralized energy supply delivers higher supply security by means of energy availability and cross-linking, as opposed to energy distribution from several centralized power stations. Distribution costs are also reduced. Of all potential technologies for small cogeneration plants, SOFC fuel cell systems offer the highest efficiency and the lowest pollutant emissions.

Gasification of biomass takes place in special devices called gasifiers, which are categorized to fixed bed and fluidized bed gasifiers. However for small-scale applications fixed bed gasifiers are the dominating technology. The biosyngas produced in the gasifiers can be fed to the SOFC, which produces heat and electricity. In order to better understand the operation of SOFCs and improve their design and performance mathematical modeling is employed. Details about gasification, SOFCs, and SOFC modeling are presented in this chapter.

2.2 Biomass Gasification

Biomass gasification is the thermochemical conversion of organically derived, carbonaceous solid fuels into a combustible gaseous product, called biosyngas, by adding oxygen, air, steam or combination of them as an oxidant. Biosyngas consists primarily of hydrogen (H$_2$) and carbon monoxide (CO). Smaller amounts of carbon dioxide (CO$_2$), methane (CH$_4$), ethane (C$_2$H$_6$), water (H$_2$O), nitrogen (N$_2$) and a variety of contaminants such as carbon particulates, tars, ash and higher hydrocarbons are also present in the producer gas. Additionally, sulfur, chlorine, alkali metals and also heavy metals are present in varying quantities depending on the type of biomass fed. The overall reaction that takes place in the gasifier could be written as follows, assuming the complete transformation of the char residue to gas [1,2]:

$$\text{Biomass} + \text{Air} \xrightarrow{HHT} H_2 + CO + CO_2 + CH_4 + C_x C_y + N_2 + Tars + Ash$$  \hspace{1cm} (2.1)

Gasification is not a single step process, but occurs in a number of sequential steps:

- Drying: vaporization of the moisture content.
- Pyrolysis: release of volatile matter (gas, vaporized tars/oils) and solid char residue.
- Gasification: partial oxidation of the char and heterogeneous reactions with CO$_2$ and H$_2$O.
- Gas phase reactions: reactions of the gaseous components formed in the first
stages.

The governing chemical reactions taking place during gasification are [3]:

- **Partial Oxidation**
  \[ C + \frac{1}{2}O_2 \rightleftharpoons CO \quad \Delta H = -268\,MJ / kg \cdot mol \]  
  (2.2)

- **Complete Oxidation**
  \[ C + O_2 \rightleftharpoons CO_2 \quad \Delta H = -406\,MJ / kg \cdot mol \]  
  (2.3)

- **Water-gas reaction**
  \[ C + H_2O \rightleftharpoons CO + H_2 \quad \Delta H = +118\,MJ / kg \cdot mol \]  
  (2.4)

- **WGS reaction**
  \[ CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H = -42\,MJ / kg \cdot mol \]  
  (2.5)

- **Methane formation**
  \[ CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad \Delta H = -88\,MJ / kg \cdot mol \]  
  (2.6)

- **Boudouard reaction**
  \[ C + CO_2 \rightleftharpoons 2CO \quad \Delta H = +172\,MJ / kg \cdot mol \]  
  (2.7)

There are different groups into which gasifiers can be classified with reference to their technology (gasifying agent, self-sufficiency in heat requirement, pressure etc.) The most usual classification is the one concerning the gasifier bed. There are two basic gasification reactor types: the fixed bed gasifier and the fluidized bed gasifier with variations within each type.

### 2.2.1 Fixed bed gasifiers

The fixed bed gasifiers have been in use for the longest [4] time and their advantage is that they are quite simple and robust. Since the bed is fixed, the design in normally very simple. Fixed bed gasification units are usually used for small-scale applications up to a few MWth. Air is mostly used as the gasification agent with oxygen and steam being alternative options. The three kinds of fixed bed reactors distinguished, are: downdraft gasifier, updraft gasifier, and the cross current gasifier.

![Figure 2.1](image.png)

**Figure 2.1:** a) Updraft, b) downdraft and c) crossdraft fixed bed gasifiers [4].

**Updraft gasifiers**

Fuel is fed at the top and the gasifying medium (air or oxygen and/or steam) is introduced at the bottom and drawn up through the fuel. The fuel bed rests on a grate through which air is supplied. Complete combustion takes place at the bottom of the bed in the oxidation zone where \(CO_2\) and \(H_2O\) are formed. The hot gases then pass through the reduction zone where they are reduced to \(H_2\) and \(CO\). Further up the bed the reducing gases pyrolyse the downward flowing...
biomass forming large amounts of tars and other products of incomplete gasification. Finally, the gases dry the incoming wet biomass and leave the reactor [4].

**Downdraft gasifiers**

Fuel is fed at the top and the gasifying medium is introduced into a downward flowing packed bed. The syngas is then drawn near the bottom. The downdraft gasifiers normally reach relatively low tar levels since the tar produced in the pyrolysis stage will be thermally cracked when it passes the homogeneous high-temperature combustion zone. A drawback with this system is that a large portion of the fuel-energy is converted into heat with a low heating value of the syngas as a result [4].

**Crossdraft gasifier**

Fuel is fed at the top and the gasifying medium is introduced from the side and drawn through the fuel. The syngas is then drawn off from the opposite side [4].

### 2.2.2 Fluidized bed gasifiers

Fluidized bed gasifiers normally use a sand bed material with a size distribution around 250 μm. The bed material enhances the heat exchange between the fuel particles and increases mixing and kinetics, thus increasing overall gasifier efficiency and fuel throughput. The risk of bed agglomeration, which is also one of the major disadvantages for biomass fuels, makes it necessary to exchange the bed material at proper intervals. The fluidization agent, often air, is normally added in several steps. The primary air is added in the bottom of the bed as fluidizing medium. Fluidized bed gasifiers are designed for mid-scale thermal capacities of 10 MWth to large-scale capacities of 100 MWth and higher. The most common types of fluidized beds are the bubbling fluidized bed (BFB) and the circulating fluidized bed (CFB). The ultimate analysis of a fuel is essential in determining the theoretical air-to-feed ratio, the higher heating value of the biomass material and in assessing the pollution potential of the feedstock [4,5].

**Figure 2.2:** a) Bubbling and b) circulating fluidized bed gasifiers [4].

**Bubbling Fluidized Bed Gasifier – BFBG**

The fuel is fed into or on top of the sand bed and the gasification agent is introduced from the bottom at speeds of 2 to 3 m/s resulting in bubbles that go up through the bed. The speed of
the fluidizing agent is of great importance for the size and speed of the bubbles and thus influencing the mixing and heat exchange between the fuel particles. The syngas is drawn off from the top of the reactor via a cyclone to separate sand and fly ash from the syngas [4,5].

Circulating Fluidized Bed Gasifier - CFBG

Fuel is fed into the sand bed and the gasifying medium is introduced from the bottom at speeds of 5 to 10 m/s. This is sufficient to suspend the bed particles throughout the entire reactor, causing a portion of the sand and char to exit the reactor along with the producer gas stream. The “entrained” particles which accompany the gas out of the gasifier unit are captured in a cyclone which recycles the bed material back into the bed. Syngas is drawn off from the top of the cyclone [4,5].

2.3 Gas cleaning

Though the gas produced is hydrogen rich, it also contains impurities like particulates, tars, sulfur compounds, halogen compounds and alkali metal compounds. These impurities can cause problems in the operation and efficiency of the system, with the fuel cell being the most sensitive. Depending on the desired hydrogen quality, various gas-cleaning systems exist. Before the biosyngas is fed to the fuel cell unit, it has to go through processing and be cleaned in order to be suitable for use. SOFCs in general demonstrate flexibility in the use of fuels and therefore gas species contained in them, as can be seen in the following table. In general, substances that can be considered as contaminants for a SOFC are particulates, tar, alkali compounds and acid gases.

<table>
<thead>
<tr>
<th>Gas species</th>
<th>PEMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
</tr>
<tr>
<td>CO</td>
<td>Poison</td>
<td>Poison</td>
<td>(&lt;0.5%)</td>
<td>Fuel</td>
<td>Fuel</td>
</tr>
<tr>
<td>CH₄</td>
<td>Diluent</td>
<td>Poison</td>
<td>Diluent</td>
<td>Fuel</td>
<td>Fuel</td>
</tr>
<tr>
<td>CO₂ &amp; H₂O</td>
<td>Diluent</td>
<td>Poison</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
</tr>
<tr>
<td>S (H₂S or COS)</td>
<td>-</td>
<td>Poison</td>
<td>(&gt;50 ppm)</td>
<td>Poison (&gt;0.5 ppm)</td>
<td>Poison (&gt;1.0 ppm)</td>
</tr>
</tbody>
</table>

Table 2.1: Fuel requirements for the principal types of fuel cells [6].

2.4 Solid oxide fuel cells

2.4.1 Fundamentals of SOFCs

Solid oxide fuel cells are energy conversion devices that produce electricity and heat directly from a gaseous fuel by electrochemical reaction of the fuel with an oxidant. A SOFC consists of an interconnect structure and a three-layer region composed of one anode and one cathode, separated by a dense ceramic electrolyte. The electrolyte material is usually yttria-stabilized zirconia (YSZ). The anode is a porous cermet made of Ni on an YSZ frame and the cathode is a porous strontium-doped lanthanum manganite (La₀.₈₄Sr₀.₁₆)MnO₃ structure. SOFCs operate at high temperatures (600-1000 °C) and atmospheric or elevated pressures. SOFCs can use H₂, CO, and hydrocarbons as fuel, and oxygen (pure or in an air stream) as oxidant. In the cell, the oxygen ions formed at the cathode migrate through the ion-conducting electrolyte to the anode/electrolyte interface where they react with the hydrogen and carbon monoxide contained in the fuel, producing water and carbon dioxide while releasing electrons that flow via an external
circuit to the cathode/electrolyte interface. When CH\textsubscript{4} or/and CO is present in the fuel stream they will produce additional amounts of hydrogen or carbon monoxide via the reforming reactions [6,7]. The overall reactions for the electrochemical oxidation of H\textsubscript{2} and CO are:

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O 
\]

\[
CO + \frac{1}{2}O_2 \rightarrow CO_2
\]

Figure 2.3: The separate anode and cathode reactions for the SOFC, when using hydrogen and carbon monoxide fuel [7].

The solid oxide fuel cell is widely expected to play a major role in the medium-sized electricity power generation industry (1–10 MW) in the coming decades. The benefits include the possibility of operation using natural gas, NH\textsubscript{3}, LPG, biosyngas or coal gases, zero emissions of nitrogen and sulphur oxides, and very high cycle efficiencies when combined with a gas turbine. Additionally, SOFC systems can make an important contribution to the energy conservation industry because decentralized cogeneration in smaller systems is an important element in the efficient utilization of fossil fuels and biogenic fuels. Decentralized energy supply delivers higher supply security by means of redundancy and cross-linking, as opposed to energy distribution from several centralized power stations. Of all potential technologies for small cogeneration plants, SOFC fuel cell systems offer the highest efficiency, highest end-user cost/benefit ratio and the lowest pollutant emissions [1,6].

The high operating temperature of SOFCs provides several advantages:

- The rate of electrochemical reactions is high, eliminating the need of expensive noble metal catalyst, and thus, SOFCs are more cost-effective than low temperature fuel cells [6,7].
• High temperature waste heat from an SOFC is of high quality and can be recovered to achieve high-energy conversion efficiency.

• In addition to hydrogen, hydrocarbon fuels such as methane, methanol, ethanol etc. can be directly used as fuel for SOFCs with internal reforming processes.

In order to calculate the cell voltage, the Nernst equation is employed. The Nernst voltage is the reversible cell voltage that would exist at given pressure and temperature. For the electrochemical oxidation of hydrogen and carbon monoxide, equations 2.10 and 2.11 are used respectively:

\[
V_r = -\frac{\Delta g_f}{2F} + \frac{RT}{2F} \ln \left( \frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}^2} \right) \quad (2.10)
\]

\[
V_r = -\frac{\Delta g_f}{2F} + \frac{RT}{2F} \ln \left( \frac{P_{CO} \cdot P_{O_2}^{1/2}}{P_{CO_2}} \right) \quad (2.11)
\]

\[
V^0 = \frac{\Delta g_f}{2F} \quad (2.12)
\]

In the above equations \( P_{H_2}, P_{O_2}, P_{H_2O}, P_{CO}, P_{CO_2} \) represent the partial pressure of the corresponding species, \( T \) represents the cell temperature, \( R \) is the universal gas constant, \( \frac{\Delta g_f}{2F} \) is the change of Gibbs free energy for the formation reaction of water divided by 2\( F \), where \( F \) is the Faraday constant and number two represents the amount of electrons transferred during the electrochemical oxidation of \( H_2 \) or \( CO \). The above ratio is also known as the standard potential for the \( H_2/CO \) oxidation reaction and is denoted by \( V^0 \).

**Ceramic electrolyte**

The most commonly used electrolyte material is zirconia (ZrO\(_2\)) doped with 8% mole yttria (Y\(_2\)O\(_3\)). This material is known as yttria-stabilized zirconia (YSZ). The role of the electrolyte is to conduct oxygen ion transport from the cathode to the anode. The YSZ electrolyte is dense (contrary to the porous electrodes), and does not allow the flow of electrons or gases. The reason that the crystal lattice of ZrO\(_2\) is doped with Y\(_2\)O\(_3\) is to create oxygen vacancies, which will be filled by oxygen ions, thus making the ion flow to the anode possible. Other materials such as CGO (ceria with the addition of gadolinium) have been proposed as electrolyte materials [6].

**Anode**

The fuel is electrochemically oxidized at the anode of the SOFC. The electrochemical reactions take place at three-phase boundary (Figure 4), i.e. the interface between the catalyst material, the anode material and gas phase. It has already been discussed that hydrogen is not the only fuel to be used in SOFCs. Carbon monoxide and light hydrocarbons can be oxidized as well. The corresponding electrochemical reactions in the anode are:

\[
H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (2.13)
\]

\[
CO + O^{2-} \rightleftharpoons CO_2 + 2e^- \quad (2.14)
\]

\[
CH_4 + 4O^{2-} \rightleftharpoons CO_2 + 2H_2O + 8e^- \quad (2.15)
\]

The advantage of SOFCs over low temperature fuel cells is that they operate at high temperatures, thus providing the required heat for direct internal reforming of hydrocarbons.
(mainly CH₄) to produce H₂. What is more, through the water gas shift reaction (WGS), SOFCs can use CO to produce H₂. Both these reactions take place directly in the anode of the fuel cell:

\[
\begin{align*}
CH_4 + H_2O & \rightarrow CO + 3H_2 & \Delta H^{0}_{298} = 206 \text{ kJ/mol} \\
CO + H_2O & \rightarrow CO_2 + H_2 & \Delta H^{0}_{298} = -41 \text{ kJ/mol}
\end{align*}
\]  

(2.16)

(2.17)

Details concerning the reforming reactions and the corresponding reaction kinetics will be further discussed in the following chapter 3 of this work.

A commonly used anode material is a cermet made of nickel and an yttria stabilized zirconia frame (Ni-YSZ). The zirconia is used in the anode for two reasons: 1) to avoid sintering of the Ni particles 2) to achieve a thermal expansion coefficient value similar to that of the electrolyte. The anode has a high porosity (20–40%) to allow rapid mass transport of reactant and product gases.

Cathode

The cathode is also porous so as not to inhibit transport of reactant and product gases. Oxygen molecules split into oxygen ions, and are transported from the cathode to the anode through the electrolyte. The reaction takes place mainly at the three-phase boundary. The most commonly used materials used are doped lanthanum manganites, such as strontium-doped lanthanum manganite (La₀.₈₄Sr₀.₁₆)MnO₃. The reaction taking place in the cathode is:

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

(2.18)

Stack design

The voltage of a fuel cell is quite small when drawing a useful current. In order to obtain a useful voltage output the cells have to be connected in series. The compilation of fuel cells in series is known as a stack. The cells are fixed in series (or in parallel) by connecting the edge of each anode to the cathode of the next cell. Bipolar plates are placed between the anode and the cathode of the next cell. The bipolar plates serve as cell interconnectors and apart from providing electrical contact with the electrodes, they are designed in such a way so that they form channels for the gas streams to flow. The following figure is a good depiction of how a fuel cell stack looks like. The channel for fuel feed in the anode and the channels for oxidant feed in the cathode are vertical (or parallel) to each other. It is important to note that though good electrical
connection is required, the fuel and oxidant supplies must be separated. There are two types of fuel cell stacks: planar and tubular.

![Diagram of a two-cell planar and tubular stack showing how bipolar plates connect the anode of one cell to the cathode of the next cell][6,22].

### 2.4.2 Thermodynamics of Fuel Cells

The first and the second law of thermodynamics allow the description of a reversible fuel cell. The second law of thermodynamics will determine the reversibility of the transport processes. The assumption of a reversible operating fuel cell requires that the chemical potentials of the fluids at the anode and the cathode are converted into electrical potentials at each specific gas composition.

![Diagram of the reversible fuel cell, its energy balance and its system boundary][2.20]

The reactants deliver the total enthalpy $\Sigma H_i$ to the fuel cell and the total enthalpy $\Sigma H_j$ leaves the fuel cell. The application of the first law of thermodynamics will lead to the following equation:

$$Q + W = \sum H_j - \sum H_i \quad \text{or} \quad Q + W = \Delta H \ (2.19)$$

The above equation implies that the molar reaction enthalpy of the fuel oxidation is the sum of work and heat. Considering the process as reversible, the second law of thermodynamics will lead to:

$$Q = Q_{rev} = T \cdot \Delta S \quad \text{and} \quad Q_{rev} + W_{rev} = \Delta H \ (2.20)$$

The reaction entropy $\Delta S$ is the entropy difference between the entropy of the species at the inlet
and outlet. Concerning the energy balance shown in Figure 2.6, the heat $Q_{rev}$ has to be transferred reversibly from the fuel cell to the environment. $Q_{rev}$ is defined as a positive value if the reversible change in entropy is positive as well, and thus the heat is transported from the environment to the fuel cell. The negative reversible work $-W_{rev}$ is transferred from the fuel cell to the environment. Combining the above equations will yield [23]:

$$W_{rev} = \Delta H - T \cdot \Delta S$$ (2.21)

The Gibbs free enthalpy will equal to the reversible work produced by the fuel cell and thus the following equation is obtained:

$$W_{rev} = \Delta G = \Delta H - T \cdot \Delta S$$ (2.22)

The reversible efficiency of the fuel cell is defined as the ratio of the Gibbs free enthalpy and the reaction enthalpy:

$$\eta_{re} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T \cdot \Delta S}{\Delta H}$$ (2.23)

The reversible work from the electrochemical oxidation of hydrogen is the sum of the reversible work from the individual conversion steps, i.e. $H_2$ compression, $O_2$ compression and $H_2O$ expansion. This can be explained by using the Figure 2.7.

![Figure 2.7: The reversible fuel cell, its energy balance and its system boundary for operation with $H_2$.](image)

The reversible work from the separate steps is summarized as:

- Compression of $H_2$: $W_{rev} = -n_{H_2} \cdot R \cdot T \cdot \ln \frac{p_0}{y_{H_2} \cdot p} = R \cdot T \cdot \ln \left( \frac{y_{H_2} \cdot p}{p_0} \right)^{1}$ (2.24)
- Compression of $O_2$: $W_{rev} = -n_{O_2} \cdot R \cdot T \cdot \ln \frac{p_0}{y_{O_2} \cdot p} = R \cdot T \cdot \ln \left( \frac{y_{O_2} \cdot p}{p_0} \right)^{1/2}$ (2.25)
- Expansion of $H_2O$: $W_{rev} = -n_{H_2O} \cdot R \cdot T \cdot \ln \frac{p_0}{y_{H_2O} \cdot p} = R \cdot T \cdot \ln \left( \frac{y_{H_2O} \cdot p_0}{p} \right)^{1/2}$ (2.26)

With:

- $W_{rev} = -\Delta G^0$ (2.27)
- $W_{rev} = \sum W_{rev}$ (2.28)

Finally, the total reversible work from the chemical reaction becomes (assuming ideal gas):

$$W_{rev} = -\Delta G^0 + R \cdot T \cdot \ln \left( \frac{y_{H_2} \cdot y_{O_2}^{1/2} \left( \frac{p}{p_0} \right)^{1/2}}{y_{H_2O}} \right)$$ (2.29)
The electrical work obtained from 1 mole of fuel in a reversible fuel cell is:
\[ W_{\text{el},r} = n \cdot F \cdot V_{\text{rev}} \]  
(2.30)

Where \( n \) = number of electrons per molecule fuel, \( F \) = Faraday constant (C/mol) and \( V_{\text{rev}} \) = reversible voltage (V). As already explained, for a reversible cell the electrical work equals the work from chemical reaction:
\[ W_{\text{el},r} = W_{\text{FC},r} \Rightarrow n \cdot F \cdot V_{\text{rev}} = W_{\text{FC},r} = -\Delta G \]  
(2.31)

Combining the above equations, the relation for the reversible voltage (known as Nernst voltage) will become:
\[ V_{\text{rev}} = -\frac{\Delta G^0}{2 \cdot F} + \frac{R \cdot T}{2 \cdot F} \ln \left( \frac{y_{H_2} \cdot y_{O_2}^{1/2}}{y_{H_2}^{1/2} \cdot y_{O_2}} \right) \]  
(2.32)

The fuel utilization \( U_f \) is defined as the ratio of the utilized fuel and the maximum available fuel:
\[ U_f = \frac{\dot{m}_{\text{fuel},\text{out}}}{{\dot{m}}_{f,in}} = 1 - \frac{\dot{m}_{\text{out}}}{{\dot{m}}_{f,in}} \]  
(2.33)

The fuel utilization \( U_f \) can also be defined as a function of current:
\[ U_f = \frac{I}{n^f \cdot \dot{n}_{f,in} \cdot F} \]  
(2.34)

The fuel determines the number of transferred electrons \( n^f \). The Faraday constant \( F \) is a constant value and the fuel inlet flow \( n_{f,in} \) is the only variable influencing the relation between fuel utilization \( U_f \) and current \( I \). Fuel utilization \( U_f \) and current \( I \) deliver the same expression if the fuel flow is kept a constant.

The maximum electrical power produced by a single fuel cell equals:
\[ P_{\text{el},\text{max}} = V_{\text{outlet}} \cdot I_{\text{outlet}} \]  
(2.35)

The Nernst voltage \( V_{\text{outlet}} \) at the outlet and the current density \( I_{\text{outlet}} \) at the outlet, are determined by the fuel utilization at the outlet of the fuel cell.

The total power \( P_d \) of a single cell at a constant cell voltage is given by:
\[ P_d = V_{\text{cell}} \cdot \int dl \]  
(2.36)

The area specific power density \( p_d \) is used to estimate the required cell area at a specific total power. When the total current is divided by the fuel cell area the average current density \( i \) is obtained.
\[ p_d = \frac{P_d}{A} = \frac{V_{\text{cell}}}{A} \cdot \int dl = V_{\text{cell}} \cdot i \]  
(2.37)

The conversion of the reacting species in fuel cells is coupled directly with the exchanged electrical current. Considering hydrogen as fuel, the molar consumption of reactants is determined by Faraday’s law:
\[ \dot{n}_{H_2,in} - \dot{n}_{H_2,out} = \frac{I}{2F} \]  
(2.38)
\[ \dot{n}_{H_2,O,out} - \dot{n}_{H_2,O,in} = \frac{I}{2F} \]  
(2.39)
\[ \dot{n}_{O_2,out} - \dot{n}_{O_2,in} = \frac{I}{4F} \]  
(2.40)

where 2 electrons per mol hydrogen and 4 electrons per mol oxygen are exchanged.
2.4.3 Solid Oxide Fuel Cell Electrochemistry

![Graph](image)

Figure 2.8: Schematic of the origin of polarization (voltage) losses in a SOFC [7]

On load, the terminal voltage of a fuel cell is lower than the Nernst potential. The characteristic shape of the voltage-current density and power-current density graphs is presented in Figure 2.8. The graph is obtained by considering four major irreversibilities (losses):

- **Activation losses**: They are caused by the extra potential energy needed to overcome the energy barrier between the electronic and ionic conductors. The activation losses are met on both the anode and the cathode [6,7].

- **Fuel crossover and internal currents**: This energy loss results from fuel passing through the electrolyte (wasted fuel), and from electron conduction through the electrolyte. These losses are met on both the anode and the cathode [6,7].

- **Ohmic losses**: The ohmic losses represent the resistance to the flow of electrons through the electrodes and the various interconnections, as well as the resistance to the flow of ions through the electrolyte. Ohmic losses are the dominant type of loss in SOFCs [6,7].

- **Mass transport or concentration losses**: These result from the change in concentration of the reactants at the surface of the electrodes as the fuel is used [6,7].

When considering the cell irreversibilities, the cell voltage becomes:

\[
V_{\text{cell}} = V_{\text{rev}} - \Delta V_{\text{activation}} - \Delta V_{\text{concentration}} - \Delta V_{\text{Ohmic}} - \Delta V_{\text{crossover}} \tag{2.41}
\]

2.5 SOFCs Coupled with Biomass Gasifier

2.5.1 SOFC operation with biosyngas and impact of gas composition

At present, the main destination for biosyngas generated by gasifiers is its combustion in engines or turbine plants for power generation. High temperature fuel cells can also use syngas as a fuel if it is sufficiently clean. Power generation systems based on fuel cells are therefore a promising method in the outlook of a clean and efficient energy economy, thanks to their high-energy conversion rates, flexible fuel utilization and very low pollutant emissions. High temperature fuel cells, such as the SOFCs, are still in the development stage, but can be integrated in small and large power plants and cogeneration units. Many system designs with
SOFCs are conceivable, but due to their high operating temperatures, integration of a SOFC with a gas turbine seems to be very attractive.

A reasonable number of studies are available in the literature, concerning integrated biomass gasification and SOFCs. Aravind et al. [9] performed such a study. In this study thermodynamic calculations were carried out to evaluate the performance of small-scale (100 kW) gasifier-SOFC-GT systems. High system efficiencies above 50% were achieved. The results obtained indicated the influence of gas cleaning (i.e. the influence of gas composition) at lower temperatures and steam addition on system efficiency. Toonsen et al. [8] studied the influence of the gasification technology (atmospheric indirect steam gasification and pressurized direct air gasification), gas cleaning technology (low and high temperature) and system scale (100 kWe and 30MW_e) on the overall performance of integrated hybrid SOFC gas turbine and gasification systems, achieving electrical exergy efficiencies of 46 - 49.9%. Toonsen et al. [10] performed a thermodynamic evaluation of different energy conversion chains based on centralized biomass gasification and decentralized heat and electricity production (μ-CHP) by a SOFC. The fuels considered were hydrogen, synthetic natural gas, and syngas from biomass gasification resulting in overall exergetic efficiencies of 21.1%, 28.4% and 30.4% respectively. Fahrad et al [11] studied the efficiency of SOFC micro-CHP systems fed with biogas. The electrical efficiencies achieved were ranging between 42.4 and 33.9% and the CHP efficiency values were in the range 76.9-80.5%.

2.5.2 Electrochemical modeling of SOFC systems

The development of SOFC is still facing some problems, such as operation lifetime, cost and efficiency in order to make energy production from SOFC viable. So, it is important to realize the internal processes and operating parameters. Since it is not only difficult but also expensive to investigate these parameters, mathematical modeling is used to identify and overcome problems related with development of SOFCs. The most important of operating parameters is the temperature distribution, because parameters that are crucial for the fuel cell performance such as material properties, chemical kinetics, current densities etc., are strongly dependent on temperature. For this reason mathematical models have been developed to predict the temperature profile of SOFC. These models are one-, two- or three-dimensional with variations in geometries, operating parameters and configurations.

Qu et al. [13] developed a three-dimensional, anode-supported, intermediate-temperature, planar SOFC unit model, using H2 fuel. This work was extended [14] using CH4 in the fuel stream. A thermo-fluid model is used for the conservation equations of mass, momentum and energy. The coupled electrochemical processes, the water gas shift kinetics and methane steam reforming kinetics of the electrochemical model are simulated by external user defined functions. The SOFC system, fed with H2 is operating on co-flow with inlet fuel and air temperatures of 973 K, and 80% fuel utilization with an output voltage of 0.8V. A relatively uniform current density distribution of approximately 5800 A/m² was achieved. Additionally, results have shown that the temperature distribution is strongly dependent on the radiation effects.

Aguiar et al. [15] presented a SOFC anode-supported model. The model comprises mass and energy balances as well as an electrochemical model that connecting the gas composition and temperature to voltage and current density. Since CH4 fuel is used, the reforming reactions are also set in the model. Maximum power densities of 0.86 W/cm² for current density of 2.1 A/cm² and cell voltage 0.42 V have been reported at 1073 K. Additionally it was reported that operation under counter-flow of the fuel and air gas streams is not a good option. The reason is that it
leads to steep temperature gradients with a consequent uneven current density distribution.

Achenbach [16] presented a three-dimensional and time dependent mathematical simulation of a planar SOFC. The results obtained from this research show that for counter-flow the highest cell efficiency is reached, while for co-flow, the most uniform current density distribution is observed. Recycling of the anode gas provided to supply the cell with steam also contributes to higher plant efficiency and more uniform current density distribution. This work also states that for co-flow of fuel and oxidant, the temperature gradient is smaller.

Ni et al. [17] developed a mathematical model to study the performance of methane (CH\(_4\)) fed SOFCs. The model takes into account the CH\(_4\) steam reforming reaction and the water gas shift reaction. The effects of electrode structural parameters on both the exchange current density and gas diffusion coefficients are fully taken into consideration. The results show that the performance can be improved by operating the SOFC at higher temperature, as all the overpotentials decrease with increasing temperature. The rate of steam reforming of CH\(_4\) and water gas shift reaction increases at high temperature, resulting in high rate of H\(_2\). Results were also obtained concerning the effect of electrode microstructure. The electrode microstructures influence the gas transport and thus influence the rate of CH\(_4\) steam reforming and water gas shift reaction. The study finally concluded that the increasing the electrode pore size decreased the concentration overpotential in the cell, while increasing the activation overpotential.

Wang et al. [18] presented a three-dimensional numerical analysis of the fluid dynamics and electrochemical kinetics for planar SOFCs. The finite volume method is employed to solve the equations for continuity, momentum, mass, energy and electrical charge conservation. The irreversibilities considered are the activation, ohmic, and concentration overpotentials. The Butler–Volmer equation, Ohm’s law, and Darcy’s gas model with constant porosity and permeability are used to determine the corresponding irreversibilities.

Colpan et al. [19] developed a thermodynamic model for a SOFC operating with direct internal reforming. The results indicate that the fuel cell performance is not significantly affected by the recirculation ratio when the cell is operated at low temperatures. On the contrary, when the cell is operating at higher current densities, then cell performance and electrical efficiency drop with increasing recirculation ratio. It is also shown that for high fuel utilization, low power output but high electrical efficiency are achieved.

Yakabe et al. [20,21] constructed a three-dimensional mathematical model for the heat transfer, mass transfer, and chemical reactions in a planar SOFC. The model included the gas diffusion in the porous electrodes. The steam reforming reactions were also integrated in the model. The study indicates that the endothermic internal reforming of CH\(_4\) causes a steep drop of fuel temperature near the inlet. The steep temperature gradients created, result in large tensile stresses in the electrolytes. There was also comparison between co- and counter-flow configurations. The co-flow pattern is preferred over counter-flow as it smooths the temperature gradient, and hence reduces the internal stresses.
Analysis and Simulation of an Anode Supported SOFC Single Channel for Operation with Biosyngas and Methane

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BFBG</td>
<td>Bubbling fluidized bed gasifier</td>
</tr>
<tr>
<td>CFBG</td>
<td>Circulating fluidized bed gasifier</td>
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<tr>
<td>LSM</td>
<td>Strontium-doped lanthanum manganite</td>
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<tr>
<td>MSR</td>
<td>Methane steam reforming</td>
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<td>SOFC</td>
<td>Solid oxide fuel cells</td>
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<td>WGS</td>
<td>Water gas shift reaction</td>
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<td>YSZ</td>
<td>Yttria stabilized zirconia</td>
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**Nomenclature**

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<thead>
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<th>Symbol</th>
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<tbody>
<tr>
<td>A</td>
<td>Cell area</td>
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<tr>
<td>F</td>
<td>Faraday constant</td>
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<tr>
<td>g</td>
<td>Gibbs free energy</td>
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<tr>
<td>H</td>
<td>Enthalpy</td>
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<tr>
<td>I</td>
<td>Current</td>
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<tr>
<td>i</td>
<td>Current density</td>
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<tr>
<td>n</td>
<td>number of moles</td>
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<tr>
<td>p</td>
<td>Pressure</td>
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<tr>
<td>P</td>
<td>Power</td>
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<td>Heat</td>
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<tr>
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<td>Entropy</td>
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<td>Temperature</td>
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<td>U_f</td>
<td>Fuel utilization</td>
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<td>V</td>
<td>Voltage</td>
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<tr>
<td>W</td>
<td>Work</td>
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<tr>
<td>y</td>
<td>Partial concentration</td>
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**Greek letters**

<table>
<thead>
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<th>Symbol</th>
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<tbody>
<tr>
<td>ΔV</td>
<td>Voltage overpotential</td>
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<td>η</td>
<td>Efficiency</td>
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**Subscripts**

<table>
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<th>Subscript</th>
<th>Description</th>
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<tr>
<td>FC</td>
<td>Fuel cell</td>
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<tr>
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<tr>
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**Superscripts**

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References:

Chapter 3: Steam reforming in SOFCs

3.1 Introduction

Solid oxide fuel cells can produce electricity by electrochemically oxidizing H\(_2\) or CO. The reactions for the electrochemical oxidation of H\(_2\) and CO are:

\[
\begin{align*}
\text{Fuel} & \quad \text{Anode reaction} & \quad \text{Cathode reaction} & \quad \text{Overall reaction} \\
H_2 & \quad H_2 + O^{2-} \rightarrow H_2O + 2e^- & \quad 1/2 O_2 + 2e^- \rightarrow O^{2-} & \quad H_2 + 1/2 O_2 \rightarrow H_2O \quad (3.1) \\
CO & \quad CO + O^{2-} \rightleftharpoons CO_2 + 2e^- & \quad 1/2 O_2 + 2e^- \rightarrow O^{2-} & \quad CO + 1/2 O_2 \rightarrow CO_2 \quad (3.2)
\end{align*}
\]

Table 3.1: Electrochemical reactions in SOFCs.

Hydrogen, which is the most commonly used fuel for fuel cells does not occur naturally and has to be generated from other gaseous fuel sources. In general H\(_2\) and CO are obtained by using natural gas, NH\(_3\), LPG, biosyngas or coal gases. One of the most common sources of H\(_2\) generation is steam reforming of CH\(_4\) [1,2,3]. Steam reforming is a technology used to produce H\(_2\) from hydrocarbons. Equation 3.3 is the chemical equation for the reforming reaction for CH\(_4\) while Equation 3.4 is the associated water gas shift reaction:

\[
\begin{align*}
\text{CH}_4 + H_2O & \rightarrow CO + 3H_2 & \quad \Delta H^0_{298} = 206 \text{ kJ / mol} \\
CO + H_2O & \rightarrow CO_2 + H_2 & \quad \Delta H^0_{298} = -41 \text{ kJ / mol}
\end{align*}
\]

Equation 3.3 is called the CH\(_4\) steam reforming reaction and equation 3.4 is the associated water gas shift reaction (WGS). They are both carried out at a high temperature range over a metal catalyst. A commonly used catalyst is Ni. The reason for making Ni a very good choice is not only that it is a suitable catalyst for the reforming reaction but is also contained in the anode cermet because of its conductivity. It is shown in the above equations that CH\(_4\) steam reforming is highly endothermic (absorbs heat), while the water gas shift (WGS) reaction is exothermic (releases heat). Both reactions are dependent on temperature, pressure, and steam-to-methane ratio in the gas flow. In steam reforming the formation of hydrogen is favoured in low pressures according to the Le Chatelier principle. The temperature required is high in order to sustain the highly endothermic reaction. Suitable temperature and pressure are important not only to sustain a sufficient rate of reaction but also to optimize the hydrogen formation. Concerning WGS, high temperature can cause the reaction to move to the left favouring the formation of CO on expense of H\(_2\) production. However this is not a major drawback because in SOFCs, CO is electrochemically oxidized as well [1,2,3].

Apart from hydrocarbons, alcohols such as CH\(_3\)OH can also be reformed, according to the following reaction:

\[
\text{CH}_3\text{OH} + H_2O \rightarrow 3H_2 + CO_2 & \quad \Delta H^0_{298} = 49.7 \text{ kJ / mol} \quad (3.5)
\]
Another type of reforming process, different than steam reforming, is dry (or CO\textsubscript{2}) reforming, which is also a highly endothermic reaction.

\[ CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H^{\circ}_{298} = 247 \text{ kJ / mol} \quad (3.6) \]

This reaction however requires catalysts other than Ni, to avoid Ni sintering and carbon formation \[1\]. Reforming equations (3.5) and (3.6) will not be further examined, as they are not considered in the present work.

Internal reforming process is preferred over external reforming in SOFC systems. The heat required to sustain the endothermic steam reforming of CH\textsubscript{4} is provided by the electrochemical reactions in the cell. Thus, the cooling required by the cell, will be much smaller (could be reduced down to 40-50\%) for internal reforming systems, compared to external reforming systems. This has a major benefit on the electrical efficiency of the system and additionally makes the system less complex. Thus internally reforming SOFCs offer significantly higher system efficiencies, reduced complexity and flexibility in the fuel choice compared to lower temperature fuel cells. Part of the steam required is obtained from the steam generated by the fuel cell reaction. Even hydrogen supply distribution could be achieved leading to even temperature distribution. One issue that arises and requires further investigation is potential instability in the coupling of the slow exothermic WGS reaction and the fast strongly endothermic CH\textsubscript{4} reforming reaction \[1,2,3\].

**Figure 3.1:** Schematic representation of direct and indirect internal reforming \[16\]

**Indirect internal reforming (IIR)**

Indirect internal reforming involves conversion of methane by reformers positioned in close thermal contact with the stack. The reformate from each plate, is fed to neighbouring cells. IIR benefits from close thermal contact between stack and reformer but suffers from the fact that heat is transferred well only from cells adjacent to the reformers and steam for the reforming must be raised separately. A variation of this type of arrangement places the reforming catalyst in the gas distribution path of each cell. With IIR, the reforming reaction and electrochemical reactions are separately held \[1,2,3\].

**Direct internal reforming (DIR)**

In direct internal reforming of SOFCs the reforming reactions take place directly in the anode of the fuel cell. The advantage of DIR is that it offers chemical integration. This means that steam produced from the electrochemical oxidation of hydrogen, can also be used for the CH\textsubscript{4} reforming and WGS reaction. DIR offers advantages over IIR. The conversion rate of CH\textsubscript{4}
is higher. The hydrogen distribution is more even, leading to even temperature distribution. This is beneficial for the cell because the temperature gradients are not that steep, so thermal cycling and thermal stresses inside the cell are smaller. This helps to avoid mechanical failure. However this could also lead to opposite effects: If the heat management is not properly controlled then sharp endothermic cooling effect could arise generating inhomogeneous temperature distributions. Heat absorption by the reforming reaction leads to higher system efficiency because the need for excess cathode air for cooling is smaller. [1,2,3]

3.2 Internal Reforming in SOFCs

3.2.1 Key requirements

The desired characteristics of the anode include good electrochemical performance, insensitivity to sulphur and other fuel impurities and carbon formation, redox stability, and the possibility for internal steam reforming or direct methane oxidation. By combining the properties of ceramics and metals, it has been possible to design and manufacture anodes fulfilling the above requirements. Ceramic and metallic materials differ in many fundamental aspects. Ceramics generally have a high melting temperature, relatively good structural strength and stability at elevated temperatures, brittle mechanical behaviour, and poor electrical conductivity. Furthermore, they are non-magnetic and their defect chemistry (ionic conductivity) varies across a large range. Metals, on the other hand, generally have an intermediate melting temperature and are ductile, that is, they show plastic deformation under stress. In addition, they possess good electronic conductivity and are magnetic materials. By combining materials from these two groups into ceramic-metal composites, cermet, many central properties can be tailored according to need [1,2,3].

Metals that can be used are Ni, Co and noble metals. The material that has been established as the most common material for SOFC anodes is a cermet made of metallic nickel and an YSZ skeleton [1,2,3]. The anode material should also have high electrical conductivity, which is achieved by 30% Ni composition in the cermet. In this case the thermal expansion of the anode has to be investigated, as it should be in compliance with the YSZ electrolyte thermal expansion to avoid thermal stresses [1,2,3]. The anode has a high porosity (20–40%) so that mass transport of reactant and product gases is not inhibited. Often a small amount of ceria is added to the anode cermet, to improve the tolerance of the anodes to temperature cycling and redox. A further advantage of using mixed conductors as anodes is that they can extend the three-phase boundary between reactant, anode and electrolyte [1,2,3].

The advantage of using a Ni-YSZ anode is that Ni serves as a good steam reforming catalyst. Thus, it is feasible to achieve reforming directly on the Ni-YSZ anode. This however requires further investigation because intense reforming activity could cause undesired steep temperature gradients. This could be treated by achieving lower operating temperatures, recycling the anode gas or by lowering the catalytic activity of the anode. During design both the need for reforming activity and for even temperature distribution should be considered [1,2,3].

3.2.2 Steam reforming catalysts

Steam reforming is a common technology for hydrogen production and a number of studies concerning the process and corresponding kinetics have been conducted. The most common catalyst used for the steam reforming process is Ni supported by MgO, α-Al₂O₃, or MgAl₂O₄ [4-8]. Concerning SOFC catalysts, Ni is still the main component, but it is mixed with
YSZ. The anode material should also have high electrical conductivity, which is achieved for 30% Ni composition and bigger size Ni particles. Apart from operating parameters such as pressure, temperature and steam-to-carbon ratio there are also structural differences that have to be further investigated to provide solution for several issues connected with SOFC steam reforming.

Steam reforming is a highly endothermic reaction absorbing the heat released from the electrochemical oxidation of hydrogen and carbon monoxide in the anode. The main issue in this case is that the reforming reaction is much faster than the electrochemical reactions, leading to cooling in the region close to the fuel cell inlet. Furthermore, CH₄ is consumed but the electrochemical reactions are still being carried out releasing heat. This is an undesired effect because it can lead to steep temperature gradients and cause thermal stresses in the fuel cell. In order to avoid large temperature gradients an even temperature distribution is required. The main reason that the reforming reaction is much faster is attributed to high Ni content. On one hand, Ni is necessary to provide high electric conductivity, but on the other hand it offers a high number of catalytic sites promoting the reforming reaction [9].

Considering the above, this means that the reaction rate of internal reforming should be lowered, while maintaining high electric conductivity and high reactivity for the electrochemical reactions. The main challenge for the steam reforming process both in industry and SOFCs is to overcome activity reductive factors such as carbon deposition, sulfur poisoning and Ni sintering [4,2].

### 3.2.3 Carbon deposition

Formation of elemental carbon and deposition on the anode catalyst will decrease the SOFC efficiency. The carbon is formed by the methane cracking mechanism, i.e. the decomposition of CH₄ when heated at temperatures above 650 °C.

\[ CH_4 \rightarrow C + 2H_2 \quad \Delta H_{298}^\circ = 75 \text{kJ} / \text{mol} \quad (3.7) \]

The problem of carbon deposition is more intense when higher hydrocarbons are present as they have the tendency to decompose easier than methane. Apart from hydrocarbons, carbon can be formed from the disproportionation of carbon monoxide, according to the Boudouard reaction:

\[ 2CO \rightarrow C + CO_2 \quad (3.8) \]

There are three types of carbon formation related to the reforming activity in SOFCs: pyrolytic carbon, gum carbon, and whisker carbon. Specifically, formation of carbon may increase pressure losses, block the active sites on the Ni catalyst surface or even destroy the catalyst structure (for whisker carbon formation) [4,9]. The deposit of carbon does not only depend on the gas properties and composition but also on the nature of the solid catalyst. For instance the Boudouard reaction is more likely to occur on a Ni catalyst, and cracking of methane is more likely to occur on acidic supports, rather than on alkaline supports [1,4,5,9].

The theoretical carbon deposition can be determined by using C-H-O ternary diagrams. These diagrams describe parameters and conditions relevant for fuel cell operation. Such diagrams have been constructed in several studies [10-15]. The ternary diagram shows the carbon deposition tendencies. Solid lines inside the triangle indicate carbon boundary lines. Above the carbon boundary line, solid carbon exists in heterogeneous equilibrium with the gas phase components. Below the carbon boundary line no solid carbon is present. Once the composition of a fuel gas is known, its coordinates in the ternary diagram can be identified.
Figure 3.2: The boundary of carbon deposition region in the C–H–O phase diagram at 1 atm. Carbon deposition is expected in the carbon-rich composition beyond the boundary at respective temperatures [14].

In Figure 3.2 it is clearly shown that for the lower temperatures investigated there is a curved line for high hydrogen content, making the ‘safe area’ surface bigger. This means that at these condition CH₄ is more stable, i.e. it is less likely for CH₄ to decompose to carbon and hydrogen. During the electrochemical reactions oxygen is transferred to the anode. This will move the coordinates away from the carbon boundary lines, but the temperature drop due to the endothermic reforming will increase the carbon deposition region. This explains why the fuel cell location where the chances of carbon deposition are higher is the area close to the inlet. The same study has indicated that though the rate of carbon deposition is increased at high temperatures, the region where the carbon is deposited decreases. This means that higher temperatures will not prevent carbon deposition, as the amount of carbon that could be deposited is higher, thus increasing the chances of deposition [9,11]. Addition of steam at high temperature will increase the fraction of oxygen and hydrogen atoms, moving the coordinates away from the carbon boundary line. Nonetheless, the steam addition should not be out of control, but there should be a balance to the steam-to-carbon ratio, which should be kept as low as possible. This is explained by the Nernst equation for SOFCs, which indicates that steam addition will lower the reversible voltage.

\[
V_r = -\frac{\Delta \bar{G}^0}{2F} + \frac{RT}{2F} \ln \left( \frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2}O} \right)
\]  

Steam to carbon ratios around 1.4 are supposed to provide safe operation for a SOFC. However, it should be pointed out that the goal is not to have a high S/C ratio. SOFCs operating at lower S/C will avoid carbon deposition as long as there is a suitable C-H-O equilibrium. This means that when the SOFC is operating with biosyngas fuel, then oxygen contained in CO or CO₂ could move the equilibrium towards the safe zone [9-12].

Step sites on the Ni catalyst particles are the most active sites for carbon formation and steam reforming as indicated by Sehested [4] and Rostrup-Nielsen et al [16]. It is suggested by Sehested [4] that the Ni steps where carbon may form, could be blocked by addition of S, Au or K. Studies conducted by Hirata et al [17] have indicated that Ni accelerates the CH₄ decomposing into carbon, while the use of Ru does not have such a catalytic effect and promotes oxidation of
CH$_4$ with O$^2$ ions, to produce hydrogen and carbon monoxide. Takeguchi et al [15] indicated that addition of CaO or SrO in the Ni-YSZ cermet will suppress the carbon deposition and also reduce the rate of steam reforming. Blocking the catalyst sites, apart from preventing carbon deposition, could also decrease the rate of methane steam reforming reaction, making it a favourable technique. Concluding, carbon deposition can be avoided (or at least limited) by addition of promoters such as Mg, Ca, Ce, Ru, Pt, Pd, Mo [9].

3.2.4 Tuning the SOFC catalyst

Mogensen et al [9] indicated a relation between the rates of the electrochemical and steam reforming reactions for a Ni-YSZ anode SOFC. They found that at the temperature range of 600-700 °C the steam-reforming rate could be decreased without significantly affecting the current density of the cell. Rostrup-Nielsen et al [16] conducted sulfur poisoning experiments on a SOFC stack. Their work has shown that there are different catalytic sites for the electrochemical and for the steam reforming reactions. Thus, it is implied that the steam reforming activity could be tuned without significantly decreasing the electrochemical activity.

The particle size of Ni will affect the performance of a cell. Smaller particles will offer a larger active surface area [9], while they can also improve stability of the anode [2]. This means that though bigger Ni particles could be used to suppress the steam reforming activity, it should be taken into account that this could lead to cell performance degradation. Rostrup-Nielsen and Christiansen [18] indicated that steam reforming over a Ni catalyst on a Mg/Al-spinel is reduced when alkali metals are added, implying that this could be a possible future technology for SOFCs. Takeguchi et al [15] studied the effect on the catalytic activity and carbon deposition of SOFCs when adding MgO, CaO, SrO and CeO$_2$ to Ni-YSZ cermets. Their work has shown that the additives affected the kinetics of the steam reforming reaction. In the case of CaO addition, CH$_4$ steam reforming was favoured, carbon deposition was suppressed, with the electrochemical activity being slightly decreased.

Changing Ni particle size, sulfur and alkali metal poisoning could also affect the electrochemical activity. So it is suggested that different anode materials could be used, always considering requirements such as conductivity, thermal expansion coefficient and pore diameter. Klein et al [19] added an Ir–CeO$_2$ catalyst layer at the anode side of a Ni-YSZ SOFC running on CH$_4$ and no degradation of the cell performance was found.

3.3 Steam reforming kinetics

There have been several studies investigating the kinetic behaviour of steam reforming both in industrial catalysts and Ni-YSZ anodes. Some of these studies will be explained in this section. The kinetics will be presented and compared, since many differences between them can be reported. This is due to the variation of reaction conditions in each study. The studies can be categorized according to the type of kinetic expressions used, as follows:

- General Langmuir-Hinshelwood kinetics.
- First order reaction with respect to methane.
- Power law expressions derived from data fitting.

Tables 3.1, 3.2 and 3.3 contain data for industrial Ni catalysts, and table 3.4 contains data concerning Ni-YSZ SOFC anode studies. When comparing data obtained from each study the fact that the Ni particle microstructure is not stable should be taken into account. The Ni grain size varies between large particles required to achieve high electrical conductivity and small
Analysis and Simulation of an Anode Supported SOFC Single Channel for Operation with Biosyngas and Methane

particles required to achieve sufficient catalytic activity. Additionally, sintering will remove active reaction sites [20]. These effects have been reported but the impact they have on the kinetics of the reaction has not been precisely evaluated.

A term that will be introduced in the following section is the activation energy, which is defined as the energy that must be overcome in order for a chemical reaction to occur. For a chemical reaction to proceed at a reasonable rate, an appreciable number of molecules with energy equal to or greater than the activation energy should exist.

3.3.1 General Langmuir-Hinshelwood kinetics

Xu et al. [7] derived equations for the CH$_4$ steam reforming, accompanied by water gas shift on a Ni/MgAl$_2$O$_4$ catalyst. The set of equations is based on a generalized Langmuir-Hinshelwood type kinetic model and suggests that the reaction of adsorbed carbon and oxygen species is the rate-determining step. The * symbol when superscripted on the chemical formula of the molecules, represents an activated molecule, while the * symbol alone denotes a free surface on the catalyst:

\[
\begin{align*}
    CHO^* + * & \rightleftharpoons CO^* + H^* \\
    CO^* + O^* & \rightleftharpoons CO_2^* \\
    CHO^* + O^* & \rightleftharpoons CO_2^* + H^*
\end{align*}
\]  

(3.10) (3.11) (3.12)

This model has been used by Wang et al [21] to make comparisons with experiments over a Ni/YSZ anode of a planar SOFC. The study has shown that high operating temperature has a positive effect on the methane conversion, while high pressures do not. It also suggested that increasing the steam-to-carbon ratio decreases the CH$_4$ conversion. The fact that molar fraction of produced hydrogen was smaller in the experimental study, was attributed to the fact that the model neglects heat and mass transfer limitations, assuming catalytic activity in the whole extent of the anode. However, in the actual anode, heat/mass transfer and diffusion limitations are significant as they limit the effective catalyst surface. Methane cracking does not seem to be affected by increasing the steam-to-carbon ratio, with carbon being formed near the inlet of the anode.

Similar kinetics have been used by Peters et al [22] and Nakagawa et al [23]. Peters et al [22] conducted a series of experiments using an anode cermet consisting of Ni-8YSZ (8 mol.% Y$_2$O$_3$-stabilized ZrO$_2$) substrate with a standard composition of 50% (mass) Ni, and have shown the influence that the gas flow velocity has on the conversion of methane. This is attributed to sufficient/insufficient mass transport from the bulk phase to the boundary layer. Anode gas recycling was employed, leading to higher CO$_2$ concentration in the inlet, which resulted in reduced CH$_4$ conversion.

Nakagawa et al [23] experimentally investigated the catalytic activity and stability of a Ni-YSZ-CeO$_2$ anode for CH$_4$ steam reforming. The measurements were conducted in the temperature range 973-1273K and steam-to-carbon ratio between 2 and 7. The rate of CH$_4$ steam reforming was calculated from the sum of the rate of production for CO and CO$_2$. The highest value of CH$_4$ conversion was 15%. The water gas shift reaction was neglected, since the rate of CO$_2$ produced is much smaller than CO produced. The anode catalytic activity is increased at increasing partial CH$_4$ pressures. The CH$_4$ conversion rate is mostly affected by the mass transfer between the gas and anode surface. It is concluded that catalytic activity of Ni-YSZ-CeO$_2$ is higher at low temperatures. The catalytic activity can also be affected by the partial
pressure of other species of the gas flow. It is deteriorated at high steam and hydrogen partial pressures and at high current density values. This study also suggested that the rate-determining factor is the mass transfer between the bulk gas and anode surface. The activation energy is 18 kJ/mol, which was lower than that of Ni-YSZ film. At low temperature range the catalytic activity of Ni-YSZ-CeO2 was higher than that of Ni-YSZ, indicating that ceria addition is beneficial for the CH4 conversion.

More recent works [2,21,24] indicate that dissociative adsorption of methane is the rate-limiting step. Mogensen et al [9] derived the following elementary reactions, which are used to obtain kinetic expressions for steam reforming:

\[
\begin{align*}
CH_4 + 2* & \rightarrow CH_3^* + H^* \\
CH_3^* + * & \rightleftharpoons CH_2^* + H^* \\
CH_2^* + * & \rightleftharpoons CH^* + H^* \\
CH^* + * & \rightleftharpoons C^* + H^* \\
H_2O + 2* & \rightleftharpoons HO^* + H^* \\
HO^* + * & \rightleftharpoons O^* + H^*
\end{align*}
\]

Neophytides et al. [25] indicated that the kinetics of steam reforming of methane on Ni-YSZ cermets involve two rate limiting steps. These steps will affect the activation energy of the reaction for various steam and methane partial pressure. The first limiting step is the activated adsorption of CH4 for the production of active species. The second limiting step is the surface reaction of the adsorbed carbon with the adsorbed oxygen, to produce CO.

Dicks et al. [26] obtained composition-dependence and non-linearity for the Arrhenius plots for Ni/ZrO2 anode. The observations made in this study are consistent with CH4 chemisorption, rapid surface reaction of methane-derived and oxygen-derived surface species, rapid desorption of CO generated and rapid dissociative chemisorption of steam and hydrogen. This study confirmed as well that low steam-to-methane ratios would decrease the reforming rate. Increasing the hydrogen partial pressure and decreasing the steam partial pressure would benefit the reforming process.

Hou et al. [27] carried out experiments on Ni/α-Al2O catalyst and based on the results obtained, they developed a kinetic model, which includes both CH4 steam reforming and water gas shift reactions. This model is based on the mechanism that both CH4 and steam are adsorbed on the catalyst with dissociation, with the CH4 dissociated into CH2 and H2 or adsorbed H, and the suggestion that the rate is being controlled by the surface reactions between adsorbed species. They also suggested that high pressure favors both forward and backward reaction rates of CH4 reforming. The research also included low temperature study of the reverse water gas shift in order to obtain estimates about the kinetics of the water gas shift reaction. The experimental study concluded that high steam-to-methane ratio and low pressure would favour the production of hydrogen and syngas.
The reaction rate was found to have a possible effect on the rate. Carbon dioxide and carbon monoxide were the primary reaction products, the carbon dioxide being formed from two to nine times faster than carbon monoxide. The water-gas shift reaction, if proceeding at all, was at a much slower rate. Belayev [29] et al studied the steam reforming of methane over a Ni-ZrO2-CeO2 anode in a solid oxide fuel cell under open- and closed-circuit conditions. Experiments were performed over a temperature range of 800-850°C and steam/methane ratios of 2-4. The reaction rate was found to be first order with respect to methane concentration. Clarke et al [30] also used a first rate equation to determine the rate of steam reforming. However their study was not on an industrial catalyst, but on a Ni/ceria anode.

Achenbach and Riensche [31] conducted experiments to determine the kinetics of CH₄

### Table 3.2: Langmuir-Hinshelwood steam reforming kinetics for Ni catalysts.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Rate of CH₄ conversion</th>
<th>Support</th>
<th>T (°C)</th>
<th>Eₚ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[7]</td>
<td>( R_{CH_4} = \frac{k \cdot P_{CH_4}}{P_{H_2O}^2} \left( 1 - \frac{Q}{K} \right) + \frac{k' \cdot P_{CH_4}}{P_{H_2O}^2} \left( 1 - \frac{Q'}{K'} \right) )</td>
<td>MgAl₂O₄</td>
<td>500-575</td>
<td>240</td>
</tr>
<tr>
<td>[23]</td>
<td>( R_{CH_4} = k \cdot \frac{K_{CH_4} \cdot K_{H_2O} \cdot P_{CH_4} \cdot P_{H_2O}}{\left( 1 + K_{CH_4} \cdot P_{CH_4} + K_{H_2O} \cdot P_{H_2O} \right)^2} )</td>
<td>YSZ-CeO</td>
<td>700-1000</td>
<td>18</td>
</tr>
<tr>
<td>[22]</td>
<td>( R_{CH_4} = k \cdot \frac{K_{CH_4} \cdot K_{H_2O} \cdot P_{CH_4} \cdot P_{H_2O}}{\left( 1 + K_{CH_4} \cdot P_{CH_4} + K_{H_2O} \cdot P_{H_2O} \right)^2} )</td>
<td>YSZ</td>
<td>700-1000</td>
<td>-</td>
</tr>
<tr>
<td>[25]</td>
<td>( R_{CH_4} = k \cdot \frac{K_{CH_4} \cdot K_{H_2O} \cdot K_{H_2} \cdot K_{OH} \cdot P_{CH_4} \cdot P_{H_2O}}{\left( 1 + K_{CH_4} \cdot P_{CH_4} + K_{H_2O} \cdot P_{H_2O} + K_{OH} \cdot P_{OH} \right)^2} )</td>
<td>YSZ</td>
<td>800-900</td>
<td>201</td>
</tr>
<tr>
<td>[26]</td>
<td>( R_{CH_4} = k \cdot \frac{P_{CH_4}}{\left( 1 + K_{CH_4} \cdot P_{CH_4} + K_{H_2O} \cdot P_{H_2O} \right)^2} )</td>
<td>ZrO₂</td>
<td>700-1000</td>
<td>154-253</td>
</tr>
</tbody>
</table>

### 3.3.2 First order kinetics with respect to methane

When the dissociative adsorption of CH₄ is considered the only step that can determine the rate of reforming reaction, then the Langmuir-Hinshelwood kinetics will result in a first order expression. Considering that no other absorbents will cover the catalyst surface, the rate of reaction will only depend on the partial pressure of CH₄. It is safe to assume that no other absorbents will cover the catalyst surface, since the operating temperature in a SOFC are high and the operating pressure is low. Kinetic and isotopic measurements for catalysts and conditions that rigorously excluded transport and thermodynamic artifacts led to a common sequence of elementary steps for reactions of CH₄ with CO₂ or H₂O and for its stoichiometric decomposition on Ni/MgO catalysts in the study conducted by Wei and Iglesia [5]. They have shown that steam reforming and WGS reaction are in quasi-equilibrium and resulted in a first order expression for steam reforming with relevance to the CH₄ partial pressure.

Akers et al [28] conducted an experimental kinetic study of the methane-steam reaction over a reduced Ni catalyst. The rate of methane conversion found, was first order with respect to methane. It is indicated the decomposition of methane is the rate-controlling step. Mass transfer was found to have a possible effect on the rate. Carbon dioxide and carbon monoxide were the primary reaction products, the carbon dioxide being formed from two to nine times faster than carbon monoxide. The water-gas shift reaction, if proceeding at all, was at a much slower rate. Belayev [29] et al studied the steam reforming of methane over a Ni-ZrO₂-CeO₂ anode in a solid oxide fuel cell under open- and closed-circuit conditions. Experiments were performed over a temperature range of 800-850°C and steam/methane ratios of 2-4. The reaction rate was found to be first order with respect to methane concentration. Clarke et al [30] also used a first rate equation to determine the rate of steam reforming. However their study was not on an industrial catalyst, but on a Ni/ceria anode.

Achenbach and Riensche [31] conducted experiments to determine the kinetics of CH₄
steam reforming reaction on a 20 wt.% Ni, 80 wt.% ZrO2 cermet, with varying temperature, CH4 partial pressure and steam-to-methane ratio. The CH4 partial pressure at the surface of the cermet had to be lower than the bulk partial pressure to allow mass flux towards the anode surface. Thus, the CH4 partial pressure at the cermet surface has to appear in the kinetic expression of the CH4 conversion because it is greatly affecting the reforming reaction. The reaction rate is very high at temperatures between 900 and 1000 °C. The most important findings are that steam partial pressure has no effect on the catalytic reforming process, and that steam-to-methane ratio has little effect on reforming. The equation proposed for the rate of reaction is proportional to the CH4 partial pressure.

\[
-R_{CH_4} = k \cdot P_{CH_4}^{\alpha} \cdot P_{H_2O}^{\beta} \cdot P_{H_2}^{\gamma} \cdot P_{CO_2}^{\delta} \cdot P_{CO}^{\epsilon}
\]

\(\gamma, \delta, \text{ and } \epsilon \) are often close to zero and are neglected. The values of \(\alpha\) and \(\beta\) vary between different studies. As can be seen in Table 3 where various studies are presented, the values for the reaction order with respect to methane vary, but are close to one. The value for the reaction order with respect to steam however shows significant variation between the studies. The difference between the studies can be attributed to the fact that the operating conditions are varying for every study.

Lee et al [32] conducted catalytic reforming tests with nickel-zirconia (Ni/ZrO2) cerments. The mechanism suggested that the initial dissociation adsorption of hydrocarbon to surface carbon species is followed by desorption of hydrogen and gasification of adsorbed carbon atoms by hydrogen or steam. The rate of reaction was found to increase with decreasing steam-to-carbon ratios and with increasing temperatures. The tested nickel-zirconia cermet compositions were 40 vol.% ZrO2, and 30 vol.% ZrO2. Higher Ni content might have been the reason that the first cermet had shown higher values for activation energy and frequency factor. Another reason given for the higher catalytic activity of the cermet was attributed to the solid microstructure differences, which could arise from the preparation procedure. Addition of sulfur in the gas flow led to decrease of the catalytic activity, i.e. the conversion rate decreased. The reaction order with respect to water was negative, varying between -1.25 and -1.28.

Ahmed and Foger [33] determined the kinetics of CH4 steam reforming. The experiments

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Rate of CH4 conversion</th>
<th>Support</th>
<th>T (°C)</th>
<th>(E_a) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[29]</td>
<td>(R_{CH_4} = k \cdot P_{CH_4})</td>
<td>ZrO2-CeO</td>
<td>800-850</td>
<td>163</td>
</tr>
<tr>
<td>[30]</td>
<td>(R_{CH_4} = k \cdot P_{CH_4})</td>
<td>Ceria</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[5]</td>
<td>(R_{CH_4} = k \cdot P_{CH_4} \cdot \left(1 - \frac{Q_s}{K_s}\right))</td>
<td>MgO</td>
<td>600-700</td>
<td>99-105</td>
</tr>
<tr>
<td>[31]</td>
<td>(R_{CH_4} = k \cdot P_{CH_4} \cdot \left(1 - \frac{Q_s}{K_s}\right))</td>
<td>ZrO2</td>
<td>700-940</td>
<td>82</td>
</tr>
</tbody>
</table>

Table 3.3: First order steam reforming kinetics for Ni catalysts

### 3.3.3 Power law expressions

The first order kinetic expressions arise by making assumptions for the rate determining steps, or for the species that are adsorbed. In order to avoid referencing back on assumptions and mechanisms employed the following expression has been proposed for the reaction rate of steam reforming:

\[
-R_{CH_4} = k \cdot P_{CH_4}^{\alpha} \cdot P_{H_2O}^{\beta} \cdot P_{H_2}^{\gamma} \cdot P_{CO_2}^{\delta} \cdot P_{CO}^{\epsilon}
\]
were done on a Ni-YSZ anode and a Ni-YSZ anode modified by the addition of a basic compound (compound not specified). The rate of conversion is higher for the unmodified anode. For the unmodified Ni-YSZ cermet the steam-to-carbon ratio required to avoid carbon deposition is 3-5, while the modified cermet operates at much lower ratios. The modified cermet shows a much higher dependency on CH\textsubscript{4} partial pressure than the unmodified one. Concerning the effect of steam partial pressure a slightly negative order dependency is obtained for both materials. The activation energy of the Ni-YSZ cermet was 95±2 kJ/mol. For the modified Ni-YSZ cermet the corresponding values are 208±10 kJ/mol. An explanation given for the large difference between the kinetic parameters of the two anodes is that the basic compound added to the catalyst has changed the number and nature of sites. This means that the reforming activity might also take place on the additive with a lower magnitude than that of Ni catalyst. The addition of the basic compound has the opposite results than ceria addition has, as reported in previous studies [31].

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Rate of CH\textsubscript{4} conversion</th>
<th>Support</th>
<th>T (°C)</th>
<th>E\textsubscript{a} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[40]</td>
<td>[R_{\text{CH}<em>4} = k \cdot P</em>{\text{CH}<em>4}^{0.75} \cdot P</em>{\text{H}_2\text{O}}^{-1.2} ]\</td>
<td>YSZ</td>
<td>-</td>
<td>191</td>
</tr>
<tr>
<td>[32]</td>
<td>[R_{\text{CH}<em>4} = k \cdot P</em>{\text{CH}<em>4}^{1.28} \cdot P</em>{\text{H}_2\text{O}}^{-1.0} ]\</td>
<td>ZrO\textsubscript{2}</td>
<td>800-1000</td>
<td>74-98</td>
</tr>
<tr>
<td>[33]</td>
<td>[R_{\text{CH}<em>4} = k \cdot P</em>{\text{CH}<em>4}^{0.35} \cdot P</em>{\text{H}_2\text{O}}^{-0.35} ]\</td>
<td>YSZ</td>
<td>850-900</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 3.4: Power law steam reforming kinetics for Ni catalysts

### 3.3.4 Kinetics over Ni-YSZ anode catalysts

The studies are categorized according to the reaction order and activation energy, and according to the reaction rate by Ni weight, surface area and anode area. It would be useful to make comparisons between the activation energies derived from each study. As already mentioned, the goal is to achieve even temperature distribution. The area on which the steam reforming reaction takes place is expected to become larger. However, even if this is achieved, there is still an issue of obtaining high electrochemical activity at lower temperatures. This means that when making considerations for a lower temperature fuel cell design, the impact on both electrochemical and reforming activity has to be investigated.

Mogensen et al [9] presented comparisons of the reaction rate, at ambient pressure, of steam reforming over Ni-YSZ reported in literature with respect to Ni content, Ni surface area and geometric anode surface area. It is suggested that there should be further investigation concerning the surface area of Ni. Hecht et al [24] studied the methane reforming kinetics within a porous Ni-YSZ SOFC anode. In the experiment, an anode is put in between two gas channels. CH\textsubscript{4}, CO\textsubscript{2} and H\textsubscript{2}O are fed to the anode through the first channel. The composition in the other channel is H\textsubscript{2}O and CO\textsubscript{2} that would be produced in a practically operating fuel cell by the electrochemical charge-transfer reactions in the reaction zone in the interface between the anode and the dense electrolyte membrane. Because the anode structure is porous, there is convective and diffusive species flux between the two flow channels. A model to investigate diffusion and reforming activity was developed. The dusty gas model used for diffusion, and the system of 42 equations for the reforming kinetics were validated, as they fitted the results obtained from the experiments.
reaction that not in equilibrium. This means that the WGS will be moved towards equilibrium by the oxidation fuel utilization. The potentials of CO and H₂

Ahmed and Foger [34] studied the reverse WGS reaction on a Ni/zirconia anode and reverse WGS reaction rate. This is because the carbonylic species formed decompose to CO and hydroxyls. Ahmed and Foger [34] studied the reverse WGS reaction on a Pt/YSZ anode of a SOFC. The study concluded that the formations of Ni-YSZ SOFC anodes.

### 3.4 Water gas shift reaction

An assumption made to simplify the calculation in SOFC modeling is that the WGS reaction is in equilibrium. However a number of experimental studies have shown that the WGS reaction is not in equilibrium [20,22,24,25,34]. Pekridis et al [35] studied the kinetics of the reverse WGS reaction on a Pt/YSZ anode of a SOFC. The study concluded that the formations of carbon intermediates and their interaction with atomically adsorbed hydrogen control the reverse WGS reaction rate. This is because the carbonylic species formed decompose to CO and hydroxyls. Ahmed and Foger [34] studied the reverse WGS reaction on a Ni/zirconia anode and concluded that the water gas shift is close to thermodynamic equilibrium only at high levels of fuel utilization. The potentials of CO and H₂ oxidation are different when the WGS reaction is not in equilibrium. This means that the WGS will be moved towards equilibrium by the oxidation reaction that will have the highest potential. Table 3.6 shows expressions for the WGS reaction.

### Table 3.5: Steam reforming kinetics and activation energies over Ni-YSZ SOFC anodes

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Rate of CH₄ conversion</th>
<th>Eₐ (kJ/mol)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[25]</td>
<td>( R_{\text{CH}<em>4} = k</em>{\text{a},\text{CH}<em>4} \cdot P</em>{\text{CH}<em>4} \cdot \left( 1 - \frac{k</em>{\text{a},\text{H}<em>2}}{k</em>{\text{a},\text{H}<em>2}} \cdot \frac{P</em>{\text{H}<em>2} \cdot P</em>{\text{CH}<em>4}}{P</em>{\text{H}_2,0}} \right) )</td>
<td>228</td>
<td>800-900</td>
</tr>
<tr>
<td>[20]</td>
<td>( R_{\text{CH}<em>4} = k \cdot P</em>{\text{CH}_4} )</td>
<td>113-124</td>
<td>650-800</td>
</tr>
<tr>
<td>[31]</td>
<td>( R_{\text{CH}<em>4} = k \cdot P</em>{\text{CH}_4} \cdot \left( 1 - \frac{Q_P}{K_P} \right) )</td>
<td>82</td>
<td>700-940</td>
</tr>
<tr>
<td>[32]</td>
<td>( R_{\text{CH}<em>4} = k \cdot P</em>{\text{CH}<em>4} \cdot P</em>{\text{H}_2,0}^{-0.28} )</td>
<td>74-98</td>
<td>800-1000</td>
</tr>
<tr>
<td>[33]</td>
<td>( R_{\text{CH}<em>4} = k \cdot P</em>{\text{CH}<em>4}^{0.65} \cdot P</em>{\text{H}_2,0}^{-0.38} )</td>
<td>95</td>
<td>850-900</td>
</tr>
<tr>
<td>[40]</td>
<td>( R_{\text{CH}<em>4} = k \cdot P</em>{\text{CH}<em>4}^{0.3} \cdot P</em>{\text{H}_2,0}^{-0.2} )</td>
<td>191</td>
<td>1000</td>
</tr>
<tr>
<td>[22]</td>
<td>( R_{\text{CH}<em>4} = k \cdot \frac{k</em>{\text{CH}<em>4} \cdot K</em>{\text{a,H}<em>2,0} \cdot P</em>{\text{CH}<em>4} \cdot P</em>{\text{H}<em>2,0}}{\left( 1 + k</em>{\text{CH}<em>4} \cdot P</em>{\text{CH}<em>4} + K</em>{\text{a,H}<em>2,0} \cdot P</em>{\text{H}<em>2,0} + K</em>{\text{a,CO}} \cdot P_{\text{CO}} \right)^2} )</td>
<td>-</td>
<td>700-1000</td>
</tr>
<tr>
<td>[42]</td>
<td>( R_{\text{CH}<em>4} = k' \cdot P</em>{\text{CH}<em>4} \cdot P</em>{\text{H}<em>2,0} - k' \cdot P</em>{\text{CO}} \cdot P_{\text{H}_2,0}^{1.3} )</td>
<td>-</td>
<td>700-950</td>
</tr>
</tbody>
</table>

### Table 3.6: WGS kinetics and activation energies over various catalysts

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Rate of CH₄ conversion</th>
<th>Catalyst</th>
<th>T (°C)</th>
<th>Eₐ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[26]</td>
<td>( R_{\text{CO}<em>2} = \frac{k</em>{\text{CO}<em>2} \cdot K</em>{\text{CO}<em>2} \cdot K</em>{\text{H}<em>2,0} \cdot R</em>{\text{CH}<em>4}^2 \cdot P</em>{\text{H}<em>2,0}}{k</em>{\text{a},\text{CO}} \cdot P_{\text{H}<em>2,0} \cdot P</em>{\text{CH}<em>4} + k</em>{\text{CO}<em>2} \cdot K</em>{\text{CO}<em>2} \cdot K</em>{\text{H}<em>2,0} \cdot R</em>{\text{CH}<em>4} \cdot P</em>{\text{H}_2,0}} )</td>
<td>Ni/YSZ</td>
<td>800-900</td>
<td>61±3.4</td>
</tr>
<tr>
<td>[4]</td>
<td>( R_{\text{CO}<em>2} = k_2 \cdot \frac{P</em>{\text{CO}<em>2} \cdot P</em>{\text{H}<em>2,0} / P</em>{\text{H}_2}^2}{K_2} )</td>
<td>MgAl₂O₄</td>
<td>500-575</td>
<td>67.13</td>
</tr>
<tr>
<td>[34]</td>
<td>-</td>
<td>Ni/Al₂O₃</td>
<td>300-500</td>
<td>87.1</td>
</tr>
<tr>
<td>[42]</td>
<td>( R_{\text{CO}<em>2} = k_2 \cdot \frac{P</em>{\text{CO}<em>2} \cdot P</em>{\text{H}<em>2,0} / P</em>{\text{H}<em>2}^{1.3} \cdot \left( 1 - \frac{P</em>{\text{CO}<em>2} \cdot P</em>{\text{H}<em>2} / K</em>{\text{H}<em>2,0} \cdot P</em>{\text{H}<em>2,0} \cdot P</em>{\text{CO}}}{K_{\text{H}<em>2,0} \cdot P</em>{\text{H}<em>2,0} \cdot P</em>{\text{CO}}} \right)}{DEN^2} )</td>
<td>Ni/α-Al₂</td>
<td>500-550</td>
<td>19</td>
</tr>
</tbody>
</table>

TU Delft, MSc Sustainable Energy Technology
3.5 Modeling internal steam reforming

Compared with experimental investigations, mathematical modeling is an economic and useful tool to predict the SOFC performance, to perform parametric analysis, to better understand SOFC mechanisms, as well as to achieve design optimization. A large number of SOFC models developed so far include internal steam reforming. SOFC models can be categorized as electrode models, cell/stack models and system models. The electrode models describe catalytic and electrochemical and heterogeneous reactions in the porous electrodes. The effects of mass and heat transfer are often taken into account [21,24]. The cell models usually are simplified concerning the electrode and electrolyte, and are used to study the gas species composition and temperature distribution along the fuel cell channels. [24,36–40]. The most often expressions used for steam reforming modeling are those suggested by Lehnert et al [42], Achenbach and Riensche [31], Xu and Froment [7] and Hecht [24].

3.6 Conclusions

The trend for the new generation SOFCs is to lower the temperature range to intermediate values around 700 °C. Apart from this it is desired to lower the methane steam reforming rate. Much work is done on fine-tuning the SOFC anode material, in order to block the active nickel step sites. One suggested solution is to use sulphur already contained in the natural gas stream fed to the fuel cell. However, in the long term this could cause degradation of the cell performance. It seems that it would be rather preferable to block the active Ni step sites by employing alkali metals instead of sulphur, making this a more viable option. Another approach is to replace part of the Ni with Cu, lowering the reforming activity without significant influence on the cell performance.

Another approach for optimizing internal steam reforming utilization is to carefully control the operating conditions so that the temperature gradients that arise will not cause any problems to the SOFC structure. Modeling is a useful tool that can help avoid problems during development. For this reason an overview of steam reforming kinetics on SOFCs is given and discussed. There are large differences in the reported steam reforming kinetics, which is reflected by the number of kinetic expressions that exist for both industrial steam reforming catalysts and on Ni-YSZ for SOFCs. The literature review has shown that although there is significant number of SOFC models a limited amount of experimental datasets is used.
Abbreviations

DIR  Direct internal reforming
IIR  Indirect internal reforming
LSM  Strontium-doped lanthanum manganite
MSR  Methane steam reforming
SOFC  Solid oxide fuel cells
WGS  Water gas shift reaction
YSZ  Yttria stabilized zirconia

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S.H. Clarke, A.L. Dicks, K. Pointon, T.A. Smith, A. Swann: Catalytic aspects of the
Chapter 4: SOFC Single Channel Model

This chapter gives the presentation of the three-dimensional CFD model of a single SOFC channel. There are two different fuel composition fed into the anode gas channel. The composition of the first fuel fed is biosyngas consisting of hydrogen, water vapor, methane, carbon monoxide and carbon dioxide (H$_2$, H$_2$O, CH$_4$, CO, CO$_2$). The composition of the second fuel is methane and steam (CH$_4$, H$_2$O). The only electrochemical reaction considered in the anode side of the fuel cell is the one between hydrogen and the oxidant ion generated in the cathode side of the cell. Electrochemical oxidation of CO is neglected. Steam reforming of CH$_4$ (MSR) and water gas shift (WGS) reactions are also considered in the model. The WGS is assumed to be in equilibrium.

The goal of the present model is to obtain data concerning the reactions taking place in the SOFC, such as the current density, the fuel component concentrations, the distribution of temperature throughout the fuel cell channel length and the effect of steam reforming kinetics on the performance. First an introduction about the mathematical model follows. The model is then described in detail in section 4.2. Sections 4.3, 4.4 and 4.5 provide information about the thermo-fluid, the electrochemical, and the internal reforming reaction model respectively.

4.1 Introduction

The advantage of SOFCs over low temperature fuel cells is that they operate at high temperatures, thus providing the required heat to the direct internal reforming of hydrocarbons (mainly CH$_4$) [1]. What is more, through the water gas shift reaction (WGS), SOFCs can use CO to produce H$_2$. There have been several studies concerning mathematical modeling of SOFC. These studies involve one-, two- or three-dimensional models for planar and tubular fuel cells and for a variety of geometries and input parameters [2-14]. One of the most important problems to be solved is the one of internal stresses caused by heat cycling. Especially when internal reforming is employed large temperature gradients will occur inside the cell [1,4]. Therefore it is very important to accurately define the temperature distribution and gradients inside the cell. In the mathematical model it is clearly shown that material properties, kinetic parameters of chemical reactions and current density are strongly dependent on temperature.

Though several heterogeneous reactions can take place in the SOFC [15,16], the most important and the only two that will be considered in this model are the highly endothermic steam reforming reaction of CH$_4$ (Equation 4.1) and the exothermic conversion of CO through the water gas shift reaction (Equation 4.2).

\[
CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{298}^0 = 206 \text{ kJ/mol} \tag{4.1}
\]

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_{298}^0 = -41 \text{ kJ/mol} \tag{4.2}
\]

H$_2$ and CO contribute to the charge transfer chemistry in SOFCs. The heat required in order to sustain the endothermic CH$_4$ reforming reaction is supplied by the exothermic electrochemical oxidation of H$_2$ (Eq. 4.3) and CO (Eq. 4.4), and the water gas shift reaction
(Eq.4.2). However, in this study, only H\textsubscript{2} is assumed to be electrochemically active and thus Equation 4.4 will not be used in the model.

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H_{298}^0 = -241 \text{kJ} / \text{mol} \tag{4.3}
\]

\[
CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad \Delta H_{298}^0 = -283 \text{kJ} / \text{mol} \tag{4.4}
\]

In the present study a three dimensional thermal-fluid model coupled with an electrochemical reaction for the anode side of the SOFC has been developed. The model considers a representative single channel in the stack. In order to avoid the end-effects of the stack, the channel considered is assumed to be in the centre of the stack. The electrochemical reactions, direct internal reforming reaction of CH\textsubscript{4}, water gas shift (WGS) reaction and heat/mass transport phenomena between the solid (electrodes, electrolyte) and gas phases (anode/cathode channel flows) have been included in the model.

The conservation equations of the thermo-fluid model presented in section 4.3 of this chapter, are solved by using the CFD software ANSYS FLUENT. The coupled electrochemical processes, the water gas shift kinetics and methane steam reforming kinetics of the electrochemical model are simulated by external user defined functions (UDFs), written in C++ programming language. Concerning the electrochemical model, an empirical equation for the cell resistance is used to determine the electrochemical parameters. The boundary conditions for the anode and cathode gas flows are known (mass flow rate, inlet flow velocity, gas composition, inlet temperature). The current density is a function of the temperature and the gas species fractions in the gas stream flows. The heat and mass transfer in the cell are simulated by combining the conservation equations of mass, momentum and energy, presented in section 4.3 of this chapter. These equations are applied to the gas (fuel and oxidant channels), solid (electrolyte, interconnectors) and porous phase (anode, cathode). The gas species concentration and temperature concentration along the channel length are calculated by these equations and afterwards, results for the current density, fuel and air utilization can be obtained. The current density depends on the resistance and the Nernst voltage of the cell, which is a function of temperature and gas species concentrations. The relation between the various cell parameters can be clearly seen in section 4.3 where the equations used in the model are presented. Figure 4.1 gives an overview of the modeling strategy used by combining the electrochemical and thermo-fluid model.

![Diagram of the modeling method](image-url)

Figure 4.1: Diagram of the modeling method
The Navier–Stokes equation and the transport equation are solved in each computational volume. The computational method used is the finite volume method. The data obtained for temperature and gas species concentrations from every computational volume of the thermo-fluid model are used in the electrochemical model to calculate the local current density, which is used to calculate the hydrogen and oxygen reaction rate, heat generated and species sources inside the channel. The current density is used to calculate the heat produced by the cell as well. The results will be the input for the next computational volume and the procedure will be iterated for every computational volume in the grid until convergence of the solution is achieved.

Figure 4.2: Flow chart of current density calculation

4.2 Model specification

The geometry of the model developed, is shown in Figure 4.3. The components are distinguished by different colours. The proposed design modeled was developed by the Energy research Center of the Netherlands (ECN). The geometry is based on an anode supported planar SOFC. The gas channels, are formed by the corrugated bipolar plates, and the current collectors are situated above and below the fuel cell active area. In order to avoid the end effects of the stack, the channel considered is assumed to be in the centre of the stack. An assumption made is that the single channel modeled here is representative for the behaviour of the whole stack except for the channels at the edge of the stack where different boundary conditions are imposed. ANSYS Gambit is used to design and mesh the geometry of the fuel cell channel. The configuration chosen for Figure 4.3 is the co-flow pattern. However, a counter-flow pattern could also be possible.

The configuration of the channel is quite complex in some regions. This is because the geometry does not consist of surfaces vertical to each other, but due to the corrugated separator plates there are many curved regions. The mesh in these regions is locally refined [14]. The following figure of the geometric model shows the grid created for the calculations. Table 4.1 shows input parameters and specifications for the model. This table provides a brief description of the material properties, geometric, operating and electrochemical parameters.
Figure 4.3: Geometric model: Three-dimensional view of a) stack b) the modeled channel and c) front view of the computational grid.

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Input data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Geometric parameters</strong></td>
<td></td>
</tr>
<tr>
<td>Anode thickness ($\tau_a$)</td>
<td>0.55 mm</td>
</tr>
<tr>
<td>Cathode thickness ($\tau_c$)</td>
<td>0.03 mm</td>
</tr>
<tr>
<td>Electrolyte thickness ($\tau_e$)</td>
<td>0.01 mm</td>
</tr>
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<td>Interconnect thickness ($\tau_i$)</td>
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</tr>
<tr>
<td>Cell length (L)</td>
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<tr>
<td>Unit channel width (W)</td>
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</tr>
<tr>
<td>Fuel channel height ($h_0$)</td>
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</tr>
<tr>
<td>Air channel height ($h_a$)</td>
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</tr>
<tr>
<td>Fuel channel inlet area ($A_{Fuel}$)</td>
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</tr>
<tr>
<td>Air channel inlet area ($A_{Air}$)</td>
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</tr>
<tr>
<td>$A_{Air} / A_{Fuel}$</td>
<td>1.59</td>
</tr>
<tr>
<td><strong>Material properties</strong></td>
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</tr>
<tr>
<td>Anode density ($\rho_A$)</td>
<td>7740 kg m⁻³</td>
</tr>
<tr>
<td>Anode thermal conductivity ($\lambda_A$)</td>
<td>6 W m⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Anode heat capacity ($C_{p,A}$)</td>
<td>0.6 kJ kg⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Anode porosity ($\gamma$)</td>
<td>30%</td>
</tr>
<tr>
<td>Cathode density ($\rho_C$)</td>
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<tr>
<td>Cathode thermal conductivity ($\lambda_C$)</td>
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<td>Cathode heat capacity ($C_{p,C}$)</td>
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<td>Cathode porosity ($\gamma$)</td>
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<td>Electrolyte density ($\rho_E$)</td>
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<td>Electrolyte thermal conductivity ($\lambda_E$)</td>
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<td>Electrolyte heat capacity ($C_{p,E}$)</td>
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<td><strong>Operating parameters</strong></td>
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<td>Pressure (P)</td>
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<td>Fuel inlet temperature ($T_{fuel, inlet}$)</td>
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</tr>
<tr>
<td>Air inlet temperature ($T_{air, inlet}$)</td>
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</tr>
<tr>
<td>Top and bottom external wall</td>
<td>Adiabatic</td>
</tr>
<tr>
<td>Operating voltage ($V_{cell}$)</td>
<td>0.8 V</td>
</tr>
<tr>
<td>Fuel feed (biosyngas)</td>
<td>2% CH₄, 10% H₂O, 18% H₂, 18% CO, 13% CO₂, 39% N₂</td>
</tr>
<tr>
<td>Air feed</td>
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</tr>
<tr>
<td>Air to fuel ratio (biosyngas)</td>
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</tr>
<tr>
<td>Fuel feed rate (biosyngas)</td>
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</tr>
<tr>
<td>Fuel feed (methane)</td>
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<tr>
<td>Air to fuel ratio (methane)</td>
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</tr>
<tr>
<td>Fuel feed rate (methane)</td>
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</tr>
<tr>
<td><strong>Electrochemical parameters</strong></td>
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</tr>
<tr>
<td>Activation energy ($E_{activation}$)</td>
<td>-101248 J mol⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Empirical parameter ($k_{0,electrical}$)</td>
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</tr>
<tr>
<td>Faraday constant (F)</td>
<td>1.8870e⁻¹⁰ ohm m²⁻¹</td>
</tr>
<tr>
<td>Universal gas constant (R)</td>
<td>8.314 J mole⁻¹ K⁻¹</td>
</tr>
</tbody>
</table>

Table 4.1. Single SOFC channel model specifications and input parameters.
4.3 Thermo fluid model

The solid and fluid domains of the model are divided into discrete meshes creating finite volumes as shown in Figure 4.3. In each computational grid created the finite volume method is applied to solve conservation equations. The conservation equations for mass, momentum, and energy are solved in each computational grid.

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = S_{\text{mass}} (4.5)
\]

\[
\frac{\partial}{\partial t} (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) + \nabla p - \nabla \cdot (\mathbf{t}) = S_{\text{momentum}} (4.6)
\]

Equations 4.5 and 4.6 are the mass and momentum conservation equations. The terms \( \frac{\partial \rho}{\partial t} \) and \( \frac{\partial (\rho \mathbf{v})}{\partial t} \) are deleted because the flow is steady state. The source term \( S_{\text{mass}} \) is the mass added to the continuous phase by user-defined sources, \( p \) is the static pressure and \( \mathbf{t} \) is the stress tensor.

\[
\mathbf{t} = \mu \left[ \left( \nabla \mathbf{v} + \nabla \mathbf{v}^T \right) - \frac{2}{3} \nabla \cdot \mathbf{v} \right] (4.7)
\]

So the final form of the momentum conservation equation is:

\[
\nabla \cdot (\rho \mathbf{v} \mathbf{v}) + \nabla p - \nabla \cdot \left[ \mu \left( \nabla \mathbf{v} + \nabla \mathbf{v}^T \right) - \frac{2}{3} \mu \nabla \cdot \mathbf{v} \right] = S_{\text{momentum}} (4.8)
\]

Where \( \mu \) is the molecular viscosity, \( I \) is the unit tensor and \( 2 \mu \nabla \cdot \mathbf{v} / 3 \) is the effect of volume dilation. The whole electrode substrates are considered to be porous media with the same properties. The additional momentum source caused by the porous media in the model is contained in the term \( S_{\text{momentum}} \). The flow velocity of the gases in the porous anode and cathode is low and can be considered as laminar flow by calculating the pore Reynolds number \( \text{Re}_p \) for both cases.

\[
\text{Re}_p = \frac{\rho |\mathbf{v}| d_p}{\mu} (4.9)
\]

where \( \mathbf{v} \) is the mean fluid velocity, \( d_p \) is the pore diameter, \( \mu \) is the dynamic gas mixture viscosity and \( \rho \) is the gas mixture density. When laminar flow through porous media is present, then the additional momentum source produced by the porous media can be simplified with Darcy’s law [2,10]. The empirical Darcy equation describes the balance between the force from the pressure gradient \( \nabla p \) and the frictional resistance from the solid material:

\[
\nabla p = -\frac{\mu \cdot \epsilon}{\alpha} \mathbf{v} (4.10)
\]

where \( \epsilon \) is the porosity (the volume fraction of void space) and \( \alpha \) is the permeability of the electrode.

Inside the cell there is transfer of gas species in the channel and in the porous electrodes. Inside the cell channel, the species are transferred by convection and in the porous electrodes by diffusion.
\[
\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i \tag{4.11}
\]

where \( Y_i \) is the species concentration, \( R_i \) is the net rate of production of species \( i \) (H\(_2\), O\(_2\), H\(_2\)O, CH\(_4\), CO\(_2\), CO) by chemical reaction and \( S_i \) is the rate of creation by adding species from the dispersed (i.e., uniformly distributed) phase plus the species from the user-defined sources (UDFs). This equation is solved for \( n - 1 \) species where \( n \) is the total number of fluid phase chemical species present in the system. Since the mass fraction of the species must sum to unity, the \( n \)th mass fraction is determined as one minus the sum of the \( n - 1 \) solved mass fractions. The term \( \vec{J}_i \) is the diffusion flux of species \( i \), which arises due to concentration gradients. The diffusion flux for laminar flows can be written as:

\[
\vec{J}_i = -\sum_{j=1}^{n-1} \rho \cdot D_{ij} \cdot \nabla Y_i \tag{4.12}
\]

In the above equation, \( D_{ij} \) is the binary diffusion coefficient. Equation 4.11 will finally be as follows:

\[
\nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \left( \sum_{j=1}^{n-1} \rho D_{ij} \nabla Y_i \right) + S_i \tag{4.13}
\]

The reaction zone created in the model is situated in the interface between the anode and the electrolyte. The gas species diffuse through the porous electrodes to reach the reaction site. The Fuller method [14] is used to calculate the binary coefficient \( D_{ij} \). The Fuller method is based on the kinetic theory diffusion coefficient. There are five gases (H\(_2\), H\(_2\)O, CH\(_4\), CO\(_2\), CO) in the anode and two gases in the cathode (O\(_2\), N\(_2\)). This means that there are 21 possible binary diffusion coefficients. The following expression is obtained for the binary diffusion coefficient of a two-gas mixture comprising species \( i \) and \( j \):

\[
D_{ij} = 0.00143 \cdot T^{1.75} \left( \frac{1}{M_{w,i}} + \frac{1}{M_{w,j}} \right)^{1/2} \tag{4.14}
\]

In the above equation, \( T \) is the temperature, \( M_{w,i} \) is the molar mass of species \( i \), and \( M_{w,j} \) is the molar mass of species \( j \).
where \( P \) is the pressure, \( V \) is the diffusion volume (see Appendix C), and \( M_W \) is the molar weight.

The energy equation solved is Eq. (4.15), where \( k_{ef} \) is the effective thermal conductivity and \( \vec{j}_j \) is the diffusion flux of species \( j \). The first three terms on the right-hand side of equation 4.15 represent heat transfer due to conduction, species diffusion, and viscous dissipation, respectively. The viscous dissipation is not considered in the present model. \( S_h \) includes the heat generated by the electrochemical reactions.

\[
\frac{\partial}{\partial t} \rho E + \nabla \cdot (\rho \vec{v} E + \rho \vec{p}) = \nabla \cdot (k_{ef} \nabla T - \sum_i \rho_i \vec{j}_i + \sum_j \rho D_j \nabla Y_j) + S_h \tag{4.15}
\]

The energy equation finally becomes:

\[
\nabla \cdot (\rho \sum_i Y_i \vec{j}_i + \rho \vec{p}) = \nabla \cdot (k_{ef} \nabla T + \sum_i \rho_i \left( \sum_j \rho D_j \nabla Y_j \right) + S_h \tag{4.16}
\]

The effective thermal conductivity in the porous medium, \( k_{ef} \), is computed as the volume average of the fluid and solid thermal conductivities:

\[
k_{ef} = \gamma k_f + (1 - \gamma) k_s \tag{4.17}
\]

**Figure 4.5: Principles of heat transfer inside the SOFC.**

A single computational cell is repeated for the whole model domain. This computational cell is assumed to be thermally isolated from all sides. The heat generated by the electrochemical reactions is transferred from the reaction zone to the gas channels, electrolyte, electrodes and interconnectors by conduction, convection and radiation (only when radiation is considered in the simulations). Heat is mainly transferred by convection between the solid parts (interconnectors, PEN structure) and the gas streams in the channels. In the porous (electrodes) and solid parts (electrolyte, interconnectors) of the cell, heat is mainly transferred by conduction. The above energy transfer equation is simplified for the solid regions (electrolyte, interconnector) of the model.

\[
\frac{\partial}{\partial t} (\rho h) + \nabla \cdot (\rho \vec{v} h) = \nabla \cdot (k \nabla T) + S_h \tag{4.18}
\]

The term on the left-hand side represents convective energy transfer. The terms on the right-hand side represent the heat transfer due to conduction, and the heat sources respectively.
The heat generated by the electrochemical reactions is transferred from the reaction zone to the gas channels, electrolyte, electrodes and interconnectors by conduction, convection and radiation (see Appendix A for effect of radiative heat transfer). The rate of heat generation $\dot{Q}$ is obtained by applying Faraday’s law to the heat balance of the cell:

$$\dot{Q} = \frac{i}{NF} \Delta H_{\text{ele, chem}} - iV_{\text{cell}}$$  \hspace{1cm} (4.19)

where, $\Delta H_{\text{ele, chem}}$ is the heat released by the electrochemical reactions, $F$ is the Faraday constant, $N$ is the number of electrons transferred during the electrochemical reaction and $V_{\text{cell}}$ is the cell voltage.

### 4.4 Electrochemical model

The electrochemical model is used to calculate the current density in the cell. The cathode gas channel flow feed is air. The oxidant is $O_2$ contained in air fed in the cathode gas channel, and is reduced at the cathode according to the reaction:

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$  \hspace{1cm} (4.20)

The oxygen ions generated at the cathode reach the reaction zone of the anode by passing through the electrolyte. When $O^{2-}$ ions reach the anode they take part in the anode electrochemical reaction, which is expressed by equation

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$  \hspace{1cm} (4.21)

The overall reaction, taking place in the SOFC is exothermic, releasing 241kJ/mol of energy.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \hspace{1cm} \Delta H^0_{298} = -241kJ/mol$$  \hspace{1cm} (4.22)

$H_2$ and CO contribute to the charge transfer chemistry in SOFCs [1]. However, in this study, only $H_2$ is assumed to be electrochemically active. There are two reasons for this: The first one is that the rate at which CO is electrochemically oxidized is by far exceeded by the rate of CO conversion in the water gas shift (WGS) reaction. The second reason is that $H_2$ charge transfer dominates over CO, when both species are present [8]. So, the electrochemical oxidation of CO is neglected and not taken into account in this model.

The cell voltage $V_{\text{cell}}$ for the electrochemical oxidation of hydrogen, is determined by the Nernst equation. The pressure and concentration of the reactants affects the Gibbs free energy, and thus the voltage. However in this model the pressure drops are considered negligible. The voltage is also affected by the temperature.

$$V_{\text{cell}} = -\Delta g^0 + \frac{RT}{2F} \cdot \ln \left( \frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}} \right)$$  \hspace{1cm} (4.23)

In the above equation $P_{H_2}, P_{O_2}, P_{H_2O}$ represent the partial pressure of the corresponding species, $R$ is the universal gas constant, $\Delta g^0$ is the change of Gibbs free energy for the formation reaction of water divided by $2F$, where $F$ is the Faraday constant and number two
represents the amount of electrons transferred during the electrochemical reaction. The above ratio is also known as the standard potential for the hydrogen oxidation reaction and is denoted by \( V_{H_2}^0 \). The value of Gibbs free energy is calculated by using equation 4.24, which is obtained by experimental studies [15].

\[
\Delta G_f = 0.053 \cdot T - 245.58
\]

(4.24)

The actual voltage \( V_{cell} \) of the SOFC equals to the value of the open circuit voltage \( V_{rev} \) minus the irreversibilities, which are activation, ohmic and concentration losses inside the cell. An empirical formula is used to calculate the total local losses \( R_{tot,loc} \), representing the total resistance of the cell components [15]. The values for the parameters \( k_{0,electrical}, E_{a,electrical}, R, T \) are taken from Table 4.1.

\[
V_{cell} = V_{rev} - i \cdot R_{tot,loc}
\]

(4.25)

\[
R_{tot,loc} = k_{0,electrical} \cdot \exp \left( \frac{-E_{a,electrical}}{RT} \right)
\]

(4.26)

The current density is calculated by rearranging the terms of equation 4.25

\[
i = \frac{V_{rev} - V_{cell}}{R_{tot,loc}}
\]

(4.27)

The gas channel is divided into discrete elements. The electrochemical reaction rate for the first element is calculated by using the inlet boundary conditions (temperature, pressure, species concentration, velocity etc.). When calculated, the outlet values of the element are used as inlet values for the following element, until electrochemical parameter values for all the elements are obtained. The material used for electrolyte in the model is YSZ, which is a pure ionic conductor. So the only component that is considered to permeate through the electrolyte is oxygen. The electrochemical reaction rates depend on the current density \( i \), according to Faraday’s law [4,5,14].

\[
\frac{\partial H_2}{\partial t} = \frac{i}{2F}
\]

(4.28 a)

\[
\frac{\partial O_2}{\partial t} = \frac{i}{4F}
\]

(4.28 b)

The terms \( \partial H_2/\partial t \), \( \partial O_2/\partial t \) represent the rates of hydrogen and oxygen molar consumption in the anode and cathode respectively. The number of moles of hydrogen and oxygen consumed and water produced is calculated according to the reaction stoichiometry of equations 4.3 and 4.4:

\[
n^\text{anode}_{H_2} = \frac{i}{2F}
\]

(4.29 a)

\[
n^\text{anode}_{O_2} = \frac{i}{4F}
\]

(4.29 b)

\[
n^\text{prod}_{H_2O} = \frac{i}{2F}
\]

(4.29 c)
4.5 Modeling Internal Reforming Reaction

The heat required to sustain the endothermic CH₄ reaction is provided by the exothermic electrochemical reactions in the cell and by the water gas shift reaction, converting CO to H₂. Thus internal reforming offers advantages concerning the operation of SOFCs. The system is less complex and cheaper, due to lack of an external reforming device. The hydrogen distribution is more even, resulting in smaller temperature gradients [1]. The efficiency is higher because heat produced by the exothermic reactions is required for the endothermic reforming, so the cooling requirements are lower. Additionally, the fuel stream becomes richer in H₂ content [1].

4.5.1 Internal Reforming Reaction

The following figure shows the internal reforming and electrochemical reaction of fuel and air in the SOFC channel. In the anode gas channel the mole fraction of the fuel is: 2% methane, 10% water vapor, 18% hydrogen, 18% carbon monoxide, 13% carbon dioxide, 39% nitrogen. The cathode airflow mole fraction composition is 21% oxygen and 79% nitrogen. Methane is reformed by water vapor in the porous anode, producing CO and H₂. The water vapor in the reforming reaction is contained either in the fuel flow, or is produced during the electrochemical oxidation of H₂. Carbon monoxide contained either in the fuel flow or produced from the CH₄ steam reforming reacts with water vapor (water gas shift reaction) to produce CO₂ and H₂. H₂ is electrochemically oxidized in the porous anode by an oxygen ion, to produce water and a pair of electrons. In the cathode, oxygen is reduced to oxide ions by electrons produced in the anode. These electrons are transferred to the cathode through the external circuit. The ions transfer from the cathode to the anode through the electrolyte. It is important to point out the current collectors are attached to the electrodes. The side view of the channel may be misleading concerning the transfer of the electrons from the anode to the cathode, as they seem to travel from the anode to the upper interconnect and from the bottom interconnect to the cathode through the gas channels. However, what actually happens is that due to the design of the fuel cell (corrugated separator plate) the interconnectors are in touch with the current collectors. (See Figure 4.3)

![Figure 4.6: Internal reforming and electrochemical reaction of fuel in the SOFC channel (side view).](image)

Figure 4.7 shows the energy balance in the single gas channel. In this figure there is no depiction of heat transfer between the gas channel and neighboring channels. All reactions are assumed to take place in the electrodes and not in the gas channels. The CH₄ steam reforming and water gas shift reactions occur in the region close to the surface of the anode, while the
electrochemical oxidation of H\textsubscript{2} takes place in the region close to the anode bottom. Heat is generated by the electrochemical reaction and by the WGS reaction. The heat is transferred to the anode and cathode gas flows and through the to the interconnectors of the cell. Part of this heat generated, is absorbed by the CH\textsubscript{4} steam reforming. When current passes through the interconnector, additional heat is generated according to Ohm’s law. However, heat generated due to electrical resistance is very small compared to heat generated by the electrochemical and heterogeneous reactions.

4.5.2 Internal Reforming Model

The highly endothermic steam reforming reaction of CH\textsubscript{4} (Eq.1) and the exothermic conversion of CO through the water gas shift reaction (Eq.2) will produce H\textsubscript{2}, CO and H\textsubscript{2}, CO\textsubscript{2} respectively. The mechanism of steam reforming on the Ni-YSZ cerments of SOFCs has been analytically reported in Chapter 3. The internal reforming kinetics affect the performance of SOFCs and have been studied in many SOFC modeling works [3-7,10,12,13,15]. The steam reforming in this model is a first order kinetic expressed suggested by Achenbach and Riensche [18-20]. It is presented in Equation 4.30. The activation energy is Ea=82 kj/mol and the pre-exponential factor is ko=4274 mol s\textsuperscript{-1}m\textsuperscript{-2}bar\textsuperscript{-1} [19].

\[
R_{\text{CH}_4} = k_0 \cdot P_{\text{CH}_4} \cdot \exp(-E_a / RT) \tag{4.30}
\]

The SOFC designed by the ECN has its highest efficiency at high fuel utilization ratio (at \(U_f=0.8\)) [15]. The water gas shift reaction is close to equilibrium at high fuel utilization ratio. The equilibrium constant \(K_{\text{w GS}} [21,22]\) is:

\[
K_{\text{w GS}} = \frac{P_{\text{CO}} \cdot P_{\text{H}_2}}{P_{\text{CO}_2} \cdot P_{\text{H}_2\text{O}}} \tag{4.31}
\]

Equation 4.32 is the expression used for the water gas shift reaction rate [5].

\[
R_{\text{W GS}} = k_{\text{W GS}} \cdot P_{\text{CO}} \cdot \left(1 - \frac{P_{\text{CO}} \cdot P_{\text{H}_2}}{P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}} K_{\text{w GS}} \right) \cdot \exp(-E_a / RT) \tag{4.32}
\]

The fuel utilization is:

\[
U_{\text{fuel}} = \frac{\left(n_{\text{H}_2} + n_{\text{CO}} + 4 n_{\text{CH}_4} \right)_{\text{idle}} - \left(n_{\text{H}_2} + n_{\text{CO}} + 4 n_{\text{CH}_4} \right)_{\text{fuel}}}{\left(n_{\text{H}_2} + n_{\text{CO}} + 4 n_{\text{CH}_4} \right)_{\text{idle}}} \tag{4.33}
\]
4.6 Conclusion

This chapter gives the presentation of the three-dimensional CFD model of a single SOFC channel using biosyngas and methane as fuels. The model considers a representative single channel in the stack. In order to avoid the end-effects of the stack, the channel considered is assumed to be in the centre of the stack. The electrochemical oxidation of hydrogen, direct internal reforming reaction of \( \text{CH}_4 \), water gas shift (WGS) reaction and heat/mass transport phenomena between the solid (electrodes, electrolyte) and gas phases (anode/cathode channel flows) have been included in the model. The electrochemical oxidation of CO is neglected.

The conservation equations of the thermo-fluid model are solved by using the CFD software ANSYS FLUENT. The coupled electrochemical processes, the water gas shift kinetics and methane steam reforming kinetics of the electrochemical model are simulated by external user defined functions (UDFs). Concerning the electrochemical model, an empirical equation for the cell resistance is used to determine the electrochemical parameters. The current density is a function of the temperature and the gas species fractions in the gas stream flows. The heat and mass transfer in the cell are simulated by combining the conservation equations of mass, momentum and energy. The Navier – Stokes equation and the transport equation are solved in each computational volume. The computational method used is the finite volume method.
## Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
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<td>C</td>
<td>Molar concentration</td>
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<td>D</td>
<td>Diffusion coefficient</td>
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## Greek

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## Subscripts

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<td>Local</td>
</tr>
<tr>
<td>M</td>
<td>Momentum</td>
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References


15. Z. Qu: Simulation and Analysis of an Anode-Supported Solid Oxide Fuel Cell and Stack.
Chapter 5: Results and discussion

5.1 Operation with biosyngas

In this section the modeling results for operation of the SOFC with biosyngas are presented. The results presented are for the gas species concentrations, temperature and current density distributions along the channel. There are also simulations for the investigation of the effect of steam reforming kinetics on the fuel cell performance. The biosyngas composition that was initially intended to be used was: CH₄ 2%, CO 20%, CO₂ 12%, H₂O 2%, H₂ 20%, N₂ 44% [1]. However as can be seen in Figure 5.5 operation with this composition was not safe for the fuel cell as there was the risk of carbon deposition. For this reason, steam was added in the fuel stream. Finally, the composition of the biosyngas used in the simulations is presented in Table 5.1.

<table>
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<td>CO₂</td>
<td>13 %</td>
</tr>
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<td>H₂O</td>
<td>10 %</td>
</tr>
<tr>
<td>H₂</td>
<td>18 %</td>
</tr>
<tr>
<td>N₂</td>
<td>39%</td>
</tr>
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</table>

Table 5.1: Biosyngas composition for simulations

The results presented are taken from five representative points of the channel, as shown in Figure 5.1 These representative points are on the upper parts of the anode, electrolyte and cathode, on the separator, and the air channel side edge bottom. All the locations apart from the air channel bottom are situated on the symmetry axis of the SOFC channel. These 5 locations are used to obtain results for the temperature, the point representing the electrolyte is used for the current density calculations, and the upper part of the anode at the interface with the anode gas channel is used to calculate the gas species concentrations.

Figure 5.1: Front view of the computational grid, and the five representative locations chosen for the simulation results.
5.1.1 Gas species concentration

The following section of this chapter is a presentation of the gas species concentrations in the fuel cell channel. The species mole fractions vary along the channel. For this reason, one representative point was chosen in the interface between the anode and the anode gas channel (Figure 5.2). Additionally, in order to obtain a more detailed view of the species concentrations, schematics including other locations of the channel will be presented (Figures 5.5-5.8).

![Figure 5.2: Representative location on the anode/anode gas channel interface](image)

5.1.1.1 Gas species concentration along the channel

![Figure 5.3: Gas species concentration in the anode gas channel along its length.](image)

Figure 5.3 shows the mole fraction profiles of H₂, H₂O, CH₄, CO, CO₂ along the fuel channel. The gas concentrations illustrate the impact of the electrochemical oxidation of H₂, the steam reforming of CH₄ and the water gas shift reaction. When H₂ enters the gas channel it is oxidized, producing water. The H₂ mole fraction curve shows an increase in the region close to the fuel inlet. This happens because the MSR and WGS reactions will produce additional H₂, which will be added to the H₂ stream that is available for oxidation. This means that the reaction rate of the MSR reaction is faster than the rate of H₂ oxidation in this region. The initial mole
fraction of $H_2$ is 18%, it slightly increases to 19.7% near the inlet, and decreases to 3% in the fuel channel outlet.

On the other hand, mole fraction of $H_2O$, which is produced during the electrochemical oxidation of $H_2$ and the reforming reactions, increases from 10% in the inlet to 27.5% in the outlet. The increase rate of $H_2O$ is lower in the region close to the inlet and is afterwards increased (see slope). In fact, the steam curve initially shows a decreasing trend. This can be explained by the fact that the amount of steam consumed by the MSR reaction is higher than the amount of steam produced by $H_2$ oxidation.

The CO concentration slightly increases near the inlet due to CO production during the $CH_4$ steam reforming reaction. As the $CH_4$ mole fraction drops, the WGS reaction dominates over reforming and the amount of CO produced by the MSR reaction, is lower than the amount of CO consumed in the WGS reaction. This explains why the mole fraction of CO is decreasing while the mole fraction of $CO_2$ increases. However near the fuel inlet (0.005 m) there is no change in the $CO_2$ concentration. The explanation for this is that $CH_4$ reforming is a mole increasing process, thus the $CO_2$ mole fraction will not increase at the very inlet of the channel. The CO initial concentration is 18%. After a slight increase near the inlet the concentration slightly rises to 18.3% and then decreases to 4.2% in the channel outlet. At this point it has to be pointed out that as previously reported, the electrochemical oxidation of CO is not implemented in the model, and thus CO is only consumed in the WGS reaction.

The $CH_4$ concentration decreases from 2% to almost 1% within a small distance from the fuel inlet (0.008 m form the inlet). At 0.036 m almost all methane has been consumed, and it is completely consumed at 0.06 m from the channel inlet. The slight increase of CO mole fraction is attributed to the fact that the $CH_4$ initial amount entering the stream is small, thus leading to low quantities of CO production when reformed. When the WGS becomes the dominant reaction over the $CH_4$ reforming reaction the concentration of CO is consumed and thus decreases, while the concentration of $CO_2$ increases. The reason that although CO is consumed in the WGS, its concentration at the outlet is not significantly decreased is explained by the high initial mole fraction. The same applies to the $CO_2$ mole fraction, because the amount produced during WGS reaction is added to the initial mole fraction of 13%. At the outlet of the fuel cell channel all the $CH_4$ has been fully consumed. The outlet gas stream composition is 27.5% $H_2O$, 4.2% CO, 3% $H_2$ and 27.4% $CO_2$.

Figure 5.4: Steam to carbon ratio along the fuel channel

Figure 5.4 presents the steam-to-carbon ratio ($S/C$) along the SOFC channel. The $S/C$ ratio varies along the channel because of the MSR and WGS reactions that consume steam, and the electrochemical oxidation of hydrogen that produces steam. The initial $S/C$ value in the
graph is 0.3 and gradually increases to 0.86 at the channel outlet. According to literature (explained in chapter 3) the S/C should be over 1.4 to avoid carbon deposition. However, the S/C ratio only gives an indication of which area is the most likely for carbon deposition to take place and it does not in any case determine if carbon deposition would take place. This is confirmed by the following ternary diagram.

Figure 5.5: Ternary diagram for operation with biosyngas. The black dot is for 2% steam concentration and the red dot is for 10% steam concentration in the fuel. The latter is below the carbon deposition boundary line and thus operation is safe concerning the risk of carbon deposition.

In order to determine whether solid carbon is formed, a ternary C-H-O diagram is needed. The position (red dot) for the ternary diagram in Figure 5.5 is calculated from the composition of the fuel at the inlet of the fuel cell channel. It is situated below the carbon deposition line, which means that the operation is safe for the fuel cell. The carbon deposition line is for atmospheric pressure and temperature 970 K. For higher temperatures the corresponding lines are situated above the existing line, and thus operation is safe in the operating temperature range of the cell.

Figure 5.6: Combined phase equilibrium diagram of Ni and NiO system from 200 ºC to 1000 ºC across a range from 10^{-40} to 10^{-10} bar. The blue dot represents the highest in the fuel gas, under the given working condition.

It is also important to predict the possibility of the formation of NiO in anode materials, since it is one of the crucial signals of the degradation of fuel cell performance. Oxygen in the fuel gas channel diffuses to the Ni based porous anode, and under certain conditions NiO might
be formed. A well-known drawback of the Ni-based cell is its susceptibility to thermomechanical failure when the anode side of the SOFC is exposed to oxidising conditions at high temperatures (redox failure). The oxidation of the Ni contained within the porous composite into NiO entails a substantial volumetric expansion and thus exerts significant stress on the ceramic backbone of the composite when the internal porosity is not sufficient to accommodate the expansion of the oxidising Ni/NiO phase. Thus a failure in the ceramic network may appear [2].

The hydrogen and steam concentration at the channel outlet were used to investigate the reforming capacity of the anode materials and the degree of oxidation of Ni from existing oxygen in anode, due to the high ratio between these two elements at this location. The corresponding concentrations are 3% and 27% respectively. The software used to draw the phase equilibrium diagram of Ni and NiO shown in Figure 5.6 is HSC Chemistry [3]. At the channel outlet temperature, 780 °C, the thermodynamic boundary for Ni/NiO lies at $1 \cdot 10^{-14}$ for the partial pressure of $O_2$. The highest value is $1.18 \cdot 10^{-19}$ under the operating conditions. This point (blue dot in the graph) is located in the safe region, below the thermodynamic boundary where metal Ni reacts to metal oxide NiO. Hence, anode materials stays in the metallic phase under the given conditions investigated in this work.

5.1.1.2 Gas species concentration close the channel inlet

![Figure 5.7: Hydrogen concentration in the middle cross section of the anode gas channel at small distance (0.02 m) from the fuel inlet.](image)

The above description for the species concentration applies for the schematics in Figures 5.7 to 5.9. The hydrogen mole fraction distribution in the middle vertical cross section of the anode gas channel is presented in Figure 5.7. The cross-section, is outlined by red colour. The enlarged part of the fuel cell channel shows the hydrogen distribution in the area close to the channel inlet. There is a clear difference in the hydrogen distribution in the fuel channel and in the anode. The electrochemical oxidation of hydrogen takes place in the reaction zone created in the interface between the anode and the electrolyte. Apart from this, there is also hydrogen production due to the MSR reaction. Thus, the amount of hydrogen produced is higher than the amount of hydrogen consumed in the electrochemical reaction. This is the reason that the concentration of hydrogen is lower in the fuel channel compared to the anode in the very inlet of the channel.

For the rest of the gas species, the reason for the difference in the concentration between the fuel channel and the anode is that all reactions (electrochemical oxidation of hydrogen, MSR, WGS) take place in the reaction zone in the interface between the anode and the electrolyte.
Their concentration fluctuates on the basis of whether the species are consumed or produced by the corresponding reactions.

Figure 5.8: Methane concentration in the middle cross section of the anode gas channel at 0.02 m from the fuel inlet.

Figure 5.9: Gas species concentration in the anode at 0.02 m from the fuel inlet (A: anode top view, B: front view) for a) methane, b) hydrogen, c) steam, d) carbon monoxide, e) carbon dioxide.
Figure 5.9 shows the contours of the gas species in the anode, in the area close to the inlet of the channel (0.02 m from the inlet). The schematics are top and front views of the anode. The reason for choosing the area close to the inlet is that the reforming reactions show high activity near the inlet (Figure 5.3). It is clearly shown that in the area underneath the inter-connector rib, the gaseous species are transported only by diffusion in the porous electrodes. This leads to lower CH$_4$, CO$_2$, H$_2$ and higher CO, H$_2$O concentrations in the area underneath the inter-connector rib compared to the channel area.

5.1.2 Temperature distribution

In this section the temperature profiles for the 5 representative locations are presented. Before the presentation of the results, it has to be specified that the single SOFC channel considered, is assumed to be thermally isolated from its surroundings.

![Temperature profiles for the components along the fuel cell channel and the initial part of the channel.](image)

**Figure 5.10**: Temperature profiles for the components a) along the fuel cell channel, and for b) the initial part of the channel.
Figure 5.10 is an illustration for the temperature distribution in specific points in the cell components. The temperature profiles are almost the same for all points examined apart from those close to the cell inlet. For this reason there is a second graph showing the initial part of the channel. There is a slight temperature drop within a short distance (0.005 m) of the cell inlet. This drop is attributed to the fact that the endothermic MSR reaction starts to take place as soon as the fuel enters the channel. However due to the small amount of methane (2%) in the fuel stream, the exothermic WGS reaction and exothermic electrochemical oxidation of H$_2$ will dominate over reforming and thus the temperature starts to increase.

Temperature differences for the five components are more significant within a small distance from the cell inlet compared to other positions along the cell. In this model a thin reaction zone has been created in the anode/electrolyte interface. The heat from exothermic reactions in anode/electrolyte interface is transferred to the porous anode, afterwards to the fuel gas flow, and from there to the upper separator plate. On the other hand, heat is absorbed in the reaction zone during the endothermic MSR reaction. This explains why within a small distance from the inlet, the temperature of the anode slightly drops from 973 K, to 969.5 K within 0.001 m from the channel inlet. After that, the temperature gradually increases till it reaches the value of 1052.46 K in the outlet.

The cathode temperature profile is not distinguished in the graph. This is explained by the fact that the cathode is too thin, it is in direct contact with the electrolyte, and is situated close to the reaction zone. The heat is conducted rapidly and thus the cathode temperature profile is the same as the electrolyte temperature profile. The reason that the PEN structure (anode, cathode, electrolyte) shows a uniform heat distribution is its high thermal conductivity. Concerning the separator due to heat transfer it follows a similar (almost the same) temperature profile with the PEN structure. However, close to the outlet where there is lower electrochemical reaction activity there is not enough heat transferred to the separator plate and thus its temperature compared to the PEN structure, is 1.2 K lower at the outlet.

Close to the inlet, the cathode gas channel has slightly higher temperature due the fact the PEN temperature drops during the MSR reaction. At the same time the air channel shows a decreasing temperature profile due to the fact that heat carried in the air stream is absorbed for the MSR reaction. As soon as MSR stops being the dominant reaction, the air channel will have lower temperature compared to the PEN structure, following an increasing profile. This is because the air apart from oxidizing the fuel, serves as a coolant in the cell. The outlet temperature of the air channel is 1047.29 K.
The average temperature gradient for the fuel cell electrolyte is 0.72 K/mm. The temperature gradient is shown in Figure 5.11. The reason that the temperature gradient is negative near the inlet is due to the steam reforming reaction. However, the temperature gradient quickly shows an increasing trend, since the CH4 concentration is low (2%) and thus the effect on the temperature is not significant. The temperature gradient increases until 0.093 m, where it reaches a peak value of 1.05 K/mm. After this the temperature gradient will gradually decrease. Figure 5.11 clearly shows that attention should be paid in the area near the inlet.

The temperature of the cell components in the outlet is almost the same due to conductivity of the materials. The difference between the minimum and the maximum temperature values in the PEN structure is 83 K. The minimum temperature is close to the cell inlet (969.5 K), and the maximum is in the cell outlet (1052.46 K). The temperature difference between inlet and outlet for the separator plate is 80.5 K. The temperature difference between inlet and outlet for the air channel bottom is 74.3 K.

Figure 5.12: Temperature distribution on a) middle cross section of the fuel cell channel b) cross section at the inlet of the fuel cell channel.
In order to obtain a complete overview of the temperature distributions, Figure 5.12 is presented. Figure 5.12 shows a detailed schematic of the temperature distribution on the middle cross section and the inlet cross section of the channel. For the middle cross section, the temperature varies between 999 and 1006 K. In the region of the separator plate, PEN (anode, cathode, electrolyte) and fuel channel the temperature is higher and evenly distributed. In the area close to the channel symmetry axis, the temperature is higher (1006 K) compared to the rest area of the other channel components. The rest area of the PEN structure (approaching to the interconnector ribs) has a slightly lower temperature (1004 K). The upper region of the air channel has the same temperature with the PEN structure (1004 K), but is decreasing from top to bottom and from the symmetry axis to the edge of the channel. The minimum temperature is observed in the air channel bottom, as determined in Figure 5.1. The reasons for the existence of regions with higher or lower temperature distributions (exothermic reactions, air serving as coolant etc.) have been explained earlier in this section.

Concerning the cross section at the inlet, it is clear that the PEN structure is at a lower temperature than the other channel components due to the endothermic MSR reaction. As can be seen, the temperature is lower at the upper part of the anode and towards the symmetry axis. This is explained by the fact that CH$_4$ concentration is higher in these areas (check Figure 5.8), and thus the MSR reaction activity is higher.

Apart from the middle cross section, the temperature distribution was investigated in the cross section of the fuel channel (A-A) and the air channel (B-B) in Figure 5.13. For the air channel the changes in the temperature distribution are bigger. The lowest temperature is found in the middle of the air channel. The single SOFC channel considered, is assumed to be thermally isolated from its surroundings and thus if there was another cell adjacent to the investigated channel, the temperature distribution would have been different.

Figure 5.13: Temperature distribution on cross section of the fuel channel and the air channel in the fuel cell channel
5.1.3 Current density profile

The current density profile along the cell length is presented in Figure 5.14. The local current density as can be seen in the electrochemical model above, is a function of the gas species concentrations, temperature and operating voltage of the cell. The current density value is in the range from 2000 to 4553 A/m². The initial current density in the cell inlet is 2005 A/m² and rapidly increases within a small distance (0.001 m) from the inlet to 3796 A/m². The current density follows an increasing profile reaching 4553 A/m² at 0.073 m and then it reduces gradually to 2211 A/m² near the channel outlet. At the outlet, the current density will rapidly drop to 970 A/m². The average current density is 4061 A/m². The fluctuations in the current density profile are attributed to gas composition (due to fuel consumption) along the channel and the effect of temperature thus making the rate of electrochemical oxidation to vary. The profile of the Nernst (reversible) voltage, resistance and current density are also shown in Figure 5.14. It has already been reported that the operating voltage of the cell is 0.8 V and thus the changes in the Nernst voltage and the resistance will determine the current density according to equation 4.27 presented in the description of the model used for the simulations.

A more clear view of the current density distribution can be seen in Figure 5.15. The current density is higher in the regions close to the symmetry axis. This is attributed to the fact that the current is calculated based on the gas species concentrations. The concentration of hydrogen (which is oxidized to produce current) is higher in those regions. The current density does not only depend on the Nernst voltage and the fuel cell resistance. These two parameters are affected by temperature, which is gradually increasing, and this partially explains why the current density reaches a region of high values at channel length ranging between 0.05 m and 0.08 m. A closer look to the graph shows that the current density is decreasing as long as the decreasing rate of Nernst voltage is higher and the decreasing rate of the resistance is lower. When the decreasing rate of Nernst voltage becomes lower and the rate of resistance decrease becomes higher, then the current density will increase.
5.1.4 Effect of reforming kinetics

The following section is an investigation on the effect that the activation energy of the methane steam reforming reaction has on the temperature profile, current density and gas species concentration. Though the concentration of CH$_4$ is low (2%), according to the steam reforming reaction of methane, one mole of CH$_4$ will produce 4 moles of H$_2$ (3 moles straight from the MSR and 1 mole from the produced CO reacting in the WGS reaction) so it is important to study its effect. There are four cases investigated for the activation energy for the methane steam reforming: case A (the one presented in the previous sections) where the activation energy is 82 kJ/kg, and cases B, C and D with activation energies 95, 118, 228 kJ/kg respectively. A detailed description for the kinetics of methane steam reforming and the values of activation energy chosen can be found in Chapter 3.

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<tr>
<td>C</td>
<td>$E_a=118$ kJ/kg</td>
</tr>
<tr>
<td>D</td>
<td>$E_a=228$ kJ/kg</td>
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</table>

Table 5.2: Cases investigated for the CH$_4$ steam reforming effect, in the SOFC channel.

5.1.4.1 Gas species concentrations comparison

The gas species concentrations for the SOFC channel components for each case (A, B, C, D), are presented in Figures 5.16-5.18. For higher activation energies the methane is consumed at a slower rate. In fact, for case B ($E_a=95$ kJ/mol) all the methane is consumed but unlike case A, it is totally consumed in the channel outlet. For case C ($E_a=118$ kJ/mol), 65% of the methane is reformed, while for case D ($E_a=228$ kJ/mol) almost no CH$_4$ is reformed (less than 0.1% of the inlet flow). This behaviour for the CH$_4$ concentration was expected, since the activation energy is the threshold for methane to start being reformed by steam.
Analysis and Simulation of an Anode Supported SOFC Single Channel for Operation with Biosyngas and Methane

Figure 5.16: Comparison for a) CH₄ and b) CO concentration in the SOFC channel for all 4 cases.

The above statement, explains the fact that the concentration of carbon monoxide, which is a steam reforming reaction by-product, is increasing for all cases near the inlet where most part of CH₄ is reformed. When the rate of steam reforming is higher, the rate of carbon monoxide produced by the MSR reaction is higher and this explains why CO concentration is higher for case A compared to cases B, C, D. The carbon monoxide concentration increases within 0.01 m from the inlet and then it decreases. This means that from this point and on, the rate of CO consumption in the water gas shift (WGS) reaction is higher than the rate of CO produced in the MSR reaction. The rate of CO production is bigger for case A compared to B, and smaller for cases C and D compared to B. Cases C and D have the same rate of CO concentration till 0.01 m and from that point and on the slope for case D becomes slightly steeper This happens because for case D, there is almost no MSR activity that would produce CO. The CO concentration at the outlet is 4.2%, 4.1%, 3.3%, 1.8% for cases A, B, C, D.

Figure 5.17: Comparison for a) CO₂ and b) H₂O concentrations in the SOFC channel for all 4 cases.

In a SOFC, hydrogen and carbon monoxide are electrochemically oxidized to produce steam and carbon dioxide. However in this study CO is not considered directly as fuel, but indirectly it acts as a fuel, since hydrogen is produced when CO reacts with steam in the WGS reaction. Apart from hydrogen, CO₂ is a product of the WGS reaction as well. Thus, CO₂ is a measure for the rate of WGS reaction. The decrease in the CO₂ concentration for the initial 0.01 m from the inlet (though it is not consumed in any of the reactions accounted for in the model), is explained by the fact that the MSR reaction is a mole increasing reaction. After 0.01 m, which is the point where the rate of CO consumption in the WGS is bigger than the rate at which CO is produced in MSR, the CO₂ concentration is gradually increasing for all cases.
The concentration of steam at the channel outlet is almost equal for all 4 cases. For cases A, B, C and D the steam concentration is 27.4%, 27.5%, 27.7% and 27.2% respectively. In the initial part of the channel (0.02 m from the inlet) the rate of increase for the steam concentration is lower compared to rate of increase for the rest part of the channel. Steam is a reactant for the reforming reactions and a product for the electrochemical oxidation of hydrogen. The steam concentration becomes higher as there is more hydrogen (as a product of MSR and WGS) available to be oxidized. From 0.02 m and until the channel outlet, there is less amount of hydrogen produced by the MSR reaction and therefore the rate at which the steam concentration increases is slightly lower.

Figure 5.18: Comparison for H₂ concentration in the SOFC channel for all 4 cases.

Hydrogen concentration is lower at the outlet of cases with higher activation energies. The graph shows that for the first 0.015 m where CH₄ is reformed by steam, the hydrogen content is higher for cases where the rate of MSR reaction is higher. After this point, the rate at which hydrogen is oxidized is almost equal for all cases. At the channel outlet, the hydrogen concentration is 3%, 3%, 2% and 0.5% for cases A, B, C and D respectively.

<table>
<thead>
<tr>
<th></th>
<th>case A</th>
<th>case B</th>
<th>case C</th>
<th>case D</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0 %</td>
<td>0 %</td>
<td>0.75 %</td>
<td>1.99 %</td>
</tr>
<tr>
<td>CO</td>
<td>4.2%</td>
<td>4.1 %</td>
<td>3.3 %</td>
<td>1.8 %</td>
</tr>
<tr>
<td>CO₂</td>
<td>27.4 %</td>
<td>27.5 %</td>
<td>28.2 %</td>
<td>29 %</td>
</tr>
<tr>
<td>H₂O</td>
<td>27.4 %</td>
<td>27.5 %</td>
<td>27.7 %</td>
<td>27.2 %</td>
</tr>
<tr>
<td>H₂</td>
<td>3 %</td>
<td>3 %</td>
<td>2 %</td>
<td>0.5 %</td>
</tr>
</tbody>
</table>

Table 5.3: Gas species concentrations at the outlet of the SOFC channel for cases A, B, C, D.

<table>
<thead>
<tr>
<th></th>
<th>case A</th>
<th>case B</th>
<th>case C</th>
<th>case D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel utilization $U_F$</td>
<td>83 %</td>
<td>83.5 %</td>
<td>81 %</td>
<td>76.5 %</td>
</tr>
</tbody>
</table>

Table 5.4: Fuel utilization for cases A, B, C, D.
Figure 5.19: Ternary diagram for operation with biosyngas, and detailed view of the ternary diagram: all 4 cases are safe. Case A: red circle, case B: green X, case C: yellow triangle, case D: blue square

It is important to predict the possibility of carbon deposition. The points in the ternary diagram in Figure 5.19 are correspondingly calculated from the point at the inlet of the fuel cell channel for each case and are situated below the carbon deposition line for the operation temperatures range. This means that the operation is safe for the fuel cell for all 4 cases.

Figure 5.20: Combined phase equilibrium diagram of Ni and NiO. The blue dot represents the highest value in the fuel gas for all cases since their values are similar.

It is also important to predict the possibility of the formation of NiO in anode materials, since it is one of the crucial signals of the degradation of fuel cell performance. Oxygen in the fuel gas channel diffuses to the Ni based porous anode, and under certain conditions NiO might be formed. The hydrogen and steam concentration at the channel outlet were used to investigate the reforming capacity of the anode materials and the degree of oxidation of Ni from existing oxygen in anode, due to the high ratio between these two elements at this location. At the channel outlet temperature, 780 °C, the thermodynamic boundary for Ni/NiO lies at $1 \cdot 10^{-14}$ for the partial pressure of $O_2$. The highest values are $1.18 \cdot 10^{-19}$, $1.38 \cdot 10^{-19}$, $2.74 \cdot 10^{-19}$, $1.62 \cdot 10^{-18}$ under the operating conditions for cases A, B, C, D respectively. These points are below the thermodynamic boundary where metal Ni reacts to metal oxide NiO. Hence, anode materials
stay in the metallic phase under the given conditions investigated here in this work.

5.1.4.2 Temperature comparison

The temperature profiles for the SOFC channel components for each case (A, B, C, D), are presented in Figures 5.21-5.22. For case B ($E_a=95 \text{ kJ/mol}$) the temperature profile for all components is slightly higher than case A ($E_a=82 \text{ kJ/mol}$). The outlet temperature for case B is 1052.31 K. The PEN temperature difference for cases A and B is ranging between 0.2 and 4.31 K. The temperature difference in the inlet is 4.11 K, it reaches its peak (4.31 K) at a distance of 0.005 m from the cell inlet and then it gradually drops to 0.2 K in the channel outlet. The PEN outlet temperature at the outlet for case C is 1053.21 K. The temperature difference for cases A and C is ranging between 0.75 and 10 K. The temperature difference in the inlet is 7 K, it gradually reaches its peak (10 K) at a distance of 0.021 m from the cell inlet and then it slightly drops to 0.75 K at the channel outlet. The PEN temperature difference for cases A and D is ranging between 0.13 K and 11.9 K in the outlet. The difference reaches its peak at 0.044 m. The outlet temperature at the outlet for case D is 1044.88 K. The reason that the temperature reaches its peak before the end of the channel can be explained by the fact that there is not any hydrogen available for electrochemical oxidation, and thus there is no heat production (Figure 5.21).

The separator plate temperature difference for cases A and B is ranging between 0.15 and 3.8 K. The temperature difference in the inlet is 2.6 K, it reaches its peak (3.8 K) at a distance 0.01 m from the cell inlet and then it gradually drops to 0.1 K in the channel outlet. The temperature difference for cases A and C is ranging between 1.05 and 9.9 K. The temperature difference in the inlet is 4.8 K, it gradually reaches its peak (9.9 K) at a distance of 0.024 m from the cell inlet and then it drops to 1.05 K in the channel outlet. The temperature difference for cases A and D is ranging between 0.47 and 11.9 K. The temperature difference in the inlet is 5 K, it gradually reaches its peak (11.9 K) at a distance of 0.046 m from the cell inlet and then it drops to 0.47 K near the channel outlet. At the channel outlet the temperature difference is 5.9 K. (Figure 5.22.a).
The air channel bottom temperature difference for cases A and B is ranging between 0.01 and 3.3 K. The temperature difference in the inlet is 0.01 K, it reaches its peak (3.3 K) at a distance 0.017 m from the cell inlet and then it gradually drops to 0.16 K in the channel outlet. The temperature difference for cases A and C is ranging between 0.015 and 9.8 K. The temperature difference in the inlet is 0.015 K, it gradually reaches its peak (9.8 K) at a distance 0.033 m from the cell inlet and then it drops to 2.12 K in the channel outlet. The separator plate temperature difference for cases A and D is ranging between 0.015 and 11.9 K. The temperature difference at the outlet is 0.7 K. The reason that the temperature is lower for cases where the rate of MSR is higher, is that the amount of heat absorbed is higher for case A compared to cases B, C, D (Figure 5.22.b).

### Table 5.5: Temperature at the outlet of the SOFC channel for cases A, B, C, D.

<table>
<thead>
<tr>
<th>Case</th>
<th>PEN Outlet temperature [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1052.46</td>
</tr>
<tr>
<td>B</td>
<td>1052.31</td>
</tr>
<tr>
<td>C</td>
<td>1053.21</td>
</tr>
<tr>
<td>D</td>
<td>1044.83</td>
</tr>
</tbody>
</table>

Figure 5.23: Temperature gradients for cases A, B, C, D.
The temperature gradients for all 4 cases are presented in Figure 5.23. The average temperature gradients are 0.73 K/mm, 0.69 K/mm, 0.68 K/mm and 0.6 K/mm for cases A, B, C and D respectively.

5.1.4.3 Current density comparison

![Figure 5.24](image-url): Current density distributions for cases A, B, C, D

The difference between the current density profiles along the cell length for cases A, B, C, and D is presented in Figure 5.24. The current density is a function of the gas species concentrations, temperature and operating voltage of the cell. For case B, the current density value is in the range between 985 and 4551 A/m$^2$. The initial current density in the cell inlet is 2030 A/m$^2$ and rapidly increases within a small distance (0.001 m) from the inlet to 3860 A/m$^2$. The current density follows an increasing profile reaching a peak at 4551 A/m$^2$ at 0.074 m and then it reduces to 2236 A/m$^2$ near the channel outlet. At the outlet, the current density will rapidly drop to 985 A/m$^2$. The average current density for case B is 4081 A/m$^2$.

For case C, the initial current density in the cell inlet is 2054 A/m$^2$ and rapidly increases within a small distance (0.001 m) from the inlet to 3966 A/m$^2$. The current density follows an increasing profile reaching a peak at 4475 A/m$^2$ at 0.064 m and then it reduces to 1165 A/m$^2$ near the channel outlet. At the outlet, the current density will rapidly drop to 435 A/m$^2$. The average current density for case C is 3950 A/m$^2$.

For case D, the initial current density in the cell inlet is 2057 A/m$^2$ and rapidly increases within a small distance (0.001 m) from the inlet to 3978 A/m$^2$. The current density follows an increasing profile reaching a peak at 4453 A/m$^2$ at 0.055 m and then it reduces to 1054 A/m$^2$ near the channel outlet. At the channel outlet the current density is too low, because there is not enough fuel left. The lack of fuel also explains the corresponding temperature drop, noticed in Figure 5.21. The average current density for case D is 3597 A/m$^2$.

<table>
<thead>
<tr>
<th>Case</th>
<th>Average current density [A/m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4061</td>
</tr>
<tr>
<td>B</td>
<td>4081</td>
</tr>
<tr>
<td>C</td>
<td>3950</td>
</tr>
<tr>
<td>D</td>
<td>3597</td>
</tr>
</tbody>
</table>

**Table 5.6**: Average current density values for cases A, B, C, D
The current density profile is lower for cases with lower activation energies for the initial 0.056 m. For cases A and B the peak value is reached at 0.074 m from the inlet. On the other hand, for cases C and D the peak is reached at 0.064 and 0.055 m respectively. After the point at which A and B reach their local peak value the current density profile for both cases is almost the same. There is a point at 0.56 m where the current density is equal for all 4 cases. From that point on, case C will have a higher current density compared to D. Apart from this, the current density for cases A and B will become larger, since the current density for cases C and D quickly decreases. This is attributed to the fact there is not significant amount of additional hydrogen produced by the MSR reaction for cases C and D.

![Figure 5.25](image)

**Figure 5.25:** a) Nernst voltage and b) cell resistance for cases A, B, C, D

The reasons leading to the differences for cases A, B, C and D are: a) methane steam reforming kinetics leading to different amounts of additional hydrogen available for oxidation for each case, b) different temperatures which will affect the electrochemical oxidation of hydrogen, c) variations of the fuel stream composition in the channel, d) effect of temperature on the cell resistance.
5.2. Results and discussion for operation with methane

In this section the modeling results for operation with methane are presented. The model employed, is the same with the one used for the simulation of operation with biosyngas. The results presented are for the gas species concentrations, temperature and current density along the channel. The effect of steam reforming kinetics on the performance is examined. There are also comparisons for operation with co- and counter-flow (presented in Appendix B) configurations and different fuel compositions. The results shown are for five representative points of the channel, as shown in Figure 5.1. These representative points are on the upper parts of the anode, electrolyte and cathode, on the separator, and the air channel side edge bottom. All the locations apart from the air channel bottom are situated on the symmetry axis of the SOFC channel. These 5 locations are used to obtain results for the temperature, the point representing the electrolyte is used for the current density calculations, and the upper part of the anode at the interface with the anode gas channel is used to calculate the gas species concentration. The activation energy used for the MSR reaction is $E_a=82\text{kJ/mol}$, similar to the simulations with biosyngas. The fuel composition is:

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>33%</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>66%</td>
</tr>
<tr>
<td>H$_2$</td>
<td>1%</td>
</tr>
</tbody>
</table>

Table 5.7: Fuel composition for simulations with methane [4]

5.2.1 Gas species concentrations

Figure 5.26 shows the mole fraction profiles of H$_2$, H$_2$O, CH$_4$, CO, CO$_2$ along the fuel channel stream. The gas concentrations illustrate the impact of the steam reforming of CH$_4$ and the water gas shift reaction at the anode, and the electrochemical oxidation of H$_2$ at the interface between the anode and the electrolyte. The methane steam reforming reaction is too fast due to the high initial concentration of CH$_4$. This can be seen by the fact that although the initial input data for the concentration is 33% in the software used (FLUENT), in the corresponding graph, the concentration has already dropped to 23%. In the initial 20 mm of the channel the methane...
concentration will rapidly drop to 2.5% (92% decrease). The same applies for steam that reacts in the MSR reaction. For the same distance from the inlet, the steam concentration will rapidly drop to 27.2% (59% decrease). Due to the fast reaction rate, the steam concentration at the cell inlet has already dropped to 51%. The CH$_4$ in the fuel has been almost completely consumed at distance 0.04 m from the inlet. During the MSR reaction, 4 moles of hydrogen per mole methane are produced (3 moles by MSR and 1 mole by WGS). Combining this with the fact that MSR reaction is happening too fast, explains why the mole fraction of hydrogen at the inlet for the anode is 19% although the initial input data for the simulations is 1%.

When H$_2$ enters the gas channel it is oxidized, producing steam, heat and electricity. Hydrogen concentration shows an increasing trend for the first 0.024 m of the channel where it reaches a peak value of 51.6%. This means that for the initial 0.024 m of the channel, the rate of hydrogen produced by the MSR and WGS reactions is higher than the rate at which hydrogen is electrochemically oxidized. From this point and on, the CH$_4$ concentration has significantly dropped and it is the WGS reaction that produces most of the additional hydrogen in the fuel cell. After the initial 0.024 m the rate at which H$_2$ reacts is higher than the rate at which hydrogen is produced by the reforming reactions, and this explains why there is a decreasing trend until the channel outlet, where H$_2$ concentration becomes 18.8%.

Concerning the steam concentration it is rapidly dropping because it is consumed in the reforming reactions (mainly in MSR). When the CH$_4$ concentration drops significantly, steam will continue to be consumed in the WGS reaction but its concentration will start to increase because of the electrochemical oxidation of hydrogen. Though CO is not present in the initial fuel composition it is produced via the MSR reaction. The amount of CO produced, reacts with steam in the WGS reaction to produce CO$_2$ and H$_2$. The fact that the concentration of CO reaches a peak at 30 mm (where the CH$_4$ concentration is too low to provide considerable amounts of hydrogen) and afterwards it decreases while consumed in the WGS reaction, leads to the conclusion that the MSR reaction dominates over the WGS reaction. Apart from CO, CO$_2$ is also present in the channel, though it was not present in the initial fuel composition. CO$_2$ is a product of the WGS, and does not take part as a reactant or as a product in any other of the reactions considered (the electrochemical oxidation of CO that produces CO$_2$ is not considered in the model). Thus, the CO$_2$ production is a measure of the amount of hydrogen produced via the WGS reaction. The concentrations of the gas species at the SOFC channel outlet are summarized in Table 5.8:

<table>
<thead>
<tr>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>CO$_2$</td>
</tr>
<tr>
<td>H$_2$O</td>
</tr>
<tr>
<td>H$_2$</td>
</tr>
</tbody>
</table>

Table 5.8: Fuel composition at the outlet.
Figure 5.27: Steam to carbon ratio along the fuel channel

Figure 5.27 presents the steam-to-carbon ratio (S/C) along the SOFC channel. The S/C ratio varies along the channel because of the MSR and WGS reactions that consume steam, and the electrochemical oxidation of hydrogen that produces steam. The initial S/C value in the graph is 1.7 and gradually decreases to 1.28 at 0.017 m. According to literature (explained in chapter 3) the S/C should be over 1.4 to avoid carbon deposition. However, the S/C ratio only gives an indication of which area is the most likely for carbon deposition. In order to determine whether carbon will be deposited, a ternary C-H-O diagram is needed. The point (blue dot) in the ternary diagram in Figure 5.28 is calculated at 0.017 m from the inlet of the fuel cell channel and it is situated below the carbon deposition line in the range of the operation temperatures. This means that methane-fed SOFCs are safe under these working conditions.

Figure 5.28: Ternary diagram for operation with methane.

It is also important to predict the possibility of the formation of NiO in anode materials, since it is one of the crucial signals of the degradation of fuel cell performance. Oxygen in the fuel gas channel diffuses to the Ni based porous anode, and under certain conditions NiO might be formed. The hydrogen and steam concentration at the channel outlet were used to investigate the reforming capacity of the anode materials and the degree of oxidation of Ni from existing oxygen in anode, due to the high ratio between these two elements at this location. The corresponding concentrations are 3.6% and 19% respectively. At the channel outlet temperature, 730 °C, the thermodynamic boundary for Ni/NiO lies at $1 \cdot 10^{-16}$ for the partial pressure of O$_2$. The highest value is $1.43 \cdot 10^{-20}$ under the operating conditions. This point is below the thermodynamic boundary where metal Ni reacts to metal oxide NiO. Hence, anode materials
stays in the metallic phase under the given conditions investigated here in this work.

**Figure 5.29:** Combined phase equilibrium diagram of Ni and NiO system. The blue dot represents the highest in the fuel gas, under the given working condition.

### 5.2.2 Temperature distribution

In this section the temperature profiles for the 5 representative locations are presented. Before the presentation of the results, it has to be specified that the single SOFC channel considered, is assumed to be thermally isolated from its surroundings.

**Figure 5.30:** Temperature profiles for the components a) along the fuel cell channel, and b) for the initial part of the channel
Figure 5.30 is an illustration for the temperature distribution in specific points in the cell components. There is also a detailed graph for temperature change at the channel inlet region where the steam reforming of methane takes place. There is a rapid temperature decrease within a short distance from the inlet. This is attributed to the fact that the endothermic steam reforming reaction starts to take place as soon as the fuel enters the channel. The MSR is too fast and this can be seen by the fact that the components of the PEN structure (anode, cathode, electrolyte) at the inlet are at a temperature much lower than the input data (973 K). The CH₄ concentration at the inlet is high and this is why the MSR reaction dominates over the exothermic WGS and electrochemical oxidation reactions.

As can be seen from Figure 5.30 the temperature differences for the five components are more significant within a small distance from the cell inlet compared to other positions along the cell. In this model a thin reaction zone has been created in the anode/electrolyte interface. The heat from exothermic reactions in the porous anode is transferred to the fuel gas flow and from there to the upper separator plate. On the other hand, the heat required for the endothermic MSR reaction is absorbed by the enthalpy carried in the gas flows, and by the heat produced during the exothermic reactions. This explains why within a small distance from the inlet, the temperature of the anode rapidly decreases to 862 K. After the anode reaches its lowest temperature value at 862 K it starts to slightly increase due to the fact that CO and H₂ become available for the exothermic WGS and electrochemical oxidation reactions. After the initial 0.02 m, the rate at which the anode temperature rises will increase (since the MSR reaction is not the dominant reaction anymore), reaching the outlet value of 1014.7 K. The rate at which the separator temperature decreases near the inlet is slower compared to the anode. Once the lowest temperature value is reached, then the separator follows the same temperature profile with the anode.

The cathode temperature profile is not distinguished in the graph. This is explained by the fact that the cathode is too thin, it is in direct contact with the electrolyte, and is situated close to the reaction zone where the exothermic and endothermic reactions take place. The heat is absorbed/conducted rapidly and thus the cathode temperature profile is the same as the electrolyte temperature profile. The reason that the PEN structure (anode, cathode, electrolyte) shows a uniform heat distribution is its high thermal conductivity. After the initial 0.02 m all three components have the same temperature. The outlet temperature of the electrolyte is 1015 K.

The cathode gas channel bottom shows the lowest temperature decrease among the rest of the channel components. This happens because this specific location is not close to the reaction zone where heat is absorbed/produced. This is the reason that the initial temperature in the graph has the same value with the provided input data (973 K). The enthalpy carried by the air stream flow is absorbed in the cell and the temperature will drop to 864 K at 0.024 m. After this point, the temperature is increasing and reaches the outlet at 1009 K.

The average temperature gradient for the fuel cell electrolyte is 1.2 K/mm. The temperature gradient along the channel can be seen in Figure 5.31. The reason that the temperature gradient is negative near the inlet resulted from the endothermic steam reforming reaction. From that point on, there are hydrogen and carbon monoxide produced, which are available for the exothermic reactions (electrochemical oxidation and WGS). It is clearly shown that attention should be paid to the area near the inlet.
5.2.3 Current density distribution

The current density profile along the cell length is presented in Figure 5.32. The current density as can be seen in the electrochemical model described earlier, is a function of the gas species concentrations, temperature and operating voltage of the cell. The current density value is in the range from 731 to 3613 A/m². The initial current density in the cell inlet is 731 A/m² and rapidly increases within a small distance (0.001 m) from the inlet to 1341 A/m². The current profile density shows a decreasing profile till 910 A/m² at 0.019 m and then follows an increasing profile reaching 3613 A/m² close to the outlet (0.108 m). The average current density is 1900 A/m². The fluctuation in the current density profile is attributed to fuel consumption along the channel, effect of temperature, gas composition and cell voltage thus making the rate of electrochemical oxidation to vary. Apart from the graph, the schematic shows that the current density is higher in the regions close to the symmetry axis. This is attributed to the fact that the current is calculated based on the gas species concentrations. The concentration of hydrogen (which is oxidized to produce current) is higher in those regions.

The current density depends on the Nernst voltage and the fuel cell resistance. The Nernst voltage is affected by species concentrations while the resistance is a function of temperature.
The graph clearly shows the effect of temperature. The current density is decreasing close to the inlet, but as the temperature rises the current density is increasing.

Figure 5.33: Current density, resistance and Nernst voltage along the length of the channel

5.2.4 Comparisons for operation with different activation energies

The following section is an investigation on the effect that the activation energy of the methane steam reforming reaction has on the temperature profile, current density and gas species concentration. According to the steam reforming reaction of methane, one mole of CH$_4$ will produce 4 moles of H$_2$ (including the WGS reaction) so it is important to study its effect, because the molar concentration of CH$_4$ is high (33%). There are four cases investigated for the activation energy for the methane steam reforming: case A (the one presented in the previous sections) where the activation energy is 82 kJ/kg, and cases B, C and D with activation energies 95, 118, 228 kJ/kg respectively. A detailed description for the kinetics of methane steam reforming and the values of activation energy chosen can be found in Chapter 3. The fuel composition used is CH$_4$: 33%, H$_2$O: 66%, H$_2$: 1%.

<table>
<thead>
<tr>
<th>Case</th>
<th>CH$_4$ Reforming Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$E_a=82$ kJ/kg</td>
</tr>
<tr>
<td>B</td>
<td>$E_a=95$ kJ/kg</td>
</tr>
<tr>
<td>C</td>
<td>$E_a=118$ kJ/kg</td>
</tr>
<tr>
<td>D</td>
<td>$E_a=228$ kJ/kg</td>
</tr>
</tbody>
</table>

Table 5.9: MSR reaction activation energies for each case investigated.

The results from FLUENT for case D were rather disappointing concerning the fuel cell performance and will not be examined in detail in this section. The cell temperature for this case dropped below 700 K and only a small amount of CH$_4$ was consumed. As a result, minimal amounts of H$_2$ and CO (for the WGS) are produced and thus there is minimal electrochemical oxidation activity.
5.2.4.2 Gas species concentrations comparison

The species concentrations of CH₄ and H₂ for the SOFC channel for each case (A, B, C, D), are presented in Figures 5.34-5.35. As already shown with biosyngas fueling, methane is consumed at a slower rate with higher activation energies. In fact, for case B (Ea=95 kJ/mol) all CH₄ available is reformed but at a slower rate compared to case A. The methane concentration becomes zero at 0.09 m, while for case A the methane has been fully consumed at 0.055 m from the inlet. For case C (Ea=118 kJ/mol) where the activation energy is higher, the reaction rate is lower and around 93% of CH₄ is reformed. For case D (228 kJ/mol) there is small amount of CH₄ reformed which leads to minimal hydrogen production and thus poor fuel cell performance. Case D will not be further investigated.

The reason that the concentration at the inlet is different for each case is explained by their activation energy values. For cases C, D where the high activation energy limits the reforming reaction, CH₄ is consumed at a slower rate and thus the initial values at the graph are almost the same as the initial input data. On the other hand, for lower activation energies the reforming reaction is so fast that the initial methane concentration is lower than the simulation input value. For cases A and B the CH₄ concentration has already dropped to 22% and 27% respectively at the channel inlet.

For cases with lower activation energy the amount of hydrogen produced by the reforming reactions is higher. At the outlet of the channel for cases A and B the hydrogen concentration is 19% and 20% respectively. For A and B, most of the hydrogen is produced close to the inlet. However, for case C, H₂ concentration is more evenly distributed and the outlet concentration is less than 10%.

When the rate of steam reforming is higher, the rate of carbon monoxide (MSR by-product) produced is higher and this explains why CO concentration is higher for cases A and B. The concentration of CO is varying in a way similar to that of H₂.

Since the electrochemical oxidation of CO is not considered in the model, the amount of CO₂ produced is entirely from the WGS reactions. Thus, the CO₂ concentration is a measure for the amount of hydrogen produced by the WGS reaction and for the amount of steam consumed in the WGS. The graph clearly shows that the amount of CO₂ produced is the same for all 3 cases. There is only a slight difference in the region 0.03-0.08 m due to the different steam concentrations. Concerning steam concentration, it is consumed at a faster rate in the areas where the rate of steam reforming is higher. The concentrations of gas species are the same at the channel outlet for cases A and B, while for case C the steam concentration is almost 70%.
As can be seen in Figures 5.34 and 5.35, the values for the gas species concentration at the inlet are different than the simulations input data. This is explained by the fact that the MSR reaction is too fast. The composition of the fuel stream at the outlet is summarized in Table 5.10.

![Graph a) showing CO2 concentration, b) CO concentration, and c) H2O concentration](image)

**Figure 5.35**: Comparison for: a) CO\textsubscript{2}, b) CO and c) H\textsubscript{2}O concentration in the SOFC channel.

<table>
<thead>
<tr>
<th></th>
<th>Ea = 82 kJ/mol</th>
<th>Ea = 95 kJ/mol</th>
<th>Ea = 118 kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{4}</td>
<td>0 %</td>
<td>0 %</td>
<td>2.5 %</td>
</tr>
<tr>
<td>CO</td>
<td>8.4 %</td>
<td>8.2 %</td>
<td>6.7 %</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>11.6 %</td>
<td>11.7 %</td>
<td>12.3 %</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>60.5 %</td>
<td>60 %</td>
<td>68.5 %</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>18.8 %</td>
<td>19.7 %</td>
<td>9.3 %</td>
</tr>
</tbody>
</table>

**Table 5.10**: Gas species concentration at the outlet for case A, B and C.

<table>
<thead>
<tr>
<th>Fuel utilization (U_F)</th>
<th>Ea = 82 kJ/mol</th>
<th>Ea = 95 kJ/mol</th>
<th>Ea = 118 kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>79.7 %</td>
<td>72 %</td>
<td>79.9 %</td>
</tr>
</tbody>
</table>

**Table 5.11**: Fuel utilization for cases A, B, C, D.

In order to determine whether carbon will be deposited, a ternary C-H-O diagram is needed. It is important to predict the possibility of carbon deposition. The points in the ternary diagram in Figure 5.36 are correspondingly calculated from the point at the inlet of the fuel cell channel for each case and are situated below the carbon deposition line for the operation temperatures range. This means that the operation is safe for the fuel cell for all 4 cases.
The hydrogen and steam concentration at the channel outlet were used to investigate the reforming capacity of the anode materials and the degree of oxidation of Ni from existing oxygen in anode, due to the high ratio between these two elements at this location. At the channel outlet temperature, 730 °C, the thermodynamic boundary for Ni/NiO lies at $1 \cdot 10^{-16}$ for the partial pressure of O$_2$. The highest values are $1.43 \cdot 10^{-20}$, $1.44 \cdot 10^{-20}$, $7.65 \cdot 10^{-20}$ under the operating conditions for cases A, B, C respectively. These points are all below the thermodynamic boundary where metal Ni reacts to metal oxide NiO. Hence, anode materials stays in the metallic phase under the given conditions investigated here in this work.

The above description for the species concentration applies for the schematics in Figures 5.38 to 5.40. The hydrogen concentration distributions in the middle vertical cross section of the anode gas channel are presented in Figure 5.38. The cross section is outlined by red colour. The enlarged part of the fuel cell channel shows the hydrogen distribution in the area close to the channel inlet (0-20 mm). There is a clear difference in the hydrogen distribution in the fuel channel and in the anode. The electrochemical oxidation of hydrogen and the reforming reactions (MSR and WGS), take place in the reaction zone situated in the interface between the
anode and the electrolyte. Thus, hydrogen is produced and this is the reason that its concentration is higher in the anode compared to the fuel channel. On the other hand, the fact that the anode has a higher hydrogen concentration will lead to hydrogen diffusion from the porous anode cermet to the fuel channel. The outline of hydrogen concentration clearly shows that for this part of the channel the MSR reaction dominates over electrochemical oxidation of hydrogen.

![Figure 5.38: Hydrogen concentration in the middle cross section of the anode gas channel at small distance (0.02 m) from the fuel inlet for cases A, B, C.](image)

Concerning the methane concentration, it is higher in the fuel channel and diffuses through the porous anode cermet, towards the reaction zone where methane is consumed. The comparison between the outlines for each case shows how the MSR reaction rate is affected by the activation energy.

![Figure 5.39: Methane concentration in the middle cross section of the anode gas channel at small distance (0.02 m) from the fuel inlet for cases A, B, C.](image)

The following figure (Figure 5.40) shows the contours of the gas species in the anode, in the area close to the inlet of the channel (0.02 m from the inlet). The schematics are top and
front views of the anode. It is clearly shown that in the area underneath the inter-connector rib, the gaseous species are transported only by diffusion in the porous electrodes. This leads to a lower CH\textsubscript{4} concentration and a higher H\textsubscript{2} concentration in the area underneath the inter-connector rib compared to the channel.

**Figure 5.40:** Gas species concentration in the anode at 0.02 m from the fuel inlet (A: anode top view, B: front view) for a) hydrogen and b) methane

**5.2.4.3 Temperature profiles comparison**

**Figure 5.41:** Comparison for the anode temperature distribution for cases A, B, C, D.
The temperature profiles for the anode for each case (A, B, C, D), are presented in Figure 5.41-5.42. For case B ($E_a=95$ kJ/mol) the temperature is higher close to the inlet than case A ($E_a=82$ kJ/mol). This is happening because the MSR reaction activity is more intense when the activation energy is low. This explains why for case C the temperature at the inlet is 963 K, while for A and B the temperature is 925 K and 940 K respectively. Apart from this, for cases A and B the temperature will rapidly drop to temperature values lower than 880K, thus introducing large temperature gradients in the SOFC channel. For case C the temperature distribution is evenly distributed compared to the other two cases investigated and this is indeed an attractive characteristic, since large temperature gradients could cause mechanical failure of the SOFC materials.

![Figure 5.42: Comparison for the a) cathode, b) electrolyte, c) separator plate and d) air channel bottom temperature distribution for cases A, B, C.](image)

The electrolyte and the separator plate follow a similar temperature profile with the anode, apart from the initial 0.015 m, for all 3 cases. The cathode has the same temperature profile with the electrolyte. Concerning the air channel bottom it follows a similar profile with the anode for all 3 cases, however its temperature is higher for the initial 0.024 m (for A, B) and 0.035 m (for C). After this point the air channel bottom has a lower temperature than the anode. This happens because this specific location is not close to the reaction zone where heat is absorbed/produced. This is the reason that the initial temperature in the graph has the same value with the provided input data (973 K). The enthalpy carried by the air stream flow is absorbed by the reforming reaction and the temperature for the air channel bottom will drop. After this, the temperature is increasing till the outlet. The difference in the temperature profiles for all 3 cases can be better depicted in the following graph showing the PEN temperature gradients for each case.

Temperature is more evenly distributed for case C. The fact that for case C the MSR reaction is taking place at a slower rate leads to a lower temperature gradient. This is an interesting fact taking into account the results already obtained for the species concentrations. However, further investigation concerning the power output is required in order to decide which case is the preferred one.
5.2.4.4 Current density comparison

The difference in the current density profiles along the cell length for cases A, B and C is shown in Figure 5.44. The current density profile has already been shown in previous section of this chapter. For case B, the current density follows a profile similar to that of case A. The initial current density in the cell inlet is 839 A/m² and rapidly increases within a small distance (0.001 m) from the inlet to 1553 A/m². The current density follows a decreasing profile reaching 1023 A/m² at 0.024 m and then it gradually increases to 4093 A/m² close to the outlet. At the outlet, the current density will rapidly drop to 2030 A/m². The average current density is 2094 A/m².

For case C the current density profile is different (almost linear throughout the channel). The initial current density in the cell inlet is 797 A/m² and rapidly increases within a small distance (0.001 m) from the inlet to 1555 A/m². The current density follows a linearly increasing profile reaching 3085 A/m² at 0.108 m. At the outlet, the current density rapidly drops to 1012 A/m². The average current density is 2260 A/m². The current density depends on the resistance and the Nernst voltage, which are affected by the temperature and species concentration. The resistance and Nernst voltage profiles are shown in Figure 5.45.

Figure 5.43: Temperature gradients for cases A, B, C.

Figure 5.44: Current density distribution for cases A (Ea = 82 kJ/mol), B (Ea = 95 kJ/mol), C (Ea = 118 kJ/mol)
## 5.2.5 Operation with pre-reformed methane

The following section is the presentation of the simulation results for operation with a mixture containing 80% methane and 20% pre-reformed methane (case E) and comparison with case C (Ea = 118 kJ/mol, CH₄: 33%, H₂O: 66%, H₂: 1%). Typical composition of pre-reformed methane mixture was found in literature [5]. Finally, the fuel composition used in the simulations for case E is presented in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Case C</th>
<th>Case E</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>33%</td>
<td>27.95%</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>0.59%</td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>0.80%</td>
</tr>
<tr>
<td>H₂O</td>
<td>66%</td>
<td>58.66%</td>
</tr>
<tr>
<td>H₂</td>
<td>1%</td>
<td>12%</td>
</tr>
</tbody>
</table>

Table 5.13: Fuel composition for cases C and E

Figure 5.46 shows the mole fraction profiles of H₂, H₂O, CH₄, CO, CO₂ along the fuel channel stream. The gas concentrations illustrate the impact of the steam reforming of CH₄ and the water gas shift reaction at the anode, and the electrochemical oxidation of H₂ at the interface between the anode and the electrolyte. The gas species concentrations for case E follow a similar profile as case C and details can be found in the previous sections. The difference between these two cases is presented in Figure 5.46.
In order to determine whether carbon will be deposited, a ternary C-H-O diagram is needed. The position (blue dot) for the ternary diagram in Figure 5.47 is calculated from the point at the inlet of the fuel cell channel. It is situated below the carbon deposition line in range of the operation temperatures, which means that the operation is safe for the fuel cell.

The hydrogen and steam concentration at the channel outlet were used to investigate the reforming capacity of the anode materials and the degree of oxidation of Ni from existing oxygen in anode, due to the high ratio between these two elements at this location. The corresponding concentrations are 19% and 58% respectively. At the channel outlet temperature, 740 ºC, the thermodynamic boundary for Ni/NiO lies at $1 \cdot 10^{-16}$ for the partial pressure of O$_2$. The highest value is $1.41 \cdot 10^{-20}$ under the operating conditions. This point is below the thermodynamic

**Figure 5.46:** Gas species concentration in the anode at 0.02 m from the fuel inlet (A: anode top view, B: front view) for a) hydrogen, b) steam, c) carbon dioxide, d) methane, e) carbon monoxide

**Figure 5.47:** Ternary C-H-O diagram for operation with a mixture containing pre-reformed methane.
boundary where metal Ni reacts to metal oxide NiO. Hence, anode materials stays in the metallic phase under the given conditions investigated here in this work.

Figure 5.48: Combined phase equilibrium diagram of Ni and NiO system from 200 °C to 1000 °C across a range from $10^{-40}$ to $10^{-10}$ bar. The blue dot represents the highest in the fuel gas, under the given working condition.

Concerning the temperature distribution for case E, it follows a similar profile as case C with temperature differences varying between 0 and 8 K. For this reason, details (effect of MSR reaction, electrochemical oxidation of hydrogen etc) concerning the temperature distribution can be found in previous sections. The temperature profile for case E, as well as the differences with case C are presented in Figure 5.49. From the following graphs it is clear that the temperature gradients are smaller for case E, and thus the chance of thermally induced stress is lower.

Figure 5.49: Temperature profiles for the components a) along the fuel cell channel for case E, b) PEN temperature comparison for cases C, E and c) air channel bottom temperature comparison for cases C, E.
Concerning the Nernst voltage, it is higher for case E while the resistance is lower. This leads to a higher current density as shown in Figure 5.50. For case E, the current density value is in the range from 1125 to 3847 A/m². The current density increases to 3847 A/m² at 0.105 m and then gradually reduces to 3703 A/m² close to the channel outlet. At the outlet, the current density rapidly drops to 1880 A/m². The average current density is 2759 A/m².

![Figure 5.50: Current density profiles for case C and E](image)

Figure 5.51: a) Nernst voltage and b) cell resistance for cases C, E.

5.3 Conclusions

5.3.1 Conclusions for operation with biosyngas

This section involves the presentation of the results obtained from the 3D SOFC single channel model for operation with biosyngas. The SOFC operation was investigated for co-flow pattern using biosyngas as fuel and air as cathode gas with inlet temperature 973 K. The main goal of this section was to investigate the effect of the MSR reaction kinetics. Though the concentration of CH₄ is low (2%), according to the steam reforming reaction of methane, one mole of CH₄ will produce 4 moles of H₂ (3 moles straight from the MSR and 1 mole from the produced CO reacting in the WGS reaction). The 4 cases investigated were: A (Ea = 82 kJ/kg), B (Ea = 95 kJ/kg), C (Ea = 118 kJ/kg) and D (Ea = 228 kJ/kg).

For case A the temperature increases to 1052.41 K at the channel outlet and the mean current density achieved is 4061 A/m². For case B the outlet temperature is 1052.31 K, but the mean current density is higher. This can be explained by the fact that for case B, methane is totally consumed (as in A) but at a slower rate, which leads to a higher temperature close to the...
inlet, decreasing the cell resistance at that location. For cases C the temperature is higher (1053.21 K) and for case D, though initially higher, due to lack of sufficient fuel at the outlet, the temperature drops to 1044.88 K. This higher temperature values are due to the fact that methane is not fully reformed and thus less amount of heat is absorbed in the endothermic MSR reaction. For case D, though the higher temperature decreases the cell resistance, no methane is reformed to provide the fuel stream with additional amounts of hydrogen and thus the current density is the lowest among all cases. On the other hand, for case C, though the initial amount of methane in the fuel is not fully reformed, the higher cell temperature will decrease the cell resistance and this is enough to generate current density slightly lower than cases A and.

In order to indicate whether the operation is safe for the fuel cell, ternary diagrams were used to predict whether carbon deposition that degrades the performance is likely to happen. According to the ternary diagrams there is no danger of carbon being deposited on the anode surface for none of the cases. Operation was found safe concerning the risk of Ni oxidation as well. The fuel utilization for all cases A, B, C, D was 83%, 83.5%, 81% and 76.5% respectively.

Simulations have shown that higher activation energies of the MSR reaction lead to higher temperature profiles, which could lead to higher temperature gradients. However, the current density gain for case B was only 20 A/m². On the other hand, for cases C and D the performance was rather degraded. This leads to the conclusion that there is no need to manipulate the MSR reaction kinetics for biosyngas with such a low CH₄ composition (2%). However it would be interesting to investigate the effect of MSR reaction kinetics on biosyngas fuel with higher CH₄ composition.

5.3.2 Conclusions for operation with methane

This section is a presentation for the simulation with methane. The goal of this section was to investigate the effect of the MSR reaction on the cell performance. The cases investigated are summarized in the following table:

<table>
<thead>
<tr>
<th>Case</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ea [kJ/mol]</td>
<td>82</td>
<td>95</td>
<td>118</td>
<td>228</td>
<td>118</td>
</tr>
<tr>
<td>CH₄</td>
<td>33%</td>
<td>33%</td>
<td>33%</td>
<td>33%</td>
<td>27.95%</td>
</tr>
<tr>
<td>H₂O</td>
<td>66%</td>
<td>66%</td>
<td>66%</td>
<td>66%</td>
<td>58.66%</td>
</tr>
<tr>
<td>H₂</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>12%</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.59%</td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.81%</td>
</tr>
</tbody>
</table>

Table 5.14: Cases investigated for operation with methane.

Concerning operation with co-flow configuration, it has been shown that for higher values of activation energy the rate of methane steam reforming is lower. Though it seems that the desired goal would be to make the MSR reaction faster in order to maximize hydrogen production, the simulation results have shown that if the reaction rate is too fast, the SOFC channel temperature drops. Low temperatures not only lead to lower current generation, but also introduce steep temperature gradients into the SOFC channel, which could cause mechanical failure of the PEN structure materials. The simulation results have shown that for case A and B there is a rapid drop around 100 K in the channel inlet area. On the other hand for case C the temperature drop due to the endothermic MSR reaction is smaller and the temperature is evenly distributed along the channel length. Higher temperature will lead to lower cell resistance and thus higher current density (average current density 2260 A/m²) compared to cases A and B.
(average current density 1900 and 2094 A/m² respectively). Apart from this, though the amount of hydrogen produced by the MSR reaction for case A and B is higher, it is not completely consumed. Case D was not further investigated, since the high MSR reaction activation energy causes minimal hydrogen production, which can’t sustain a sufficient supply to electrochemical oxidation reaction and thus the cell temperature drops. Apart from operation with methane, there were also simulations with a mixture containing 20% pre-reformed methane (case E). This mixture has a lower mole fraction of methane and a higher mole fraction of hydrogen, which leads to a lower temperature decrease near the inlet, i.e. more evenly distributed temperature, but also higher current density.

To summarize, the effect of the rate of reforming reaction rate is significant on the SOFC operation and it is desired to slow down the MSR reaction activity to a certain extent. However, this is not the only solution to improve the SOFC performance. Operation with a mixture containing 20% externally pre-reformed methane not only smooths the temperature distributions but also generates higher current (average current density 2759 A/m² for case E, 2260 A/m² for case C).
References

Chapter 6: Conclusions and Recommendations

6.1 Conclusions

Mathematical modeling is a useful tool that can help avoid problems related to the development of a SOFC stack. The main part of this MSc Thesis was to investigate the three-dimensional CFD model of a single SOFC channel. The fuel fed into the anode gas channel is biosyngas consisting of hydrogen, water vapor, methane, carbon monoxide and carbon dioxide. The only electrochemical reaction considered in the anode side of the fuel cell is the one between hydrogen and the oxidant ion generated in the cathode side of the cell. Electrochemical oxidation of CO is neglected. Steam reforming reaction of CH$_4$ (MSR) and water gas shift (WGS) reaction are considered as well in the model.

This chapter includes a summary of the results obtained from the simulations as well as conclusions drawn and recommendations for further work. The quantitative conclusions have already been presented in the corresponding sections of previous chapters. This chapter contains the qualitative conclusions drawn from this work, i.e. the answers to the questions set in the introductory chapter of this assignment:

- **Is operation with biosyngas from air gasification of biomass safe for the SOFC design considered in this study (Ni oxidation, carbon deposition)?**

  Simulations have shown that operation with the specific biosyngas is safe for the operation of the SOFC concerning the risk of carbon deposition as well as the oxidation of nickel contained in the anode. The hydrogen and steam concentrations at the channel outlet are used to investigate the reforming capacity of the anode materials and the degree of oxidation of Ni from existing trace oxygen in anode. The rationale for using the concentrations of these two species at the channel outlet to calculate the possibility of Ni oxidation is that the ratio between these two gases is high at this location, and thus is the most probable area for NiO formation to take place. Indeed, the phase equilibrium diagram drawn clearly shows that there is no trend of Ni oxidation under given working condition.

  For the carbon deposition, the most probable region for solid carbon to be formed is at the channel inlet. The C-H-O ternary diagram shows that the fuel composition is out of the carbon deposition region under this working condition and thus the operation is safe. Even when simulations with different activation energies for the MSR reaction were performed, operation was still safe.

- **Is operation with methane safe for the SOFC (Ni oxidation, carbon deposition)?**

  The same applies to operation with methane for both compositions used (methane and methane with 20% pre-reformed methane). There is no danger of NiO formation, and the composition is far below the carbon deposition equilibrium line. This is explained by the fact that there is high concentration of steam in both fuel compositions, while the methane molecule itself contains 4 hydrogen atoms. When simulations with different activation energies for the MSR reaction were performed, operation was still safe.
• What is the impact of different fuel compositions on SOFC performance?

Three different fuels were used in the simulations: Biosyngas (2% CH₄, 10% H₂O, 18% H₂, 18% CO, 13% CO₂, 39% N₂), methane (33% CH₄, 66% H₂O, 1% H₂) and a mixture of methane with addition of pre-reformed methane (27.95% CH₄, 58.66% H₂O, 12% H₂, 0.59% CO, 0.8% CO₂). The results have shown that operations with biosyngas produces 208% and 170% higher current density on average, compared to operation with methane and the mixture containing pre-reformed methane. Apart from this, operation with biosyngas shows smooth temperature gradient, while fueling with methane introduces steeper temperature gradient in the channel inlet region. Such a big difference in the generated current density between biosyngas and methane is attributed to the high amount of steam in the latter case, while the endothermic MSR reaction decreases the channel temperature, thus leads to higher resistance values.

It is important to point out, that the fuel input was 1.8 times higher for operation with biosyngas than operation with methane, and this has played a major role in this difference in the current density output. Unfortunately it was not possible to increase the methane inflow (or decrease the biosyngas inflow) in the CFD simulations, in order to make comparisons with similar values for the fuel input. The reason was that if either of these would happen: a) the results returned by the simulation would be rather disappointing (too low temperature, too low current output), b) the simulations would return no results at all c) the fuel utilization would significantly drop. For this reason the software Cycle-Tempo (see Appendix D) was used. The results in Cycle-Tempo have shown that this difference in the current density is mostly attributed to the different rate of fuel inflow and the temperature distribution.

• What is the impact of the steam reforming reaction kinetics of methane on the SOFC performance for operations with biosyngas and methane?

The goal of investigating internal steam reforming kinetics is to find out a more appropriate reaction rate for steam reforming and hence a suitable anode catalyst for steam reforming which can maintain high electric conductivity and keep the high reactivity of the electrochemical reactions, while providing a better temperature distribution simultaneously. The reaction rate of the MSR reaction can be slowed down with the methods suggested in chapter 3 of this thesis.

Simulations for operation with biosyngas have shown that slowing down the MSR reaction will increase the current density output only by 0.5-1%. This is explained by the low methane concentration in the fuel stream. For operation with methane, slowing down the MSR reaction rate is indeed beneficial for the performance. Not only is the current density output higher, but also the temperature is evenly distributed making the fuel cell safer concerning thermally induced stress. Operations are safe concerning the risk of both carbon deposition and Ni oxidation for all investigated cases.

• What constructive suggestions can be made for further development of SOFCs?

Simulations with biosyngas fuel have shown that the effect of the MSR kinetics is not significant on the SOFC performance. This is explained by the low methane concentration in the fuel stream. However it would be interesting to investigate this effect for biosyngas compositions containing higher amount of CH₄. The reason that makes this suggestion interesting is that one mole of CH₄ will produce 4 moles of H₂ (including the MSR and the associated WGS reactions). Concerning the risk of carbon deposition, since the operating point examined is below the
carbon deposition equilibrium line, but not far below from it, further investigation is required. So that operations with different biosyngas compositions should also be investigated to guarantee the safety.

Concerning operation with methane, simulations have shown that operation is safe and the operating points examined are located far below the carbon deposition equilibrium line. This means that operation would still be safe with different methane compositions. Simulations have shown that different MSR reaction kinetics lead to different cell performances, we can get desired cell performance by choosing appropriate anode materials. Although the methane is not fully reacted, the fact that the lower temperature decrease at the inlet will lead not only to higher current density, but also to more even temperature distribution.

### 6.2 Recommendations

The simulations performed have helped to obtain useful results concerning the operation of a SOFC. Of course this model includes only the simulation of a single SOFC channel and before moving to cell and stack level modeling there should be some improvements in the present channel model.

1. The effect of radiative heat transfer should be included in further development of the present model. There is a simple simulation of radiation in Appendix A, which indeed indicates that the temperature distribution is affected. However, radiative heat transfer is a complex phenomenon and for this reason, it was not further studied. Another reason is that the model is a single SOFC channel. Radiation would be more effective and thus more interesting to be investigated in case that a whole cell was modeled.

2. Changing the MSR reaction kinetics can also lead to smoother temperature distribution apart from achieving higher current density. Especially for operation with methane, the temperature gradients, which are indications to thermal stresses are steeper close to the inlet. In order to determine whether the operation is safe, a stress analysis should be made for operation with biosyngas and methane as well.

3. Apart from the co-flow pattern, the counter-flow pattern should be further investigated. Appendix B is the presentation of the simulations with methane as the fuel gas and air as the oxidant under counter flow. The current density output is higher, but accompanied by large temperature gradients that could harm the cell. It would be really interesting to extent investigation on counter-flow configuration fueling biosyngas as well.

4. The only electrochemical reaction considered in the anode side of the fuel cell is the one between hydrogen and the oxidant ion generated in the cathode side of the cell. Electrochemical oxidation of CO is neglected because the other electrochemical reactions will dominate over it. Including the electrochemical oxidation of CO in the simulations would make the model more complete and realistic on one hand, but it would also bring more complexity into the model on the other hand.
5. It is recommended that more simulations need to be performed with different biosyngas compositions so as to determine whether the operation will still be safe (concerning the risk of Ni oxidation and carbon deposition).

6. It is recommended that more simulations should be performed with different biosyngas compositions containing higher amounts of CH₄, so as to determine whether the MSR reaction kinetics can affect the performance.
Appendix A

Effect of radiation for operation with biosyngas

In this section the temperature profiles for the 5 representative locations are presented. There are two cases investigated: case I, in which the effect of radiative heat transfer is neglected, and case II in which the radiative heat transfer is considered in the model. Before the presentation of the results, it has to be specified that the single SOFC channel considered, is assumed to be thermally isolated from its surroundings.

<table>
<thead>
<tr>
<th>Case</th>
<th>Radiative heat transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>No</td>
</tr>
<tr>
<td>II</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table A.1: Cases investigated for temperature distribution in the SOFC channel.

The SOFC is operating at high temperatures, thus the radiative heat transfer is also considered in the model. The radiative heat transfer equation is solved with the discrete ordinates (DO) radiation model. The equation is solved for a finite number of discrete solid angles, each associated with a vector direction $\hat{\Omega}$ fixed in the Cartesian system $(x,y,z)$. The DO model considers the radiative transfer equation (RTE) in the direction $\hat{\Omega}$ as a field equation. The radiative transfer equation (RTE) for an absorbing, emitting, and scattering medium at position $\vec{r}$ in the direction $\hat{\Omega}$ is:

$$\frac{dI(\vec{r},\hat{\Omega})}{ds} + (\hat{\Omega} + \sigma_s) \cdot I(\vec{r},\hat{\Omega}) = a_r \frac{\sigma T^4}{\pi} + \frac{\sigma_s}{4\pi} \int_0^{4\pi} I(\vec{r},\hat{\Omega}') \cdot \Phi(\hat{\Omega} \cdot \hat{\Omega}') d\Omega' \quad (A.1)$$

The above equation is simplified by considering the gases as transparent media. This means that the absorption coefficient $a_r$ is zero. Only the radiative heat transfer between interconnects, electrodes and electrolyte are considered, with an emissivity value 0.9.
A.1 Temperature distribution for case I

![Temperature distribution graph]

Figure A.1: Temperature profiles for the components along the fuel cell channel (case I - no radiative heat transfer)

![Initial temperature profile graph]

Figure A.2: Temperature profiles for the fuel cell channel components for the initial part of the channel (case I - no radiative heat transfer)

Figures A.1 is an illustration for the temperature distribution in specific points in the cell components for case I. The temperature profiles are almost the same for all points examined apart from those close to the cell inlet. For this reason there is a second graph showing the initial part of the channel in Figure A.2.

There is a slight temperature drop within a short distance (0.005 m) from the cell inlet. This drop is attributed to the fact that the endothermic MSR reaction starts to take place as soon as the fuel enters the channel. However due to the small amount of methane (2%) in the fuel stream, the exothermic WGS reaction and exothermic electrochemical oxidation of H₂ will dominate over reforming and thus the temperature starts to increase.

Temperature differences for the five components are more significant within a small distance from the cell inlet compared to the other positions along the cell. In this model a thin reaction zone has been created in the anode/electrolyte interface. The heat from exothermic reactions in anode/electrolyte interface is transferred to the porous anode, afterwards to the fuel.
gas flow, and from there to the upper separator plate. On the other hand, heat is absorbed in the reaction zone during the endothermic MSR reaction. This explains why within a small distance from the inlet, the temperature of the anode slightly drops to 970.5 K within 0.001 m from the channel inlet. After that, the temperature gradually increases till it reaches the value of 1051.80 K in the outlet.

The cathode temperature profile is not distinguished in the graph. This is explained by the fact that the cathode is too thin, it is in direct contact with the electrolyte, and is situated close to the reaction zone. The heat is conducted rapidly and thus the cathode temperature profile is the same as the electrolyte temperature profile. The reason that the PEN structure (anode, cathode, electrolyte) shows a uniform heat distribution is its high thermal conductivity. Concerning the separator due to heat transfer it follows a similar (almost the same) temperature profile with the PEN structure. However, close to the outlet where there is lower electrochemical reaction activity there is not enough heat transferred to the separator plate and thus its temperature is 1.2 K lower.

Close to the inlet, the cathode gas channel has a slightly higher temperature due to the fact the PEN temperature drops during the MSR reaction. At the same time the air channel shows a decreasing temperature profile due to the fact that enthalpy carried in the air stream is absorbed for the MSR reaction. As soon as MSR stops being the dominant reaction, the air channel will have lower temperature compared to the PEN structure, following an increasing profile. This is because the air apart from oxidizing the fuel, serves as a coolant in the cell. The outlet temperature of the air channel is 1045.9 K.

The average temperature gradient for the fuel cell electrolyte is 0.72 K/mm. The temperature gradient is shown in Figure A.3. The reason that the temperature gradient shows a decreasing trend near the inlet is due to the steam reforming reaction. However, the temperature gradient quickly shows an increasing trend, since the CH$_4$ concentration is low (2%) and thus the effect on the temperature is not significant. The temperature gradient increases until 0.093 m, where it reaches a peak value of 1.13 K/mm. After this the temperature gradient will gradually decrease. Figure A.3 clearly shows that attention should be paid to the area near the inlet. It is the only area of the temperature gradient curve where a fluctuation (non-linear behaviour) is met, and thus it is the area that thermal stresses are more likely to appear.

![Figure A.3: Temperature gradient profile along the fuel cell channel (case I - no radiative heat transfer)](image)

The temperature of the cell components in the outlet is almost the same due to conductivity of the materials. The difference between the minimum and the maximum temperature values in the PEN structure is 81.5 K. The minimum temperature is close to the cell inlet (970.5 K), and the maximum is at the cell outlet (1052 K). The temperature difference...
between inlet and outlet for the PEN and separator plate is 80.5 K and 79.24 K respectively. The temperature difference between inlet and outlet for the air channel bottom is 72.9 K.

A.2 Comparison between case I and II

The difference in the temperature profiles for both cases I and II, is shown in Figure A.4. For the PEN structure, the temperature for case I is lower in the initial part of the channel. However this temperature difference shows a decreasing trend until 0.07 m, where the two cases have the same temperature. From this point on, the temperature profile for case II is lower. For the separator, the temperature for cases I and II is the same close to the inlet, and from 0.02 m and after the temperature difference is increasing, with case II following a lower temperature profile. For the air channel bottom the temperature profile is the same for both cases for the initial 0.01 m and after this point the temperature profile for case II is higher than case I.

![Figure A.4: Temperature profiles for the PEN structure, separator and air channel bottom of the fuel cell channel along its length for cases I and II (without and with radiative heat transfer).](image)

In order to obtain a complete overview of the temperature distribution and the effect of radiative heat transfer in the fuel cell channel, Figure A.5 is presented. Figure A.5 shows a detailed schematic of the temperature distribution in the middle cross section of the channel for both cases I and II. For case I, the temperature varies between 996 and 1002 K. In the region of the separator plate, PEN (anode, cathode, electrolyte) and fuel channel, the temperature is higher and evenly distributed. In the area close to the channel symmetry axis, the temperature is higher (1002 K) compared to the other channel components. The rest area of the PEN structure (approaching to the interconnector ribs) has a slightly lower temperature (1001 K). The upper region of the air channel has the same temperature with the PEN structure (1002 K), but is decreasing from top to bottom and from the symmetry axis to the edge of the channel. The minimum temperature is observed in the air channel bottom. The reasons for the existence of
regions with higher or lower temperature distribution (exothermic reactions, air serving as coolant etc.) have been explained earlier in this section of the chapter.

For case II, the heat is transferred from/to the fuel cell channel components either when produced by the exothermic reactions or when absorbed by the steam reforming reaction, and apart from conduction and convection, it is as well affected by thermal radiation. When the effect of radiative heat transfer is considered (case II), the temperature will vary between 993 and 1002 K, i.e. the temperature difference observed between the highest and the lowest temperature value in this section of the channel is 9 K, on contrary to 6 K for case I. When comparing schematics for both cases, there are differences for all channel components, but the main difference in the temperature distribution is observed for the air channel. Contrary to case I, for case II the region with the lowest temperature is located in the centre of the air channel and towards the symmetry axis. The highest temperature is observed for the PEN structure (1002 K). The temperature is slightly decreasing in the areas away from the reaction zone and the symmetry axis. In this case, the part of the separator plate that is not in direct contact with the PEN structure has a lower temperature (1000 K). Though the temperature gradients for the fuel cell channel for case I seem to be smaller, it should be noted that case II which takes into account radiative heat transfer, is a more realistic approach.

![Cross section on the middle of the cell](image)

Figure A.5: Temperature distribution on middle cross section of the fuel cell channel for cases I and II.

Apart from the middle cross section, the temperature distribution was investigated in the cross sections of the fuel channel (A-A) and the air channel (B-B) of the fuel cell for both cases. Figures A.6 and A.7 actually confirm the conclusions drawn from the previous figures, that the radiation affects the temperature distribution. It can be seen that for the fuel channel the distribution is changing however the temperature profile have a similar form for both cases. For the air channel the changes in the temperature distribution are more significant. The lowest
temperature is found in the middle of the air channel for case II. The single SOFC channel considered, is assumed to be thermally isolated from its surroundings and thus if there was another cell adjacent to the investigated channel, the temperature distribution would have been different.

**Figure A.6:** Temperature distribution on cross section of the fuel channel and the air channel in the fuel cell channel for case I (without radiation).

**Figure A.7:** Temperature distribution on cross section of the fuel channel and the air channel in the fuel cell channel for case II (with radiation).
Appendix B

Counter-flow configuration for operation with methane

The effect of counter-flow configuration (case F, $E_a = 118$ kJ/mol, $\text{CH}_4$: 33%, $\text{H}_2\text{O}$: 66%, $\text{H}_2$: 1%) is investigated in this section. Figure B.1 shows the co-flow and counter-flow configurations for operation with methane. The two cases compared in this section are summarized in the following table:

<table>
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<th>Case</th>
<th>Details</th>
</tr>
</thead>
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<td>C</td>
<td>Co-flow: $E_a = 118$ kJ/mol, $\text{CH}_4$: 33%, $\text{H}_2\text{O}$: 66%, $\text{H}_2$: 1%</td>
</tr>
<tr>
<td>F</td>
<td>Counter-flow: $E_a = 118$ kJ/mol, $\text{CH}_4$: 33%, $\text{H}_2\text{O}$: 66%, $\text{H}_2$: 1%</td>
</tr>
</tbody>
</table>

Table B.1: Cases investigated for comparison between co-flow and counter-flow.

![Figure B.1: Co-flow and counter-flow configurations for the SOFC channel (side view)](image)

B.1 Gas species concentration

Figure B.2 shows the mole fractions of $\text{H}_2$, $\text{H}_2\text{O}$, $\text{CH}_4$, CO, CO$_2$ along the fuel channel stream for the counter-flow configuration. The gas concentrations illustrate the impact of the steam reforming of $\text{CH}_4$ and the water gas shift reaction at the anode, and the electrochemical oxidation of $\text{H}_2$ at the interface between the anode and the electrolyte. The gas species concentrations follow a similar profile with differences compared to the co-flow configuration. The MSR reaction is too fast due to the high initial concentration of $\text{CH}_4$. The comparisons for the gas species concentrations between both configurations are shown in Figure B.3. For the counter-flow pattern methane is consumed faster. The same applies to steam that reacts in the MSR reaction. The fact that the MSR is faster for the counter-flow configuration explains the higher $\text{H}_2$ concentration near the inlet. CO is not present in the initial fuel composition but it is produced via the MSR reaction, which is faster, and thus the CO concentration will be higher for the counter flow pattern as long as the MSR is the reaction dominating in the channel region.
Apart from the difference in the concentration of CH₄, H₂O, H₂, CO, which are attributed to the faster MSR reaction rate in the counter-flow pattern, there is also the CO₂ concentration, which is an indicator for the WGS reaction. CO₂ production is a measure of the amount of hydrogen produced via the WGS reaction and thus it is concluded that the amount of H₂ produced via the WGS reaction is higher with counter-flow compared to the co-flow configuration.

Figure B.2: Concentration of gas species for the anode (counter-flow)

Figure B.3: Comparison between concentrations of gas species for the anode for co-flow (blue line) and counter-flow (red dashed line)
Figure B.4: Comparison between co-flow (blue line) and counter-flow (red dashed line) S/C ratios for the anode

The S/C ratio varies along the channel because of the MSR and WGS reactions that consume steam, and the electrochemical oxidation of hydrogen that produces steam. For co-flow, the S/C ratio will rapidly drop to 0.99 and then begins to rise until the value 2.25 is reached at the channel outlet. For the counter flow, the lowest S/C value is 0.91. The point chosen (blue dot) in the ternary diagram in Figure B.5 is the point at 0.022 m from the inlet of the fuel cell channel and it is situated below the carbon deposition line for the operation temperatures range. This means that the operation is safe for the fuel cell.

Figure B.5: Ternary diagram for operation with methane (counter-flow)

B.2 Temperature distribution

Figure B.6 is an illustration for the temperature distributions in specific points in the cell components for counter flow. Contrary to what happens for the co-flow configuration, there is no temperature decrease in the inlet, though the rate at which methane is consumed is higher. This can be explained by the fact that the amount of hydrogen produced by the WGS reaction (see CO and CO₂ concentration) is higher and this will lead to an additional amount of heat produced by the electrochemical oxidation of hydrogen. One other possible reason could be the fact that the cathode air has higher temperature and thus does not absorb any heat at this area of the channel.

The anode temperature at the inlet is 978 K and gradually increases to 1045 K at 0.04 m. After 0.04 m, the temperature starts to decrease, due to the fact that the rate at which hydrogen is produced by the MSR and WGS reactions is reduced. In other words, the available fuel has
reached a peak and therefore the rate of the exothermic reactions becomes smaller and leads to a temperature drop. The anode temperature at the outlet is 983 K. Similar temperature changes apply to the separator plate, which follows the same temperature change with the anode after 0.01 m.

Figure B.6: Temperature profiles for the components along the fuel cell channel, and for the initial part of the channel (counter-flow)

The cathode temperature profile is not distinguished in the graph. This is explained by the fact that the cathode is too thin, it is in direct contact with the electrolyte, and is situated close to the reaction zone where the exothermic and endothermic reactions take place. The heat is absorbed/conducted rapidly and thus the cathode temperature is the same as the electrolyte temperature. The reason that the PEN structure (anode, cathode, electrolyte) shows a uniform heat distribution is its high thermal conductivity. After the initial 0.002 m all three PEN components have the same temperature.

The cathode gas channel bottom shows the highest temperature among the other channel components close to the fuel inlet. The air provided in the SOFC channel apart from an oxidant is a coolant as well, and this explains why the air channel bottom shows a higher temperature profile compared to the other channel components. After 0.038 m where the air channel bottom reaches the same temperature with the PEN structure, its temperature starts to decrease. The rate of exothermic reactions is decreasing and thus the amount of heat produced in the channel is less, leading to lower temperatures. The rate of temperature decrease for the air channel is larger than the corresponding rate of temperature decrease of the PEN. This is because air serves as a coolant, and there is less amount of heat to be absorbed. The outlet temperature for the air channel bottom is 998 K.

Figure B.7 shows the difference between the temperature changes for the co- and counter-flow patterns. While in a co-flow SOFC the temperature increases along the air and fuel flow direction by heat accumulation, with the maximum temperature at the exit, in a counter-flow cell the temperature has a peak after a short distance from the channel middle (0.04 m) and the operation is characterised by higher average cell temperatures and steeper local temperature gradients. Though the rate at which CH₄ is reformed is faster for counter-flow, there is no temperature drop at the inlet.

This can be explained by the fact that more H₂ has been produced by WGS and MSR (see H₂ concentration curves), and thus the exothermic WGS and electrochemical oxidation reactions dominate over MSR and compensate for the heat absorbed. One main issue with counter-flow is
that although the high temperature can lead to a higher current density (Figure B.3), the local temperature gradient are steeper (Figure B.8) and could induce thermal stresses, and cause mechanical failure of the PEN material.

**Figure B.7:** Temperature profiles for a) PEN structure b) air channel bottom of the fuel cell channel along its length for co-flow and counter-flow

**Figure B.8:** Temperature gradients in the fuel cell channel along its length for co-flow and counter-flow

**B.3 Current density distribution**

Figure B.9 shows the difference between the current density distribution for co- and counter-flow operation. For counter-flow operation the current density value is in the range from 1097 to 5765 A/m². The current density follows an increasing profile reaching 5765 A/m² at 0.039 m and then reduces to 2515 A/m² near the channel outlet. At the outlet, the current density rapidly drops to 1286 A/m². The average current density is 4282 A/m². The fluctuation in the current density profile is attributed to the fuel composition and the effect of temperature along the channel, thus making the rate of electrochemical oxidation and cell resistance to vary. At 0.04 m from the inlet, the increasing temperature reaches a peak, which leads to a resistance decrease, and thus the current density rises. Although the Nernst voltage is lower for the counter-flow configuration, the resistance is affected by temperature and this is why the current density is much higher for the counter-flow pattern. Apart from the graph, the schematic shows that the current density is higher in the regions close to the symmetry axis. This is attributed to the fact that the current density is calculated based on the gas species concentrations.
The differences in the current density distribution between these two cases are attributed to the differences in both the resistance and Nernst voltage, which are affected by the temperature distribution as well as gas species concentration. The resistance and Nernst voltage are shown in Figure B.10.

**Figure B.10:** a) Nernst voltage and b) resistance in the fuel cell channel along its length for co-flow and counter-flow
Appendix C

Properties of gases in SOFCs

C.1 Density

The gas species’ density depends on the temperature. In order to obtain a more accurate model this effect has to be taken into account. The modeled SOFC operates at low pressure and high temperature and thus the gas species can be assumed as ideal gases. The density of an ideal gas is:

\[
\rho = \frac{P}{(R/M_w) \cdot T} \quad \text{(C.1)}
\]

\( \rho \) = density of gas [g/m³]
\( P \) = pressure [Pa]
\( R \) = universal gas constant [8.314 J/mol·K]
\( M_w \) = molecular weight [g/mol]
\( T \) = temperature [K]

Because the fuel used for the simulations is a mixture then equation (C.1) becomes:

\[
\rho = \frac{P}{RT \cdot \sum_i \frac{Y_i}{M_{w,i}}} \quad \text{(C.2)}
\]

\( Y_i \) = mass fraction of species
\( M_{w,i} \) = molecular weight of species \( i \) [g/mol]

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Molecular weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
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<tr>
<td>O₂</td>
<td>31.999</td>
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<td>H₂O</td>
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<td>CO</td>
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<tr>
<td>N₂</td>
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</tbody>
</table>

Table C.1: Molecular weight of the gas mixture species

C.2 Heat capacity of gases

Because of the fact that the pressure is low and the gas species are assumed to be ideal gases, the molar heat capacity is calculated by the following equation, proposed by Todd and Young [1]

\[
C_p = \sum_{i=a}^6 a_i \cdot \tau^i \quad \text{(C.3)}
\]

\( C_p \) = molar heat capacity [J/mol·K]
\( a_i \) = coefficients of molar heat capacity [-]
\( \tau = T/(\text{K})/1000 \)
Analysis and Simulation of an Anode Supported SOFC Single Channel for Operation with Biosyngas and Methane

\[ \alpha_0 \alpha_1 \alpha_2 \alpha_3 \alpha_4 \alpha_5 \alpha_6 \]

\[ \begin{align*}
\text{CH}_4 & \quad 47.964 & -178.59 & 712.55 & -1068.7 & 856.93 & -358.75 & 61.321 \\
\text{H}_2\text{O} & \quad 37.373 & -41.205 & 146.01 & -217.08 & 181.54 & -79.409 & 14.015 \\
\text{CO}_2 & \quad 4.3669 & 204.60 & -471.33 & 657.88 & -519.9 & 214.58 & -35.992 \\
\text{CO} & \quad 30.429 & -8.1781 & 5.2062 & 41.974 & -66.346 & 37.756 & -7.6538 \\
\text{H}_2 & \quad 21.157 & 36.036 & -150.55 & 199.29 & -136.15 & 46.903 & -6.4725 \\
\text{N}_2 & \quad 29.027 & 4.8987 & -38.040 & 105.17 & -55.554 & 214.58 & -10.350 \\
\text{O}_2 & \quad 34.850 & -37.975 & 203.68 & -300.37 & 231.72 & -91.821 & 14.776 \\
\end{align*} \]

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<td>231.72</td>
<td>-91.821</td>
<td>14.776</td>
</tr>
</tbody>
</table>

Table C.2: Molar heat capacity coefficients (273-1473 K) \[1\]

Equation C.3 will eventually become:

\[
C_p = \sum_{i=1}^{n} X_i \cdot C_{p,i} 
\]

\[\text{(C.4)}\]

\[X_i = \text{mass fraction of species} \]

\[M_w = \text{molecular weight of species } i \ [\text{g/mol}] \]

C.3 Dynamic viscosity

The dynamic viscosity of species is obtained by the following equation:

\[
\mu_i = \sum_{k=0}^{b} b_k \cdot \tau^k 
\]

\[\text{(C.5)}\]

\[\mu = \text{dynamic viscosity } [\text{j/mol} \cdot \text{K}] \]

\[b_k = \text{coefficients of dynamic viscosity} \ [-] \]

\[\tau = \frac{T}{1000} \text{(K)} \]

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</table>

Table C.3: Dynamic viscosity coefficients (273-1473 K) \[1\]

Because the gas species are assumed to be ideal gases the mixture dynamic viscosity is calculated by Fluent as:

\[
\mu = \sum \left( \sum_{j=1}^{n} \phi_{ij} \cdot X_j \cdot \mu_j \right) 
\]

\[\text{(C.6)}\]

\[
\phi_{ij} = \begin{align*}
\left[ 1 + \left( \frac{\mu_j}{\mu_i} \right)^{0.5} \cdot \left( \frac{M_{w,j}}{M_{w,i}} \right)^{0.28} \right]^{-2} & \\
\left[ 8 \cdot \left( 1 + \frac{M_{w,j}}{M_{w,i}} \right)^{0.5} \right]^{-2} &
\end{align*}
\]

\[\text{(C.7)}\]

where,

\[X_i = \text{mole fraction of species} \]

\[M_w = \text{molecular weight of species } [\text{g/mol}] \]

C.4 Thermal conductivity

The thermal conductivity is obtained by equation C.8
\[ \lambda = 0.01 \sum_{k=0}^{6} c_k \cdot \tau^k \]  
(C.8)

\[ \lambda = \text{thermal conductivity [W/m·K]} \]
\[ c_k = \text{coefficients of molar heat capacity [-]} \]
\[ \tau = \frac{T(K)}{1000} \]

Table C.4: Thermal conductivity coefficients (273-1473 K) [1]

<table>
<thead>
<tr>
<th>species</th>
<th>( c_0 )</th>
<th>( c_1 )</th>
<th>( c_2 )</th>
<th>( c_3 )</th>
<th>( c_4 )</th>
<th>( c_5 )</th>
<th>( c_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>0.4796</td>
<td>1.8732</td>
<td>37.413</td>
<td>-47.440</td>
<td>38.251</td>
<td>-17.283</td>
<td>3.2774</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>2.0103</td>
<td>-7.9139</td>
<td>35.922</td>
<td>-41.390</td>
<td>35.993</td>
<td>-18.974</td>
<td>4.1531</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>2.8888</td>
<td>-27.018</td>
<td>129.65</td>
<td>-101.12</td>
<td>38.251</td>
<td>-17.283</td>
<td>18.698</td>
</tr>
<tr>
<td>CO</td>
<td>-0.2815</td>
<td>13.999</td>
<td>-23.186</td>
<td>36.018</td>
<td>13.379</td>
<td>-2.3224</td>
<td>-2.2741</td>
</tr>
<tr>
<td>H(_2)</td>
<td>1.5040</td>
<td>62.892</td>
<td>-47.190</td>
<td>47.763</td>
<td>11.972</td>
<td>-1.8954</td>
<td>-1.8954</td>
</tr>
<tr>
<td>O(_2)</td>
<td>-0.1857</td>
<td>11.118</td>
<td>-7.3734</td>
<td>6.7130</td>
<td>1.4910</td>
<td>0.2278</td>
<td>-0.2278</td>
</tr>
</tbody>
</table>

The gas species are assumed to be ideal gases the mixture dynamic viscosity is calculated as:

\[ \lambda = \sum \sum X_i \cdot \lambda_i \cdot \sum X_j \cdot \phi_{ij} \]  
(C.9)

\[ \phi_{ij} = \frac{1}{\left( 1 + \left( \frac{\lambda_i}{\lambda_j} \right)^{0.5} \left( \frac{M_{w,i}}{M_{w,j}} \right)^{0.5} \right)^2} \]
\[ \left[ 8 \left( 1 + \frac{M_{w,i}}{M_{w,j}} \right)^{0.8} \right] \]  
(C.10)

C.5 Binary diffusion coefficient

The reaction zone created in the model is situated in the interface between the anode and the electrolyte. The gas species have to diffuse through the porous electrodes to reach the reaction site. The Fuller expression [1] is used to calculate the binary coefficient \( D_{ij} \). The Fuller method is based on the kinetic theory diffusion coefficient. There are five gases (H\(_2\), H\(_2\)O, CH\(_4\), CO\(_2\), CO) in the anode and two gases in the cathode (O\(_2\), N\(_2\)). This means that there are 21 possible binary diffusion coefficients. The following expression is obtained for the binary diffusion coefficient of a two-gas mixture comprising species i and j:

\[ D_{ij} = \frac{0.00143 \cdot T^{1.75} \left( \frac{1}{M_{w,i}} + \frac{1}{M_{w,j}} \right)^{1/2}}{\sqrt{2} \cdot P \cdot \left( V_{i}^{1/3} + V_{j}^{1/3} \right)} \]  
(C.11)

where \( P \) is the pressure, \( V \) is the diffusion volume, and \( M_{w} \) is the molar weight.

Table C.5: Gas species diffusion volumes (273-1473 K) [1]

<table>
<thead>
<tr>
<th>Gas species</th>
<th>( V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>6.12</td>
</tr>
<tr>
<td>O(_2)</td>
<td>16.3</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>13.1</td>
</tr>
<tr>
<td>CO</td>
<td>18</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>26.9</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>25.14</td>
</tr>
<tr>
<td>N(_2)</td>
<td>18.5</td>
</tr>
</tbody>
</table>
Analysis and Simulation of an Anode Supported SOFC Single Channel for Operation with Biosyngas and Methane

However, the data from this table can't be introduced into Fluent for the simulations. In order to transform the term $D_{ij}/T^{1.75}$ into a polynomial equation the term $T^{1.75}$ is expanded by using Taylor series: $1.69556571810^8 + 304.9108571 \cdot (T-973.15) + 0.1174963483 \cdot (T-973.15)^2 - 0.0001006151400 \cdot (T-973.15)^3 + O((T-973.15)^4)$. Thus, the input data are shown in Table C.6.

### Table C.5: Binary diffusion coefficient

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>$D_{ij}/T^{1.75}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>$O_2$</td>
<td>3.792924 + 1.3921E-05</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>CO</td>
<td>3.761185 + 1.0292E-05</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>$CH_4$</td>
<td>3.855283 + 6.2488E-06</td>
</tr>
<tr>
<td>$N_2$</td>
<td></td>
<td>3.581797 + 2.5683E-06</td>
</tr>
<tr>
<td>$O_2$</td>
<td>$H_2O$</td>
<td>23.05225 + 6.2519E-06</td>
</tr>
<tr>
<td>CO</td>
<td>29.87214 + 3.5912E-06</td>
<td></td>
</tr>
<tr>
<td>$CO_2$</td>
<td>37.05535 + 1.7756E-06</td>
<td></td>
</tr>
<tr>
<td>$CH_4$</td>
<td>21.37128 + 9.6991E-07</td>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
<td>29.87377 + 3.4549E-06</td>
<td></td>
</tr>
<tr>
<td>$H_2O$</td>
<td>CO</td>
<td>21.92764 + 4.3722E-06</td>
</tr>
<tr>
<td>CO</td>
<td>25.56551 + 2.205E-06</td>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
<td>16.97208 + 1.1104E-06</td>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
<td>21.92851 + 4.2028E-06</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>$CO_2$</td>
<td>34.23311 + 1.82O3E-06</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>20.40125 + 9.8329E-07</td>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
<td>28.01197 + 3.449E-06</td>
<td></td>
</tr>
<tr>
<td>$CH_4$</td>
<td>$CO_2$</td>
<td>23.51434 + 8.7872E-07</td>
</tr>
<tr>
<td>$N_2$</td>
<td>34.23524 + 2.9109E-06</td>
<td></td>
</tr>
<tr>
<td>$CH_4$</td>
<td>$N_2$</td>
<td>20.40201 + 3.3311E-06</td>
</tr>
</tbody>
</table>

### Table C.5: Polynomial function of binary diffusion coefficient

### References

Appendix D

Analysis with Cycle-Tempo

Apart from simulations with Fluent, a macroscopic analysis of the SOFC is performed using the energy and exergy analysis tool Cycle-Tempo [www.3me.tudelft.nl]. The computer program Cycle-Tempo was developed within the Energy Technology section of TU Delft as a modern tool for the thermodynamic analysis and optimization of energy systems.

D.1 Energy balance

The energy balance of an open system is given by the following equation:

\[ \frac{dE}{dt} = Q - W_v + \dot{m}_m \left( h_v + \frac{v^2}{2} + g \cdot z_v \right) - \dot{m}_{out} \left( h_{out} + \frac{v^2}{2} + g \cdot z_{out} \right) \]  

(D.1)

Neglecting the potential energy for a steady state and adiabatic fuel cell, equation (D.1) is simplified:

\[ \frac{dE}{dt} = Q - W_v + \dot{m}_m \left( h_v \right) - \dot{m}_{out} \left( h_{out} \right) \]  

(D.2)

The work in a SOFC is performed by the transport of electrons, thus:

\[ W_v = I_{cell} \cdot V_{cell} \]  

(D.3)

Combining equations (D.2) and (D.3) for a the inlet and outlet surface, will yield:

\[ \int \int \dot{m}_{in} \left( \dot{m}_m \cdot h_v + \dot{m}_w \cdot \frac{v^2}{2} \right) dA = \int \int \dot{m}_{out} \left( \dot{m}_{out} \cdot h_{out} + \dot{m}_{out} \cdot \frac{v^2}{2} \right) dA + W_v \]  

(D.4)

D.2 Irreversibility

Exergy is defined as the availability of energy, and the exergy of a system is the maximum work obtainable from the system until it is in equilibrium with the environment. In the SOFC operation, the portion of the total available exergy of the fuel cell that is not converted into usable work is irreversible entropy production. The rate of exergy change of a system can be calculated by the following equation:

\[ \frac{dEx}{dt} = \sum_{\text{boundary,i}} \left( 1 - \frac{T_i}{T_j} \right) \dot{Q}_i - \left( \dot{W}_v - p_v \frac{dV_v}{dt} \right) + \sum_{\text{inlet}} \dot{m}_{in} \cdot ex_{\text{flow,in}} - \sum_{\text{outlet}} \dot{m}_{out} \cdot ex_{\text{flow,ou}} - T_0 \cdot \dot{\sigma}_v \]  

(D.5)

In the above equation the last term is used to express the exergy losses. Considering no control volume change, steady state operation and adiabatic fuel cell, equation (D.5) is simplified to:

\[ \sum_{\text{inlet}} \dot{m}_{in} \cdot ex_{\text{flow,in}} - \sum_{\text{outlet}} \dot{m}_{out} \cdot ex_{\text{flow,ou}} = I_{cell} \cdot V_{cell} + T_0 \cdot \dot{\sigma}_v \]  

(D.6)
D.3 SOFC system Cycle-Tempo model

The Cycle-Tempo models presented are for operation with biosyngas and methane for all cases investigated (according to MSR reaction activation energy). The inputs provided can be summarized in Table D.1. The inputs are taken from the results obtained in the CFD simulations (see Chapter 5: Results and Discussion):

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Operation with biosyngas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow configuration</td>
<td>Co-flow</td>
</tr>
<tr>
<td>Fuel composition</td>
<td>2% CH₄, 18% H₂, 18% CO, 13% CO₂, 10% H₂O, 39% N₂</td>
</tr>
<tr>
<td>Pressure drop of fuel and oxidant</td>
<td>Neglected</td>
</tr>
<tr>
<td>Active channel (cell) area</td>
<td>0.000448 m²</td>
</tr>
<tr>
<td>Cell resistance [ohm · m²]</td>
<td>Ea=82 kJ/mol: 3.6e-05, Ea=95 kJ/mol: 3.54e-05, Ea=118 kJ/mol: 3.28e-05, Ea=228 kJ/mol: 3.19e-05</td>
</tr>
<tr>
<td>Fuel inlet temperature</td>
<td>973 K</td>
</tr>
<tr>
<td>Air inlet temperature</td>
<td>973 K</td>
</tr>
<tr>
<td>Operating temperature [K]</td>
<td>Ea=82 kJ/mol: 1006, Ea=95 kJ/mol: 1010, Ea=118 kJ/mol: 1013, Ea=228 kJ/mol: 1015</td>
</tr>
<tr>
<td>Outlet temperature</td>
<td>Ea=82 kJ/mol: 1052.46, Ea=95 kJ/mol: 1052.31, Ea=118 kJ/mol: 1053.21, Ea=228 kJ/mol: 1044.83</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>1 bar</td>
</tr>
<tr>
<td>Average current density [A/m²]</td>
<td>Ea=82 kJ/mol: 4061, Ea=95 kJ/mol: 4081, Ea=118 kJ/mol: 3950, Ea=228 kJ/mol: 3597</td>
</tr>
<tr>
<td>Fuel utilization</td>
<td>Ea=82 kJ/mol: 0.83, Ea=95 kJ/mol: 0.835, Ea=118 kJ/mol: 0.81, Ea=228 kJ/mol: 0.765</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Operation with methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow configuration</td>
<td>Co-flow</td>
</tr>
<tr>
<td>Fuel composition</td>
<td>33% CH₄, 1% H₂, 66% H₂O</td>
</tr>
<tr>
<td>Pressure drop of fuel and oxidant</td>
<td>Neglected</td>
</tr>
<tr>
<td>Active channel (cell) area</td>
<td>0.000448 m²</td>
</tr>
<tr>
<td>Cell resistance [ohm · m²]</td>
<td>Ea=82 kJ/mol: 1.3e-04, Ea=95 kJ/mol: 1.21e-04, Ea=118 kJ/mol: 6.3e-05</td>
</tr>
<tr>
<td>Fuel inlet temperature</td>
<td>973 K</td>
</tr>
<tr>
<td>Air inlet temperature</td>
<td>973 K</td>
</tr>
<tr>
<td>Operating temperature [K]</td>
<td>Ea=82 kJ/mol: 919, Ea=95 kJ/mol: 928, Ea=118 kJ/mol: 961</td>
</tr>
<tr>
<td>Outlet temperature</td>
<td>Ea=82 kJ/mol: 1015, Ea=95 kJ/mol: 1027, Ea=118 kJ/mol: 1018</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>1 bar</td>
</tr>
<tr>
<td>Average current density [A/m²]</td>
<td>Ea=82 kJ/mol: 1900, Ea=95 kJ/mol: 2094, Ea=118 kJ/mol: 2260</td>
</tr>
<tr>
<td>Fuel utilization</td>
<td>Ea=82 kJ/mol: 0.797, Ea=95 kJ/mol: 0.72, Ea=118 kJ/mol: 0.799</td>
</tr>
</tbody>
</table>

Table D.1: Input parameters for Cycle-Tempo model of the SOFC system

The composition of the fuel remains the same as in the CFD calculations. For biosyngas the composition is 2% CH₄, 18% H₂, 18% CO, 13% CO₂, 10% H₂O, 39% N₂ and for methane, it is 33% CH₄, 1% H₂, 66% H₂O. The pressure drops of the fuel and the oxidant are neglected. The cell resistance varies for each case (according to the activation energy Ea). The values of the resistance for each case, were obtained by the CFD simulations in Chapter 5. The active cell area of the channel is 0.000448 m². For all cases the inlet temperature is 973 K, and the corresponding outlet temperatures are the values obtained from the CFD simulation (Chapter 5). The average temperature is set as the operating temperature for each case. The same applies to the current density and fuel utilization values used, which are also the values obtained in Chapter 5.

The modeling results for operation with biosyngas have shown that the power output for the cases investigated varies between 0.0013 and 0.0015 kW. The efficiencies are in a narrow range close to 50%. These simulations actually confirm the conclusion drawn from the CFD
simulations, that the effect of the reforming kinetics is not significant when the concentration of methane in the biosyngas is too low (only 2%). The results are summarized in Table D.2.

The modeling results for operation with methane have shown that the power output for the cases investigated varies between 0.0006 and 0.0008 kW, which is expected since the input for the current density is obtained in chapter 5 and is much lower than the corresponding values for biosyngas. The air to fuel ratio is lower compared to operation with biosyngas because less coolant air is required due to the endothermic MSR reaction. The difference in the energy efficiencies is attributed to the fact that for operation with methane and $E_a=118 \text{ kJ/mol}$ the average temperature is higher leading to lower resistance (Table D.1), thus making current flow easier.

Figures D.1 and D.2 show the process flow scheme along with information about the input and the output and Tables D.2 and D.3 show the corresponding results.

![Figure D.1](image.png)

**Table D.2:** Results for operation with biosyngas

<table>
<thead>
<tr>
<th>Cycle Tempo Results</th>
<th>Operation with Biosyngas</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a = 82 \text{ kJ/mol}$</td>
<td>$E_a = 95 \text{ kJ/mol}$</td>
</tr>
<tr>
<td>Power [kW]</td>
<td>0.0014</td>
</tr>
<tr>
<td>Power density [kW/m²]</td>
<td>3.22</td>
</tr>
<tr>
<td>Voltage [V]</td>
<td>0.7939</td>
</tr>
<tr>
<td>Air utilization [%]</td>
<td>6.96</td>
</tr>
<tr>
<td>Fuel flow [kg/s]</td>
<td>$9.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Air flow [kg/s]</td>
<td>$7.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>Efficiency [%]</td>
<td>50.63</td>
</tr>
</tbody>
</table>
Figure D.2: Process flow scheme for operation with methane

<table>
<thead>
<tr>
<th>Cycle Tempo Results</th>
<th>Operation with Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Case</strong></td>
<td><strong>Ea = 82 kJ/mol</strong></td>
</tr>
<tr>
<td>Power [kW]</td>
<td>0.0006</td>
</tr>
<tr>
<td>Power density [kW/m²]</td>
<td>1.4</td>
</tr>
<tr>
<td>Voltage [V]</td>
<td>0.7371</td>
</tr>
<tr>
<td>Air utilization [%]</td>
<td>7.68</td>
</tr>
<tr>
<td>Fuel flow [kg/s]</td>
<td>3.95·10⁻⁶</td>
</tr>
<tr>
<td>Air flow [kg/s]</td>
<td>1.4·10⁻⁷</td>
</tr>
<tr>
<td>Efficiency [%]</td>
<td>56.43</td>
</tr>
</tbody>
</table>

Table D.3: Results for operation with methane

One issue that can be answered with the aid of Cycle-Tempo is the one raised in Chapters 5 and 6 about the current density output for operation with biosyngas and methane. Indeed the CFD simulations have shown that for operation with biosyngas the average current density output is 2.08 times higher compared with operation with methane (4081 to 2260 A/m²). This difference can be partially attributed to the fact that the temperature distribution is higher for operation with biosyngas and this could affect the resistance value and thus current density. Indeed this argument is confirmed by the CFD results (3.54·10⁻⁵ for biosyngas and 6.3·10⁻⁵ for methane).

It is important to point out, that for the CFD simulations the fuel input was 1.8 times higher for operation with biosyngas than operation with methane, and this has played a major role in this difference in the current density output. Unfortunately it was not possible to increase the methane inflow (or decrease the biosyngas inflow), in order to make comparisons with similar values for the fuel input. The reason was that if either of these would happen: a) the results returned by the simulation would be rather disappointing (too low temperature, too low current output), b) the simulations would return no results at all c) the fuel utilization would significantly drop. For this reason the software Cycle-Tempo was used.
In the extra simulations performed, the input data was the same as in Table D.1, with the only difference, that the desired current density output for operation with methane was the same as with operation with biosyngas (4081 A/m²). The results are summarized in Table D.4. Operation with biosyngas has still higher power output but the output for operation with methane has significantly increased. This is due to the fact that the fuel input 3.27 times higher (check Table D.3).

These results confirm the fact that the main reason for the difference in the current density between operation with biosyngas and methane is due to the fuel inflow. However, as already explained it was not possible to perform CFD calculation with the same fuel inflow of biosyngas and methane.

<table>
<thead>
<tr>
<th>Cycle Tempo Results</th>
<th>Biosyngas</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ea [kJ/mol]</td>
<td>95</td>
<td>118</td>
</tr>
<tr>
<td>Power [kW]</td>
<td>0.0015</td>
<td>0.0013</td>
</tr>
<tr>
<td>Power density [kW/m²]</td>
<td>3.24</td>
<td>2.91</td>
</tr>
<tr>
<td>Voltage [V]</td>
<td>0.7933</td>
<td>0.7137</td>
</tr>
<tr>
<td>Air utilization [%]</td>
<td>6.9</td>
<td>7.47</td>
</tr>
<tr>
<td>Fuel flow [kg/s]</td>
<td>9.43·10⁻⁶</td>
<td>8.71·10⁻⁶</td>
</tr>
<tr>
<td>Air flow [kg/s]</td>
<td>7.7·10⁻⁷</td>
<td>3·10⁻⁷</td>
</tr>
<tr>
<td>Efficiency [%]</td>
<td>50.9</td>
<td>54.7</td>
</tr>
</tbody>
</table>

Table D.4: Comparison of results for operation with biosyngas and methane
Appendix E

User defined functions

E.1 Oxygen mass sink

```c
#include "udf.h"
#define MW_H2 2e-3 /* Mole weight of Hydrogen [kg/mol] */
#define MW_O2 32e-3 /* Mole weight of Oxygen [kg/mol] */
#define MW_H2O 18e-3 /* Mole weight of Water [kg/mol] */
#define R 8.314 /* Gas constant */
#define F 96485.0 /* Faraday constant [C]*/
#define Length 112.0e-3 /* the length of the anode reaction layer [m] */
#define Width 2.0e-3 /* the width of the anode reaction layer [m] */
#define Height 0.1e-3 /* the height of the anode reaction layer [m] */

/**********************************************************/
/* Oxygen mass sink                                        /
/**********************************************************/
DEFINE_SOURCE(sink_mass_O2, cell, thread, dS, eqn)
/* sink_mass_O2 is an (arbitrary) name for the mass sink of O2 [kg/m3-s] */
/* cell holds a cell ID provided by the Fluent solver */
/* thread holds a thread ID provided by the Fluent solver */
{
    real r[ND_ND]; /* the position vector; ND_ND returns the number of dimensions of the problem */
    real I;           
    real sink; /* the returned source term */
    real z;          /* accesses the cell’s centroid coordinate */
    C_CENTROID(r, cell, thread); 
    /* pick the z-coordinate from the position vector */
    /* I=10769927718*z*z*z*z*z*z - 492688349*z*z*z*z*z*z + 772503805*z*z*z*z*z*z - 62428830*z*z*z*z + 2642934*2*z*z + 39474.91*z + 5733; */
    I = C_UDMI(cell, thread,0); 
    sink = -(I*MW_O2)/(4*F*Height); /* the oxygen mass source in the cell [kg/m3s] */
    dS[eqn] = 0.0;
    return sink;
}
```

E.2 Oxygen mass source

```c
#include "udf.h"
#define MW_H2 2e-3 /* Mole weight of Hydrogen [kg/mol] */
#define MW_O2 32e-3 /* Mole weight of Oxygen [kg/mol] */
#define MW_H2O 18e-3 /* Mole weight of Water [kg/mol] */
#define R 8.314 /* Gas constant */
#define F 96485.0 /* Faraday constant [C]*/
#define Length 112.0e-3 /* the length of the anode reaction layer [m] */
#define Width 2.0e-3 /* the width of the anode reaction layer [m] */
#define Height 0.1e-3 /* the height of the anode reaction layer [m] */

/**********************************************************/
/* Oxygen mass source                                    /
/**********************************************************/
DEFINE_SOURCE(source_mass_O2, cell, thread, dS, eqn)
/* source_mass_O2 is a (arbitrary) name for the mass source of O2 [kg/m3-s] */
```
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```plaintext
/* cell holds a cell ID provided by the Fluent solver */
/* thread holds a thread ID provided by the Fluent solver */
{
  real r[ND_ND];
  /* the position vector; ND_ND returns the number of dimensions of the
   problem */
  real I;
  real z;
  real source; /* the returned source term */
  C_CENTROID(r, cell, thread);
  /* accesses the cell's centroid coordinate */
  z = r[2]; /* pick the z-coordinate from the position
    vector */
  /* I = 10769927718*z*z*z*z*z*z - 4926868349*z*z*z*z*z + 772503805*z*z*z*z -
   6242883*z*z + 2642934*z - 39474.91*z + 5733; */
  /* A/m2 */
  I = C_UDMI(cell, thread, 0);
  source = (I*MW_O2)/(4*F*Height); /* the oxygen mass source in the
    cell [kg/m3s] */
  dS[eqn] = 0.0;
  return source;
}

E.3 Define execute on loading

#include "udf.h"
#define NUM_UDM 1
static int udm_offset = UDM_UNRESERVED;
DEFINE_EXECUTE_ON_LOADING(set_udms_on_loading, libname)
/* sink is the name for the energy sink in reaction layer [W/m3] */
{
  if(udm_offset == UDM_UNRESERVED)
    udm_offset = Reserve_User_Memory_Vars(NUM_UDM);
  if(udm_offset == UDM_UNRESERVED)
    Message("\nYou need to define up to %d extra UDMs in GUI and then
reload current library %s\n", NUM_UDM, libname);
  else
    {
      Message("%d UDMs have been reserved by the current library
%sn", NUM_UDM, libname);
      Set_User_Memory_Name(udm_offset, "Current density [A/m2]"),
    }
  Message("\nUDM offset for Current Loaded Library = %d\n", udm_offset);
}

E.4 Define on demand

#include "udf.h"
#define MW_H2 2e-3 /* Mole weight of Hydrogen [kg/mol] */
#define MW_O2 32e-3 /* Mole weight of Oxygen [kg/mol] */
#define MW_H2O 18e-3 /* Mole weight of Water [kg/mol] */
#define STOIC_H2 1.0
#define STOIC_O2 0.5
#define STOIC_H2O 1.0
#define R 8.314 /* Gas constant */
#define F 96485.0 /* Faraday constant [C] */
#define k0 1.887e-10
#define Ea -101248.0
#define Length 112.0e-3 /* the length of the anode reaction layer [m] */
#define Width 2.0e-3 /* the width of the anode reaction layer [m] */
#define Height 0.1e-3 /* the height of the anode reaction layer [m] */
DEFINE_ON_DEMAND(set_udms)
/* sink is the name for the energy sink in reaction layer [W/m3] */
{
  Domain *d;
  Thread *t; /*=Lookup_Thread(d,ID);*/
  cell_t c;
}
```
real $\text{ConcenH}_2, \text{ConcenO}_2, \text{ConcenH}_2\text{O}$; /* Mole concentration of species [mol/m$^3$]*/
real $\text{MoleH}_2\text{C}, \text{MoleO}_2\text{C}, \text{MoleH}_2\text{O}\text{C}$; /* Mole fraction of species [%]*/
real density,temp;
real Gibbs, heat_sink;
real Rohm, E, Vohm, V, Power;
real I;
d = Get_Domain(1);
thread_loop_c(t,d)
{
    if (THREAD_ID(t)==5)
    {
        begin_c_loop(c,t)
        {
            density = C_R(c,t);
            temp = C_T(c,t);
            V = 0.8;
            \text{ConcenH}_2 = \text{density} \times C_YI(c,t,0)/\text{MW_H}_2; /* Get mole concentration of Hydrogen [mol/m$^3$]*/
            \text{MoleH}_2\text{C} = \text{ConcenH}_2/(\text{ConcenH}_2 + \text{ConcenH}_2\text{O}); /* Get mole fraction of Hydrogen [%]*/
            \text{ConcenH}_2\text{O} = \text{density} \times C_YI(c,t,2)/\text{MW_H}_2\text{O}; /* Get mole concentration of Water [mol/m$^3$]*/
            \text{MoleH}_2\text{OC} = \text{ConcenH}_2\text{O}/(\text{ConcenH}_2 + \text{ConcenH}_2\text{O}); /* Get mole fraction of Water [%]*/
            \text{MoleO}_2\text{C} = 0.21; /* = 0.416*2+2.188*z*z;*/
            \text{Gibbs} = (0.053 \times \text{temp}-245.582)*1000; /* Gibbs free energy [J/mol] */
            \text{E} = -\text{(Gibbs)/(2*F)} + \text{R*temp*(log(\text{MoleH}_2\text{C})*0.5*log(\text{MoleO}_2\text{C})*log(\text{MoleH}_2\text{O}))/2*F}; /* The Nernst equation*/
            \text{Rohm} = k_0 \times \exp(-\text{Ea}/(\text{R*temp})); /* Get the electric resistance [ohm.m$^2$]*/
            \text{I} = (\text{E-V})/\text{Rohm};
            if (\text{I}>200)
            {
                \text{C_UDMI(c,t,0)} = \text{I};
            }
            else
            {
                \text{C_UDMI(c,t,0)} = 200;
            }
        }
        end_c_loop(c,t)
    }
    else
    {
        begin_c_loop(c,t)
        {
            \text{C_UDMI(c,t,0)} = 0;
        }
        end_c_loop(c,t)
    }
}

E.5 Set udms

#include "udf.h"
#define \text{MW_H}_2 2e-3 /* Mole weight of Hydrogen [kg/mol] */
#define \text{MW_O}_2 32e-3 /* Mole weight of Oxygen [kg/mol] */
#define \text{MW_H}_2\text{O} 18e-3 /* Mole weight of Water [kg/mol] */
#define \text{STOIC_H}_2 1.0
#define \text{STOIC_O}_2 0.5
#define \text{STOIC_H}_2\text{O} 1.0
#define \text{R} 8.314 /* Gas constant */
#define \text{F} 96485.0 /* Faraday constant [C]/*/
#define \text{k}_0 1.887e-10
#define \text{Ea} -101248.0
#define \text{Length} 112.0e-3 /* the length of the anode reaction layer [m] */
#define \text{Width} 2.0e-3 /* the width of the anode reaction layer [m] */
#define \text{Height} 0.1e-3 /* the height of the anode reaction layer [m] */
DEFINE_INIT(set_udms_init,d)
/* sink is the name for the energy sink in reaction layer [W/m$^3$] */

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E.6 Sink

/***************************************************************************/
/* UDF for specifying an energy sink for the single channel of fuel cell */
/***************************************************************************/
#include "udf.h"
#define MW_H2 2e-3 /* Mole weight of Hydrogen [kg/mol] */
#define MW_O2 32e-3 /* Mole weight of Oxygen [kg/mol] */
#define MW_H2O 18e-3 /* Mole weight of Water [kg/mol] */
#define STOIC_H2 1.0
#define STOIC_O2 0.5
#define STOIC_H2O 1.0
#define R 8.314 /* Gas constant */
#define F 96485.0 /* Faraday constant [C]*/
#define k0 1.887e-10
#define Ea -101248.0

{ Thread *t;/*=Lookup_Thread(d,ID);*/
cell_t c;
real r[ND_ND];
real I,z;
d=Get_Domain(1);
thread_loop_c(t,d)
{
  if(THREAD_ID(t)==4)*/
  {
    begin_c_loop(c,t)
    {
      C_CENTROID(r,c,t);
      z=r[2];
      I=500+40600*z;/*10^769927718*z*z*z*z*z*z -
      4926868349*z*z*z*z*z + 772503805*z*z*z*z + 62428830*z*z + 2642934*z*z -
      39474.91*z + 5733; /* A/m2 */
      C_UDMI(c,t,0) = I;
      C_UDMI(c,t,1) = 0.21;
    }
    end_c_loop(c,t)
  }
  begin_c_loop(c,t)
  {
    C_UDMI(c,t,0) = 0;
  }
  end_c_loop(c,t)*/
}
#define Length 112.0e-3  /* the length of the anode reaction layer [m] */
#define Width 2.0e-3     /* the width of the anode reaction layer [m] */
#define Height 0.1e-3    /* the height of the anode reaction layer [m] */
DEFINE_SOURCE(sink, cell, thread, dS, eqn)
/* sink is the name for the energy sink in reaction layer [W/m3] */
{
  real ConcentH2,ConcenO2,ConcenH2O;    /*Mole concentration of species [mol/m3]*/
  real MoleH2C,MoleO2C,MoleH2OC;       /*Mole fraction of species [%]*/
  real density,temp;
  real Gibbs,heat_sink;
  real Rohm,E,Vohm,V,Power;
  real I;
  I = C_UDMI(cell, thread,0)
  V=0.8;
  Power = V*I/Height; /*Get the fuel cell power [W/m3]*/
  heat_sink = - Power; /*Get the energy sink[W/m3]*/
  dS[eqn] = 0.0;
  return heat_sink;
}
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Ηλεκτρικά ναρκωτικά με ταξιδεύουν, μέσα από γυάλινα κουτιά με κοροϊδεύουν

Free translation: Electric drugs are driving me, mocking me through their boxes of glass