Modeling a Solid Oxide Fuel-Assisted Electrolysis Cell in Cycle Tempo

MASTER OF SCIENCE THESIS

For the degree of Master of Science in Sustainable Energy Technology at Delft University of Technology

Floris Karel Boudewijn Wijers
October 7 2011

Supervisors and reviewers:

Dr. P.V. Aravind
Ir. T. Woudstra
Ir. T.P. van der Stelt
Dr. K. Hemmes
Prof. Dr. Ir. A.H.M. Verkooijen

Faculty of Mechanical, Maritime and Materials Engineering
Master Sustainable Energy Technology
Department of Process and Energy
Delft University of Technology
Report No. 2477
ACKNOWLEDGEMENTS

The subject of this thesis is an elaboration of previous performed work by the author. Prior to the thesis, a compulsory research was performed, named SIPII (Systems Integration Project II). During this project, the theoretical foundation was laid for the final simulation of the SOFEC. Due to many overlapping components, the author and his supervisors decided that the thesis report would best benefit from combining both researches into one final report. These are marked individually, shown in the table of contents, named part I and II.

From the university’s perspective, a thesis is an individual research of a student’s capability. When it comes to thinking and writing, the process is indeed individual. The completion of a thesis, however, is something that is never done alone. Therefore, the author would like to extend his gratitude to a number of people that have contributed to the development of this thesis. The author would like to thank -in the first place- his direct thesis supervisors: Dr. P.V. Aravind and Ir. T.P. Woudstra. Their advice, support, valuable comments and trust have made working on this thesis an enjoyable experience. Furthermore, the author would like to thank Ir. T. van der Stelt for his immensely valuable help with all matters related to the actual Fortran programming of Cycle Tempo.

A special thanks goes out to the author’s parents. The author’s mother, who spent many hours during her vacation, helping to make this report readable and understandable. The author’s father, who’s enthusiasm and perpetual support have helped to keep the end goal in sight, and for his shared opinion on the relationship between financial security and getting the most out of your student time. Also, the author would like to thank his girlfriend. While once a student herself, working for two years and living with a student must not have been an easy task. Her support and compassion have greatly helped the author.

Finally, the author would like to thank his grandparents: Ir. H.C. Blauwkuip MSc. and H.M. Blauwkuip-Wylacker for their endless inspiration. To study at Delft University, to taste the good student-life, and to be their first grandchild to graduate from Delft University.

*It makes me proud that they, at age 87 and 86, are able to stand next to me.*

Floris K.B. Wijers
1174304
Delft, October 7, 2011
f.wyers@gmail.com
Abstract

This research forms a basis for the process of quantifying and simulating the reactions occurring within a Solid Oxide Fuel-Assisted Electrolysis Cell and the results emanating from it. This relatively new alternative application within the known SOFC is a subject of great interest. Initial laboratory tests predict it’s highly efficient hydrogen production ability. A summation of previous works will be followed by a detailed explanation of the theory behind the SOFEC. In the whole report, comparisons will constantly be made with a SOFC, in an attempt to better understand the processes involved. This theoretical knowledge is expanded with a mathematical description of the internal processes involving the cell voltage, current density, resistance and voltage drop. These variables are linked together through a single equation.

Based on the known SOFC equation, a SOFEC variant is proposed. This is done by breaking down the steps performed within Cycle Tempo. These are analyzed individually, an alterations are made. Afterwards, the actual programming code is analyzed, and all alterations are summarized. They are changed according to the proposed theory. With a working program, the results are finally analyzed and compared to the theory. This is followed by a chapter covering explaining the basics of the hydrogen economy. The advantages and problems occurring from this are summarized and a possible future implementation of the SOFEC is given. The report end with a conclusion and recommendations.
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Part I.

Theory and Mathematics

1. Introduction

With an ever increasing demand for energy, industries, research facilities and governments are constantly increasing their efforts to find alternatives to a finite reserve of fossil fuels. Global warming forms a major threat to the life people are now accustomed to. It is obvious that with this demand and the rise of the third world countries, alternatives will have to be found. The attention is focussed on renewable energy sources and hydrogen as a possible ultimate energy carrier.

This research focusses on a promising technology, that is capable of producing hydrogen from water and electricity, with the help of a fuel cell used as an electrolyzer. The original fuel cell technology dates back to 1838. But it wasn’t till the last couple of decades, that this technology started showing results as a viable alternative to the current polluting systems with their harmful exhausts. In particular, the Solid Oxide Fuel Cell (SOFC) will be discussed and it’s different methods of operation. At this moment, the SOFC is one of the most efficient methods of turning hydrogen into usable electrical energy.

Now, almost 95% of the world hydrogen production is created by large scale methane steam reforming facilities. It’s high efficiency makes it so popular, while some drawbacks exist. There is still a need for fossil fuels, and for hydrogen production to be economically viable, a large scale plant is needed with a big constant load. This limits the production to centralized plants located near hydrogen consuming industries. Apart from not being as readily available as, for example: gasoline or methane, the transportation of hydrogen also forms large barriers. This is discussed in chapter 8, explaining the problems resolving around transportation and storage of hydrogen. All combined, the advantages of fossil fuels outweigh those of hydrogen. Therefore, fossil fuels will still, for the next couple of decades, remain the first choice for all countries running their economy.

An alternative to hydrogen production through steam reformation is the electrolysis of water. By applying a voltage over two electrodes placed in water, hydrogen and oxygen can be created. This process is very inefficient due to the high decomposition voltage of water. Research to increase the yield has led to the use of a SOFC as an electrolysis device. This
is called a Solid Oxide Electrolysis Cell (SOEC), while nowhere near the efficiency of the large scale methane reformation, the SOEC is still a step in the right direction. Further research has led to dozen’s of electrolysis spin-offs, with one of the newest being the Solid Oxide Fuel-Assisted Electrolysis Cell (SOFEC). While only just patented in 2000, preliminary results are promising. A laboratory test shows a decrease in electrical energy needed of 85% compared to the best electrolysis alternatives. By adding methane to the anode, the decomposition voltage of water can be lowered. This leads to a lower power usage and a higher conversion ratio of electricity to hydrogen.

Furthermore, the SOFEC is particularly interesting due to its versatility. As a compact system, it allows the user to produce hydrogen on-site. The price of the final hydrogen will even be able to compete with large scale methane reformation plants. The transportation factor will not play a role of interest anymore as one of the most important cost drivers. Therefore, locally placed SOFEC’s generating hydrogen will allow a much larger availability throughout the country. While this solution is still not carbon free as renewable energy sources as methane is still used, it does lend itself to becoming a good intermediate solution. Methane is readily available in all modern countries and, with a well developed distribution infrastructure, the SOFEC’s can literally be placed anywhere.

This report will focus mainly on the theory and technology behind the SOFEC and is divided into several of chapters. To start, a summary is given of the research already performed on the SOFEC. This will be continued with a chapter covering the basics of fuel cells with the SOFC, SOEC and SOFEC in particular. The following chapter will contain a proposed mathematical model based on work already performed by A. de Groot [4]. The next chapter describes the steps taken to create a new model within Cycle Tempo, and is broken down in different paragraphs. Firstly, an introduction to Cycle Tempo is given. This is followed by a chapter describing the step sequence used by the program. This is used to propose a new flow chart, which will be capable of simulating the SOFEC. Afterwards, the flow chart and proposed changes are translated to actual code. The next chapter will demonstrate all the changes made within the source code and the effect they will have. The chapter is concluded by a summarization of the obstacles encountered and recommendations for further research. The next chapter will briefly cover the hydrogen economy and how the SOFEC will be able to fit into this economy. Lastly, the report will end with the overall drawn conclusions and recommendations.
2. Summary of related work

In 2000, Pham et al. [9] patented the first idea of adding fuel to the anode. By doing this, they reduced the voltage required for the electrolysis process. The idea was proposed, where they only indicated there was an increase in efficiency, based purely on the change in thermodynamic energy. Their fuel cell was able to run in two different operational modes that described how the methane reacted. In the partial oxidation mode, the catalyst on the anode side will promote the partial oxidation of natural gas to carbon monoxide and hydrogen. The resulting mixture, called syn-gas, can be used in large industrial processes, as well as react further into hydrogen and carbon dioxide. The result of this system is that hydrogen is produced at the anode and cathode side. The total oxidation mode entails the direct oxidation of the added methane with the oxygen molecules formed by the diffused oxygen ions. This will result in a lowered potential difference over the membrane, reducing the electricity consumption. Either way, it wasn’t till a few years later that Martinez-Frias, Pham, Alceres [6] created a working model. The newly created system was compared to the best alternative at the time: HOT ELLY. This was a high temperature steam electrolyzer, while the most advanced of its sort, was still only capable of generating hydrogen at twice the price of large scale steam reformation. According to their analysis, 80% of the total hydrogen production costs came from the electricity costs. This was mainly attributed to the high cell voltage, that needed to be overcome as a result of the high decomposition voltage of water. According to Martinez-Frias, Pham and Alceres, in the case of their NGASE (Natural Gas Assisted Steam Electrolyzer), the operating voltage of the fuel cell could be lowered as much as 1volt (from $\sim 1.2V \rightarrow 0.2V$). This would result in an increase of electrical energy to hydrogen conversion, making the final hydrogen price a viable competitor to industrially reformed methane.

This maximum was achieved after certain adjustments were made: for instance by an increased anode porosity. They stated that the efficiency was greatly influenced by the anode, as this limited diffusion was mainly creating a large over-potential. They also stated that increasing the temperature would increase the amount of carbon deposition at the anode. This could then be counteracted by adding more steam to the anode gas flow, which in turn would have a negative effect on the thermodynamic properties. An optimal balance would be an important aspect when designing the operating parameters of the fuel cell.
The idea for adding a fuel as proposed in the NGASE, was quickly adopted by other groups. Gopalan et al. [5] proposed a new system using a molten silver electrode. The molten Ag electrode would allow the system to still run in the partial and total oxidation modes mentioned by Pham, but would increase the electrode diffusibility. They theorized that the use of coal at the anode, would have a similar effect to the system proposed by Pham. The coal, at high temperature and with added steam, would gasify in CO and CO$_2$. This could unfortunately not be compared to an actual system, as it was only a paper study. The idea was continued by Pati et al. [7], who included a working cell, and an extensive electrochemical modeling and characterization.

Back to the Martinez-Frias study, which had a general assumption suggesting that the anode porosity limited the fuel cell operation. This idea was continued by Wang et al. [14], who agreed on the diffusion limited Ni/YSZ cermet anode. They also recognized that it would be prone to hydrocarbon deposition (coking). They proposed an alternative consisting of a YSZ backbone, impregnated with CeO$_2$, and various amounts of metallic compounds: Cu, Co and Pd. Their results showed that a Pd-Cu-CeO$_2$-YSZ anode was found to have the highest catalytic activity, and gave the largest reductions in operating potential, and thus the lowest diffusion limitations.

Though, apart from the above mentioned, no extensive research was performed of the SOFEC, which is a more general form of the NGASE, the idea stands solid. Anode porosity, adding metals to the electrodes and hydrocarbon coking all effect the performance of the fuel cell. This research must, for the sake of simplicity, focus only on the most simple type of SOFEC. Therefore, only methane will be used as fuel in the anode. Coking is still too undeveloped and unpredictable and will therefore not be taken into consideration. The anode, cathode and electrolyte used, will be the same as the most common currently used within SOFC. This will become clear in the next chapter. Further experimentation will be needed to be able to predict what actually will happen. For this theoretical study, simplification is the key to achieving viable results.
3. Fuel Cell explained

Before explaining the inner works of the SOFEC model, it is best to start with the model from which it is deduced, the Solid Oxide Fuel Cell (SOFC). This is a fuel cell which is capable of turning the chemical energy of fuel added (hydrogen, methane, butane etc) into electrical energy. The fuel cell operation is based on the natural tendency of oxygen to react with hydrogen to create water. By controlling the means by which such a reaction occurs and by directing the reaction through a device, it is possible to harvest the energy yielded by the reaction.

At this moment, there are six distinct types of fuel cells. Fuel cells are primarily classified by the kind of electrolyte they use. The electrolyte will be discussed in more detail later on. In essence one can think of the electrolyte as the membrane sandwiched between the positive and negative electrode, which determines which particles can pass through it, and which cannot. This classification also determines the kind of catalyst required, the temperature range in which the fuel cell operates, the fuel required and other factors.

These characteristics, in turn, affect the applications for which the fuel cells are most suitable. The temperature ranges from 20 - 1100°C. This obviously forms one of the most determinant characteristics. A lot of research is currently being performed on these different types of fuel cells, each with their own spin-offs within the classifications. Each cell has its own advantages, limitations and applications.

A commonly asked question is: why one would want to use a fuel cell? The answer is partially given in the introduction where reason for the search for clean energy converters has become ever so important. Another important reason is its efficiency. When compared to the traditional Internal Combustion Engine (ICE), the fuel cell is able to achieve a much higher efficiency. This efficiency is described as the amount of usable work retrieved, divided by the total energy entering the 'converter', and thus stored in the fuel used. The rest of the energy is 'lost' to heat and normally unusable. In the case of a gasoline powered car, it is described by a thermal cycle: the Otto cycle. This is a realistic version of the theoretical Carnot Cycle which emulates a perfect system containing no irreversible heat losses. The efficiency of the ICE is determined by the compression ratio of the gasses and the operating temperature. Theoretically speaking, in the most efficient Carnot Cycle situation, the efficiency of the engine could reach efficiency of 50-60%+, however modern combustion engines have an efficiency of around 20 -25% (combined thermal and mechanical conversion).
The fuel cell on the other hand does not work using the Carnot Cycle. The cell limits itself only by the enthalpy (energy of the fuel entering fuel cell) and Gibb’s free energy (useful retrievable energy) chemically stored in its fuel. Its theoretical thermodynamic limit lies around 83% energy conversion (chemically stored energy to useable electrical energy) at 298K. However, taking irreversible losses into account, the actual efficiency varies per fuel cell, but for the SOFC, efficiencies in the range of 60 - 65% have been reached. Similar to a car using its waste heat to heat up the car, a fuel cell can be placed in a combined heat and power plant (CHP), increasing its overall efficiency, reaching almost 80%. Next to an increased efficiency, one of the most important arguments to use a fuel cell is its fuel: hydrogen. There are ICE’s running on hydrogen, however the supplied oxidant must be pure oxygen to prevent pollutant nitrous-oxides in the exhaust. The fuel cell does not have this problem, resulting in only water and unused air at the exhaust. Lastly, the fuel cell contains no moving parts subject to wear and tear as with a car engine, making them run for much longer periods. All these advantages have contributed to the (recently) increased interest in these fuel cells. The research intensified and resulted in the discovery of the SOFEC.

The following chapter will be subdivided into three parts describing the different operational modes of this particular type of fuel cell. Firstly the common SOFC is explained. Then an explanation is given in how this cell can be used in regenerative mode, and finally the newly acquired knowledge is applied to SOFEC system.

3.1. SOFC: Solid Oxide Fuel Cell

The Solid Oxide Fuel Cell is the fuel cell with the longest continuous development period, starting in the late 1950’s. The name reveals one of the most important components of the fuel cell: Solid Oxide. As mentioned earlier, the fuel cells are categorized by the electrolyte and the type of particles they allow to pass. In this situation, one is dealing with a ceramic solid oxide electrolyte able to conduct oxygen ions. The fuel cell is capable of converting chemical energy into electrical energy. The most important advantages of the SOFC when compared to the other fuel cells are summarized below:

- **Fuel flexibility.** As will become clear later on, the SOFC has a wide variety of suitable fuels. The flexibility comes from the fact that the fuel cell is operated at a very high temperature, allowing fuel that enters the anode to be converted into hydrogen before oxidizing.
• **High efficiency.** The high operating temperature generally results in a higher thermal conversion efficiency when compared to lower temperature fuel cells. Even so, the waste heat of the SOFC is also very high, making it perfect in combination with a steam turbine. The waste heat is used to create steam to drive a turbine which can generate electricity.

• **Long-term stability.** The SOFC is able to run for long periods of time without any change in performance or temperature. However, due to their long startup time, they aren’t suitable as backup power systems, but better for system requiring a constant base-load system.

• **Solid Electrolyte.** Due to the solid electrolyte, the cell can be cast into various shapes, such as planar and tubular. It also allows precise engineering of the three-phase boundary and avoids electrolyte movement or flooding in the electrodes.

• **Low costs and emissions.** All the materials used within the fuel cell are readily available, and are of much lower cost when compared to low temperature fuel cells. Due to its high operating temperature, there is no need for an expensive catalyst like platinum used in a PEMFC. Furthermore, emissions in a SOFC are only water, if pure hydrogen is provided as fuel.

The largest advantage of the SOFC, is also it’s largest disadvantage: the high temperature. Operating a fuel cell at such high temperatures requires special care. Though the materials used to construct the device are affordable, the high operating temperature makes these materials prone to degradation. The SOFC also has a long startup time, as a result of its high operating temperature. The expansion coefficient of the materials determines the material expansion due to increase in temperature. When increasing the temperature rapidly, the fuel cell, which is hermetically sealed, would become subject to large stresses in the materials. This could damage and create leaks which would seriously effect the safety and efficiency of the cell. This means that, depending on the specific type of SOFC, the startup time could vary from 24 - 72 hours. The SOFC is at best use when running under a constant base-load.

Unlike most other types of fuel cells, SOFC are fabricated with different geometries. During this research, use will be made of the planar fuel cell design geometry. This is the typical “sandwich type geometry” employed by most types of fuel cells. SOFCs can also be made in tubular geometries, where either air or fuel is passed through the inside of the tube and the other gas is passed along the outside of the tube. The tubular design is advantageous because it is much easier to seal air from the fuel. The performance, on the other hand, of
the planar design is currently better than the performance of the tubular design. This is
due to its lower resistance. This research will focus only on the planar type SOFC.

The planar SOFC [10] used in this research is shown in the following figure 1, showing
the different components.

![Illustration of a SOFC](image)

**Figure 1**: Illustration of a SOFC

The figure shows the reaction occurring, and the flow of gases in the different components
of the fuel cell. In short: what happens is that fuel is added to the anode. In this case, the
most simple example of hydrogen, as a fuel, is given. This fuel will react with the diffused
oxygen ions (O$^{2-}$) coming from the cathode through the electrolyte to the anode. Under an
oxidation reaction, the oxygen ions react with the hydrogen, releasing energy and electrons,
resulting in the creation of water. The electrons are fed back to the cathode through an
external circuit fitted with a load, indicated by a light bulb. At the other side, oxygen is
fed to the cathode. Again, the most simple example is given where pure oxygen is used. In
real life situations, this would be air containing a certain amount of oxygen. The oxygen
reacts with the newly arrived electrons forming oxygen ions which can then diffuse through
the electrolyte, completing the circle. The electrolyte only allows the ions to pass and not
the oxygen molecules. If this would happen, the hydrogen would burn and therefore skip
the external circuit.

The three main components of a typical SOFC [3] are:

1. **Anode: nickel and YSZ (yttria stabilized zirconia) cermet.** The anode must
   be able to conduct electrons and its main task is to allow the electrochemical reaction
to occur between the hydrogen and oxygen ions. During this reaction, heat, water and
electrons are released. The anode is always the negative (external) terminal indicating
electrons emit from this electrode. The anode consists of a combination of a ceramic
(cer) and a metal (met). It must be very porous to allow the fuel to flow towards the
electrolyte. The YSZ is added to the nickel to help stop the grain growth of Ni. This layer is also the thickest in the SOFC and provides the mechanical strength of the whole fuel cell.

2. Electrolyte: YSZ. The electrolyte is a layer of dense ceramics that functions as a membrane to prevent oxygen and fuel mixing. This material starts becoming a good ionic conductor at around 600°C, and therefore also forms the lower temperature boundary of the SOFC.

3. Cathode: LSM, LSCF or LSCM. The cathode is a thin porous ceramic layer placed on the electrolyte. Here the oxygen reduction reaction takes place. This means that the electrons are combined with the oxygen atom to form an ion. The cathode is (externally) positive, as this is the electrode where the electrons flow too. The cathode must be electrically conductive and is made up of one of the three industry standard perovskite mixed ionic/electronic conductors: LSM (lanthanum strontium manganite), LSCF (lanthanum strontium cobalt ferrite) or LSCM (lanthanum strontium chromium manganite). Depending on the fuel cell requirements, a choice will be made between these three.

These three components are placed on top of each other and must be bound tightly to form an airtight seal, which is also stress resistant. Operating the fuel cell at such high temperatures requires a well crafted device, as the slightest imperfection will quickly degrade the fuel cell. During this research no further attention will be paid to the actual construction of the fuel cell, nor will degradation play any part. Here, just the "theoretically perfect" device will be considered.

As shown in figure 1, the reactions taking place at the anode and cathode keep each other in balance. These reactions are dependent on each other, so it is important that the fuel cell is provided with a correct flow of fuel and oxidant, to keep the cell running at maximum efficiency. The reactions that take place at the anode and cathode are called the half-cell reactions and are summarized next in table 1.

<table>
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<th>Table 1: SOFC half-cell reactions</th>
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<tr>
<td><strong>Anode</strong></td>
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<td>$H_2 + O^{2-} \rightarrow H_2O + 2e^{-}$</td>
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When adding the anode and cathode reactions together, the left and right side of the arrow contains similar components. These can be removed from the equation resulting in

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F.K.B. WIJERS
T.U. Delft
the bottom overall reaction. This reaction shows that 1 mole of H\textsubscript{2} will react with half a mole of O\textsubscript{2} resulting in one mole of H\textsubscript{2}O, which is the basic principle of a fuel cell. The next information of interest is knowing how much energy is needed or released to let this reaction occur. Before this question can be answered, a couple of thermodynamic quantities need to be introduced, which will be used throughout the rest of the report. They have been obtained from Schroeders Introduction to Thermal Physics [11]:

- **Enthalpy** is a measure of the total energy of a thermodynamic system. This is a combination of internal energy and the amount of energy needed to make room for it while establishing its volume and pressure (\(H = u + PV\)). When using enthalpy, not the total enthalpy, but the change in enthalpy is used. A negative enthalpy (enthalpy of the products minus the enthalpy before the reaction) indicates an exothermic reaction, meaning: it will occur spontaneously. A positive reaction enthalpy indicates an endothermic reaction which will only occur when energy is provided.

- **Entropy** is the quantitative measure of disorder in a system. It is a thermodynamic property that can be used to determine the energy available for useful work in a thermodynamic process. The higher the entropy, the higher the disorder in a system and the lower the amount of energy which can be used for work. The change in entropy is stated as the change in heat divided by the temperature (\(\Delta s = \Delta Q/T\)).

- **Gibb’s free energy** is a thermodynamic potential that measures the ”useful” or process-initiating work obtainable from an thermodynamic system. In the case of a fuel cell, it allows the calculation of the electrochemical potential from the reactions occurring at the anode and cathode. It is defined as the enthalpy minus the change in entropy multiplied by the temperature (\(\Delta G = \Delta H - T\Delta s\)).

The Gibb’s free energy is the actual energy that is free to perform work. This is the total energy (enthalpy) minus the entropy times the temperature. This will be explained in more detail later on. In the case of the SOFC, the enthalpy and entropy of the reactions occurring at the anode and cathode can be added. This will be equal to the overall equation, and are summarized in table 2. Important to note is that these energies are based on the reaction occurring under standard circumstances. This means: temperature \(T = 298K\) (25°C) and pressure \(p = 1\) bar (atmospheric pressure). At higher temperatures and pressures these values will differ. For this sake, all values found in enthalpy tables in books and on the internet, are all formulated under standard conditions, as only then will comparison be possible.
Table 2: Gibbs free energy of a SOFC (H₂O liquid)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Enthalpy [kJ]</th>
<th>Entropy [J/K]</th>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} )</td>
<td>( 0 + \frac{1}{2} \cdot 0 \rightarrow -285.8 )</td>
<td>( 130.7 + \frac{1}{2} \cdot 205.1 \rightarrow 69.9 )</td>
<td>( \Delta H = -285.8 \text{ kJ} )</td>
<td>( \Delta S = -163.7 \text{ J/K} )</td>
</tr>
</tbody>
</table>

Table 2 summarizes the resultant energies from the overall reaction. For each energy, the resultant energy minus the energy before the reaction is calculated and stated in the right column. The enthalpy is negative, therefore the oxidation reaction of hydrogen and oxygen is exothermic. Energy is released, and this energy can be used to deliver power. The enthalpy and entropy are known values, and with these energies, the Gibb’s free energy can be calculated, shown in the following equation 2:

\[
\Delta G = \Delta H - T \Delta S
\]  

The Gibb’s free energy \( G \) is equal to the change in enthalpy \( H \) minus the change in entropy \( S \) times the temperature. The enthalpy is given in kilo joules, and the entropy in kilo joules per Kelvin. Multiplying the entropy with temperature will also result in joules, allowing it to be subtracted from the enthalpy. In the case of the fuel cell, operating at a temperature of 298K and filling this in to equation 2 will result in the following:

\[
\Delta G = \Delta H - T \Delta S \rightarrow -285.8 - 298 \cdot (-0.1637) = -237.13 \text{ [kJ/mole]}
\]  

This exothermic reaction occurs spontaneously, and within the fuel cell, this value can be converted into a cell voltage. Using Faraday’s law, the following cell voltage can be calculated:

\[
E_0 = -\frac{\Delta G}{n \cdot F} = -\frac{(-237130)}{2 \times 96485} = +1.23 \text{V}
\]  

while using the following variables:

\[
\begin{align*}
\Delta G & = \text{Gibb’s free energy [kJ/mole]} \\
n & = \text{Number of electrons freed during reaction per atom} \\
F & = \text{Faraday’s Constant (96485 C/mole electrons)}
\end{align*}
\]  

Faraday’s law describes the relationship between the Gibb’s free energy and the reversible cell voltage at standard conditions. The fuel is capable of providing this potential when the
redox (reduction-oxidation) reaction occurs at the anode and cathode. This particular fuel cell is therefore capable of providing 1.23V when all the reactions occur at 298K and 1 bar.

There is one more condition that needs to be taken into account. The water used in the previous calculation is in its liquid form. In the case of the SOFC, running at temperatures much higher than the boiling point of water, steam is used, which also requires energy. The evaporation energy of water must be subtracted from the total energy and has an effect on the enthalpy and entropy resulting in the following energies as shown in table 3.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} )</th>
<th>( \Delta H = -241.8 \text{ kJ} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy [kJ]</td>
<td>( 0 + \frac{1}{2} \cdot 0 \rightarrow -241.8 )</td>
<td>( \Delta S = -44.6 \text{ J/K} )</td>
</tr>
<tr>
<td>Entropy [J/K]</td>
<td>( 130.7 + \frac{1}{2} \cdot 205.1 \rightarrow 188.7 )</td>
<td></td>
</tr>
</tbody>
</table>

This will result in the following Gibb’s free energy: \[-241.8 - (298) \cdot (-0.0446) = -228.5 \text{ kJ}\]. The energy is less than the Gibb’s energy of liquid water, and therefore will result in a lower cell voltage. Important to note is: this equation is a little odd. It assumes an enthalpy of steam at 298K, which, of course, isn’t possible. This must be disregarded in the future and just used as it is. Qualitatively speaking: this is the cell voltage at standard conditions assuming water vapor as reactant. When filled into Faraday’s law, this results in the following cell voltage:

\[
E_0 = -\frac{\Delta G}{n \cdot F} = -\frac{-228509}{2 \times 96485} = +1.18 \text{V}
\]  
(5)

During this research, the SOFC will not be operating under standard conditions. The temperature will be much higher, and the pressure is dependent on what the user wants. To account for these different operating conditions, the Nernst equation was devised by Walter Nernst in the early 1900’s. This equation adjusts the standard cell voltage by subtracting an extra factor shown in the following equation:

\[
E_{rev} = E_0 + \frac{RT}{n \cdot F} \cdot \ln(Q)
\]  
(6)

With the following variables:

\[
\begin{align*}
R &= \text{Gas constant } 8.314 \text{ JK}^{-1}\text{mol}^{-1} \\
T &= \text{Temperature in K} \\
Q &= \text{Thermodynamic reaction quotient} \\
F &= \text{Faraday’s constant } (96485 \text{ C/mole electrons}) \\
n &= \text{number of electrons freed during reaction per atom}
\end{align*}
\]
This equation adjusts the standard cell voltage to account for the different temperature and pressure by subtracting a certain factor. This factor consists of a $\frac{RT}{2}F$ part which takes into account the temperature of the fuel cell and the amount of electrons involved in one reaction, and the reaction quotient $Q$. The Nernst equation calculates what is called the Nernst potential or the reversible cell voltage of the fuel cell.

The reaction quotient is a factor that incorporates the amount of the gasses actually used, while operating the fuel cell. Hydrogen entering the fuel cell will only be used to a certain amount. Let’s say this is 80%, meaning that the fuel utilization will be 0.8. Looking at the anode reaction ($H_2 + \frac{1}{2}O_2 \rightarrow H_2O$), it is now possible to say how much hydrogen and how much water will exit the anode. 80% of the hydrogen is converted, meaning the outlet gas will contain 80% water. 20% is not converted, and therefore the outlet gas will contain 20% hydrogen. The final composition of the exiting anode gas will contain certain components with their own partial pressures (denoted as concentration $y$. Gasses at similar temperature and pressure have the same volume, meaning the partial pressures are equal in ratio to their concentrations of the total anodic or cathodic flow). These pressures are used in the thermodynamic reaction quotient and have an important effect on the final cell voltage. The partial pressures of the SOFC, and how they contribute to the Nernst equation are shown in equation 7.

$$Q = \left( \frac{y_{H_2} \cdot y_{O_2}^{1/2}}{y_{H_2O}} \cdot \left( \frac{p_{cell}}{p_0} \right)^{1/2} \right)$$

(7)

The partial pressures can easily be calculated and are summarized in the following table:

<table>
<thead>
<tr>
<th>$y_{H_2}$</th>
<th>1 - fuel utilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_{H_2O}$</td>
<td>Fuel utilization</td>
</tr>
<tr>
<td>$y_{O_2}$</td>
<td>Oxidant utilization (=1)</td>
</tr>
<tr>
<td>$p_{cell}$</td>
<td>Operating pressure fuel cell</td>
</tr>
<tr>
<td>$p_0$</td>
<td>Standard pressure</td>
</tr>
</tbody>
</table>

The operating pressure of the fuel cell is also of influence and it’s contribution is shown above. During this research, the operating pressure is constantly assumed to be equal to ambient pressure and therefore does not contribute to this situation (dividing it by $p_0$, results into the dimensionless value of 1. The concentrations are also dimensionless resulting in a logarithm being taken from a dimensionless value).

Important to note is the partial pressure of oxygen. The cathode is fed with pure oxygen, and once used in the reaction, has no effect on the composition of the cathodic exit flow.
Therefore, the partial pressure remains 1. In the case of a SOFC running on air, the partial pressure will change. The cathodic entrance flow will contain a different concentration of oxygen at the entrance and exit of the fuel cell.

So, to summarize: by analyzing the Nernst equation, one can see that depending on the partial pressures of the reactants and products, the standard cell potential will be altered. It becomes clear that by increasing the temperature, the cell voltage decreases. Increasing the pressure has a positive effect on the electrochemical kinetics, and therefore increases the cell voltage. These are just a few of the instruments at the disposal of a fuel cell designer, and shows how much difference this can make.

3.2. SOEC: Solid Oxide Electrolysis Cell

The previous chapter forms the basis for the electrolyzer cell, which is the intermediate step between the SOFC and SOFEC. The Solid Oxide Electrolysis Cell (SOEC) is in essence the same as the SOFC, with the only difference that it creates hydrogen from water, while using electric energy. It contains the same three parts, and just as with the SOFC, oxygen ions diffuse through the membrane. A typical SOEC is shown in figure 2.

![Illustration of a SOEC](image)

The anode and cathode have been explained in the previous chapter and were defined by the type of reaction occurring within the specific electrode. For the case of the SOEC, the anode and cathode have changed places. Water must be electrolyzed, and for this reaction to occur, electrons must be taken up. This is an oxidation reaction, and therefore requires this electrode to be the cathode. At the other side, oxygen ions recombine to oxygen molecules while releasing electrons equivalent to the oxidation reaction. This must now be the anode. The electrodes have switched places, and therefore also the electron flow. The rest of the fuel cell remains unchanged.
The energy analysis can be performed in a similar way to the SOFC. The reactions are summarized below in table 4:

<table>
<thead>
<tr>
<th>Anode</th>
<th>( \text{O}_2^- \rightarrow \frac{1}{2} \text{O}_2 + 2e^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>( \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + \text{O}_2^- )</td>
</tr>
<tr>
<td>Overall</td>
<td>( \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2 )</td>
</tr>
</tbody>
</table>

The reactions are the same, but the arrow has turned around. This has an effect on the energy, as stated in table 5. (This analysis directly assumes the use of water vapor as described earlier).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 )</th>
<th>( \Delta H = +241.8 \text{ kJ} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy [KJ]</td>
<td>-241.8 \rightarrow 0 + \frac{1}{2}0</td>
<td></td>
</tr>
<tr>
<td>Entropy [J/K]</td>
<td>188.7 \rightarrow 130.7 + \frac{1}{2}205.1</td>
<td>( \Delta S = +44.6 \text{ J/K} )</td>
</tr>
</tbody>
</table>

The result is obvious. A voltage must be applied to the fuel cell to allow the disassociation of water molecules to occur.

With the SOFC and SOEC explained, the SOFEC remains. The idea of generating hydrogen is similar to the SOEC, but the reactions occurring differ significantly and will be discussed in the next paragraph.

### 3.3. SOFEC: Solid Oxide Fuel-Assisted Electrolysis Cell

The Solid Oxide Fuel-Assisted Electrolysis Cell is the main subject of this report. This is a remarkable fuel cell, with the potential of producing hydrogen cheaper than current electrolysis devices.
3.3 SOFEC: Solid Oxide Fuel-Assisted Electrolysis Cell

The whole principle of the SOFEC is based on the idea of replacing a certain amount of the expensive high valued electricity with cheaper, lower value methane. The main reason is to increase the efficiency of the electrolysis process. This is best explained with the help of a simple electrolysis example.

Recall the earlier SOFC energy calculations. When working with liquid water, it was shown that oxidizing H$_2$ led to a fuel cell operating at a voltage of +1.23V. For the opposite reaction to occur, electrolysis of water, a voltage of 1.23V is needed to be applied. This means that if two electrodes are placed in a bucket of water, and a voltage difference of 1.23V or more is applied across them, the water might electrolyze and O$_2$ and H$_2$ gas will form at the electrodes. This reaction will take place very slowly, because only the minimum voltage of 1.23V is applied. To increase the speed, and therefore the amount of hydrogen created per unit time, a greater voltage must be applied. However, applying a greater voltage also results in a lower volume of hydrogen per amount of electricity, decreasing its efficiency.

This problem was also noted by Pham et al [9], and a solution was proposed with the Natural Gas Assisted Steam Electrolyzer (NGASE), which is similar to the SOFEC described in this report. They theorized, and later confirmed with a working laboratory model, that adding methane to the anode would lower the electrolysis voltage. The main driver for this process was the fact that methane could replace the electricity at 25% of the cost. (A quick comparison shows that 1m$^3$ of CH$_4$ contains 8 times as much energy as 1 kWh of electricity at twice the price).

In his paper, Pham distinguished two different types of reactions that could occur within the anode, when an extra fuel was added, namely the total and partial oxidation of CH$_4$:

1. **Total Oxidation.** When operating the SOFEC in this mode, Pham noticed that the added methane reacted directly with the oxygen ions. Methane would oxidize directly according to the following reaction: \( \text{CH}_4 + 4\text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^- \)

2. **Partial Oxidation.** The second mode of operation was based on a partial oxidation of CH$_4$. This was a combination of different reactions:

   - *Anode(1), Steam Reforming reaction:* \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \)
     
     This is called the steam reform reaction, as is currently the most common way of producing hydrogen. At high temperature, the CH$_4$ will react with the steam which is also fed in to the anode. The products are: CO and 3H$_2$. The carbon monoxide can then react further with a reaction called:
• **Anode(2)**. *Water gas shift reaction*: \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)

This shift reaction also occurs before any reaction with the diffused oxygen ions occurs. Adding *Anode\(^1\)* and *Anode\(^2\)* will result in an overall 'pre-oxidation' reaction, shown next.

• **Anode\(^{(1+2)}\)**: \( \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \)

The newly created \( \text{H}_2 \) particles can then react with the oxygen ions in the same way they would in a normal SOFC.

• **Anode\(^{(3)}\)**: \( \text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \)

Both oxidation methods ensure methane reacts within the anode. At the cathode, oxygen molecules will become ions, diffuse through the electrolyte and react at the anode. Dependent on the type of methane oxidation, they will react directly with the methane or with the steam reformed hydrogen. Both cathode reactions, belonging to the different oxidation methods of methane, are summarized in the table 6.

<table>
<thead>
<tr>
<th>Table 6: SOFEC. Total and partial oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Oxidation</strong>, direct oxidation of methane</td>
</tr>
<tr>
<td>Anode</td>
</tr>
<tr>
<td>Cathode</td>
</tr>
<tr>
<td>Overall</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Partial Oxidation</strong>, steam reform and water gas shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>1+2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>Anode</td>
</tr>
<tr>
<td>Cathode</td>
</tr>
<tr>
<td>Overall</td>
</tr>
</tbody>
</table>

Obviously, both oxidation methods have the same resultant reaction. The most important difference between these reactions is the steam added to the anode. Total oxidation does not require the user to add steam to the anode. Pham did however mention that in his test set-up, he added steam. This was to ensure a minimum carbon deposition. As always, when a reaction has \( \text{CO}_2 \) as end-product, there is the possibility of some carbon forming on the electrode, resulting in a lower efficiency. To counteract this deposition, steam is added. But, once steam is added, the partial oxidation reaction can also occur. So there is actually no telling which reaction will eventually occur. After careful consideration, it seems obvious to assume the partial oxidation to be the dominant reaction. The steam must be
added to inhibit the carbon deposition which then ensures the reformation reaction to occur.

The SOFEC, and its intermediate steps, are summarized in the following figure 3.

![Diagram of a SOFEC](image)

**Figure 3:** Illustration of a SOFEC

The figure shows the in- and outlet gasses. Inside the callout box, the reforming reactions are noted. One can assume that these reactions occur very fast, and are therefore in good balance with the incoming CH\textsubscript{4}. This means that all the CH\textsubscript{4} entering the fuel cell, is almost instantly converted into CO and H\textsubscript{2} followed by the watergas shift reaction which also has no significant delay. Remarkable is, that this type of reaction is already a much used reaction for the SOFC. At the beginning of this chapter, fuel flexibility was mentioned as advantage of the SOFC. When methane and steam is added to the anode, the reformation reaction occurs. This is called a SOFC with **direct internal reforming**.

Looking at figure 3, one might have noticed that the anode and cathode have changed back when compared to the SOEC. This seems counterintuitive, as the SOFEC in essence performs the same reaction as the SOEC, namely the electrolysis of water. However, when looking closely at the oxidation and reduction reaction, it becomes obvious this is the only setup possible.

Lastly, a quantification of the involved energies must be made. The Gibb’s free energy musts be calculated to see what the new cell voltage will be. Due to its more complex nature, this will be the main subject of the next chapter. A full mathematical model will be proposed. The model will show how the cell voltage changes and how the resistance of the fuel cell affects the fuel cells performance.
4. Mathematical Model

The final goal will be to model a SOFEC in Cycle Tempo. Before this can be done, a distinction must be made between the different mathematical steps followed. A similar approach to the previous chapter will be used, where the SOFC and SOEC will be discussed independently. These will then be combined and applied to a model for the SOFEC.

4.1. Approach for the SOFC

The following mathematical model was devised from work already performed by A. de Groot [4]. During his research, he contributed to the actual implementation of the fuel cell model in to Cycle Tempo. His work will form the basis for both electrolysis fuel cells.

As mentioned in chapter 3, the reversible cell voltage at standard conditions of a fuel cell, will not change when using hydrogen as fuel. The (actual) reversible cell voltage will change depending on the temperature of the fuel cell, pressure and fuel utilization. To illustrate this, the following figure 4 is given that shows how the cell voltage changes while the temperature is increased. The following operating parameters are used:

- \( T \) = from 298 to 1300K
- \( U_F \) = 0.85
- \( P_{cell} \) = 1 bar
- \( Fuel \) = Hydrogen (\( H_2 \))

Recalling last chapter, equation 5 states that the standard reversible cell voltage of a hydrogen fuel cell is \(+1.18 \text{V}\). This will have to be adjusted according to the above mentioned parameters with the use of the Nernst equation (partial pressures are constant over the whole temperature range). As a result, \( E_{rev} \) will decrease while while the temperature rises, shown in the next figure.

![Reversible Cell Voltage vs Temperature](image)

_Figure 4: Reversible Cell voltage at changing temperature_
Figure 4 shows how the reversible cell voltage decreases when temperature increases. To familiarize the reader with all the different voltages, they are summarized below:

- \( E_0 \): Reversible Cell voltage at standard conditions. This voltage is shown in figure 4 as the upper dashed line at 1.18 V. This is the voltage the cell delivers under standard conditions without taking any resistances into account, leading to voltage drops.

- \( E_{\text{rev}} \): Reversible cell voltage or Nernst Potential. This is shown by the downward sloped straight line calculated by the Nernst equation. This is the maximum voltage the fuel cell is capable of achieving when using the operating parameters stated earlier.

- \( E_{\text{cell}} \): Cell Voltage. This voltage isn’t shown in the figure. \( E_{\text{cell}} \) indicates the actual output of the fuel cell once the voltage drops created by internal resistances are taken into account. This will be discussed in more detail later on.

Applying this knowledge to figure 4, the reversible cell voltage is visible below the reversible cell voltage at standard conditions. This corresponds with the factor, subtracted from the theoretical maximum cell voltage at standard conditions, as done in the Nernst equation. The reversible cell voltage (Nernst Potential) decreases, when the temperature increases. This means that the voltage, from which usable work can be retrieved, decreases and the heat losses increase. Normally, one would assume heat to be unusable and therefore no energy (work) can be retrieved from it. For a low temperature fuel cell, this is most definitely the case. For the SOFC on the other hand, the rest heat can even be hotter than 1000°C. This means that it could easily be used in an external turbine circuit to generate electricity. However, during this research no consideration will be given to using the rest heat. Only the actual cell voltage, current and delivered power will be used.

The SOFC gives a lower output voltage when the temperature is increased. This is unfavorable, as the output power will decrease with the same amount of current. However, for the SOEC and SOFEC, the voltage must be kept as low as possible. Therefore, the power supplied will be lower, but then the required heat must be higher.
Though the figure shows the dependency of the reversible cell voltage on the temperature, this is still not the whole case. The reversible cell voltage is the theoretically maximum voltage the fuel cell can deliver. In this case, no losses are taken into account that arise from a current passing through the cell. However, when the voltage is measured at 0 current, it is actually slightly less than the reversible cell voltage. This is called the Open Circuit Voltage (OCV). The output power of the fuel cell depends on the operating voltage of the fuel cell and the current passing through it. Higher voltage indicates lower resistances. This can also be an indication of less current passing through the fuel cell. The trick is to keep the voltage as high as possible with the largest current density. How the internal resistance of the fuel cell is accounted for, is shown in the following equation 9.

\[ E_{\text{cell}} = E_{\text{rev}} - \Delta V \]  

This shows that the actual cell voltage is calculated by subtracting the voltage drop, due to internal resistance, from the reversible cell voltage (OCV). The voltage drop \( \Delta V \) incorporates all the different voltage losses the current is subject to within the fuel cell and can be categorized in the following groups:

\[ \Delta V = \Delta V_{\text{pol,activation}} + \Delta V_{\text{pol,ohmic}} + \Delta V_{\text{pol,concentration}} \]  

These resistances are called polarizations or over-potentials. They are the result of several different factors including small imperfections in the materials, the specific microstructure and the design of the fuel cell. A brief description of the different losses, taken from the Fuel Cell Handbook [12], is given next.

- **Activation Polarization.** The voltage drop is due to complex kinetics involved with each electrochemical reaction. Without going into detail, this polarization essentially is a result of slow and inefficient electrochemical reactions. Catalysts are generally used to increase the and efficiency, and fuel cell performance critically depends on using the correct catalyst.

- **Ohmic Polarization.** The voltage drop due to this polarization is a result of the ionic resistance of the electrolyte and the electrodes and the electronic resistance of the electrodes, current collectors and contacts. Electrons are transported through an external circuit and in general undergo less resistance the the ions. These are often much larger and more massive than the electrons. The must travel through the electrolyte. This process, when compared to electron transportation, is much less efficient and can represent a significant resistance loss, reducing cell performance.
• **Concentration Polarization.** During the reactions occurring within the fuel cell, at least one product will be created. In the case of a hydrogen fuel cell, water will be created at the anode. If this water is not removed from the fuel cell, it will build up and eventually mix with the incoming fuel. Therefore, it is of importance that this is dealt with in order to prevent any voltage drops.

All these voltage drops can be quantified. The losses become more prominent in their contribution while in different current density ranges. The following figure illustrates the voltage drop, and is a typical representation of a flat geometry type fuel cell. The curve can differ slightly for different types of fuel cells.

![Figure 5: Different polarizations within the SOFC](image)

Throughout this report, only the flat plate/geometry type fuel cell will be considered. This type of fuel cell has a similar structure as the illustrations shown in the previous chapter and is one of the most commonly used geometries. Another often used geometry is the tubular form, but will not be discussed any further. Figure 5 shows the non-linear shape of the voltage drop. This curve indicates that precise simulation, within a mathematical model, will become quite elaborate and difficult. Due to the symmetry of the flat type fuel cell, numerous simplifications can be applied.

In general, a flat type cel has a resistance that is negligible over the length of the electrodes (electrodes run over the whole length of the fuel cell and electrons undergo only a very small resistance) in comparison to the ion transportation resistance through the electrolyte. This leads to the assumption that the voltage drop, over the electrodes in the direction of the flow of gasses (entrance to exit of anode or cathode), can be discarded. It can be assumed that the cell voltage ($E_{\text{cell}}$) is constant over the whole cell: $E(x) = E = \text{Constant}$. 

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From now on, the cell voltage will be noted as $E$ without the cell subscript. The local reversible cell voltage, however, will change within the fuel cell. This value depends on the partial pressure of the gasses and changes accordingly to the amount of used reactants. Therefore, the $E_{rev}$ will be position dependent: $E_{rev}(x)$. Lastly, the voltage drop, which follows Ohm’s law ($V = i \times R$), that depends on the changing local current density and constant resistance. This value is also position dependent resulting in an overall voltage drop that depends on it’s location: $\triangle V(x)$.

When taking these position dependent arguments into account, the rewritten version of equation 9 follows:

$$E = E_{rev}(x) - \triangle V(x) \quad (11)$$

Looking back at figure 5, and assuming negligible electrode resistances, the only thing left is the almost linear ohmic polarization. For sake of simplicity, the total voltage drop/loss will be linearized. It is therefore assumed that the whole voltage drop of the fuel cell is position dependent and equivalent to the local current density times a constant resistance.(Ohm’s Law: $V = i \cdot R$). This is shown in the following relationship:

$$\triangle V(x) = i(x) \cdot R_{ASR} \quad (12)$$

This can then be substituted into equation 11, resulting in:

$$E = E_{rev}(x) - i(x) \cdot R_{ASR} \quad (13)$$

In this equation, the **Area Specific Resistance**, $R_{ASR}$, is introduced and is given in [ohm m$^{-2}$]. The $R_{ASR}$ incorporates all the different resistances one might encounter. This includes ohmic, activation and concentration losses due to local resistance. N. Perdikaris et al. [8] performed a research on this, where they calculated the specific resistances of certain anode/electrolyte/cathode combinations. This is particularly handy when designing a fuel cell and determining the total resistance of the whole fuel cell.

The next step will be to create a model that can be used by Cycle Tempo. Firstly, an equation must be formulated describing the course of the voltage drop throughout the fuel cell. The best approach is dividing the fuel cell into many smaller subcells. Calculating these cells individually and then integrating over the whole fuel cell, will give a good representation of the local reversible cell voltage and current density.
To calculate the current of a subcell, the local current density must be multiplied by the area of the subcell dA:

\[ dI = i(x) \cdot dA \]  

(14)

By multiplying the local current density with the total amount of subcells, the total current of the fuel cell can be calculated. The local current can also be calculated through its relationship with the amount of electrons, Faraday’s constant and fuel flow. This will become particularly important later on.

\[ dI = zF d\epsilon_e \]  

(15)

This equation describes the change in current (dI) by multiplying the amount of electrons released during a reaction (z=2 for oxidation of hydrogen) with Faraday’s constant (F, amount of charge of 1 mole of electrons) and the change in fuel (d\epsilon_e). Substituting this into equation 14, and rewriting to local current density will result in the following:

\[ i(x) = \frac{dI}{dA} = \frac{zF d\epsilon_e}{dA} \]  

(16)

By rewriting equation 13,

\[ E = E_{rev} - i(x) \cdot R_{ASR} \rightarrow i(x) = \frac{E_{rev} - E}{R_{ASR}} \]  

(17)

and substituting equation 14 into this, the following formula can be obtained:

\[ zF d\epsilon_e = \frac{E_{rev}(x) - E}{R_{ASR}} \cdot dA \]  

(18)

A relationship is given where the amount of fuel used is directly proportional to the local voltage drop \( E_{rev} - E \) times the area of the subcell. The amount of fuel used is described in the reaction coordinate \( d\epsilon_e \). This parameter shows the reaction rate of the fuel in moles/s and is based on the amount of moles of H\(_2\). It is known that the SOFC is capable of running on a variety of fuels. After several different (depending on the used fuel) reactions, the incoming fuel is eventually converted into H\(_2\). In the case of CH\(_4\), the reformation and water-shift reaction turn 1 mole methane into 4 moles H\(_2\). When CO is used as fuel, 1 mole is shifted into 1 mole of H\(_2\). To incorporate this, the reaction coordinate can be rewritten:

\[ \epsilon_{e}^{max} = \varphi_a(x \cdot _{H_2}^0 + x \cdot _{CO}^0 + 4x \cdot _{CH_4}^0) \]  

(19)

The rewritten equation above illustrates that the maximum reaction coordinate is equal to the molar flow of the anode (\( \varphi_a \)) times the individual concentrations \( x \) of the components.
The max superscript above the reaction coordinate assumes a total utilization of the incoming fuels. This means, for instance, that one mole of methane would be converted into four moles of hydrogen. If this was used directly, 100% of the newly created hydrogen would be consumed within the anode. Obviously, this cannot be the case as it would create a problem when using the Nernst equation. Therefore, the maximum fuel flow is multiplied by the fuel utilization ($0 < U_F < 1$) to give the fuel flow as restricted by the fuel utilization. This is shown in equation 20:

$$I = zF_{e}^{max}U_F$$

(20)

The next step will be to incorporate this into equation 18. The problem is that this equation is based on the change in reaction coordinate, while equation 20 calculates the total fuel flow. This problem can be solved by introducing a new dimensionless variable:

$$d\lambda = \frac{de_e}{\epsilon_{max}}$$

(21)

The new lambda is a ratio of how much the local fuel flow divided by the total fuel flow is. The local fuel flow cannot exceed the fuel utilization. The maximum fuel flow is of course equal to 1 (100%). Therefore, the maximum value of $\lambda$ is bound by the fuel utilization, and will run from $0 - U_F$. Rewriting equation 21, where the local fuel flow is expressed in lambda and total fuel flow, and substituting this into equation 18 results in the following equation:

$$zF d\lambda \epsilon_{max} e = \frac{E_{rev}(\lambda) - E}{R_{ASR}} \cdot dA$$

(22)

The reader might have noticed that the $x$ has been changed for the dimensionless $\lambda$. This can be done because the fuel utilization, just as $x$, runs over the whole length of the fuel cell. It can therefore be assumed when at $x = 0$ the fuel utilization $U_F$ will also be zero, and $x = max$ at the end of the cell will be equal to the defined fuel utilization. The $E_{rev}$ can therefore also be integrated over $\lambda$. To calculate the whole fuel cell, the equation must first be rewritten to $dA$ equals:

$$dA = zF_{e}^{max} R_{ASR} \cdot \frac{d(\lambda)}{E_{rev}(\lambda) - E}$$

(23)

The whole fuel cell can now easily be calculated by integrating the left and right side. The left side must contain the total area of the fuel cell. The right side must be integrated over the total length of the fuel cell, which is equal to the fuel utilization.
4.2 Adjusting approach for a SOEC

The integration of dA leads to the area of the fuel cell which leads to the following equation:

\[ \frac{A}{zF\epsilon_{e}^{\text{max}}} = R_{ASR} \int_{0}^{U_{F}} \frac{d\lambda}{E_{\text{rev}}(\lambda) - E} \]  

Finally, by substituting the definition of I from equation 20, a new expression is given:

\[ \frac{I}{A} = \frac{U_{F}}{R_{ASR} \int_{0}^{U_{F}} \frac{d\lambda}{E_{\text{rev}}(\lambda) - E}} \]  

This final equation shows the correlation between I, V and A, with only the Nernst voltage depending on local partial pressure. This can be linked directly to \( \lambda \), allowing the integration of \( E_{\text{rev}} \) over \( \lambda \). The equation can be solved numerically, and that is exactly what Cycle Tempo currently does. The next step will be to adapt this equation for the situation involving hydrogen generation.

4.2. Adjusting approach for a SOEC

As shown in the last chapter, for a SOFC, the cell voltage is equal to \( E = E_{\text{rev}} - \Delta V \). This means that the cell voltage will be lower than the reversible cell voltage. For a SOEC, a different situation arises.

A SOEC electrolyzes water and will need a certain potential applied to it. A minimum voltage will be needed to electrolyze water plus an extra voltage to overcome the voltage drop. Therefore the cell voltage can be written according to the following relationship:

\[ E = E_{\text{rev}} + \Delta V \]  

Similar to the SOFC from figure 5, the voltage drop can be illustrated when increasing the current density [10]:

Again, the cell resistance over the electrodes in case of a flat plate type fuel cell is negligible. The same assumption can be made that the cell voltage will be constant over the whole length of the fuel cell. The \( E_{\text{rev}} \) and \( \Delta V \) are still position dependent, allowing equation 11 to be rewritten accordingly:

\[ E = E_{\text{rev}}(x) + \Delta V(x) \]  

T.U. Delft
F.K.B. WIJERS
4.3 Creating the SOFEC model

The final step will be to use these two mathematical models and combine them to make the SOFEC model. There are, however, some difficulties with the SOFEC. This device is a combination of the SOFC and SOEC. It electrolyzes water as the SOEC, but also oxidizes hydrogen as the SOFC. The final mathematical equations for the SOFC and SOEC are summarized below in table 7 as a quick reference:

With the basics covered, a start can be made for the SOFEC model. To show how it differs...
4.3 Creating the SOFEC model

**SOFC**

\[ E_{SOFC} = E_{rev} - \Delta V \]

**SOEC**

\[ E_{SOEC} = E_{rev} + \Delta V \]

\[ I = \frac{U_F}{R_{ASR} \int_{0}^{\lambda} \frac{d\lambda}{E_{rev}(\lambda) - E}} \]

\[ I = \frac{U_F}{R_{ASR} \int_{0}^{\lambda} \frac{d\lambda}{E_{rev}(\lambda) - E}} \]

<table>
<thead>
<tr>
<th>Table 7: Summary of the equations of the SOFC and SOEC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SOFC</strong></td>
</tr>
<tr>
<td>[ E_{SOFC} = E_{rev} - \Delta V ]</td>
</tr>
<tr>
<td><strong>SOEC</strong></td>
</tr>
<tr>
<td>[ E_{SOEC} = E_{rev} + \Delta V ]</td>
</tr>
</tbody>
</table>

Table 8: Summary of the equations of the SOFC and SOEC

From the SOEC model, it is best to create a simple example illustrating the differences in terms of cell voltage and power usage.

To begin with, an energy balance is given. It is known that adding CH\(_4\) has a de-polarizing effect, meaning that it is safe to predict that the SOFEC model will consume less power than the SOEC. This is best illustrated in the following table: a summarization of the energies associated with the different reactions occurring in the SOFEC.

<table>
<thead>
<tr>
<th>ANODE</th>
<th>Enthalpy</th>
<th>Entropy</th>
<th>Gibbs Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Steam Reform</strong></td>
<td>CH(_4) + H(_2)O \rightarrow 3 \cdot H(_2) + CO</td>
<td>-74.8 + (-241.8) \rightarrow 3 \cdot 0 + (-110.5)</td>
<td>(\Delta H = 206.0 \text{ kJ/mol})</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>Entropy</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Watergas shift</strong></td>
<td>CO + H(_2)O \rightarrow H(_2) + CO(_2)</td>
<td>-110.53 + (-241.8) \rightarrow 0 + (-393.5)</td>
<td>(\Delta H = -41.2 \text{ kJ/mol})</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>Entropy</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>H(_2) Oxidation</strong></td>
<td>4 \cdot H(_2) + 2 \cdot O(_2) \rightarrow 4 \cdot H(_2)O</td>
<td>4 \cdot 0 + 2 \cdot 0 \rightarrow 4 \cdot (-241.8)</td>
<td>(\Delta H = -967.2 \text{ kJ/mol})</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>Entropy</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CATHODE</th>
<th>Enthalpy</th>
<th>Entropy</th>
<th>Gibbs Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H(_2)O Electrol.</strong></td>
<td>4 \cdot H(_2)O \rightarrow 4 \cdot H(_2) + 2 \cdot O(_2)</td>
<td>4 \cdot (-241.8) \rightarrow + 4 \cdot 0 + 4 \cdot 0</td>
<td>(\Delta H = +967.2 \text{ kJ/mol})</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>Entropy</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>Enthalpy</td>
<td>206 - 41.2 - 967.2 + 967.2</td>
<td>(\Delta H = 164.8 \text{kJ/mol})</td>
</tr>
<tr>
<td>Entropy</td>
<td>214.7 + (-30.7) + (-177.7) + 177.7</td>
<td>(\Delta S = 184 \text{ J/K})</td>
<td></td>
</tr>
<tr>
<td>Gibbs energy</td>
<td>(\Delta G = \Delta H - T(298K)\Delta S)</td>
<td>(\Delta G = 110\text{kJ/mol})</td>
<td></td>
</tr>
</tbody>
</table>

The anode reactions are summarized and the associated enthalpy and entropy changes are given. The initial reformation is endothermic, followed by the exothermic watergas shift reaction. Finally, the newly created hydrogen oxidizes while releasing energy. At the cath-
ode, water is electrolyzed while energy is provided. The most important conclusion that can be drawn from this table is: the oxidized hydrogen at the anode, and the electrolyzed water at the cathode effectively counteract each other. Therefore, the only energies of importance are those of the reformation and watergas shift reaction. Subtracting these values from each other results in a positive enthalpy of 164.8kJ/mol. The same can be done for the entropy, shown under the total row. From this, the final Gibb's free energy can be calculated under standard conditions. This results in a Gibb's energy of 110kJ/mol of CH$_4$. The fuel cell will require at least 110kJ per mole of CH$_4$ to create 4 moles of H$_2$. Compare this to the energy needed per mole of H$_2$ by the SOEC, and it is obvious how much more efficient the SOFEC is.

This total net energy, however, cannot be used directly in the Nernst equation. The reversible cell voltage is calculated, based on the electrons through the external circuit. This means that the reformation reaction plays no part in the actual calculation of the Nernst potential. The reformation of methane occurs at the entrance of the anode, and all reactions happen instantaneously. The only reactions left are the oxidation of hydrogen at the anode and the electrolysis of water at the cathode. From table 8, one can see that these reactions have an enthalpy and Gibb's free energy that are equal, but opposite, in absolute amount. The Nernst potential is therefore only based on the difference in concentrations of reactants and products in the anode and cathode. For the SOFC, the Nernst equation is straightforward, but for the SOFEC, a few additional steps need to be taken into account. Instead of giving it directly, the next paragraph will show how it is obtained from the fundamental thermodynamics.

**4.4. Reversible work retrieved from a fuel cell**

The SOFC is based on the oxidation reaction of hydrogen with the diffused oxygen ions. To calculate the amount of reversible work retrievable from this reaction, it must be split up in the following parts:

1. **Compression** of H$_2$
2. **Compression** of O$_2$
3. **Expansion** of H$_2$O

The first two compression processes are to bring the reactants to standard pressure. Therefore, when they react in the reversible process, the work retrievable will also be at standard
pressure and temperature. It will be equal to Gibb’s free energy released during the oxidation of hydrogen calculated earlier, which is also at standard conditions. Once the reversible process has taken place, the resultant water must then be returned to the original operating conditions, and is therefore expanded. The three reactions mentioned above can be coupled as shown in the following figure:

![Diagram of reversible work from the oxidation of hydrogen](image)

**Figure 7:** Reversible work from the oxidation of hydrogen [2]

First, both reactants are compressed to standard pressure ($p_0$). At standard pressure, they react to form water while also releasing energy. The product (water) must then be expanded to the same pressure as the reactants before the reaction. This also involves work and summed up, they form the reversible work retrievable from a fuel cell. This can be calculated through basic thermodynamics stated in the following equation:

$$W_{rev} = -\int_{in}^{out} V \cdot dp$$ (33)

Depending on whether a compression or expansion is calculated, the integral will run from either $p_0$ to $p_i$ or the reverse of that.

Because the volume is constant it can therefore be substituted with the ideal gas law stated shown next:

$$PV = nRT$$ (34)

Substituting this into equation 33, the following equations can be deduced describing the work obtainable from either a compression or expansion of a gas:

$$W_{rev}(compression) = R \cdot T \cdot \ln \left( \frac{p_i}{p_0} \right)$$ (35a)
\[ W_{\text{rev}}(\text{expansion}) = R \cdot T \cdot \ln \left( \frac{p_0}{p_i} \right) \]  

(35b)

Applying this knowledge on the different (compression and expansion) steps shown in figure 7, the following equations can be stated:

<table>
<thead>
<tr>
<th>Table 9: Reversible isothermal combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression ( \text{H}_2 )</td>
</tr>
<tr>
<td>Compression ( \text{O}_2 )</td>
</tr>
<tr>
<td>Expansion ( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Reversible Reaction</td>
</tr>
</tbody>
</table>

In this table, the reversible work has been adjusted according to the partial molar flows of the different components and the reaction ratio between the reactants. The \( y \) indicates their partial molar flow, equal to the earlier discussed partial pressures derived from the fuel utilization. Because the volume of a gas only depends on temperature (which is constant in an isothermal combustion) and pressure, and not on the molecule it is made up of, these partial pressures must add up to 1. Finally, the superscript indicates the ratio at which the reactants interact with each other. By summing the individual contributions, the reversible work retrievable from the fuel cell can be calculated:

\[ W_{FC,\text{rev},SOFC} = \sum_n W_{\text{rev}} \]

\[ = R \cdot T \cdot \ln \left( \frac{y_{\text{H}_2} \cdot \text{p}}{p_0} \right)^1 + R \cdot T \cdot \ln \left( \frac{y_{\text{O}_2} \cdot \text{p}}{p_0} \right)^{0.5} \]

\[ + R \cdot T \cdot \ln \left( \frac{p_0}{y_{\text{H}_2\text{O}} \cdot \text{p}} \right)^1 - \Delta G \]

\[ = -\Delta G + R \cdot T \cdot \ln \left( \frac{y_{\text{H}_2} y_{\text{O}_2}^{0.5}}{y_{\text{H}_2\text{O}}} \left( \frac{\text{p}}{p_0} \right)^{0.5} \right) \]

(36)

This equation looks very similar to the Nernst equation (equation 6) stated earlier. The reversible work obtained from 1 mole of fuel in a reversible fuel cell is equal to:

\[ W_{\text{electr,rev}} = -n \cdot F \cdot E_{\text{rev}} \]

(37)

Dividing the last line of equation 36 by \( n \cdot F \), allows the calculation of the Nernst voltage. This process can also be done for the SOEC, where now the combustion and expansion
processes have switched places. This results in the following reversible work:

<table>
<thead>
<tr>
<th>Table 10: Reversible isothermal combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Expansion $\text{H}_2$</td>
</tr>
<tr>
<td>Expansion $\text{O}_2$</td>
</tr>
<tr>
<td>Reversible Reaction</td>
</tr>
</tbody>
</table>

The reversible work from the electrolyzer can be retrieved in a similar way:

$$W_{\text{FC,rev,SOEC}} = \sum_n W_{\text{rev}}$$

$$= -\Delta G + R \cdot T \cdot \ln \left( \frac{y_{\text{H}_2\text{O}}} {y_{\text{H}_2} \cdot y_{\text{O}_2}^{0.5}} \cdot \left( \frac{p_0} {p} \right)^{0.5} \right)$$

(38)

The next step will be to combine these two to create the Nernst equation for the SOFEC.

This simplified SOFEC will look as follows:

![Illustration of a simplified SOFEC](image)

From this figure, it could be deduced that the reversible work of the SOFEC will be a combination of the reversible work from the SOFC and SOEC. The combined Gibb’s free energy at standard conditions of both reactions must result to 0. They are equal in size, but with opposite signs.

However, directly adding the reversible work of SOFC and SOEC will result in a correct final equation, but it is important to understand that for the SOFEC, there is no concentration of oxygen. There are only oxygen ions created at the cathode and consumed at
4.4 Reversible work retrieved from a fuel cell

the anode. Therefore, oxygen does not take part in the partial pressures of the anode and cathode gas flow. Taking this into account, a new expansion and compression figure can be given as shown next:

![Diagram](image_url)

Figure 9: Illustration of a simplified SOFEC

In this case, oxygen has been taken out of the equation. Now, the hydrogen from the anode and the water from the cathode must be compressed to standard pressure. In the reversible process, both the oxidation and electrolysis reaction take place. Therefore, the $\Delta G$ will be zero. Once the reactions have taken place, the final products must again be expanded. If each process is dealt with separately according to the definition of work, the following reversible work is retrievable, summarized in the next table:

<table>
<thead>
<tr>
<th>Process</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression $\text{H}_2(\text{a})$</td>
<td>$W_{\text{rev}} = R \cdot T \cdot \ln \left( \frac{y_{\text{H}_2(\text{a})}P}{p_0} \right)^1$</td>
</tr>
<tr>
<td>Compression $\text{H}_2\text{O}(\text{c})$</td>
<td>$W_{\text{rev}} = R \cdot T \cdot \ln \left( \frac{y_{\text{H}_2\text{O}(\text{c})}P}{p_0} \right)^1$</td>
</tr>
<tr>
<td>Expansion $\text{H}_2\text{O}(\text{a})$</td>
<td>$W_{\text{rev}} = R \cdot T \cdot \ln \left( \frac{p_0}{y_{\text{H}_2\text{O}(\text{a})}P} \right)^1$</td>
</tr>
<tr>
<td>Expansion $\text{H}_2(\text{c})$</td>
<td>$W_{\text{rev}} = R \cdot T \cdot \ln \left( \frac{p_0}{y_{\text{H}_2(\text{c})}P} \right)^1$</td>
</tr>
<tr>
<td>Reversible Reaction</td>
<td>0</td>
</tr>
</tbody>
</table>

Similar to how the SOFC equation was deduced, now all the reversible work contributions can be added as follows:
4.4 Reversible work retrieved from a fuel cell

\[ W_{FC,rev,SOFEC} = R \cdot T \cdot \ln \left( \frac{y_{H_2(a)} \cdot p}{p_0} \right)^1 + R \cdot T \cdot \ln \left( \frac{y_{H_2O(c)} \cdot p}{p_0} \right)^1 \]
\[ + R \cdot T \cdot \ln \left( \frac{p_0}{y_{H_2O(a)} \cdot p} \right)^1 + R \cdot T \cdot \ln \left( \frac{p_0}{y_{H_2(c)} \cdot p} \right)^1 \]
\[ = R \cdot T \cdot \ln \left( \frac{y_{H_2(a)} \cdot y_{H_2O(c)}}{y_{H_2O(a)} \cdot y_{H_2(c)}} \right)^1 \] (39)

This final equation allows the calculation of the reversible work obtained from a SOFEC running on pure hydrogen. It is only dependent on the partial pressures of hydrogen and water at the anode and cathode. Oxygen has been removed completely from the equation. Furthermore, the operating pressure of the fuel cell is no longer of influence.

From this equation, it can easily be deduced that if the fuel utilization is 0.5, the reversible cell voltage will be exactly 0. The partial pressure of each component will be 0.5, resulting in a logarithm of 1.

Changing the ratio at which \(H_2O\) enters the cathode will also alter the reversible cell voltage. Each ratio of molar flows will have its own fuel utilization for which the logarithm will become 0. The following figure shows the change in reversible cell voltage when cathodic flow of water is changed at \(T = 1273K\):

![Reversible Cell voltage with changing molar flow cathode at T=1273K](image)

**Figure 10:** \(V_{rev}\) at changing cathodic \(H_2O\) flow
Important to note out is that when changing the cathodic flow of water, the utilization of the water will also change. The only situation in which the utilization of hydrogen at the anode and water at the cathode can be the same is in the situation of equal molar flows.

This graph also indicates at what cathodic water flows and fuel utilization this SOFEC can either produce or consume power. Consider the case for $U_F$ is 0.5 and the ratio between $H_2$ and $H_2O$ flow is 1:1. To the left of $U_F=0.5$, the SOFEC will be able to produce (as well as consume) power, and to the right, only power consumption is possible. The graph looks similar to the SOFC, while also having the ability to generate hydrogen. This will be explained next.

4.5. Comparing all three models

The mathematical models describe the relationship between the current density, cell voltage and reversible cell voltage of all fuel cells. The next step will be to plot their cell voltages as a function of current density. The voltage drops of a SOFC and the SOEC are shown in figure 5 and figure 6. The SOFEC curve will be in the same current density region as the SOFC (both positive). However, the reversible cell voltage at standard conditions will be 0, as shown in equation 39. If the current is increased (fuel is being used), the reversible cell voltage will be greater than 0 up until the point where the concentrations of hydrogen and water at the anode and cathode are equal. Once the current density increases further, the reversible cell voltage will become smaller than 0.

This is shown in the following figure:
From the top figure (which is based heavily on SOEC voltage curve taken from Rauch [10]), it becomes clear how the voltage of the different fuel cells change according to the change in current density. The SOFC has a cell voltage smaller than the reversible cell voltage when increasing the current density. The SOEC must consume power and has a cell voltage larger than the reversible cell voltage, in accordance to equation 7. The SOFEC curve has been taken from the previous paragraph. At low current densities, the reversible cell voltage can be positive. Increasing the current density decreases the voltage up to a point where it becomes negative. Its effect is best shown in the power graph.

The second graph shows the power production or consumption of the different fuel cells while increasing the current density (The values for this graph are calculated based on cell voltage and current density of the top graph). From the multiplication of the voltage with current density, the power graph can be drawn. The SOFC has a positive volt and current density, and therefore a positive power production. This same logic can be applied to the SOEC and SOFEC, where they either have a negative or positive current density or cell voltage resulting in a power consumption or production. (Looking closely at the power curve of the SOFEC, one can see the power is positive up till a certain current density). From the power curves, it becomes obvious that the fuel cells cannot be scaled linearly indefinitely. At the beginning and end of the curves, the activation and concentration overpotentials have
a dominant effect, resulting in proportionally larger power changes. The straight parts are caused by the predominantly linear contribution of the ohmic overpotential.

The most obvious conclusion that can be drawn from the power curves is the difference between the SOEC and SOFEC. The theoretical power distributions are given, and the accentuated area shows the difference in power consumption between both devices. This power consumption is compensated in the SOFEC due to the added methane. As mentioned in the introduction, it is much cheaper to provide this power from methane than electricity, which makes this device so interesting.

A mathematical foundation is laid for the new SOFEC model. Fortunately, this was widely based on the well developed SOFC model, following the same cell voltage calculation \( E = E_{\text{rev}} - \Delta V \). Adaptation for the regenerative model only required modest changes. It must be noted that these graphs are highly theoretical. The exact curve of the cell voltage will, of course, differ per fuel cell, making a generic model hard to formulate. It does, however, show the potential of the SOFEC in contrast to the SOEC. An obvious decrease in power usage would normally be used just to overcome the initial decomposition voltage of water. In the next chapter, this mathematical description will be implemented into Cycle Tempo.
Part II.

Programming and Simulation

5. Cycle Tempo

Cycle-Tempo is an elaborate thermodynamic system simulator designed at the TU Delft. This simulator has been in development since the 1980’s, and has had numerous updates since then. It wasn’t till Arend de Groot [4], who made it part of his PhD research, that the fuel cell model was introduced into Cycle Tempo. The program is capable of simulating almost all different types of fuel cells. As new applications for fuel cells are constantly being developed, so also must Cycle Tempo be updated to be able to facilitate these new modes of operations. Due to the complexity of the program and the limited research performed on SOEC’s and SOFEC’s, integration will require a breakdown into different steps.

In the appendix A, an introduction to Cycle Tempo is given. Basic setup instructions and all parameters used in the following paragraphs are covered.

This chapter starts with a flow chart of the SOFC model, describing the steps performed by Cycle Tempo. Within the different steps, certain mathematical subroutines are distinguished. These are broken down and analyzed. A theorized flow chart follows for the SOEC and SOFEC. It contains the new and altered steps needed to facilitate these adjusted modes of operation.

5.1. SOFC

The SOFC model, shown in the previous chapter, is modeled and calculated according to strict procedures within Cycle Tempo. The followed routine is shown in the next figure, which gives a simplification of all steps taken. It outlines the input and output parameters, most important for this particular fuel cell situation.
5.1.1. SOFC Flow Chart

The following figure shows the inputs, operational steps and outputs of Cycle Tempo. The inputs are linked directly to outputs through different calculation steps. The operations performed by Cycle Tempo can be categorized in different steps, as is shown in the following figure:

![Flow Chart SOFC](image)

**Figure 12: Flow Chart SOFC**

The flow chart is divided into three columns that each contain different steps:

1. **INPUT.** The left side of the flow chart shows the different inputs of importance. Though all mentioned inputs, described in appendix A are used, only the most important are highlighted here: **UFL** (fuel utilization), **PFCELL** (pressure of the fuel cell), **TFCELL** (operating temperature of the fuel cell), **RCELL** (area specific resistance). Next to these, the parameters used in equation 26, described in the mathematical approach, are given: **CDENS** (current density), **VOLT** (fuel cell voltage), **POWER** (power of fuel cell), **FLOW** (flow of H2).
and **POWER** (fuel cell power output). They will be discussed in detail later on.

2. **OPERATIONS.** The middle column shows the steps taken within Cycle Tempo. These consist of reading in the user defined inputs, performing calculations and then outputting the results. Depending on the user-defined input, the routine sequence will change for the SOEC and SOFEC, as will be discussed in the following paragraphs.

3. **OUTPUT.** The right column consists of all the outputs of Cycle Tempo. These results describe how the fuel cell has functioned under the user-defined inputs.

Instead of the Input, the operations of Cycle Tempo will be discussed first. This column, and its steps, form the back-bone of Cycle Tempo. It will provide an overall idea of how the source code is built up. The first five steps are performed unconditionally. Though certain checks are performed, verifying user input and its feasibility, these steps will not change. During step 6, the conditional inputs, VOLT, CDENS and POWER, that define how the program continues, are used. They will be mentioned individually afterwards. The output speaks for itself, and requires no further explanation. Next follows a summarization of the procedure, shown in the operational column. The numbers correspond to those, used in the flow chart, and will from now on be called 'steps'.

1. In this step, the composition of the **incoming anode flow** at the active cell area is calculated, depending on what type of fuel cell the user has defined, Cycle Tempo allows the option to choose whether the system will make use of reforming. In this situation: the simple SOFC, no reforming will be used at all. This is confirmed by the use of pure hydrogen as fuel. This simplifies step 1 drastically. Therefore, the incoming composition will be the same as the composition at the active cell area, reducing step 1 to merely writing the input to the output **YAN[1:NCOMP]**.

2. During this step the **outgoing flow of the anode** is calculated. On the left hand side, one can see that the first parameter entered by the user is used: **UFL**. This UFL determines the amount of fuel used, and is therefore important to calculate the outgoing anode flow composition. By multiplying the inlet composition with the utilization: 100% H\textsubscript{2} \times UFL, the output composition is obtained. This is shown in the figure to the right of step 2, where is is written to **CONC[LAOUT.1:NCOMP]**.

3. This step becomes more complicated, where the **outgoing composition of the cathode** will be calculated. This is broken down in the following parts:
   - Calculating the amount of **H\textsubscript{2} equivalents** that exist in the anode.
     This is done with help of the anode entrance flow. With a known incoming
fuel, and whether or not reforming takes place, calculation of the amount of H\textsubscript{2} equivalents is straightforward. (See the mathematical model equation 19, where different fuels are taken into consideration)

- Once the equivalents are known, it is multiplied with the UFL to give the amount of H\textsubscript{2} used. This then determines the minimum amount of oxidant needed. Cycle Tempo knows that per H\textsubscript{2} equivalent it will need $\frac{1}{2}$O\textsubscript{2}. The ratio between those two is called the OFRAT (oxygen fuel ratio).

- Depending on the incoming composition of the cathode, Cycle Tempo can now calculate the outgoing composition.
  In a normal situation, air would be added to the cathode, and therefore the outgoing composition would change depending on the amount of O\textsubscript{2} used. This model uses pure oxygen meaning the composition won’t change, only the mass flow.

4. During this step, all enthalpies, pressures and temperatures are obtained. Depending on the user input, Cycle Tempo will calculate:
   - Any pressure drops over either anode or cathode.
   - Temperature changes associated with difference in inlet, outlet and operating temperatures.
   - Correct enthalpies according to the components of the anode and cathode flow.

5. At this point, the reversible cell voltage (EREV) is calculated.
   The Nernst equation, with the predefined UFL and the Gibb’s free energy of the reactions at the anode and cathode, is used.

6. The final step connects the dots. Depending on the input, Cycle Tempo will perform iterations, if necessary, to calculate the remaining values. As shown in figure 12, the user is able to choose between different inputs. Providing more than one of these values, will create an error as these values are all dependent of each other. (This is shown in equation 26).

The importance of this step will become clear later on, where a detailed description is given of the possible sub-routines. These sub-routines are also subject to change with the implementation of the SOEC and SOFEC models.
If all the user defined values are within a remotely plausible range, the program will give a correct output with the amount of iterations performed. Once finished, a whole range of figures and tables can be evoked. They can come in handy when performing an efficiency analysis. This efficiency analysis will not be discussed any further in this report.

As mentioned in step 6*, Cycle Tempo contains a couple of important equations, where the following table 12 shows the dependence of the different inputs: CDENS, VOLT and POWER. They are all used in one and the same equation. Depending of the variable given, the formula is either filled in directly or the voltage is iterated. An explanation of this process follows.

### Table 12: Equations used in the subroutines

<table>
<thead>
<tr>
<th>Equation</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta V_{SOFC/SOFEC}$</td>
<td>$\Delta V = \left( \int_0^{U_F} \frac{dx}{E_{rev}(x)-E} \right)^{-1}$</td>
<td>Voltage drop derived in the previous chapter (SOFEC follows same derivation as SOFC, as for SOFEC: $E = E_{rev} - \Delta V$ also holds.</td>
</tr>
<tr>
<td>$\Delta V_{SOEC}$</td>
<td>$\Delta V_e = \left( \int_0^{U_F} \frac{dx}{E-E_{rev}(x)} \right)^{-1}$</td>
<td>Voltage drop for either the SOEC (Subscript e stands for electrolysis)</td>
</tr>
<tr>
<td>$V_{CDR}$</td>
<td>$i = \frac{U_F}{R_{ASR}} \times \left( \int_0^{U_F} \frac{dx}{E_{rev}(x)-E} \right)^{-1}$</td>
<td>Voltage as a function of current density and cell resistance. Same equation as CD_{VR}, but the voltage is retrieved through iteration.</td>
</tr>
<tr>
<td>$CD_{VR}$</td>
<td>$i = \frac{U_F}{R_{ASR}} \times \Delta V$</td>
<td>Current density as a function of cell voltage and cell resistance.</td>
</tr>
<tr>
<td>$V_{PDR}$</td>
<td>$P = i \times E = \frac{U_F}{R_{ASR}} \times \Delta V \times E$</td>
<td>Voltage as a function of power density and cell resistance. Again, the voltage is retrieved through iteration.</td>
</tr>
</tbody>
</table>

In the following paragraphs, each of the routines will be explained separately. They are
evoked when either of the inputs is given. (CDENS, VOLT or POWER).

To begin, the subroutine used when CDENS (current density) is given. Furthermore, in each situation, the user is required to define an ACELL (area of the fuel cell) and RCELL (resistance of the fuel cell) in order for the voltage drops to be calculated correctly. This will not be discussed anymore in the following paragraphs, only the calculation process is shown and the variables required by Cycle Tempo to correctly perform its calculations.

5.1.2. CDENS provided

The following parts of code are obtained from the fuel cell manual, written by T. van der Stelt [13], who currently co-provides support for Cycle Tempo. This is not the actual code, but a simplified version written in 'pseudo' code. This is more intuitive and easier to understand without having any knowledge in Fortran programming. The actual code, and its adjustments, will be discussed in detail in the next chapter.

\[
\begin{align*}
\text{if given CDENS then} \\
\text{VOLT} &= V_{\text{CDR}} \\
\text{CURR} &= \text{CDENS} \times \text{ACELL} \\
\text{POWER} &= \text{CURR} \times \text{VOLT} / 1000 \\
\text{FLFUEL} &= \text{CURR} / (X_{\text{H2EQ}} \times \text{UFL} \times 2 \times \text{FAR})
\end{align*}
\]

Table 13: SOFC 1\textsuperscript{st} Subroutine: CDENS

The code shown in the Table 13 shows the operations performed with CDENS as the starting point.

First off, the voltage is calculated with the \texttt{V\_CDR} routine. This equation is similar to the \texttt{CD\_VR} routine, except that $\Delta V$ is rewritten explicitly to show the dependence on the cell voltage $E$.

The $\Delta V$, also shown in the table as the first equation, is almost exactly the same as the equation from the mathematical chapter, with the only difference being that the $\lambda$ has been changed for an $x$. This has no effect on the end result, and to maintain resemblance to the Cycle Tempo code, $x$ will be used from now on.

The second line of code describes how the voltage is retrieved from the \texttt{V\_CDR} subroutine. The user defined current density is the solution of the equation, where the voltage must be iterated. Cycle Tempo calculates a voltage from the equation by repeatedly filling in different voltages and checking if it is equal to the user provided current density. Since Cycle Tempo has no idea where to start, the user must define an \texttt{ESTVLT}. This is an estimated voltage, where one assumes the cell voltage will lie around. The estimated cell voltage must be provided in all situations where no VOLT is given.
Once the voltage is calculated the current is obtained with the user-defined CDENS multiplied by the fuel cell area.

Afterwards, the power is obtained from the newly calculated voltage and Joule’s law: $P = V \cdot I$, resulting in the power provided by the fuel cell.

The final flow of fuel is calculated with Faraday’s law: $I = zF\epsilon_{e}^{max}U_{F}$. Recalling equation 19, one can see how $\epsilon_{e}^{max}$ can be split into its composition components of $\text{H}_2$ equivalents per type of fuel ($\text{H}_2$, CO or $\text{CH}_4$) times the mass flow. By rewriting Faraday’s law to the mass flow of fuel in terms of the rest, as shown in the code, the FLFLOW can be calculated. The amount of fuel needed can be used, in combination with UFL, and OFRAT to calculate all remaining unknown mass flows of the anode and cathode. (Remember that in steps 1-3 of the flow chart, the compositions are calculated. Final mass flows are obtained after FLFLOW is calculated)

### 5.1.3. VOLT provided

In this situation, VOLT is provided and Cycle Tempo will now calculate the CDENS and POWER from this.

The code as retrieved from the manual:

```java
if given VOLT then
  CDENS = CD\_VR
  CURR = CDENS \cdot ACELL
  POWER = CURR \cdot VOLT / 1000
  FLFUEL = CURR / (XH2EQ \cdot UFL \cdot 2 \cdot FAR)

Table 14: SOFC 2\textsuperscript{nd} Subroutine: VOLT
```

This first step involves calculating the current density with help of the subroutine CD\_VR. All the provided input parameters are used and with VOLT already given, no ESTVLT is needed. With the acquired CDENS, the rest of the steps are straightforward. Current density multiplied by the area of the fuel cell equals the current. To calculate the power delivered by the fuel, this is then used in combination with the cell voltage. Afterwards, the fuel flow is calculated in a similar way as the CDENS situation.

### 5.1.4. POWER provided

Lastly, the situation involving a user provided power. This is a more common approach than the others. The power is probably the most important design parameter for a fuel cell
developer. One would want a fuel cell which is capable of delivering a certain amount of output power. The following subroutine will be invoked:

```
if given POWER then
    PDENS = POWER * 1000 / ACELL
    VOLT = V_PDR
    CDENS = PDENS / VOLT
    CURR = CDENS * ACELL
    FLFUEL = CURR / (XH2EQ * UFL * 2 * FAR)
```

Table 15: SOFC 3rd Subroutine: POWER

An extra step has to be made here. As for the first two routines, Cycle Tempo is calculating in densities. Therefore, the POWER will first need to be converted into a power density. This is why for the first code line, the needed power is divided by the fuel cell area. Afterwards the V_PDR equation is used. This equation, again, is very similar to the earlier mentioned formula V_CDR. By multiplying it with an extra voltage (E) and then iterating with ESTVLT to make the right side of the equation equal to the provided POWER, a cell voltage can be obtained. The next step is to calculate the current density. This is done by dividing the power density by the newly obtained cell voltage.

Once the current density is known, this is multiplied by the cell area, resulting in the current. Again, the current is a direct measure of the amount of electrons passing through per second, and can therefore be converted into fuel flow with Faraday’s law finishing the calculation cycle.

### 5.1.5. FLFUEL provided

The last approach allows the user to define the amount of fuel added to the fuel cell. Cycle Tempo will then calculate the VOLT, CDENS and POWER based on the amount of hydrogen fed to the anode. This is shown in the following table:

```
if given FLFUEL then
    CURR = FLFUEL * (XH2EQ * UFL * 2 * FAR)
    CDENS = CURR / ACELL
    VOLT = V_CDR
    POWER = CURR * VOLT / 1000
```

Table 16: SOFC 4th Subroutine: FLFUEL

This approach is also straightforward. The current is retrieved from the fuel flow, and more specifically, the H₂ equivalents. Based on the fuel, this will differ. Afterwards, the
current density can be derived from this, which is then used to iterate the cell voltage. Finally, the power can be obtained by multiplying the cell voltage times the current.

In the case of an electrolyzer, these approaches must be modified. The fuel cell will now consume power to create hydrogen. The approach devised is shown in the following paragraphs.

5.2. SOEC

The reverse oxidation reaction brings along some elementary changes to the flow chart. With no hydrogen present to oxidize, the reaction is now restricted by the utilization of water.

5.2.1. SOEC Flow Chart

An altered flow chart is given in the following figure, illustrating the changes made when compared to the SOFC. Recalling figure 2 of the SOEC, one will have noticed the fact that the cathode is now the electrode where the main reaction occurs. Cycle Tempo is based on performing it’s calculations from the perspective of the anode. To facilitate this change, two options have been researched:

1. **Maintaining a calculation based on the anode exiting flow.** (Only oxygen will be exiting the anode).

   Designing a SOEC based on the anode output of oxygen, and then calculating the remaining flows at the cathode. There would be no use for the UFL at the anode, as this amount is in direct proportion to the amount of electrons freed at the cathode and the total current. The UFL would now be applied to the water, being electrolyzed at the cathode. Summarized this would mean:

   - The user defines the flow of O\(_2\) coming out of the anode.
   - This flow must then be converted into a current (one mole O\(_2\) is equal to 4 mole electrons). The current will be directly proportional to how much water is electrolyzed.
   - The electrolyzed water is equal to the amount of H\(_2\) and half the amount of O\(_2\) exiting the cathode.
   - The exiting water at the cathode is equal to 1 minus the water utilization.
   - The incoming cathode-water can be calculated by dividing the amount of electrolyzed water by the fuel utilization.
This approach does not seem very intuitive, and would only allow the user to define his fuel cell by the amount of oxygen exiting the cathode. Furthermore, only the FL-FUEL subroutine (which will be discussed later on) would be able to calculate this operational mode, and even then, it would have to be modified.

The other option is a cathode based calculation. This leads to the next option:

2. **The cathode will become the defining electrode.**

The amount of entering H$_2$O and its conversion will now be design parameters of the fuel cell. The user will provide a utilization that will be used to calculate the outgoing cathodic H$_2$. The most radical change must now be a flow chart that uses the cathode as starting point. From there on, the hydrogen equivalents will be calculated, resulting in an oxidant fuel ratio and finally in an anodic exit flow of oxygen. This approach is harder to implement, but is much more logical. The user will now be able to design a fuel cell based on the amount of H$_2$ he wants it to produce. This is merely dividing the H$_2$ by the water utilization to get the amount of H$_2$O needed at the cathode entrance.

After careful consideration, the *second option* has been chosen. It is more logical, but will also be more challenging when actually adding it to the code.

Based on this approach, the following flow chart for the SOEC can be given. The new and altered blocks have been accentuated.
The most obvious change is the switch from anode to cathode. The cathode is now used as starting point. The individual steps are discussed next. Many of these steps will be similar to those shown in the SOFC situation.

1. First, the incoming fuel (water) composition of the cathode at the active cell area will be calculated.
   Just as with the SOFC, 100% pure fuel is assumed, and therefore the incoming concentration $\text{CONC}[\text{LK},1:\text{NCOMP}]$ will be the same as the new output variable: $\text{YKA}[1:\text{NCOMP}]$, which is similar to the variable used in the SOFC mode (based on the anodic approach).
2. In step 2, the outgoing cathode flow will be calculated.
The amount of fuel (water) converted will be calculated. This conversion will be limited by the UFL, with which the resultant output flow can be calculated. The variable \( \text{CONC[LKOUT,1:NCOMP]} \) will contain information about the amount of \( \text{H}_2\text{O} \) left, and the amount of \( \text{H}_2 \) created.

3. During step 3, calculations are performed on the outgoing composition of the anode.
This step will be much simpler than the SOFC. Since no gas is added to the anode, only the amount of \( \text{O}_2 \), which can be formed from the diffused oxygen ions, needs to be calculated. As with the SOFC, first the \( \text{H}_2 \) equivalents need to be calculated. This will be equal to incoming cathode flow times UFL (resulting in the amount of \( \text{H}_2\text{O} \) electrolyzed). The ratio of this flow, with the outlet anode flow, will result in the OFRAT. Quick comparison of the reactions shows that this will be half of the flow of the cathode, \( \text{H}_2\text{O} : \text{O}_2 \rightarrow 2:1 \).

4. Step 4 will be the same as the SOFC and will calculate all the pressures, temperatures and enthalpies.

5. Step 5 will calculate the reversible cell voltage \( E_{\text{REV}} \). The Nernst equation shown in 38, will be used. (This will need to be coded into Cycle Tempo).

6. Step 6. As with the SOFC, this step will be discussed in more detail in the following paragraph.

The most important differences are accentuated within the flow chart. Overall, the chart looks similar to the SOFC, with the cathode as starting point. Next to the program scheme, additional adjustments must be made, shown next.

5.2.2. Additional SOEC adjustments

As a result of the mathematical derivation for the SOEC, the voltage drop will need to be changed accordingly. The following equation, which is similar to equation 32 derived earlier with only the \( \lambda \) changed into an \( x \), will be used within Cycle Tempo.

\[
\Delta V_{\text{SOEC}} = \left( \int_0^{U_F} \frac{dx}{E - E_{\text{rev}}(x)} \right)^{-1}
\]  
(40)
As mentioned in the theory chapter, the SOEC will have a negative voltage, due to its positive Gibbs free energy. However, in the mathematical chapter, the voltage was considered to be positive to make comparison with the SOFC easier. Here also, the cell voltage will be positive.

Before treating the different mathematical subroutines as done with the SOFC, certain assumptions need to made, based on the results found within the mathematical derivation.

- The fuel cell will now consume power to perform its operations. The power is therefore negative. However, the cell voltage is chosen to be positive, meaning the current (density) must be negative.

- When calculating the voltage drop for the SOEC, the actual cell voltage and reversible cell voltage have changed places. However, due to the 'chosen' positive voltage of the cell (reversible voltage and cell voltage), and the fact that \( E > E_{\text{rev}} \), the voltage drop will be positive.

For these prerequisites to hold, certain adjustments need to be made the mathematical subroutines. The following paragraphs will cover all the adjustments needed for the different approaches used depending on the user defined cell requirements (CDENS, VOLT, POWER and FLFUEL)

5.2.3. CDENS provided

The CDENS must now be negative (See figure 11). Recall the code shown in table 13. The new \( \Delta V_{SOEC} \), used in the subroutine, will calculate a voltage drop based on the cell voltage being larger than the reversible cell voltage. The cell voltage will be calculated by iterating the following equation (The added "e" will be used in all further subroutine modifications. This indicates that the electrolysis process is being calculated with the new voltage drop):

\[
V_{\text{CDRe}} \rightarrow i = \frac{U_F}{R_{\text{ASR}}} \times \Delta V_{\text{SOEC}}
\]

The provided negative current density will restrict Cycle Tempo to calculate a negative voltage drop. This can only be the case if \( E_{\text{rev}} \leq E \). However, for the SOEC situation, the cell voltage must be higher than the reversible voltage. The voltage drop can only be positive, and therefore a negative sign must be placed in front of the \( V_{\text{CDRe}} \) equation. The code will look as follows:

\[
\text{5.2 SOEC 5 CYCLE TEMPO}
\]

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After multiplying the iterated negative cell voltage with $-1$, the CURRENT calculation will follow. This will now also be negative, due to the negative current density. Multiplying the negative current with a positive voltage will result in a negative power. This will indicate that the fuel cell is consuming this amount of power, instead of generating it. The most noticeable difference will be that the newly calculated VOLT will be higher than the voltage for the SOFC. This is, of course, in accordance with what is proven in the mathematical model.

Finally, the flow of water is calculated with Faraday’s equation and the amount of current passing through the SOEC. Because the current is negative, the calculated fuel flow will also be negative. This cannot be the case, and therefore will require a new minus sign in front of it to make it positive again.

This approach can also be adopted for the other subroutines.

### 5.2.4. VOLT provided

As for an electrolysis fuel cell, the $\text{VOLT} > E_{\text{rev}}$. Cycle Tempo is programmed to give an error if this happens. Therefore, this must also be programmed in to Cycle Tempo (This will be shown in the next chapter, covering the actual coding). The first step consists of calculating CDENS with the CD\_VR routine.

\[
\text{CD\_VR} \rightarrow i = \frac{U_F}{R_{ASR}} \times \Delta V_{SOEC}
\]

The calculated value must be negative, but due to the positive voltage drop the resulting current density must be multiplied by $-1$, as shown next:

\[
\begin{align*}
\text{if given VOLT then} \\
\text{CDENS} &= -1 \times (\text{CD\_VR}) \\
\text{CURR} &= \text{CDENS} \times \text{ACELL} \\
\text{POWER} &= \text{CURR} \times \text{VOLT} / 1000 \\
\text{FLFUEL} &= -1 \times (\text{CURR} / (XH2EQ \times UFL \times 2 \times FAR))
\end{align*}
\]

<table>
<thead>
<tr>
<th>Table 17: SOEC 1st Subroutine: CDENS</th>
</tr>
</thead>
<tbody>
<tr>
<td>if given CDENS then</td>
</tr>
<tr>
<td>VOLT = -1 * (V_CDRe)</td>
</tr>
<tr>
<td>CURR = CDENS * ACELL</td>
</tr>
<tr>
<td>POWER = CURR * VOLT / 1000</td>
</tr>
<tr>
<td>FLFUEL = -1 * (CURR / (XH2EQ * UFL * 2 * FAR))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 18: SOEC 2nd Subroutine: VOLT</th>
</tr>
</thead>
<tbody>
<tr>
<td>if given VOLT then</td>
</tr>
<tr>
<td>CDENS = -1 * (CD_VR)</td>
</tr>
<tr>
<td>CURR = CDENS * ACELL</td>
</tr>
<tr>
<td>POWER = CURR * VOLT / 1000</td>
</tr>
<tr>
<td>FLFUEL = -1 * (CURR / (XH2EQ * UFL * 2 * FAR))</td>
</tr>
</tbody>
</table>

This approach can also be adopted for the other subroutines.
The negative current density is multiplied with the area of the fuel cell, resulting in a negative current. As also shown within the CDENS subroutine, the negative CURR is again used to calculate the negative flow of H\textsubscript{2}O. Again, this must the be multiplied by $-1$ to give the positive flow of water at the cathode.

### 5.2.5. POWER provided

First, the new voltage drop must be incorporated, resulting in the following V\textsubscript{PDRe} equation:

$$V_{PDRe} \rightarrow P = i \times E = \frac{U_F}{R_{ASR}} \times \Delta V \times E$$  \hspace{1cm} (43)

This will result in the following adjustments in the code:

<table>
<thead>
<tr>
<th>Code Snippet</th>
</tr>
</thead>
<tbody>
<tr>
<td>if given POWER then</td>
</tr>
<tr>
<td>PDENS = POWER * 1000 / ACELL</td>
</tr>
<tr>
<td>VOLT = -1 * (V\textsubscript{PDRe})</td>
</tr>
<tr>
<td>CDENS = PDENS / VOLT</td>
</tr>
<tr>
<td>CURR = CDENS * ACELL</td>
</tr>
<tr>
<td>FLFUEL = -1 * (CURR / (XH2EQ * UFL * 2 * FAR))</td>
</tr>
</tbody>
</table>

**Table 19:** SOEC 3\textsuperscript{rd} Subroutine: POWER

With the user provided ESTVLT, the VOLT is iterated. The CDENS is then calculated by dividing the negative PDENS by the positive VOLT. Multiplying this with the area of the cell and substituting it in to Faraday’s law will again result in a negative fuel flow. Multiplied by $-1$, this will calculate the H\textsubscript{2}O entering the cathode.

### 5.2.6. FLFUEL provided

Lastly, the FLFUEL approach. Using the same V\textsubscript{CDRe} as before, a similar approach to the last three can used used, resulting in the following code:

<table>
<thead>
<tr>
<th>Code Snippet</th>
</tr>
</thead>
<tbody>
<tr>
<td>if given FLFUEL then</td>
</tr>
<tr>
<td>CURR = -1 * (FLFUEL * (XH2EQ * UFL * 2 * FAR))</td>
</tr>
<tr>
<td>CDENS = CURR / ACELL</td>
</tr>
<tr>
<td>VOLT = V\textsubscript{CDRe}</td>
</tr>
<tr>
<td>POWER = CURR * VOLT / 1000</td>
</tr>
</tbody>
</table>

**Table 20:** SOEC 4\textsuperscript{th} Subroutine: FLFUEL

The user will provide a flow of H\textsubscript{2}O, which must result in a negative current. Therefore, the minus sign is added in front of Faraday’s law. The resultant negative current is then used to calculate the current density. This is then used to iterate a positive cell voltage that,
of course, can only be achieved by placing a minus sign in front of the \( V_{CDRe} \) equation. Finally, a negative power is calculated using the negative current.

To summarize: certain steps within the flow chart will need to be rearranged, the user will have to pay special attention to the inputs used. All the subroutines will have to be adjusted to facilitate the negative inputs. The modifications are listed below:

1. Create new cathode outlet variable: \([YKA[1:NCOMP]]\)
2. Change of voltage drop: \( \Delta V_{SOFC} \to \Delta V_{SOEC} \)
3. Remove internal check allowing \( \text{VOLT} > \text{EREV} \)
4. (neg) \( \text{CDENS} \to \text{V}_{CDRe} \)
5. (pos) \( \text{VOLT} \to \text{CD}_{VR} \)
6. (neg) \( \text{POWER} \to \text{V}_{PDRe} \)
7. (pos) \( \text{FLFUEL} \to \text{V}_{CDRe} \)

Next to these changes, the most challenging part will be to instruct Cycle Tempo to use the cathode as 'defining' electrode. Whether the first (anode based) or second (cathode based) approach is used, it has become clear the complexity involved when implementing it in Cycle Tempo is great. However, as will become clear in the next chapter, the SOFEC is surprisingly easier to model. This is due to its striking resemblance to the SOFC, as will become clear in the following paragraph.

\section*{5.3. SOFEC}

This final paragraph will describe the process followed for the SOFEC. In contrast to the SOEC, the SOFEC is actually less complicated when it comes to programming. Recall figure 3 where the reactions within the anode (methane reform and \( \text{H}_2 \) oxidation) can be used as defining characteristics. For the SOEC, it seemed more logical to pursue a cathode based calculation process, for the SOFEC, the anode is the preferred route. However, because this fuel cell is able to consume and generate power, an extra paragraph will be dedicated in explaining the intricate nuances that lay the restrictions on the operating parameters. This will be discussed in detail right after the flow chart.
5.3.1. SOFEC Flow Chart

The SOFEC flow chart is shown in the following figure, where the new and altered blocks compared to the SOEC have been accentuated:

![Flow Chart SOFEC](image)

This flow chart is almost identical to the SOFC flow chart. The order, in which the steps are performed, stays the same with the anode functioning as the defining electrode. Steps 1 through 6 will be discussed similar to the SOFC.

1. Step 1 is the same as with the SOFC. The inlet anode concentration is calculated.

For the SOFC, pure H\_2 was assumed to be entering the anode. This means that the inlet concentration of the anode is equal to the concentration of the gas at the active cell area. Within the SOFEC model this will change, but similar to a SOFC using internal reforming. The inlet concentration \texttt{CONC[LA, 1:NCOMP]} will show CH\_4 and H\_2O entering the anode. Due to internal reforming, the concentration of the gasflow will change, resulting in the extra components H\_2 and CO\_2. The process of...
reforming and the change in concentration is calculated and delivered as an output: 
\text{YAN}[1: \text{NCOMP}].

2. During step 2, the anode outlet flow will be calculated similar to the SOFC.
The inlet flow concentration will be multiplied with the user defined \text{UFL} resulting in the outlet concentration: \text{CONC}[\text{LAOUT}, 1: \text{NCOMP}].

3. In step 3, the calculation of the outlet concentration of the cathode will consist of two parts:
   - First the H\textsubscript{2} equivalents are calculated from the anode flow at the active cell area.
     This will be equal to the amount of H\textsubscript{2} resulting from the methane reformation.
   - Next, the \text{OFRAT} will be calculated. This results from the anode H\textsubscript{2} equivalents
times the UFL and the amount of electrolyzed water at the cathode needed
to oxidize the hydrogen. This will be one of the most important steps during
the calculation process. Cycle Tempo will have to be told how the electrolysis
reaction happens, and how much oxygen is results from this, in order to oxidize
the hydrogen in the anode. In essence, Cycle Tempo must recognize H\textsubscript{2}O as an
oxidant.

4. In step 4, the pressures, temperatures and enthalpies will be calculated.
The enthalpies changes must now be equal to those calculate in table 8. The H\textsubscript{2}
oxidation at the anode, and the steam electrolysis at the cathode are perfectly evened
out. This means that Cycle Tempo will only need to calculate the enthalpy associated
with the endothermic reform and exothermic watergas shift reaction.

5. Step 5 will calculate the \text{EREV}.
   As shown in equation 39, the Nernst equation will look significantly different. Also, the
Gibb’s free energy at standard conditions must be zero. The oxidation and electrolysis
reaction are supposed to counteract each other perfectly. This will be elaborated on
extensively in the following chapter covering the coding process.

6. The final step will involve the mathematical subroutines. They will all be discussed
independently in the next paragraph.

This system is surprisingly less complicated than the SOEC model. It must be noted
that this model does not allow the user to design his SOFEC based on the amount of H\textsubscript{2}
exiting the cathode. This problem, encountered during the coding process, will be discussed
in more detail at the end of the next chapter.
The following subroutines will be similar to those of the SOEC and will be discussed next.

5.3.2. SOFEC principles applied to Cycle Tempo

Depending on the user defined fuel utilization, oxidant fuel ratio and operating voltage of the fuel cell, the SOFEC will either consume or produce power. As shown for the SOEC, the condition of consuming power required major adjustments in the code, and in particular the mathematical subroutines. In the case of the SOFEC, its operation is similar to the SOFC. However, whether the correct values are calculated depend mainly on the user defines the operating conditions accordingly. This is best explained by dividing the SOFEC operational modes according to two conditions:

1. **Produce** power.
2. **Consume** power.

Recall figure 11. The reversible cell voltage of the SOFEC based on a reversible cell voltage of 0 volt at standard conditions, it does not seem possible for a SOFEC to produce power. In fact, in normal operating conditions, the SOFEC will not produce power as this requires the fuel cell to run very inefficiently. To explain this, the following figure is given

![Figure 15: SOFEC power explained](image)

Because the SOFEC is based on the concentrations of hydrogen and water in both the anode and cathode, there is a situation in which the fuel cell will produce power. For this to be true, the concentrations in the nominator must be larger than the concentrations in the denominator (see equation 39). The anodic concentration of hydrogen and the cathodic concentration of water must be larger than its products after either the oxidation or electrolysis
reaction has taken place. During the whole mathematical chapter, the concentrations of the reactants are assumed to be at the end of the fuel cell. This means that in the process of running the fuel cell, the incoming reactants will react to form their products, where their final concentrations are used to define the reversible cell voltage. This is true, but consider the situation at the beginning of the cell. Both reactions are just starting to take place, meaning that the hydrogen and water concentrations are still larger than the end products they will react into. Because the fuel utilization will be smaller at this point, the local reversible voltage will be positive. If the user has defined a $U_F$ which is small enough, it is possible to have a positive reversible cell voltage at the entrance and exit, which will allow the user to produce electrical power.

The fuel cell will produce power till the moment where the reactants and products are equal in quantity. At this moment, the concentrations will be 0.5 (50% of anodic hydrogen oxidized and 50% water electrolyzed). The reversible cell voltage will be zero, as shown in the graph above as the point where the $E_{rev}$ curve intersects the x-axis. The reason for laying the emphasis on this again is because in Cycle Tempo, a distinction is made of the reversible cell voltage at the entrance and at the exit of the fuel cell. These will differ due to the local fuel utilization at that point. This will be of particular importance in the following paragraph where the mathematical subroutines are explained.

5.3.3. CDENS provided

As shown in the mathematical chapter, the SOFEC differs only slightly from the SOFC when it comes to calculations performed. The current density of the SOFEC is positive, determined by the direction the electrons flow (independent on power production or consumption). Therefore, only the cell voltage (positive or negative), will determine whether the SOFEC will produce or consume power. If this knowledge is applied to the mathematical subroutine, it becomes obvious that no changes are needed:

```
if given CDENS then
  VOLT = V_CDR
  CURR = CDENS * ACELL
  POWER = CURR * VOLT / 1000
  FLFUEL = CURR / (XH2EQ * UFL * 2 * FAR)
```

Table 21: SOFEC 1st Subroutine: CDENS

With help of the $V_{CDR}$ function:

$$i = \frac{U_F}{R_{ASR}} \times \left( \int_0^{U_F} \frac{dx}{E_{rev}(x) - E} \right)^{-1}$$

(44)
the power production and consumption scenarios can be explained:

1. **Power production.** The SOFEC has a positive current density (always). Therefore, the voltage drop (term in between the brackets of the previous equation) is required to be positive as well. This requires the \( E < E_{rev} \). However, because the fuel cell is producing power, the cell voltage must also be larger than 0. This means that the fuel cell voltage will lie in the region: \( 0 \leq E < E_{rev} \). With these restrictions, the voltage drop can never be larger than \( E_{rev} \). Recalling the definition of the voltage drop (\( \Delta V = i \cdot R_{ASR} \)), it becomes obvious that the fuel cell is now restricted to low current densities in order for it to produce power. This translates directly to a low fuel utilization, which in terms results in a low efficiency. Therefore, in real life situations, one can assume that the SOFEC will always be consuming power in order to keep the fuel utilization and efficiency up.

2. **Power consumption.** Again, the SOFEC will keep its positive current density. The current density times the resistance must be larger than the reversible cell voltage. As long as this is the case, will a cell voltage be iterated which is negative. However, the user must keep in mind that the ESTVLT he provides **MUST** be negative. This forces Cycle Tempo to iterate a negative cell voltage.

To summarize, the operating conditions are shown in the next table (where the \( E_{rev} \) has been given a value of \( \pm 0.2\) V in order to give sense to the magnitude of the cell voltage):

<table>
<thead>
<tr>
<th>Condition</th>
<th>( E_{rev} )</th>
<th>ESTVLT</th>
<th>( i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production</td>
<td>(~0.2) V</td>
<td>( 0 \leq E &lt; E_{rev} )</td>
<td>((i \cdot R_{ASR} = \Delta V) \leq E_{rev})</td>
</tr>
<tr>
<td>Consumption</td>
<td>(~0.2) V</td>
<td>( E &lt; 0 )</td>
<td>((i \cdot R_{ASR} = \Delta V) &gt; E_{rev})</td>
</tr>
</tbody>
</table>

**Table 22:** CDENS conditions for a SOFEC

Though the code requires no adjustments, it is important to realize how the fuel cell will be operating. Assuming a positive ESTVLT with a current density that is too large will give an error. This will happen due to the fact that the calculated cell voltage will be larger than \( E_{rev} \), which cannot be the case. Following the above stated restrictions, the code will calculate the remaining fuel cell parameters. The current will be positive. The power of the fuel cell will depend on the voltage iterated from \( V_{CDR} \). Finally, the fuel flow will be calculated with the positive current resulting in an amount of hydrogen needed at the anode.

A similar approach is used for the other subroutines, as will be discussed in the following paragraphs.
5.3.4. VOLT provided

The VOLT situation is actually the most simple, and will be the same as for the SOFC:

\[
\begin{align*}
\text{if given VOLT then} \\
\text{CDENS} &= C_{D,VR} \\
\text{CURR} &= \text{CDENS} \times \text{ACELL} \\
\text{POWER} &= \text{CURR} \times \text{VOLT} / 1000 \\
\text{FLFUEL} &= \frac{\text{CURR}}{(XH2EQ \times UFL \times 2 \times \text{FAR})}
\end{align*}
\]

Table 23: SOFEC 2\textsuperscript{nd} Subroutine: VOLT

Similar to the CDENS subroutine, the current density will be calculated depending on the user provided cell voltage. Keeping the previous stated requirements in mind, a positive or negative power will be calculated. The size of the current then determines the amount of fuel needed. This approach is the most simple and will form the starting point of the coding process in the next chapter.

5.3.5. POWER provided

Upholding the requirements stated at the CDENS subroutine, the user will must comply with his defined ESTVLT. The positive power is severely restricted in size, and may require a few tries before Cycle Tempo allows it in combination with the provided ESTVLT. Nevertheless, the code will stay unchanged in comparison to the SOFC:

\[
\begin{align*}
\text{if given POWER then} \\
\text{PDENS} &= \text{POWER} \times 1000 / \text{ACELL} \\
\text{VOLT} &= V_{PDR} \\
\text{CDENS} &= \text{PDENS} / \text{VOLT} \\
\text{CURR} &= \text{CDENS} \times \text{ACELL} \\
\text{FLFUEL} &= \frac{\text{CURR}}{(XH2EQ \times UFL \times 2 \times \text{FAR})}
\end{align*}
\]

Table 24: SOFEC 3\textsuperscript{rd} Subroutine: POWER

5.3.6. FLFUEL provided

This subroutine will allow the user to define the amount of hydrogen converted at the anode. The code will stay unchanged in comparison to the SOFC:

\[
\begin{align*}
\text{if given FLFUEL then} \\
\text{CURR} &= \text{FLFUEL} \times (XH2EQ \times UFL \times 2 \times \text{FAR}) \\
\text{CDENS} &= \frac{\text{CURR}}{\text{ACELL}} \\
\text{VOLT} &= V_{CDR} \\
\text{POWER} &= \frac{\text{CURR} \times \text{VOLT}}{1000}
\end{align*}
\]

Table 25: SOFEC 4\textsuperscript{th} Subroutine: FLFUEL
Similar to the POWER approach, the user must be aware of the fact that the fuel flow is indirectly proportional to the current passing through the fuel cell (amount of converted fuel in H₂ equivalents is equal to the current). Low fuel flow results in a low current and current density. Providing a positive (but smaller than \( E_{\text{rev}} \)) ESTVLT, will result in a positive voltage being iterated from \( V_{\text{CDR}} \). The cell will produce power. Increasing the fuel flow will increase the current, and the fuel cell will start consuming power requiring a negative user provided ESTVLT.

Depending on the approach used, the user must be well aware of the requirements of the fuel cell. All except the VOLT approach, require the user to define two values. The provided ESTVLT is of great importance, as it determines whether the SOFEC produces or consumes power.
With the subroutines discussed, the next step involves the actual coding. The SOFEC will be modeled according to the simplified version involving a direct inlet of hydrogen at the anode. Future versions will, of course, be updated in order for the SOFEC to run on methane, but are not discussed any further in this chapter.

The core code describing the calculation of the fuel cell within Cycle Tempo can be found in Ap_FCel.for, that contains over 3400 lines. It is divided into routines, each with their own specific tasks.

Routines in Cycle Tempo are designed to perform specific calculations. They are categorized by the calculations they perform and their dependency on each other. Within each routine, there are different types of externally defined variables and functions, which can be evoked. The variables are subdivided into two types:

1. Argument variables, that can be adjusted and rewritten to the array so that following routines can use them.
2. Local variables, which will only be used within the routine.

The local variables may be changed within the routine, but will retain their original value once evoked in a different routine.

Furthermore, there are also functions that perform a specific small calculation, used within different routines. Instead of copying the same code into each routine, these functions are placed at the end of the file, where they can be called upon.

Important to note is: within the existing code, the SOFC has been used as the base for the SOFEC. Therefore, each notation with SOFC can be referred to as the new SOFEC model. (Every following text written in this font refers to pieces of code from the Fortran file).

After all calculation steps are altered for the SOFEC, and the model works as wanted, the graphic user interface will need to be updated for the SOFEC. Afterwards, the SOFC code will be added again.

The next paragraphs will discuss, in detail, the different routines and the alterations that need to be made in order to calculate the SOFEC.
6.1 DfFCel and DfGmFCel routine

These are the first two routines the user will see when opening the Fortran file. Their sole purpose is to write all the user inputed thermodynamic and geometry information into neatly organized arrays. From there, the next calculation routines can retrieve their information. It performs checks on certain values entered by the user to see whether they are correct and viable. An example would be the check to see if the fuel utilization lies between 0 and 1. If not, it will give an error message, when running the simulation within Cycle Tempo, indicating this condition is not met.

As these routines are very straightforward, no detailed information will be given. All the possible inputs that will be used for the SOFEC are already defined and will require no adjustments.

6.2 CmFCel Routine

This is the first actual calculation routine and has the following tasks:

1. Incoming gas concentration at active cell area calculation.
2. Outgoing anode gas concentration calculation.
3. Outgoing cathode gas concentration calculation.

These tasks correspond to step 1-3 of the flow chart, shown in the previous chapter. For the SOFEC, H$_2$ will be added to the anode. The entering concentration of hydrogen will be the same as the "gas concentration at the active cell area of the anode". The next step will comprise of the calculation of the exiting anode gas, which is merely defined by the fuel utilization UFL.

Task 3 comprises of calculating the outgoing cathode gas. For a normal SOFC, only air (or more specifically O$_2$) is detected at the cathode as oxidant. However, for the SOFEC, H$_2$O must be used as oxidant. When Cycle Tempo calculates the oxidant fuel ratio, it will need to know how many oxygen it can retrieve from water. This will need to be added to the code so that Cycle Tempo can recognize water as a valid oxidant for the reaction in anode.
To allow the routine to recognize water at the cathode, several adjustments need to be made:

1. First: water needs to be added as a local variable.
   This is done by adding $\text{H}_2\text{O}$ as an integer. As an integer, it may only take on a whole value, and is used in the COMP function. This function defines the components present; where water is now 'detectable'. Water must also be added to the so called REAL(8) variables. This is a floating point value and is allowed to contain decimals. Here, $\text{YH}_2\text{O}$ is added as water concentration. (Hence the Y)

2. Secondly, with water 'detectable', there must now also be an argument stating that once it is detected, it is written to the COMP (composition) array. This is shown in the following code: (all adjusted code will be accentuated)

   ```fortran
   *==========================================================================*
   * 4. Calculation of cathode outlet composition. *
   *==========================================================================*
   IF (DEBUG)CALL Pause( 'Calculation cathode outlet composition')
   *
   * Store indices of O2 and CO2 in systemarrays
   DO J = 1, NCOMP
       IF (COMP(J) == 'O2' ) THEN
           O2 = J
       ELSE IF (COMP(J) == 'CO2' ) THEN
           CO2 = J
       ELSE IF (COMP(J) == 'H2O' ) THEN
           H2O = J
       ENDIF
   ENDDO
   *
   3. Finally, the detected water is used when calculating the oxidant fuel ratio.

   Step 3 involves calculating the oxidant fuel ratio: OFRAT. For the SOFEC, each oxidized $\text{H}_2$ at the anode will require an $\text{O}^{2-}$ ion. This will be retrieved from from one electrolyzed $\text{H}_2\text{O}$ molecule in the cathode. For the SOFC, the OFRAT is calculated through the following code:

   $$\text{OFRAT} = 0.5 \times \frac{\text{YH}_2\text{EQ}}{\text{CONC(LK,O2)}} \times \frac{\text{UFL}}{\text{UMAX}}$$

   The ratio is calculated by dividing the $\text{H}_2$ equivalents ( $\text{YH}_2\text{EQ}$ ) by the concentration of $\text{O}_2$ at the cathode. The factor 0.5 accounts for the reaction ratio of $\text{H}_2$ and $\text{O}_2$. The
amount of H\(_2\) reacting at the anode is bound by the fuel utilization, and therefore YH2EQ is multiplied by UFL. The fuel ratio will be verified later on in the PrF Cel routine (discussed in the next paragraph) using the mass flows. The UMAX shown, is the maximum oxidant utilization and is set to 0.95 by Cycle Tempo at the beginning of the routine. This is not a required value for the user to fill in, but ensures that under any situation it never exceeds this value. Later on in the code, the actual oxidant utilization is calculated and overwritten, but for now, this default value is used. Fuel utilizations above this value are not realistic and have serious consequences for the logarithm in the Nernst equation.

For the SOFEC, some modifications must be made to the OFRAT calculation. Instead of retrieving the amount of oxygen atoms (from the cathode) needed by YH2EQ in the anode from oxygen molecules, the oxygen atoms must now be taken from water. Obviously, oxygen molecules have twice as much oxygen atoms as water. Therefore, the 0.5 multiplication can be removed. In this configuration, the correct amount of oxygens atoms can be taken from the concentration of water (CONC(LK,H2O)) at the cathode. This is shown in the following code: (Not all the code is shown, only the header followed by the first couple of lines, where to modifications have been made)

```fortran
*--------------------------------------------------------------------------*
* Determine oxidant/fuel ratio OFRAT.                                     *
*--------------------------------------------------------------------------*
IF ( Given(UOXUSR)) THEN
    OFRAT = YH2EQ / CONC(LK,H2O) * UFL / UOX
ELSE
    IF (ITM == 0) THEN
        OFRAT = YH2EQ / CONC(LK,H2O) * UFL / UMAX
    ENDIF
*--------------------------------------------------------------------------*

With the OFRAT, the oxidant utilization can be calculated. This must also be adjusted for the water in the cathode:

```fortran
*--------------------------------------------------------------------------*
* Calculate and check oxidant utilisation UOX calculated from OFRAT.       *
*--------------------------------------------------------------------------*
UOX = YH2EQ / CONC(LK,H2O) * UFL / OFRAT
IF (UOX > 1) THEN
    WRITE (13,940) IAP, ITM, UMAX
    CALL WarningIncrement()
    OFRAT = YH2EQ / CONC(LK,H2O) * UFL / UMAX
ENDIF
```

T.U. Delft
F.K.B. WIJERS
No further alterations are made in CmFCel. The most important step is telling Cycle Tempo that H₂O is now the oxidant, that is needed to let the H₂ at the anode react. Later on, the electrolysis reaction will be introduced.

6.3. PrFCel Routine

The next routine is PrFCel, that calculates several thermodynamic properties of the fuel cell (pressures, temperatures, enthalpies, power and fuel flow). Just as with CmFCel, YH₂O has been added at the beginning as a floating point local variable.

Though the routine performs a variety of tasks, the only part that needs adjustment, is the recalculation of the oxidant utilization. The oxidant utilization must now correspond to the newly calculated mass flows.

This routine is divided into the following steps:

1. Step 1 involves the initialization process. All the apparatus data are retrieved from arrays already defined earlier. Within the array, they are given a number. Therefore, to make things less confusing while reading the code, they are again assigned their original name as used in the graphic user interface.

2. Step two then uses these values to calculate the change in pressures and temperatures. To keep this model simple, there will only be minimal modifications. It is required by Cycle Tempo to have a change in entrance and exit temperature of the anode and cathode for it to be able to perform its calculations. The pressure of the incoming gasses and of the fuel cell are both set to standard pressure (1 bar).

3. During step three, the electrical properties and fuel mass flow are calculated. The SOFEC is based on the utilization of the hydrogen entering the anode. This will be the same as for the SOFC and no adjustments are needed (hydrogen is converted into water). This routine also performs the calculations based on the user defined inputs CDENS, VOLT, POWER and FLFUEL. As discussed earlier, for the SOFEC, the mathematical subroutines require no adjustments.

4. Step four calculates the temperature from the energy balance when working with a cooling cycle. However, during this research no use has been made of the cooling cycle, nor has it been discussed. For the SOFEC, no modifications will be needed.

5. Step five will calculate the mass flow of the oxidant based on the energy balance. These important parts can be distinguished:
a) First the inlet enthalpies of the fuel and oxidant, $H_{\text{INFL}}$ and $H_{\text{INOX}}$ are retrieved. (Easily done based on the user defined operating parameters: temperature and pressure)

b) The outlet enthalpy is then calculated with function $H_{\text{PTW}}$. This function makes use of the user defined pressure, temperature and the components (calculated before) of the gasses exiting the fuel cell.

c) With the inlet and outlet enthalpy, the change ($\Delta H$) can be calculated, specific for the reaction occurring. The change in enthalpy can be used to calculate the amount of oxidant used. With the amount of oxidant used, the final cathodic mass flow can be calculated: $M_{\text{INOX}}$

d) Finally, the cathode mass flow can then be used to recalculate the OFRAT. As always: water will need to be added as possible component:

\[
\begin{align*}
&\text{* Calculate new utilisations for O}_2, \text{ CO}_2 \text{ and H}_2\text{O correspond. to mass flows.} \\
&\text{* Recalculate oxidant / fuel ratio} \\
&\text{OFRAT} = M_{\text{INOX}} / M_{\text{INFL}} * \text{AVERG(LA)} / \text{AVERG(LK)} \\
&\text{DO J = 1, NCOMP} \\
&\quad \text{IF (COMP(J) == 'O2') } YO2 = \text{CONC(LK,J)} \\
&\quad \text{IF (COMP(J) == 'CO2') } YCO2 = \text{CONC(LK,J)} \\
&\quad \text{IF (COMP(J) == 'H2O') } YH2O = \text{CONC(LK,J)} \\
&\text{ENDDO}
\end{align*}
\]

As shown earlier, the OFRAT calculation is based on oxygen in the cathode. Again, this must be changed for the SOFEC in order to recognize water as oxidant (oxygen supplier for the anode).

\[
\begin{align*}
&\text{* Calculate and check oxidant utilisation} \\
&\text{UOX} = Y_{\text{H2EQ}} / Y_{\text{H2O}} * U_{\text{FL}} / \text{OFRAT} \\
&\text{IF (UOX >= 1) THEN} \\
&\quad \text{UOX} = \text{UMAX} \\
&\quad \text{TLOW} = .\text{TRUE.} \\
&\quad \text{OFRAT} = Y_{\text{H2EQ}} / Y_{\text{H2O}} * U_{\text{FL}} / \text{UMAX} \\
&\text{ENDIF}
\end{align*}
\]

6. Step 6 calculates the outlet temperature based on a system with a cooling cycle. This is not of importance for the SOFEC.

7. Finally, the routine ends by storing the calculated values to an array. They can be then used in the following WrFCel routine, which writes the data to an output file.
This concludes all the main routines used by Cycle Tempo. The previously mentioned WrFCell only recalls all the calculation results and writes them neatly into an output file. (If the user wishes to view any additional information, that is not shown in the primary output of the fuel cell, he can call upon the aforementioned output file through the text output command in the graphic user interface)

Next to the main routines, there are also supporting functions, explained in the next paragraph.

### 6.4. Supporting functions

The supporting functions are evoked on different occasions throughout the whole code. They are routines by themselves, but are named "supporting functions" as they perform calculations used, within the other main routines. There are several different supporting functions. The most important supporting functions are listed below:

1. **AnOutCmp.**
   This function performs the actual calculation of the anode outlet composition. It is used several times in the previous routines, and for the SOFEC it needs no adjustments. The reformation reaction can already be calculated in Cycle Tempo.

2. **CaOutCmp.**
   The CaOutCmp function calculates the cathode outlet composition with the help of the H\textsubscript{2} equivalents at the anode, the fuel utilization and the oxidant / fuel ratio. Firstly, H\textsubscript{2} has been added as an integer. (This is not found in the cathode in any of the other fuel cells). Now that hydrogen can be detected, it must also be written to the composition array, as shown in the following code:

   ```
   ELSE IF (COMP(J) == 'H2' ) THEN
     H2 = J
   ENDIF
   ENDDO
   ```

Next the CMOLES is calculated:

\[
\text{CMOLES} = \text{YH2EQ} \times \text{UFL} / \text{OFRAT}
\]

This is the hydrogen equivalents multiplied by the fuel utilization, which tells Cycle Tempo how much hydrogen has been converted. It is then divided by OFRAT, in
order to adjust to possible different cathodic oxidant flows. CMOLES is a change in percentage (given in a value between 0 - 1, that tells how much of the entering hydrogen has been converted, and then adjusts that percentage for the cathode. It takes into account the fact that the cathodic flow can be larger than the anode, and dividing by OFRAT compensates for this change. A worked out example is given in paragraph 7.1) Then, the exiting composition of the cathode is calculated by subtracting CMOLES from the incoming composition and writing it in the same spot in the array:

\[
Y_{CA}(O_2) = Y_{CA}(O_2) - \frac{\text{CMOLES}}{2}
\]

Here, the actual used CMOLES is the amount of oxygen atoms used. Therefore, the outgoing flow will have been reduced by half that amount in \( O_2 \) molecules. For the SOFEC case, the code has been adjusted as followed to again incorporate \( H_2O \):

```fortran
*--------------------------------------------------------------------------*
* Determine outlet composition.                                           *
*--------------------------------------------------------------------------*
ELSE IF (TYPE == 'SOFC-ER' .OR. TYPE == 'SOFC-IIR' .OR. TYPE == 'SOFC-DIR') THEN
  YCA(H2O) = YCA(H2O) - CMOLES
  YCA(H2)  = YCA(H2)  + CMOLES
ENDIF
```

This means that the cathodic water will be reduced by CMOLES, which is the exact amount at which hydrogen is created at the cathode. To the concentration of hydrogen entering the cathode, CMOLES amount of hydrogen is added. Together, the concentration of water and hydrogen exiting the cathode must be 1. Also, the CMOLES does not have to be divided by two. This can easily be deduced from the amount of oxygen atoms released during the electrolysis reaction.

3. \( H2\text{eq} \).

Calculates the amount of \( H_2 \) equivalents in the anode fuel. No modifications are needed.

4. \( E_{\text{rev}} \).

This function calculates the reversible cell voltage. The Erev function contains the Nernst equation. As shown earlier, the reversible cell voltage at standard conditions needs to be changed. This is based on the Gibb’s free energies of the overall reaction. For the SOFC, this is shown in the following code:

\[
E_0H2 = -\frac{G(H2O)}{2.d0 * \text{FAR}}
\]
The Gibbs free energy of H\(_2\) and \(\frac{1}{2}\)O\(_2\) have been subtracted from H\(_2\)O, but because these are zero, only H\(_2\)O is left. This is then divided by n(=2 electrons) \(\times\) Faraday’s constant.

For the SOFEC, this will be \(E_{0SOFC} = 0\), as shown in paragraph 4.4, where the Gibb’s free energy at standard conditions is 0. Next, the reversible cell voltage is calculated:

\[
E_{Rev} = E_{0SOFC} + \frac{R \cdot TK}{2 \cdot FAR} \cdot \log\left(\frac{(YAN(H2) \cdot YCA(H2O))}{(YAN(H2O) \cdot YCA(H2))}\right)
\]

5. **Vloss** No changes need to be made for the SOFEC as the voltage drop is determined in the same way as the SOFC. For the SOEC this must be changed, and shown in the appendix for the SOEC programming.

6. **CD_VR, V_CDR and V_PDR.**

   Again, these are the same for the SOFEC as for the SOFC and require no modifications.

All the changes were made, and finally the program was run. The results are shown in the next chapter.
7. Results

The goal of this paragraph is to determine whether Cycle Tempo performs its calculations correctly. Its outputted values must be in accordance with the theoretical values calculated in the mathematical chapter.

To generate all the results shown next, extra pieces of code are added that tell Cycle Tempo to output certain values in the output box. This is done because not all values necessary for comparison are generally given directly. They are used within the program itself to finally calculate the operating parameters of the fuel cell, but not shown to the user.

The general outlay of the information in the output screen of Cycle Tempo is given as follows:

```
===================================
Calculate CMOLES
===================================
CMOLES = 0.500000000000000
YH2EQ = 1.000000000000000
UFL = 0.500000000000000
OFRAT = 1.000000000000000
CMOLES = YH2EQ * UFL / OFRAT

===================================
EREV concentrations
===================================
Entrance FUEL CELL for EIN
Hydrogen ANODE YAN_0(H2) = 1.000000000000000
Water ANODE YAN_0(H2O) = 0.000000000000000E+000
Hydrogen CATHODE YCA_0(H2) = 0.000000000000000E+000
Water CATHODE YCA_0(H2O) = 1.000000000000000

Exit FUEL CELL for EOUT
Hydrogen ANODE YAN(H2) = 0.500000000000000
Water ANODE YAN(H2O) = 0.500000000000000
Water CATHODE YCA(H2O) = 0.500000000000000
Hydrogen CATHODE YCA(H2) = 0.500000000000000

===================================
EIN & EOUT
===================================
EIN = 1.000000000000000E+020
EOUT = 0.000000000000000E+000
```
7 RESULTS

Most of this information does not show up in Cycle Tempo. In particular the ratio of the concentrations of the incoming and outgoing flows. This is important information when determining the reversible cell voltage, and was of great importance during the debugging process.

The first 5 values are important in determining whether the electrolysis reaction takes place as it is supposed to. The \textbf{YH2EQ} tells the user the concentration of entering hydrogen at the anode. In this specific case it is 100%. The fuel utilization (UFL) is 0.5, meaning half of the incoming hydrogen in converted. Furthermore, the OFRAT determines the relative ratio of molar flows between the anode and cathode. In this case CMOLES is 0.5, meaning that half of the incoming water at the cathode is electrolyzed to accommodate the oxidized hydrogen in the anode.

The second group of values shows the incoming and exiting concentrations of the anode and cathode. The first 4 values confirm that the entrance anode flow is indeed 100% hydrogen. The next values show the exiting concentrations of the anode and cathode. The exiting anode flow must now contain 50% hydrogen, and 50% oxidized hydrogen which is converted into water. The exiting values of the cathode flow show that 50% of the water is electrolyzed. From that electrolyzed water (50%), all the oxygen has diffused through the electrolyte, and the remaining hydrogen molecules now form 50% molar flow of the cathode.

Finally the entrance (EIN) and exit (EOUT) reversible voltages are calculated. In this case, EIN has an unrealistic value. This is due to the fact that during the calculation of the reversible cell voltage at the entrance of the fuel cell, the logarithm of 0 is taken, as shown in the following formula taken from equation 39:

\[
\ln \left( \frac{Y_{AN}(H2) \ast Y_{CA}(H2O)}{Y_{AN}(H2O) \ast Y_{CA}(H2)} \right) = \ln \left( \frac{1 \ast 1}{0 \ast 0} \right)
\]  

Instead of giving an error, Cycle Tempo assumes a default value. This is done for all cases involving a division by 0. To prevent this, there must always be a small concentration of water added to the anode, and hydrogen added to the cathode. This is also the case for a normal SOFC. While running Cycle Tempo, the user is required to always provide a small amount of steam to the anodic hydrogen flow.

While calculating EOUT, the same calculation operation is performed but then with the exiting anodic and cathodic flow. The simplified calculation will look as follows:
7.1 Changing OFRAT

\[ \ln \left( \frac{YAN(H2) \cdot YCA(H2O)}{YAN(H2O) \cdot YCA(H2)} \right) = \ln \left( \frac{0.5 \cdot 0.5}{0.5 \cdot 0.5} \right) \]

(46)

Theoretically speaking, this will result in the logarithm being taken of 1 resulting in 0. This is exactly what happens in Cycle Tempo, and EOUT = 0. These values are in accordance to figure 10. Here the \( E_{\text{rev}} \) is shown while increasing the \( U_F \). At an oxidant fuel ratio of 1, the reversible cell voltage must be zero, as shown by the intersection of the curve with the x-axis at \( U_F = 0.5 \).

It works as theorized, and the next step will be to check how much power the fuel cell produces. For this specific (and all calculations following), the following operating parameters have been used:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature entrance</td>
<td>1000(^\circ)C</td>
</tr>
<tr>
<td>Temperature exit</td>
<td>1023(^\circ)C</td>
</tr>
<tr>
<td>Fuel cell Area</td>
<td>10m(^2)</td>
</tr>
<tr>
<td>Area specific resistance ( A_{ASR} )</td>
<td>7.5e-05 ( \Omega \cdot m^2 )</td>
</tr>
</tbody>
</table>

These values have been chosen to keep the model simple. The difference between the entrance and exit temperature is necessary for Cycle Tempo to perform its calculations. In the theorized model, the temperature doesn’t change, but that isn’t realistic for a real life fuel cell. It is required by Cycle Tempo to be different in order for the temperature calculations to be performed correctly. (No further attention will be paid to these values, and are kept constant for all future calculations).

For the all next calculations, each series is calculated where every time 1 variable is changed in order to see what Cycle Tempo does. These are discussed, and compared to the theoretical calculations and their predictions. For all calculations, the VOLT approach has been used. As discussed in chapter 5.3.4, this approach is easiest to model, as only the cell voltage must be taken into consideration. All other approaches require the user to define a correct current density, power or fuel flow as well as an ESTVLT with the correct sign. As of now, the program is not capable of running in these modes and require more research in order for them to work correctly.

7.1 Changing OFRAT

To see whether Cycle Tempo correctly makes use of different cathodic flows of water, the OFRAT has been changed with each calculation. For this (and all following calculations),
the anodic flow is assumed to contain 90% hydrogen and 10% water. The cathodic flow is altered in a similar way and will now contain 90% water and 10% hydrogen. The new reversible cell voltage (at different oxidant fuel ratio’s) as a function of the fuel utilization is shown in the next figure:

![Graph showing reversible cell voltage with changing molar flow cathode at T=1273K using 90:10 H2:H2O anodic and 90:10 H2O:H2 cathodic entrance flow.]

Figure 16: Simplified SOFEC reversible cell voltage

There are some significant differences between this figure and figure 10. Obviously, there is no asymptotic activity at $U_F = 0$, because there will always be a small entrance flow of water at the anode and hydrogen at the cathode. Based on this graph, the results from Cycle Tempo will be checked in order to confirm it runs correctly.

To indicate how the respected values are retrieved from Cycle Tempo, the following situation is given. The OFRAT is set to 5, so Cycle Tempo should calculate values in accordance to figure 16. The output of Cycle Tempo is given as follows:
7.1 Changing OFRAT

Calculate CMOLES

CMOLES = YH2EQ * UFL / OFRAT

EREV concentrations

Entrance FUEL CELL for EIN
Hydrogen ANODE YAN_0(H2) = 0.899999999999558
Water ANODE YAN_0(H2O) = 0.100000000000442
Hydrogen CATHODE YCA_0(H2) = 0.100000000000442
Water CATHODE YCA_0(H2O) = 0.899999999999558

Exit FUEL CELL for EOUT
Hydrogen ANODE YAN(H2) = 0.179999730000723
Water ANODE YAN(H2O) = 0.819998770003777
Water CATHODE YCA(H2O) = 0.756000000000000
Hydrogen CATHODE YCA(H2) = 0.244000000000000
E0H2 = 0.000000000000000E+000

EIN & EOUT

EIN = 0.245412908534171
EOUT = -2.152724385757411E-002

In the ‘Calculate CMOLES’ box, several values are given and calculated:

- The YH2EQ indicates what the concentration of hydrogen equivalents is in the entrance anode flow. As this comprises of 90% hydrogen, the value will be 0.9.

- The UFL and OFRAT are the user defined values.

- On top, CMOLES is given. This indicates how much of the cathodic water must be converted. This is calculated by multiplying the entrance hydrogen equivalents with the fuel utilization and then divided by the OFRAT. For this specific situation, the entrance flow containing 90% hydrogen will oxidize. The amount if defined by the fuel utilization. By multiplying 0.9 with 0.8 (UFL), it is obvious that 0.72 of the initial 0.9 H2 is converted. However, 0.72 of the anodic entrance flow will not be the same for the cathode, as the entrance flow will be 5 times as large. Therefore, this value (0.72), must be divided by 5 in order to calculate its relative electrolysis of water. So, 72% converted hydrogen in the anode equals 0.144 (=0.72/5) electrolysis of the total cathodic water flow.
With this information, the values in the 'EREV concentrations' box can be calculated. These are summarized below:

- First are the entrance flows of hydrogen and water at the anode and cathode. These speak for themselves.

- The exiting flow of the anode is calculated according to the fuel utilization and CMOLES. The exiting hydrogen will be equal to the entering hydrogen minus that which is converted (0.9 - 0.72 = 0.18). The resultant water will be equal to the entrance amount plus that which is created from the oxidized hydrogen. (0.1 + 0.72 = 0.82). Together they must be 1.

- The exiting flow of the cathode is calculated similarly, but uses CMOLES as percentage of electrolyzed water. In this situation, CMOLES = 0.144, so this must be subtracted from the entering water flow (0.9 - 0.144 = 0.756). The newly created hydrogen must be added to the initial flow (0.1 + 0.144 = 0.2144). Together, of course, they must be 1.

In the last section, the reversible voltage at the entrance and exit of the fuel cell is calculated. The value can be confirmed by hand:

\[
\frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{0.9 \times 0.9}{0.1 \times 0.1} \right) = 0.235 V
\]  

or it can be verified in figure 16. Either way, Cycle Tempo correctly calculates the value. The reversible cell voltage at the exit of the fuel cell can be checked in a similar way. Figure 16 can be checked. Following the OFRAT = 5 curve up till \( U_F = 0.8 \) shows indeed a very small negative voltage.

This calculation has been performed several times for different OFRATS, and are shown in the following table:

<table>
<thead>
<tr>
<th>OFRAT</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>UFL</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>EOUT th.</td>
<td>-0.155</td>
<td>-0.08</td>
<td>-0.0477</td>
<td>-0.0226</td>
<td>0.00258</td>
</tr>
<tr>
<td>VCELL</td>
<td>-0.2</td>
<td>-0.2</td>
<td>-0.2</td>
<td>-0.2</td>
<td>-0.2</td>
</tr>
<tr>
<td>CT EOUT</td>
<td>-0.1693</td>
<td>-0.0756</td>
<td>-0.0474</td>
<td>-0.02152</td>
<td>0.00308</td>
</tr>
<tr>
<td>POWER</td>
<td>-4.13kW</td>
<td>-6.39kW</td>
<td>-7.02kW</td>
<td>-7.57kW</td>
<td>-8.57kW</td>
</tr>
</tbody>
</table>

Table 26: Operating parameters with changing OFRAT (1)

For this calculation, the UFL is kept constant at 0.8. The EOUT is calculated by hand before the program is run. This done to prevent the user form defining an invalid cell voltage. Based on that restriction, the cell voltage in the first situation is set to -0.2V. It must
be smaller than EOUT in order for Cycle Tempo to not give an error. According to figure 16, increasing the OFRAT will make the EOUT less negative. This is confirmed by the values calculated by Cycle Tempo. This means that the voltage drop between the EOUT and the user defined VCELL becomes larger. Therefore, at the same VCELL, the power increases, as the amount of current passing through the fuel cell also increases when the OFRAT is increased.

At $U_F = 0.8$, it is obvious that there is only a small window in which the SOFEC can produce power. This scenario is best explained with the following table, where the UFL has been set to 0.5. For this situation, the SOFEC will produce power at a much lower OFRAT as shown in the following table:

<table>
<thead>
<tr>
<th>OFRAT</th>
<th>UFL</th>
<th>EOUT th.</th>
<th>VCELL</th>
<th>CT EOUT</th>
<th>POWER</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>-0.022</td>
<td>-0.1</td>
<td>-0.024</td>
<td>-2.16kW</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.03</td>
<td>0.01</td>
<td>0.0296</td>
<td>-2.73kW</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>0.06</td>
<td>0.01</td>
<td>0.0296</td>
<td>0.10kW</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.072</td>
<td>0.01</td>
<td>0.0697</td>
<td>0.132kW</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.072</td>
<td>0.01</td>
<td>0.0697</td>
<td>0.157kW</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>0.087</td>
<td>0.01</td>
<td>0.088</td>
<td>0.45kW</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>0.087</td>
<td>0.01</td>
<td>0.088</td>
<td>0.1768kW</td>
</tr>
</tbody>
</table>

Table 27: Operating parameters with changing OFRAT (2)

Using a smaller fuel utilization (UFL), figure 16 predicts that the tipping point between producing and consuming power will come much faster (at a lower OFRAT). The first calculation shows indeed that the fuel cell is only capable of consuming power as the EOUT is smaller than 0. However, at OFRAT = 2, the EOUT becomes positive. From this point on, increasing the OFRAT will only increase the EOUT, allowing the user to define a increasingly larger VCELL resulting in a higher power output. This is exactly the case for the following calculations. For OFRAT 5, the voltage is increased from 0.01 to 0.05V. It can actually be increased all the way up to 0.0697, as long as it is smaller than the Cycle Tempo calculated EOUT.

7.2. Changing UFL

Changing the UFL will also have a very distinctive effect of the fuel cell. Figure 16 shows that a low UFL will allow the fuel cell to produce power, as long as the user defines a positive VCELL. Using an anodic 90:10 and cathodic 90:10 entrance flow, the following results are obtained as shown in the following table:
<table>
<thead>
<tr>
<th>UFL</th>
<th>EOUT th.</th>
<th>VCELL</th>
<th>C’T EOUT</th>
<th>POWER</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.05</td>
<td>0.05</td>
<td>0.059</td>
<td>0.85kW</td>
</tr>
<tr>
<td>0.4</td>
<td>0.018</td>
<td>0.015</td>
<td>0.0179</td>
<td>0.73kW</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.022</td>
<td>-0.5</td>
<td>-0.0241</td>
<td>-44.25kW</td>
</tr>
<tr>
<td>0.55</td>
<td>-0.022</td>
<td>-0.1</td>
<td>-0.0241</td>
<td>-3.44kW</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.06</td>
<td>-0.1</td>
<td>-0.0642</td>
<td>-3.27kW</td>
</tr>
</tbody>
</table>
| 0.7 | -0.11   | -0.1  | ERR      | /  
| 0.77| -0.165  | -0.2  | -0.111   | -8.95kW |
| 0.8 | -0.11   | -0.2  | -1.693   | -8.57kW |

Table 28: Operating parameters with changing UFL

From this table, several interesting pieces of information can be retrieved.

- Firstly, it is obvious that that increasing the UFL will decrease (more negative) the EOUT. This follows the curve shown in figure 16. For this reason, the VCELL of the first (UFL 0.3) and second (UFL=0.4) calculation have different cell voltages. At an UFL of 0.3, the EOUT is 0.059. This allows the user to define a VCELL up to 0.059 V. If the user defined value lies between this value and 0, the fuel cell will produce power. Lowering the VCELL below 0 will automatically make the fuel cell consume power. However, decreasing the voltage that much only increases the voltage drop, and therefore the current passing through the fuel cell. The current is directly linked to the hydrogen production, so more current equals more hydrogen production.

- Secondly, there are two situations where increasing the UFL with constant VCELL, actually decreases the POWER consumption (UFL = 0.5 & 0.6 with VCELL = -0.1 and UFL = 0.7 & 0.8 with VCELL = -0.2) . This might sound contradictory, as UFL should decrease the reversible cell voltage. However, this result is easily explained by taking a closer look at the voltage drop equation and its relationship with the current density and cell voltage:

\[ i = \frac{U_F}{R_{ASR}} \times \left( \int_0^{U_F} \frac{dx}{E_{rev}(x) - E} \right)^{-1} \]  \hspace{1cm} (48)

This equation states the the voltage drop is determined by the difference between the reversible cell voltage and the operating cell voltage. At a low \( U_F \), the difference between the EOUT and cell voltage is larger than at a higher \( U_F \). Therefore, keeping the cell voltage constant results in the voltage drop becoming smaller when increasing the \( U_F \). At \( U_F = 0.8 \), the difference between EOUT and E is less than at \( U_F=0.7 \), for VCELL=-0.2. The voltage drop decreases, and using its definition (\( \Delta V = i \cdot R_{ASR} \)), the current density must also decrease. However, decreasing the current density while keeping the cell voltage constant will result in reduced power consumption. This is exactly the case in this situation, as the power consumption becomes less negative (and smaller).
Lastly, there is also a column containing ERR. This indicates that Cycle Tempo has given an error in its initial calculation. Looking closely at the values, it becomes obvious that the user has defined an invalid VCELL. This can NEVER be larger than EOUT. Cycle Tempo’s built in checks resolve this problem by giving an error, and automatically reducing the UFL. It is know that reducing the UFL will increase the EOUT. This action will continuously be performed up to the point where indeed the VCELL is smaller than EOUT.

7.3. Changing cell voltage

Lastly, there is the possibility of changing the cell voltage. The rest of the input variables are kept constant. The same molar ratio of the anode and cathode are used as in the previous approach. Furthermore, the $U_F$ is kept constant at 0.8 and the OFRAT is 1.

The results are shown in the following table:

<table>
<thead>
<tr>
<th>VCELL</th>
<th>POWER</th>
<th>EIN</th>
<th>EOUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.3</td>
<td>-16.9kW</td>
<td>0.2454</td>
<td>-0.169</td>
</tr>
<tr>
<td>-0.4</td>
<td>-28.06kW</td>
<td>0.2454</td>
<td>-0.169</td>
</tr>
<tr>
<td>-0.5</td>
<td>-41.82kW</td>
<td>0.2454</td>
<td>-0.169</td>
</tr>
<tr>
<td>-0.6</td>
<td>-56.26kW</td>
<td>0.2454</td>
<td>-0.169</td>
</tr>
<tr>
<td>-0.7</td>
<td>-77.36kW</td>
<td>0.2454</td>
<td>-0.169</td>
</tr>
<tr>
<td>-0.8</td>
<td>-86.26kW</td>
<td>0.2454</td>
<td>-0.169</td>
</tr>
</tbody>
</table>

Table 29: Operating parameters with changing VCELL

As could be expected, the power consumption will increase with an increasing (more negative) cell voltage. However, the power does not scale linearly with the increase in cell voltage. This can be explained by the power, that is defined by the cell voltage and the current density. The current density is directly proportional with the voltage drop. From the voltage drop equation, it becomes obvious that this increases when the difference between the reversible cell voltage and actual cell voltage increases. Changing the cell voltage, therefore, effects the power in two ways. Firstly because the cell voltage (is changed) is multiplied by the current density. And secondly, because the current density also increases with the voltage drop. For example: running the fuel cell at -0.4V and -0.5V does not increase the power consumption by 25% (increase % of voltage), but almost 50%.

7.4. Conclusion

Summarizing the results, Cycle Tempo performs according to predictions. The simplified SOFEC only runs on hydrogen and the calculations are based on the VOLT approach. However, the results are in accordance with the theory, confirming the correct SOFEC code implementation. For anyone wishing to produce power with his SOFEC, these results indi-
cate nicely in what regions the fuel cell must operate in order for it to produce power. It has also become clear that the amount of power produced by the fuel is severely limited. The VCELL must be smaller than EOUT, but larger than 0. Also, the amount of current through the fuel cell is also restricted by the difference between EOUT and VCELL.

Future research should involve creating new restrictions within the code for the user defined ESTVLT, stating that it must be positive or negative based on the other input values. At this moment, the EOUT is calculated by hand in order to define a correct VCELL.
8. SOFEC in the H₂ society

Though the SOFEC isn’t the only or the cleanest way to produce hydrogen, it does seem to be a perfect intermediate model between the current fossil fuel driven economy and a future that is totally carbon-free. To put the SOFEC into perspective, this chapter will cover the most important aspects of the hydrogen society and propose how the SOFEC fits into this.

The hydrogen economy and all its aspects can globally be divided into the following sections: production, delivery, storage and conversion & applications. (U.S. Department of Energy [1])

8.1. Production

Hydrogen can be produced from a variety of sources. The most important ones include fossil fuels, biomass, heat powered thermochemical reactions, renewable energy sources and electrolyzers.

At present, most of the world’s hydrogen production is used in a variety of industries, including the production of chemicals and petroleum, metal treating and electrical devices. In most cases, hydrogen is used as an intermediate chemical for larger processes. On a much smaller scale, it is used as an energy carrier, for instance in the transportation sector.

Hydrogen is the most abundant chemical element of the universes chemical elemental mass, namely 75%. However, it does not naturally exist on earth. It must always be produced out of other compounds, including water, fossil fuels or biomass. There are a lot of different production methods. All production methods need their own energy sources and will generate different by-products and emissions.

Currently, the reformation of methane, as also occurs inside the anode of the SOFEC, is the most popular method of hydrogen production. This accounts for 95% of the hydrogen production. This method is the most cost efficient production method, that delivers hydrogen with CO₂ as byproduct. The drawback is that for a cost effective production, it is necessary to produce the hydrogen in large scale production facilities, requiring a constant and large load. Though this system outperforms any other method of hydrogen production, it is the SOFEC’s versatility that makes it a promising alternative. The reformation process of methane is bound to large centralized plants, while the SOFEC, being much more compact, will be able to be placed throughout the country, producing hydrogen locally.
8.2. Delivery

The transportation of hydrogen is a large contributor to the price the end consumer must pay. Currently, hydrogen is delivered through pipes, cylinders and cryogenic tankers. The piping system is similar to those currently used for natural gas transportation. Due to the high diffusibility of hydrogen, pipes are restricted to a short distance. This can be increased by upgrading the pipes, which will require a substantial investment. Either way, losses are significant with this method of delivery using current technologies. The next option is the transportation inside pressurized cylinders on trucks. This also has a limited range of around 200 - 400km. Add the fact that pressurizing the H\textsubscript{2} will cost energy, increasing the price per amount of hydrogen. The last option involves using super insulated cryogenic tankers, which have a range of 2000 km. As with pressurizing, this also requires massive amounts of energy to cool and pressurize the hydrogen into a liquid state before it can enter the tanker.

It seems obvious that all current forms of transportation require extra costs before hydrogen can be delivered to the end-user. A possible future vision could therefore consists of:

1. A large scale infrastructure for transportation to high-demand area’s.

2. On-site production for rural and lower-demand area’s.

The second option is, of course, where the SOFEC comes into play. The SOFEC is a great alternative for small scale on-site hydrogen production.

8.3. Storage

Storage of hydrogen is also a problem. Hydrogen has a low volumetric and gravimetric energy density. Its kilo joules per liter or kg are very low compared to, lets say: gasoline. The following table lists a couple of the currently used fuels and their energy densities:

<table>
<thead>
<tr>
<th>Storage Type</th>
<th>Specific energy (MJ/kg)</th>
<th>Energy Density (MJ/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane: 1 bar &amp; 15°C</td>
<td>55.6</td>
<td>0.0378</td>
</tr>
<tr>
<td>Gasoline</td>
<td>44.6</td>
<td>34.2</td>
</tr>
<tr>
<td>H\textsubscript{2}: 1 bar &amp; 15°C</td>
<td>143</td>
<td>0.01079</td>
</tr>
<tr>
<td>H\textsubscript{2}: 700 bar</td>
<td>143</td>
<td>5.6</td>
</tr>
<tr>
<td>H\textsubscript{2}: liquid</td>
<td>143</td>
<td>10.1</td>
</tr>
</tbody>
</table>
It becomes clear that though hydrogen has a high specific energy density, its volumetric energy density leaves much to be desired. The specific energy density of hydrogen is obviously the same in any state it is in, and is considerably higher than the other substances. Yet, the volumetric density is of importance when using hydrogen in, for example: the transportation sector. The goal is to carry as much 'energy' in a compact volume as possible. Even when liquifying hydrogen, which requires a lot of energy, its energy density is still only $\frac{1}{3}$ of that of gasoline. The low energy density forms one of the most important reasons why no full scale hydrogen implementation has been realized yet. Gasoline is still much cheaper, and its technologies are much more advanced. The society suffers from a technological 'lock-in'.

However, research has intensified drastically over the past decade, with frequent new discoveries. A few of the most promising technologies have been listed below:

- **Gas tanks.**
  This, obviously, involves pressurizing the gas. Currently, tanks are pressurized till around 300-400 bar. Current research shows stable tanks at 700 bar. Even then, the energy density is still about 17% of that of gasoline. Higher pressures will be possible, but will need a total new design of the tanks, that are currently used.

- **Liquid hydrogen.**
  Already widely applied and has a much higher energy density than pressurized hydrogen. The main problem is the cost, associated with pressurizing and lowering the temperature of hydrogen. Hydrogen becomes liquid at -253°C.

- **Metal Organic Framework.**
  MOF for short, which involves injecting hydrogen in to open spaces of a metal-organic crystal lattice. This new technique has potential, but is still in early stages of development.

- **Metal Hydride.**
  This type of 'chemical' storage shows great promise. It involves a liquid, that binds very strongly with hydrogen. The reverse reaction of releasing the hydrogen is also possible, and only requires a minimum amount of added energy to do so. In current research, tests show a higher volumetric energy density than liquid hydrogen. Research into metal hydrides is one of the main researches performed here at the TU Delft.

Next to these, other options are also being researched. The most important issue, next to safety, is the energy density. Once this reaches a competitive level, people will start seeing
much more hydrogen vehicles arriving.

8.4. Conversion and Applications

The conversion and applications of hydrogen refer to all devices that are capable of using hydrogen and what they are intended for. For a car running on hydrogen, while using an internal combustion engine, the conversion will be to mechanical energy. However, during this conversion, the maximum usable energy retrievable to perform mechanical work is limited by the Otto thermal cycle. The other option is the use of a fuel cell. In this situation, the chemical energy stored in the hydrogen is converted directly into electrical energy. The efficiency is much higher than directly combusting the hydrogen.

It is obvious that the use of the application determines which type of conversion is used. Applications vary from car engines to power supplies. Either way, it is obvious that the fuel cell is on the winning team, as its conversion to electrical energy is much higher than direct combustion of hydrogen. Currently, hydrogen is used almost solely for large scale industrial processes. Once the energy density of the storage of hydrogen can be increased, it is safe to predict that the fuel cell will be used in much more applications where keeping the system compact plays a large role. Most importantly, the transport sector will benefit greatly from any progress made in this field.

8.5. SOFEC in the $\text{H}_2$ economy

In the previous paragraphs, a brief overview has been given of all aspects involved for a hydrogen economy. There are still a lot of problems that need to be addressed in order for hydrogen to become an important part of the modern society. The SOFEC also has a place between the previously mentioned aspects of the $\text{H}_2$ economy. Dependent on how the SOFEC is used, will can it be placed in either production, conversion or application. The SOFC/SOFEC (can produced power as a SOFC when $\text{H}_2\text{O}$ cathode feed is stopped) can adapt to a variety of situations, where it will produce hydrogen cheaply, but also functions as a stationary power usply. An example of how the SOFEC could be used in the future is given in the following figure:
This figure of the SOFEC is a prime example as to what extent the fuel cell can be used. Its connected to a methane pipe, where it is safe to assume that all western countries are in possession of an adequate infrastructure to deliver it. Furthermore, it is connected to a couple of renewable energy sources: solar cells and wind turbines. The SOFEC could be connected to any energy source, any of which is available at that location. Furthermore, it is also connected to a grid. This to ensure there is always available electricity in times of little wind and sun. Fueling stations will be placed closely to the SOFEC’s and therefore the transportation costs of the newly created hydrogen can be brought to a minimum. There are a great amount of other functions the SOFEC can fulfill like:

- Function as a backup generator for a hospital. Assuming the grid should fail and the hydrogen tanks are full, the SOFEC could use the hydrogen to supply emergency power.
• If the tanks are full, and no cars need refueling, the fuel cell could, just as the renewable energy sources, be used to provide electricity to the grid.

• In a situation that lots of cars need hydrogen during a windless night, the SOFEC could draw power from the grid and still provide enough hydrogen.

These are just a few examples, but it clearly shows the possibilities.

8.6. Conclusion

In the future, hydrogen is to become the premier energy carrier. Ultimately, one will want to reduce the dependance on imported petroleum. Hydrogen, and its clean production, will drastically reduce the pollution and greenhouse gas emissions. The largest challenge, trying to achieve this vision of abundant clean fuel, is the cost. Now, hydrogen production costs are high, in relation to conventional fuels. With most of the current hydrogen being produced from hydrocarbons, the cost, per unit energy, is higher than the hydrocarbon itself.

Current large scale, well-developed delivery infrastructures for natural gas, oil, coal and electricity keep the energy prices low, making it hard for hydrogen to compete. Next to this, current large scale hydrogen production systems produce large quantities of CO$_2$ and is considered damaging for the environment. This will, however, not be much better with the SOFEC, as it still needs methane to cheaply produce hydrogen. An important goal, whether using large scale methane reformation plants or a SOFEC, will be to supply electricity from renewable energy. Ultimately, a SOEC powered by renewable energy would be the perfect option as no hydrocarbons are used at all.

Lastly, public awareness is still a serious problem. People do not want to work with or invest in hydrogen. A basic understanding of the effect and advantages of hydrogen need to brought to the public. Maybe if governments and producers of hydrogen will invest more in demonstrations of the advantages, confidence in hydrogen will be created in society.

All the factors form major barriers that prevent the hydrogen economy to be implemented. Research has intensified greatly over the past years, however, it wont be any time soon till hydrogen powered cars will be the preferred form of transportation.
9. Conclusion and recommendations

The SOFEC technology has the potential to lower the cost of electrolysis produced hydrogen. The technique is fairly new, and was only patented in 2000. Though the solution isn’t without CO$_2$ exhausts, it is an intermediate step towards a future using only renewable energy.

The theory is straightforward: the added methane is reformed at the anode, resulting in hydrogen (and CO$_2$). This hydrogen will oxidate at the anode as if it were a SOFC, resulting in a negative Gibb’s free energy. At the other side, water is fed to the cathode. This will electrolyze, as if it were a SOEC, and provide oxygen ions for the oxidation reaction in the anode. The Gibb’s free energy needed for the electrolysis reaction will be provided by the oxidation reaction at the anode. These will effectively counteract each other, resulting in a lower electrical demand for the hydrogen production than directly electrolyzing water with a SOEC.

This report has made a start to transferring the theory into a working simulation. Due to its complexity, the SOFEC has been simplified. Instead of adding methane to the anode and taking all reactions and reactants into consideration, the option was chosen to model the SOFEC with pure hydrogen added to the anode. Firstly, the theory of the SOFC and SOEC are explained. This knowledge is then applied to the SOFEC, which is quite straightforward. This is then backed mathematically, with which a start was made for the actual programming. The transfer to Cycle Tempo is divided into three steps, where firstly the flow charts of the program are discussed. Based on this, the most important mathematical subroutines are shown, where the modifications are listed per type of fuel cell: SOFC, SOEC and SOFEC. Finally, these modifications are coded into the source code. Each step is documented and explained, finally resulting in a working program. The calculation results from running the program are listed afterwards, where these are compared to the theory and mathematics discussed earlier. The following conclusions can be drawn on the theory and programming:

- **SOFEC theory**
  
The idea of adding a fuel to the anode does not seem very difficult to understand. However, while mathematically describing its behavior, several problems were encountered. The SOFEC contains elements of both a SOFC and a SOEC. A fuel cell capable of producing as well as consuming power with a positive current was only explained when the assumption was made that the cell voltage could either be positive or negative. This lead to the cell voltage curves showing it intersect the x-axis at certain fuel
utilizations. Nevertheless, the theory now stands solid and will help any wishing to start a research on SOFEC’s.

- **SOFEC programming**

  The initial idea was that the SOFEC was an electrolyzer with a lower reversible cell voltage. The power consumption would be lower, as was expected. However, during this research, it become more and more apparent that it contained more resemblance to the SOFC. Both currents were positive, and the mathematical subroutines needed no modifications. Finally programming the SOFEC was less complicated that initially presumed. Summarized, the current SOFC code needed only to be equipped with the electrolysis reaction, the possibility of a negative cell voltage, and an altered reversible cell voltage at standard conditions. The electrolysis reaction was easily programmed, based on the assumption that the amount of oxygen (used during oxidation or as a result of electrolysis) was equal. Because the incoming flows were only restricted to water and hydrogen, the exiting flows could easily be defined. The changing reversible cell voltage was a direct result from the Nernst equation, and the different mathematical subroutines used in Cycle Tempo were perfectly capable of calculating this for the SOFEC. The only major adjustment lies in the reversible cell voltage at standard conditions. Because the oxidation reaction and electrolysis reaction counteract each other, the reversible cell voltage at standard conditions results to zero.

- **Results**

  The results retrieved from running Cycle Tempo were in direct accordance to the results calculated by hand. This was the most important step in confirming the correct execution of the program. The results also showed how the power changes with different OFRAT’s and UFL’s. Though only a handful of calculations were performed, the next step would be analyze the power production/consumption versus current density. It would give great insight into knowing at which UFL, OFRAT and VCELL, the production of hydrogen would be the most efficient and whether the fuel cell will consume or produce power.

However, the results given do show that Cycle Tempo performs its calculations accordingly, there are some adjustments recommended for future users in order to make the program more user friendly:

- The current code is only capable of using the VOLT approach (as opposed to designing a SOFEC based a specific current density, power or fuel flow). Further
research should incorporate the other approaches allowing the user to define his fuel cell based on fuel flow, power consumption and current density.

- The current fuel flow is based on the amount of hydrogen oxidized. Another approach would be to design a fuel cell based on the possible amount of hydrogen output at the cathode. This will require extensive coding, as the fuel cell must now be designed using the cathode a defining electrode. This subject has been discussed briefly during the SOEC approach and dismissed due to the amount of extra work it would cost.

- Extra warnings must be added to alert the user on his ill-chosen operating parameters. The SOFEC is able to consume and produce power. Therefore, in any other approach than the VOLT approach, Cycle Tempo must be equipped with the ability to tell the user that his defined ESTVLT is not correct.

- Finally, the user interface must be updated. This report is based on the recoding of the normal SOFC. Future versions of Cycle Tempo must add the 'extra' SOFEC fuel cell option in order to keep the program universal for every type of fuel cell.

Though the program runs as it is supposed to, there are still several adjustments and improvements that can be made in order to make this model even more versatile. This model is based on a SOFEC running on hydrogen. This is, of course, not a realistic model, as there is no sense in using pure hydrogen to create hydrogen. However, the mechanics of this fuel cell can be used for a SOFEC running on any type of fuel. Future research will show how different fuels affect the cell voltage and current density. If its results are then compared to the current hydrogen production methods, a real conclusion can be drawn on the effectiveness and energetic efficiency of the SOFEC.

Next to the essential technical knowledge, an economical analysis would also be a welcome addition. As with all fuel producing devices, the most important driver is always it’s economic viability. Observing these results of the SOFEC model, some careful conclusions can be drawn as to the fact that this system could produce hydrogen at a lower cost than the SOEC alternative. Compared to large scale methane reformation plants, this statement cannot be made. A more in-depth comparison between the two should resolve this issue. However, there is no denying that the SOFEC is much more compact and versatile than a large scale plant, which definitely contributes to it applicability for different situations.

Time shall tell if the world is ready to adopt hydrogen as its premier energy carrier. The SOFEC could certainly help pave the road to this scenario.
A. Cycle Tempo Introduction

The program is fairly small (25MB) and must be installed in combination with another product also created here at the TU: Fluid Prop. This program contains most of the fluid transport and thermodynamic properties, used within Cycle Tempo. Once the program is booted, certain visual aids are recommended to be turned on which have also been used in the following figures. (Options → Show Numbers, Show Grid, Show Connections points).

This fuel cell model will consist only of the basic parts needed to simulate the system. No consideration will be given to any external cooling systems, heat transfer or auxiliary fuel sources. The model will contain two gas sources, two gas sinks and the fuel cell. These will all be connected with gas connection lines.

First, a fuel cell must be added. This is located in the tool bar on the right hand side. Next, the gas sinks and sources must be added, also within the same tool box. To connect these, the tool box containing the connection lines is selected. In here, the Gas line must be selected. By dragging from the sources to the entrances of the cathode and anode, gas connection lines are made. The same procedure is needed for the outputs. These steps are shown in the following figure 18:

![Fuel cell model](image.png)

(a) Selecting the fuel cell and sink / source  (b) Connecting the gas lines  (c) Final fuel cell model

Figure 18: Steps taken to make our simple fuel cell model
The next step requires the input of parameters. These are found by double clicking the aforementioned components. Gas composition is changed by clicking the inlet pipes. There, the edit composition button is selected. H2 is chosen at 100% mole composition. This is illustrated in the figure 19.

![Figure 19: Altering the gas composition of the anode inlet](image)

The process is repeated for the cathode inlet, where O2 is selected from the gas components. For simplicity, pure oxygen is chosen instead of air, containing only a certain amount of oxygen.

Instead of clicking the sinks and sources independently to adjust their parameters, this can all be combined in one step. For this reason, the sinks and sources will not be adjusted anymore throughout the whole modeling process.
Double clicking the fuel cell displays pop-up box shown in figure 20.

![Figure 20: Fuel cell normal input parameters](image)

For sake of simplicity, only the absolutely necessary parameters are chosen. These are summarized and explained in table 31.

<table>
<thead>
<tr>
<th>Normal Input Data</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EEQCOCD = 1</td>
<td>Should always be 1, except if a cooling cycle is used (then use 2). During this research no cooling is used, and the pressures and temperatures are provided by the user, from which the mass flow of the gasses is calculated.</td>
</tr>
<tr>
<td>PINAN = 1 bar</td>
<td>Inlet pressure of the anode</td>
</tr>
<tr>
<td>TINAN = 1023 °C</td>
<td>Inlet temperature of the anode</td>
</tr>
<tr>
<td>TOUTPS = 1023 °C</td>
<td>Outlet temperature of the anode and cathode</td>
</tr>
<tr>
<td>PINCA = 1 bar</td>
<td>Inlet pressure of the cathode</td>
</tr>
<tr>
<td>TINCA = 1000 °C</td>
<td>Inlet temperature of the anode</td>
</tr>
<tr>
<td>POWER = 0.2 MW</td>
<td>Output power of the fuel cell</td>
</tr>
<tr>
<td>DCAC = 1</td>
<td>Direct current to alternating current efficiency.</td>
</tr>
<tr>
<td>TFCELL = 1023 °C</td>
<td>Operating temperature of the fuel cell</td>
</tr>
</tbody>
</table>

Table 31: Fuel cell input parameters

By adjusting input parameters of anode and cathode, there is no need to do this within the sinks and sources themselves. This makes future alterations easier and more clear. If they are, by some chance, doubly defined by the user within the sink or source, Cycle Tempo
will directly output an error and terminate the simulation process.
In the case of different pressures at inlet and outlet, the user must define a pressure drop: DELPAN and DELPCA.

Next to the above mentioned parameters, which are located under the 'normal input data', there is also the possibility of changing the geometry options. The Geometry input data is shown in figure 21 with the most important input values summarized in table 32.

![Figure 21: Fuel cell Geometry input parameters](image)

<table>
<thead>
<tr>
<th>Geometry input data</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCELL</td>
<td>7.5e-05 ohm m$^2$</td>
<td>Cell Area specific resistance $R_{ASR}$ as used in the mathematical model</td>
</tr>
<tr>
<td>ACELL</td>
<td>200 m$^2$</td>
<td>Total area of the fuel cell (combined area of the stacked fuel cells)</td>
</tr>
<tr>
<td>ESTVLT</td>
<td>0.8 V</td>
<td>Estimate of the cell voltage</td>
</tr>
</tbody>
</table>

Table 32: Fuel cell geometry input parameters

Though not as many options are filled in as the normal input, these are critical for the mathematical subroutines. In this situation, the power is already defined, meaning that CDENS and VCELL and any mass flows are calculated by Cycle Tempo and therefore must not be filled in. By defining a RCELL and ACELL, Cycle Tempo will be able to calculate the total resistance of the fuel cell by multiplying these with each other. The final input is the ESTVLT that tells Cycle Tempo which cell voltage the user predicts the fuel
cell will have.

The final input parameters are found under the More input data button as shown in figure 22. Here, only the UFL: the fuel utilization, is defined. This is used within the Nernst equation and defines the partial pressures of the gasses within the anode and cathode.

![Figure 22: Fuel cell more input parameters](image)

When all the above mentioned parameters are filled, the program is run. If all goes well, meaning are parameters are correct, the fuel cell will be calculated, as depicted in figure 23.
By pressing the the call-out button xxx,yy within the tool-box panel and clicking on the fuel cell and all the gas connections, the extra information boxes are added. These contain important information and summarize the values filled in, and the values calculated. Next to the fuel cell, some new values are shown. The cell voltage is calculated, 0.798V which lies close to the ESTVLT used.

This fuel cell is a simple model which contains a few of the numerous other options. For a full description of the other inputs possible, see the the Cycle Tempo manual [13].
B. SOEC coding

During the process of coding the SOFEC, the SOEC approach has also been discussed. Initial thoughts presumed both fuel cells to have similar properties. Later on, this idea was negated as it became clear that the SOFEC had more in common with the SOFC. Nevertheless, the results from this research will form a good start for anyone attempting to program the SOEC.

The code differs only slightly from the SOFC, with the most important differences summarized below according to the corresponding routine or function:
• **PrFCel** The most obvious change lies in the altered mathematical subroutines as mentioned in the SOEC chapter.

```plaintext
IF (Given(CDENS)) THEN
  VOLT = -V_CDR( IAP, TYPE, FLOW, NCOMP, COMP, YAN, YCA,
                & CDENS, RCELL, ESTVLT, UFLH, OFR, PFCELL,
                & TFCELL, G, TH2OOS, XSHIFT, EPS, FAIL,
                & SPFC_OD)
  CURR = CDENS * ACELL
  POWER = CURR * VOLT / 1.d3
  FLFUEL = -1*(CURR / (YH2EQ * UFL * 2 * FAR)) ! Faraday's law
ELSE IF (Given(VOLT)) THEN
  CDENS = -CD_VR( IAP, TYPE, FLOW, NCOMP, COMP, YAN, YCA,
                 & VOLT, RCELL, UFLH, OFR, PFCELL, TFCELL, G,
                 & TH2OOS, XSHIFT, EPS, FAIL, SPFC_OD)
  CURR = CDENS * ACELL
  POWER = CURR * VOLT / 1.d3
  FLFUEL = -1*(CURR / (YH2EQ * UFL * 2 * FAR)) ! Faraday's law
ELSE IF (Given(POWER)) THEN
  PDENS = POWER * 1.d3 / ACELL
  VOLT = -V_PDR( IAP, TYPE, FLOW, NCOMP, COMP, YAN, YCA,
                 & PDENS, RCELL, ESTVLT, UFLH, OFR, PFCELL,
                 & TFCELL, G, TH2OOS, XSHIFT, EPS, FAIL,
                 & SPFC_OD)
  CDENS = PDENS / VOLT
  CURR = CDENS * ACELL
  FLFUEL = -1*(CURR / (YH2EQ * UFL * 2 * FAR)) ! Faraday's law
ELSE
  FLFUEL comes from MKGS or ESTMFL or is estimated
  FLFUEL = EstFuel( NLIN, ITM, LA, MKGS, AVERG, ESTMFL)
  CURR = -1*(FLFUEL * YH2EQ * UFL * 2 * FAR) ! Faraday's law
  CDENS = CURR / ACELL
  VOLT = -V_CDR( IAP, TYPE, FLOW, NCOMP, COMP, YAN, YCA,
                 & CDENS, RCELL, ESTVLT, UFLH, OFR, PFCELL,
                 & TFCELL, G, TH2OOS, XSHIFT, EPS, FAIL,
                 & SPFC_OD)
```

• **Vloss.** This function calculates the voltage losses by numerical calculation of the integral shown in table 12. The actual calculation of the voltage drop integral is performed with Simpson’s 1/3 rule. Cycle Tempo performs two checks before actually calculating the integral. It determines whether the cell voltage is too high, compared to reversible cell voltage. From the mathematical chapter for the SOFC, it is given that the cell voltage must be lower than the reversible cell voltage. This is due to the fact that that voltage drop is subtracted from the reversible cell voltage. Cycle Tempo therefore
performs a check at the entrance of the fuel cell and at the exit. This check means it will calculate the EREV at $x = 0$ and at $x = UFL$. Both values called: \( EIN \) and \( EOUT \), must be smaller than EREV, otherwise a loop is evoked, lowering the UFL by 5\% till the arguments hold. In the SOEC situation, the cell voltage needs to be higher than EREV.

This has been incorporated as follows:

```fortran
*-------------------------------------------------------------------------*
* Check if V > Erev over whole range of conversion                      *
*-------------------------------------------------------------------------*

* Calculation Erev x=0
    DCONV = 0.d0
    CONV = 0.d0
    EIN = Erev(IAP, TYPE, FLOW, NCOMP, COMP, YAN_0, YAN, YCA_0,
                  & UFL, CONV, DCONV, OFRAT, PFCELL, TFCELL, G,
                  & TH2OOS, XSHIFT, FAIL)

    IF (EIN > VOLT) THEN
        WRITE (13,900) IAP, EIN, VOLT
        CALL ErrorIncrement()
        Vloss = Unknown()
        FAIL = .TRUE.
        RETURN
    ENDIF

* Calculation Erev x=L (DCNV still equals 0)
    CONV = UFL
    EOUT = Erev(IAP, TYPE, FLOW, NCOMP, COMP, YAN_0, YAN, YCA_0,
                 & UFL, CONV, DCONV, OFRAT, PFCELL, TFCELL, G,
                 & TH2OOS, XSHIFT, FAIL)

    DO WHILE (EOUT > VOLT)
        UFL = 0.95d0 * UFL
        WRITE (13,901) IAP, EOUT, VOLT, UFL
        CALL WarningIncrement()

        DCONV = 0
        CONV = UFL
        EOUT = Erev(IAP, TYPE, FLOW, NCOMP, COMP, YAN_0, YAN, YCA_0,
                     & UFL, CONV, DCONV, OFRAT, PFCELL, TFCELL, G,
                     & TH2OOS, XSHIFT, FAIL)
    ENDDO
```

After the used-defined cell voltage is checked to be greater than the reversible cell
voltage, the integration is performed.

The following code shows this:

```
*-------------------------------------------------------------------------*
* Numerical calculation with simpsonrule of integral dx/(E-V) "*
*-------------------------------------------------------------------------*
F0 = 1 / (VOLT - E0)
F1 = 1 / (VOLT - E1)
F2 = 1 / (VOLT - E2)
```

Instead of subtracting the cell voltage from the reversible cell voltage, they have switched places. Using Simpson’s 1/3 rule, Cycle Tempo now calculates the integral by taking three steps, spaced closely to each other. These are E0, E1 and E2, and are the reversible cell voltage at a certain location of the fuel cell. Then, the average is taken from these three values. When performing this a predefined amount of times, the resulting in the voltage drop profile over the length of the fuel cell will be calculated.

In essence, the SOEC should run correctly. However, this code has never been checked, as it was not one of the goals of this research.
References


