# Role of Fuel assisted Solid oxide Electrolysis in the Renewable Energy Scenario: A Feasibility Study

BY

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# ABSTRACT

Fuel assisted electrolysis has the advantage of reducing the power demand of hydrogen production by solid oxide electrolysis with the help of assisting fuel. This thesis presents a feasibility study on the use of biogas fuelled solid oxide fuel assisted electrolysis (SOFEC) for hydrogen production on an industrial scale. The biogas is supplied as a source of hydrogen to the anode of the solid oxide electrolyser where hydrogen gets oxidised and provides electrons for the steam splitting taking place at the cathode. This results in upgrading of biogas to hydrogen and reduction in the electrical power demand. However, steam reforming of biogas (methane) is an endothermic reaction and hence, heat has to be supplied externally.

The SOFEC system is modelled in Cycle Tempo and the modelling results are used to perform the feasibility study based on technical, economic and social aspects. Further, to corroborate the results from the study, a case study scenario of integration of SOFEC in a steel mill is presented.

With regard to technical aspects, the SOFEC cathode and electrolyte materials were found to be in practice commercially, adequate biogas supply could be ensured by biogas production at waste water treatment plants and heat supply from high temperature waste heat sources was proposed to meet heat demand of methane reforming. Based on these conditions, the SOFEC system has high prospect of being technically feasible.

Further, for economic analysis, the net production cost of SOFEC was estimated to be less than 4.5 Eur/kg  $H_2$  which is lower than that of low temperature (7.32 Eur/kg  $H_2$ ) and high temperature electrolysis (5.54Eur/kg  $H_2$ ). Considering high temperature heat, recovered from molten slags in steel mills, being used as heat supply followed by a predicted drop in electrolyser capital costs, the SOFEC is able to compete with lower production costs of steam methane reforming (3 Eur/kg  $H_2$ ). Thus, low electrolyser capital costs and availability of low cost waste heat supply are the main driving factors for SOFEC to be economical.

In social aspects, the operational safety and social acceptance of SOFEC were investigated. It was concluded that for hydrogen storage challenges, existing commercial hydrogen storage solutions can work and with hydrogen fuel cells being socially accepted, the SOFEC was assumed to be accepted the same. Also the SOFEC was shown to have low  $CO_2$  (2 kg  $CO_2$  equivalent / kg  $H_2$ ) and low  $SO_2$  emissions provided sufficient desulfurisation of biogas is done. Therefore, it is concluded that the SOFEC has high potential to be socially feasible.

Although, the SOFEC has been presented to be a feasible technology, uncertainties such as degradation in performance due to interruptions in biogas supply, absence of anode materials which can withstand reducing environments, absence of low cost high temperature heat and high costs of electrolyser systems are obstacles which have to be resolved.

# **EXECUTIVE SUMMARY**

The thesis work analyses multiple facets involved in determining the feasibility of a a biogas fed solid oxide fuel assisted electrolyser (SOFEC) on an industrial scale. The concept involves using biogas fuel at the anode of a solid oxide electrolyser cell (SOEC). Here, the biogas, in presence of steam, is reformed to produce hydrogen which, in turn, gets oxidised to steam generating electrons. Further, the electrons travel to the cathode through the external circuit and take part in the steam splitting reaction at the cathode. This results in the upgrading of biogas to hydrogen at the anode and a reduction in the electrical power demand for the steam splitting process. In contrast to steam reforming of methane, the hydrogen stream exiting the cathode is hydrocarbon free and only requires steam-hydrogen mixture separation. Thus, the SOFEC produces hydrogen with electricity demand lower than the SOEC and does not require major gas cleaning units.

In Chapter 3, a literature study on how to perform a feasibility analysis was done. It was inferred that performing a feasibility study comprises of analysing three facets, namely, technical, economic and social feasibility. Technical aspects determine the construction and operational feasibility of SOFEC whereas economic aspects cover the production costs and profitability of the SOFEC. The social part involves considering social acceptance and the environmental impact of the electrolyser.

Further, a review on the current status of SOFEC was presented. While the process of fuel assisted electrolysis has been used in the aluminium industry for ore purification since the late 19th century, research on its application for hydrogen production has taken place only in the last two decades. Also, the SOFEC is an immature technology as it has only been tested on lab scale using methane or carbon monoxide as fuel with methane. In addition, the advantage of reduced power demand of SOFEC over SOEC diminishes when the fuel supply is inadequate. Thus, the various sources and consistent supply of biogas are integral in determining the operational feasibility of SOFEC.

As the SOFEC is based on the SOEC, the SOFEC structure and cell design is similar to the SOEC with fuel, instead of oxygen, at the anode. Further, with the fuel being reformed inside the fuel cell, methane present in the fuel can crack to form carbon which deposits on the anode deactivating the electrode. Therefore, steam is added at the anode to reform the methane and avoid carbon formation. However, steam reforming of methane is an endothermic reaction and heat has to be provided for the reaction. Therefore, in addition to consistent biogas supply, thermal input is also required to operate the SOFEC.

Further, in Chapter 4 and 5, the SOFEC is modelled and simulated in Cycle Tempo to provide data on fuel and steam massflows; electrical parameters and thermal demand. While the initial approach to develop a SOFEC model was to build a SOEC model and then adapt it to operate in fuel assisted mode. However, due to requirement of complex coding and time consuming process of getting the code debugged, this approach was dropped. Therefore, the SOFEC model was developed using the existing solid oxide fuel cell model present in Cycle Tempo. However, this method had some implications on the simulation results. When the SOFEC model was simulated with any fuel input and increasing fuel utilisations from 0.5 to 0.9, the cell voltage dropped whereas it should actually increase due to higher extent of hydrogen oxidation at the anode and higher current densities. Further, the simulation results presented power production, instead of the power consumption, and incorrect cathode and anode outlet temperatures. Thus, balance of plant components such as heat exchangers and blowers could not be integrated with the SOFEC model and their losses have not been considered in the model. However, the cell voltages at certain current densities for fuel utilisation of 0.8 matched with the experimental data from literature. Thus, the mass flows and electrical parameter data for fuel utilisation of 0.8 were considered for feasibility studies. A SOFEC unit of 25 stacks with 400 cells each was considered. Thermal demand calculations were done by calculating the T $\Delta$ S and heat demand by steam reforming of methane based on the mass flows and operating temperature.

In Chapter 6, the feasibility analysis was conducted based on technical, economic and social aspects.

In the technical feasibility analysis, the availability and performance of construction materials, biogas and heat inputs for operation of the SOFEC on an industrial scale were considered. With regard to the construction materials, the cathode and electrolyte materials were found to be in commercial practice. However, little research has been done on the materials for anode and use of SOFC anodes requires addition of excess steam to avoid carbon deposition, which in turn, increases power demand. Thus, the SOFEC development depends on the performance and availability of anodes which support reducing environments.

For fuel input, if biogas is produced using biomass to meet the remaining demand, it will compete with the land usage for food crops. Therefore, the operation of the SOFEC unit in the vicinity of biogas and wastewater treatment plant (WWTP) was proposed to ensure adequate supply. In addition, handling and use of biogas requires pretreatment for removal of water and sulfur which can corrode pipes and compressors. The use of commercially available desulfurisers and condensers was suggested.

The SOFEC unit operates at a temperature of  $800^{0}$ C and also requires additional heat for steam reforming occurring at the anode. Therefor, use of a heat recovery system used in SOFCs, with preheater and heat exchangers, was suggested which would recover heat from the anode and cathode off gases at a temperature of  $800^{0}$ C. Alternatively, use of waste heat in industries with high temperature effluents could be used to meet the thermal demands. In Chapter 7, a case study was performed for the integration of SOFEC in a steel mill. Here, the waste heat recovered from molten steel slags was used for the heating of biogas and steam flows. However, the current waste heat recovery systems are inefficient and most of them have not been tested on an industrial scale.

Therefore, the SOFEC could be technically feasible with a commercialised efficient waste heat recovery method, adequate supply of biogas and availability of anode materials.

In the economic feasibility analysis, the net production costs of hydrogen production (NPC) were calculated using the modelling results and literature data. The capital costs of SOFEC units, heat exchangers and other auxiliary equipment was considered as the capital expenditure (CAPEX) and the costs of electricity, fuel, water and operation and maintenance as the OPEX. It was found that the NPC for SOFEC was less than 7 Eur/kg H2 which is lower than the literature values of NPC of biomass gasification (8.25 Eur/kg H<sub>2</sub>) and low temperature electrolysis (7.34 Eur/kg H<sub>2</sub>). A major part of NPC calculation for SOFEC were the capital costs of electrolyser and operating costs of external electric heating. However, based on a 40% drop in future electrolyser costs predicted by Schmidt et al., 2017, the net production costs drop to 3 to 4 Eur/kg H2. Further, when waste heat recovery systems are incorporated, the large recurring heating costs are replaced by much lower capital costs. In the case study, waste heat is recovered from molten slag leads to a reduction of net production costs to about 2 Eur/kg H2. Thus, for the SOFEC operation to be economical, low capital costs of electrolyser and low cost external heat sources are desired.

For the social feasibility analysis, the safety in SOFEC operation, social acceptance of hydrogen technologies and environmental impact of SOFEC were considered.

In operational safety, desulfurisation of biogas to concentrations below 250ppm was suggested as it could erode the pipes and heat exchange equipment. Further, for hydrogen storage, salt caverns were proposed to be the best method for safe large scale hydrogen storage. Due to limited availability of salt caverns, other commercial methods such as metallic tanks for small scale long term storage and cryogenic storage for large scale small term storage were suggested. However, the leakage of hydrogen in metallic tanks reduce its storage efficiency and chance of hydrogen explosion in cryogenic storage requirement of concrete walls for protection.

With regard to social acceptance, the hydrogen technologies were shown to have high support. Surveys showed that there was support for hydrogen where the local communities were not aware of hydrogen fuel cell technologies. Thus, spreading awareness on the benefits of such technologies is required to ensure local support.

Further, the environmental impact of the SOFEC was studied on basis of acidification potential (AP) and global warming potential. THe value of acidification potential was found to be higher than other renewable based electrolysis processes. This was due to the presence of sulfur in the biogas which might form sulfur oxide and siloxanes when used in biogas. Further, the composition of biogas varies with sources and hence, removal of sulfur using a desulfuriser is essential. The GWP value for SOFEC with renewable electricity was calculated to be 2 to 3 kg CO<sub>2</sub>-equivalent/kg H<sub>2</sub> which was among the lowest values compared to renewable based conventional electrolysis and other hydrogen production methods.

# PREFACE

This thesis marks the culmination of my masters degree in Sustainable Energy Technology at TU Delft. The past three years have been very educational and have helped me develop on a personal as well as professional level. While I was introduced to the process of electrolysis in one of the subjects of my course, it really captured my interest when I did my internship on alkaline electrolysis at Zero Emission Fuels B.V., Delft. Having acquired experimental knowledge in electrolysis, my new goal was to learn how to model an electrolyser and its components so as to understand the process on both component and system levels.

When I met Dr. Kas Hemmes and Ir. Theo Woudstra in my second year to discuss about the thesis topic, I was very fascinated by the process of fuel assisted electrolysis and hence, decided to take it as the subject of my thesis.

I highly appreciate Dr. Kas Hemmes for sharing his knowledge and most importantly, for his patience to supervise me even after his retirement. Even when it took me a lot of time to understand my thesis topic very well, he was very patient and supportive.

I would also like to thank Ir. Theo Woudstra and Teus van der Stelt for all their assistance in Fortran coding and Cycle Tempo model simulations. Without their help, I believe it would have been a highly difficult task.

I highly value the help and support provided by Dr. Linda Kamp and academic counsellor Leonie Boortman. While Dr. Linda Kamp helped me organize my work and meet the deadlines, Leonie Boortman helped me to cope with all the stress. Thus, I am really thankful to both of them.

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# **INTRODUCTION**

The use of fossil fuels as a major source of energy has led to the rise in carbon dioxide and other greenhouse gas emissions causing global warming, air pollution and climate change. In response to the effects on the environment, the Paris Climate Agreement was introduced and adopted by 190 countries to avoid climate change by limiting global warming to well below 2°C and pursuing efforts to limit it to 1.5°C (IRENA, 2019). To curb the emissions, countries have focused on reducing emissions in the energy industry by introducing and scaling up renewable energy infrastructures such as wind and solar energy. While electrification by renewable sources, such as wind and solar, is said to reduce emissions to a great extent and cater to the energy needs, issues of intermittency, long term energy storage and lack of sustainable fuel and feedstock for chemical process industries hamper the energy transition.

While batteries have been used to store electricity in the short term, power to gas technologies has been adopted as the solution for long term energy storage. Power to gas (PtG) involves converting excess renewable electrical energy to chemical energy in gases such as hydrogen via water electrolysis. Hydrogen, formed by electrolysis can then be stored in tanks for a long duration. Subsequently, when the demand for energy is high, the hydrogen can be used as fuel or again electrochemically oxidised to give water(Ni et al., 2008). Also, the hydrogen can further be used to form chemicals such as methane, methanol and formic acid which can be used as feedstock in the chemical process industries. Thus, hydrogen is a promising alternative for fossil fuels.

While water electrolysis has its advantage of being a pollutant free process, its electricity demand is very high. Electrolysis can be done at high temperatures (steam electrolysis) to utilize waste heat from industry, remarkably reduce the electricity demand and increase reaction and hydrogen production rate. Solid oxide electrolysis cell (SOEC) is a high temperature electrolysis, operating at 600<sup>0</sup>C to 800<sup>0</sup>C, which has been researched extensively but is yet to be commercialised(Luo et al., 2014). Although a part of the electricity demand is replaced by high temperature heat demand, electricity is still the major energy consumption for electrolysis.

From the economic point of view, hydrogen production through electrolysis is influenced by the electrolyser capital costs, operating duration and the electricity purchase price during the time of operation. To balance the high capital cost, the electrolyser is run for long duration (atleast 3000 to 6000 hrs/year) (Ball and Weeda, 2016). However, this tilts the balance towards the cost of electricity incurred to operate it. Also, the cost of production through water electrolysis is 2 to 3 times that of commercial hydrogen production by steam reforming of methane. Thus, to reduce the electricity consumption costs, it is essential to minimize the electricity demand as much as possible.

Solid oxide fuel assisted electrolysis cell (SOFEC) is a novel approach to electrolysis introduced in 2000 Glass et al., 2000. The SOFEC, as opposed to SOEC, adds a fuel input in addition to steam which significantly reduces the electricity consumption in comparison to the SOEC and thus, reduces the dependency of hydrogen production economics on electricity. The fuel added can be hydrogen, methane or biogas. While it is a promising technology, it will take many years of research to be commercialised and used in the industry. In conclusion, with the SOFEC, the overall cost of hydrogen production can be lower than a SOEC.

In recent years, few researchers have conducted experiments to study the electrical performance of SOFEC (Martinez-Frias et al., 2003)(W. Wang et al., 2008). Others have performed mathematical simulation to study the electrochemical and kinetic characteristics of SOFEC (Patcharavorachot et al., 2016)(Luo et al., 2014). A previous work done by Wijers, 2011 developed a SOFEC model in Cycle Tempo and presented its simulations. However, this model was not experimentally validated. Thus, there was also interest in developing a SOFEC model in Cycle Tempo and obtaining results which can be experimentally validated. In addition, only one report of work done by (van Nielen, 2016) was found. In this work, a techno-economic assessment of the solid oxide fuel cell (SOFC) and SOFEC was performed for future Dutch energy systems using Python based modelling. The report concludes that while the costs of SOFEC are expected to decrease in future, they become competitive only when capital costs are low. However, the report uses a linear simplified model for the SOFEC input-output calculations and thus, the author suggests the use of a non linear model (such as the fuel cell model in Cycle Tempo) for more accurate results.

Hence, there is interest in performing SOFEC feasibility studies and therefore, developing a SOFEC model in Cycle Tempo is necessary. Further, a feasibility study with a SOFEC system should provide understanding on whether the development of a SOFEC is feasible and how the SOFEC can play a role in the sustainable energy transition.

### **1.1.** AIMS OF RESEARCH

The thesis work aims to assess the feasibility of a SOFEC system based on technical, economic and social aspects. The main research question and sub-questions are as follows:

- Is the biogas fuelled SOFEC system a feasible technology?
  - 1. Is the SOFEC system technically feasible?
  - 2. Is the SOFEC system economically feasible?
  - 3. Is the SOFEC system socially feasible?

## **1.2.** THESIS OUTLINE

Initially, **Chapter 2** provides a research methodology on how the feasibility studies will be performed to provide answers for the research questions.

**Chapter 3** outlines the literature review done on improving the performance of solid oxide electrolysis and provides the scope of the thesis study. This is followed by a detailed explanation of working principle and reactions involved in SOFC, SOEC and SOFEC. In addition, a description of cell design parameters such as fuel cell support and reforming configurations along with voltage losses in fuel cells is given.

Further, **Chapter 4** at first delineates the Cycle Tempo SOFC model. This includes the assumptions made, mass and energy balance, voltage calculations and the program code flow. This is followed by an explanation of SOFC and SOEC operation which is used to describe how the SOFEC is different in its operation as compared to both the SOFC and SOEC. Further, the approach used to adapt the Cycle Tempo SOFC model for SOFEC operation is given. In addition, the major model adjustments to the model are also stated.

Then, **Chapter 5** presents SOFEC model simulations for parameter studies. Initially, the SOFEC model is validated followed by the parametric sensitivity analysis. Further, a system model with heat integration is described.

Further, **Chapter 6** presents the feasibility study done to answer the research questions. Initially, the technical feasibility study is performed to determine if the SOFEC can be manufactured realistically. This is followed by economic feasibility where the cost of hydrogen production by SOFEC system is calculated. Further, a social feasibility study on the SOFEC is done where safety and social acceptance of the technology is discussed.

After determining the feasibility of SOFEC system, **Chapter 7** provides an illustration of the use of a SOFEC system by delineating a scenario for the integration of biogas fuelled SOFEC in a steel mill. This will include a description of the fuel supply, waste heat recovery for SOFEC thermal inputs and hydrogen supply for steel production.

**Chapter 8** discusses the results from the feasibility and case studies and lays out the conclusions to answer the research questions of the thesis work.

Finally, **Chapter 9** discusses the limitations of the model and provides recommendations for future work on the feasibility of SOFEC based systems.

# 2

# **RESEARCH METHODOLOGY**

To determine whether a biogas fuelled SOFEC system is feasible choice for a renewable energy scenario, a feasibility study has to be performed. The steps taken are shown in Figure 2.1.



Figure 2.1: Schematic of steps taken to perform the feasibility study

In the figure, initially literature review is done to gain the current knowledge on fuel assisted electrolysis process and further how to determine whether it is feasible and what parameters are required to do so. Further, a SOFEC model is developed and simulated to provide parameter data such as fuel, electricity and heat requirement. This data is used to determine whether the SOFEC is technically, economically and socially feasible. In addition, a case study is also presented to sketch out how the SOFEC should perform in a niche market. Now each step will be described in further detail.

## **2.1.** LITERATURE REVIEW

A literature review presents the current knowledge and significant findings on the subject or work. It helps in establishing the context of the work and to understand the problem definition. As the interest in research on SOFEC for hydrogen production was established in the year 2000 (Glass et al., 2000), there have been only a few research groups from the years 2000 to the present which have contributed in developing the process for hydrogen production. A summary of the research done and conclusions drawn by the researchers is made to get a good understanding of SOFEC technology. In addition, knowledge on the technicalities of solid oxide cells and the various parameters affecting its performance such as fuel cell supports and reforming configurations is required to design or model the SOFEC. Also, since the electrochemistry and physics involved in the design and operation of SOFEC is similar to high temperature solid oxide cells, a literature study is also performed on SOFC and SOEC to understand the configuration of the cell and materials used in its development. As the sole purpose of the SOFEC model is to be used for feasibility studies, it is essential to know what parameters and indicators are considered for technical, economic and social feasibility analysis and how to perform the studies. This was done by performing literature study on several techno-economic and social impact studies done on SOFC and SOEC.

Literature on fuel assisted electrolysis, solid oxide fuel cells and electrolysers is found in peer reviewed journals such as 'Journal of Power Sources', 'International Journal of Hydrogen Energy' and 'Energy Conversion and Management' which are published by Elsevier. Other journals referred mainly for feasibility studies were 'Process Safety and Environmental Protection', 'Journal of Sustainable Development of Energy, Water and Environment Systems'. They were accessed through the website sciencedirect.com using the keywords 'solid oxide fuel cell','solid oxide electrolysis' and 'fuel assisted electrolysis'.

## **2.2. SOFEC MODEL DEVELOPMENT**

To carry out feasibility studies, it is necessary to first develop a SOFEC model and simulate it to obtain the data for parameters such as fuel usage, electricity and heat demand used in all the three feasibility studies. Thus, the next measure is to develop a SOFEC model in Cycle Tempo. The first step in developing the SOFEC model is the type of of model required. The model can either be a lumped model (zero dimensional, 0-D) or one dimensional (1-D). In 0-D, the model uses average values of parameters such as temperature, pressure etc whereas a 1-D model considers spatial distibution of parameters along any one of the dimensions. A 1-D model is preferred as it provides more accurate results.

Another important aspect of the model development encompasses the inclusion of both Nernst and polarisation losses in the calculation of cell voltage. EStandaert's work (Standaert et al., 1996) on analytical fuel cell modelling provides a relationship for cell voltage calculation which includes both Nernst and polarisation losses. While the voltagecurrent relationship currently used in the Cycle Tempo fuel cell model includes both the losses, it differs from the model presented by Standaert's work. Thus, to resolve this ambiguity, both the models will be described and compared. Based on the comparison, it can be concluded whether the Cycle Tempo can be used for the SOFEC model.

Further, the SOFEC model has to be made compatible with Cycle Tempo for simu-

lation studies. Thus, the SOFEC model will be developed by adapting the Cycle Tempo solid oxide fuel cell (SOFC) model Fortran code to operate as a SOFEC. As the SOFC model apparatus is also a 1-D model, modifying it is convenient. The changes in the code include altering the electrochemical reactions involved, the voltage-current relationship considered for power calculations and mass and energy balances.

Finally, the Fortran code will be integrated with Cycle Tempo and parameter values can be provided in Cycle Tempo for electrolyser simulations.

## **2.3.** PARAMETER STUDY AND SYSTEM MODEL

Once the model is developed in Cycle Tempo, the simulation results need to be validated with experimental results. Thus, the experimental results presented by Wang et. al's work (W. Wang et al., 2008) will be used to validate the SOFEC model results.

Further, to obtain the parameter data for feasibility studies, the SOFEC model will be simulated and their results will be plotted. This consists of acquiring and plotting values of power density, cell voltage and efficiency for a given current density by varying other operating parameters such as fuel utilisation, steam utilisation and operating temperature.

The next step is to develop a SOFEC system model. A system model generally comprises of the balance of plant/auxiliary components such as heat exchangers, compressors, reformers, controllers, etc. required to operate the technological component in a plant. For the SOFEC, heat exchangers will be used for cathode and anode product heat recovery. The system model will be developed using the existing apparatus modules present in Cycle Tempo.

## **2.4.** FEASIBILITY STUDY

With the system model developed and all the SOFEC parameter data available, the technical, economic and social feasibility study can be performed. A feasibility study is an analysis of the viability of a project based on technical, economic and social factors relevant to the project. The book on feasibility study of sustainable systems by Herriott et al., 2014 was mainly used to determine how to perform each of the feasibility studies. Thus, to understand the feasibility of a SOFEC system, the following points are taken into account:

#### **2.4.1.** TECHNICAL FEASIBILITY

In this section, the technical feasibility of the SOFEC system will be tested based on the electrolyser materials, electricity and heat input to the system and fuel usage.

When operating at high loads, the SOFEC structure has to withstand the oxidising and reducing environments in the cell along with providing structural strength. As SOFEC, SOFC and SOEC essentially have the same structure, the structural material degradation will be similar. Thus, a literature review on the material degradation in SOFC and SOEC will be conducted to assess the availability of materials for scaling up the SOFEC system. (Laguna-Bercero, 2012) presents the electrode and electrolyte materials currently used in the SOFCs and SOECs while W. Wang et al., 2007 provides insights on materials which perform best when used in a fuel assisted electrolyser cell. Based on this literature, it will be concluded whether the materials for SOFEC development are currently available.

Further, the SOFEC being a high temperature electrolyser requires electricity and heat inputs. For the renewable energy scenario, the SOFEC should use electricity generated by renewable sources such as wind and solar. On the other hand, F. Wang et al., 2021 and Martinez-Frias et al., 2003 work on heat recovery systems for SOEC and SOFEC were referred for heat inputs respectively. Based on this literature, it can determined whether the electricity and heat demands of the SOFEC can be met.

In addition, to be completely integrated in the renewable energy scenario, the SOFEC system will use green fuels such as biogas. However, biogas has impurities which can corrode and degrade the materials used in the SOFEC structure (Trendewicz and Braun, 2013,Saadabadi et al., 2018). Further, the production of biogas from energy crop based biomass can be erratic if it competes with the land usage for food supply (Ridjan et al., 2013). Based on the referred literature, it will be inferred whether biogas can be used as fuel for SOFEC operation.

Based on these factors, it can be be determined whether the SOFEC system is technically feasible.

#### **2.4.2.** ECONOMIC FEASIBILITY

The SOFEC system can be said to be economically feasible if it is able to compete with production costs incurred in commercial technologies, such as low temperature electrolysis and steam reforming of methane, which are currently used globally. This will enable the SOFEC system to attract investments for its commercialisation. To compare these costs, several economic parameters such as internal rate of return on investment (IRR) and net production costs over the technology's lifetime. (Trendewicz and Braun, 2013, H. Zhang and Desideri, 2020).

Initially, the total capital costs for the process equipments (such as the electrolyser stack, heat exchangers, etc.) and operational costs will be calculated for the SOFEC system. As the SOFEC is similar to the SOFC and SOEC in structure and operations and SOFC having been researched extensively in the past, the SOFEC capital costs (CAPEX) and operating costs (OPEX) can be estimated by examining the net production cost calculations done for SOFC systems. H. Zhang and Desideri, 2020 have calculated the net production costs for co electrolysis of  $CO_2$  and steam in solid oxide electrolysers. Further, a similar approach is followed by Herz et al., 2021 for economic assessment of electrolysis for power to liquid processes. Thus, based on the cost calculations in these two studies, the total costs for SOFEC system as well as the net production costs will be calculated.

Further, the calculated net production costs will be compared with the costs for com-

peting technologies such as steam methane reforming, low temperature electrolysis, biomass gasification, etc. The values for these technologies will be acquired from the economic review and evaluation of numerous hydrogen production methods performed by Dincer et al. (Dincer and Acar, 2015) and IRENA report on hydrogen energy (Gielen et al., 2019).

Finally, based on the comparison of production cost values, conclusions will be drawn on whether the SOFEC system is economically feasible method of hydrogen production.

#### **2.4.3.** SOCIAL FEASIBILITY

In general, social feasibility of the SOFEC system should involve studying its impact on the location and the communities to which it is catered. As the SOFEC system is still developed only on a lab scale and is only affected by the location when considering the biogas fuel supply, the SOFEC system scenario should technically be able to integrate with any process plant having hydrogen demand.Thus, the study will consider process safety, social acceptance on a global scale, and impact of greenhouse gas (GHG) emissions on the environment and community to determine the social feasibility of the system.

Process safety for SOFEC involves safety measures in SOFEC operation and handling and storage of raw materials and products especially hydrogen. Ustolin et al., 2020 and Hansen, 2020 provide details on hydrogen storage and precautionary measures for hydrogen handling respectively. These details will help determine if the SOFEC can be operated safely.

Further, social acceptance of the SOFEC will be determined by analysing the attitude of the community towards hydrogen ,fuel cells and use of biogas as raw material. Oltra et al., 2017 and Korbag et al., 2021 have analysed the acceptance of hydrogen fuel cells and use of biogas in Europe respectively. Finally, to understand the effect of SOFEC operation on the environment, environmental impact factors such as the global warming potential (GWP) and acidification potential (AP) for the system will be calculated. These values will then be compared with GWP and AP for other hydrogen production methods such as low temperature electrolysis, biomass gasification and steam methane reforming. These values are taken from life cycle analysis done by Dincer and Acar, 2015 and Ozbilen et al., 2013.

Based on the analysis of process safety, social acceptance and environmental impact, it can be determined whether the SOFEC system is socially feasible.

## **2.5.** CASE STUDY: SOFEC INTEGRATION IN STEEL MILL

Further, a case study is presented to illustrate whether it is feasible to integrate the SOFEC in a steel mill for hydrogen based iron ore reduction process. With the emerging interests in usage of hydrogen in steel industry (Vogl et al., 2018), the SOFEC can play an integral role in providing hydrogen at high efficiencies. The integration of SOFEC in the system will be done with the following steps :

1. **Waste heat availability:** Operating at high temperature, the SOFEC requires external heat input to maintain a temperature of about 1000<sup>0</sup>C. While the heat input can be provided by external electrical heating, it is beneficial to utilise waste heat

produced in the steel plant as heat input. Quader et al. (Quader et al., 2015) provide a comprehensive review on the waste heat sources and recovery technologies in the steel industry. Based on their research, the waste heat source and recovery technology will selected for the SOFEC system model.

- 2. **Process Flow Development:** The next step is the development of process flow diagram, starting from heating the input streams and ending at the supply of hydrogen to the iron oxide reduction process. Bhaskar et al., 2020 and Vogl et al., 2018 have developed process flow diagrams for the hydrogen based iron ore reduction. This includes incorporating heat exchangers; various flow streams such as biogas and steam input, anode off gases, etc. with their temperature and compositions; the SOFEC unit and iron ore reduction shaft.
- 3. **Hydrogen demand and SOFEC sizing:** The hydrogen demand will be calculated based on the hydrogen production and iron ore consumption provided in literature (Bhaskar et al., 2020 and Patisson and Mirgaux, 2020). Based on the demand, the SOFEC model will be used to calculate the inputs such as fuel supply, electricity and waste heat energy input required to cater to the hydrogen demand and ultimately the SOFEC unit capacity.
- 4. **Feasibility Analysis:** With the SOFEC unit capacity and waste heat calculations, the net production cost of hydrogen and syngas and the  $CO_2$  emissions avoided will be calculated. Based on these results, it would be determined whether integration of SOFEC will be feasible in this scenario

# 3

# **LITERATURE REVIEW**

This chapter initially presents a literature review on how each of feasibility studies are performed. Further, a summary of the previous research done regarding fuel assisted solid oxide electrolysis is presented. The chapter then explains the concepts of solid oxide fuel cells (SOFC), solid oxide electrolysis cell (SOEC) and solid oxide fuel assisted electrolysis (SOFEC) with their working principles, reactions involved and Nernst equations. Furthermore, the parameters affecting fuel cell operation such as the voltage losses (activation, ohmic and concentration) and how they affect anode, cathode and electrolyte supported fuels cells will be given. Finally, the fuels which can be used for SOFEC with different types of reforming configurations (Direct Internal vs Indirect Internal vs External Reforming).

## **3.1.** REVIEW ON FEASIBILITY STUDY:

In order to perform the feasibility study, a literature review was done to understand how the study is carried out and what factors have to be take into account. A book on feasisbility analysis for sustainable technologies by Herriott et al., 2014 states that feasibility analysis of a sustainable technology generally determines whether it is technically, economically and socially viable.

In determining the technical feasibility of a system, they suggest asking the questions such as whether the technology can be developed and operated with the existing materials and equipments?, how does the technology compare with other commercial ones in terms of efficiency and lifetime? what are the constraints and issues in its operation and can they be solved?. In the technical paper by Saadabadi et al., 2018, the potential and constraints of using biogas in SOFCs is investigated. Here, the operational challenges for biogas fuelled SOFC are assessed by determining whether the biogas can be handled safely, will the materials used in the SOFC be able to withstand the reactions taking place and avoid degradation due to contaminants such as hydrogen sulfide, and what are the energy and exergy efficiencies of the process. Such an analysis is also done by Kamalimeera and Kirubakaran, 2021 and Barelli et al., 2020 for biogas and ammonia

fed SOFCs. Thus, these questions will have to be answered for the SOFEC system to be technically feasible.

Further, to determine the economic feasibility of a system, Herriott et al., 2014 states that the initially the total costs of production are to be calculated. They address it to be a sum of the fixed costs such as the cost of equipment, installation costs and variable operational costs such as cost of fuel and utilities. These costs can be spread through the lifetime of the technology to provide levelised costs of production. Further, they state that methods such as internal rate of return (IRR) and net present value (NPV) are used to gauge the profitability of the technology. The IRR is determined by initial investment and the amount and timing of cashflows in return. On the other hand, NPV of a technology provide the present value of benefits minus the investment required. Siefert and Litster, 2014 performed the economic analysis for a biogas fuelled SOFC system by calculating the normalised capital costs (\$ kW<sup>-1</sup>). This was done by dividing the total capital costs by the total power generated by the system in a year. To add the operating and maintenance costs, the author calculated the IRR by assuming the maintenance costs and the cashflows required. On the other hand, economic analysis of SOFC done by Trendewicz and Braun, 2013 and Barelli et al., 2020 does not consider NPV or IRR and includes the operation and maintenance costs in the cost of electricity and levelised cost of electricity as a measure of economic analysis respectively. Kothari et al., 2008 and Dincer and Acar, 2015 performed economic analysis on various hydrogen production methods and have only considered the net production cost per kg of hydrogen produced as an economic parameter. This can be speculated to be due to lack of information on cashflows for the technology. Therefore, while IRR and NPV provide the profitability of the technology, it requires data on the returning cashflows of the technology to be available.

Finally, with regard to social feasibility analysis for energy systems, most of the researchers have focussed on the environmental impacts of the technology.For instance, Dincer and Acar, 2015 and Ozbilen et al., 2013 have both calculated and reviewed the effect on the environment by calculating the global warming potential (GWP) and acidification potential (AP) for different hydrogen production methods such as electrolysis and biomass gasification. On the other hand, Schubert et al., 2015 investigate the importance of other factors such as social acceptance, transparency of data and political feasibility in energy scenarios in Germany. A review on global social acceptance of hydrogen technologies was done by Oltra et al., 2017. It suggests that while there is a lot of support for hydrogen technologies, there is not enough awareness about it among the citizens.

Therefore, while environmental impact is an important factor in social feasibility, other factors such as social acceptance should also be included in the analysis.

## **3.2.** PRIOR RESEARCH ON FUEL ASSISTED ELECTROLYSIS

The concept of fuel assisted electrolysis has been researched and used in the aluminium manufacturing industry since the late 19th century. The manufacturing process, known

as Hall-Héroult process, involves electrolysis of alumina (Al<sub>2</sub>O<sub>3</sub>) dissolved in molten cryolite-based electrolyte (Na<sub>3</sub>AlF<sub>6</sub>) to obtain pure aluminium at a temperature of  $1000^{\circ}$ C (Grjotheim and Kvande, 1993). Here, at the cathode, alumina gets reduced to aluminium and oxide ions. The oxide ions are conducted throught the electrolyte to the anode. Carbon fuel electodes are used as anodes which react with which get oxidised and form carbon dioxide, thus, preventing the formation of oxygen gas was considered undesirable. The application of this concept for hydrogen production was done by Glass et al., 2000. In 2000, Pham, Glass and Wallman first patented the idea of natural gas assisted steam electrolysis which was claimed to reduce the electricity consumption as compared to existing SOECs. This claim was established on the idea of a high temperature process being thermodynamically favourable and reduction in electrode polarisation based losses. Their electrolyser had two operational modes namely, partial oxidation and total oxidation. In partial oxidation mode, nickel catalyst (Ni cermet) partially oxidised natural gas to form syngas (carbon monoxide and hydrogen) which can react further to form carbon dioxide to give hydrogen at both anode and cathode. In contrast, total oxidation mode enables the natural gas to be completely oxidised by oxygen ions produced by electrolysis at the cathode and diffused to the anode. This reduces, the potential difference across the electrolyser membrane and hence, lower the electricity consumption.

The idea was further developed in a few years by Martinez Frias, Pham and Aceves (Martinez-Frias et al., 2003) who proposed a novel, high efficiency natural gas assisted SOEC (NGASE). In their experiment, total oxidation of natural gas was performed at the anode at  $700^{\circ}$ C which lowered the operating voltage by as much as 1 volt compared to a conventional SOEC. They also observed that a higher temperature ( $800^{\circ}$ C -  $900^{\circ}$ C) increased the amount of carbon deposition at the anode. To suppress it, a high amount of steam would have to be added to anode gas flow which was undesirable as it leads to increased endothermic steam reforming reaction, thus, having negative effects on the thermodynamics. Thus, a trade off is to be made to ensure optimal peformance with low carbon deposition.

Over the years, many research groups adopted the NGASE and worked to optimize its performance further. In 2007, Wang et al. (W. Wang et al., 2007) experimented on improving the catalytic properties of the anode by replacing Ni-YSZ (Yttria Stabilised Zirconia) anodes with YSZ impregnated with aqueous solutions of Cu-CeO<sub>2</sub>, Cobalt (Co) and Palladium (Pd). These anodes were said to have higher porosity and did not promote coking in presence of hydrocarbons. Thus, they were tested in a SOE cell in presence of reducing gases  $H_2$ , CO and  $CH_4$ . It was found that Pd-C-CeO<sub>2</sub>-YSZ anode showed best catalytic performance and reduced the open circuit voltage (OCV) by the highest margin.

In recent times, research has focused on feeding either, a mixture of a methane and steam, or syngas at the anode of the SOEC. One such work is shown by Tao et al. (Tao et al., 2011). In their research, syngas ( $CO + H_2$ ) is fed at the anode while steam is passed at the cathode. The cell is operated as a SOFC to give  $CO_2$  and steam at the anode and pure humidified hydrogen at the cathode, thus, eliminating need of gas cleaning unit for hydrogen usage. Such a cell is termed to be a solid oxide fuel assisted electrolyser cell (SOFEC).According to experiments conducted by Tao, Butler and Virkar performed

for SOEC and SOFEC, the OCV of the SOFEC is observed to be 1V lower than that of the SOEC. Also, as the current direction of SOFC and SOFEC is the same, the researchers have analysed the configuration and performance of SOFEC-SOFC hybrid unit.

In addition, Luo et al. (Luo et al., 2014) also developed a one dimensional kinetic model of SOFEC based on the elementary reactions to compare the performance of  $H_2$ ,CO and CH<sub>4</sub> assisted SOFEC. Their results show that CO and CH<sub>4</sub> assisted SOFEC perform better than that of  $H_2$  with  $CH_4$  giving best results. Their reaction mechanism shows that methane is first converted to carbon monoxide and H<sub>2</sub> through steam reforming which is followed by electrochemical oxidation of hydrogen at anode. Thus, electricity is generated at anode while also producing hydrogen at cathode. A similar approach was taken by Patcharavorachot et al. (Patcharavorachot et al., 2016) where a more detailed electrochemical model is developed by including the activation, concentration and ohmic voltage losses. It is shown that the SOFEC can do both, generate electricity and produce hydrogen, in the negative net cell voltage region while only produce hydrogen in the positive region. Thus, SOFEC is a promising concept. However, the advantage of fuel assistance is present only when there is adequate fuel supply to the anode. Cinti et al., 2016 experimented using fuel assistance in SOEC and investigated the performance of the cell as function of fuel and reactant utilisation. Their results showed that if inadequate fuel is supplied to the anode and fuel utilisation is kept at 100%, all the fuel gets oxidised between the inlet and the outlets and the fuel assisted electrolysis changes into conventional electrolysis, thus, producing oxygen. Thus, the cell voltage and performance becomes equivalent to that of conventional electrolysis and the benefit of fuel addition in reducing the electrical power demand disappears. Therefore, Cinti et al., 2016 conclude that sufficient fuel has to be supplied when performing fuel assisted electrolysis and fuel utilisation should be below hundred percent.

Based on the above literature research, it is clear that the concept of SOFEC is a more general form of NGASE with more flexibility of fuels used. Also, only two research groups have developed models to explain the electrochemical and kinetic behaviour of the reactions at anode and cathode. Thus, these two research groups Patcharavorachot et al., 2016 and Luo et al., 2014 will be referred for development of the electrochemical SOFEC model. Further, fuel assisted electrolysis is only beneficial when there is adequate supply of fuel. Thus, the supply of fuel plays a major role in the performance of the SOFEC.

# **3.3.** FUEL CELL BACKGROUND

To understand the modelling of SOFEC, it is essential to have basic understanding of the technical aspects of fuel cells and electrolyser cells, mainly, solid oxide fuel cell (SOFC) and solid oxide electrolyser cell (SOEC). A fuel cell is an electrochemical device which produces electrical power and heat using chemical energy of a fuel. Fuel cells generally consist of an ion conducting electrolyte sandwiched between two electronic conductors, namely, an anode and a cathode. The fuel and oxidant flow over the anode and

cathode while the electrolyte membrane facilitates the transport of ions (Giddey et al., 2012). There are various fuel cell designs which differ in the choice of fuel and electrolyte and are named after the electrolyte material used.

## 3.3.1. SOFC

Solid oxide fuel cells, as the name suggests, use a solid oxide ceramic electrolyte which conducts oxygen ions. They operate at high temperatures (650<sup>0</sup>C to 1000<sup>0</sup> which improve reaction kinetics and allow oxygen ions to be conducted through the solid ceramic electrolyte. Fig 3.1 shows the schematic representation of different parts of an SOFC and the reactions that occur at anode and cathode.



Figure 3.1: Schematic of SOFC anodic and cathodic reactions (Cells, 2015)

#### WORKING PRINCIPLE AND REACTIONS INVOLVED

As shown in Fig 3.1, the fuel enters in the channel along the anode and air in the channel along the cathode. Oxygen from air diffuses into the cathode to form  $O^{2-}$  ions. The solid oxide electrolyte conducts the oxide ions to the anode. Hydrogen from fuel diffuses into the anode and is oxidised by oxide ions to form water. This takes place at an interface called the Triple Phase Boundary (TPB) where the anode, the electrolyte and gas phase are all in contact with each other.

$$At \ anode: H_2 + O^{2-} - > H_2O + 2e^- \tag{3.1}$$

$$At \ cathode: 1/2O_2 + 2e^- - > 2O^{2^-}$$
(3.2)

Overall Reaction: 
$$H_2 + 1/2O_2 - - > H_2O$$
,  $\Delta H = -248.3 kJ/mol$  (3.3)

Other reactions may also take place depending on the fuel used at the anode. Hydrocarbon fuel such as natural gas or methane can provide hydrogen to the anode by steam reforming (Eqn 3.4) and water gas shift (Eqn 3.5) reactions. Other reactions occur in parallel, but these have lower rates (Wendel et al., 2016) and are only relevant in detailed studies of kinetic effects at the fuel electrode.

$$CH_4 + H_2O - - > CO + 3H_2, \quad \Delta H = 225.6kJ/mol$$
 (3.4)

$$CO + H_2O - - > CO_2 + H_2, \quad \Delta H = -34kJ/mol$$
 (3.5)

## 3.3.2. SOEC

A solid oxide electrolysis cell is primarily a SOFC working in the reverse direction. While the structure of a SOEC and a SOFC are identical, their electrical connections are reversed. Fig 3.2 represents a schematic of the reactions occurring at the and air electrodes respectively.



Figure 3.2: Schematic of SOEC cathodic (steam) and anodic (air) reactions

#### WORKING PRINCIPLE AND REACTIONS INVOLVED

Here, steam is passed at the cathode (steam electrode) which dissociates into hydrogen and oxide ions. Hydrogen ions combine to form molecular hydrogen gas while oxide ions conduct to the anode (air electrode) through the solid oxide electrolyte. The oxide ions further recombine to form oxygen gas and exit the anode channel.

At anode: 
$$O^{2^{-}} - > 1/2O_2 + 2e^{-}$$
 (3.6)

$$At \ cathode: H_2O + 2e^- - > O^{2^-} + H_2 \tag{3.7}$$

$$Overall \ Reaction: H_2O - -> H_2 + 1/2O_2, \ \Delta H = 248.3 kJ/mol$$
(3.8)

#### 3.3.3. SOFEC

Solid oxide fuel assisted electrolysis is a novel approach towards solid oxide electrolysis. Here, steam is reduced to hydrogen at the cathode whereas the fuel (Eg.  $CO,H_2,CH_4$ , etc.), instead of oxide ions ( $O^{2-}$ ), is oxidised at the anode to form steam and other fuel based products. Fig 3.3 shows the operation of SOFEC. Thus, from operational point of view, the SOFEC could be understood as the combination of the anode of SOFC and the cathode of SOEC.



Figure 3.3: Schematic of SOFEC operation

#### **REACTIONS INVOLVED**

At the cathode, steam is electrolysed to give oxide ions and hydrogen gas. On the other hand, at the anode, hydrogen from the fuel undergoes electrochemical oxidation and produces steam. Depending on the fuel used, water gas shift 3.5 and steam methane reforming 3.4 both can occur at the anode.

At cathode: 
$$H_2O + 2e^- - > O^{2^-} + H_2$$
 (3.9)

At anode: 
$$H_2 + O^{2-} - > H_2O + 2e^-$$
 (3.10)

 $Overall \ Reaction: H_2O \ (cathode) + H_2 \ (anode) - - > H_2 \ (cathode) + H_2O \ (anode) \ (3.11)$ 

It can be seen from the equations that the overall cell reaction is close to equilibrium and thus, the net cell voltage required to drive the hydrogen production is very close to zero. Also, as the hydrogen is always produced at the cathode, it is pure without any carbon compounds and hence, other than steam removal, no gas treatment is required to acquire and store the produced hydrogen (Tao et al., 2011). In addition, the SOFEC and SOFC have the current flowing in the same direction. Thus, both of them can be electrically connected in series and the hydrogen produced in the SOFEC can be used in the SOFC (Tao et al., 2011).

# **3.4.** Cell Design parameters

The design parameters for a fuel cell vary from the component materials and direction of feed flow to the type of fuel used. The main design parameters are explained as follows:

## **3.4.1.** FUEL FLEXIBILITY

A variety of fuels can be used in a SOFC or SOFEC such as methane, natural gas, syngas, biogas and other hydrocarbons. Biomass can be used as source to produce such fuels. The biomass processing methods include fermentation, anaerobic digestion and supercritical gasification can produce fuels such as biogas and syngas which are compatible with SOFCs (Archer and Steinberger-Wilckens, 2018).

While biogas has been used previously in low conversion technologies such as internal combustion engines and gas burners, they have a total efficiency below 50% (Saadabadi et al., 2018). Thus, biogas usage benefits tremendously when used in high efficiency technologies such as fuel cells. However, there are some disadvantages of using biogas such as high costs of contaminant removal and enrichment of biogas. Also, the local supply of biomass near the plant competing for land usage with food supply limits the availability of biogas (Ridjan et al., 2013).

### 3.4.2. FUEL CELL SUPPORT

Fuel cell generally have a support layer which holds the components together and provides strength to the structure. These supports are either made by thick electrodes (anode/cathode) or thick electrolyte layer. Their respective characteristics are given as follows:

#### ELECTRODE SUPPORTED FUEL CELL

Fuel cells with thick electrode as support structure have the benefit of having a thin electrolyte membrane. This reduces the ohmic loss associated with electrolyte thickness enabling operation at low temperatures and higher performance. Lower temperature also helps in reducing degradation of electrodes and supporting materials, thus, enhancing its lifetime. However, a thicker electrode leads to higher resistance towards gas diffusion at the electrode surface, thus, limiting the rate of reactions at the surface. Thus, it is essential that the electrode materials should have a high porosity to promote gas diffusion. In addition, it is found that anode supported fuel cells have lower activation losses compared to the cathode supported ones and thus, have received more attention in recent years (Yang et al., 2013).

#### **ELECTROLYTE SUPPORTED FUEL CELL**

In contrast to the anode and cathode supported, electrolyte supported cells have a dense electrolyte membrane and thin anode and cathode electrodes. The dense electrolyte membrane provides strong structural support. In addition, using electrode supports over long duration leads to delamination of electrode-electrolyte interface. This is due

to electrode volume expansion caused by prolonged re-oxidation of electrode material (Tiwari and Basu, 2013), which is avoided when using electrolyte supported cells. Also, a thin electrode greatly reduces diffusion resistance at the triple phase boundary. The downside to this approach is the thick electrolyte increases ohmic losses resulting in lower power density. Therefore, this cell type requires higher operating temperature to achieve equivalent performance.

#### **3.4.3.** REFORMING CONFIGURATIONS

One of the advantages of solid oxide fuel cells is the high operating temperature which allows the use of hydrocarbons such as natural gas to be used as fuel. However, the fuel needs to be reformed using steam to form hydrogen for SOFC operation. While reforming can be done using a separate external reformer, being an endothermic process, it requires heat input which, based on the operating conditions, varies from 40% to 70% of the heat produced in the fuel cell (Aguiar et al., 2002). Thus, the reforming process can be made more efficient by performing it internally which is known as internal reforming.

#### INTERNAL REFORMING

There are two approaches to internal reforming, namely, Indirect Internal Reforming (IIR) and Direct Internal Reforming (DIR). In the first approach, steam reforming is done in a separate reformer but in close thermal contact with the anode (IIR). This ensures that the reforming reaction and the electrochemical reaction occur separately in the fuel cell stack. It should be noted that the heat from reaction is transferred only to the cells adjacent to the reformer and steam for reforming has to be provided separately (Larminie, 2003).

The second approach has reforming taking place directly at the anode with the anode material being the catalyst. This allows both good heat transfer and provision of product steam at the anode for reforming. Though, there are two main issues with direct reforming. One problem is the decomposition of methane may lead to coke formation which deactivated the anode material, thus, reducing system efficiency (Larminie, 2003).

$$CH_4 - - > C + 2H_2$$
 (3.12)

This can be avoided either by adding steam in excess or reducing the operating temperature (Martinez-Frias et al., 2003). Another issue is the highly endothermic steam reforming which results in a cooling effect causing large temperature gradients in the fuel cell. To reduce this effect, the fuel can be partially pre-reformed to reduce the reforming taking place in the cell and thus, suppress the thermal stress in the cell. In addition, anode gas recycling (Aguiar et al., 2002).

## **3.5.** ELECTRICAL PARAMETERS FOR FUEL CELLS

#### **3.5.1.** NERNST VOLTAGE

The Nernst equation is used to calculate the reversible voltage (electromotive force), also known as 'Nernst voltage', at a given temperature and pressure. The Nernst equation for SOFC is given as follows:

$$E_{SOFC} = E_T^0 + \frac{RT}{2F} ln \left( \frac{p_{O_2}^{\frac{1}{2}}(ca) * p_{H_2}(an)}{p_{H_2O}(an)} \right)$$
(3.13)

where  $E_T^0$  is the standard reversible voltage for hydrogen and  $p_x$  is the partial pressure of the gas phase x. 'ca' and 'an' represent the cathode and anode respectively. This is the maximum voltage a SOFC can achieve as when current is drawn from it, the voltage drops due to various voltage losses (will be discussed in the next section).

The standard reversible voltage for SOFC is calculated using the Gibbs free energy and is given as follows:

$$E_T^0(SOFC) = -\frac{\Delta G^0}{zF} \tag{3.14}$$

where z is the number of electrons liberated during the reaction per hydrogen atom and is equal to 2, F is Faraday's constant = 96485 C/mole.

For a SOEC, the Nernst equation is given as follows:

$$E_{SOEC} = E_T^0 + \frac{RT}{2F} ln \left( \frac{p_{H_2}(ca) * p_{O_2}^{\frac{1}{2}}(an)}{p_{H_2O}(ca)} \right)$$
(3.15)

This is the minimum voltage required by the SOEC to electrolyse steam into hydrogen and oxygen.

The standard reversible potential for SOEC has the same value but with a negative sign as the voltage developed in the reverse direction to that of the SOFC.

Now, the SOFEC can be considered as a SOEC coupled to a SOFC as the anode of the SOFEC (fuel electrode) is equivalent to that of the SOFC and the cathode of the SOFEC is equivalent to the cathode (steam electrode) of the SOEC. The main reactions which play a role in the calculation of cell voltage are the hydrogen oxidation and water splitting reactions. However, as both these reactions have an equal and opposite standard Nernst potential, the Nernst voltage is only dependant on the partial pressures of the reactants and the products at the anode and cathode (Papalexis, 2016,Patcharavorachot et al., 2016). The Nernst voltage for SOFEC can be given as follows:

$$E_{SOFEC} = \frac{RT}{2F} ln \left[ \frac{p_{H_2}(an) * p_{H_2O}(ca)}{p_{H_2O}(an) * p_{H_2}(ca)} \right]$$
(3.16)

Where 'ca' means cathode and 'an' means anode.

#### THERMODYNAMICS OF ELECTROLYSIS

With the Nernst voltage described, it is also important to understand the thermodynamics of hydrogen oxidation and water splitting which affects the open circuit voltage. In fuel cells, hydrogen oxidation reaction occurs spontaneously and produces energy in the form of heat and useful work. The useful work at a constant temperature and pressure is given as follows:

$$\Delta G = \Delta H - T\Delta S$$

$$\implies \Delta H = \Delta G + T\Delta S$$
(3.17)

where  $\Delta G$  is change in Gibbs free energy and represents the useful work done by the fuel cell in the form of electricity generation,  $\Delta H$  is the total change in enthalpy of reaction and  $T\Delta S$  represents the heat dissipated to the environment.

The opposite happens in electrolysis of water where energy in the form of heat and electricity has to be supplied to split water molecules into hydrogen and oxygen atoms. In low temperature electrolysis, the  $T\Delta S$  term is small and thus, electrolysis mainly requires only electricity. However, at higher temperatures,  $T\Delta S$  rises and theoretically both electricity and heat are required for electrolysis of water (Penchini et al., 2014). Fig 3.4 shows the variation in the values of  $\Delta G$ ,  $\Delta H$  and  $T\Delta S$  as a function of temperature. While the total energy demand ( $\Delta H$ ) increases only slightly, the electrical energy demand decreases while the thermal energy demand increase with rising temperatures. Thus, for SOEC, the electrical energy demand ( $\Delta G$ ) is reduced and the thermal demand has a significant contribution to the total energy demand ( $\Delta H$ ).

Now, the reversible voltage (open circuit voltage), as discussed earlier, is the minimum voltage required to split water and is calculated using the Gibbs free energy change of the reaction. The Gibbs free energies of water and steam splitting are 237.2 kJ/mole at  $25^{\circ}$ C and 179.9 kJ/mole at  $1000^{\circ}$ C respectively (Harrison et al., 2010). The reversible voltages for both are calculated as follows:

At 
$$25^{\circ} C$$
,  $E_{rev} = \frac{-\Delta G}{nF} = 1.23 V$   
At  $1000^{\circ} C$ ,  $E_{rev} = \frac{-\Delta G}{nF} = 0.98 V$  (3.18)

However, such a case is only possible if the heat demand  $(T\Delta S)$  is supplied by the surrounding environment which can lead to cooling in the cell and the electrolysis process will eventually cease (Ju et al., 2018). Therefore, to ensure that the process continues, the thermal demand has to be supplied by having a cell voltage higher than the reversible voltage. This is cell voltage is known as the thermo-neutral voltage ( $E_{the}$ ) and is expressed using the total enthalpy change ( $\Delta H$ ) as follows

$$E_{rev} = \frac{-\Delta H}{nF} \tag{3.19}$$

#### **3.5.2.** VOLTAGE LOSSES

The cell voltage of a fuel cell decreases with increasing current density due to polarisation losses made up of activation, ohmic and concentration losses. In case of an electrolyser, cell voltage increases with increasing current density as the losses are considered as overpotentials which are added to the cell voltage which increases the power demand for water splitting. Fig 3.5 shows the regions in which each of the polarisation losses play a major role in the decrement of voltage in a fuel cell.

#### **ACTIVATION LOSSES**

A proportion of voltage generated is lost in overcoming the activation energy required for driving electro-chemical reaction for transfer of electrons to or from the electrode.



Figure 3.4: Plot of total energy, electrical energy and heat demands for water electrolysis as a function of temperature at atmoshpheric pressure. Plot values are taken from (Lide, 2004 and Ju et al., 2018)



Figure 3.5: Drop in cell voltage with increasing current density due to polarisation losses (Adapted from Agaesse, 2016)

Such voltage losses are known as activation losses (Winterbone and Turan, 2015). The activation losses can be calculated using the Butler-Volmer equation. To lower the activation losses, it is crucial to have suitable catalysts and a large active area exposed at the electrolyte interface. This can be done by increasing the porosity of electrode ma-

terial. The activation overpotential is calculated by the following equations (Noren and Hoffman, 2005):

$$V_{act} = \frac{RT}{\alpha F} * sinh^{-1} \left[ \frac{J}{2J_0} \right]$$
(3.20)

where R is universal gas constant (in J/mol K), J is current density (A/m2),  $J_0$  is the exchange current density and  $\alpha$  is the charge transfer coefficient taken as 0.5. The exchange current density is calculated as

$$j_0 = A \exp\left(\frac{-E_a}{RT}\right) \tag{3.21}$$

where A is the pre-exponential factor and E<sub>a</sub> is the activation energy

#### **OHMIC LOSSES**

Ohmic polarization originates from resistance to ionic flow through the electrolyte and the electrical resistance of the electrode. These losses can be minimised using highly conductive electrodes and reducing the thickness of electrolyte.Larminie, 2003. While reducing electrolyte thickness, the strength and support provided by electrolyte should be compensated by making thicker electrodes. Sometimes the choice of material for the bipolar plates and interconnects also reduce such losses. The ohmic overpotential is calculated as follows (Aguiar et al., 2004):

$$V_{ohmic} = J * R_{ohm}$$
where  $R_{ohm} = \frac{Anode \ Thickness}{Anode \ Electric \ conductivity} + \frac{Cathode \ Thickness}{Cathode \ Electric \ conductivity} + \frac{Electrolyte \ Thickness}{Electrolyte \ Ionic \ conductivity}$ 

$$(3.22)$$

#### **CONCENTRATION LOSSES**

Concentration losses are mass transfer losses which occur at the active area of the electrode . This is caused by rate of inflow of reactants and outflow of products being limited by diffusion and is slower than the discharge current (Winterbone and Turan, 2015). This lowers the partial pressure of the fuel and oxidant gases , thus, resulting in the drop in cell voltage.

#### HEATING DUE TO LOSSES

Overpotentials due to activation, ohmic and concentration losses cause resistive heating in the cell and increase almost proportionally with the current density. In such a case, when current is applied, the Nernst voltage caters to the electrical demand while the overpotentials partly or fully cover the thermal demand (Petipas, 2013). When the heating is enough to compensate the thermal demand (T  $\Delta$  S) for electrolysis, the total cell voltage including the overpotentials at that current density is equal to the thermoneutral cell voltage.



Figure 3.6: Polarisation (J-V) curve for an electrolysis cell (Petipas, 2013)

Fig 3.6 shows the three operating modes of an electrolyser. In the endothermic mode, the resistive heating only partially compensates for the thermal demand as the cell voltage is lower than the thermo neutral-voltage. In this case, the thermal energy from the environment is taken leading to decrease in cell temperature. When the heating fully compensates for the thermal demand, the cell is in thermoneutral mode. In exothermic mode, the voltage is higher than the thermoneutral voltage and thus, resistive heating is in excess. The excess heat dissipates into the environment leading to a rise in cell temperature.

# 4

# **SOFEC MODEL DEVELOPMENT**

After the literature review, the next step taken is to develop a SOFEC model in Cycle Tempo. As explained in the research methodology, the purpose of the model is to provide SOFEC performance parameter data such as fuel supply, operating current densities at a certain cell voltage, etc. This data will be used for the technical, economic and social feasibility calculations.

Cycle Tempo is a flowsheet program which can analyse, operate and optimize the thermodynamics of an energy system. It was developed at TU Delft and is being distributed by Asimptote B.V. The fuel cell model for Cycle Tempo was developed by Aren de Groot (Groot, 2004) as a part of his PhD research. THe model is coded in Fortran programming language. Since the fuel cell model is complex and is adapted from the current Cycle Tempo SOFC model, the development of the SOFEC model will be done in steps.

Initially, the Cycle Tempo SOFC model will be explained in detail to provide a clear understanding of model structure. It includes the assumptions made in the model, the electrical parameters taken, the isothermal fuel cell model used and the mass and energy balances considered Further, based on the SOFC model, the SOFEC model approach and program flow will be discussed. Finally, the modifications made to the SOFC model code to form the SOFEC model will be provided.

# 4.1. CYCLE TEMPO SOFC MODEL

The Cycle Tempo SOFC model enables the modelling of fuel cells based on reforming (external and internal reforming) and flow type (co-flow and counter-flow). The fuel cell model assumes a planar geometry due to lower resistance, high power density and lower production costs. The thermodynamic properties of fluids (fuel, air, oxygen, etc.) used in the model are calculated using the software package FluidProp by Asimptote. The following are the assumptions made while developing this model:
#### 4.1.1. ASSUMPTIONS

- 1. A one dimensional model of the active surface is considered . Thus, temperatures, pressures and compositions are considered constant in a cross section perpendicular to direction of flow.
- 2. Only hydrogen is oxidised in the electrochemical reaction. Other fuels will be converted through chemical reactions.
- 3. The water-gas shift reaction and internal reforming reaction always occur at equilibrium on the electrode area, at the cell temperature and pressure.
- 4. All the processes in the model occur at constant temperature and pressure. Thus, an average cell temperature and pressure is used.
- 5. High temperature of SOFC provides enough activation energy for electrochemical reactions and thus, voltage losses due to activation are negligible
- 6. Voltage losses on level of electrodes are negligible in direction of fuel flow and thus, voltage is constant across the fuel cell.

#### 4.1.2. ELECTROCHEMICAL ISOTHERMAL FUEL CELL MODEL

In the basic isothermal fuel cell model, the fuel cell considered is a rectangular flat plate cell and is represented as an equivalent electrical circuit as shown in Fig



Figure 4.1: Schematic of fuel cell represented as an equivalent circuit

The anodic surface area of the cell is given by BL, where L is the length and B is the breadth of the cell. For flat plate type cells, voltage losses due to resistances in the plane of the electrodes are significantly smaller than the losses occurring in the electrochemical reactions or due to the transport of ions through the electrolyte. Thus, the cell voltage can be assumed to be constant across the whole cell (represented as  $V_{cell}$ ).

Hence, the local equilibrium overpotential  $(\eta(X))$  can be described as the difference between the local equilibrium potential  $(V_{eq})$  and the cell potential  $(V_{cell})$  at which the current is produced. Assuming that the local overpotential varies linearly with the local

current density and quasi ohmic resistance (r), the local overpotential is given as follows (Standaert et al., 1996,Eqn 1):

$$\eta(X) = V_{eq}(X) - V_{cell} = r(X).i(X)$$
(4.1)

The quasi-ohmic resistance, also known as area specific resistance (ASR), accounts for voltage losses due to ohmic, activation and concentration losses lumped into a single resistance. To make the relation more simple, as the quasi-ohmic resistance is mainly dependent on the temperature and the temperature is the same across the cell (isothermal), we can assume the resistance is uniform throughout the cell i.e. r(X) = r for all X.

$$i(X) = \frac{V_{eq}(X) - V_{cell}}{r}$$
(4.2)

Now, the above equation can be developed and solved to obtain a relation between the cell voltage, current density and change in fuel composition. Two reseachers, namely Arend de Groot (Groot, 2004) and F. Standaert (Standaert et al., 1996) have previously developed the isothermal fuel cell model taking Nernst losses into account. Their approaches seem to be different and their resulting model equations are as follows:

Arend de Groot's Equation (Groot, 2004, Pg 138, Section 6.2.2.1, Eqn 6.8):

$$\frac{I_{out}}{A} = \frac{Uf}{r * \int_0^{Uf} \frac{du}{V_{eq}(\lambda) - V_{cell}}}$$

F. Standaert's Equation(Standaert et al., 1996, Pg 233, Eqn A17)::

$$V_{cell} = \int_0^{uf} V_{eq}(u).du - \frac{r}{i_{out}} \int_0^1 i(x)^2.dx$$

From the above two equations, it can be seen that they are very different from each other. For both the models to be correct, their resulting models should either be the identical or should be derivable from one another. Thus, to get clarity on the differences in the model and to decide which one is the most appropriate, both the approaches and results will be described and compared with each other.

#### STANDAERT'S APPROACH

In this approach, an ordinary differential equation (ODE) is established for fuel utilisation (u) formed on the equation regarding the equilibrium overpotential (Standaert et al., 1996, section 2). This is done by considering Nernst law which states that the local equilibrium potential mainly depends on the local fuel and oxidant composition. Assuming that the oxidant flow is very large and homogenous, the equilibrium potential depends only on local fuel composition. As this composition can be determined as a function of local fuel utilisation (u(X)), the local equilibrium potential is represented in terms of the fuel utilisation (u(X)).

To obtain an equation for fuel utilisation, the output current  $(I_{out})$  and equivalent input current  $(I_{in})$  for the fuel cell are considered. Here, the equivalent input current  $(I_{in})$  represents the maximum amount of current that is drawn in the hypothetical instance of complete utilisation of fuel. Thus, the total fuel utilisation is given as follows (Standaert et al., 1996, Eqn 14):

$$U_{total} = \frac{I_{out}}{I_{in}} \tag{4.3}$$

Analogous to the above equation, the local fuel utilisation (u(X)) is defined as the fraction of the equivalent input current produced between the cell inlet and position X (Standaert et al., 1996,Eqn 2).

$$u(X) = \frac{B}{I_{in}} \int_0^X i(\epsilon) \ d\epsilon, \ (0 \le u \le 1)$$
(4.4)

Substituting the expression for i(X) from Eq 4.2 in the above equation and differentiating with respect to X, the following differential equation is obtained (Standaert et al., 1996,Eqn 3).

$$\frac{du}{dX} = \frac{B}{r.I_{in}}(V_{eq}(u) - V_{cell}), \ (0 < X < L)$$
(4.5)

Now, for X=0 (at the cell inlet), u = 0. Also, at length of cell L, total fuel utilisation (uf) is achieved.

Hence, scaling the equivalent input current ( $I_{in}$ ) to BL and the X-coordinate to L (Standaert et al., 1996,Eqn 5).

$$i_{in} = \frac{I_{in}}{BL}, \ x = \frac{X}{L}, \ (0 < x < 1)$$
 (4.6)

Substituting and scaling Eq 4.5 using Eq 4.6, the following boundary value problem is obtained (Standaert et al., 1996, BVP).

$$\frac{du}{dx} = \frac{1}{r.i_{in}} (V_{eq}(u) - V_{cell}), \ (0 < x < 1)$$
(4.7)

where u(0) = 0 and u(1) = uf. Eq 4.7 can be rewritten as follows

$$\frac{du}{(V_{eq}(u) - V_{cell})} = \frac{dx}{r.i_{in}}, \ (0 < x < 1)$$
(4.8)

Integrating utilisation dependent terms from u = 0 to u = uf and dx from x = 0 to x = 1, the following final equation is obtained,

$$\int_{0}^{uf} \frac{du}{(V_{eq}(u) - V_{cell})} = \frac{1}{r.i_{in}}$$
(4.9)

Thus, Eq 4.8 can now be used to numerically calculate the current density and cell voltage. Now, to present the inclusion of both Nernst and polarisation losses, the above equation is rearranged and multiplied by du/dx on both sides to get the following equation.

$$\left(\frac{du}{dx}\right)^{2}.dx = \frac{1}{i_{in}.r}.(V_{eq}(u) - V_{cell}).du$$
(4.10)

Integrating left hand side from x = 0 to x = 1 and right hand side from u = 0 to u = uf, we get (Standaert et al., 1996, Pg 225).

$$\int_{0}^{1} \left(\frac{du}{dx}\right)^{2} dx = \int_{0}^{uf} \frac{1}{i_{in} r} (V_{eq}(u) - V_{cell}) du$$
(4.11)

Now, based on Eq 4.4, utilisation u(x) is given as follows (Hemmes, 2004, Eqn 78):

$$u(x) = \frac{1}{i_{in}} \int_0^x i(x) \, dx, \ (0 < x < 1)$$

Converting it into differential form (Hemmes, 2004, Eqn 79)

$$\frac{du}{dx} = \frac{i(x)}{i_{in}} \quad (0 < x < 1) \tag{4.12}$$

Substituting values of du/dx and  $i_{in}$  from Eq 4.12 and Eq 4.3 respectively into Eq 4.11 and solving further, the following equation is obtained

$$\frac{r.uf}{i_{out}} \int_0^1 i(x)^2 dx = \int_0^{uf} (V_{eq}(u) - V_{cell}) du$$
(4.13)

Finally, solving the integral for  $V_{cell}$  on right hand side and rearranging the equation, the following equation is acquired (Standaert et al., 1996, Eqn A17)

$$V_{cell} = \int_0^{uf} V_{eq}(u).du - \frac{r}{i_{out}} \int_0^1 i(x)^2.dx$$
(4.14)

Eq 4.14 has two integral terms on the right hand side. The first term is the Nernst potential averaged over the cell from u = 0 (at cell entry) to u = uf (at cell exit). This term is lesser than the open circuit voltage leading to the Nernst losses which represent thermodynamic reversible losses (Hemmes, 2004). The second integral provide the polarisation losses in form of local irreversible heat dissipation integrated over the length of the cell.

#### AREND DE GROOT'S APPROACH

In Groot's approach, the cell is divided into subcells with each having area dA (Groot, 2004, section 6.2.2.1). The local current density is initially expressed in terms of the total output current of a subcell (dI) and area of subcell dA as shown (Groot, 2004, Section 6.2.2.1, Eqn 6.2)

$$i(X) = \frac{dI}{dA} \tag{4.15}$$

Further, the output current is calculated using the Faraday law (Groot, 2004, Section 6.2.2.1, Eqn 6.3)

$$dI = z.F.d\varepsilon \tag{4.16}$$

where  $\epsilon$  is defined as the number of hydrogen moles consumed in the reaction over a period  $\Delta t$ .

Combining the values of dI and i from Eq 4.15 and Eq 4.16 and substituting in Eq 4.2, the following quasi-ohmic relation is obtained (Groot, 2004, Section 6.2.2.1, Eqn 6.4)

$$z.F.d\varepsilon = \frac{V_{eq} - V_{cell}}{r}.dA \tag{4.17}$$

Further, Groot defines the maximum reaction coordinate ( $\epsilon^{max}$ )obtained as the reaction coordinate (moles/sec) when all the fuel is converted and relates it with the total output current. (Groot, 2004, Section 6.2.2.1, Eqn 6.5)

$$I = z.F.\epsilon^{\max}.Uf \tag{4.18}$$

where Uf is the final fuel utilisation at the end of the cell Now, to relate Eq 4.17 and Eq 4.18, a dimensionless reaction coordinate is defined by dividing the reaction coordinate by the maximum value of the reaction coordinate as shown below (Groot, 2004, Section 6.2.2.1, Eqn 6.6)

$$\lambda(X) = \frac{\epsilon(X)}{\epsilon^{max}}$$

$$d\lambda = \frac{d\epsilon}{\epsilon^{max}}$$
(4.19)

Substituting this expression of the reaction coordinate into Eq 4.17 gives (Groot, 2004, Section 6.2.2.1, Pg 138):

$$dA = z.F.\epsilon^{max}.r. \frac{d\lambda}{V_{eq}(\lambda) - V_{cell}}$$
(4.20)

While the area of subcell can be directly integrated to obtain total cell area A (Groot's approach), it can also be alternatively integrated similar to Standaert's approach to obtain the same result as follows:

$$dA = B.dX = B.L.dx$$
 where  $x = \frac{X}{L}$  (4.21)

Here, dx will be integrated from x = 0 (cell entry) to x = 1 (cell exit) to obtain BL which is the total area 'A'.

The limits for the dimensionless reaction coordinate are given as when x = 0,  $\lambda = 0$  and at x = 1,  $\lambda = Uf$ .

Thus, integrating Eq 4.20 gives (Groot, 2004, Section 6.2.2.1, Eqn 6.7)

$$\frac{A}{z.F.\epsilon^{max}.r} = \int_0^{Uf} \frac{d\lambda}{V_{eq}(\lambda) - V_{cell}}$$
(4.22)

Substituting z.F.*e*<sup>max</sup> with I/Uf (Eq 4.18, we get (Groot, 2004, Section 6.2.2.1, Eqn 6.8)

$$\frac{I}{A} = \frac{Uf}{r * \int_0^{Uf} \frac{du}{V_{eq}(\lambda) - V_{cell}}}$$
(4.23)

This is the final correlation derived by Arend de Groot which can be numerically solved to calculate the total output current I at a certain cell voltage Vcell.

#### COMPARISON BETWEEN THE TWO MODELS

Now, since both the approaches and resulting models have been derived, one can argue that while both the approaches are different, resulting equation is the same. This can be explained by comparing the models at two main distinguishable points

#### 1. Dimensionless reaction coordinate vs utilisation:

In Groot's approach, the local equilibrium voltage  $V_{eq}$  is a function of dimensionless reaction coordinate  $\lambda$  (Eq 4.20). However, by its given definition,  $\lambda$  is the ratio of moles of hydrogen converted and maximum conversion when all the moles are converted (Eq 4.19). Thus, it is identical to the local fuel utilisation (u(X)) as used in Standaert's approach (Eq 4.4).

#### 2. Final correlation between current and cell voltage:

Considering Eq 4.18 from Groot's derivation, the output current is related with the final fuel utilization Uf and maximum reaction coordinate  $\epsilon^{max}$ . Here, it can be seen that the expression  $zF\epsilon^{max}$  is maximum current drawn when all the fuel is converted which is the same as the equivalent input current.

$$I = z.F.\epsilon^{max}.Uf = I_{in}.Uf$$

Further, Eq 4.23 can rewritten as the following

$$\frac{A}{I_{in}.r} = \int_0^{Uf} \frac{d\lambda}{V_{eq}(\lambda) - V_{cell}}$$

 $\implies$ 

$$\frac{1}{i_{in}.r} = \int_0^{Uf} \frac{d\lambda}{V_{eq}(\lambda) - V_{cell}}$$

This resultant equation is the identical to the resultant boundary value equation (Eq 4.7) derived in Standaert's approach. Further, this equation can be solved to present the inclusion of Nernst and polarisation losses as done in Standaert's approach (from Eq 4.9 to Eq 4.14).

Thus, from the above two comparisons, it can be concluded that while Groot's and Standaert's approaches seem different, they produce the same resultant equation.

As a matter of fact, Cycle Tempo is currently using the fuel cell model derived by Arend de Groot and is given as follows:

$$\frac{I}{A} = \frac{Uf}{r * \int_0^{Uf} \frac{du}{V_{eq}(u) - V_{cell}}}$$
(4.24)

#### 4.2. SOFEC APPROACH

To discuss the approach to model a SOFEC, the operation and sign conventions of SOFC and SOEC will be described and based on this knowledge, the approach towards SOFEC will be explained. This is followed by the changes made to the Cycle Tempo fuel cell mode to operate as a SOFEC.

#### 4.2.1. SIGN CONVENTION AND OPERATION

With the basic fuel cell model and associated mass and energy balance explained, the SOFEC mode can be explained by comparing it with the SOFC and SOEC. This is followed by the description of all the changes made to the fuel cell model to operate in the SOFEC mode.

The solid oxide cells modes can be understood using the IV curves as shown in the Fig 4.2 (from Tao et al., 2011). The figure shows the IV curves for SOFC, SOEC and SOFEC with different inputs. Here the focus is only on cell votage and current density axes. As discussed in the literature review, the SOFC mode involves formation of steam from hydrogen and oxygen. It is a spontaneous and exothermic process ( $\Delta$  G and  $\Delta$  H is negative) which produces heat and generates an electric current. Thus, the voltage and current density is considered to be positive. The figure shows the SOFC IV curve with an open circuit voltage of about 1 volt.On the other hand, the SOEC mode involves splitting of steam into hydrogen and oxygen. This process demands electricity and heat and the electron movement is in the opposite direction as compared to a SOFC. Thus, the voltage remains positive but the current density is considered as negative.



Figure 4.2: Comparison of IV curves for SOFC, SOEC and SOFEC modes (Tao et al., 2011)

For the SOFEC, Fig 4.2 shows two curves, one in quadrants 1 and 4 and the other in quadrants 2 and 3. Only the latter curve will be considered in this report. This is done as the latter curve is in the SOEC direction and helps in the performance comparison with

the SOEC. Here, the current density is negative while the voltage moves from being negative to positive. To explain the SOFEC mode of operation clearly, the Nernst equation for the SOFEC can be recalled.

In Chapter 3, the SOFEC Nernst equation (Eqn 3.5.1) was discussed. It should be noted that this Nernst equation is obtained when electrical connections are equivalent to that of SOFC i.e.when the fuel electrode is connected to the positive terminal and the steam electrode is connected to the negative terminal.For the SOFEC operating in the SOEC direction, the Nernst equation becomes as follows (Patcharavorachot et al., 2016,Luo et al., 2014):

$$E_{SOFEC} = \frac{RT}{2F} ln \left[ \frac{p_{H_2}(ca) * p_{H_2O}(an)}{p_{H_2O}(ca) * p_{H_2}(an)} \right]$$
(4.25)

In terms of mole fractions of the gases, it is stated as

$$E_{SOFEC} = \frac{RT}{2F} ln \left[ \frac{y_{H_2}(ca) * y_{H_2O}(an)}{y_{H_2O}(ca) * y_{H_2}(an)} \right]$$
(4.26)

Now, the SOFEC mode of operation in SOEC direction can be divided into three different cell voltage scenarios:

#### • When voltage is negative (V<0):

At low current densities, the concentration of hydrogen is higher at the fuel electrode than at the steam electrode. Thus, a spontaneous flow of electrons liberated by the oxidation of fuel at the fuel electrode flow to the steam electrode through the external circuit. From the Nernst equation, it is evident that the cell voltage is negative ( $V_{rev} < V_{cell} < 0$ ) which is shown in the quadrant 3 of Fig 4.2. In this case, the cell produces hydrogen as well as electricity (little amount). Electricity is produced as it is a spontaneous process and Gibbs free energy change ( $\Delta G$ ) is negative (such as in a SOFC).

#### When voltage is zero (V=0):

With increase in current densities, the hydrogen concentration at the steam electrode becomes equivalent to the fuel electrode. In this case, the cell voltage becomes zero. Here, the enthalpy of the assisted fuel is just enough to compensate with the electricity demand. Thus, hydrogen is produced without any electricity demand or generation.

#### • When voltage is positive (V>0:

At higher current densities, the hydrogen is produced at a higher rate at the steam electrode as compared to the fuel one leading to a positive cell voltage. In this case, the irreversible losses are high and electricity input is required, in addition to the enthalpy from assisting fuel, to produce hydrogen at the steam electrode.

#### **4.2.2.** Changes to Cycle Tempo model

To develop the SOFEC model in Cycle Tempo, it was suggested to modify an existing fuel cell model to work as a SOFEC. Thus, the direct internal reforming SOFC apparatus

(SOFC-DIR) in Cycle Tempo was considered for this purpose. In addition to the changes described below, the changes in the code and consideration to run the model are provided in the Appendix.

The first method for SOFEC development was to develop a SOEC model and provide the addition of fuel at the oxygen electrode of the electrolyser. In this way, it would have been possible to use the same model to obtain results for a SOEC and a SOFEC and compare their results. However, the main issue with this approach is that the existing fuel cell model takes the anode (fuel electrode) as the defining electrode. This means that all cathode gas compositions and electrical parameters are calculated w.r.t the anode. In the report by Wijers, 2011, two approaches were discussed to develop a SOEC model. They are as follows:

#### 1. Calculation based on oxygen electrode exiting flow:

In this approach, fuel utilisation is applied to the electrolysed steam at the steam electrode. Now, the user inputs oxygen flow exiting the oxygen electrode. Back calculating the number of electrons released by the oxygen, the current is calculated and further, the current is used to calculate how much steam is electrolysed at the steam electrode. The amount of steam provides the amount of hydrogen and oxygen flow exiting the steam electrode. The amount of steam inflow at the cathode can then be calculated by dividing the amount of electrolysed water by fuel utilisation.

In this case, the main drawback is that the oxygen exiting the oxygen electrode (anode) is the only parameter which can be defined to calculate all the remaining parameters

2. **Calculation based on cathode as the defining electrode:** In this method, the cathode (steam electrode) acts as the starting point for all the calculations. Also, the steam inflow at the cathode and the steam utilisation are user defined inputs which calculate the hydrogen concentration at the cathode exit. Finally, based on the hydrogen concentration, the oxygen flow at the anode can be calculated.

In this thesis work, the second approach was used as it being more intuitive and provided more freedom in deciding the parameters. However, it was very complex to implement in the code. In addition, the debugging software, used to create an executable file for Cycle Tempo, was incompatible with the operating system in use. Thus, the code had to be sent to Teus van der Stelt for debugging for everytime a change was made in the code. This made developing this model highly time consuming.

Thus, owing to time constraints and code complexity, the idea to develop a SOEC model was dropped.

On the other hand, a SOFEC model was easier to develop using the SOFC model as the anode could still be used as the defining electrode and only had to be replaced with steam. The major changes made to the Cycle Tempo model to operate as a SOFEC are shown as follows:

#### • Isothermal Fuel cell model:

To operate the SOFEC mode using the Cycle Tempo model, the existing electrochemical isothermal fuel cell model is used as shown in Eqn 4.1.2. However, upon using the model, errors were encountered with Cycle Tempo being unable to use negative current densities for power calculations. Changes were made in the fuel cell mode code for current density and power calculations to allow negative currents and fix this issue but the errors persisted. Finally, due to time constraints, an approach based on the work by Wijers, 2011 was taken and change was made to isothermal fuel cell model such that the current densities calculated are positive. This is done by reversing the voltage difference in the denominator of Eqn 4.1.2. Thus, the modified fuel cell model is as follows:

$$\frac{I}{A} = \frac{Uf}{r * \int_0^{Uf} \frac{du}{V_{cell} - V_{eq}(u)}}$$
(4.27)

While this change is intuitive since the cell voltage is higher than the reversible voltage for an electrolyser, it leads to changes in the sign convention and ambiguity in power density and efficiency calculations. Based on this change, Cycle Tempo will produce the following results:

- 1. When cell voltage is negative, the voltage difference is positive and hence the current density is positive. Thus, while there is electricity generation in this scenario, the power density calculated will have a negative sign.
- 2. When cell voltage is positive, current density is still positive. Thus, while there is a demand for electric energy here, the calculated power density will still have a positive sign.

#### **Nernst Equation:**

The Nernst equation currently used in this model is that of a SOFC. This will be replaced by the Nernst equation developed for SOFEC operating in electrolyser direction as shown earlier in Eqn 4.2.2. Operating the SOFEC in the electrolyser direction helps in and will be as follows:

$$E_{SOFEC} = \frac{RT}{2F} ln \left[ \frac{y_{H_2}(ca) * y_{H_2O}(an)}{y_{H_2O}(ca) * y_{H_2}(an)} \right]$$
(4.28)

## 5

### **SOFEC MODEL AND SIMULATIONS**

This chapter initially validates the Cycle Tempo SOFEC model with experimental results obtained from literature. Further, it compares the performance of the model with that of a SOEC using current density - voltage (J-V) curves. This is followed by a parameter study of the model where the effect of parameter changes on the model performance will be studied. Finally, the SOFEC system will be developed by adding balance of plant components.

#### **5.1.** MODEL VALIDATION

To validate the SOFEC model, its simulation results must be compared with the experimental results found in the literature. This is done by comparing the J-V curves acquired from the model simulations and experimental work done on fuel assisted electrolysis. From literature, W. Wang et al., 2008 have performed lab scale experiments on carbon monoxide and methane assisted electrolysis for optimal electrode material study while Martinez-Frias et al., 2003 performed system level experiments and studied the effect of fuel utilisation on energy efficiency. As the validation of SOFEC model will be done on a component level, the experimental results by Wang et al. will be considered for validation.

Wang et al. experimented using SOFEC for hydrogen production at an operating temperature of 973 K. They used a cathode supported button fuel cell which consisted of 50  $\mu$ m thick YSZ electrolyte disc sandwiched between 15  $\mu$ m (anode) and 300  $\mu$ m (cathode) thick electrodes (as listed in Table 5.1) which makes it a cathode supported cell. The cathode stream inlet composition consisted of steam to hydrogen ratio (H<sub>2</sub>O:H<sub>2</sub>) of 13:1. Various anode streams were used as shown in Fig 5.1. For the purpose of model validation, the curves for 50% and 80% conversion are considered as the anode gas composition for only is given. For 50% and 80% methane conversions, anode stream was made up of a fuel mixture consisting of methane to steam to carbon dioxide (CH<sub>4</sub>:H<sub>2</sub>O:CO<sub>2</sub>) ratio of 10:20:10 and 10:40:80 respectively. The researchers added CO<sub>2</sub> to the fuel mixture to replicate high conversion efficiencies as their button fuel cell couldn't operate in

Parameter	Symbol	Value	Unit
Anode Thickness	На	15	μm
Cathode Thickness	Hc	300	μm
Electrolyte Thickness	Не	50	μm

Table 5.1: Geometric Parameters for one cell

Table 5.2: Physical Properties

Parameter	Symbol	Value	Unit
Anode Electric Conductivity	$\sigma_{a}$	8 x 10^4	ohm-1m-1
Cathode Electric Conductivity	$\sigma_{\rm c}$	8.4 x 10^3	ohm-1m-1
Electrolyte Electric Conductivity	$\sigma_{ m e}$	33400 exp (-10300/T)	ohm-1m-1
Pre-exponential factor	k	854 x 10^9	ohm-1m-2
Activation Energy	Е	-140 x 10^3	J mol-1

such conditions. In addition to the experimental parameters listed above, other physical parameters were taken from Patcharavorachot et al., 2016 paper as listed in Table 5.1. These properties are used to calculate the area specific resistance (ASR) using the formulae for activation and ohmic losses discussed in Chapter 3 (Eqn 3.20,3.21 and 3.22) for the Cycle Tempo model.

The J-V curves for 50% and 80% methane conversion at 973K are shown Fig 5.1 by the green and red arrow respectively. It should be noted that these curves are obtained when the SOFEC is operated with the SOFC connections. Thus, they can be plotted for electrolyser connections by taking a transpose of the curve as was done in the previous chapter. Patcharavorachot et al., 2016 have used this method to validate their model with the experimental results from W. Wang et al., 2008 as shown in Fig 7.3.



Figure 5.1: J-V curves plotted for fuel assisted electrolysis as a function of various anode gas composition: (+) H2 + 3%H2O, (Diamond symbol) CH4, 10% conversion, (O) CH4 + 3%H2O, ( $\Delta$ ) CH4, 50% conversion, and (X) CH4, 80% conversion. The cathode gas consisted had H2O/H2 = 13 and P<sub>H2O</sub>H2O = 0.57 atm (Adapted from W. Wang et al., 2008)



Figure 5.2: SOFEC Model validation performed by Patcharavorachot et al., 2016 using experimental results of W. Wang et al., 2008 for  $CH_4:H_2O:CO_2=10:40:80$  and  $CH_4:H_2O:CO_2=10:20:10$ . Here the SOFEC is operated in the SOEC direction

The Cycle Tempo SOFEC model was also validated for 80% and 50% methane conversions as shown in Fig 5.3. The J-V Curve produced by the Cycle Tempo model for 80% conversion is in good agreement with the experimental result. The maximum deviation found was +0.005V at 900 A/m<sup>2</sup>. However, Cycle Tempo was unable to calculate the cell voltages for current densities below 100 A/m<sup>2</sup>. This was due to failure in convergence of the Simpsons integral method which is used in Cycle Tempo to iteratively calculate the cell voltage for a given current density and fuel utilisation. Thus, the reversible voltage is predicted using the slope of the previous points (as shown in Fig 5.3) and is found to be 0.065V which matches with the experimental results.

On the other hand, the J-V curve for 50% methane conversion with 50% steam conversion also match with the experimental results as shown in Fig 5.6. While the most of initial simulation curve points match the experimental ones, the simulated voltages after 1500 A/m2 current densities are lower than that of the experimental ones. This is attributed to the exclusion of concentration losses in this model (as mentioned in the assumptions in previous chapter) and thus, the overpotentials are not added in the cell voltage calculations.



Figure 5.3: Cycle Tempo SOFEC Model validated using J-V plot for  $CH_4$ : $H_2O:CO_2 = 10:40:80$  from W. Wang et al., 2008



Figure 5.4: Model validation using J-V plot for CH<sub>4</sub>:H<sub>2</sub>O:CO<sub>2</sub> = 10:20:10 from W. Wang et al., 2008

#### **5.2.** MODEL SIMULATION RESULTS

#### **5.2.1.** Electrical savings of SOFEC over SOEC

The SOFEC model voltage vs current density curve can be compared with that of the SOEC to calculate the voltage difference and hence, the savings in electrical power consumption. Papalexis, 2016 experimented with both SOEC and hydrogen fuelled SOFEC and compared their voltage vs current density curves. The highest difference recorded in their voltages was 1.11 V with power consumption savings of about 65%. Similar results were provided by Tao et al., 2011 with a voltage difference of about 1V.

However, as discussed in Chapter 4, it was not possible to develop a SOEC model in Cy-

cle Tempo due to complexity of the model code and time constraints. Alternatively, it is possible to compare the operating voltages of both type of electrolyser cells if the cell resistance and gas composition for the SOEC is provided. An experiment on performance analysis of SOEC done by Penchini et al., 2014 uses steam electrode gas compositions of 50% H<sub>2</sub> and 50% H<sub>2</sub>O with cell resistance value of 0.5 ohm m<sup>2</sup> at an operating temperature of  $800^{0}$ C. The cell has a current density of 5000 A/m<sup>2</sup> at cell voltage of 1.21 V (From Fig 5.5). Using the same steam electrode gas composition, cell resistance, operating temperature and current density, the SOFEC model calculates and presents a cell voltage of 0.1554 V for fuel electrode composition of methane:steam ratio of 1:2 as shown in Fig 5.5. The electrical power saving by the SOFEC model is calculated as follows:

Power Saving (%) = 
$$\frac{i.(V_{SOEC} - V_{SOFEC})}{i.V_{SOEC}} * 100 = \frac{1.21 - 0.1554}{1.21} * 100 = 86.3\%$$
 (5.1)

Thus, a electrical power saving of 86.3% is obtained when a methane fuelled SOFEC is operated when compared with that of a SOEC.



Figure 5.5: I-V plot of SOEC for operating temperature of 1073K, area specific resistance = 0.5 ohmcm<sup>2</sup> and total active cell area of 320 cm<sup>2</sup> (Adapted from Penchini et al., 2014)



Figure 5.6: J-V plot for operating temperature of 1073K, area specific resistance = 0.5 ohmcm<sup>2</sup> and CH<sub>4</sub>:H<sub>2</sub>O = 1:2

#### 5.2.2. SOFEC INLET AND OUTLET MASSFLOWS

The SOFEC massflows for fuel utilisation of 0.8 and current density of 5000A/m<sup>2</sup> have been presented in the table 5.3. The anode inlet has biogas (60 % methane and 40% carbon dioxide) and steam in the ratio 1:2 to prevent carbon deposition at the anode. The anode outlet consists mainly of steam (67.33%) and carbon dioxide (21.24%) with small amount of hydrogen and traces of carbon monoxide. Such a mixture can be useful in producing syngas and can find use in methanol production. However, the benefits of sell the hydrocarbon mixture has not been explored in this work. Further, from the table, the ratio of biogas to hydrogen output massflows is calculated to be approximately 2:1 i.e. for every kg of hydrogen output, twice the amount of BOFEC.

#### **5.2.3.** EFFECT OF FUEL UTILISATION

The effect of varying fuel utilisation on the cell voltage is given in Fig 5.2.3. Fuel utilisation (UFL) is varied from 0.3 to 0.8 while keeping the steam utilisation constant at 0.8. While the cell voltage initially increase till the UFL value of 0.5. Upon increasing the UFL further, the cell voltage starts to drop. This is not possible as with higher fuel utilisation, even more hydrogen oxidises and emits more electrons, increasing the current density. This, in turn, increases the cell voltage and voltage losses. The model could not be fixed to provide appropriate results due to time constraints and inadequate knowledge of the Cycle Tempo fuel cell model code.

Streams	Mass Flows (in g/s)	Gases	Composition ( in %)
		CH4	20
Anode inlet	3.41	CO2	13.333
		H2O	66.67
Cathodo Inlot	ode Inlet 2.36	H2O	90
Californe fillet		H2	10
		CO2	21.24
Anode Outlet	5.07	CO         2.57           H2O         67.33	2.57
	5.07		67.33
		H2	8.86
Cathode Outlet 31	210	H2O 18	
	510	H2	82

Table 5.3: Mass flows and composition of SOFEC anode and cathode inlet and outlet flow respectively



Figure 5.7: Effect of varying fuel utilisation on voltage

#### 5.2.4. EFFECT OF STEAM UTILISATION

The effect of steam utilization at the cathode side of the SOFEC on its performance is presented in Fig 5.2.4. Steam utilization is varied from 0.3 to 0.9 and fuel utilization is fixed at 0.8. From the result depicted in the figure, the increase of steam utilization increases the voltage. High steam utilization causes high hydrogen production at the cathode side; thus, cell voltage and all voltage losses are higher.



Figure 5.8: Effect of varying steam utilisation on voltage and power density



Figure 5.9: Effect of varying operating temperature on voltage and power density

#### **5.2.5.** EFFECT OF CELL OPERATING TEMPERATURE

In fig. 5.2.5, the operating temperature is varied from 873 K to 1273 K, is a key parameter on performance of the SOFEC. From the figure, it can be seen that power consumption decreases with increasing operating temperature. Not only the electrochemical reac-

tion but also the steam reforming reaction at the anode has a faster reaction time when the operating temperature is higher. In addition, the reduction of electrical energy consumption occurs when the operating temperature increases according to the thermodynamics of the SOEC. When the SOFEC operates at a higher operating temperature, cell voltage, activation overpotential and ohmic loss can be reduced. Consequently, high temperature operation can improve the performance of the SOFEC. However, a limitation due to the cell materials at high temperature should be noted.

For thermal demand and electrolyser calculations in following sections, the operating parameters presented in table 5.3 will be used. This is done as the model was only validated appropriately for a fuel utilisation of 0.8.

Parameter	Value	Unit
Fuel Utilisation	0.8	-
Steam Utilisation	0.8	-
Operating Temperature	1073	Kelvin
Operating Pressure	1	bar
Area Specific Resistance	0.5	Ohm cm2

Table 5.4: Operating parameters for SOFEC unit

#### **5.3.** SOFEC THERMAL MANAGEMENT:

Considering the operating temperature of SOFEC to be  $800^{0}$ C, the fuel and steam mass flows to the anode and cathode of SOFEC respectively have to be heated to  $800^{0}$ C. Further, the hot off gases at the anode exit and the hot mixture of steam and hydrogen at cathode exit have to be cooled to ambient temperature. Therefore, using heat exchangers, the high temperature heat contained in the gases at anode and cathode exits can be reused in heating the input mass flows. For the SOFEC model in Cycle Tempo, the heat exchanger modules available in Cycle Tempo were added to the electrolyser unit as shown in Fig 5.3.1.

However, upon running the simulation, the results did not converge with a Fortran error being displayed. To understand the source of the error, the parameter values, such as heating and cooling fluids temperatures and heat transfer coefficient etc., of heat exchangers were changed. However, the error was still present. In addition, Cycle Tempo was also wrongly calculating the temperatures of anode off-gas and hydrogen-steam mixture at the cathode. Instead of having higher temperatures at higher current densities due to Joule heating, a reverse trend was observed where tempratures dropped with higher current densities. For instance, for methane to steam ratio of 1:2 at anode inlet, the outlet temperature of anode off gas should be about 700<sup>o</sup>C whereas it showed as 280  $^{\circ}$ C at 700 A/m<sup>2</sup>. This value reduced further as the current density was increased and an outlet temperature of 93<sup>o</sup> C at 3000A/m<sup>2</sup>. Further, it was found that these values varied when the fuel at anode was changed. For instance, when a hydrogen and steam mixture (9:1 ratio) was used as fuel input at anode, the temperatures at the anode and



Figure 5.10: Cycle Tempo SOFEC model with heat exchangers

cathode outlet rose to 823  ${}^{0}$ C at 700 A/m<sup>2</sup> and dropped to 640 ${}^{0}$ C at 3000 A/m2<sup>2</sup>. Finally, this issue was discussed with Theo Woudstra and Teus van der Stelt (Cycle Tempo) to understand and resolve it but to no avail. Therefore, as the issue could not be resolved, the heat exchangers were not used in the model and the heat calculations were done manually.

#### **5.3.1.** HEAT CALCULATIONS:

#### SOFEC MODE OF OPERATION

As discussed earlier, a heat input equivalent to  $T\Delta S$  is required for electrolysis to take place.  $T\Delta S$  can be calculated by initially calculating the molar change in entropy. Wijers, 2011 had calculated the standard molar change in enthalpy and standard molar change in entropy by considering the steam reforming of methane, watergas shift, hydrogen oxidation and water electrolysis reactions as shown in Fig 5.11.

Here,  $\Delta$  S is calculated on basis of 1 mole of methane. Also, 1 mole of methane produces 3 moles of hydrogen. Therefore, T $\Delta$ S on basis of hydrogen at 800<sup>0</sup>C is calculated to be about 65.8kJ/mol.

Further,  $T\Delta S$  has to be compensated by irreversible polarisation losses and is calculated as follows using the formula from Luo et al., 2014 :

$$T\Delta S \times \frac{I}{2F} = I \times (V - V_{OC})$$
(5.2)

where  $V_{OC}$  is the open circuit voltage. The former is the heat demand while the latter is heat loss due to voltage losses. Based on this formula, a thermoneutral point with current density of 4890 A/m2 at cell voltage of 0.141V was calculated. Thus, below this current

	III(ODE	
Steam Reform	$CH_4 + H_2O \rightarrow 3 \cdot H_2 + CO$	
Enthalpy	$-74.8 + (-241.8) \rightarrow 3 \cdot 0 + (-110.5)$	$\triangle H = 206.0 \text{ kJ/mol}$
Entropy	$186.3 + 188.8 \rightarrow 3 \cdot 130.7 + 197.7$	$ riangle S = 214.7 \; \mathrm{J/K}$
Watergas shift	$\rm CO + H_2O \rightarrow H_2 + CO_2$	
Enthalpy	$-110.53 + (-241.8) \rightarrow 0 + (-393.5)$	$ riangle H = -41.2  ext{ kJ/mol}$
Entropy	$186.3 + 188.8 \rightarrow 130.7 + 213.7$	$ riangle S = -30.7 \; \mathrm{J/K}$
H <sub>2</sub> Oxidation	$4 \cdot H_2 + 2 \cdot O_2 \rightarrow 4 \cdot H_2 0$	
Enthalpy	$4 \cdot 0 + 2 \cdot 0 \rightarrow 4 \cdot (-241.8)$	$\triangle H = -967.2 \text{ kJ/mol}$
Entropy	$4 \cdot 130.7 + 2 \cdot 205.1 \rightarrow 4 \cdot 188.8$	$ riangle S = -177.7 \; J/K$
	CATHODE	
$H_2O$ Electrol.	$4 \cdot H_2 O \rightarrow 4 \cdot H_2 + 2 \cdot O_2$	
Enthalpy	$4 \cdot (-241.8) \rightarrow + 4 \cdot 0 + 4 \cdot 0$	$\triangle H = +967.2 \text{ kJ/mol}$
Entropy	$4 \cdot 188.8 \rightarrow 4 \cdot 130.7 + 2 \cdot 205.1$	$ riangle S = +177.7  \mathrm{J/K}$
TOTAL		
	IOIAL	

TOTAL		
Enthalpy	206 - 41.2 - 967.2 + 967.2	$ riangle H = 164.8 \mathrm{kJ/mol}$
Entropy	214.7 + (-30.7) + (-177.7) + 177.7	$\triangle \mathrm{~S} = \mathrm{184~J/K}$
Gibbs energy	$\triangle \mathbf{G} = \triangle \mathbf{H} - \mathbf{T}(298\mathbf{K}) \triangle \mathbf{S}$	$ riangle {G} = 110 \mathrm{kJ/mol}$

Figure 5.11: Calculation of standard molar entropy and standard molar entahlpy for SOFEC (Wijers, 2011)

density, the SOFEC operates in endothermic mode. Further, for electrolyser sizing , a unit structure by Petipas, 2013 is considered. Here, an active SOFEC cell area of 100cm<sup>2</sup> is chosen and a SOFEC unit structure of 25 stacks with 400 cells each is taken. The total power rating is calculated as follows:

Total Voltage = Cell Voltage × 400cells Total Current = Current Density × Cell area × 25stacks Total Power rating = TotalVoltage × TotalCurrent

(5.3)

#### HEAT TRANSFER

The heat calculations were done by performing an energy balance consisting of heat demand for input streams and cooling demand for outlet streams.

The heating and cooling demand for the input and output mass flow streams was calculated using the following formula:

$$Q = m \times \int_{T_1}^{T_2} Cp \times dT \tag{5.4}$$

where Q is the enthalpy flow (in kW), m is the mass flow rate (kg/sec), Cp is the heat capacity of the fluid (in kJ/kgK) and  $T_1$  and  $T_2$  are the initial and final temperatures of the gas.

The heat capacity values were calculated based on the formula provided in the paper

by Todd and Young, 2002 on thermodynamic and transport properties of gases. The formulae are given as follows:

$$C_p = \sum_{i=0}^{i=6} a_i \tau^i$$
  

$$\tau = \frac{T(K)}{1000}$$
  

$$C_{pmix} = \sum C_{pi} X_i$$
(5.5)

where T is the fluid temperature and X is the mole fraction of the specie.

The energy balance used is as follows:

$$\Delta H_{biogas} + \Delta H_{steam} + \Delta H_{rxn} = (\Delta H_{anoff} + \Delta H_{catoff}) \times \eta + External heat (5.6)$$

where  $\Delta H_{biogas}$  is the enthalpy change in heating biogas flow from 298K to 1073K;  $\Delta H_{steam}$  is the enthalpy change in heating water flow from 298K to 1073K and is the sum of enthalpy change of water from 298K to 373K, latent heat of vaporisation and enthalpy change of steam from 373K to 1073K;  $\Delta H_{anoff}$  is the enthalpy change in cooling of anode off gases from 1073K to 298K) and  $\Delta H_{catoff}$  is enthalpy change in cooling of cathode off gases from 1073K to 298K). The latter two include condensation of steam and cooling of water to ambient temperature.

 $\Delta H_{rxn}$  is the net heat demand of steam reforming of methane and water gas shift reaction and  $\eta$  is the heat exchanger effectiveness.

For the heat exchange, a counter flow heat exchanger with a constant effectiveness of 0.85 was considered for simplicity in calculations. Change in effectiveness of heat exchanger due to change in area of heat exchanger will require different massflow rates through it. Therefore, the total heat exchanged is obtained by calculating the enthalpy flow change for the input streams from ambient temperature to  $800^{0}$ C and enthalpy flow change of output streams from  $800^{0}$ C to ambient temperatures. The net heat transferred is computed to be the minimum of the two enthalpy flows.

## 6

### **SOFEC FEASIBILITY ANALYSIS**

Now, with the SOFEC model explained in detail in Chapter 4 and the system model developed in Chapter 5, it can be determined if the SOFEC system is feasible technically, economically and socially. Initially, the technical feasibility study is performed to determine whether the SOFEC system can be built and operated in a practical manner. This is followed by the economic feasibility study which makes an assessment of what the SOFEC will cost. Finally, the social feasibility decides whether the system can be accepted by the community. The mass flow data used for the economic and social feasibility are provided in Appendix B

#### **6.1.** TECHNICAL FEASIBILITY

To determine if the fuel assisted electrolyser is technically feasible, as discussed in the literature review, this section delves into the ability to manufacture and operate the SOFEC realistically. Therefore, The feasibility study can consider various elements such as degradation of electrolyser materials, effect of scaling up over fuel distribution in the anode, safe processing and storage of products from the electrolyser, catalysts for redox reactions occurring at the anode/cathode-electrolyte interface,etc.

Now, some of the major factors which will be considered to assess the manufacturability of the SOFEC are described as follows:

#### **6.1.1.** Electrolyser Component Materials

The electrolyser operates at about  $800^{0}$ C where its components (anode, cathode and electrolyte) also have to withstand oxidising and reducing environments. Now, considering the electrolyte, it has the function of transporting O<sup>2-</sup> ions from the steam electrode to the fuel electrode. This condition is also present in the SOFC and SOEC. The most commonly used material for the electrolyte is Yttria stabilised Zirconia (YSZ). This is due to it high ionic conductivity and chemical stability (Larminie, 2003). Other electrolyte materials such as scandia doped zirconia and lanthanum based electrolytes have also been found to provide higher ionic conductivity than YSZ (Laguna-Bercero, 2012).

However, as the latter materials consist of rare metals which will be very expensive and scarce, YSZ is the preferred electrolyte material.

At the fuel electrode (anode), the hydrocarbon fuel will be oxidised and thus, the anode material needs to withstand the reducing environments. Generally, Ni-based YSZ are used in SOFCs to achieve it (Aguiar et al., 2004). However, they suffer from metal dusting (process of metal dissociation at high temperatures) and sulphur poisoning (Jain Subodh, 2019). Alternatives such as Nickel cermets of ceria and Cobalt doped copper-ceria integrated YSZ anodes for SOFECs have been tested by Wang et al. (W. Wang et al., 2007) and have found to provide great thermal stability and catalytic activity in reducing environments. However, only one such research work has been reported. Also, Wang states that anodes used in commercial SOFCs cannot be used in SOFECs due to carbon deposition (coking) occurring in the steam reforming of methane. Therefore, further research is still required for the selection of anode materials. For cathode, Nickel doped ceria electrodes will be used as they have high reaction sites and low electronic resistance (Laguna-Bercero, 2012). Further, the SOEC and SOFC with the above stated materials have been found to degrade by 2-3% per 1000h at current densities of about -0.3 to -0.5 Acm<sup>-2</sup> (Laguna-Bercero, 2012). The main issue for SOEC is the delamination of the nickel based cathode. However, research is continuing on improving the microstructural performance of these materials and thus, it can be assumed that the materials will perform better when the SOFEC is developed.

In addition, new SOECs and SOFCs have microtubular design configuration as opposed to planar ones, as they provide increased power density, simple sealings, lesser startup or shutdown time and reduced damage due to redox cycling (Laguna-Bercero, 2012). Thus, the SOFEC can also adopt this design configuration. While the materials for electrolyte and cathodes are used in practice, further research is required in selection of anode materials for the SOFEC. Assuming that in addition to cathode, the materials for anode are also researched and are available when the SOFEC is developed, the development of the SOFEC will be feasible in terms of component materials.

#### 6.1.2. FUEL INPUT:

With regard to fuel input at the anode of the SOFEC, the fuel is required to undergo electrochemical oxidation. Hydrocarbon fuel such as methane and carbon monoxide have been used as fuel for fuel assisted electrolysis (Martinez-Frias et al., 2003,W. Wang et al., 2008). However, to reduce  $CO_2$  emissions of the SOFEC, biogas will be used as fuel input. Assuming that the biogas is produced from biomass and organic matter which consume  $CO_2$  from the atmosphere, usage of biogas as fuel in the SOFEC can make the process carbon neutral. Further, using biogas as fuel has the advantage of upgrading of biogas to hydrogen.

Trendewicz and Braun, 2013 report that the biogas has to be pretreated before using in fuel cells. Biogas has some water content which oxidises the hydrogen sulphide ( $H_2S$ ) at high temperatures to form sulfuric acid which, in turn, corrodes the pipes and compressors pumping the biogas. Thus, a desulfuriser and condenser (for water removal) will be used to treat the biogas before usage. Velasco et al., 2019 have performed desulfurisation on a pilot scale using biological processes and such a system can be used for the SOFEC.

Further, they also state that biogas is generally stored for short term (hourly) at low pressures as long term storage at high pressures requires a lot of energy (10% of the energy of biogas used). Thus, the SOFEC system will have to be operated with a biogas plant in the vicinity. Pilot plants in Barcelona and Italy have tackled this issue by installing biogas based fuel cells and using the biogas generated in the waste water treatment plants (WWTP) to produce power and heat (Saadabadi et al., 2018).

Lanzini and Leone, 2010 have compared using biogas and biohydrogen (biogas upgraded to hydrogen) as fuel in a SOFC. They report that internal reforming of biogas by steam reforming or dry reforming with  $CO_2$  is required to avoid carbon deposition at the anode. While using biohydrogen helps to avoid reforming and gives a steady output, it has a low production rate as its production by fermentation is still being researched and cannot be used in a scaled up SOFEC (Trendewicz and Braun, 2013). Thus, steam will be supplied at the anode to avoid carbon deposition in the SOFEC.

Since biogas has been used in fuel cells before and desulfurisers and condensers for pretreatment of biogas have been developed in a pilot plant scale, it can be said that using biogas as fuel for the SOFEC system is technically feasible.

#### 6.1.3. THERMAL INPUT:

As the electrolyser operates at high temperature, external heat input is required to heat the input flows (fuel at the anode and steam at the cathode). In addition, the internal reforming of biogas taking place at the anode of the electrolyser is an endothermic reaction and thus, consumes heat from its surroundings. A part of the heat required can be recovered from the anode and cathode offgases through a heat recovery system while the remaining is provided externally. Martinez-Frias et al., 2003 employed a heat recovery system consisting of heat exchangers and a preheater, with air as heating fluid, for their lab scale natural gas assisted steam electrolyser. Thus, similar heat recovery systems can be used for heat integration in SOFEC. Alternatively, the electrolyser can be integrated with waste heat from processes having high temperature effluents. Such a waste heat integration system has not been tested practically as solid oxide electrolysers (SOE) have yet to be commercialised on a large scale. However, SOEs have been modelled by few researchers to include waste heat recovery from effluents. F. Wang et al., 2021 have presented a model on the integration of solid oxide electrolyser with waste heat recovery from a marine engine. For the SOFEC operating at 800<sup>0</sup>C, ceramic plate fin type exchangers should be used as they are compact, have high heat transfer area to volume ratio. Such heat exchangers are being commercially used in the gas turbine plants for hot gas heat recovery (X. Zhang et al., 2018). Depending on the application, the heat integration for the SOFEC will vary from waste heat recovery to product gas heat recovery. As such systems have been developed on a lab scale, they can be developed for the SOFEC system and are technically feasible.

#### **6.2.** ECONOMIC FEASIBILITY

Now, with knowledge of the various additional auxiliary equipments required, it can be determined if the SOFEC is economically viable. Various methods have been used, in

general, in literature to measure the economic value of a project. In Chapter 3, the net production cost and internal rate of return were discussed.

Siefert and Litster, 2014 performed economic analysis on a biogas fuelled SOFC system by calculating the internal rate of return on investment (IRR) of the power plant. It provides the average rate of return on investment that an investor would acquire if the dividends are invested back into similar projects. IRR is calculated by estimating the interest rate i which makes the net present value (NPV) equal to zero of the net income or loss in the period 0 year to N years (as shown in equation below)

$$NPV = 0 = \sum_{t=0}^{N} \frac{C_t}{(1+i)^t}$$
(6.1)

where  $C_t$  is the cash-flow time-series and N is total lifetime of the power plant. However, IRR calculation is complex in calculation and it requires to estimate the cashflows over the time period. Siefert and Litster, 2014 had assumed the price of electricity sold to calculate the cashflows. In addition, it is difficult to estimate the price of hydrogen. Also, the SOFEC is not commercialised and there is no past data to estimate the discounted cash flows over time. Thus, calculating the IRR for the SOFEC is not possible.

Further, Herz et al., 2021 have performed the economic analysis on electrolyser based power to liquid processes by considering the net production costs(NPC) using the following formula:

$$NPC = CAPEX + OPEX$$

$$CAPEX = ACC + AC$$

$$OPEX = DC + LC + IT$$
(6.2)

Here, CAPEX refers to the capital expenditure which includes the annualised capital costs (ACC), insurance and taxes (IT) and administrative costs (AC). OPEX is the operating expenditure which consists of direct costs i.e. cost of raw materials required for production, labour costs and insurance and taxes. For CAPEX, annualised capital costs (ACC) depends on the fixed capital investment (FCI) which, in turn, depends upon the estimated equipment cost. For the SOFEC, the net production cost per kg of hydrogen will be used to measure its economic value.

As the SOFEC is currently developed only on a lab scale, the equipment costs for it will be estimated using the cost estimations for SOFC and SOEC in the literature. This consideration is supported by the fact that the materials used in SOFEC are similar or based on the materials used in development of SOEC and SOFEC. Now, to fix a power rating and electricity demand for the SOFEC, the modelling results from Chapter 5 section 5.3 were considered. To have higher efficiency of SOFEC, an endothermic mode of operation was chosen and a current density of 3600 A/m<sup>2</sup> was considered. With 3 units of SOFEC producing 112 kg/hr of hydrogen, a 700kW SOFEC system was considered which consisted of 25 electrolyser stacks with 400 electrolyser cells each.

For the calculation of CAPEX, the cost of electrolyser unit and cost of heat exchanger and other auxiliary equipments will be considered. The cost of SOFEC unit was based

Expenditure type	Price	Price Unit	Total Cost	Unit
CAPEX				
SOFEC Unit	4000	Eur/kW	2.1	Mil Euros
Heat exchangers and other Auxiliarry equipments	20 % of Electrolyser Cost	-	0.42	Mil Euros
	TOTAL		2.52	Mil Euros
OPEX				
Electricity	40	Eur/MWh	0.196	Mil Euros/year
Fuel	0.2	Eur/kg	0.31	Mil Euros/year
Water	8	Eur/m3	0.048	Mil Euros/year
	TOTAL		0.554	Mil Euros/year
Hydrogen Production	112	kg/hr	784	tons/year

Table 6.1: CAPEX and Annual OPEX values for the SOFEC system (Adapted from Anghilante et al., 2018, Petipas, 2013 and H. Zhang and Desideri, 2020) (Mil = Million)

upon the cost evaluation of the SOEC systems done by Anghilante et al., 2018. They investigated the SOEC system models developed by several researchers. The costs of electrolyser decrease with increase in capacity. For instance, electrolysers with less than 1MW power rating have costs greater than 2000 Eur/kW (3000 to 5000 Eur/kW) whereas those in the range of 10MW to 100MW cost about 400 Eur/kW. Thus, as the SOFEC will be a new technology in the market and the electrolyser capacity considered is below 1 MW, an upper end cost of 4000 Eur/kW was chosen.

Further, H. Zhang and Desideri, 2020 have presented the costs for heat exchangers and other auxiliary equipments to be 20% of the electrolyser cost. The same is assumed for the SOFEC system.

For calculation of OPEX, the costs of electricity and biogas fuel were considered. European Commission, 2020 presented the electricity prices for industrial and household demands with an electricity price of 40 Eur/MWh for industries. Thus, this price was taken for electricity demand calculations. Further, the price of biogas was taken as 0.24 USD/kg (0.2 Eur/kg) methane for fuel in the SOFEC was chosen from the biogas technology report by Renewable Energy Agency, 2018. The amount of fuel required is calculated using the Cycle Tempo SOFEC model and fuel to hydrogen output ratio of 2:1 is considered. Thus, amount of fuel required in a year is twice the amount of hydrogen produced. In addition, water costs have been considered to be 8 Eur/m3 EurEau, 2020.

Based on the Cycle Tempo electrolyser sizing in Chapter 5, a hydrogen production of kg/hr was taken. Further, H. Zhang and Desideri, 2020 have used a capacity factor of about 80% for their electrolyser model i.e. the electrolyser will operate for 80% of the total hours in a year. Thus, the same is assumed for the SOFEC as well. Based on the above considerations, the annual CAPEX and OPEX are calculated and shown in the table 6.1.

Park et al., 2014 have performed economic analysis for SOFC operation and they calculated their operation and maintenance costs (O&M) to be about 18 to 19% of the OPEX. Thus, for the SOFEC, O&M costs equivalent to 19% of the OPEX will be added to the OPEX. The electricity demand, fuel and water supply calculations are provided in the

Type of Process	Net production cost	Unit
Low temperature electrolysis	7.34	Eur/kg H <sub>2</sub>
Solid oxide electrolysis	5.54	Eur/kg H <sub>2</sub>
Biomass gasification	8.25	Eur/kg H <sub>2</sub>
Steam Methane Reforming	3.11	Eur/kg H <sub>2</sub>
Solid oxide fuel assisted electrolysis	4.05	Eur/kg H <sub>2</sub>

Table 6.2: Net production costs for various hydrogen production processes (From Dincer and Acar, 2015 and Yukesh Kannah et al., 2021)

Appendix B.1.1.

Siefert and Litster, 2014 have considered the lifetime of their SOFC plant to be 20 years with SOFC stacks being replaced three times over the lifetime. The same assumptions are considered for the SOFEC plant as well. The total CAPEX, OPEX and Hydrogen production is calculated as follows:

Total CAPEX = (SOFEC system costs × 3) + Other Equipment Costs (Heat exchanger, blower, etc.)

Total OPEX = (Sum of Annual Costs of Electricity, Fuel, Water and Maintenance)× Plant Lifetime

Total Hydrogen Production = Annual Hydrogen Production × PlantLifetime

The total net production cost per kg of hydrogen is calculated as follows:

$$Net Production \ cost = \left[\frac{Total \ CAPEX + Total \ OPEX}{Total \ hydrogen \ production}\right] = 4.055 \ Eur \ / \ kgH_2 \quad (6.3)$$

Further, from table 6.1, it can be seen that while the SOFEC unit takes a major share of the CAPEX, the fuel costs dominates the OPEX. Also, a major part of electricity costs (about 60%) account for heating demand of SOFEC.

A comparison of the net production costs can be done with the net production costs of other competing technologies considered in review done by Dincer and Acar, 2015 and Yukesh Kannah et al., 2021. They are shown in the table 6.2.

From the table 6.2, it can be seen that the SOFEC estimated production cost is about 1.5 euros less than that of solid oxide electrolysis. This is mainly due to the fact that the while the biogas costs of SOFEC add up (as seen in table 6.1), SOFEC has much lower electricity demand as compared to SOEC which lead to lower costs of electricity. Steam methane reforming, being the most widely used method, has the lowest production cost of  $3.11 \text{ Eur/kg H}_2$  and biomass gasification has the highest net production cost of  $8.25 \text{ Eur/kg H}_2$ . Thus, even with lower electricity demand for the SOFEC unit, the SOFEC unit costs is still the major factors in reducing the net production cost. In addition, it

is assumed that there is an uninterrupted supply of biogas and electricity. If the biogas supply is interrupted, the power demand of the SOFEC will become equivalent to that of the SOEC and thus, increase the production costs tremendously. Schmidt et al., 2017 predict the future cost (2030) and performance of water electrolysis by consulting with industry and academic experts. For SOEC, with investment in research and development and production scale up, they suggest the capital costs can drop by about 40% to the range 1500 to 1800 Eur/kW. Thus, the capital costs for SOFEC can be assumed to have the same trend. In addition,W. Wang et al., 2008 experimented with different electrode materials and showed that electrodes with better catalytic properties can reduce electricity demand required to produce the same amount of hydrogen. Martinez-Frias et al., 2003 changed their anode material properties and were able to more than double the current density obtained at a given cell voltage. Further, Laguna-Bercero, 2012 presented the recent developments in solid oxide electrolyser materials and have stated that research on better catalytic materials for electrodes is ongoing. Hence, it can be assumed that with better electrode materials, the electric power will drop by 20%

Thus, based on the assumptions that capital cost of SOFEC is about 1800 Eur/kW and the electric power demand reduces by 20 %, the production cost of SOFEC will be about 3 Euros per kg hydrogen and will be able to compete with steam methane reforming. In conclusion, based on the cost estimates made, the SOFEC system should be economically feasible.

#### **6.3.** SOCIAL FEASIBILITY

As discussed in Chapter 3, social feasibility involves determing the social acceptance and environmental impact of the technology. Therefore, process safety, social acceptance and environmental impact have been considered. Unsafe operation and handling of raw materials such as hydrogen in a system can cause hazardous situations and accidents leading to loss of life and property. This makes process safety a very important aspect in deciding the feasibility of a technology. In addition, technology awareness and acceptance by the public and consumers is essential to attract investments for SOFEC's development. Taking the environment into perspective, if the SOFEC has reduced emissions, it can help in competing with commercial technologies such as steam reforming of methane and low temperature electrolysis. Analysing all these factors can help determine whether the SOFEC system is socially feasible.

#### 6.3.1. PROCESS SAFETY

For a SOFEC system, process safety involves the safety measures in handling and storage of biogas and hydrogen and the operation of fuel assisted electrolysis. The safety considerations in the latter part will be equivalent to those taken for SOFC due to the structural and operational similarities (Tao et al., 2011). Further, SOFC being a more mature technology provides assurance that the SOFEC can be operated safely. Thus, the focus of process safety is on the measures taken for biogas and hydrogen handling. As mentioned earlier, biogas consists of hydrogen sulfide (H<sub>2</sub>S) is flammable, poisonous and colourless gas which can also oxidise to form sulfuric acid and corrode process equipments. Thus,

desulfurisation of biogas to reduce the  $H_2S$  levels to less than 250ppm is recommended (Saadabadi et al., 2018). Other trace impurities in biogas such as ammonia and siloxanes can be extracted in the biogas plants itself.

Further, hydrogen storage and handling becomes the main concern when producing large quantities of hydrogen. The steam and hydrogen mixture exiting the electrolyser at the steam electrode can be partially condensed to extract hydrogen from the mixture and store it.Generally, hydrogen is produced and consumed industrially at the same site to avoid safety issues (Ustolin et al., 2020). For later use, hydrogen is either stored as compressed gas or as liquid. Compressed hydrogen gas is stored industrially at 200 to 300 bar pressure in metallic tanks with a low mass storage efficiency of 1 wt% (Barthelemy et al., 2016). However, hydrogen in contact with metal surfaces causes embrittlement ( $H_2$  dissolution in metal surface) leading to cracks and metal surface degradation and further the risk of hydrogen leakage. Hydrogen leakage occurs more frequently as compared to explosions in metallic tanks and can be avoided by baking the tanks to 220<sup>0</sup>C making the hydrogen diffuse out of the metal (Hansen, 2020).

On the other hand, cryogenic (liquid) storage stores hydrogen at  $-253^{0}$ C enabling high energy density storage and hydrogen embrittlement is negligible at temperatures lower than  $-150^{0}$ C. However, liquid H<sub>2</sub> storage is still an energy intensive with energy equivalent to 40% of hydrogen content being used for long term storage as compared to 10% in case of compressed gas storage (Ustolin et al., 2020). To ensure that safety in both the storage methods, the storage tanks can be surround by high concrete walls to avoid the impact of hydrogen explosions (Hansen, 2020). Another method of hydrogen storage is storing in man-made cylindrical underground caverns in salt deposits. They can store large amounts of hydrogen safely at 200 bar or higher pressures(Michalski et al., 2017) as these salt caverns protect the hydrogen from external environmental influences. The main limitation to this method is the availability of suitable salt deposit sites where these caverns can be made.

For hydrogen transportation, compressed gas storage at 250 bar in tanks with composite and polymer liners is used for short distance while cryogenic hydrogen storage is seen as a promising solution for long distance as large amounts can be transported at once (Barthelemy et al., 2016).

Thus, it can be inferred that for the hydrogen storage in a SOFEC system, compressed hydrogen tanks can be used for small scale long term storage due to their cost effectiveness and cryogenic storage can be used for short term large scale storage due to its high energy density storage. A salt cavern is the safest and best hydrogen storage option provided that there are salt deposits present in the vicinity of the hydrogen production facility. With the knowledge and means for safe biogas and hydrogen handling already present in the industry, the SOFEC is socially feasible in terms of process safety.

#### **6.3.2.** SOCIAL ACCEPTANCE

Social acceptance is the positive attitude of the public and consumers towards the adoption of a technology. Many studies performed to examine the awareness, familiarity and understanding of citizens in European countries on hydrogen and hydrogen fuel cell technologies. The results from a majority of them have shown that while people in have a meager knowledge about hydrogen, there is high support for hydrogen fuel cell technologies for vehicles and residential applications. (Oltra et al., 2017). Thus, it can be assumed that SOFEC system will also be accepted by the people in the vicinity of the plant. Further, acceptance of biogas for energy generation in SOFCs is hampered due to the presence of hydrogen sulfide and siloxanes which create health and environmental concerns (Saadabadi et al., 2018). However, countries such as Germany and UK have set laws and guidelines to regulate the production of biogas in waste water treatment plants (WWTs) and ensure safety measures are taken (Korbag et al., 2021). This helps in instilling confidence in people about the use of biogas in SOFC and SOFEC. Currently, biogas from WWTs has been used in SOFC to provide heat and power(Saadabadi et al., 2018). Alternatively, SOFECs can use this biogas to produce hydrogen and WWTs can earn revenue by selling the produced hydrogen to chemical and energy industries. In such a case, biogas is upgraded to hydrogen which is a more valuable fuel and raw material.

Based on the net production costs estimated in the previous section, SOFEC might also be a more cost effective hydrogen production method from an industry perspective as compared to low temperature electrolysis. Thus, based on social acceptance, the SOFEC can be said to be socially feasible.

#### **6.3.3.** ENVIRONMENTAL IMPACT:

Hydrogen has been considered to play a significant role as a zero emission fuel and energy carrier to replace the use of highly polluting and depleting fossil fuels. However, it is necessary to take into account the hydrogen production method as it determines the extent to which hydrogen can be regarded as a environmentally benign energy carrier. Parameters such as acidification potential (AP) and global warming potential (GWP) are used to gauge the impact of a hydrogen production method on the environment (Dincer and Acar, 2015). Many researchers such as Dincer and Acar, 2015,Ozbilen et al., 2013 and Bhandari et al., 2014 have focused mainly on GWP and AP as the parameters for environmental impact analysis. Thus, as the literature values for GWP and AP are available, this section will focus on only these two parameters.

Acidification potential (AP) relates the discarding of acidifying pollutants in surface waters, ground water, soil and ecosystems affecting the natural environment and human health. Ozbilen et al., 2013 state that sulfur dioxide and  $NO_x$  emissions are the major contributors for AP. They have performed life cycle analysis (LCA) on electrolysis based on several sources and have presented their AP results as shown in the table 6.3.

It can be seen that biomass gasification has the highest AP value (34 g SO<sub>2</sub>) equivalent) followed by biomass based electrolysis (34 g SO<sub>2</sub>) equivalent) . Here biomass is used for fuel generation by gasification. The fuel obtained is used in a combined cycle gas turbine for electricity generation and further this electricity is used in low temperature electrolysis. Steam reforming of methane has higher AP than electrolysis based on other sources. In case of SOFEC, the main source of SO<sub>2</sub> is the biogas used as assisting fuel. However, as explained earlier, biogas has to be desulfurised below 250ppm for use in SOFC and SOFECs In addition, the major contributor to the the AP value of steam

Hydrogen Production Method	Acidification Potential (g SO2- equivalent/kg H2)
Solar based Electrolysis	8.06
Wind based Electrolysis	2.58
Biomass based electrolysis	29.03
Biomass gasification	34
Nuclear based high temp Electrolysis	4.84
Steam Reforming of methane	15
SOFEC with Renewable Electricity	5

Table 6.3: Values of acidification potential (AP) for electrolysis with different hydrogen production methods (From Ozbilen et al., 2013)

Table 6.4: Values of GWP for various hydrogen production methods (From Dincer and Acar, 2015

Hydrogen Production Method	Global Warming Potential (kg CO2- equivalent/kg H2)
Solar based Electrolysis	2.5-3
Biomass gasification	4
Wind based electrolysis	1
Nuclear based high temp Electrolysis	2.5-3
Steam Reforming of methane	8
Electrolysis with Grid electricity	30
SOFEC with Renewable electricity	2-3

methane reforming is based on source from which the methane is obtained. Thus, the value of AP for SOFEC can be estimated to be between that of methane reforming and solar based electrolysis (between 8.06 and 15 g SO<sub>2</sub> equi.). The value of AP for SOFEC can be even lower based on the source of electricity as seen by the differences in WInd, solar and nuclear based electrolysis.

The other parameter GWP, is defined as the impact of human emissions on the thermal radiation absorption by the atmosphere leading to climate change affecting the ecosystem and human health (Ozbilen et al., 2013). The GWP is calculated in terms of kg  $CO_2$  equivalent as the  $CO_2$  is considered as the major contributor to greenhouse gas emissions. The GWP values for various hydrogen production methods have been presented by (Dincer and Acar, 2015) and are shown in table 6.4.

From table 6.4, it can be observed that electrolysis supplied by grid electricity has the highest GWP of 30 kg  $CO_2/kg$  H2. This is due to the grid electricity being supplied completely by fossil fuel. This is followed by steam methane reforming which, in addition to  $CO_2$  production and hydrogen, also uses grid electricity for post production processes such as compression and separation. Wind based electrolysis has the lowest GWP of 1 kg  $CO_2$  equi. per kg H<sub>2</sub>.

For the SOFEC, if it is assumed that all the electrical (including compression and separation) and heat demand is catered to by renewable electricity (wind and solar), the  $CO_2$  emissions mainly depend on the assisting fuel which is taken as biogas. Based on the Cycle Tempo SOFEC simulation results, a carbon dioxide output to hydrogen produced ratio of 2:1 is considered. Thus, a SOFEC running on renewable electricity is estimated

to have the GWP of 2 to 3 kg CO<sub>2</sub> per kg H<sub>2</sub> produced.

In conclusion, the acidification potential for SOFEC is higher than electrolysis based on other sources and can be reduced further based on how the electrical demands are met. Further, the GWP for SOFEC is estimated to be between 2 to 3 kg  $CO_2$  per kg H<sub>2</sub> produced for complete renewable electricity supply. Thus, with lower  $CO_2$  and  $SO_2$  emissions than steam methane reforming, the SOFEC is environment friendly.

# 7

### CASE STUDY: SOFEC INTEGRATION IN STEEL MILL

The results from the feasibility study in the previous chapter show that a biogas fuelled SOFEC system can be feasible to be build and operate. To further corroborate this inference, a scenario can be presented for the SOFEC system.

One of the main requirements for the SOFEC is the availability of external heat input for it to operate at high temperatures. Thus, an energy intensive industry which produces a lot of heat and utilizes hydrogen in its processes can be a desirable scenario to consider for the SOFEC system. One such industry is the steel manufacturing industry. Iron and steel mills lose about 20% to 50% of the energy input as waste heat in form of exhaust gas, molten slag and cooling water (Quader et al., 2015).

In addition, to meet the zero emission policy of the Paris Agreement, steel manufacturers are working on 'breakthrough technologies' as the current technologies reduce the emissions by only 15% to 30% (Åhman et al., 2017). One such technology is the hydrogen based direct reduction of iron. It involves the use of hydrogen to reduce iron oxides (Fe<sub>2</sub>O<sub>3</sub>) to pure iron which is further used in the steel making process. Commercially, iron oxide reduction in steel mills is done using carbon monoxide or pure carbon which, in turn, produces carbon dioxide as a by-product. For every kg of iron oxide reduced, 1.5 to 3 kgs of  $CO_2$  is produced (Patisson and Mirgaux, 2020). This is avoided when hydrogen is used as the reducing agent with the by-product being water as shown in the equations below.

$$Fe_2O_3 + 1.5C = 2 Fe + 1.5CO_2$$
  

$$Fe_2O_3 + 3 CO = 2 Fe + 3 CO_2$$
  

$$Fe_2O_3 + 3 H_2 = 2 Fe + 3 H_2O$$
(7.1)

In recent years, several companies have shown interest in adopting this technology. In 2015, Energiron, a supplier of natural gas based DRI shaft furnaces, successfully tested

direct reduction of iron ore with gas having more than 90 % hydrogen concentration and claimed that it would also work on 100% hydrogen (Bhaskar et al., 2020). Further in 2016-17, a collaboration by European steel companies SSAB, LKAB and Vattenfall initiated a major project called HYBRIT which uses hydrogen based iron ore reduction with an aim for entire fossil free value chain for steel production (Vogl et al., 2018). However, hydrogen production using low temperature electrolysis and SOEC can be very expensive. Bhaskar et al., 2020 presented a model of hydrogen based iron ore reduction using a low temperature electrolyser power demand accounted for 70% of their operating costs. In contrast, the SOFEC has a much lower power demand compared to low temperature electrolysers and SOEC which can reduce the operating costs to a great extent. Thus, in such a scenario, SOFEC can be a promising solution.

Therefore, with abundance of external heat input and hydrogen demand, hydrogen based iron ore reduction is chosen as a case study scenario for the SOFEC system. The process of hydrogen based steel making shown in the Fig 7.1. The process involves initially reducing iron ore to produce direct reduced iron (DRI) using hydrogen. This is followed by the steel making occuring in the electric arc furnace and further, liquid steel is turned and rolled into coils. In this scenario, only the electrolysis with iron ore reduction part (red encircled area) will be considered.



Figure 7.1: Hydrogen based steel making process (Patisson and Mirgaux, 2020)

#### **7.1. SOFEC INTEGRATION**

To describe how the SOFEC will be used in the steel mill, first the waste heat source used as external heat input for the SOFEC will be explained. This is followed by an explanation of the process flow diagram of the SOFEC integration with the iron ore reduction process. Further, the hydrogen demand by the iron oxide process is calculated and the electrolyser sizing is done.

#### 7.1.1. WASTE HEAT UTILISATION

To heat the biogas and steam inflow to the SOFEC, waste heat from steel mills can be utilised as a source of heat. The main sources of waste heat are the molten slag  $(1400^{\circ}C to 1500^{\circ}C)$  and off gases (up to 1800  $^{\circ}C$ ) generated in the production of steel in electric arc furnaces (Quader et al., 2015). While the high temperature off gases produced can be

a source of waste heat, they consist of high amounts of dust, fly ash and other impurities which causes damage to the heat exchange equipment and its heat recovery is still being researched (Steinparzer et al., 2014). Thus, heat recovery from molten slag will be considered in this scenario.

Heat recovery from molten slag can be either done using physical or chemical methods. Physical methods involve mechanical processing of the slag and recovering heat from it using air as a medium for heat exchange. On the other hand, chemical methods involve carrying out endothermic reactions such as steam reforming of methane and coal gasification in presence of molten slag to recover the sensible heat from the slag. Here, the product gases are then used as a heat source (H. Zhang et al., 2013).

For the purpose of the thesis work, only physical methods are considered as chemical methods are still in a research phase and for the SOFEC, the reforming reactions occur inside the fuel cell. Physical methods include mechanical stirring, air blasting and centrifugal granulation. H. Zhang et al., 2013 provides a review of all the physical methods. They state that mechanical stirring is energy intensive and has a low heat recovery rate (30-50%); air blasting is also energy intensive with 50% heat recovery but has been tested for industrial use and centrifugal granulation has the highest heat recovery rate (59%) but is still being researched and yet to be commercialised. Therefore, as air blasting is the only method tested for industrial scale, it is chosen for the waste heat recovery.

Air blasting involves the use of high speed and high pressure gas to impinge the molten slag and recover the sensible heat of the slag. Fig 7.1 shows the air blasting technology developed by POSCO (Pohang Iron and Steel Company) in 2012. In air blasting, heat recovery rate is 50% heat with hot air temperature of  $460^{\circ}$ C to  $500^{\circ}$ C (Quader et al., 2015). However, for the SOFEC, heat has to be recovered at a temperature of atleast  $800_{0}$ C.

Therefore, waste heat for the SOFEC will be recovered from the molten slag using air blasting method. For simplicity, it will be assumed that the residence time for air recovery is increased and heat can be recovered at hot air temperature  $900^{0}$ C.

#### 7.1.2. PROCESS FLOW

To develop the process flow for integration of SOFEC in the iron reduction process, models for hydrogen based iron reduction developed by Vogl et al., 2018 and Bhaskar et al., 2020 were referred. In these models, hydrogen was supplied to an iron reduction shaft where iron oxide was reduced to iron at about  $500^{\circ}$ C. For hydrogen production, alkaline electrolyser was used and hydrogen produced was heated to  $500^{\circ}$ C using electrical heating.

A schematic of the integration of the SOFEC system for iron oxide reduction is shown in Fig 7.2. Streams of biogas at  $25^{\circ}$ C (F1) and steam at  $100^{\circ}$ C (F2) are initially heated in heat exchangers HEX2 and HEX1 respectively. Anode off gases from the previous process run (F6), is initially used to heat the two streams F1 and F2. This is followed by the heat exchangers HEX3 and HEX4 using hot air at  $900^{\circ}$ C, from the molten slag heat recovery which heats the biogas (F4) and steam (F3) streams to  $800^{\circ}$ C. Now, some of the steam from F3 is added to stream F4 such that biogas to steam mass ratio is 1:2. This is done to


Figure 7.2: Slag heat recovery technology using air blast developed by POSCO (Quader et al., 2015)

ensure that the avoid carbon deposition during the reforming reaction in the SOFEC.

The SOFEC operates in endothermic mode and the heat demand by steam reforming of methane occurring at the anode will be compensated by the hot air recovered from molten slag heat recovery. Electrical input for the SOFEC is considered to from renewable sources. The hydrogen produced by the SOFEC (F5) is at  $800^{\circ}$ C and is sent to the iron oxide reduction shaft. In the shaft, iron oxide entering from the top is reduced and direct reduced iron (DRI) is obtained at the bottom. Off gases containing steam and hydrogen (F7) are added to the F1 stream after the first heat exchanger. The off gases are obtained at temperature range of  $250^{\circ}$ C to  $500^{\circ}$ C and have to be heated before it is fed to the cathode of the SOFEC. Finally, the anode off gases (F7) are cooled to ambient temperature and water is extracted from it to give a hydrocarbon mixtrue which can be sent to methanol production plants as feedstock.

#### 7.1.3. SOFEC SIZING

With the process flow explained, the hydrogen demand by the iron reduction process and further, sizing of SOFEC can be done. With the SOFEC capacity calculated, the levelised cost of hydrogen (LCOH) and can be estimated for the scenario and it will be possible to determine whether the integration of SOFEC is feasible.

For SOFEC sizing, both the hydrogen and heating demand have to be taken into account.

For hydrogen demand calculations, a basis of 1 ton of steel production per hour is considered. The results obtained by the iron reduction model by Bhaskar et al., 2020 showed that to produce 1 ton of molten steel, 1.06 ton of reduced iron is required. By stoichiom-



Figure 7.3: Integration of SOFEC in the iron ore reduction process

etry, 54 kg of hydrogen is required to reduce iron oxide ores and obtain 1 ton of reduced iron (Patisson and Mirgaux, 2020). However, practically a much higher amount of hydrogen is required. Further, Vogl et al., 2018 states that the ratio of the actual hydrogen requirement to that of the stoichiometric amount is 1.6 which means 60% higher consumption of hydrogen. Thus, the total hydrogen requirement is as follows:

$$H2 \ requirement = 54 \times 1.06 \times 1.6 = 91.6 \ kg \tag{7.2}$$

With the actual hydrogen requirement established, the SOFEC capacity can be determined.

Using the model parameters from table 5.2.5, the Cycle Tempo SOFEC model was simulated and hydrogen production was calculated for current densities from  $2000 \text{ Am}^{-2}$  to thermo neutral mode (4890 Am<sup>-2</sup>). It was found that from current densities  $3000 \text{ Am}^{-2}$  and above, the hydrogen requirement is met. The mass flow and energy data used for the economic feasibility are provided in Appendix B

For the thermal demand, the basic heat calculations done in Chapter 5 section 5.3 were carried out for biogas and steam massflows at 3000 A m<sup>-2</sup>. However, here anode off gas and hot air from the molten slag heat recovery system will be used to heat the steam and biogas mass flows. Based on the literature review on plate type heat exchangers done by X. Zhang et al., 2018, the effectiveness of the four heat exchangers used is taken as 0.85.

Table 7.1.3 shows the mass and heat flows of heating and cooling streams. The mass flow of hot air required was back calculated such that it only caters to the heat demand left when the anode off-gases are cooled to ambient temperature.

Further, the heat demand by steam reforming of methane (206 kJ/mol) and heat produced by water gas shift reaction (-41 kJ/mol) in the anode of the SOFEC were considered and a net heat demand was calculated.

Therefore, using the SOFEC unit structure from the feasibility studies (25 stacks with 400 cells each), the SOFEC unit power was calculated to be 14.7 kW with cell voltage of 0.0491V and current density of 3000A/m<sup>2</sup>. Further, 3 units of SOFEC will be used to produce about 91.8kg/hr of hydrogen.

	Streams	Mass Flows (in g/s)	Heat Flows (Q)(inkW)
Heating Streams	Biogas	51.24	78.15
	Steam (including latent heat)	198.35	975
Cooling Streams	oling Streams Anode Off-gas		522.3
	Hot air	838.89	844

Table 7.1: Mass and heat flows of heating and cooling streams for three units of SOFEC

#### 7.1.4. FEASIBILITY ANALYSIS

The feasibility analysis will consider the effectiveness of the waste heat recovery system (technical aspect), cost of hydrogen (COH) and cost of products (COP) (economic aspect) and  $CO_2$  emissions avoid (social aspects).

#### WASTE HEAT RECOVERY SYSTEM

In the thermal demand calculations, it is assumed that only the calculated amount of hot air is obtained in the waste heat recovery system. Also, it is assumed that molten slag is available for heat recovery. However, this is not practical. L. Wang et al., 2021 showed that a heat recovery of 59% from 90 kg of slag required air mass flow of 4.2 kg/s. Such a large mass flow of air will contain 2000 to 3000 kW of sensible heat which is in excess and will require huge amounts of cooling water. Further, this recovery method requires a lot of area for the slag to flow.

Therefore, other methods with lower energy intensity and better efficiency such as centrifugal granulation and heat recovery from furnace off-gases have to be developed and commercialised to make the SOFEC integration feasible. Alternatively, conversion of waste heat into thermo-electric power using semiconductors is also being explored which can help in reducing electricity costs for the SOFEC in addition to the cooling duty. Considering these technologies are developed and commercialised in the furture, the use of waste heat recovery in the SOFEC system can then be feasible.

#### COST OF HYDROGEN AND SYNGAS PRODUCTION

With the SOFEC power rating calculated, the cost of hydrogen and cost of combined syngas and hydrogen production can be calculated. The costs per unit for all the CAPEX and OPEX calculations were taken from table 7.1.4. The cost of waste heat recovery system Table 7.2: Annual CAPEX and OPEX values for the SOFEC system with waste heat recovery (Adapted from Anghilante et al., 2018, Petipas, 2013 and H. Zhang and Desideri, 2020) (Mil = Million)

Expenditure type	Price	Price Unit	Total Cost	Unit
CAPEX				
SOFEC Unit	4000	Eur/kW	0.138	Mil Euros
Heat exchangers, waste				
heat recovery system	40 % of Floctrolycor System Cost	-	0.84	Mil Euros
and other Auxiliary	40 % of Electrolyser System Cost			
equipments				
	TOTAL		0.958	Mil Euros
OPEX				
Electricity	40	Eur/MWh	0.0128	Mil Euros/yr
Fuel	0.2	Eur/kg	0.258	Mil Euros/yr
Water	8	Eur/m3	0.04	Mil Euros/yr
	TOTAL		0.3108	Mil Euros/yr
	·	•	•	•
Hydrogen Production	91.8	kg/hr	642600	tons/yr

was not found in literature and thus, an assumption of additional 40% of electrolyser cost was added in the heat exchanger and auxiliary systems.

The operational and maintenance costs are assumed to be about 25% of the OPEX when taking the operation of waste heat recovery system into consideration. The total net production cost per kg of hydrogen is calculated as follows:

$$Net Production cost = \left[\frac{Total CAPEX + (Annual OPEX * Lifetime)}{Total hydrogen production over lifetime}\right] = 2.09Eur perkg H2$$
(7.3)

Comparing the calculated production cost with the net production costs for steam methane reforming in table 6.2, the calculated costs are 1 Eur/kg  $H_2$  lower than that of steam methane reforming. This is due to the availability of waste heat which nullifies the heating costs incurred in operating the SOFEC. Thus, the SOFEC can be economically feasible in the steel mill scenario.

#### REDUCTION IN CO<sub>2</sub> EMISSIONS

Replacing carbon based iron ore reduction with hydrogen highly reduces the amount of  $CO_2$  emitted. As shown in Eqn 7.1, for every 2kg of reduced iron, 3 kg of carbon dioxide is produced. With hydrogen based iron oxide reduction, it is replaced with 3kg of steam. Also, based on the stoichiometry, about 1 ton of reduced iron is required to produce 1 ton of steel. Thus, for every ton of steel, at least 1.5 ton of  $CO_2$  is produced the annual  $CO_2$  emissions avoided by using the SOFEC is calculated as follows:

$$kgCO_2 = 1.5 \times 7200 hrs = 10800 tonsof CO_2$$
(7.4)

# 8

## **DISCUSSION**

The goal of the thesis was to determine whether a biogas fuelled SOFEC is a feasible technology. To achieve it, a feasibility analysis was performed. From the literature review, it was observed that the research on SOFEC for hydrogen production has only been done in recent years. Also, SOFEC holds the potential of producing hydrogen at lower voltages as compared to the SOEC.Further, from Chapter 3, the SOFEC was understood to be a combination of the anode of the SOFC and cathode of SOEC and the hydrogen is always produced at the cathode and hence, except steam removal, no other gas treatment is required. However, it has only been tested using experimental setups and has never been operated on an industrial scale.

## **8.1.** TECHNICAL FEASIBILITY

In the technical feasibility, the limitations and considerations of construction materials, fuel and heat inputs for operation of the SOFEC on an industrial scale have been discussed and solutions for them have been provided. With regard to the construction materials, the cathode and electrolyte materials were found to be in commercial practice. However, little research has been done on the materials for anode and SOFC anodes cannot be used due to carbon deposition in reforming methane (W. Wang et al., 2007). While carbon deposition can be alleviated by using excess steam, presence of excess steam increases the SOFEC electrical power demand. Further, it was assumed that with the research continuing for the improvement of cathode materials (Laguna-Bercero, 2012), anode materials will also be researched and be available when the SOFEC is developed. Thus, the SOFEC development depends on the performance and availability of anode materials.

Further, biogas was proposed as the assisting fuel for SOFEC. While the use of biogas helps in upgrading the fuel to hydrogen, it has issues in handling and has limitations in its availability. Biogas before use in the SOFEC has to be pretreated for removal of water and sulfur which can corrode pipes and compressors (Trendewicz and Braun, 2013).

Thus, use of commercially available desulfurisers and condensers was proposed. On the other hand, the operation of the SOFEC unit in the vicinity of biogas and wastewater treatment plant (WWTP) was considered as the solution for limited availability of biogas. However, on an industrial scale, the biogas provided by the WTP may not completely meet the fuel demands of the SOFEC. Further, if biogas is produced using biomass to meet the remaining demand, it will compete with the land usage for food crops. For the SOFEC, the availability of adequate biogas is essential as lack of assisting fuel can lead to the SOFEC operating as a conventional SOEC diminishing benefit of the assisting fuel (Cinti et al., 2016). Therefore, inadequacy of biogas for the SOFEC might pose a problem on an industrial scale.

With regard to thermal demands of the SOFEC unit, use of a heat recovery system, with preheater and heat exchangers, was suggested which would recover heat from the anode and cathode off gases at a temperature of 800<sup>0</sup>C. Such systems have been used in SOFCs to maintain the operating temperature and can be used for temperature control in SOFECs. However, external electrical heating might be required to meet heating demands when operating the SOFEC on a large scale due to heat losses in the pipes and heat exchangers. This will increase the costs of operation and in turn, costs of hydrogen production. Further, use of waste heat in industries with high temperature effluents was proposed to meet the thermal demands. In the case study, the waste heat recovered from molten steel slags was used for the heating of biogas and steam flows. However, such waste heat recovery systems have not yet been developed on an industrial scale. In steel mills, physical methods such as mechanical stirring, air blasting and centrifugal granulation have been developed. However, only air blasting has been tested on an industrial scale and has been proven to be highly energy intensive with heat recovery of 50% at 460 to  $500^{0}$ C (Quader et al., 2015). Therefore, more efficient waste heat recovery methods will have to be developed commercially for the operation of the SOFEC to be feasible.

### **8.2.** SOFEC CYCLE TEMPO MODEL

To acquire data on hydrogen production, fuel consumption and SOFEC power demand required for the economic and social feasibility calculations, a SOFEC model was developed in Cycle Tempo. Initially there was ambiguity in the Cycle Tempo fuel cell model by Groot, 2004 as the resultant equation differed from the result obtained by Standaert et al., 1996. This ambiguity was resolved by deriving both the equations and comparing them. Further, the initial approach to develop a SOFEC model was to develop a SOEC model and then adapt it to operate in fuel assisted mode. However, due to requirement of complex coding and time consuming process of getting the code debugged, this approach was dropped. Therefore, the SOFEC model was developed using the existing fuel cell model present in Cycle Tempo. In this case, while the current density remained positive, with increasing current density, the cell voltages moved from being negative (combined production of electricity and hydrogen) to positive (production of hydrogen with elecectricity consumption). However, this had many implications on the proper functioning of the model. While the model was validated with experimental results from (W. Wang et al., 2008), it simulated incorrect cell voltages when fuel utilisation was varied from 0.3 to 0.8 with only correct value being at 0.8. Further, while changes were made to the

electrochemical equations fuel cell model, no change was made to the energy balance. The Gibbs free energy change ( $\Delta$  G), the enthalpy change ( $\Delta$  H) and the change in entropy (T  $\Delta$  S) values were calculated incorrectly which led to power production, instead of power comsumption, in the SOFEC and errors in anode and cathode outlet temperatures. Thus, the SOFEC model was not integrated with heat exchangers and was used only for the electrical and mass flow values at a fuel utilisation of 0.8. Based on the SOEC unit model by Petipas, 2013, a SOFEC unit of 25 stacks with 400 cells each was considered and a cell area of 100 cm<sup>2</sup> was taken. For heat demand calculations, T  $\Delta$  S value of 65.8 kJ/mol calculated by Luo et al., 2014 for methane assisted solid oxide electrolysis at operating temperature of 800<sup>0</sup>C was considered. By comparing the reversible heat demand by entropy change and irreversible heat losses by overpotentials, a thermoneutral potential of 0.07979V at 3637  $A/m^2$  was obtained. While, a heat exchange effectiveness was considered, the heat losses incurred by other balance of plant components such as blowers, pipes and compressors was not considered in the calculations. However, on a industrial scale, these heat losses can lead to changes in the energy balance and increase in heat demand.

### **8.3.** ECONOMIC FEASIBILITY:

For the economic feasibility analysis, the net production costs of hydrogen production were calculated using the modelling results from Chapter 4. For CAPEX, the capital costs of SOFEC units, heat exchangers and other auxiliary equipment was considered and taken from literature (Anghilante et al., 2018, H. Zhang and Desideri, 2020). On the other hand, for OPEX, the costs of electricity, fuel, water and operation and maintenance were considered. From the net product cost (NPC) calculations, it was found that the NPC value for SOFEC (4.05 Eur/kg H<sub>2</sub>) lesser than most of the costs for competing technologies such as biomass gasification(8.25 Eur/kgH<sub>2</sub>), low temperature electrolysis (7.34 Eur/kg H<sub>2</sub>) and SOEC (5.54 Eur/kg H<sub>2</sub>) taken from literature (Dincer and Acar, 2015). However, the NPC value of steam methane reforming was still lower than the SOFEC at 3.11 Eur/kg H<sub>2</sub>. The highest costs involved in the NPC calculation for SOFEC were the capital costs of electrolyser and operating costs of electricity and fuel. While the high cost of electrolyser is expected as the technology is yet to mature, the high costs of electricity is mainly due to the large heating costs of steam and biogas. With fuel massflow being twice that of the hydrogen produced, costs of fuel is also a major factor. However, based on a 40% drop in future electrolyser costs predicted by Schmidt et al., 2017, the net production costs drop to 2 Eur/kg H<sub>2</sub>. Further, when waste heat recovery systems are incorporated, the large recurring heating costs are replaced by much lower capital costs. In the case study, waste heat is recovered from molten slag leads to a reduction of net production costs to about 2 Eur/kg  $H_2$ . Thus, for the SOFEC operation to be economical, low capital costs of electrolyser and low cost external heat source are desired.

## **8.4.** SOCIAL FEASIBILITY:

For the social feasibility study, aspects including safety in SOFEC operation, social acceptance of hydrogen technologies and environmental impact of SOFEC were considered.

In the analysis of operational safety, desulfurisation of biogas to concentrations below 250ppm was suggested as it could erode the pipes and heat exchange equipment. Further, for hydrogen storage, salt caverns were proposed to be the best method for safe large scale hydrogen storage. However, the main limitation for it is the limited availability of salt deposit sites where such caverns can be constructed. Other commercial methods such as metallic tanks for small scale long term storage and cryogenic storage for large scale small term storage were suggested. However, the leakage of hydrogen in metallic tanks reduce its storage efficiency and chance of hydrogen explosion in cryogenic storage requirement of concrete walls for protection.

With regard to social acceptance, the hydrogen technologies were shown to have high support. However, surveys showed that there was support for hydrogen where the local communities were not aware of hydrogen fuel cell technologies. Thus, spreading awareness on the benefits of such technologies is required to ensure local support.

Further, the environmental impact of the SOFEC was studied on basis of acidification potential (AP) and global warming potential. THe value of acidification potential was found to be higher than other renewable based electrolysis processes. This was due to the presence of sulfur in the biogas which might form sulfur oxide and siloxanes when used in biogas. Further, the composition of biogas varies with sources and hence, removal of sulfur using a desulfuriser is essential. The GWP value for SOFEC with renewable electricity was calculated to be 2 to 3 kg CO<sub>2</sub>-equivalent/kg H<sub>2</sub> which was among the lowest values compared to renewable based conventional electrolysis and other hydrogen production methods.

# 9

# **CONCLUSIONS AND RECOMMENDATIONS:**

The purpose of this thesis is to determine whether a biogas fuelled SOFEC system is a feasible technology. This is achieved by performing a feasibility study considering technical, economic and social aspects. Further to corroborate the results of the study, a case study scenario of the feasibility of integration of SOFEC in a steel mill was presented. Based on the results and discussions on the feasibility study and case study, the research questions can be answered.

#### 1. Is the SOFEC system technically feasible?

In technical aspects, the performance and availability of SOFEC component materials, handling and adequate supply of biogas as assisting fuel and heating systems to compensate for thermal demands were addressed.

Based on literature review, it was shown that anode materials which can withstand reducing environments have to be researched as exisiting SOFC anodes are susceptible to carbon deposition and deactivation . Further, desulfurisers and condensers were proposed to make biogas devoid of corrosive sulfur and safe for handling. Further, operation of SOFEC in the vicinity of waste water treatment plants was suggested to maintain adequate supply of biogas. To meet the thermal demands of endothermic reforming reaction, heat recovery systems with anode and cathode offgas heat recovery were suggested. In addition, with the case study, the advantage and feasibility of high temperature waste heat recovery from molten slags in steel mills was presented. With existing technologies being suggested for the SOFEC operation and solutions proposed to tackle challenges posed by anode material and thermal demands, the development of the SOFEC system is possible. Therefore, it can be concluded that biogas fuelled SOFEC system is technically feasible.

#### 2. Is the SOFEC system economically feasible?

For the economic feasibility, the net production costs (NPC) of hydrogen for SOFEC were

considered. Based on the modelling results and maximum capital and operational costs incurred in development and operation of SOFC and SOECs, the net production cost of hydrogen production using SOFEC was estimated to less than 4.5 Eur/kgH<sub>2</sub>. The calculated cost was found to be higher than steam reforming of methane (3.11 Eur/kg H<sub>2</sub>) but lower than the NPC of biomass gasification (8.25 Eur/kgH<sub>2</sub>), low temperature electrolysis (7.34Eur/kgH<sub>2</sub>) and high temperature solid oxide electrolysis(5.54 Eur/kgH<sub>2</sub>). To alleviate the SOFEC costs further, a predicted reduction in electrolyser costs and use of better electrode materials were proposed. Further, it was shown through the case study that reduction in heating costs using waste heat recovery systems would reduce the NPC of SOFEC to less than 3 Eur/kg H<sub>2</sub> allowing it to compete with steam reforming of methane. Thus, with the capability of SOFEC to compete with other hydrogen production methods and possible solutions to make it the one of the more economical methods, it can be said that the SOFEC system has high potential to be economically feasible

#### 3. Is the SOFEC system socially feasible?

For the social feasibility study, aspects including safety in SOFEC operation, social acceptance of hydrogen technologies and environmental impact of SOFEC were considered.

In operational safety, desulfurisation of biogas to concentrations below 250ppm was suggested. Further, for hydrogen storage, salt caverns were proposed to be the best method for safe large scale hydrogen storage. Other commercial methods suggested included metallic tanks for small scale long term storage and cryogenic storage for large scale small term storage.

With regard to social acceptance, the hydrogen technologies were shown to have high support. As surveys showed that there was support but not enough awareness of hydrogen technologies among the local communities, spreading awareness on the benefits of such technologies was suggested.

Further, the environmental impact of the SOFEC was studied on basis of acidification potential (AP) and global warming potential. While the value of AP for the SOFEC found to be higher than other electrolysis due to sulfur in biogas ( $8g SO_2$ -equivalent/kg H<sub>2</sub>), desulfurisation of biogas below 250 ppm was suggested to reduce the value. The GWP value for SOFEC with renewable eelctricity was calculated to be 2 to 3 kg CO<sub>2</sub>-equivalent/kg H<sub>2</sub> which was among the lowest values compared to renewable based conventional electrolysis and other hydrogen production methods. With all the equipments suggested being in practice and solutions provided for issues addressed, it can be concluded that the SOFEC system is capable of being socially feasible.

With the sub research questions answered, the main research question can be answered.

#### Is the biogas fuelled SOFEC system a feasible technology?

By performing technical, economic and social feasibility studies and presenting solutions for each roadblocks for the development of SOFEC, it has been concluded that the SOFEC system is highly capable of being technically, economically and socially feasible. Therefore, based on this conclusion, the biogas fuelled SOFEC system is highly likely to be feasible.

### **9.1.** RECOMMENDATIONS FOR FUTURE RESEARCH

With the findings of the thesis work discussed and conclusions drawn from them, several recommendations can be made for future expansion of this work.

- 1. In the literature review, it was shown that the research in only few researchers have actually performed fuel assisted electrolysis using methane and carbon monoxide. Also, the use of biogas as fuel was never explored for fuel assisted electrolysis. Thus, it is recommended to experiment with the usage of biogas as fuel for SOFECs on a larger scale such as with a pilot plant.
- 2. In Chapter 4, it was observed that while the Cycle Tempo fuel cell model was adapted to operate as a fuel assisted electrolyser, it was simulating the power consumption and energy balance parameters incorrectly which made it incompatible with heat exchangers. This was speculated to be due to the SOFEC being modelled using a fuel cell rather than through an electrolyser model. Thus, for any future work, it is recommended that first a electrolyser model be made in Cycle Tempo which can then be operated in fuel assisted electrolysis mode. Further, the model was only operated at a fuel utilisation of 0.8 as this was the only value at which the model simulated experimentally validate results. Therefore, this issue will have to be fixed to validate the effect of fuel utilisation and inadequate supply of biogas on SOFEC.
- 3. In the technical feasibility study, while the fuel and heat inputs are considered, the source of electricity has not been considered and it is assumed that electricity is provided by renewable source. In addition, the capability of the SOFEC to adapt to fluctuations in electricity and integration in future energy systems have not been considered in the model. These factors should be considered for future work as it can have a great impact on the operational load of SOFEC and provide insights in how the SOFEC will react to shortage of electricity input.
- 4. In the economic feasibility study, while the reduction in costs by waste heat recovery was investigated, other factors such as subsidies and carbon tax were not considered due to lack of research. Further, the depreciation in capital costs over time and equipment replacement costs were not considered in the calculation of net production costs. Therefore, it is recommended to take these factor into account to provide a more accurate estimation of the hydrogen production costs using a SOFEC.
- 5. Finally, in the social feasibility study, the effect of the SOFEC in providing employment and providing a business case for the local waste water treatment plants was not investigated. This can greatly affect the local economy of the towns in vicinity

of the plants. While use of hydrogen was shown to be socially accepted, the conclusions were drawn from very few surveys. Thus, it is recommended that more research is done in understanding the social acceptance of hydrogen based technologies on a global scale.

In conclusion, the SOFEC is a promising concept with a major advantage of reduced power demand over SOEC and biogas upgrading. However, it should be feasibile only when conditions such as uninterrupted biogas supply, waste heat availability and better anode materials are acheived. Thus, if these conditions are met in the future, the SOFEC can prove to be a competitive hydrogen production method.

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# A

# **APPENDIX A**

# **A.1.** CHANGES TO THE FUEL CELL CODE: **A.1.1.** CHANGES TO CMFCEL SUBROUTINE:

IF (DEBUG)CALL Pause( 'Calculation cathode outlet composition')

Figure A.1: Original Part

```
IF (DEBUG)CALL Pause( 'Calculation cathode outlet composition')
Store indices of 02 and CO2 in systemarrays
DO J = 1, NCOMP
IF (COMP(J) == '02' ) THEN
02 = J
ELSE IF (COMP(J) == 'CO2' ) THEN
CO2 = J
ELSE IF (COMP(J) == 'H2O' ) THEN
H20 = J
ENDIF
ENDDO
```

Figure A.2: Changed Part

```
Calculate mole flows 02 in cathode inlet pipe and pipe IPUOX
FM02P = MKGS(IPP) * CONC(IPP,02) / AVERG(IPP)
FM02K = MKGS(LK) * CONC(LK,02) / AVERG(LK)
```

Figure A.3: Original Part

```
Calculate mole flows 02 in cathode inlet pipe and pipe IPUOX

IF ( TYPE(:4) == 'SOFC') THEN

FM02P = MKGS(IPP) * CONC(IPP ,H2O) / AVERG(IPP)

FM02K = MKGS(LK) * CONC(LK ,H2O) / AVERG(LK)

ELSE

FM02P = MKGS(IPP) * CONC(IPP,02) / AVERG(IPP)

FM02K = MKGS(LK) * CONC(LK ,02) / AVERG(LK)

ENDIF
```

Figure A.4: Changed Part

```
* Determine oxidant/fuel ratio OFRAT. *
*
IF ( Given(UOXUSR)) THEN
OFRAT = 0.5 * YH2EQ / CONC(LK,02) * UFL / UOX
ELSE
```

#### Figure A.5: Original Part

```
* Determine oxidant/fuel ratio OFRAT. *
*
IF ( Given(UOXUSR)) THEN
IF ( TYPE(:4) == 'SOFC') THEN
OFRAT = YH2EQ / CONC(LK,H2O) * UFL / UOX
ELSE
OFRAT = 0.5 * YH2EQ / CONC(LK,O2) * UFL / UOX
ENDIF
ELSE
ELSE
```

Figure A.6: Changed Part

```
*_____*
* Calculate and check oxidant utilisation UOX calculated from OFRAT.
*
UOX = 0.5 * YH2EQ / CONC(LK,02) * UFL / OFRAT
IF (UOX > 1) THEN
WRITE (13,940) IAP, ITM, UMAX
CALL WarningIncrement()
OFRAT = 0.5 * YH2EQ / CONC(LK,02) * UFL / UMAX
ENDIF
ENDIF
```

Figure A.7: Original Part

```
* Calculate and check oxidant utilisation UOX calculated from OFRAT. *
* Calculate and check oxidant utilisation UOX calculated from OFRAT. *
* .....*
IF (TYPE(:4) == 'SOFC') THEN
UOX = YH2EQ / CONC(LK,H2O) * UFL / OFRAT
ELSE
UOX = 0.5 * YH2EQ / CONC(LK,O2) * UFL / OFRAT
ENDIF
IF (UOX > 1) THEN
WRITE (13.940) IAP, ITM, UMAX
CALL WarningIncrement()
OFRAT = 0.5 * YH2EQ / CONC(LK,H2O) * UFL / UMAX
ENDIF
```

#### Figure A.8: Changed Part

#### A.1.2. CHANGES TO PRFCEL SUBROUTINE:

```
*_____*
*
     Calculate new utilisations for O2 and CO2 corresp. to mass flows. *
*
       Recalculate oxidant / fuel ratio
       OFRAT = MINOX / MINFL * AVERG(LA) / AVERG(LK)
       DO J = 1, NCOMP
         IF (COMP(J) == '02') YO2 = CONC(LK,J)
         IF (COMP(J) = 'CO2') YCO2 = CONC(LK,J)
       ENDDO
       Calculate and check oxidant utilisation
       UOX = 0.5 * YH2EQ / YO2 * UFL / OFRAT
       IF (UOX >= 1) THEN
         UOX = UMAX
         TLOW = .TRUE.
         OFRAT = 0.5 * YH2EQ / YO2 * UFL / UMAX
       ENDIF
```

Figure A.9: Original Part

```
Recalculate oxidant / fuel ratio
 OFRAT = MINOX / MINFL * AVERG(LA) / AVERG(LK)
 DO J = 1, NCOMP
    IF (COMP(J) == '02') YO2 = CONC(LK,J)
    IF (COMP(J) == 'CO2') YCO2 = CONC(LK,J)
   IF (COMP(J) == 'H2O') YH2O = CONC(LK,J)
 ENDDO
 Calculate and check oxidant utilisation
 IF (TYPE(:4) == 'SOFC') THEN
UOX = YH2EO / YH2O * UFL / OFRAT
 ELSE
 UOX = 0.5 * YH2EQ / YO2 * UFL / OFRAT
 ENDIF
 IF (UOX >= 1) THEN
    UOX = UMAX
    TLOW = .TRUE.
   IF (TYPE(:4) == 'SOFC') THEN
    OFRAT = YH2EQ / YH2O * UFL / UMAX
    ELSE
    OFRAT = 0.5 * YH2EQ / YO2 * UFL / UMAX
    ENDIF
 ENDIE
```

Figure A.10: Changed Part

A.1.3. CHANGES TO CAOUTCOMP SUBROUTINE:

```
*_____*
* 6. Calculation of outlettemperature from energy balance for EEQCOD = 2. *
*_____*
     IF (EEQCOD == 2) THEN
       IF (DEBUG) CALL Pause('Temp. from energy bal. for EEQCOD = 2')
       Calculate oxidant utilisation. This calculation is just done
*
       to be able to display the correct value of UOX in WrFCel.
       DO J = 1, NCOMP
         IF (COMP(J) == '02' ) Y02 = CONC(LK,J)
IF (COMP(J) == 'H20' ) YH20 = CONC(LK,J)
       ENDDO
       IF (TYPE(:4) == 'SOFC') THEN
       UOX = YH2EQ / YH2O * UFL / OFRAT
       ELSE
       UOX = 0.5 * YH2EQ / YO2 * UFL / OFRAT
       ENDTE
```

Figure A.11: Original Part

Figure A.12: Changed Part

A.1.4. CHANGES TO EREV SUBROUTINE:

```
*
* Identify system components for reaction.
*
DO J = 1, NCOMP
IF (COMP(J) == 'H2O' ) THEN
H2O = J
ELSE IF (COMP(J) == 'CO2' ) THEN
CO2 = J
ELSE IF (COMP(J) == 'O2' ) THEN
O2 = J
ENDIF
ENDDO
```

Figure A.13: Original Part



Figure A.14: Changed Part

Figure A.15: Original Part

```
ELSE IF (TYPE == 'SOFC-ER' .OR. TYPE == 'SOFC-IIR' .OR.

TYPE == 'SOFC-DIR') THEN

YCA(H2O) = YCA(H2O) - CMOLES

YCA(H2) = YCA(H2) + CMOLES
```

Figure A.16: Changed Part

```
ELSE IF (TYPE(:4) == 'SOFC' .OR. TYPE == 'AFC') THEN

IF (YAN(H2O) > 0) THEN

ERev = E0H2 + R * TK / (2 * FAR) *

XLOG(XSQRT(YCA(O2)) * YAN(H2) * XSQRT(PFCELL) /

YAN(H2O))

ELSE

ERev = 1.d20

ENDIF
```

Figure A.17: Original Part



Figure A.18: Changed Part

A.1.5. CHANGES TO VLOSS SUBROUTINE:

```
DCONV = 1 - (1 - CONV2) / (1 - CONV1)

CONV = CONV1

E2 = Erev( IAP, TYPE, FLOW, NCOMP, COMP, YAN_0, YAN,

YCA_0, UFL, CONV, DCONV, OFRAT, PFCELL,

TFCELL, G, TH2OOS, XSHIFT, FAIL)

ESAV = E2

F0 = 1 / (E0 - VOLT)

F1 = 1 / (E1 - VOLT)

F2 = 1 / (E2 - VOLT)

PHI = PHI + F0 + 4*F1 + F2

ENDDO
```

Figure A.19: Original Part



ENDDO

Figure A.20: Changed Part

#### A.1.6. CHANGES TO VCDR SUBROUTINE:

```
*_____
                 _____
   Calculate estimations for two values of V: V0 and VN
*_____
    IF (Given(ESTVLT)) THEN
      V0 = ESTVLT
      VN = 0.5 * (EIN + EOUT) - CDENS * RCELL
      IF (VN >= V0) VN = 0.9 * V0
    ELSE
      V0 = EIN - CDENS * RCELL
      VN = EOUT - CDENS * RCELL
      IF (V0 >= EOUT) THEN
        V0 = 0.9 * EOUT
        VN = 0.9 * V0
      ENDIF
    ENDIF
```

#### Figure A.21: Original Part

```
*_____*
 Calculate estimations for two values of V: V0 and VN *
*_____*
    IF (Given(ESTVLT)) THEN
      VN = ESTVLT
      V0 = CDENS * RCELL - (0.5 * (EIN + EOUT))
      IF (VO \ge VN) THEN
      V0 = 0.9 * VN
    ELSE
      VN = CDENS * RCELL - EIN
      V0 = CDENS * RCELL - EOUT
      IF (VN <= EOUT) THEN
        VN = 1.2 * EOUT
        V0 = 0.9 * VN
      ENDIF
    ENDIF
    IF (ABS(VN-V0) < 0.01) V0 = V0 * 0.9
```

Figure A.22: Changed Part

# B

# **APPENDIX B**

## **B.1.** CYCLE TEMPO SIMULATION DATA FOR FEASIBILITY STUDY

Streams	Mass Flows (in g/s)	Gases	Composition ( in %)
		CH4	20
Anode inlet	61.49	CO2	13.333
		H2O	66.67
Cathode Inlet	237.75	H2O	90
		H2	10
Anode Outlet	273.75	CO2	21.24
		CO	2.57
		H2O	67.33
		H2	8.86
Cathode Outlet	38.25	H2O	18
		H2	82

Table B.1: Mass flows for 3 SOFEC units at a current density of 3600 A/m2

Table B.2: Energy flows for 3 SOFEC units at a current density of 3600 A/m2

	Streams	Heat Capacity (kJ/kgK)	<b>Q</b> ( in kW)	
Heating	Biogas	1.967	93.78	
Domand	Steam			
Demanu	(including	2.066	991.96	
	latent heat)			
	Reaction heat	-	305	
Cooling	Anode Off gas	2.956	627.1	
Demand	Cathode off gas	12.416	368.07	

### **B.1.1. OPEX CALCULATIONS**

 $\begin{array}{l} Total \ Electricity \ Demand \ = \ SOFEC \ Power \ \times \ Capacity \ Factor \ (80\%) \ \times \ Total \ hours \ in \ a \ year \ (B.1) \\ Total \ Fuel \ Demand \ = \ Fuel \ Supply \ (in \ kg/hr) \ \times \ Capacity \ Factor \ (80\%) \ \times \ Total \ hours \ in \ a \ year \ (B.2) \\ Total \ Water \ Demand \ = \ Water \ Supply \ (in \ m^3/hr) \ \times \ Capacity \ Factor \ (80\%) \ \times \ Total \ hours \ in \ a \ year \ (B.3) \\ \end{array}$ 

## **B.2.** CYCLE TEMPO SIMULATION DATA FOR CASE STUDY

Streams	Mass Flows (in g/s)	Gases	Composition ( in %)
		CH4	20
Anode inlet	51.2	CO2	13.333
		H2O	66.67
Cathode Inlet	198.35	H2O	90
		H2	10
Anode Outlet	228	CO2	21.24
		CO	2.57
		H2O	67.33
		H2	8.86
Cathode Outlet	21.5	H2O	18
	51.5	H2	82

Table B.3: Mass flows for 3 SOFEC units at a current density of 3000 A/m2

Table B.4: Mass flows for 3 SOFEC units at a current density of 3600 A/m2

	Streams	Heat Capacity (kJ/kgK)	<b>Q</b> ( in kW)
Heating	Biogas	1.967	78.148
Demand	Steam		
Demanu	(including	2.066	828.33
	latent heat)		
	Reaction heat	-	254.6
Cooling	Anode Off gas	2.956	522.3
Demand	Hot Air from		
	waste heat	1.15	589.52
	recovery		