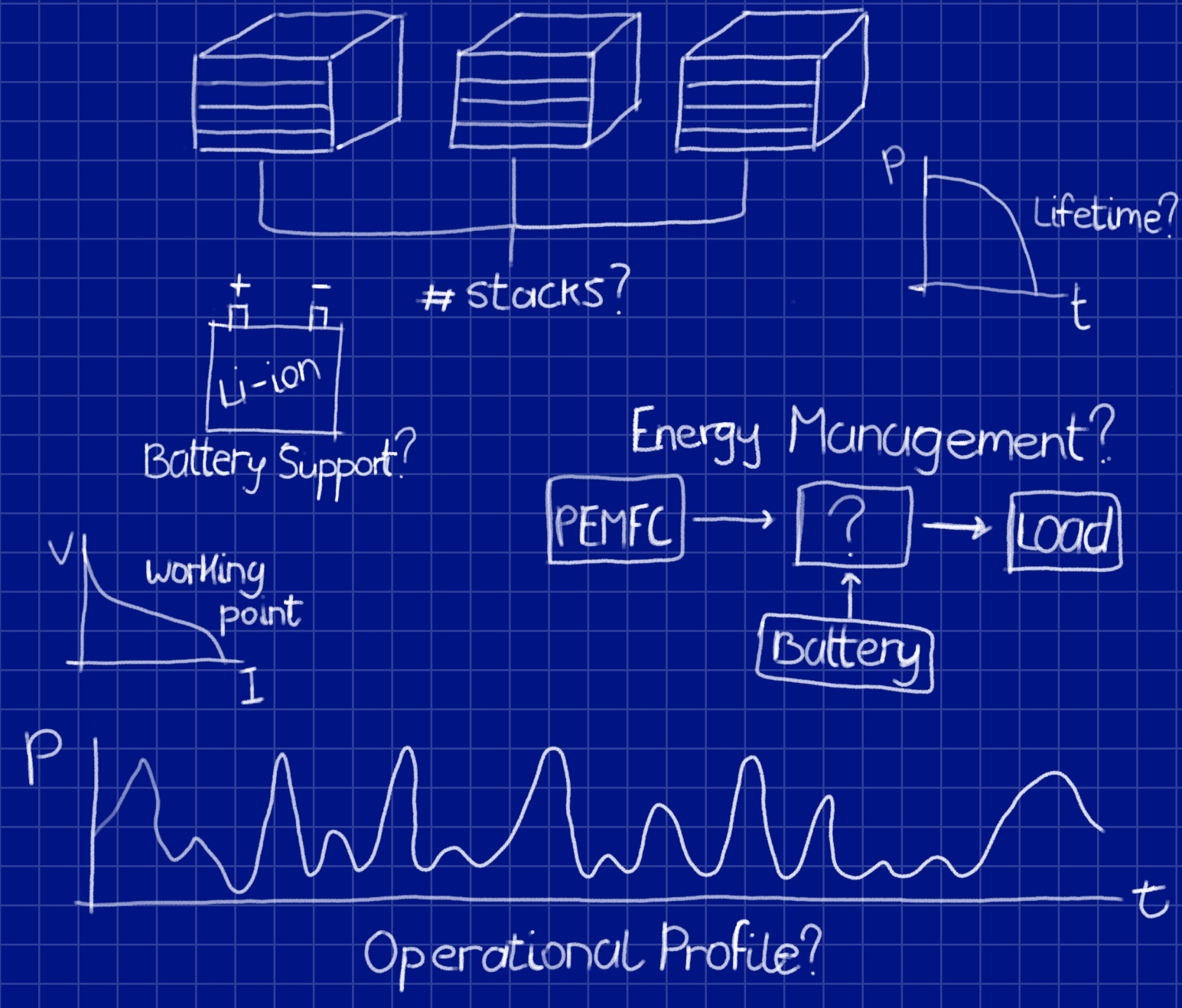
Master Thesis

Lifetime predictions for a Proton Exchange Membrane Fuel Cell system in maritime applications

SDPO.21.020.m.

J.R. Kuipers



TU Delft

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Master Thesis

Lifetime predictions for a Proton Exchange Membrane Fuel Cell system in Maritime applications

by

J.R. Kuipers

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TU Delft

Summary

Global warming is one of the biggest challenges society faces today and it is partly caused by burning fossil fuels. Therefore, the Dutch Ministry of Defence aims to reduce its use of fossil fuels by 70% by the year 2050 compared to the benchmark year 2010. As part of this reduction, future ships of the Royal Netherlands Navy will have to use alternative energy sources/carriers. Hydrogen is a possible candidate as it can be produced with a sustainable method. One of the ways hydrogen can be converted into electric energy is by using a fuel cell. This study will focus on one type of fuel cell in particular; the Proton Exchange Membrane Fuel Cell (PEMFC).

Degradation is currently considered to be the biggest technological bottleneck of a PEMFC. At the same time, PEMFC degradation is not yet fully understood and it is heavily dependent on usage. Additionally, the effect of the PEMFC system layout had not been investigated. Therefore, ship designers cannot take PEMFC lifetime into account when designing leading to the motivation of this research. To obtain more insight into the degradation of a PEMFC system in a maritime environment the corresponding research question is:

> *"How is the lifetime of a proton exchange membrane fuel cell in a hybrid system in combination with a battery affected by the system design parameters and maritime operations?"*

To find the answers to this question a discrete fixed time-step model has been created in Matlab/Simulink that estimates PEMFC lifetime based on the load profile and PEMFC system layout. The PEMFC lifetime is estimated using a method based on load conditions from Pei et al [52]. The base model represents an energy generation system consisting of a PEMFC system and a battery system that is managed by an energy management system. To answer the research question, four experiments are conducted that each study the influence of a variable on PEMFC lifetime. The proposed variables are load profile, PEMFC size, energy management and PEMFC module shutdown. For each variable, a variation on the base model is made and simulations are performed for a set range. The simulations are performed with a recorded load profile of a ship from the Royal Netherlands Navy.

It was found that the load profile used resulted in vastly different load conditions compared to the automotive industry. Less than 10% was caused by start-stop or load change conditions compared to 90% from the original experiment from Pei et al with automotive applications. Experiment 1 showed that an increase in installed PEMFC power leads to a decrease in PEMFC degradation. This is due to the lower part-load conditions the PEMFC system experiences with higher installed PEMFC power. PEMFC generally experience lower degradation at lower part-load conditions [52]. In experiment 2 it was found that energy management strategies that charge faster experience more degradation compared to slower charging energy management strategies. It was found that the faster charging strategies spend more time in high load conditions and have more load changes, which are both considered to be less beneficial for PEMFC lifetime. Experiment 3 shows that shutting down modules can prolong the operational lifetime. However, shutting down too early is less beneficial due to a vast increase in load changes and time in high power conditions. From experiment 4 can be learned that dividing the system into modules and actively shutting one down when not needed can prolong PEMFC lifetime. Furthermore, it was found that the lifetime increased with the number of modules for the range tested.

This research has studied the effect of the load profile and system layout on PEMFC lifetime and discovered relations that describe the correlation between a PEMFC system parameter and PEMFC lifetime.

Preface

Dear reader,

In front of you lies the report of my master thesis on the subject of: "Lifetime predictions for a Proton Exchange Membrane Fuel Cell system in maritime applications". It concludes my time at the TU Delft where I followed both the bachelor 'Maritieme Techniek' and the master 'Marine Technology' for which this master thesis is the final piece of the puzzle.

During my research, I have received a lot of support, for which I would like to express my gratitude. First of all, my daily supervisor at the DMO, Dorien Stroeve. Thank you for your enthusiasm and positive mindset that helped me find my focus. Dorien always made time for me (even during her vacation) to help me search for data, brainstorm or to help me with numerous problems. I was lucky to have such an involved supervisor! I would also like to thank Isaac Barendregt, my second supervisor at the DMO. Isaac helped me stay on track by asking critical questions during our meetings and often provided the 'helicopter view' that I much needed.

Lindert van Biert, my daily supervisor at the TU Delft, thank you for thinking along when the perspective of my original research topic wasn't so bright. Lindert supported me with his extended knowledge of fuel cells and doing research in general. I have learned a lot from Lindert and he helped me appreciate the value of my work. I also enjoyed our discussions about fuel cells and related items! I would also like to thank Klaas Visser, chairmen of my committee and second TU Delft supervisor, for the in-depth discussions that helped me position my research and all the effort put in to help me graduate on time.

I would also like to thank my parents, for all the support not only for the duration of my graduation but also throughout my whole study period. It has been a fun but also challenging period and I could not have done it without your support! And last but certainly not the least, Kirsten van Kooij. Thank you very much for all the help reviewing my work, commenting and the fresh look you brought to my work. And of course, for all the support you have given me these last few intense months!

J.R. (Jarno) Kuipers
Delft, August 2021

Abbreviations

AC	Alternating Current
BOP	Balance Of Plant
CL	Catalyst Layer
C-rate	(dis)Charge Rate
CO	Carbon Monoxide
DC	Direct Current
DMFC	Direct Methanol Fuel Cell
DMO	Defensie Materieel Organisatie
EMS	Energy Management System
GDL	Gas Diffusion Layer
HT-PEMFC	High Temperature Proton Exchange Membrane Fuel cell
LT-PEMFC	Low Temperature Proton Exchange Membrane Fuel Cell
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
MPL	Micro-Porous Layer
NiCd	Nickel-Cadmium
NiMH	Nickel-Metal-Hydride
OCV	Open Circuit Voltage
PEMFC	Proton Exchange Membrane Fuel Cell
PMS	Power Management System
PPM	Parts Per Million
PPB	Parts Per Billion
PTFE	PolyTetraFluorEtheen
RNLN	Royal Netherlands Navy
SOC	State Of Charge
SOFC	Solid Oxide Fuel Cell
TPB	Triple Phase Boundary
TRL	Technology Readiness Level

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1. Introduction

Increasing temperature, rising seawater level and more weather extremes are all considered to be the result of global warming [59]. Greenhouse gases are seen as a large contributor to global warming and society has realised that action has to be taken. Although the shipping industry is responsible for over 3% of the total greenhouse gas emissions according to the IMO [62], the industry has not been subjected to strict regulations for a large part of the past decades. The emission of greenhouse gases is directly related to the type of fuel combined with fuel consumption and there is an increasing demand for cleaner and more economical ships, leading to a growing interest in alternative fuels. The Dutch Ministry of Defence adopted a reduction of greenhouse gas emissions into their strategy for the coming years by aiming for a reduction of the use of fossil fuels of 70% by the year 2050 compared to the benchmark year 2010 [4].

Reducing the use of fossil fuels can be done in various ways. For example by using synthetic fuel [36] or going full electric with battery-powered ships [33]. However, one of the most promising solutions is the use of hydrogen as a fuel, in combination with a fuel cell, if the hydrogen is produced sustainably. Fuel cells have been around since the 1960s and found their first use in the space industry [38]. There are various types of fuel cells but this research will focus on Proton Exchange Membrane Fuel Cells (PEMFC) because of their good transient behaviour and commercial availability. The lifetime of a PEMFC is at the time of writing considered to be the largest technological bottleneck for PEMFC usage on a large scale [52]. There are various degradation mechanisms that occur under different conditions and are often categorised on the location where the degradation occurs [72]. Most of these mechanisms are still being researched and no conclusive method to determine the total degradation based on these mechanisms has been found yet. This is because the amount of degradation of each mechanism cannot be summed to obtain the total degradation. Taking the sum of all the individual degradation processes can only be done if they have no influence on each other.

PEMFC degradation can also be approached from a load characteristics point of view. For example, Moein-Jahromi et al [48] and Garcia-Sanchez et al [25] researched degradation due to cyclic load conditions or Zhang et al [76] who provided a literature review of various work on degradation due to start-stop conditions. Pei et al [52] divided the load characteristics into four conditions: 1) start-stop, 2) load changing, 3) idle and 4) high power. Using these conditions, Chen et al [10] developed a method to estimate the lifetime based on the load characteristics. When a PEMFC is combined with a (supporting) battery pack it is often called a hybrid fuel cell system. An energy management system will then regulate the energy flow in the system between the two power sources and the load [41]. The energy management system can also be used to optimise for fuel economy as done by Zhang et al [77] and Kim et al [35].

Despite the extensive research into PEMFC degradation and hybrid fuel cell system management no methods exist for estimating PEMFC lifetime based on the load profile and system characteristics. Additionally, the relation between the number of modules, the sizing of the battery pack and the influence of naval operational load characteristics on the lifetime of a PEMFC are still unknown. Therefore, an engineer who wants to implement a hybrid fuel cell system in a ship has no methods to estimate the PEMFC lifetime beforehand. This is relevant due to the life-cycle of (naval) ships. Diesel engines are currently the standard and last up to 100.000 hours with a major overhaul around 16.000 hours [44]. The time between overhauls roughly matches the docking period that has to be done every five years. PEMFC stacks have to be replaced instead of overhauled which means that all the stacks have to be replaced completely when the end of lifetime is reached. Therefore, the goal is to have a PEMFC lifetime of at least 16.000 hours to ensure that the PEMFC system is able to last the period between dockings.

1.1 Problem definition

It has been broadly accepted that greenhouse gas emissions contribute to global warming, which results in all kinds of climate changes. Climate changes pose a threat to human society and the environment. Therefore the urge arises around the world to reduce emittance of polluting emissions into the environment. The maritime industry also plays a role in the global warming problem and is exploring ways to limit their emissions but has not found a suitable solution yet. Various solutions are being researched including fuel cells which show promising results but also challenges.

This research focuses on PEMFC's due to their high Technology Readiness Level (TRL) and availability, which is important for the Defensie Materieel Organisatie (DMO) for whom this research is carried out. At the time of writing, the limited lifetime of PEMFC's is considered to be one of the largest technological bottlenecks of this technology. PEMFC applications in the automotive industry typically last about 5000 hours before the end of lifetime is reached which is insufficient for maritime applications. PEMFC lifetime is mainly determined by the design of the PEMFC (choice of materials and fabrication method) and the degradation mechanisms as a result of usage [38].

Although the choice of materials and fabrication method has a large impact on PEMFC lifetime, this research will focus on the latter and will study the effect of the load profile and PEMFC system characteristics. To study the effect on PEMFC lifetime, a method must be found to compute PEMFC degradation based on the load profile and system characteristics. Therefore a literature study will be performed to study PEMFC degradation and the different mechanisms that cause it to develop/find a method for lifetime estimation. A lifetime of less than 16.000 hours is deemed too short for maritime applications [44]. Therefore, the lifetime of a maritime operational profile must be investigated. Not only the operational profile of a ship differs from that of an application in the automotive industry, but also the power, system layout and energy management are expected to be different. It is expected that these differences in system layout will result in different use of the PEMFC and thus a different estimated lifetime. However, the relation between system component sizing and PEMFC lifetime has not yet been discovered. This also applies to energy management systems of PEMFC in maritime applications. Previous research on PEMFC energy management systems mainly focused on system efficiency and optimising for fuel consumption. Therefore, the relation between energy management systems and PEMFC lifetime is still unknown.

1.1.1 Research questions

The goal of this thesis is to study the degradation of a PEMFC system in maritime conditions including the load profile, system layout and energy management. The aim is to discover relations that can be used as an aid for designing maritime PEMFC systems with maximum lifetime. Correspondingly, the following research question has been defined:

> *"How is the lifetime of a proton exchange membrane fuel cell in a hybrid system in combination with a battery affected by the system design parameters and maritime operations?"*

To help answer the research questions four sub-questions have been defined that each answer a part of the main research question more accurately and more in-depth:

- How can the degradation of a proton exchange membrane fuel cell be determined based on a load cycle?
- How do the size of the fuel cell and the battery in a hybrid system contribute to the lifetime of a proton exchange fuel cell?
- In what way does energy management of the hybrid system influence PEMFC degradation?
- How does the number of active fuel cell modules affect the operational lifetime expectancy of the proton exchange membrane fuel cells?

1.1.2 Scope

Modelling the degradation of a PEMFC due to load in a hybrid system is extensive and not everything can be taken into account in detail. To ensure that the quality of the work is high enough and with sufficient depth, a scope has been defined. The scope entails what will be in this research and which subjects will not be taken into account or assumed to be constant. To define the scope the following constraints are proposed:

- Only performance loss of the fuel cell will be considered. Degradation or deterioration of any of the other components of the system is considered to be non-existent.
- This model will only optimise for lifetime. Although it is possible, no optimisation will be done for cost, size, performance or any other characteristics.
- No degradation due to contaminated air or fuel. This means that we assume a supply of 100% hydrogen and clean air.
- The computed values are not considered representative since the input used for the degradation computation is not representative for the fuel cell stacks used.
- Since this research is done for the DMO, the test case will be a representative naval vessel. Any findings and conclusions are considered only valid for this type of ship.
- Lithium-ion batteries will be used for the test case. Other types of batteries result mainly in different sizes and weights which are not important for this research.

1.2 Outline

This thesis consists out of three parts. The first part, chapter 2, contains a literature review to provide a clear overview on the state of the art on hybrid fuel cell systems and PEMFC degradation in particular. Also, a method to estimate the lifetime of a PEMFC will be introduced. The second part, chapter 3, elaborates on the method for this research. A model will be used to study the effects on PEMFC lifetime by performing simulations in four different experiments. The topology of the model will be discussed including the alterations made during the experiments. The third part, chapter 4, contains the results of the experiments. The results are given per experiment with additional findings at the end of the chapter. Additional figures and tables are provided in appendix A.

2. Literature review

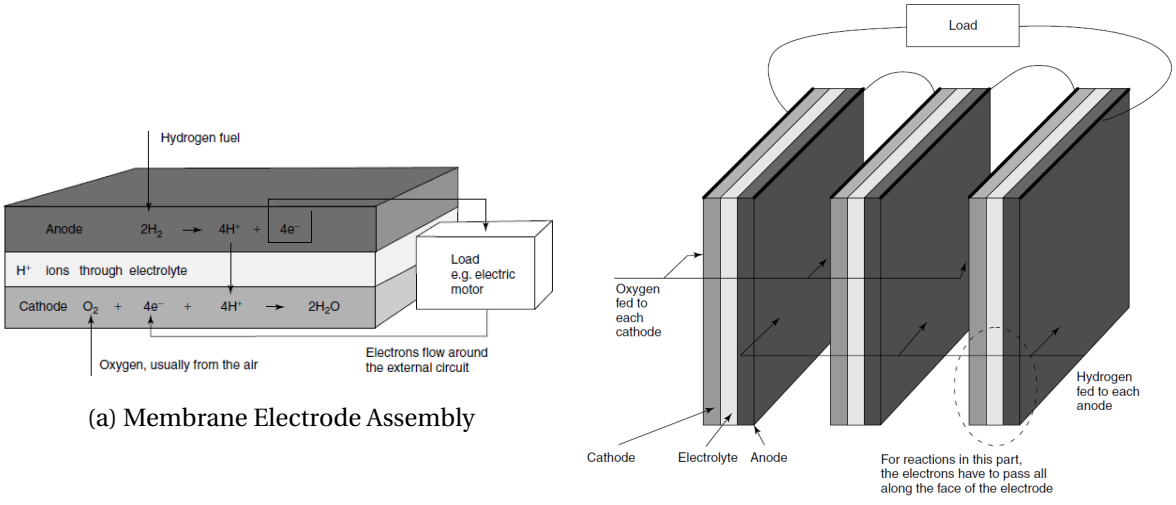
This literature review covers four subjects 1) Proton Exchange Membrane Fuel Cell (PEMFC) system, 2) PEMFC degradation, 3) Battery systems and 4) Power management. These subjects will provide the state of the art and the knowledge needed to answer the problem stated in the problem definition.

2.1 Proton Exchange Membrane Fuel Cell systems

This section will provide information on the proton exchange membrane fuel cell, its components, auxiliary components and fuel. Together with the state of the art, this section will provide the background needed for the sections that will follow.

2.1.1 Working principle

A Proton Exchange Membrane Fuel cell works on the principle of reverse electrolysis (figure 2.1a). During this electrochemical process, hydrogen and oxygen recombine into water producing an electric current. The hydrogen gas ionises at the anode and thus releases H^+ ions and electrons. The electrolyte is made of an ion conduction material and thus conducts H^+ ions to the cathode side. At the cathode side, the H^+ ions react with oxygen and electrons to form water. The contact between the electrodes should be as large as possible and the distance as small as possible in order to produce a reasonable amount of current. For PEMFC this usually results in a plate-like construction as shown in figure 2.1a. The electrodes are made out of a porous structure allowing gas to flow through them. This also maximises the contact area between the electrode, the electrolyte and the gas. The reaction rate at the electrodes is slower at low temperatures for most chemical reactions, including the reactions happening inside a PEMFC, compared to high temperatures. To compensate for the slow reaction rate a Low-Temperature Proton Exchange Membrane Fuel cell (LT-PEMFC) uses platinum as a catalyst to obtain a faster reaction rate [14]. The electrodes are composed of a catalyst layer (CL) and a gas diffusion layer (GDL), on which more information can be found in section 2.2.1 and 2.2.2. In the case of a PEMFC, the electrolyte (called the membrane) consists out of a proton-conducting wetted solid polymer, often Nafion ® is used [56]. Together with the electrodes, the membrane forms the Membrane Electrode Assembly (MEA). The membrane of a PEMFC must be hydrated to have good H^+ conducting properties. However, the water content of the membrane must be balanced. Too dry will reduce the proton-conducting properties and too wet will flood the electrodes blocking the pores in the porous structure and thus increasing the mass transfer losses at the electrodes. Therefore, membrane hydration is a challenge of the PEMFC and requires close monitoring and mitigation.



(a) Membrane Electrode Assembly

(b) Multiple cells

Figure 2.1: Schematic overview of fuel cell composition [38]

The voltage of a single fuel cell is rather small, roughly 1 volt. To obtain the desired amount of power multiple cells are placed together to form a stack as shown in figure 2.1b. In a PEMFC hydrogen must be fed to the anodes and oxygen (air) must be fed to the cathode. In the configuration of figure 2.1b the oxygen and hydrogen would mix. Therefore, a bipolar plate is put between the electrodes as shown in figure 2.2. The bipolar plate has channels running along both sides of the plate for separate hydrogen and oxygen transportation across the electrodes.

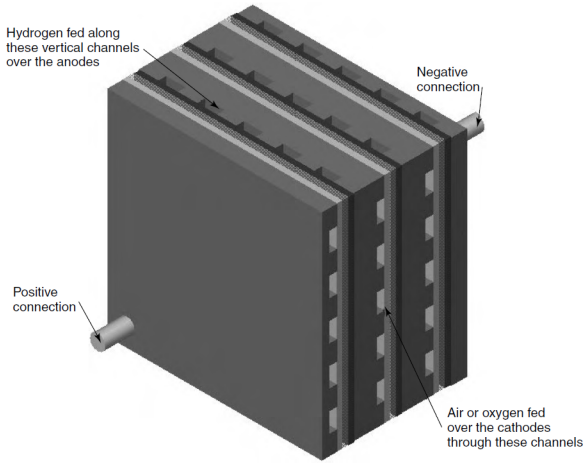


Figure 2.2: A three cell stack using bipolar plates [38]

The theoretical open-circuit voltage (OCV) of a hydrogen fuel cell is given by equation 2.1, where E is the potential, $-\Delta\overline{g}_f$ is the Gibbs free energy and F is Faraday's constant. For an operating temperature lower than 100°C this gives a value of 1.2 volts based on the reaction of oxygen and hydrogen into water vapour.

$$E = \frac{-\Delta\overline{g}_f}{2F} \tag{2.1}$$

However, the actual open circuit voltage is lower due to various losses, as figure 2.3 shows. Therefore, the theoretical OCV is also called the no loss voltage. The difference between the no loss voltage and the actual open voltage circuit is called the over-potential or over-voltage.

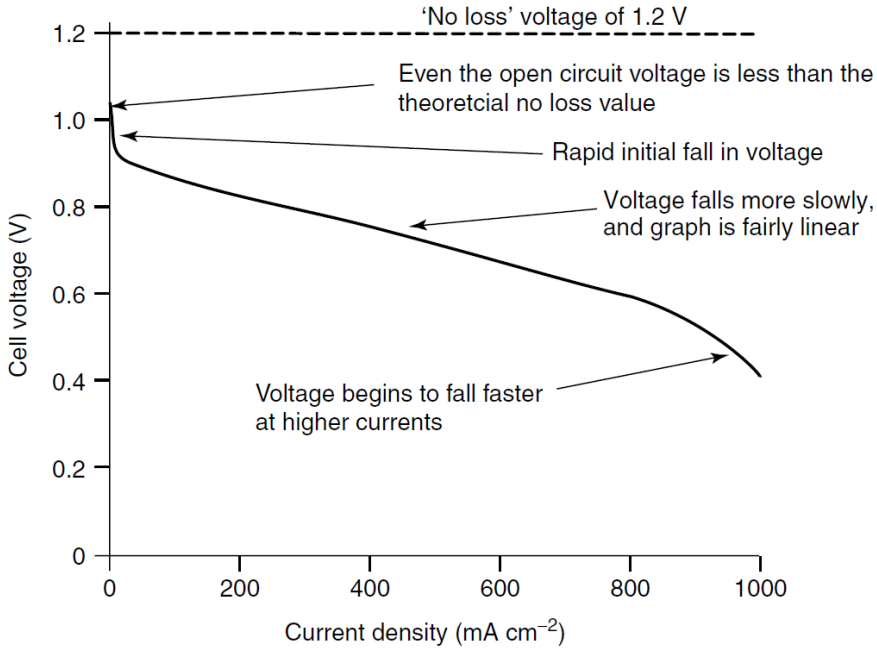


Figure 2.3: Open circuit voltage for a typical low temperature, air pressure, fuel cell [38]

The voltage drop depicted in figure 2.3 resulted from four irreversible losses:

- Activation losses - caused by the slow reaction rate at the electrodes. Some of the energy is lost to driving the chemical reaction that transfers the protons.
- Fuel crossover / internal currents - hydrogen can pass through the membrane, wasting energy on transport. Also, leakage can occur, both ionic as electronic.
- Ohmic losses - caused by the resistance in the electrodes and connections. Also partly caused by the resistance of the flow of ions through the membrane.
- Mass transport/concentrations losses - caused by differences in concentration at the surface of the electrodes as the fuel is used. Also, the resistance of the mass transport plays a role.

Standard key figures are used to describe the performance of a fuel cell. These key figures allow engineers or scientists to compare different fuel cells to each other and other systems. To compare electrolytes and electrodes often current per unit area $[\frac{mA}{cm^2}]$ is used, which is called the current density. Current density is specific for the voltage at which the fuel cell operates and thus the current density is often given at a specific operating voltage. The power density of a PEMFC system is described as the power output of the fuel cell stack divided by the volume of the stack and the balance of plant $[\frac{kW}{m^3}]$ or $[\frac{kW}{L}]$. The term specific power is used for the amount of power per unit mass $[\frac{kW}{kg}]$. Again the mass includes the whole balance of plant. Fuel cells degrade over time (which is described further in section 2.2) and this is usually described as a loss of voltage per 1000 hours $[\frac{mV}{1000h}]$.

2.1.2 PEMFC Fuels

A PEMFC requires hydrogen in the gaseous state to be fed to the anode side. An LT-PEMFC usually runs on pure hydrogen [37], but there are examples of fuel cells that run on other types of fuels. Examples of such fuel cell types are Solid Oxide Fuel Cell (SOFC), Molten Carbonate Fuel cells (MCFC), Direct Methanol Fuel Cell (DMFC) or High-Temperature Proton Exchange Membrane Fuel Cells (HT-PEMFC). [27].

An LT-PEMFC uses pure hydrogen as fuel. The term 'pure' is relative in this case. Many manufacturers state in their product information sheet the purity needed for their fuel cell [78]. Purity is often described as a percentage of the fuel that contains hydrogen (i.e. 99.999% purity). However, purity is actually not used to show the amount of hydrogen in the fuel; it displays the number of contaminants in the fuel. A PEMFC has a low tolerance of impurities in the fuel. Too much CO can poison the Pt catalyst and reduce the lifetime of a PEMFC quite rapidly. Therefore, a maximum of 10 ppm of CO in the fuel is often considered the maximum by most PEMFC manufactures. The same applies to sulphur, as much as 1 ppb can be enough to poison the anode catalyst.

Nonetheless, it is possible to extract hydrogen from another fuel to use in a PEMFC by reforming the fuel [27, 37]. Reforming can be done by various chemical processes and are divided into two categories: 1) internal reforming and 2) external reforming. As the name suggests, internal reforming takes place in the fuel cell itself and thus fuel is directly fed to the fuel cell (figure 2.4). When external reforming is applied, the reforming process is done outside of the fuel cell and only the hydrogen that is extracted is fed to the fuel cell. However, both of these processes require heat for the chemical reaction to take place. The high-temperature fuel cell produces heat at a sufficient temperature for the internal reforming process but an LT-PEMFC does not reach temperatures high enough for internal reforming [22]. Thus only external reforming is a possibility for using a fuel other than pure hydrogen for an LT-PEMFC. However, an external reforming process requires extra energy which lowers the overall efficiency of the fuel cell [38].

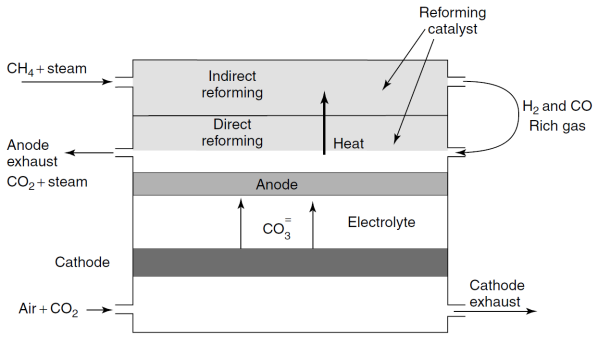


Figure 2.4: Schematic representation of direct and indirect internal reforming [38]

The storage of hydrogen for fuel cell applications can be divided into two categories: 1) compressed hydrogen (H2), usually compressed at 350 or 700 bar which are the standard in the automotive industry, 2) cryogenic hydrogen (LH2), which is stored at ambient pressure at a temperature of -253°C. There are more methods available to store hydrogen such as binding the hydrogen to metal hydrides (for example natriumborhydride NaBH4). However, these methods are still being researched and therefore left out of the scope of this research.

2.1.3 Balance Of Plant

Besides the fuel stack itself, auxiliary components are needed for a working fuel cell system. Auxiliary components are often called the Balance Of Plant (BOP). The composition of the BOP depends on the type of fuel cell used. For example, high-temperature fuel cells often include heat exchangers and fuel reforming equipment while low-temperature fuel cells do not need them. Because this research focuses on LT-PEMFC we will only consider components used for low-temperature fuel cells. Figure 2.5 shows a typical schematic overview of a BOP for low-temperature fuel cells, however not all BOP are configured like this. The BOP components are relatively large compared to the fuel cell stack and take up a large part of the space needed for the overall system. It must be noted that most of the BOP components require energy and thus reduce the overall efficiency of the fuel cell system.

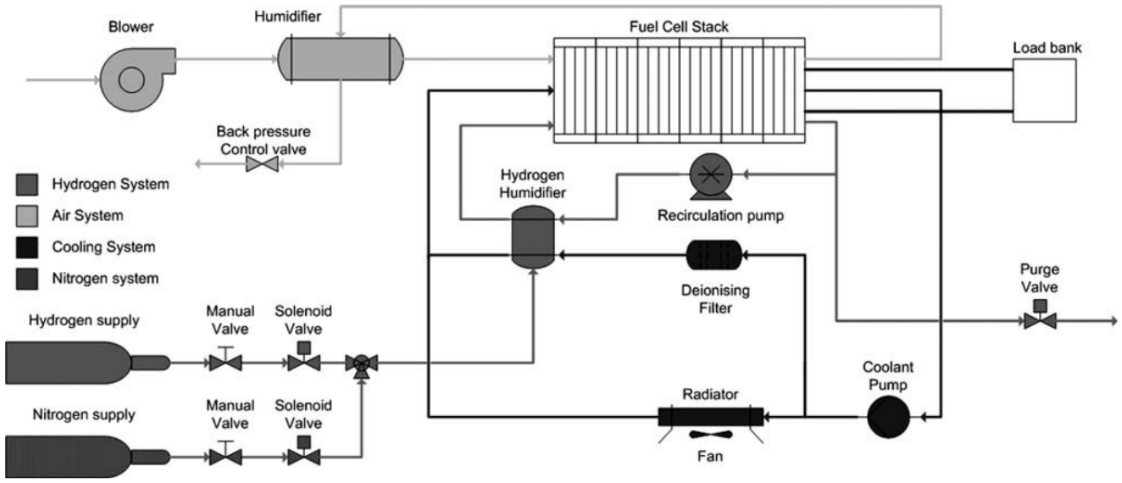


Figure 2.5: Schematic example of a BOP [71]

Fuel supply

Hydrogen is often stored compressed using tanks. Tanks for compressed hydrogen are relatively large and heavy due to the high pressure of the hydrogen [79]. From the tank the hydrogen is fed to the humidifier to prevent dehydration of the membrane. The pressure at which the hydrogen is kept is often high enough to drive the hydrogen through the system without the need for an additional pump. After the humidifier the hydrogen is fed to the fuel cell. The excess hydrogen is

recirculated using a pump into the humidifier, after which it is again fed to the fuel cell. Sometimes the fuel supply chain is equipped with a nitrogen supply [71]. Nitrogen is then used to purge the remaining hydrogen when the fuel cell is shut down. As will be explained in section 2.2 this prolongs the lifetime of the fuel cell.

Oxidant supply

Most systems use oxygen from the air subtracted out of the environment as an oxidant supply. Either a blower or a compressor is used to drive the air into the system depending on the desired pressure at the cathode. Similar to hydrogen, the air must be (de)humidified to prevent the membrane from over (de)hydration. After the humidifier, the air is fed into the fuel cell. In a PEMFC H_2O is formed at the cathode as a result of the chemical reaction within the fuel cell. The air fed to the cathode also serves as a water remover. The excess air carries the water vapour away from the cathode. That water is then later used to humidify the incoming air in the humidifier.

Cooling system

Fuel cells are not 100% efficient and most of the energy losses are converted into heat. For smaller fuel cells (<1 kW) air cooling is sufficient. For larger systems often water cooling is used. The cooling water is circulated through the system using a pump. Water is fed to the fuel cell where it flows through channels in the bipolar plate. The enthalpy of the water can be removed using a radiator (heat exchanger) to disperse the heat to the surroundings or it can be used for heating purposes of other systems. The fuel cell system is then called a Combined Heat and Power plant (CHP). However, this is not often done with an LT-PEMFC due to its low operating temperature.

Power electronics

Fuel cells generate DC power with a variable current and voltage depending on the load of the fuel cell. To be able to use the generated power often some sort of power conditioning is used. Most DC systems require a constant voltage, the variable voltage must then be converted to a fixed voltage. However, not all systems run on the same voltage thus a DC to DC converter is needed to adjust the voltage. Alternatively, some systems require an AC voltage for which a DC to AC inverter is needed.

2.2 PEMFC Degradation

Fuel cells degrade over time due to various processes [72] which will be explained in the following sections. Degradation leads to an increase in fuel consumption [23] and ultimately in loss of power [7] to the point that the fuel cell cannot deliver its rated power. A general rule of thumb is that a fuel cell is considered at its end of life when it has lost 10% of its power [52]. The sections below give an overview of the most researched degradation processes. The processes are organised by the location the degradation takes place within the fuel cell.

2.2.1 Catalyst layer degradation

As described in section 2.1.1 a MEA consists out of electrodes with a membrane in between. The electrodes are covered with platinum particles (figure 2.6) which act as a catalyst for the chemical reaction. This is also called the catalyst layer (CL) and is typically 5-25 μm thick. The CL generally has three functions: 1) to act as a binder between the platinum/carbon particles, 2) to provide a proton conductive link to the membrane and protonic current flow and 3) to make the platinum catalyst electrochemically active by transferring protons to and from the catalyst [74].

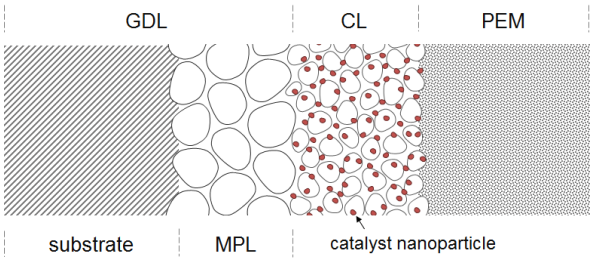


Figure 2.6: Schematic cross section of a PEMFC [67]

For the catalyst layer mainly three degradation processes are known. The degradation of the catalyst itself (Platinum oxidation, dissolution and ripening), the support (Carbon corrosion) and the ionomer (Chemical degradation)[55].

Catalyst degradation

The catalyst of choice for a PEMFC is often platinum (Pt) [38]. Platinum particles are spread across a carbon support structure. By scattering the small platinum particles the maximum surface area is achieved. The performance of the catalyst depends on the surface area of the catalyst. Increasing the surface area increases performance due to the larger area where reactions can take place. The surface area of the catalyst is sometimes also called the Triple Phase Boundary (TPB). Reducing the TPB thus has a negative effect on the performance of a PEMFC and can be seen as degradation [72]. Several degradation mechanisms have been proposed for the degradation of the catalyst: oxidation, dissolution and ripening [75].

Platinum oxidation and platinum dissolution are chemical degradation processes that occur under the influence of a potential. According to Meyers et al [46] platinum dissolution is negligible at low and high potentials, but is significant for medium potentials. Formulas 2.2, 2.3 and 2.4 show the chemical processes of platinum dissolution, platinum oxide film formation and chemical dissolution of platinum oxide respectively [75]. Obviously, all three reactions reduce the amount of platinum in the catalyst layer.

$$Pt \longrightarrow Pt^{2+} + 2e^- \tag{2.2}$$

$$Pt + H_2O \longrightarrow PtO + 2H^+ + 2e^- \tag{2.3}$$

$$PtO + 2H^+ \longrightarrow Pt^{2+} + H_2O \tag{2.4}$$

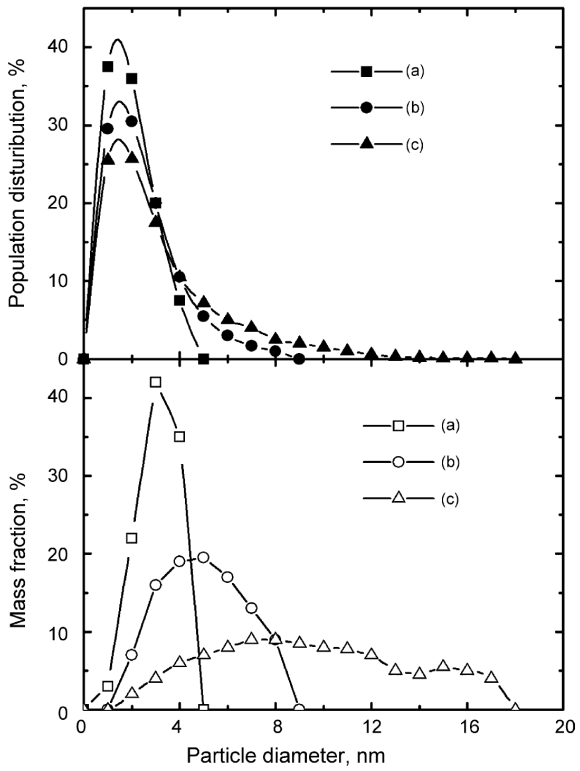


Figure 2.7: *Top:* Particle-size population distributions of Pt in PEMFC cathodic catalysts. *Bottom:* Mass distributions of Pt in catalysts. (a) Fresh catalyst; (b) catalyst after 1320 h of operation; (c) catalyst after 2200 h of operation [70]

The clustering of multiple Pt particles, also called ripening, is caused by the Ostwald ripening mechanism [70]. Two or more particles clustered together form a bigger particle. However, this reduces the total available area of the platinum catalyst. Figure 2.7 shows the clustering process over time [75].

Support degradation

The carbon support degrades mainly due to a chemical reaction[23], see formula 2.5. The already present water reacts with the carbon support. The equilibrium potential (using Butler-Volmer) of reaction 2.5 equals $E^0 = 0.207V$ at a temperature of 298 K. A cell usually operates at a voltage larger than 0.207 V (figure 2.3) and thus carbon corrosion cannot be avoided. However, the reaction rate of reaction 2.5 shows slow kinetic behaviour during normal operation [15].

$$C + H_2O \longrightarrow CO_2 + 2H^+ + 2e^- \tag{2.5}$$

According to Tang et al [64] presence of oxygen at the anode side of the fuel cell promotes carbon corrosion. There are two ways oxygen can find its way to the anode: 1) fuel starvation [23], causing an oxygen crossover from the cathode to the anode, 2) leaking after shutdown [64], air can diffuse into the anode side after shutdown if the anode exhaust port is not closed. When an oxygen/hydrogen mixture is formed at the anode side a reverse current between the electrodes is induced, which promotes the cathode carbon oxidation i.e. carbon corrosion. Thus carbon corrosion leads to thinning of the cathode resulting in a smaller active area and therefore lower cell performance. Figure 2.8 shows the chemical reactions and potentials that cause carbon corrosion.

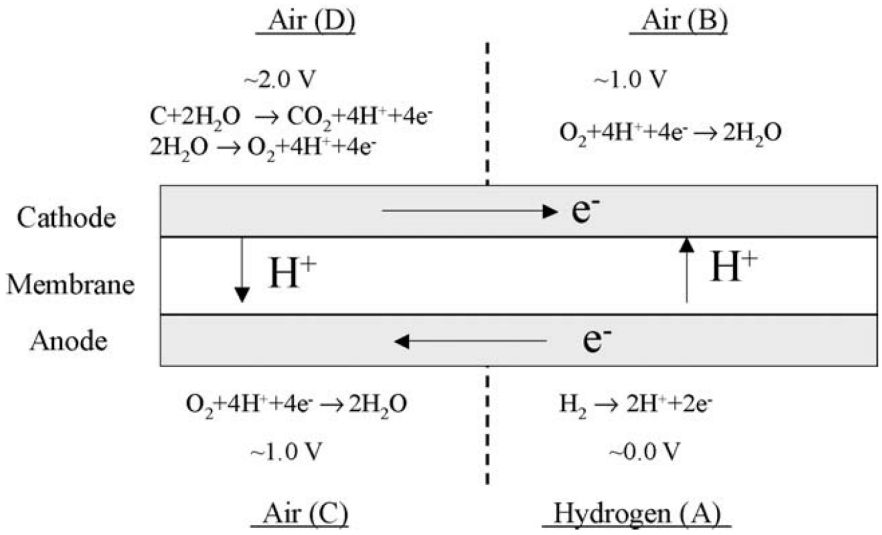


Figure 2.8: A schematic illustration of reactions in four distinct regions when an air/fuel boundary is formed at the anode [64]

Ionomer degradation

Experiments have shown that dissolution of Nafion ® or polytetrafluoretheen (PTFE), material from the membrane, leads to a change in hydrophobic characteristics of the catalyst layer during normal operational conditions [73]. As a result, the water management properties and the electrode mass transportability are reduced [72].

2.2.2 Gas Diffusion Layer degradation

The gas diffusion layer (GDL) is placed on the electrode and positioned on the outside of the MEA (see figure 2.6). Transporting the reactant gas from the flow channel to the catalyst layer is critical for the performance of the fuel cell. However, it is not the only function of the GDL. The GDL also removes excess reactant water from the CL, conducts the current from the CL with low resistance and it keeps the membrane hydrated when the gas humidity is low. The most common form of a GDL consists out of two layers: 1) a microporous substrate and 2) a microporous layer (MPL) both made out of carbon. The macroporous substrate and the MPL have different functions. The macro-porous substrate (made out of fibres) distributes the gas from the flow channel to the MPL and eventually the CL and also conducts the current from the CL. The microporous layer (made out of powder and a hydrophobic agent) helps manage the hydration of the membrane. The hydrophobic agent of the MPL repels the water which is beneficial for water evaporation.

It is clear that the GDL is an important part of the fuel cell. Therefore, degradation of the GDL has an immediate influence on the performance of the fuel cell. Park et al [50] distinguishes two categories of degradation (figure 2.9): 1) mechanical degradation and 2) chemical degradation. Using extensive literature research he identified five common degradation mechanisms that affect the durability of the fuel cell, which are described below.

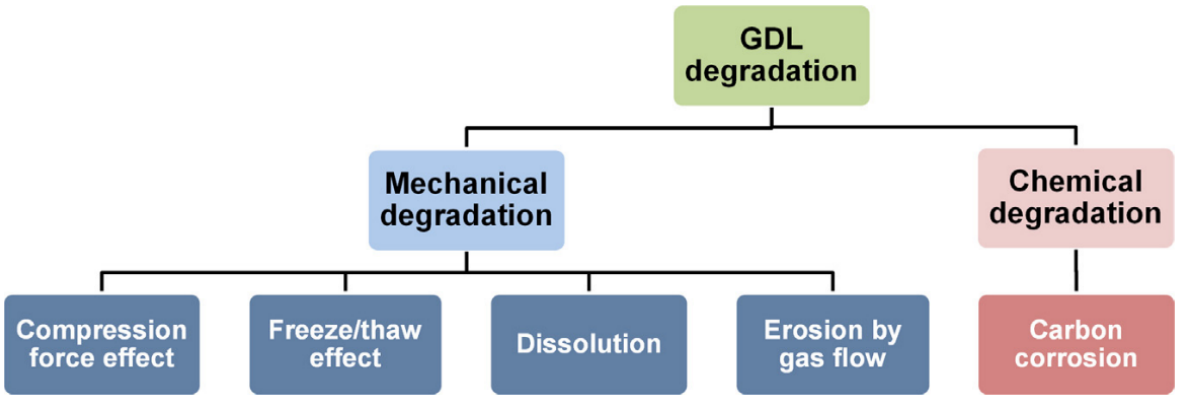


Figure 2.9: Degradation mechanisms of the GDL [50]

Compression force effect

The first of the five common degradation mechanisms is the compression force effect. The GDL is placed on the outside of the MEA between the MEA and a bipolar plate. To avoid leakage and to ensure good/low resistance contact between the components high compression is applied holding the components together [50]. Of those components, the GDL is the most compressible component due to it's structure. Though compression is necessary, it also affects the characteristics of the GDL and the connection properties between the GDL and CL/bipolar plate which in the end affects the fuel cell performance. Nitta et al [49] has captured the different effects in an overview (figure 2.10). When the GDL is compressed the pore volume of the structure and gas permeability decreases. This limits the gas mass transport through the GDL causing a higher mass transport overpotential [42]. While compression has a negative influence on the mass transfer through the GDL, it has a positive influence on the contact between the GDL and other components. The improved contact enhances the electrical en thermal conductivity between the components resulting in a lower ohmic resistance (and thus overpotential) and smaller temperature differences over the interfaces of the components. This also holds for the contact within the GDL. The carbon fibres which form the structure of the GDL are compressed, improving electrical and thermal conductivity [8]. Thus the GDL experiences positive and negative effect due to compression. Several studies have been done to investigate the effects of compression and the resulting trade-off. Lin et al [42] found that there can be an optimum compression ratio for a given fuel cell.

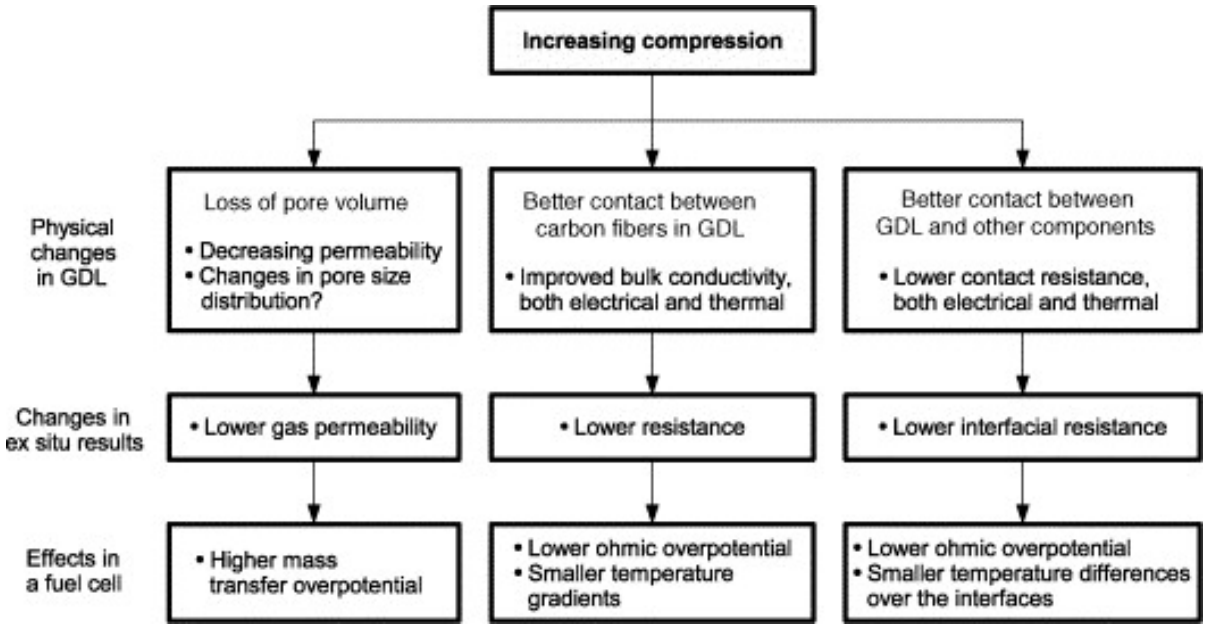


Figure 2.10: Compression force effects [49]

Freeze/thaw effect

After the shutdown of the fuel cell often a small amount of reactant water stays behind in the fuel cell. When the temperature of the fuel cell reaches a temperature below 273 K the remaining water will freeze. During the phase change from water to ice, water significantly increases in volume leading to mechanical stress on cell components. Figure 2.11 shows different forms of mechanical stress caused by freezing water in or near the GDL. Lee et al [39] has investigated the degradation of the GDL due to repetitive freezing. Repetitive freezing of the fuel cell can have a negative influence on the porosity of the DGL, can cause deformation of the DGL and can increase the resistance between the DGL and the CL or polar plate. Freezing of the fuel cell only occurs when the fuel cell is shut down because the operating temperature of an LT-PEMFC is far above 273 K. To avoid water being present after shutdown the cathode can be purged using air to remove the leftover water.

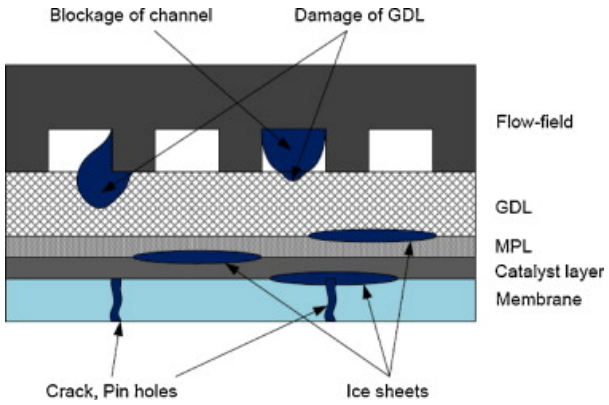


Figure 2.11: Conjectured mechanism of the degradation of PEMFCs in freezing conditions obtained from [40]

Dissolution

The GDL is exposed to water or oxidative conditions when operating under normal conditions [50]. As water is formed by the electrochemical reaction it hydrates the GDL. The water formed on or in the GDL can dissolve the carbon structure of the GDL and generate hydroxide, other oxides and other species [11, 28]. Dissolving carbon is degradation of the GDL. This results in a loss of hydrophobicity, a reduction in its transportability and reduces the hydration level of the membrane because it holds water instead of returning it to the membrane [12]. In order to reduce this form of GDL degradation researchers investigated the use of (PTFE),an hydrophobic agent that is often also used in the membrane. Fairweather et al [21] found that the concentration of PTFE does not create a consistent difference in results. However, as Das et al [17] pointed out, a higher concentration of PTFE is helpful to reduce the rate of degradation of the GDL.

Erosion by gas flow

One of the functions of the GDL is to transport gas from the bipolar plate to the CL. However, the transport of the gas can cause erosion of the carbon structure. Chun et al [13] conducted accelerated experiments for 14 days using both dry and humid air and found that most of the damage to the MPL is caused by humid air. Chun found that water concentrates on cracks in the surface of the MPL. Removing the surface cracks from the MPL could improve the durability of the MPL.

Carbon erosion

Similar to the CL, the GDL is vulnerable to carbon corrosion. However, for carbon corrosion at the GDL, the chemical reaction is caused by the lack of hydrogen instead of the presence of water. A lack of hydrogen at the cathode can occur during start/stop conditions or in the case of local fuel starvation. The shortage of hydrogen is replaced with air (thus oxygen). The presence of oxygen is caused by fuel crossover or leakage of the MEA.

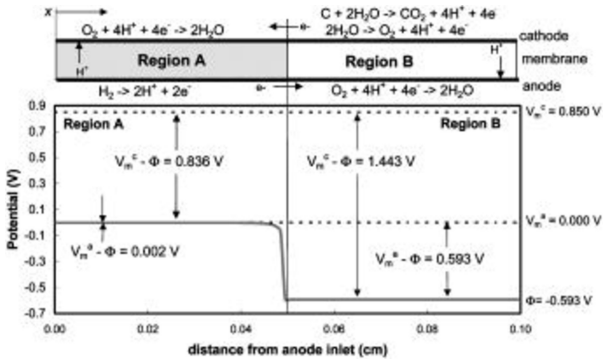


Figure 2.12: Chemical reaction in the GDL causing carbon corrosion [54]

When oxygen is present at the anode, reaction 2.6 and reaction 2.7 take place as figure 2.12 shows. This reaction leads to a high difference in potential at the locations air is present [54]. Similar to carbon corrosion at the CL this causes a reverse current leading to corrosion of the carbon fibres of the GDL at a potential difference of 1.44 V.

$$H_2 \longrightarrow 2H^+ + 2e^- \tag{2.6}$$

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \tag{2.7}$$

The rate of oxidation is often described as the corrosion current. Frisk et al [51] found that the corrosion current increases if the applied voltage to the GDL also increases. Thus, carbon corrosion of the GDL happens at a faster rate for higher voltages. Degradation due to carbon corrosion has a significant impact on the performance of the fuel cell because the GDL has a heavy influence on the performance of the fuel cell. According to Park et al [50], the mass transport resistance can increase up to 22% and the charge resistance even up to 40%. Huang et al [30] showed that carbon corrosion of the GDL happens mostly on the MPL. This is confirmed by experiments performed by .... [9], where the inner side of the GDL is significantly more corroded than the outside.

2.2.3 Membrane degradation

The membrane forms the centre of the MEA, as figure 2.1a shows. The polymer electrolyte membrane has multiple functions. It is a conductor for protons from the anode to the cathode, it prevents the hydrogen and oxygen from the electrodes from reacting and it acts as an electronic insulator. The reduction (degradation) of any of these functions has a direct impact on the performance of the fuel cell. For simplicity reasons a membrane made out of Nafion ® will be taken as an example since the majority of the commercial membranes are made out of this material. Membrane degradation can be mechanical or chemical. However, it is generally accepted that mechanical degradation plays a small role and that most of the degradation is of a chemical nature [47]. For a long period of time, the hypothesis [47] has been that the degradation of a PEMFC happens via a complex multi-step mechanism, existing of two steps: 1) the formation of membrane degrading species and 2) attack of the membrane. The formation of membrane degrading species are mainly caused by two mechanisms: a) H_2O_2 formation at the anode which is then decomposed into radicals [45, 61] and b) the formation of intermediate radicals during the oxygen reduction reaction (ORR) at the cathode [1, 53]. The mechanism of the attack of the membrane is dependent on the material of the membrane. For membranes based on Nafion ® the extraction of H from the reactive end groups of the polymer (COOH) by the radicals formed in the first step is the most common form of attack. The removal of H reduces the proton-conducting ability of the membrane and therefore reduces performance [16].

$$H_2 + O_2 \xrightarrow{pt} X \tag{2.8}$$

In recent years, a new hypothesis has been formed [18, 47] that states that a radical is formed in the presence of platinum (reaction 2.8). This radical is believed to be the true cause of the chemical degradation of the membrane. However, the exact mechanism is not fully understood yet. It is indicated that the reaction is independent of the potential and thus chemical in nature. The surface of the CL is believed to have an influence on the mechanism but this is still under investigation.

2.2.4 Load characteristics degradation

The lifetime of a PEMFC is the limiting factor for commercial use [2]. Sections 2.2.1, 2.2.2 and 2.2.3 discussed the various degradation mechanisms that reduce the lifetime of a PEMFC. A part of the degradation can be lead back to the design of the fuel cell and the choice of material, which can only be improved by redesigning the fuel cell [76]. However, a part of the degradation mechanisms are caused by the conditions at which the fuel cell operates. This can be environment conditions but also load conditions. A PEMFC used for as a fixed power supply can reach a lifetime up to 30.000 hours [69] while a PEMFC used in automotive applications usually lasts only 2500-3000 hours [10]. This is far less than the industry standard, the marine diesel engine, which has a lifetime expectancy between overhauls of 25.000 hours.

It must be noted that PEMFC degradation due to load conditions are not new degradation mechanisms, but it describes the conditions under which the mechanisms described in sections 2.2.1 to 2.2.3 occur. Various research has been done to understand the degradation due to load characteristics such as Moein-Jahromi et al [48] and Garcia-Sanchez et al [25] who investigated the degradation of the CL under cyclic load and provided a method for lifetime prediction. Shan et al [60] investigated the influence on degradation of dynamic cycles which applies well to the automotive application of PEMFC. Uchimura et al [66] pointed out that not only the change in load is important for the degradation but also the transient behaviour of this load. He performed measurements using different cycle profiles (figure 2.13) and concluded that the profile had an influence on the performance of the fuel cell. And Zhang et al [76] provided a literature review of various work on degradation due to start-stop conditions. Durst el al [20] further showed that during start-stop conditions heterogeneities play an important role.

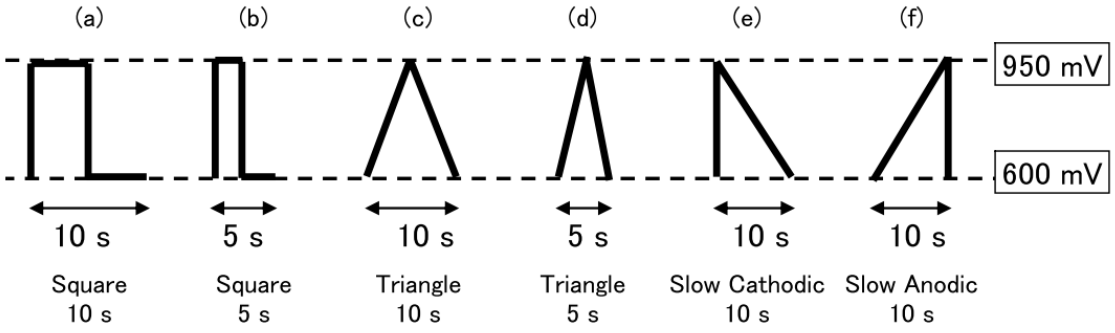


Figure 2.13: Schematic of voltage cycle profiles used in the study by Uchimura et al with upper potential limit of 0.95 V and lower potential limit of 0.60 V. a) square 10 s; b) square 5 s; c) triangle 10 s; d) triangle 5 s e) asymetrical triangle, slow cathodic 10 s; f) asymetric triangle, slow anodic, 10 s [66]

Despite the extensive research done over the past decades, there is still no conclusive method to quantify the total PEMFC degradation based on the load characteristics. Research, as cited above, all review one or a few of the total degradation mechanisms that occur during normal operation. Even though some of the research is able to quantify the degradation accurately, superposition cannot be applied because the degradation mechanisms are not independent of each other. This means that the degradation as calculated in the literature cannot be summed to obtain the total degradation. Further research must be done into the relation between degradation mechanisms in order to accurately quantify the total degradation of a PEMFC during load.

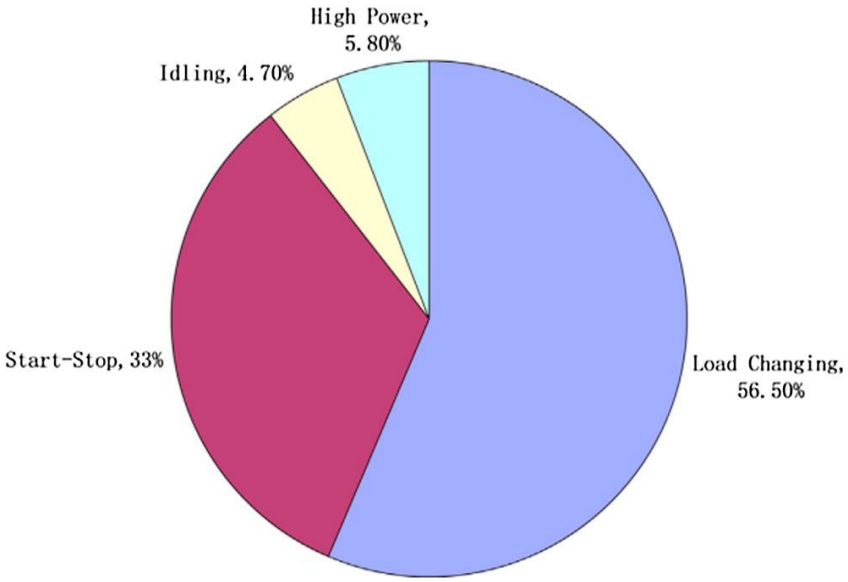


Figure 2.14: Degradation contribution of the four different conditions during practical operation experiments with a bus [52]

However, research has shown that the degradation of a PEMFC and load characteristics are connected. Instead of looking from the degradation mechanism perspective, one could also approach the problem from the load characteristic side. The load characteristics can be divided into different load conditions as done by Pei et al [52] who distinguished four conditions: 1) start-stop, 2) load changing, 3) high power and 4) idle. As can be seen in figure 2.14 start-stop and load changing conditions contribute more to the total degradation of the fuel cell than idle or high load conditions for this particular operational profile.
Being able to quantify the degradation of a PEMFC based on the load characteristics can be useful and the academic society has not been able to do so analytically yet. The method Pei et al [52] uses can be described as a phenomenological model. A phenomenological model describes an empirical relationship of phenomena without a direct derivation from theory [24]. Therefore, a phenomenological model can be used when the relationship cannot be explained but can be described using empirical results from former experiments.

Evaluating method for PEMFC degradation due to load

With the phenomenal model of Pei et al, degradation can be described using the load characteristics and experiments. It must be noted that the empirical values used for the model are only valid for the model the experiments are performed on. Therefore, if one were to adopt this method, experiments must be conducted using the exact type of fuel cell one wants to use. Pei et al tested the degradation rate for each condition using the experiments listed below.

1) Start-stop cycling:
For the start-stop process, a protocol was used: running at idle for 1 minute at a constant current density of 10 mA/cm^2, then stop, purge the remaining hydrogen from the fuel cell using nitrogen gas, wait until the voltage of the stack has dropped to zero and then repeat. Every 10 cycles the performance of the fuel cell was recorded (see figure 2.15) and the testing was carried out for 80 hours in total. For this experiment, a linear decrease in performance could be established of 0.00196% per cycle.

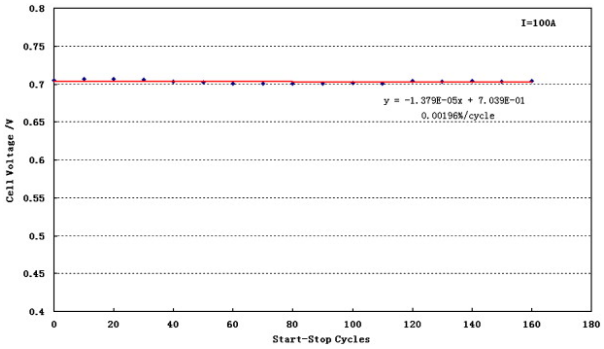
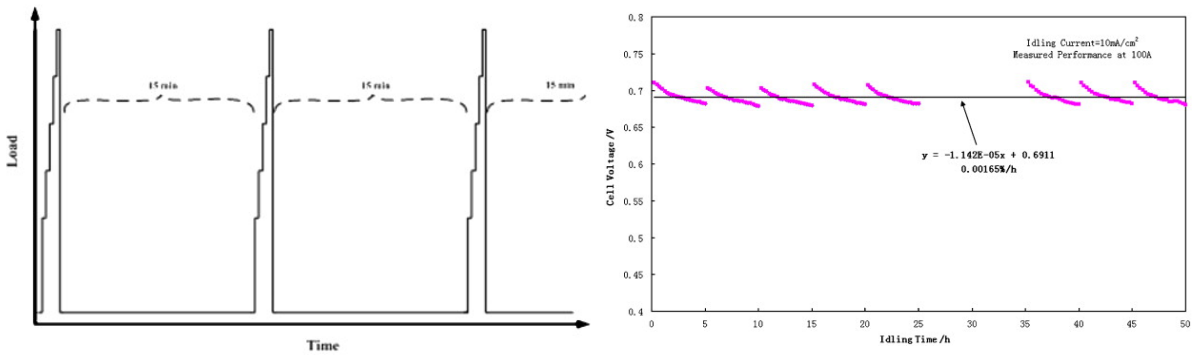


Figure 2.15: Performance change in start-stop cycles [52]

2) Continuous idle operation

For the continuous idle operation process the following protocol was used: continuous operation at a current density of 10 mA/cm^2 for 5 hours at a time. The period of 5 hours was chosen because it resembles the idle condition of a bus during normal operation for a day. After the test period, the fuel cell was stopped and started again, allowing the fuel cell to recover some of its degradation. Figure 2.16b shows the degradation over a period of 50 hours using a measurement interval of 15 minutes (figure 2.16a). A degradation of 0.00126% per hour was established.



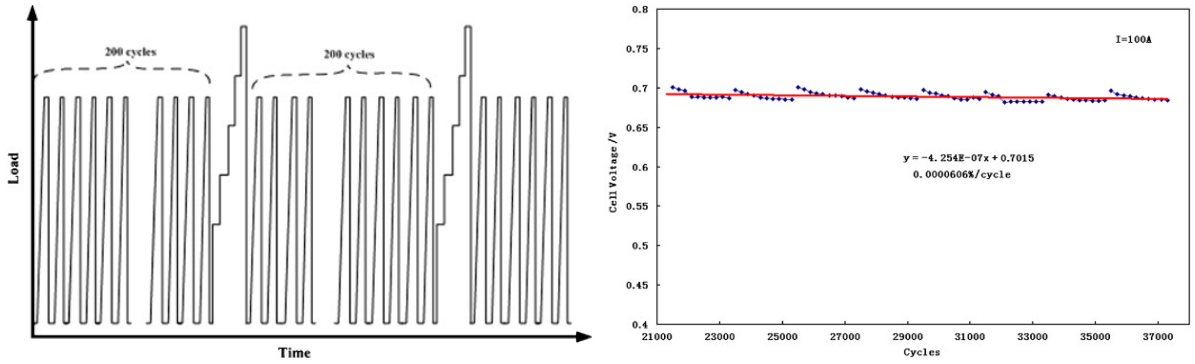
(a) Idle test cycles

(b) Idle performance change

Figure 2.16: Idle experiments [52]

3) Load changing operation

The load changing operation performs cycles from idle condition to its rated power as shown in figure 2.17a. First, the fuel cell performed a warming-up cycle by running 30 minutes at idle, after which 2000 cycles were performed. In total this experiment was conducted for a period of 80 hours. Using this experiment a degradation of 0.0000593% per cycle could be established (figure 2.17b)



(a) Load changing cycles

(b) Load changing performance change

Figure 2.17: Load changing experiments [52]

4) High load operation

The high load operation started with a warm-up period of 30 minutes after which the fuel cell was run at its rated power. The high load operation was run for 5 hours after which the fuel cell was stopped and started again the next day. Measurements were taken every 15 minutes to record the performance decay as shown in figure 2.18. From this experiment a degradation rate of 0 00147% per hour could be established.

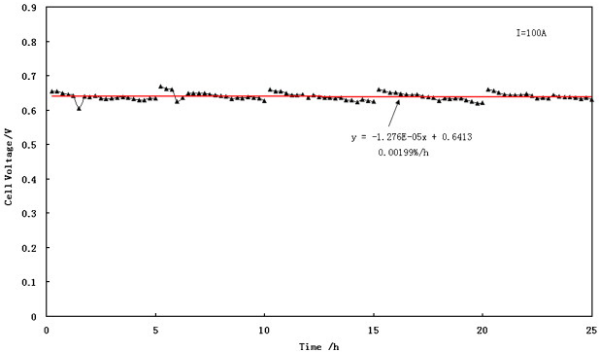
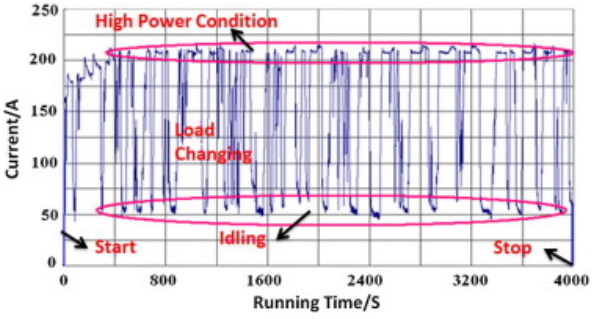
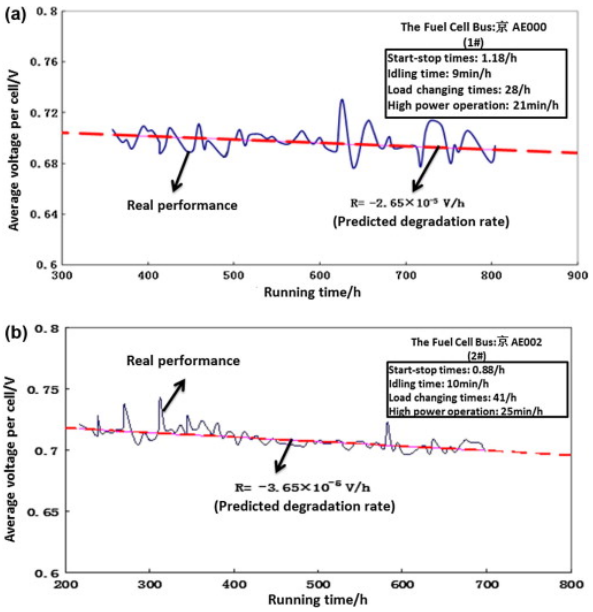


Figure 2.18: High load performance change [52]

The obtained degradation rates are all derived in lab conditions. Verification must take place to ensure the found degradation rates accurately describe degradation during actual use. Pei et al used two busses equipped with the same type of fuel cell to verify the results. Over the period of one year the two busses were deployed on a specific bus line, during which the load characteristics were monitored as shown in figure 2.19a. This allowed the researchers to verify the phenomenal model made with results from lab experiments with actual degradation. Figure 2.19b shows the predicted degradation rate versus the monitored degradation rates from the busses.



(a) Example of actual measured load profile [10]



(b) Phenomenal model verification [10]

Figure 2.19: Load characteristics and model verification [10]

PEMFC lifetime prediction method

To provide a lifetime expectation, first it must be defined when a PEMFC is at the end of its life. A widely accepted definition is that a PEMFC is at the end of its life when it has lost 10% of its voltage at a calibration current [52]. According to Pei et al many fuel cell lifetime tests have shown that degradation of a fuel cell shows a linear trend over time. Therefore, the expected lifetime of a PEMFC can be described using relation 2.9, where T_f is the expected lifetime in hours, ΔP is the difference between the end of lifetime and the beginning in percentage and r_d is the decay rate of the fuel cell in percentage.

$$T_f = \frac{\Delta P}{r_d} \tag{2.9}$$

The decay rate is here taken as a single number but is actually composed using the four conditions described above. Pei et al described a method for analysing the load characteristics and combine them with the degradation rates found using experiments. For each condition of the driving cycle (Driving cycle = $\{n_1, t_1, n_2, t_2\}$) a parameter is used to describe the duration or the frequency of each condition.
Here n_1 is the number of times a start-stop cycle is performed per hour, t_1 is the duration at idle in one hour, n_2 is the number of load changes per hour and t_2 is the time at high load in one hour. Together they form the load spectrum of the driving cycle.
The degradation rates obtained during experiments are denoted as: V_1 is the degradation rate due to start-stop cycles, U_1 is the degradation rate due to idle condition, V_2 is the degradation rate due to load changes and U_2 is the degradation due to high load conditions.

$$n_1 V_1 + t_1 U_1 + n_2 V_2 + t_2 U_2 = r_d \tag{2.10}$$

The load spectrum of the driving cycle and the degradation rates can be put together to obtain the total degradation rate r_d using equation 2.10. Additionally, Pei et al proposed a factor k which resembles the acceleration due to environmental conditions such as polluted air that cause an increase in degradation rate. Combining equation 2.9, equation 2.10 and the factor k we obtain the relation (2.11) for lifetime prediction of a PEMFC dependent on the load spectrum.

$$T_f = \frac{\Delta P}{k(n_1 V_1 + t_1 U_1 + n_2 V_2 + t_2 U_2)} \tag{2.11}$$

To conclude, it is possible to predict the lifetime of a fuel cell based on the load spectrum. Using experiments and a decomposition of the load spectrum an estimation can be made to predict the lifetime of a PEMFC. It must be noted that this prediction is only valid for the type of fuel cell used for the experiments. Also, the accuracy of the lifetime prediction is only as accurate as the load spectrum used for the calculation.

2.3 Battery systems

This chapter will elaborate on the basics of battery characteristics. Each type of battery has different characteristics which are dependent on the chemistry, size and structural design of the battery. For this research, only basic knowledge of battery characteristics is necessary to be able to adapt batteries in a model together with fuel cells.

2.3.1 Power

Power is a unit measured in watts (W) that is used to describe the batteries' ability to charge and discharge at high current rates. The amount of power a battery can deliver is called the power rating of a battery. In order to compare the power rating of batteries power density can be used as shown in figure 2.20. Power density can be expressed in volumetric density ($\frac{W}{L}$) or in gravimetric density ($\frac{W}{kg}$). However, power density often refers to the volumetric density and specific power is used for the gravimetric density.

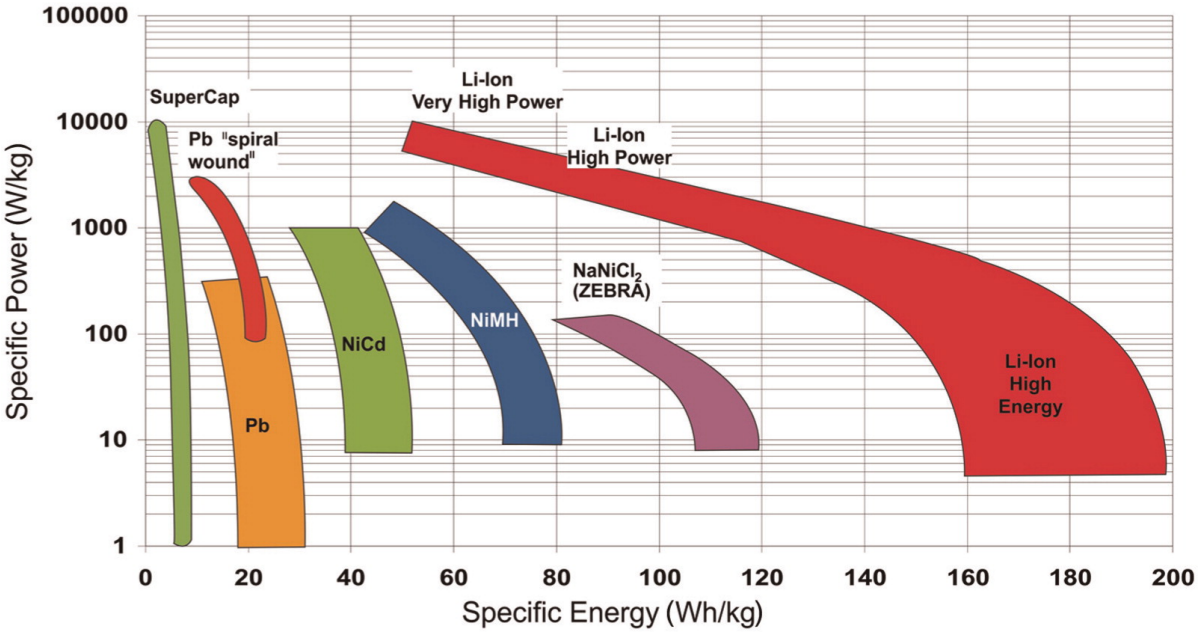


Figure 2.20: Overview of the power density of different battery types [6]

For this research, batteries are used as part of a hybrid fuel cell system. Because of this supporting role, the batteries have to be able to deliver power fast allowing the fuel cell to increase its power at its transient speed. A higher power rating means that the battery is able to charge/discharge faster. For a battery to have a high power-rating the internal resistance of the battery has to be as low as possible [26]. Usually, low internal resistance can be achieved by using thin electrodes, which increases the active surface area and thus decreases the internal resistance. It must be noted that the opposite is true for capacity. Therefore, a balance must be found in order to have a battery with a high power-rating and still have sufficient capacity.

The speed of charging and discharging of a battery is described by the C-rate. The C-rate is defined as the charge or discharge of current the battery (I) divided by the battery capacity (Q) as shown by equation 2.12. Therefore, a C-rate of 1 means that the entire capacity of the battery is charged or discharged in one hour. If the same battery is charged or discharged with a C-rate of 2 or 0.5 the battery is charged or discharged in half an hour and two hours respectively. Thus an increase of the C-rate means an increase in the current and a decrease in time for the same battery capacity. However, increasing the current increases the internal losses and decreases the efficiency of the battery [65].

$$\text{C-rate} = \frac{I}{Q} \tag{2.12}$$

2.3.2 Capacity

A widely accepted definition of battery capacity is the maximum usable energy it can store measured in kilo-Watt-hours (kWh). However, to prolong the lifetime of a battery, often a minimum and maximum State Of Charge (SOC) is used, which reduces the usable capacity of a battery. In equations, the capacity of a battery is often expressed with Q. Similar to power, capacity density is used to compare the capacity of batteries as shown in figure 2.20. Capacity density can be expressed volumetric ($\frac{\text{kWh}}{L}$) or gravimetric ($\frac{\text{kWh}}{kg}$).

The capacity is mainly influenced by three battery properties [43]: 1) chemistry, 2) electrode structure and 3) electrolyte structure. The energy of a battery is stored in the electrodes. The energy storage characteristics are different for different materials. Thus the material an electrode is made of has an influence on the capacity. For example, in lithium-ion batteries materials that have a higher affinity with lithium ions can increase energy storage. Because the energy is stored in the electrodes the size also plays a role when it comes to capacity. Opposite compared to power density, thicker electrodes increase the capacity of a battery because there is more material to store energy in. The structure of the electrolyte determines its capability to transfer ions from the anode to the cathode. When the electrolyte does not have enough transportation capability it decreases the capacity of the battery.

2.3.3 Battery types

Several battery types have been developed during the last decades but three types of batteries are considered interesting for this research due to their characteristics and Technology Readiness Level (TRL) [32]: 1) Lead-acid, 2) Nickel-based and 3) Lithium-ion batteries. In this section, the main characteristics are provided per type of battery.

Lead-acid batteries

The lead-acid battery has been around since 1859 and is very common [57]. For example, most cars use a lead-acid battery. Although they have been around for over 150 years, the lead-acid battery remains very popular due to its ability to recharge, low cost, robustness and low self-discharge. However, the lead-acid battery has a low energy density compared to other battery types and has a larger negative impact on the environment [57]. Lead-acid batteries are named after the materials used. The anode is made out of lead metal, the cathode out of lead dioxide and the electrolyte out of sulphuric acid. The lifetime of a lead-acid battery is usually around 200-300 cycles due to corrosion at the cathode [19].

Nickel based batteries

There are several battery types that use nickel, but two types are most common: 1) Nickel-cadmium (NiCd) and 2) Nickel-metal-hydride (NiMH). The NiCd battery uses a nickel-oxide-hydroxide cathode, a cadmium anode and a potassium hydroxide solution as electrolyte. A NiMH battery also uses a nickel-oxide-hydroxide cathode and a potassium hydroxide solution electrolyte but uses a hydrogen-absorbing metal alloy instead of cadmium. Nickel-based batteries have a relatively long cycle life of around 1000 cycles if properly maintained. This maintenance entails periodical full discharge of the battery to avoid a decrease in performance. If a full discharge is not done periodically crystals form within the battery, decreasing its performance, called the memory effect. Compared to other types of batteries nickel-based batteries have a relatively high self-discharge rate of around 40% in three months time [34]. NiMH is a newer form of nickel-based battery and its main advantage is a higher energy density compared to NiCd (see figure 2.20), but the self-discharge rate increases as well.

Lithium-ion batteries

Lithium-ion batteries are relatively new compared to other batteries but have great potential. Lithium-ion batteries are considered one of the lightest batteries currently available. Lithium is the lightest metal and has one of the highest electrode potential (3.04 V) [68]. The low weight and the large potential of the battery give it a very high energy density compared to other batteries. Further advantages of the lithium-ion battery are low maintenance and no memory effect. Furthermore, the self discharge rate is less than half that of nickel based batteries [5] and it has a lifetime of up to 7000

cycles [65] which is a large improvement over the other types. However, the lithium-ion battery is vulnerable to a thermal runaway. This is an exothermic process that can be triggered by physical or electrical abuse such as over (dis)charging, short circuit or external heating.

Overview

Figure 2.21 show the battery characteristics as mentioned in the sections above. The data shows clearly that lithium-ion outperforms the other types on almost each criterion, but is also the most expensive one.

Battery type	Lead-acid	Nickel-based	Lithium-ion
Costs (€/kWh)	€100 - €200	€300 - €600	€250 - €1500
Energy (Wh/kg)	30 - 50	45 - 120	100 - 250
Power (W/kg)	50 - 180	150 - 1000	250 - 3000
Cycle life	200 - 300 cycles	300 - 1100 cycles	300 - 7000 cycles
Safety	Average	Good	Sub-type dependent
Temperature	-20°C - 50°C	-40°C - 70°C	-20°C - 60°C
Typical C-rates	0.1 C	0.1 - 10 C	0.3 - 10 C

Figure 2.21: Overview of battery characteristics per type. Table from [65] data from [5]

2.3.4 Battery degradation

Similar to fuel cells batteries are subjected to a loss in performance due to degradation. The loss of performance is loss of capacity and/or loss of power. The degradation mechanisms of batteries are often divided into two categories of characteristics: 1) cycle life and 2) calendar life [26]. Degradation due to calendar life is the decrease of performance over time and degradation due to cycle life is caused by the usage of the battery.

Various factors have an influence on these characteristics such as temperature, state of charge, C-rate and the cycling profile. The degradation mechanisms are chemical reactions that take place at the electrodes. Usually, a high reactivity is good for battery performance, but this also increases the chemical reactions that cause degradation and thus decreases the lifetime of the battery [65]. Therefore, a balance must be found between battery performance and lifetime. The materials of a battery have a large impact on the lifetime because of the chemical nature of the degradation process. Therefore the choice of material is key to obtain a battery with good lifetime characteristics. Often additives are added to the materials to prolong the lifetime of a battery by slowing down the reaction rate and decreasing the performance of the battery and increasing the lifetime.

2.4 Energy management systems for hybrid fuel cell systems

A typical power-train system of a PEMFC contains a battery pack, fuel cell, converter and Energy Management System (EMS) [35], figure 2.22. Proton exchange membrane fuel cells have relatively good transient behaviour compared to for example solid oxide fuel cells [3]. However, the transient speed of a PEMFC is often not high enough to meet the dynamic load conditions for a power train [41]. Combining the fuel cell with a battery resolves this problem. When the load is larger than the fuel cell can deliver, the battery delivers the difference between the load and the power of the fuel cell. The same holds the other way around [29]; if the load is less than the fuel cell delivers the excess of power can be used to charge the battery for later use. Fuel cell systems that also use a battery are often called a hybrid fuel cell system [35].The time scale of the model will have a great influence on which effects are taken into account in the model such as transient behaviour of the PEMFC or the battery. Nowadays these systems often also equip a super-capacitor to account for the fast changes even a battery cannot handle. However, the time scale used in this research is too large to take a super-capacitor into account and will therefore not be modelled.

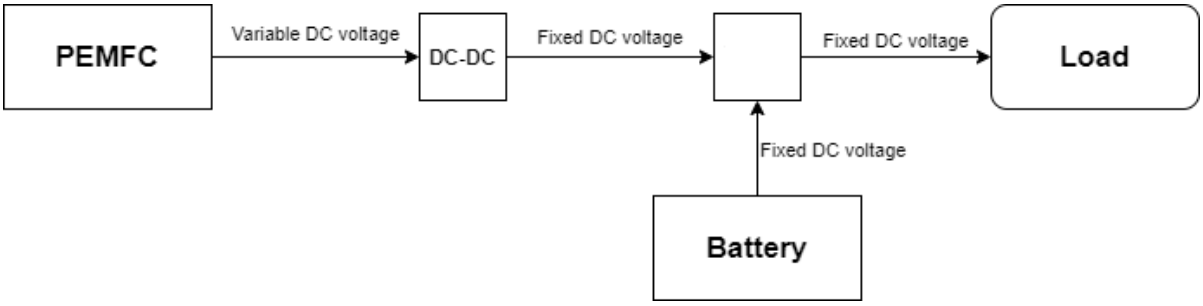
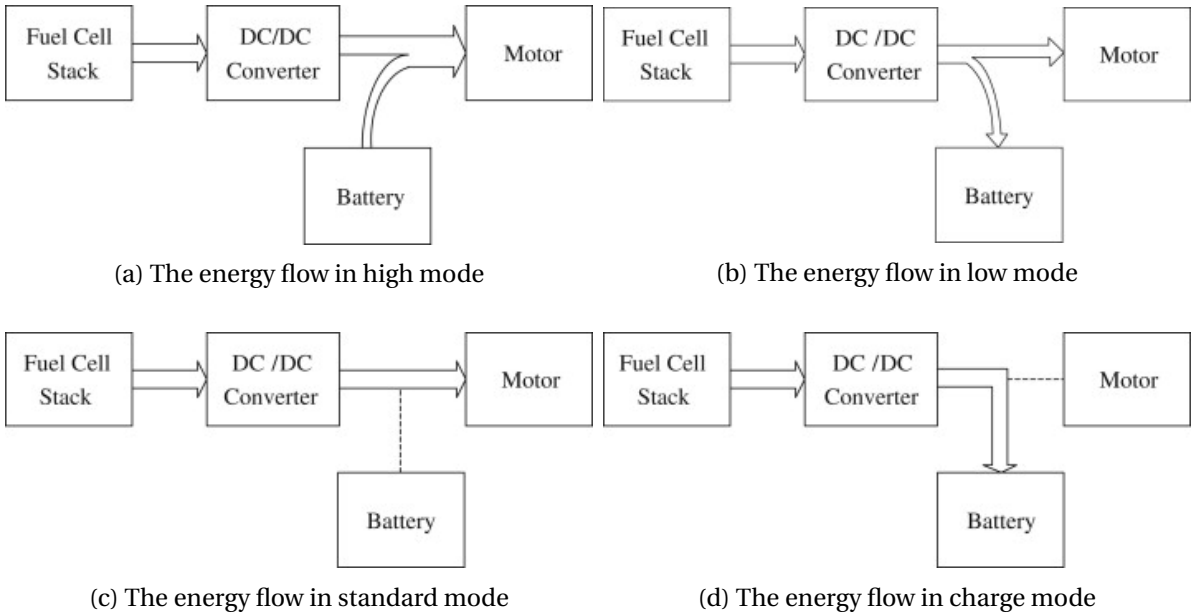


Figure 2.22: Schematic overview of a PEMFC hybrid system

To use fuel cells in systems with dynamic load conditions batteries and an EMS are used. The energy management system determines when and how energy is drawn from the fuel cell and battery. Energy management systems can be based on all kinds of principles and can be real-time or predetermined. One of the simplest forms is a management system based on a set of rules and boundary conditions by which it determines where and how to draw energy from. The decision if energy can be drawn from the battery is often made based on the SOC. Over (dis)charging is harmful to the battery and must be avoided. Therefore, energy management systems often keep the state of charge of a battery between 40 and 80%.

Hwang et al [31] proposed 4 operating modes, figure 2.23, of a hybrid fuel cell system: 1) high power mode, 2) low power mode, 3) standard power mode and 4) charging mode. These energy modes describe the way energy flows during each condition. During high power mode, figure 2.23a, the energy demand is larger than the fuel cell can deliver. Therefore, the fuel cell and battery both supply energy to the load. During low power mode, figure 2.23b, the fuel cell delivers more energy than is needed by the load. The excess energy is then used to charge the battery. Standard power mode, figure 2.23c, describes the condition between high and low mode. During standard mode, the fuel cell is able to deliver the amount of energy that is needed for the load but no more than that. Thus no excess energy is used to charge the battery. The fourth power mode is charging mode, figure 2.23d, when the fuel cell is running but there is no energy demand by the load, all the energy of the fuel cell is used for charging the battery.

The size of the fuel cell and the battery depend both on the operational modes, energy management rules and the operational profile [35]. The energy management system determines when an operational mode is used based on the load given by the operational profile. The whole power train should be able to deliver energy at all times while avoiding the start-stop cycles of the fuel cell [50]. For example, this means that if the system experiences high load conditions for longer periods it most likely will need a larger battery [63]. Or, when the load is fairly constant, the fuel cell energy will probably be close to the load with a small battery that allows small deviations.



(a) The energy flow in high mode

(b) The energy flow in low mode

(c) The energy flow in standard mode

(d) The energy flow in charge mode

Figure 2.23: Energy modes as described by [31]

As mentioned earlier, energy management systems describe how, when and from which energy source energy is drawn. However, there is not only one way to manage a hybrid fuel cell system. A distinction can be made when applying an EMS between limits and boundaries that are chosen because of a favourable effect or because there are physical boundaries in place. It is clear that the second set of limits cannot be altered but the first set of limits can. Therefore, one could set the first set of limits to be optimised for a specific purpose. Various optimisation purposes exist and have been studied. Like most power supply systems, fuel economy or efficiency is important.

Therefore, optimising for fuel economy using an energy management system has been the subject of many studies [29, 35, 63, 77]. These studies either focus on sizing fuel cell system components or on optimising the dynamic conditions of the fuel cell. While both aim for the same result the method is different. By optimising the size of components often energy is saved because the BOP needs less energy, while optimising for the dynamic conditions saves fuel by choosing the operation conditions in favour of fuel efficiency.

Related to fuel economy is cost. Energy management systems can also be used to optimise for cost. This can be for example operational cost, cost of ownership or initial investment. Although the PEMFC developments are still ongoing the price remains relatively high per kW [3]. Therefore, it is worthwhile to perform optimisation for cost in most cases.

Last but not least is the optimisation for fuel cell degradation. In section 2.2.4 it was shown that the load conditions of a PEMFC can have an impact on the degradation of a fuel cell. If the load spectrum is known then that knowledge can be used to optimise for degradation. For example, it is proven that start-stop conditions contribute significantly to the overall degradation of a PEMFC. By choosing a battery large enough the number of starts and stops can be reduced and thus the degradation can be reduced as well.
It must be noted that most optimisations only hold for the situation the optimisation has been done for. PEMFC's are not often equipped in naval vessels at the time of writing. Therefore, little experience is available and thus the conditions for which is optimised is based on little experience and could be less accurate.

3. Method and model

The knowledge obtained from theory on PEMFC's, recorded information of an Royal NetherLands Navy (RNLN) ship and lifetime prediction models from the literature study is used to build a model to show the effects of component sizing, energy management strategies and the number of active modules. In this chapter the composition and the justification of the model will be discussed, as well as the experiments conducted with this model.

3.1 Approach

The various factors that influence the lifetime of a PEMFC can be approximated in a comprehensive model that computes the lifetime using the method of Pei et al [52]. This model and its sub-models will be discussed later in section 3.2 including the assumptions and limitations in section 3.3. It is the hypothesis that component sizing, energy management strategies and selective use of PEMFC modules will have an effect on the lifetime of a PEMFC. The influences of these factors are investigated by modelling a PEMFC-battery hybrid power-train of a ship of the RNLN and simulating a typical journey. The model will be adapted to systematically explore the effect of the three factors (section 3.4).

The environment chosen to build the model in is Matlab®/Simulink ®. Matlab is a software package that offers an environment for (technical) scripting, especially with the Simulink extension. Simulink is particularly suitable for simulations in various domains, including the time domain. With Simulink, a graphical representation of the actual drive-train can be created using blocks and sub-systems which are connected by signal lines containing various types of information.

3.2 Model structure

The model has multiple functions; distributing the load amongst the fuel cell and battery system, monitoring fuel consumption and state or charge of the battery, and analyse PEMFC degradation. The model is constructed using five sub-models to comply with these functions. Each of these sub-models represents a part of the power train system, as either a physical component or the output from a group of components, for example, the load from a ship. Figure 3.1 displays a schematic overview of the model and the five sub-systems. The black arrows between the blocks represent the flow of information. The sections 3.2.1 to 3.2.5 describe the five subsystems of the base model in further detail. For the experiments, additional adaptations to the base model have been made which will be further explained in section 3.4.

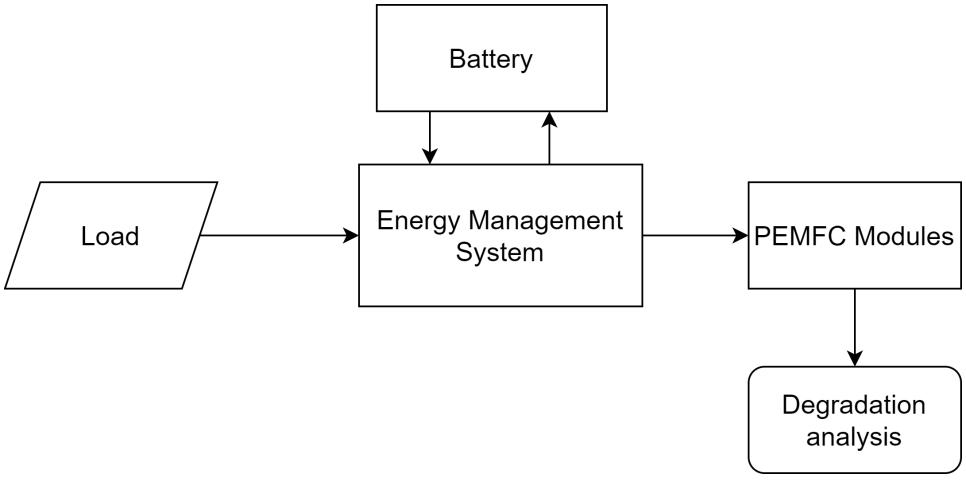


Figure 3.1: Schematic overview of the model

The model runs a simulation in the time domain with time steps of one second, which is equal to the time step of the provided load. Analysis of the time step showed that an increase of the time step up to 5 seconds does not give a lifetime or load spectrum with a deviation larger than 0.5%. However, because all simulations could be run in the available time, it was decided to run at the native time step of the data of one second. Using a discrete model with a fixed time step means that the model is quasi-static and that transient behaviour is neglected.

3.2.1 Load

For the simulations, a load profile of an existing RNLN ship will be used. The load profile contains the power demand from the propulsion as well as the power demand from the auxiliaries on board the ship. In other words; the total power demand of the ship. This load profile is provided by the RNLN and recorded during one of its operations. The load profile contains data from a period of two weeks recorded at an interval of one second, which corresponds to roughly 1.2 million samples. Before the load profile can be used the original recording is converted to a $.CSV$ file which can be loaded directly into Matlab for further processing.

The load block directly imports the load profile from Matlab and submits the corresponding value of the power demand of the ship at the correct time step during the simulation. As the load profile is loaded from Matlab the block only contains one output; the power demand $[kW]$.

3.2.2 Energy management system

The energy management system decides if power is drawn from the PEMFC, battery, both or neither. The energy management system block has two inputs; the load from the load block and the SOC from the battery block, and three outputs; PEMFC load, battery charge and battery discharge.

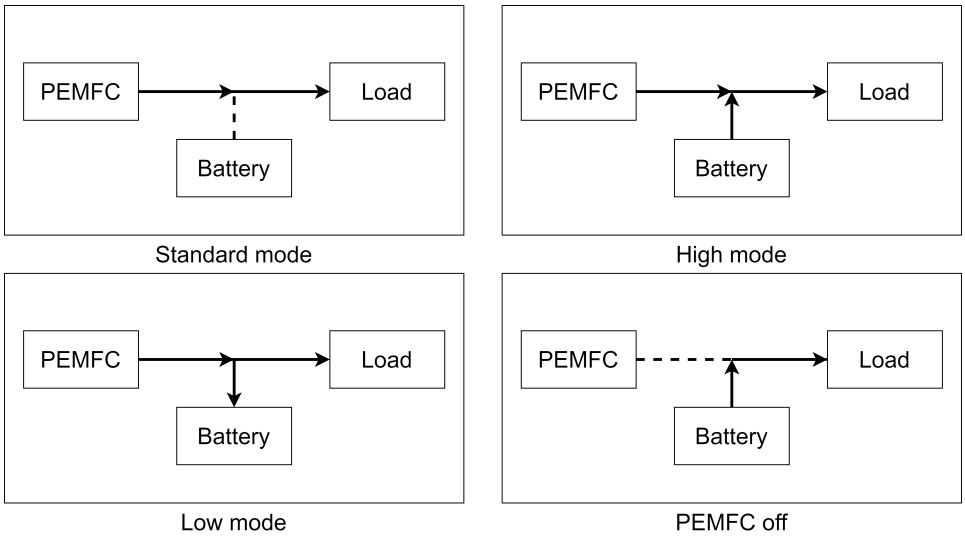


Figure 3.2: Energy flow for the described power modes

The base model is based on four energy settings, figure 3.2. Variations on these energy settings are made during the experiments, but will be discussed later in section 3.4. The first energy setting is standard mode, which is active between 30% and 100% of the rated PEMFC power. Basically, standard mode is the range in which the PEMFC can operate. For this model, the idle power condition is assumed to be at 30% of the rated PEMFC power. This means that standard mode is active when the power demand is in the range of what the PEMFC system is capable of. The second energy setting is the high power mode. When the energy demand is larger than the PEMFC system can deliver, above 100% of the rated PEMFC power, the battery system will replenish the energy supply to the level of the energy demand. Therefore the rated power of the PEMFC system plus the rated power of the battery system must be equal or larger than the largest energy demand from the load. The third energy setting is the low power mode, which is activated when the load is less than the idle power of the PEMFC system. The energy management system will keep the PEMFC power at idle and use the excess power to charge the battery system. The management system will also keep

track of the state of charge of the battery system. Although the degradation of the battery system is not a part of this research the SOC of the battery system is kept between 20% and 80% to prolong the lifetime of the battery system. If the load drops below the idle condition of 30% and the SOC of the battery is larger than 80% the system will go to the fourth and final energy setting: PEMFC off. In this mode the PEMFC system is shut down and all of the energy is supplied by the battery system. Figure 3.3 displays a decision tree for the energy setting selection.

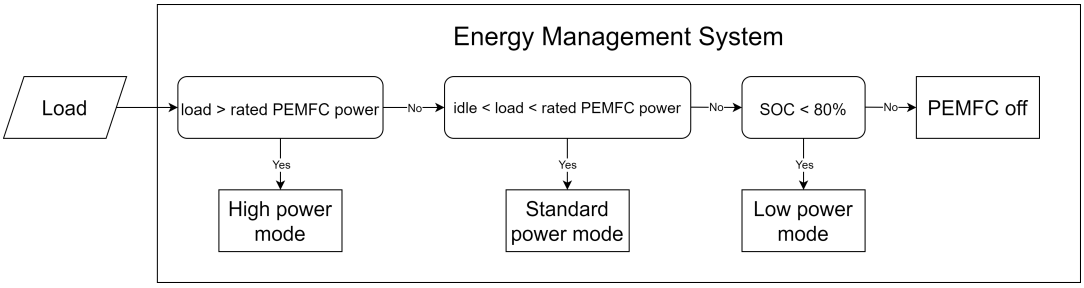


Figure 3.3: Flow chart of the energy management system process

3.2.3 Battery

The battery block resembles the battery system that is part of the power train. For simplicity reasons the battery system is considered as a whole, meaning that no distinction is made between the individual batteries. Furthermore, the battery system uses lithium-ion batteries for which a power to capacity ratio of 3 to 2 is assumed. The capacity, and thus the power, of the battery, is predetermined and dependent on the simulation that will be further explained in section 3.4.

The block has two inputs; battery charge and battery discharge, which originate from the energy management system. The block has one output, the state of charge from the battery system, which is set to 80% at the beginning of the simulation. Over time the charge and discharge input is integrated with an offset of the initial SOC, resulting in the real-time SOC of the battery system.

3.2.4 PEMFC

The PEMFC block resembles the PEMFC system including the BOP. The block has one input; the energy demand from the energy management block, and one output; the energy delivered by the PEMFC modules leading to the analysis block. The reason that the energy demand has to go through the PEMFC block is due to one of the experiments, where the PEMFC system is split into modules. Inside the PEMFC block, the fuel consumption is estimated using an efficiency curve composed of efficiency curves from literature and commercially available PEMFC's, see figure 3.4

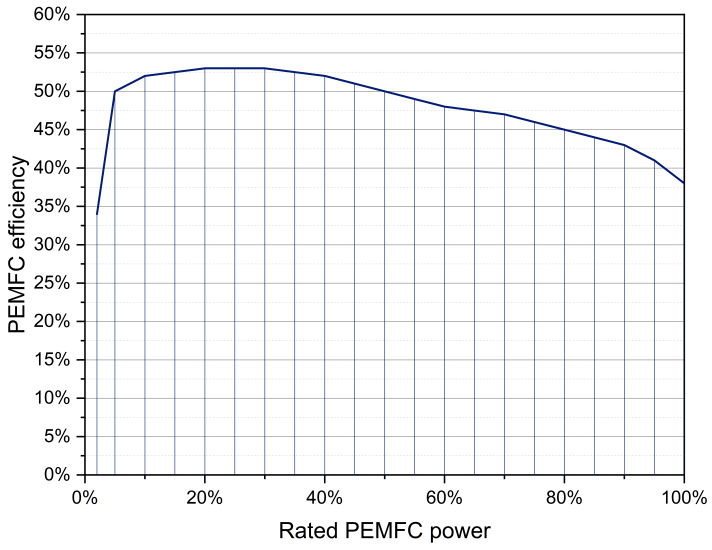


Figure 3.4: The adopted PEMFC efficiency curve

Using a lookup table and linear interpolation the efficiency of the PEMFC is estimated for the energy demand of that time step. The corresponding hydrogen consumption is then computed using the lower heating value of hydrogen (120 MJ/kg). Integrating the hydrogen consumption over time using a discrete integration method with a time step of one second gives the total hydrogen consumption in kilograms. The effect of PEMFC degradation on the fuel consumption is negligible for short periods of time and is therefore not taken into account.

3.2.5 Analysis and Lifetime estimation

The method of Pei et al [52] and Chen et al [10] is adopted to estimate the lifetime of a PEMFC based on the load as felt by the PEMFC. This method uses four conditions to estimate the lifetime of a PEMFC; 1) Start-stop, 2) Load changes, 3) High power and 4) Low power. The low/high power condition will be called low/high load condition in this thesis, because the low/high power condition refers to the load as felt by the PEMFC and to avoid confusion as the term power is already used for multiple definitions. As will be explained in section 3.3.2, the PEMFC parameters as deducted by Pei et all will be used in this research. Table 3.1 shows the adopted values of the four conditions.

Table 3.1: PEMFC parameters as deducted by Pei et al [52]

PEMFC parameter	Value	Unit
1) Start-Stop	13.79	μV / cycle
2) Load changes	0.4185	μV / cycle
3) High Load	10.00	μV / hour
4) Low Load	8.662	μV / hour

The Start-stop condition (1) is defined as one cycle every time the PEMFC has to shut down and start again. For example, if the PEMFC has to shut down twice during a simulation the number of times the start-stop condition has occurred is three due to the initial start-stop. The load change condition (2) is defined as a 20% difference from a moving average over a period of 5 seconds. This definition is deducted from the ramp-up/downtime of an average PEMFC which often can go from idle to full power in a few seconds, such as the HyPM-HD 180 from Hydrogenics for example. Using a 20% average from the moving average ensures that load changes that exceed the ramp-up time of a PEMFC are taken into account as well as the load changes prior to this time step, but load changes that occur over large periods of time are ignored. The high load condition (3) is defined as above 70% of the rated PEMFC power. The low load condition (4) is defined as below 50% of the rated PEMFC power. The definitions of the low/high load condition are deduced from figures from the work of Pei et all, exact numbers were not mentioned. Table 3.2 provides an overview of the definitions of the conditions.

The analysis block is programmed to remain in either the low or high load condition until the load crosses the threshold for the other condition. Since the start-stop and load changes condition are cycle based instead of time based, the degradation due to start-stop and load changes condition is complementary to the degradation obtained in the low or high load condition.

Table 3.2: Definition of load conditions

Condition	Definition
Start-Stop	Complete shut down of the PEMFC system
Load changes	20% difference between the load and a moving average over the previous 5 seconds
High Load	>70% rated PEMFC power
Low Load	<50% rated PEMFC power

The analysis block analyses the load from the PEMFC block and divides it into the four conditions. The conditions are described by the parameters $\{n_1, n_2, t_1, t_2\}$ that describe the occurrence for condition 1 and 2 and the duration for condition 3 and 4. The PEMFC parameters, table 3.1, are described by $\{V_1, V_2, U_1, U_2\}$.

Using the PEMFC parameters, the load spectrum and equation 3.1 the lifetime of the PEMFC is estimated. Furthermore, with this method the individual contribution of each condition can be determined. The contribution of all four conditions together form the load spectrum.

$$T_f = \frac{\Delta P}{k(n_1 V_1 + t_1 U_1 + n_2 V_2 + t_2 U_2)} \tag{3.1}$$

3.3 Assumptions and limitations

3.3.1 Data confidentiality

As this research is done for the RNLN, a test case is built around one of their vessels. However, due to confidentiality the ship characteristics and energy profile cannot be disclosed in this document. Therefore, this thesis will not go into detail on matters that are related to the load profile or the ship. Although the data is not publicly accessible, it is made available to the supervisors.

3.3.2 PEMFC parameters

Unfortunately, it was not possible to perform tests on PEMFC's that fit the purpose of this research. Therefore, the values derived by Pei et al will be used in this research, see table 3.1. It is acknowledged that these values are not representative and that the estimated lifetime will not comply with the actual lifetime. However, using these values it is possible to adopt the method of Pei et al and study the influences of various factors on the lifetime. Idle conditions are assumed to be at 30% of the rated PEMFC power. The efficiencies as used in the PEMFC block are also assumed based on various existing PEMFC's.

3.3.3 Load

The load is a recording of the energy usage of an actual ship of the RNLN, which was recorded for the duration of two weeks with a time step of 1 second. Although this gives over 1.2 million data points, it only represents two weeks of operations. By only using this data set the assumption is made that these two weeks are representative of the whole lifetime of the ship. It is most likely that the actual operation profile of the ship will vary from the given profile. However, in collaboration with DMO and RNLN, it is decided that the profile is sufficient for this research.

3.3.4 Influence maritime environment

As mentioned the parameters for the PEMFC system are borrowed from research from the automotive industry. Possibly the (harsh) maritime environment could play a role in the degradation of the PEMFC. Yet it is unknown what the effect of the (high) salt content in the air is on the degradation. Another environmental factor that could play a role is the BOP. The BOP in a ship is of a whole other scale than the automotive industry. For example, differences in cooling characteristics could affect the degradation of the PEMFC. The effect of the maritime environment on the degradation of a PEMFC is therefore presumed to be zero for this research.

3.3.5 Balance Of Plant

During the experiments, the size of the PEMFC and battery system and the way they are used is changed. Most likely the BOP changes accordingly. This could affect the efficiency of both the PEMFC and the battery system. However, it is difficult to determine this accurately without designing the whole system in detail. Therefore, the influence of the BOP is considered to be relatively equal for all the experiments and is included in the PEMFC degradation parameters.

3.3.6 Fuel purity

The literature study showed that fuel impurities can lead to degradation of the PEMFC. However, degradation due to impurities is left out of the scope of this research because it is highly dependent on the purity of the fuel used.

3.3.7 Battery degradation

The battery system itself will also degrade over time. Various factors will influence the degradation of the battery including the SOC and C-rate used for (dis)charging. To remain focused on the PEMFC the degradation of the battery system is considered to be zero. However, in future work, it can be implemented using the method of Ten et al [65], for example.

3.3.8 Rule based energy management strategy

This research applies rule based energy management strategies only. Although it is a practical approach, it also limits the possibilities. Possible alternatives are for example; fuzzy rule based method, global optimisation or real time optimisation [58].

3.4 Experiments

The influence of three factors is the topic of this research; the size of system components, energy management strategies and module shutdown. To investigate the influence of these factors four experiments are conducted of which two are combined into one larger experiment. The experiments consist of a series of simulations in which one of these factors is changed with predetermined steps. Each of the experiments will run the same simulation using the load profile from the RNLN, but the relevant parameters are varied for each experiment. For each of the simulations the lifetime, load spectrum, battery capacity and hydrogen consumption are logged.

It was chosen to study the influence of PEMFC and battery size (experiment 1) because it is one of the most important parameters of any power plant. PEMFC power has a strong correlation with weight, volume and cost which are important parameters for each power plant.
The research of Pei et all showed that the operational profile has a strong relation with the degradation of the PEMFC. Therefore, it was chosen to study the influence of different energy management strategies, because they have a direct influence on the operational profile. In experiment 2, four energy management strategies are proposed to study the influence on PEMFC lifetime.
Inspired by the Active Cylinder Termination technology of Volkswagen, experiment 3 and 4 look into the possibility of increasing PEMFC lifetime by shutting down a part of the PEMFC system. Experiment 3 investigates two effect of timing and experiment 4 studies the effect of the number of modules a PEMFC system is divided into. Table 3.3 contains an overview of the four experiments and the variable that is changed during the experiments.

Table 3.3: Experiments conducted

Experiment	**Variable**	**Range**
1 - Component sizing	PEMFC power	1700-2500 kW
2 - Energy management strategy	Charging power and timing	30% - 50% - 70% - variable
3 - Module shutdown timing	Shutdown threshold	30% - 50%
4 - Module shutdown amount	Number of modules	1-2-3-4-5

3.4.1 Experiment 1 & 2 - Component sizing and energy management strategies

Experiment 1 (component sizing) and experiment 2 (Energy Management Strategies) are combined into one experiment where both parameters are systematically varied to obtain a matrix of results. Experiment 1 and 2 are combined because it is expected that the size of the components will have an effect on energy management and vice versa. By combining the two experiments more insight will be created into the correlation between the two factors.

Experiment 1 - Component sizing

The hybrid PEMFC system consists, amongst others, out of a PEMFC system and a battery system. The size of these components is mainly determined by the load profile to which they have to comply. Furthermore, the size of the PEMFC system and the battery system are negatively correlated with respect to the minimum energy requirements.

Since the PEMFC system is the subject of this research, the size of the battery system is based on the size of the PEMFC system. In total five combinations are simulated with a PEMFC rated power from $2500kW$ to $1700kW$ with steps of $200kW$. The battery system is sized depending on the load profile and the PEMFC power. Therefore, the simulations start with a battery system of $100kWh$ which is increased by another $100kWh$ if the combination of the PEMFC and the battery does not comply with the load profile. For this purpose, two checks are performed: Power check; the combination of PEMFC and battery must be able to deliver the maximum load of the load profile

and a capacity check; the state of charge cannot dip below 20% of the rated battery capacity. The smallest PEMFC-battery combination is found when the simulation complies with both checks.

Experiment 2 - Energy Management Strategies

In total four energy management strategies (table 3.4) are proposed; low charge, medium charge, high charge and smart charge. The standard and high low load mode are equal for all four charge strategies. The only differences between the strategies are when and at what power the battery system is recharged, see table 3.3. The low charge strategy will only charge if the load is less than 30%. The battery will then be charged with 30% of the rated PEMFC power minus the load. The medium charge strategy works in a similar way; it will charge the battery if the load dips below 50% with 50% of the rated PEMFC power minus the load. This also holds for the high charge strategy; it will charge the battery if the load dips below 70% with 70% of the rated PEMFC power minus the load. The smart charge strategy will decide when to charge or when the power is used to charge based on the SOC of the battery system. At a lower SOC, the system will charge sooner and faster than at a high state of charge. The smart charge strategy will charge at 30% if the SOC is larger than 70%, at 50% if the SOC is smaller than 70% but larger than 50%, and at 70% if the SOC is smaller than 50%. It is the hypotheses that this will result in a smaller battery.

Table 3.4: Charge strategies

Charge strategy	Threshold	Charge power
Low charge	30% of rated power	30%
Medium charge	50% of rated power	50%
High charge	70% of rated power	70%
Smart charge	SOC >70%	30%
	50% <SOC <70%	50%
	SOC <50%	70%

3.4.2 Experiment 3 & 4 - Active Module Shutdown

The stacks of the PEMFC system can be combined into modules. These experiments will investigate the influence of shutting down one of the modules when the load drops beneath a set threshold. The idea behind this experiment is that when not all modules are needed, one module can be shut down, possibly reducing the degradation of that particular module. A reduction in degradation will only occur if the degradation saved by being inactive is larger than the degradation caused by the start-stop sequence. For these experiments, the Smart charge strategy is chosen because of the results obtained during experiment 1 and 2 (see chapter 4).

Experiment 3 - Shutdown threshold

For the module shutdown, a threshold will be used to determine when to shut down one of the modules. This experiment will try two different thresholds; the idle condition of 30% and 50%. The threshold of 30% is chosen because this is also the condition at which the PEMFC system usually will shut down. The second threshold of 50% is chosen in order to see if shutting down sooner increases the benefits of shutting down a module.

Experiment 4 - Number of modules

The approach for experiment 4 is similar to that of 1 and 2. The PEMFC system is divided into 1, 2, 3, 4 or 5 modules of which one is shut down when low power mode is active. For each of these module settings, the simulation is run for a PEMFC power from $1700kW$ up to $3100kW$ with an interval of $200kW$. This will, again, result in a matrix of results. To achieve an even degradation among the modules, the degradation is monitored and the module with the largest degradation will shut down.

4. Results

In this chapter, the results from the experiments described in section 3.4 are presented. Only the most relevant results are provided. A complete overview of the results can be found in appendix B and additional figures can be found in appendix A.

4.1 Component sizing and energy management

Experiments 1 & 2 looked into the effect of PEMFC power and energy management strategies on PEMFC lifetime. With five component combinations and four energy strategies, a matrix can be formed of 20 solutions. The capacity of the battery is unique for each combination, because of the trial and error method used to obtain them as explained in section 3.4. Figure 4.1 displays the battery capacity in combination with PEMFC power obtained during experiments 1 & 2. The variation of the results is relatively large when looking at fuel cell sizing, but small between the different energy management strategies. Systems with less PEMFC power depend more often on the battery system, which thus has to be larger. Due to this relation, the capacity depends also on the load profile. For this particular profile the capacity increases (on approximation) exponentially with respect to the decrease of the PEMFC power. It is expected that battery systems with a capacity of 1000 kWh or more are not suitable for the RNLN ship the load originates from due to the large volume of the system.

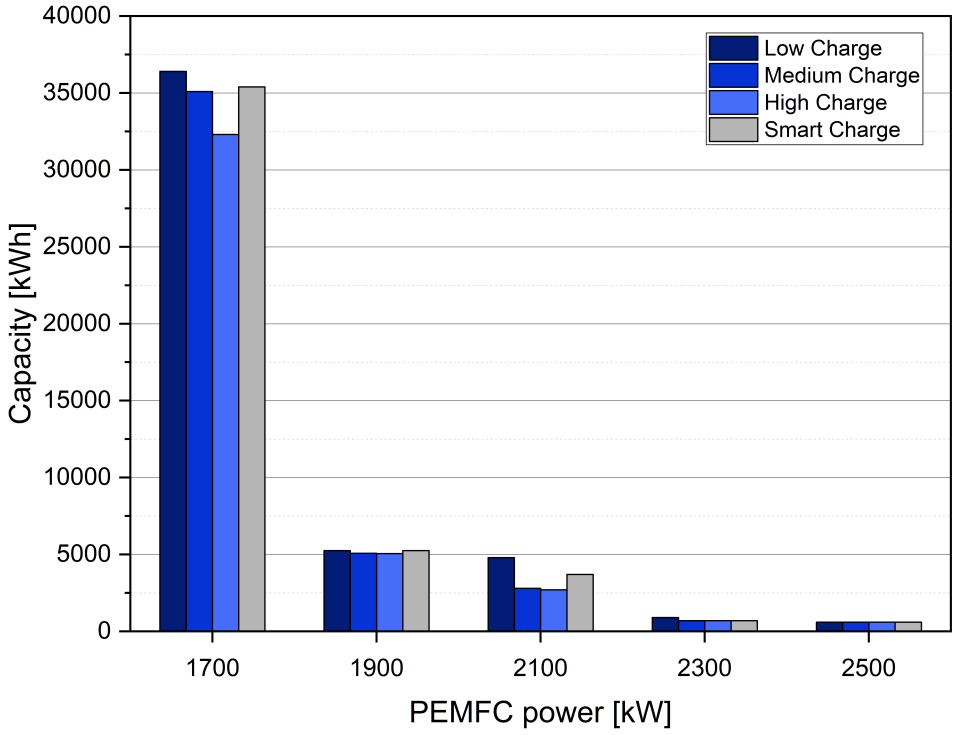


Figure 4.1: Battery capacity obtained during simulations vs PEMFC power - experiment 1 & 2

4.1.1 Component sizing

The simulated lifetime of the 20 combinations is shown in figure 4.2. It can be observed that as the PEMFC power decreases also the lifetime decreases in most cases. Furthermore, low charge outperforms medium and high charge for all the combinations. Additionally, the best performing management strategy overall seems to be the smart charge, which is especially effective for the lower PEMFC power combinations.

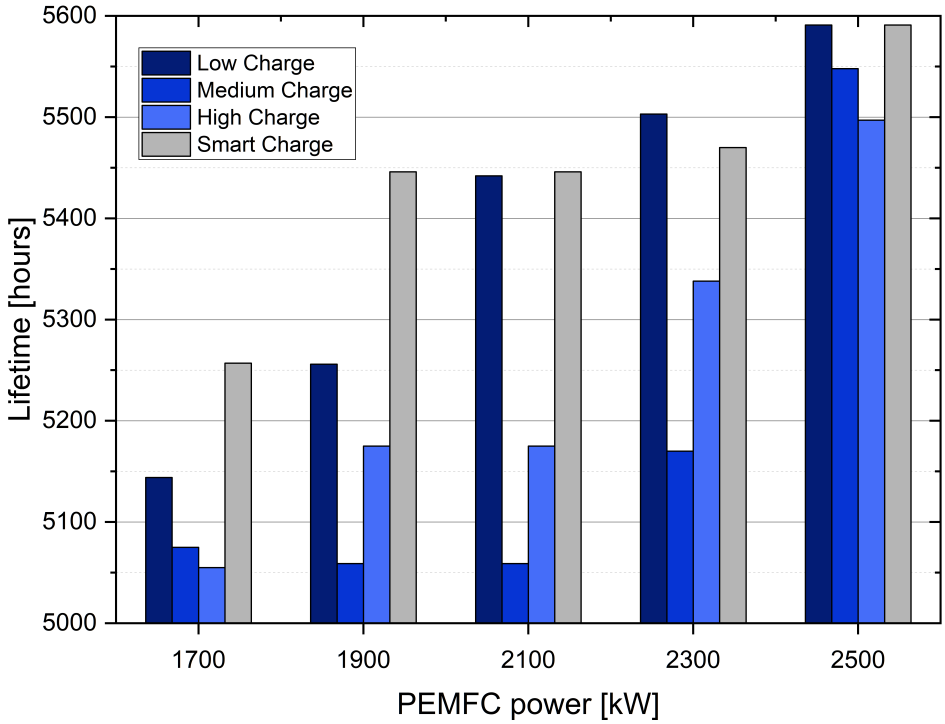


Figure 4.2: Lifetime vs PEMFC power - experiment 1 & 2

The decrease in lifetime for decreasing PEMFC power can be explained by the increase of the time spent in the high load condition, as shown in figure 4.3. Smaller fuel cells will spend relatively more time in the high load condition than larger fuel cells for the same energy profile. The PEMFC parameters used for the simulation show that the PEMFC degrades faster in high load condition compared to the low load condition. Spending more time in the high load condition will thus lead to a decrease in PEMFC lifetime.

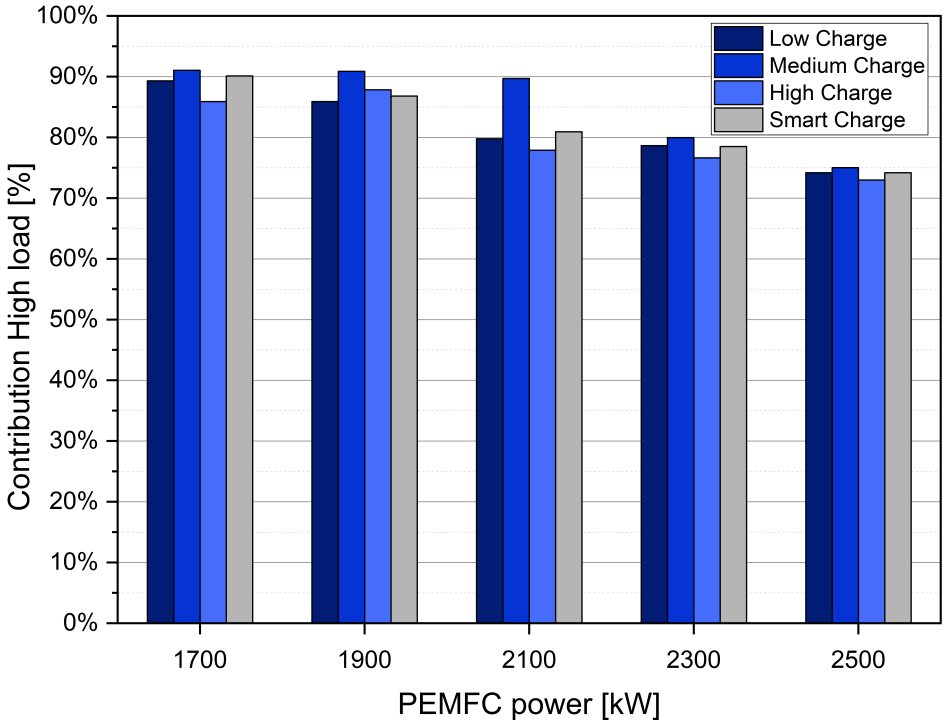


Figure 4.3: Contribution high load condition vs PEMFC power - experiment 1 & 2

4.1.2 Energy management

Although a difference in lifetime due to management strategies can be observed, the differences are smaller compared to the sizing experiment. Figure 4.4 shows the estimated lifetime for each management strategy. Note, this figure represents the data from figure 4.2 sorted by energy management strategy. It can be observed that the low charge strategy performs better than the medium and high charge strategy. Although the low charge strategy performs better for the combination of 2300 and 2500 kW, the smart charge strategy has a better performance overall.

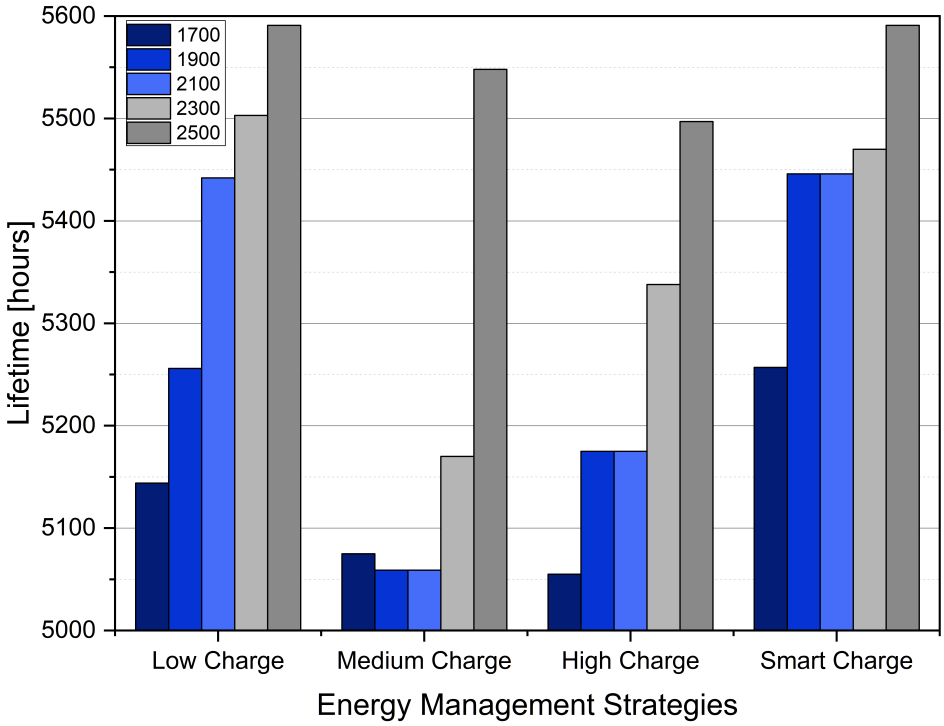


Figure 4.4: Lifetime vs energy management strategies - experiment 1 & 2

The differences in degradation can be explained by the number of load changes, figure 4.5, and time spend in high load condition, figure 4.6. It is clear that the medium and high charge strategies experience up to 5 times as many load changes as the low charge strategy. Although the smart charge strategy is a combination of the other three strategies, it does not experience as many load changes and in some cases even less than the low charge strategy.

Based on the contribution of the number of load changes, the medium charge strategy would perform better than the high charge strategy. However, figure 4.6 shows that the medium strategy spends a large amount of time in the high load condition, from which is known that it leads to more degradation than the low load condition. The differences of the load changes and high load condition together explain the lifetime estimations from figure 4.4.

The degradation as a result of an energy management strategy can be lead back to the load spectrum that is derived from the experiment. The degradation conditions that occur during the simulation partly depend on the strategy that is chosen.
It is expected that values of the load spectrum of the medium strategy lie between the values of the low and high strategy. However, the experiments show that this is not the case. This is most likely due to an unforeseen unfortunate combination of load profile and energy management strategy. The load will then cycle around the boundary between low and high load condition, causing an increase in load changes.

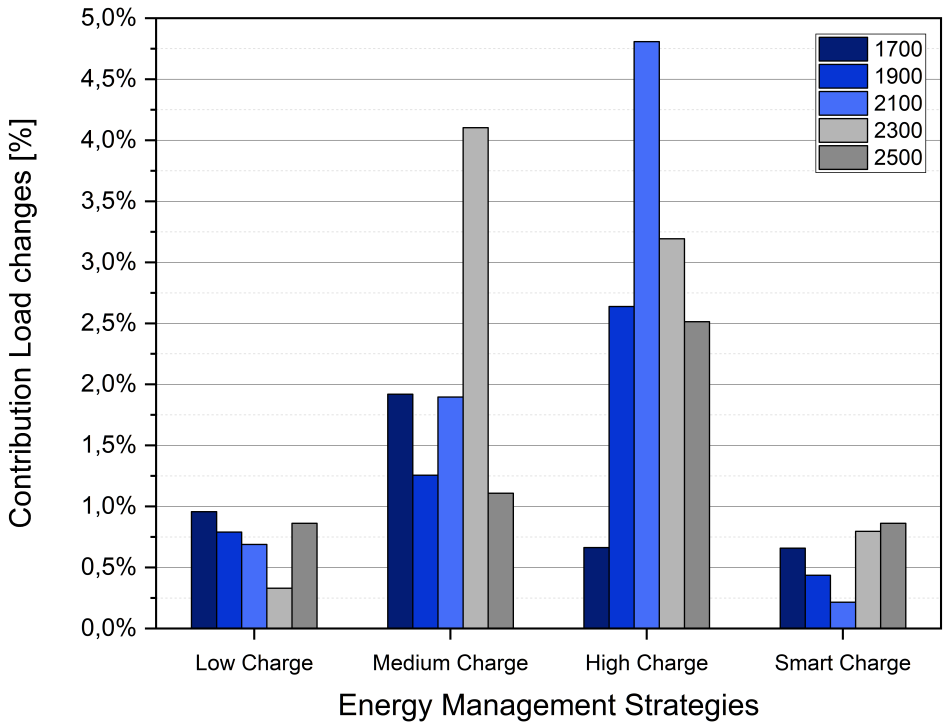


Figure 4.5: Contribution load change condition vs energy management strategies - experiment 1 & 2

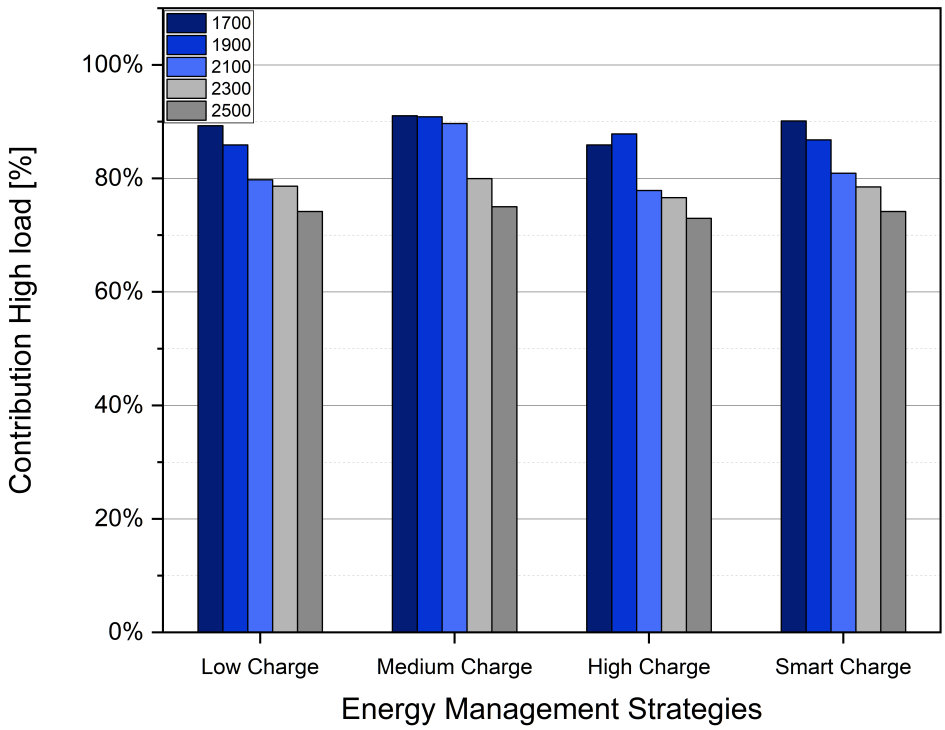


Figure 4.6: Contribution high load condition vs energy management strategies - experiment 1 & 2

4.1.3 Conclusion experiment 1 & 2

The results and conclusions from experiments 1 and 2 together answer the second sub-question: "How do the size of the fuel cell and the battery in a hybrid system contribute to the lifetime of a proton exchange fuel cell?"

It can be concluded that PEMFC systems with a larger power show less degradation due to less time spend in the high load condition, which has a higher degradation rate than the low load condition. Furthermore, the experiments showed that management strategies do have an influence on the lifetime of a PEMFC. Strategies with a faster charging setting showed more degradation than less powerful strategies. This can be explained by the increase in load changes caused by the charging. Additionally, it is found that some combinations of energy management strategy and load profile can cause unexpected deviations from the results.

4.2 Module shutdown

The third experiment looked into the effect of shutting down a part of the PEMFC system (module) and more specifically, the moment or threshold at which the module is shut down. The smart charge strategy is used for the modules shut down experiment because of its performance overall. Experiments 3 and 4 are performed for the range of PEMFC power. However, the top of the range is extended from $2500kW$ to $3100kW$ resulting in a range from $1700kW$ tot $3100kW$ with steps of $200kW$. The range is extended because it is expected to show large improvements in PEMFC lifetime for large PEMFC power in this experiment. The model will monitor the load for each module and will compose a load spectrum accordingly. The load spectrum will then be used to estimate the lifetime for each module of which the average is taken to obtain the average estimated lifetime of the PEMFC system.

4.2.1 Shutdown threshold

Two variants of the smart charge strategy are simulated in experiment 3. Both of the variants contain three modules that together form the whole PEMFC system. The results from these two variants are compared with the results of the smart charge strategy from experiment 2, which is not divided into modules. The first variant will shut one of the modules down if the load drops below 30% and the second at 50%. Figure 4.7 shows the estimated lifetime for all three variants for the selected range of PEMFC power.

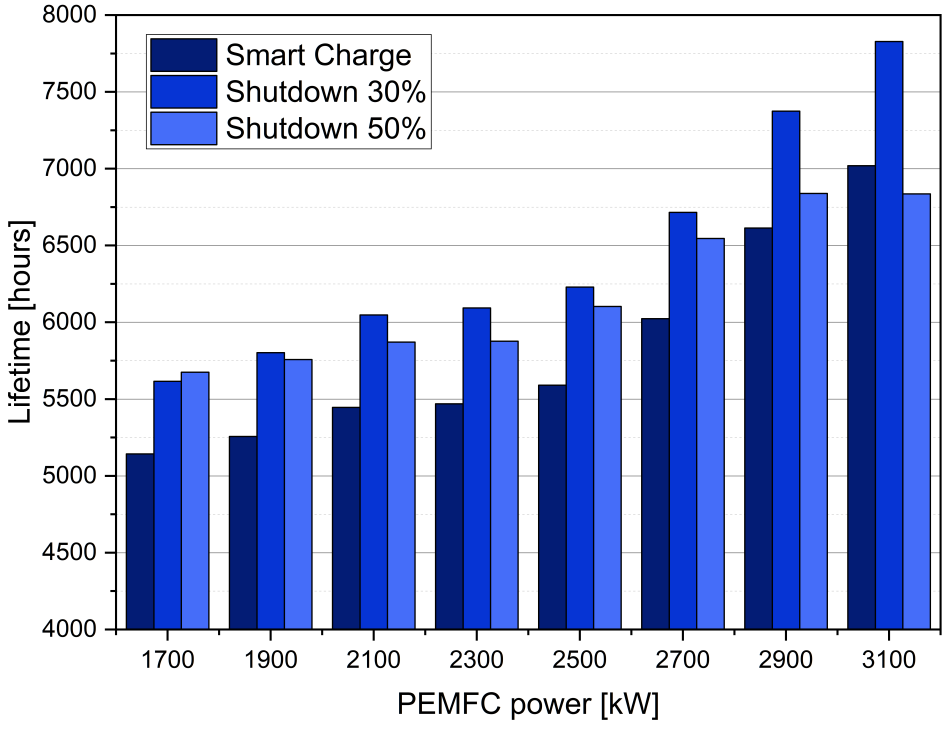


Figure 4.7: Lifetime vs PEMFC power - experiment 3

Figure 4.7 shows that, as expected, the lifetime for all variants decreases when the PEMFC power also decreases, which is explained in section 4.1.1 using experiment 1. Furthermore, the 30% variant shows significant improvement in lifetime over the whole range. The 50% variant has a larger estimated lifetime than the standard smart charge strategy, except for the largest PEMFC power. However, in most cases, the 50% variant shows less improvement compared to the 30% variant.

The differences between the 30% and the 50% variant can again be explained with the time spend in the high load condition and the contribution of the number of load changes, as figures 4.8 and 4.9 show below. It is observed that the 50% variant spends significantly more time in high load condition. This can be explained by the effect of shutting down modules. When one of the modules is inactive the other two modules will have to work 1.5 times as hard and thus spend more time in high load condition. This effect is most noticeable at the high end of the PEMFC range where most of the time low load condition is active. A second explanation comes from a significant increase in load changes as figure 4.9 shows. The 50% variant will shut one of the modules down sooner than the 30% variant. This will lead to more load changes because the other modules have to work harder.

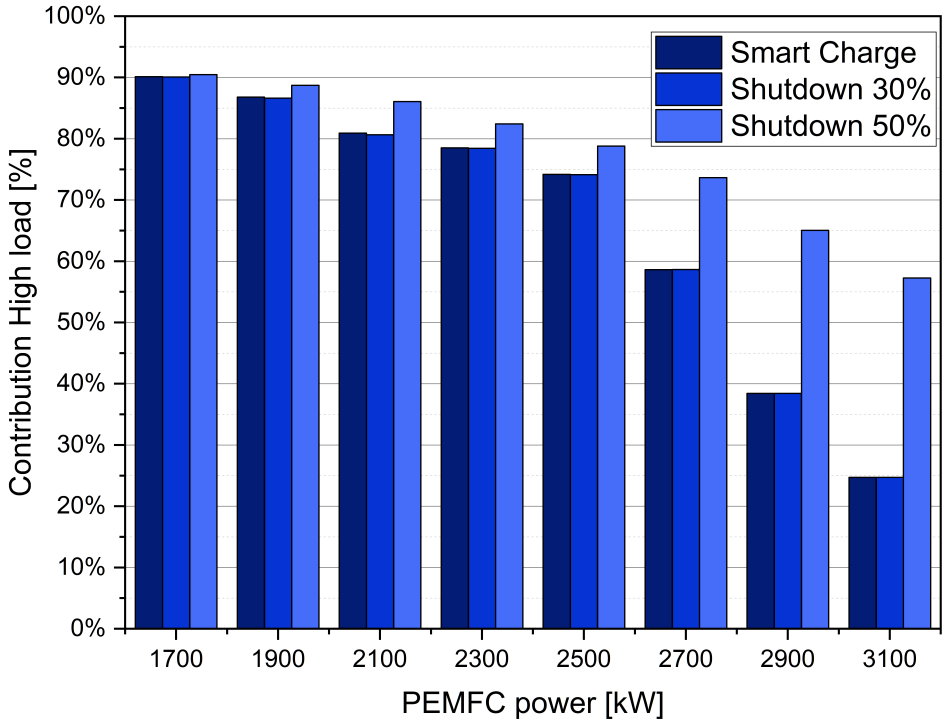


Figure 4.8: Contribution high load condition vs PEMFC power - experiment 3

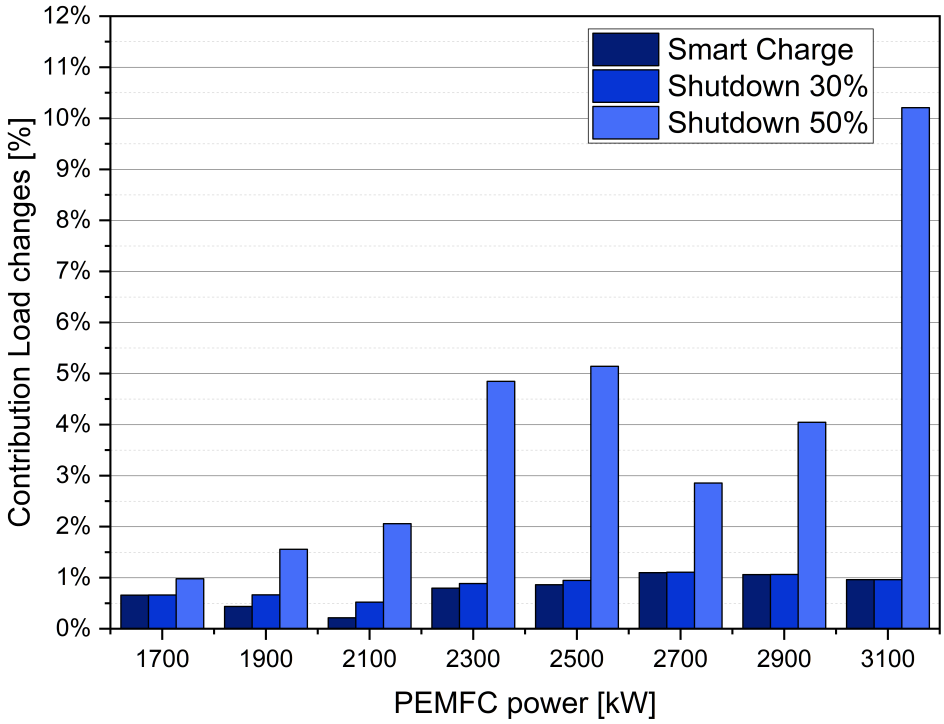


Figure 4.9: Contribution load change condition vs PEMFC power - experiment 3

Although the effects on PEMFC lifetime appears to be limited it is interesting to look at the contribution of the start-stop condition. Figure 4.10 shows that the differences are relatively small between the smart charge strategy and the 30% variant. One might expect the 30% variant to show more degradation due to the start-stop condition when more starts and stops are made. However, when the load drops below 30% only one of the three modules will shut down, thus preventing the other two from having to shut down. Therefore, the number of shutdowns per module appears to be roughly equal to the number of shutdowns with the standard smart charge strategy.
The 50% variant shows an even lower contribution of the start-stop condition. Due to the lower shutdown threshold, the modules are not only shut down sooner, but they also remain inactive for a longer period of time until the limit of 50% is crossed again. This decreases the number of start-stop movements. However, the decrease in start-stop movements is not enough to compensate for the increased amount of time spend in high load condition and the increased number of load changes.

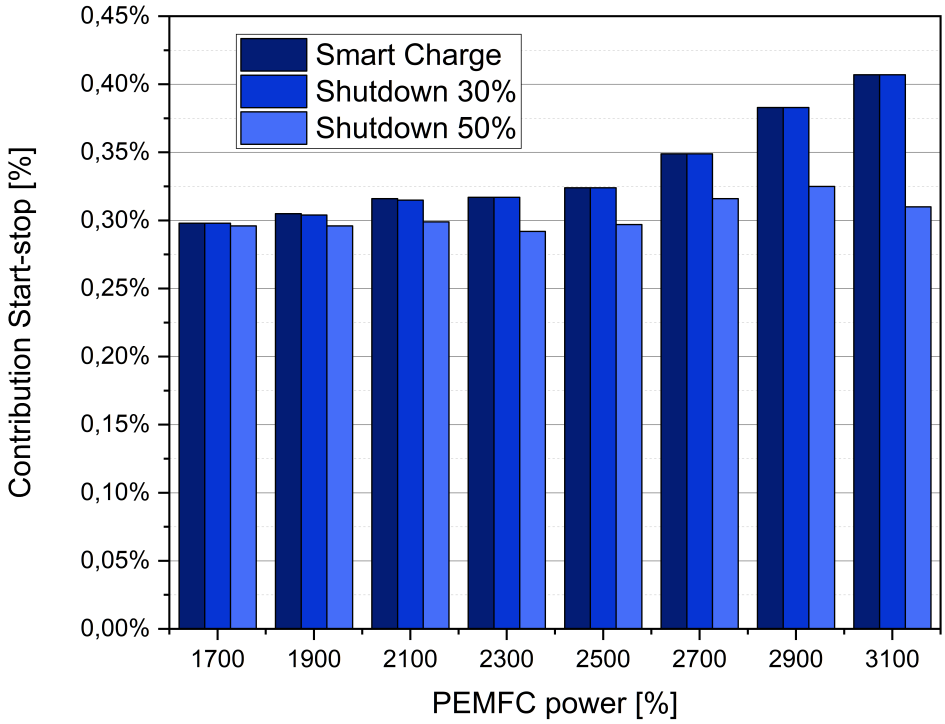


Figure 4.10: Contribution start-stop condition vs PEMFC power - experiment 3

4.2.2 Number of modules

The last experiment, number 4, studies the influence of the number of modules in which the PEMFC system is divided. During this experiment, a range of 1 to 5 modules is simulated. The configuration with 1 module is the baseline, which is the smart charge strategy with a PEMFC power range from $1700kW$ to $3100kW$. Each variant shuts down one module at the 30% threshold.

The estimated lifetime for each variant is shown in figure 4.11. The lifetime of the different variants is expressed in operational time for a more accurate comparison. The lifetime estimated by the model is divided by the time the modules are active to obtain the operational lifetime. By doing so the estimated lifetime is extrapolated to the time the PEMFC can be operational. In general, the estimated lifetime increases with the number of modules with the exception of the 2 modules variant. Furthermore, the 3 and 4 modules variants appear to perform equally good in terms of lifetime. The sections below will first explain why the 2 modules variant deviates, followed by an explanation on why the variants with module shutdown perform better than without and last the reason the 5 modules variant has a significant better lifetime performance is mentioned.

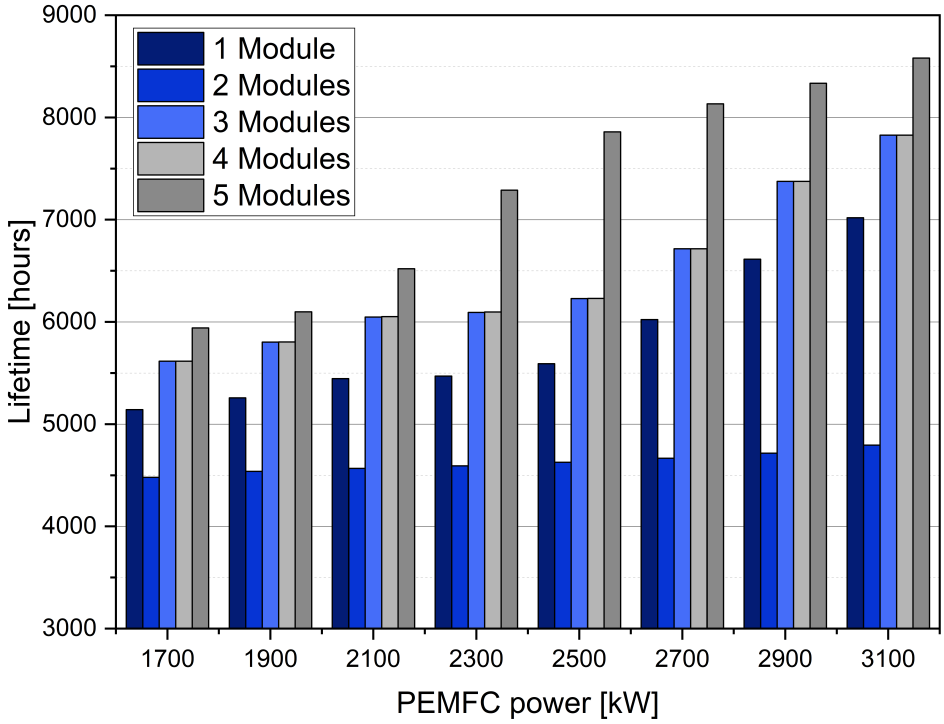


Figure 4.11: Lifetime vs PEMFC power - experiment 4

The variant with 2 modules has deviating results compared with the other variants. As figure 4.12 shows, this can be explained by the significant increase in the number of load changes. The increase in load changes can be explained by the number of modules. When a module is shut down, load is divided amongst the remaining modules. Systems with more modules will have a relatively large load when one module is inactive compared to systems with fewer modules. For example, a system with 5 modules has 80% of its rated power active with one module inactive and a 3 module system only 66.67%. Therefore, the system with 2 modules will switch more often between high and low load condition.

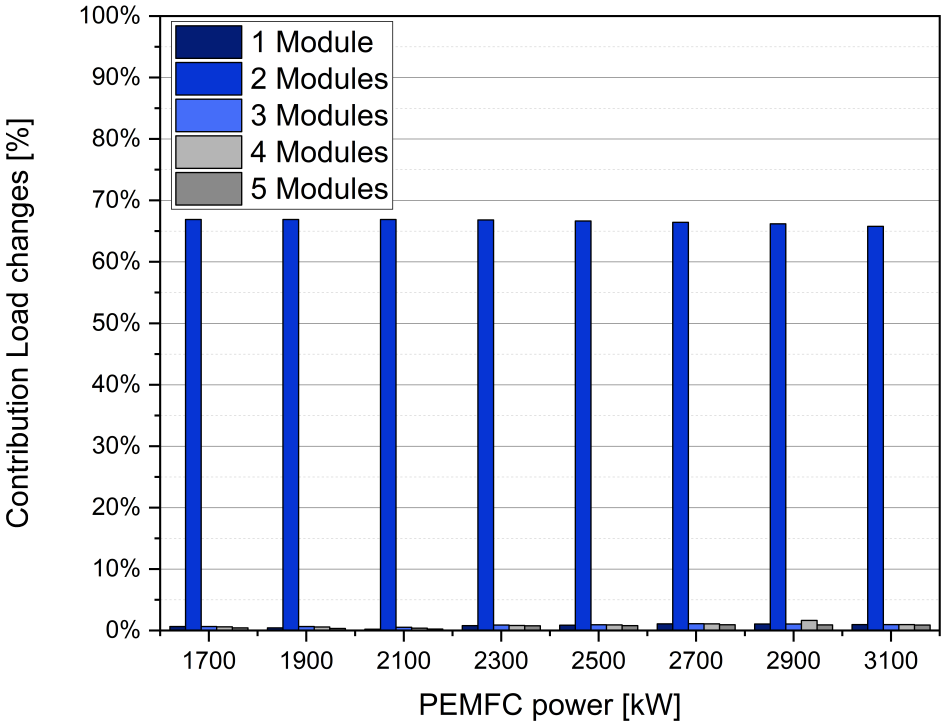


Figure 4.12: Contribution load changes condition vs PEMFC power - experiment 4

During previous experiments, the differences between variants are explained using the load spectrum. However, the differences in the load spectrum are not large enough to justify the differences in lifetime for variants with or without module shutdown. For example, the contribution of the high load condition, figure 4.13, is fairly equal for the 1, 3 and 4 module variants. Hence the differences are not because of the load conditions as felt by the PEMFC. Since the load conditions only describe the degradation of the PEMFC when it is active the answer must lie in the time the PEMFC is inactive. Figure 4.14 show the average time each module is active for the different variants. It shows that the 3, 4 and 5 module variants have an active module time of roughly 90%. Which explains the ≈ 10% increase in lifetime of the 3 and 4 module variant. However, the 5 module variant also has an active time of ≈ 90% but has an even higher estimated lifetime. This can be explained by the load spectrum, which shows a decrease in the high load condition for the 5 module variant as can be seen in figure 4.13.

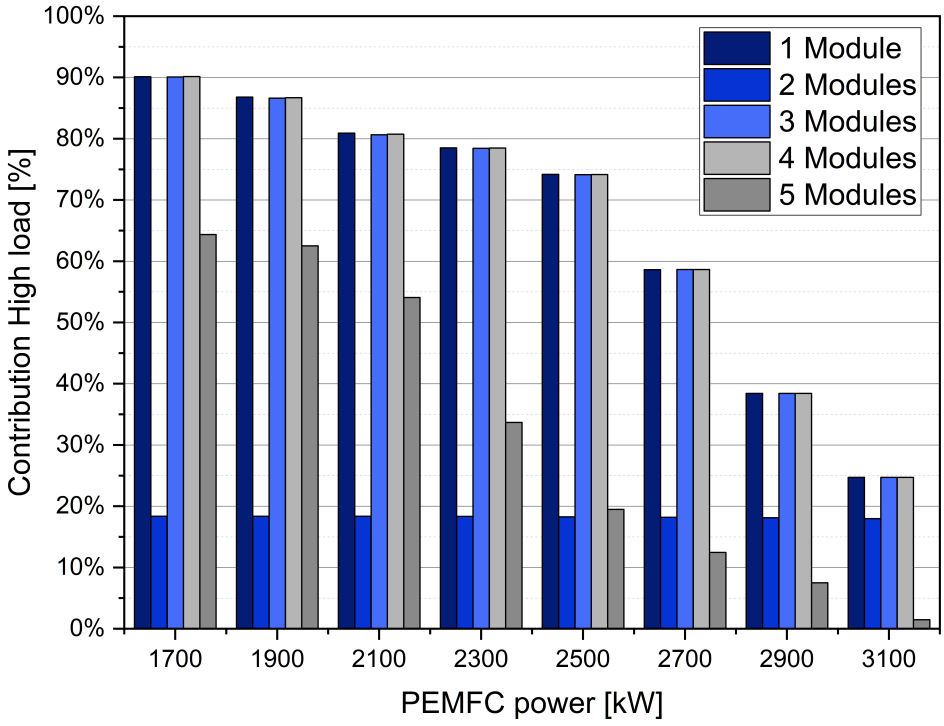


Figure 4.13: Contribution high load condition vs PEMFC power - experiment 4

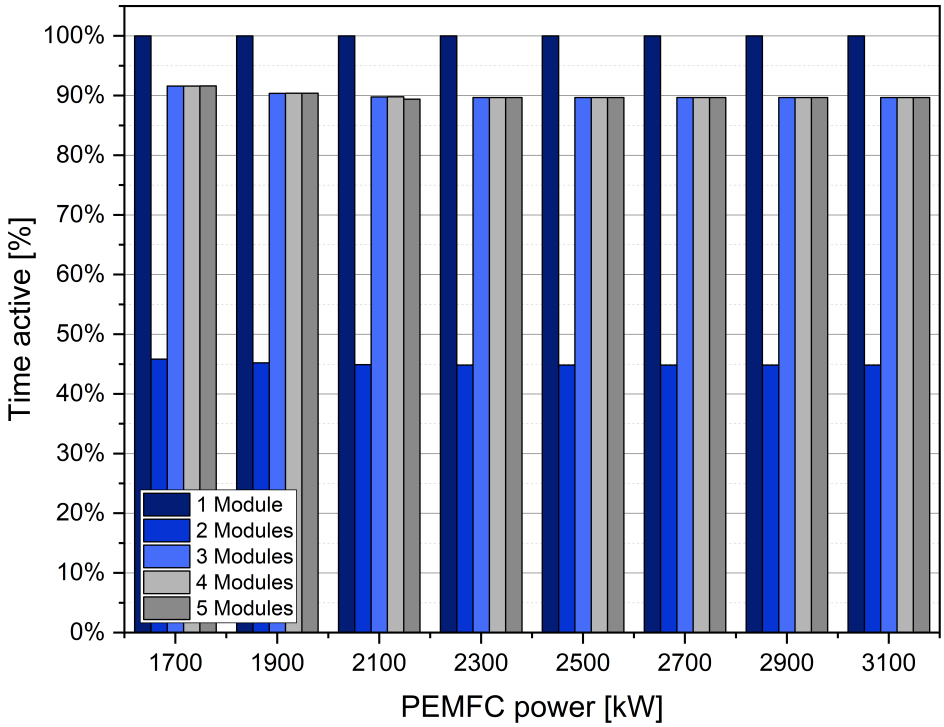


Figure 4.14: Average active time per module vs PEMFC power - experiment 4

The deviation of the 2 module variant, the 5 module variant and the fact that there is no big difference between 3 and 4 modules show that there are multiple factors that play a role. The combination of the number of modules, load profile and energy management strategy together determine the lifetime of the PEMFC. When the load profile fluctuates around a power level where a management setting is in place or a module shuts down, unexpected situations can occur that can cause more/less degradation.

4.2.3 Conclusion experiment 3 & 4

The results from experiment 3 and 4 show that shutting down modules can increase the number of hours the PEMFC system can operate. However, timing is of the essence. Experiment 3 showed that shutting down a module too soon can counteract this effect because of an increase in load changes and more time in the high load conditions. Experiment 4 showed that the number of modules can have a positive or a negative influence on the lifetime. In general, more modules tend to result in a longer lifetime.

The results from both experiments also showed that the combination of load profile, energy management strategy and number of modules together can result in unexpected results due to unfortunate coincidences. It shows that despite general trends certain combinations can still lead to less performance and thus must be investigated beforehand.

With these results, the third sub-question can be answered: "Does the number of active fuel cell modules have an influence on the operational lifetime expectancy of the proton exchange membrane fuel cells?"

4.3 Fuel consumption

As explained in section 3.4 the fuel consumption is estimated using a generic fuel consumption curve based on the load. Figure 4.15 shows the fuel consumption for experiments 1 and 2. Note that these results are a rough figure and do not include the various losses, e.g. due to charging. From this figure an overall trend is observed; the fuel consumption is larger for smaller fuel cells. This can be explained by the efficiency of the fuel cell. The efficiency curve that is used shows that the efficiency is larger for smaller loads and thus decreases for larger loads. The smaller fuel cells operate more often in high load condition and will thus have a larger fuel consumption.
Furthermore, it can be observed that the high charge strategy has the largest fuel consumption. This is because the high charge strategy will put the fuel cell more often in high load condition and uses more energy to charge the battery system.

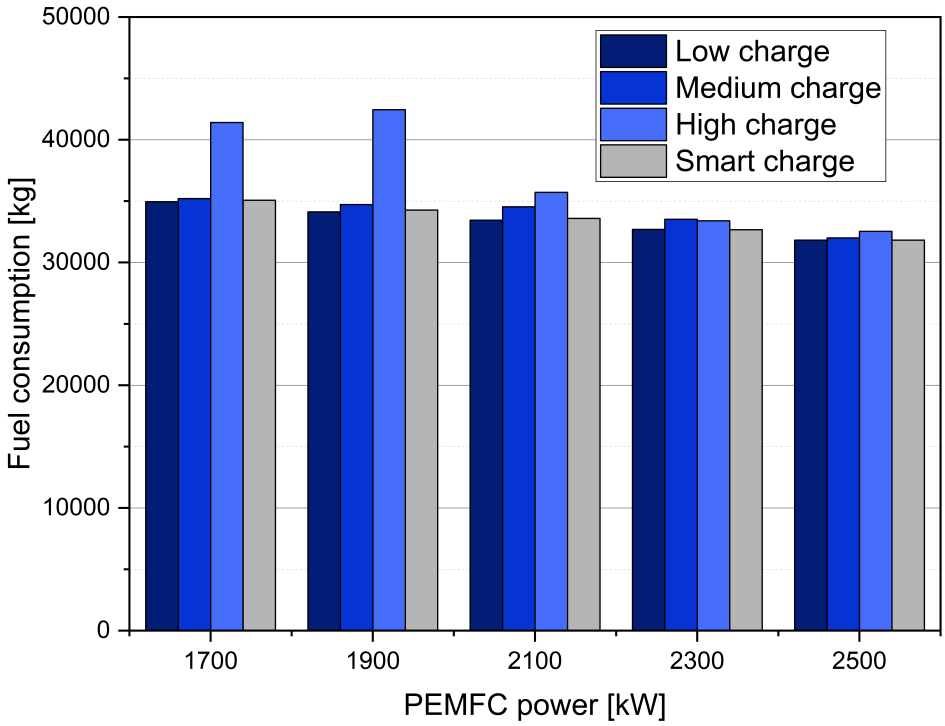
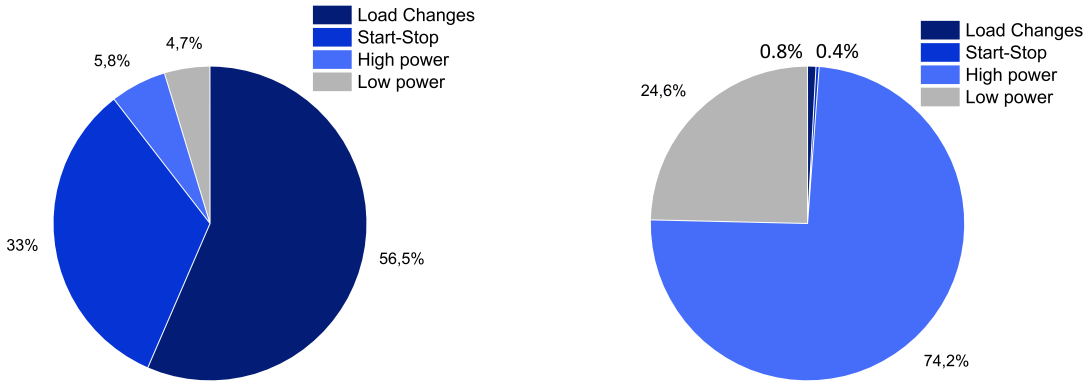


Figure 4.15: Estimated fuel consumption vs PEMFC power - experiment 1 & 2

4.4 Sensitivity study

The lifetime estimations in this research depend on two factors; the load spectrum and the corresponding PEMFC parameters. All four experiments show a vastly different load spectrum than obtained by Pei et all during the original studies as figure 4.16 shows. The spectrum of Pei, figure 4.16a is from a line bus which endures much more load changes and stops than the naval profile used for the second spectrum of figure 4.16b. Although the load spectrum is different for each combination during the experiments, the overall trend is that load changes and start-stop conditions have a negligible contribution to the overall degradation. Because the same PEMFC parameters are used as the spectrum from Pei it can be concluded that the difference comes from the load profile.



(a) Load spectrum from [52]

(b) Load spectrum smart charge 2500kW

Figure 4.16: Load spectrum experiment 1 & 2

One of the assumptions of this research is that the PEMFC parameters of Pei are valid. However, it is most likely that they are not representative since the tests are done over 15 years ago on a much smaller fuel cell. Therefore, a sensitivity analysis of the PEMFC parameters is necessary to find whether the results of this research are still valid if the PEMFC changes significantly. For this purpose, it is assumed that the load spectrum of figure 4.16b is representative for all experiments. It can be seen that if the load change parameter or start-stop parameter are five times larger than they are now, the load spectrum would still look roughly the same. Hence the method is relatively insensitive for the load changes and start-stop parameter. However, if the high or low load condition parameter were to change with a factor of five the results could be totally different. However, this would only be the case if only the low *or* the high load condition parameter changes.

5. Discussion

The goal of this thesis is to study the influences of component sizing, energy management strategies and modules shut down on the lifetime of a proton exchange membrane fuel cell. For this purpose, a model is created that simulates a typical power generation system using a PEMFC and a lithium-ion battery. In this model, the lifetime estimation method of Pei et al is adopted to find the expected lifetime of the PEMFC and the load spectrum obtained from simulations. To test the model, four experiments were conducted using the model to study the influences on PEMFC lifetime. Although the absolute results are of limited value due to assumptions and limitations, the observed relations between the parameters offer valuable insights into the driving mechanisms. This chapter will discuss the results, limitations and assumptions and their effect on the conclusions of this research.

Results

The results from experiment 1 show that increasing the installed PEMFC power leads to decreasing degradation. This can be explained by the fact that PEMFC systems with larger rated power will experience relatively lower part-load conditions compared to lower power PEMFC systems. Low power conditions lead to less degradation because various degradation mechanisms occur less often at a lower power, such as for example fuel starvation [38]. Although a general trend can be observed from the experiment, the results do not show an optimal PEMFC size. Repeating the experiment with a much larger range could lead to an optimum. It is expected that at higher PEMFC power, the load drops below the idle condition too often causing the PEMFC system to shut down, increasing the degradation due to start-stops. If the increase in degradation becomes larger than the decrease due to the PEMFC power increase an optimum is reached. Furthermore, the component sizing experiment has not looked into the volume and weight of the simulated systems. It is possible that the weight/volume/cost limit of a to be designed ship is reached before the optimum lifetime is reached. Adding weight and volume computations to the simulations will provide more insight into the feasibility of the system.

Experiment 2 showed that energy management strategies that charge earlier and with more power cause more degradation due to an increase in load changes and more time spend in the high load condition while only small decreases in battery capacity are obtained. One of the reasons a battery system is added is to avoid the PEMFC from having to shut down. The results show that the benefit of fewer shutdowns is outweighed by the increase in load changes and time in high power condition. Experiment 2 showed the effect of the chosen management strategies on the lifetime of a PEMFC system. However, many more management strategies could be applied such as done by Hwang et al. [31] and Kim et al. [35]. Also, the battery system shows degradation due to cycling loads. Future research should also look into battery degradation to study the relation between PEMFC and battery lifetime as a consequence of management strategy.

Shutting down modules is beneficial for PEMFC lifetime if the degradation saved, because the PEMFC is inactive, is larger than the extra degradation due to increased load changes and high power condition. Experiment 3 shows that shutting down modules can prolong the operational lifetime. However, shutting down too early is less beneficial due to a vast increase in load changes and time in high power condition. In other words, shutting down modules increases lifetime if the module remains inactive long enough. Although only two options were explored, there must be an optimal moment to shut down a module. The optimal moment could be dependent on the number of modules the PEMFC is composed of. Future research could look into the possibility of optimising the shutdown moment. Furthermore, the possibility of human interaction should be looked into, because the crew might know in advance whether the module can remain inactive for a longer period or not. This can be done either by onboard experiments or by the use of algorithms that predict future demand.

The main observation from experiment 4 is that dividing the PEMFC system on more modules seem to improve PEMFC operational lifetime. This can be explained, for the range the experiment is performed in, using the load spectrum. Due to the large improvements obtained during this experiment further research is recommended. It is expected that extending the range of modules will lead to further improvement of PEMFC lifetime and possibly an optimum number of modules for this particular combination of load, energy management and PEMFC size. Furthermore, shutting multiple modules down simultaneously could expand the possibilities and improve PEMFC lifetime even further. Experiment 4 only studied the effect on PEMFC lifetime. However, the number of modules is likely to have an effect on the efficiency at which the PEMFC system operates and the complexity of the system. Complexity due to the increased number of components and system size but also with respect to maintenance.

It must be noted that although all four experiments show an overall trend, some of the results show outliers, as can be seen in figures 4.2, 4.9 and 4.12. However, as explained in chapter 4, all of these outliers are due to the particular combination of load, energy management, PEMFC size and number of modules. These outliers are not considered to be important for this research, because they can be easily fixed if such an unfortunate combination would occur in an actual system. The management systems software could be changed to a strategy more beneficial for the PEMFC lifetime.

Monitoring the hydrogen consumption during all four experiments has led to two findings: 1) larger PEMFC systems are more efficient and 2) charging the battery costs energy and thus increases the fuel consumption. Although fuel economy is not in the scope of this research these findings should be included in future research. Together with the PEMFC lifetime, fuel consumption can be used to compute the total cost of ownership for a period of time.

The sensitivity analysis showed that the sensitivity for the PEMFC parameters is limited. It is likely that the estimated lifetime will differ. However, the discovered relations will probably still be valid. Furthermore, it is observed that the load profile has the largest effect on the estimation of PEMFC lifetime using the method of Pei et al. Although the relations are expected to remain valid, further studies of the degradation behaviour of PEMFC based on the load spectrum for newer and more powerful PEMFC is advised. It is expected that newer and larger PEMFCs will show less degradation per hour or per cycle than the one used by Pei et al. This will result in a longer estimated lifetime as advertised by most manufacturers.

Limitations and assumptions

The results obtained with the model are only valid for the load profile that is used. Although the load profile is representative for a range of ships and operations it does limit the applicability of the results. From the experiments, it has become clear that the load has a large influence on the load spectrum as figure 4.16 shows. Furthermore, the experiments showed that some specific combinations can result in an unexpected short lifetime in which the load plays an important role.

Due to limited availability, the PEMFC parameters from another study were used. These parameters originate from a $10kW$ fuel cell from over 15 years ago. This limits the validity of using these parameters for this research. However, due to a lack of an alternative, it was chosen to use these parameters. This research has shown that the method used is suitable for investigating the chosen influences on PEMFC lifetime. Further studies must be conducted to obtain representative PEMFC parameters that can be used for more accurate PEMFC lifetime predictions. Investigating multiple PEMFC's from different sizes and manufactures is recommended because the PEMFC lifetime estimation is heavily dependent on the PEMFC parameters.

The maritime environment can be harsh for equipment because of the high or low (water) temperatures, the salt content of the air or the vibrations due to other equipment. The influence of this environment on PEMFC lifetime is not yet clear and is not taken into account in this research. The research used for this study all originates from the automotive industry where the maritime environment is not applicable. It is therefore recommended to perform further studies into the

influence of the maritime environment on PEMFC lifetime.

The performance of the balance of plant is directly related to the operating temperature, water content and purging procedures during start-stop conditions. Therefore the BOP is likely to have an influence on the lifetime of a PEMFC. During the experiments, a range of PEMFC power is simulated of which it is likely that the BOP also changes. The effect of the BOP is considered to be equal for all combinations of PEMFC in the range. It is expected that the differences in a lifetime are negligible, but this has to be verified through additional studies.

It is known that PEMFC's have a low tolerance for fuel impurities [38], in particular for carbon-monoxide and sulphur. These effects are not taken into account in this research, but they can have a large effect on the lifetime of the PEMFC and the catalyst layer in particular[67]. It is expected to have a significant influence on the lifetime of a PEMFC. Future research is particularly interesting when the combination of internal/external reforming is taken into account.

The results and the developed method of this research can be applied in future studies. For example in lifetime cost estimations. PEMFC power generation on board of ships is still relatively new and will in most places replace a diesel engine or something similar. For most applications, cost is an important factor and will have a large impact on the system design. Another example of a future study is research into the lifetime of PEMFC systems for various operational profiles, to study the effect of ship type or operation on PEMFC lifetime.

6. Conclusion

This research aimed to provide insight into the influences of component sizing, energy management strategies and shutting down modules on the lifetime of a proton exchange membrane fuel cell. The goal was to be able to take PEMFC lifetime into account in the design phase of a power generation plant of a ship. Using simulations, valuable relations are discovered that are useful when designing for maximum PEMFC lifetime. Although limitations are in place, the method used has proven its applicability to study the influence of system parameters on PEMFC lifetime.

For this thesis, the following main research question was defined: *"How is the lifetime of a proton exchange membrane fuel cell in a hybrid system in combination with a battery affected by the system design parameters and maritime operations?"*

The research question is answered using the answers to the sub-questions as defined in chapter 1.

- *How can the degradation of a proton exchange membrane fuel cell be determined based on a load cycle?* - The literature study showed that methods exist to quantify PEMFC degradation based on operating conditions. One method in particular showed that the load profile can be analysed leading to a load spectrum of four load conditions. The corresponding PEMFC degradation parameters for each condition can be found using laboratory tests.
- *How do the size of the fuel cell and the battery in a hybrid system contribute to the lifetime of a proton exchange membrane fuel cell?* - Experiment 1 showed that PEMFC systems with a larger rated power show less degradation due to less time spend in the high load condition, which has a higher degradation rate than the low load condition.
- *In what way does energy management of the hybrid system influence PEMFC degradation?* - From experiment 2 it can be concluded that energy management strategies have an influence on the lifetime of a PEMFC. Strategies with a faster charging setting showed more degradation than slower strategies. This can be explained by the increase in load changes caused by the charging.
- *How does the number of active fuel cell modules affect the operational lifetime expectancy of the proton exchange membrane fuel cells?* - Experiments 3 and 4 show that shutting down modules during low load conditions can be beneficial for PEMFC lifetime. However, it was shown that timing is of the essence. Additionally, the number of modules the PEMFC system is divided into has a large impact on the lifetime gained from shutting down modules. The estimated lifetime increased for each added module for the range tested.

Additionally, it was found that generally speaking, higher rated PEMFC power leads to a lower fuel consumption due to the higher efficiency in part load. Furthermore, charging the battery system reduces the overall efficiency and thus increases fuel consumption. With the model, relations between PEMFC lifetime and system parameters can be made based on the load profile, the system layout and the energy management strategy. However, due to the limitations and assumptions that are in place, the lifetime estimation is not accurate. This can be improved by extending the model and performing additional studies as suggested in chapter 7.

7. Recommendations

This research aimed to uncover the influences of important design parameters on PEMFC lifetime. The literature study and the experiments have successfully led to the discovery of relations between component size, energy management strategy, shutting down modules and PEMFC lifetime. Additionally, the limitations and results of this research show that more research needs to be done for a more accurate lifetime estimation. This chapter will elaborate on the future research that needs to be done:

- **Extending the range of experiment 1:** Experiment 1 is conducted for a limited range of PEMFC rated power. It is recommended to extend the range of experiment 1 to investigate the possibility of a (local) optimum for PEMFC power and PEMFC lifetime. The current range of experiment 1 showed an increasing line, but it is expected that the lifetime will drop beyond a certain PEMFC power due to an increase in start-stop movements. Additionally, weight and volume could be added to the experiments to incorporate the feasibility of such a system. It might be the case that the optimum PEMFC size is too large, heavy or expensive for its purpose.
- **Include battery lifetime:** During this research only the effect on the lifetime of the PEMFC is taken into account. It is unknown what the effect of the system parameters is on the lifetime of the battery system. It is recommended to include battery degradation in order to be able to ensure both PEMFC and battery lifetime.
- **Human interaction:** This research has applied rule based energy management strategies. Although effective and simple it does not take into account what will happen in the future, it will base its outcome on the current situation. Possibly, the crew will know in advance if a module can be shutdown for a long period or not. This will avoid unnecessary shut down of modules and an increase in PEMFC lifetime. It is recommended that the effect of human interaction on energy management and thus PEMFC lifetime is researched.
- **Extended module shut down experiments:** Experiment 4 showed promising results by prolonging the PEMFC lifetime with up to 20%. However, only a small range of modules was tested. Testing with a larger range could result in an even larger increase in PEMFC lifetime or an optimum number of modules. Additionally, shutting down more than one module at the time should be investigated in combination with the extended range to study the relation between the number of active modules and PEMFC lifetime. Furthermore, as cost and complexity increase with the number of modules, it is expected that a maximum number of modules will be found during this research.
- **Load profile sensitivity:** The experiments are all conducted for one load profile of two weeks and, as shown in section 4.4, resulted in quite a different load profile compared to an automotive application. It is recommended to perform additional simulations with a variety of load profiles to study the influence of the load profile on the findings of chapter 4.
- **PEMFC parameters:** The PEMFC parameters used for this research originate from the work of Pei et al [52]. However, these parameters were derived from a $10kW$ PEMFC of 15 years ago. It is expected that this PEMFC is not representative for applications with larger power and modern PEMFC systems. Therefore, it is highly recommended that additional lab test are performed on modern PEMFC systems of suitable rated power.
- **Maritime environment:** Most of the literature used for this research originates from the automotive industry. This raises questions such as the PEMFC parameters but also about the influence of the maritime environment. It is recommended to study the influences of the maritime environment on PEMFC lifetime such as salt content in the air, balance of plant and fuel impurities. It is likely that these conditions are different compared to the automotive industry and could affect the PEMFC lifetime.

8. Bibliography

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A. Appendix A: Results

A.1 Experiment 1

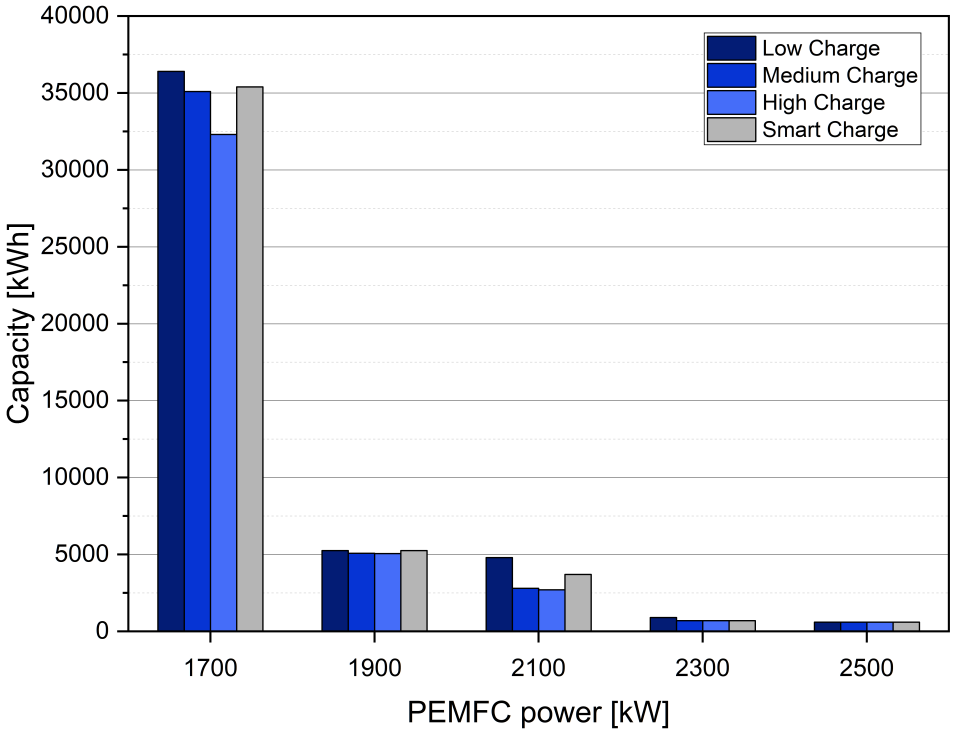

Figure A.1: Battery capacity for fuel cell power / energy management strategy combinations - experiment 1

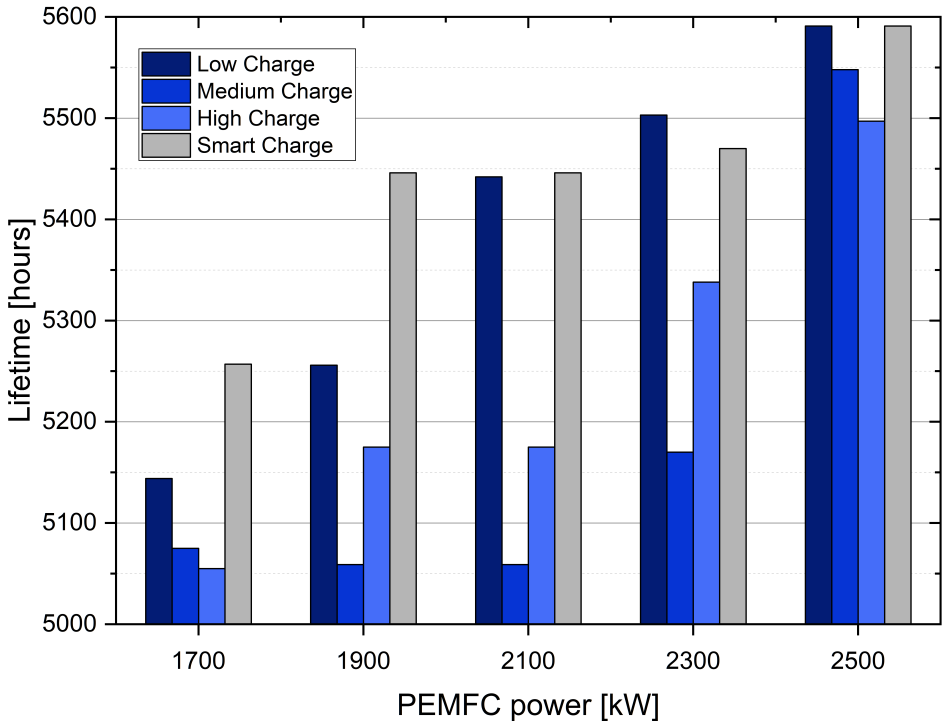

Figure A.2: PEMFC lifetime for fuel cell power / energy management strategy combinations - experiment 1

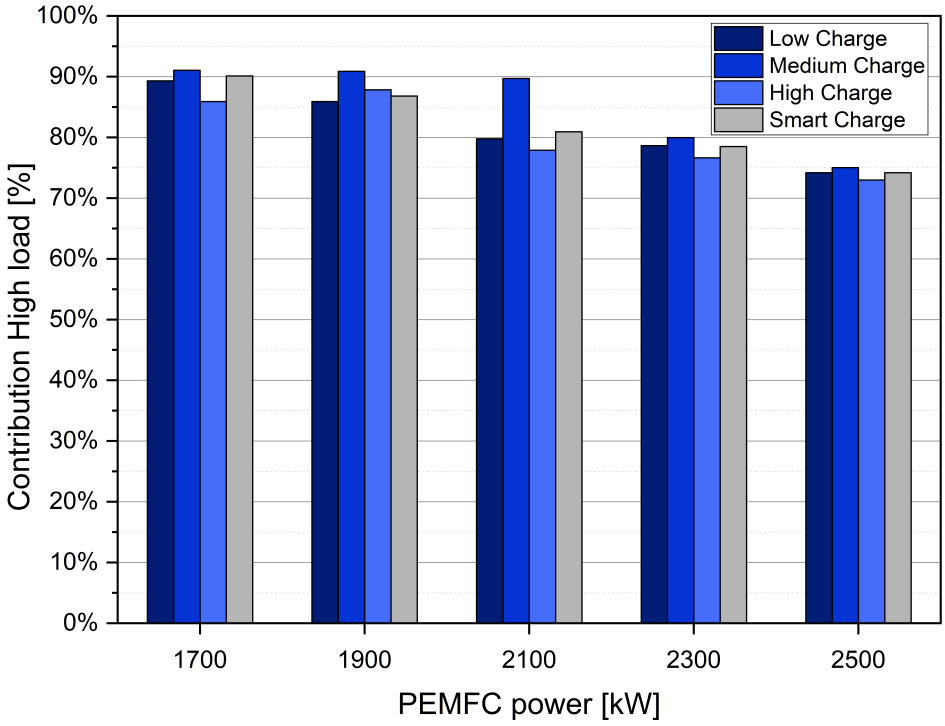

Figure A.3: Contribution High load condition for fuel cell power / energy management strategy combinations - experiment 1

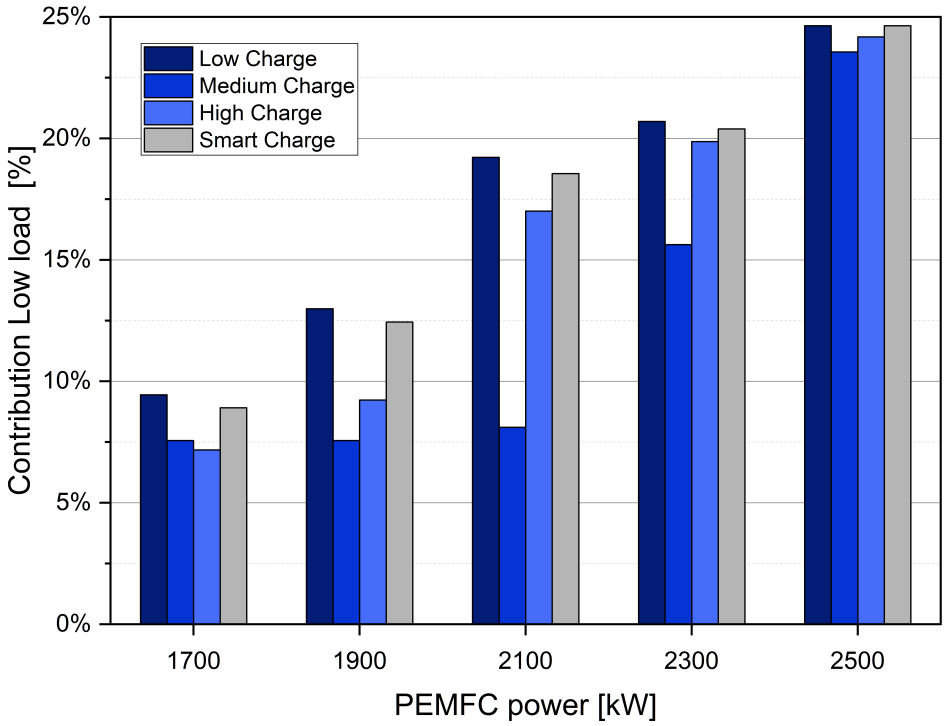

Figure A.4: Contribution Low load condition for fuel cell power / energy management strategy combinations - experiment 1

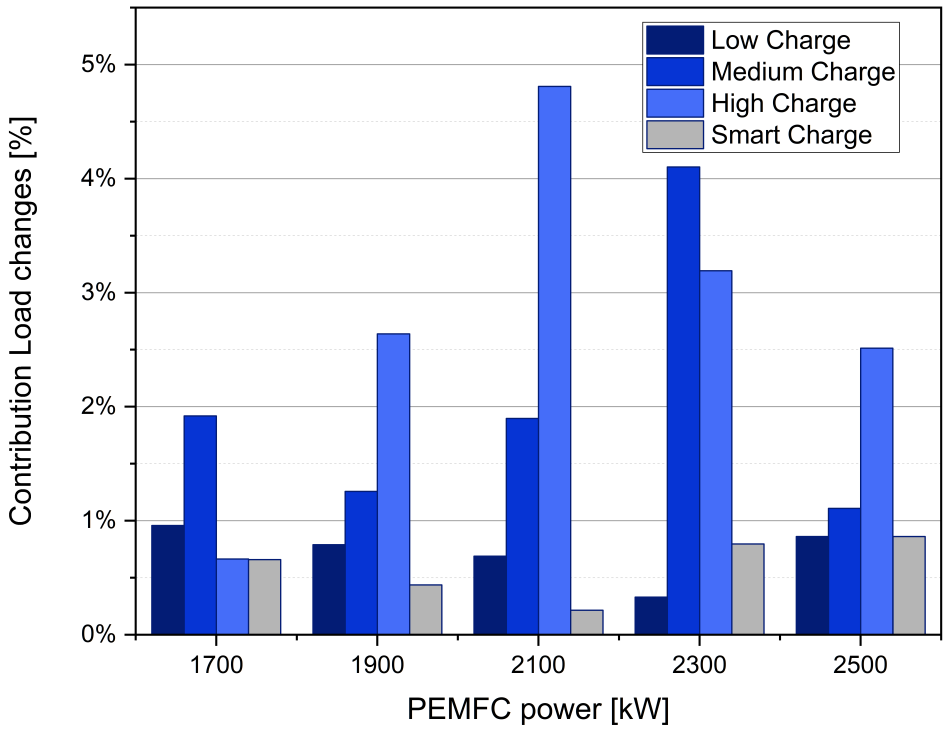

Figure A.5: Contribution Load changes condition for fuel cell power / energy management strategy combinations - experiment 1

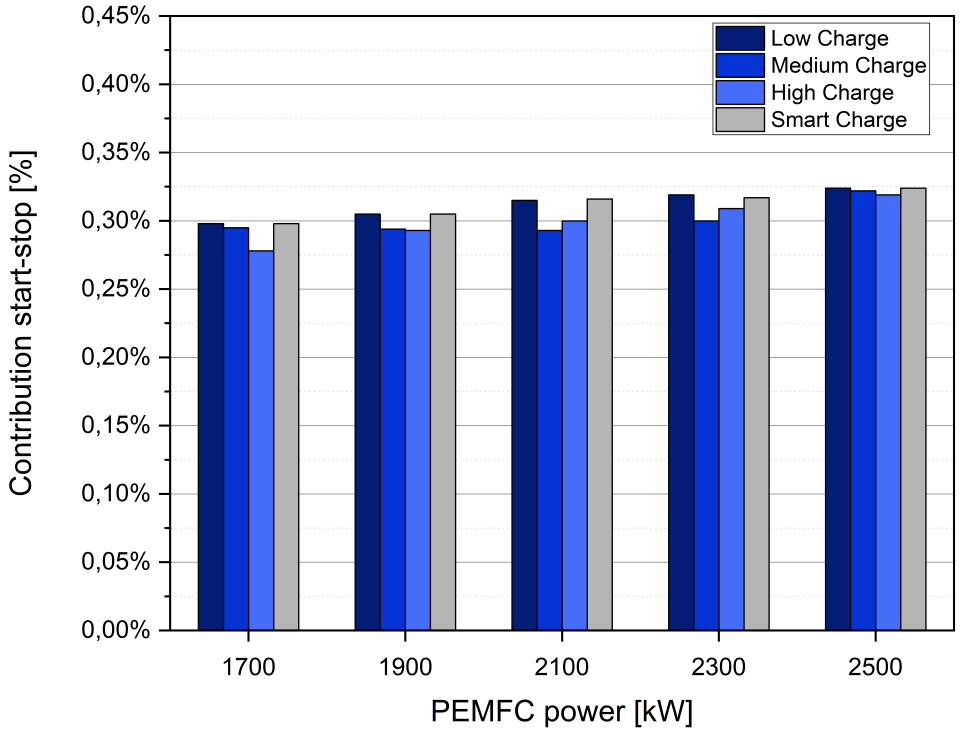

Figure A.6: Contribution Start-stop condition for fuel cell power / energy management strategy combinations - experiment 1

A.2 Experiment 2

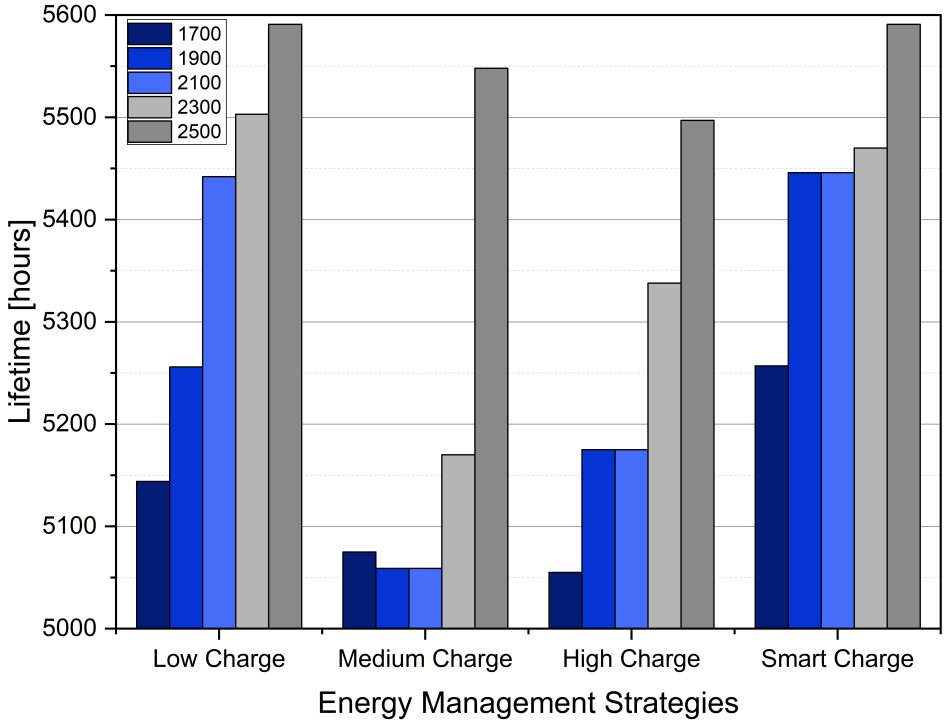

Figure A.7: PEMFC lifetime for fuel cell power / energy management strategy combinations - experiment 2

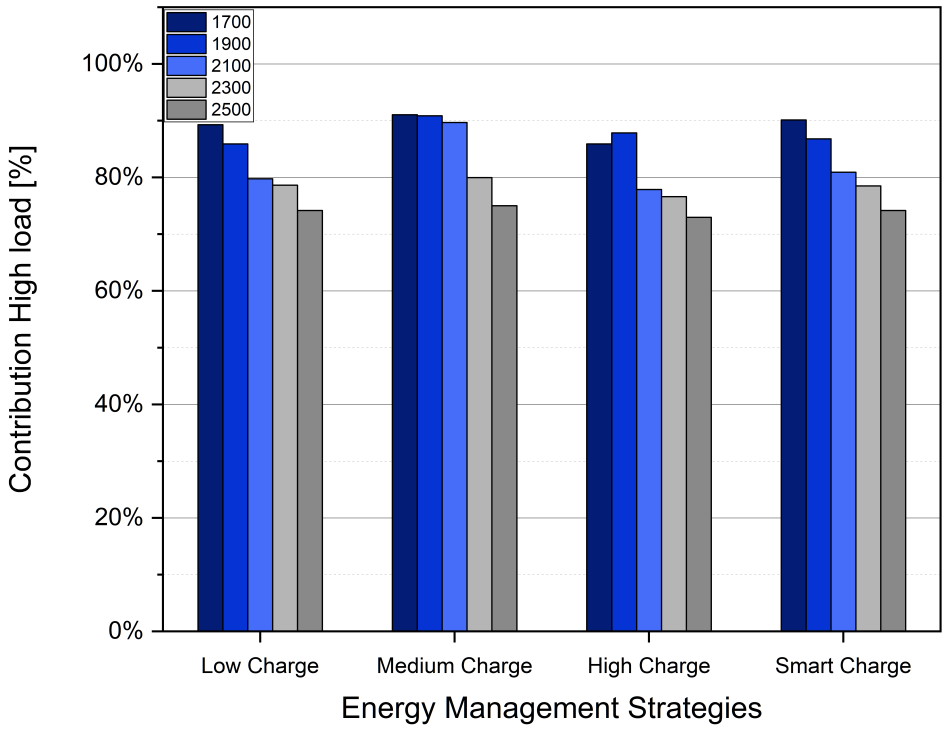

Figure A.8: Contribution High load condition for fuel cell power / energy management strategy combinations - experiment 2

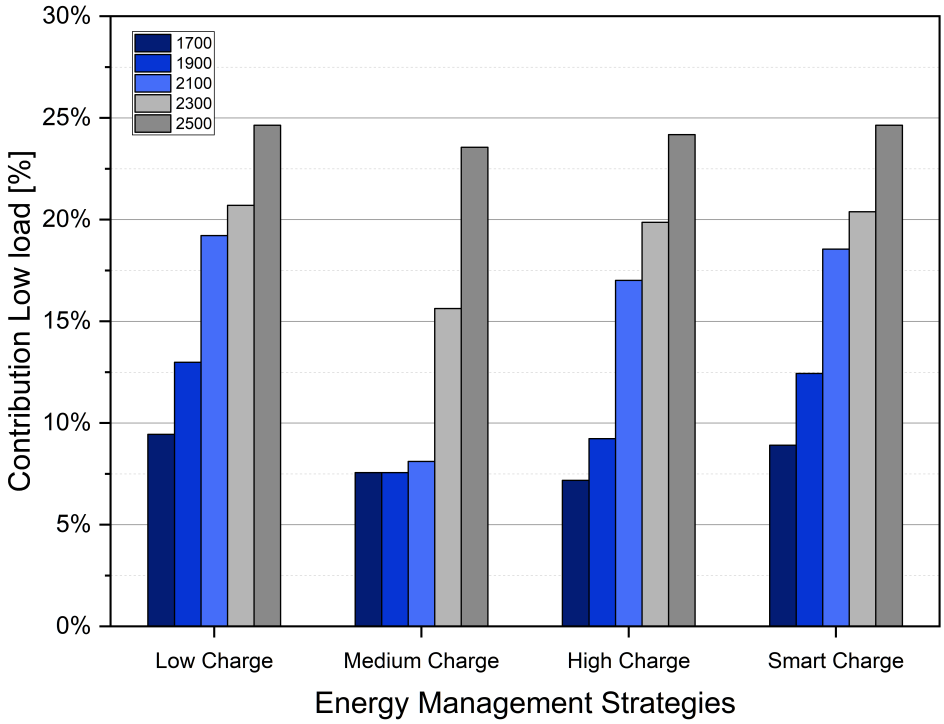

Figure A.9: Contribution Low load condition for fuel cell power / energy management strategy combinations - experiment 2

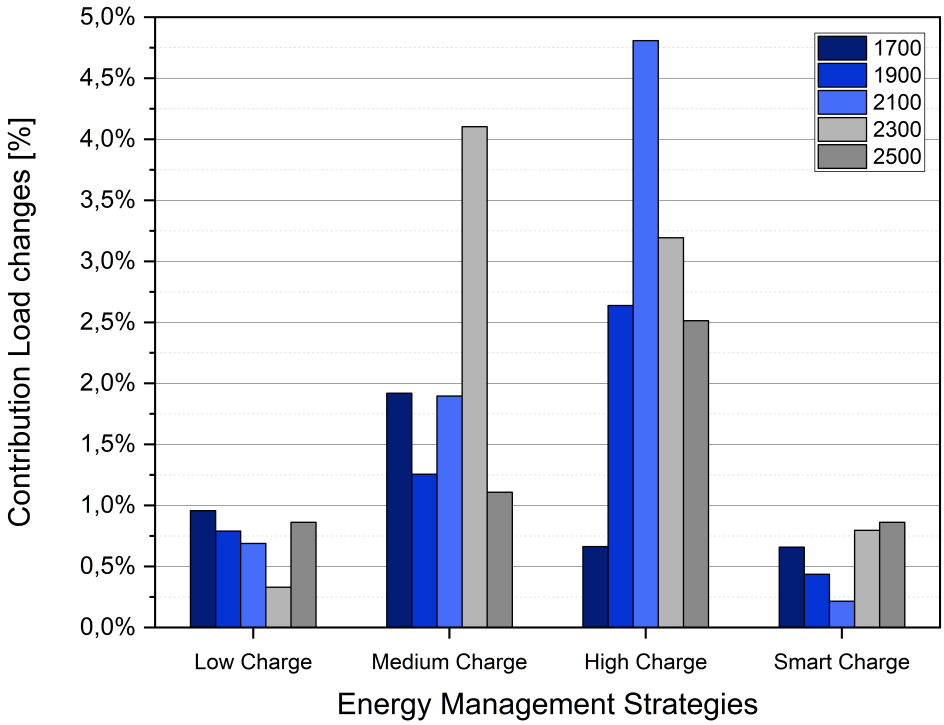

Figure A.10: Contribution Load changes condition for fuel cell power / energy management strategy combinations - experiment 2

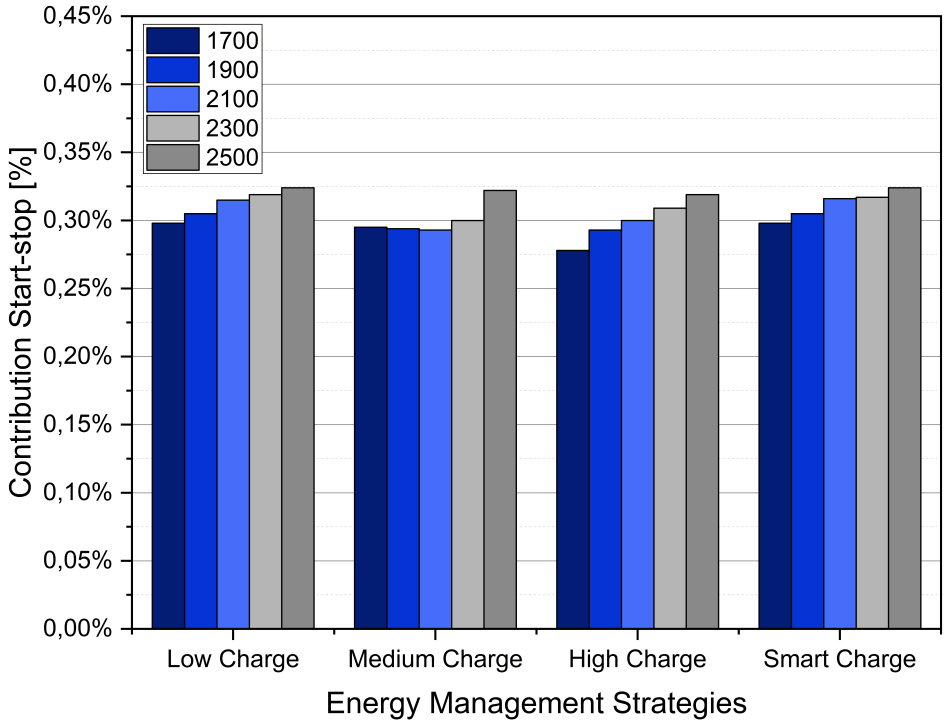

Figure A.11: Contribution Start-stop condition for fuel cell power / energy management strategy combinations - experiment 2

A.3 Experiment 3

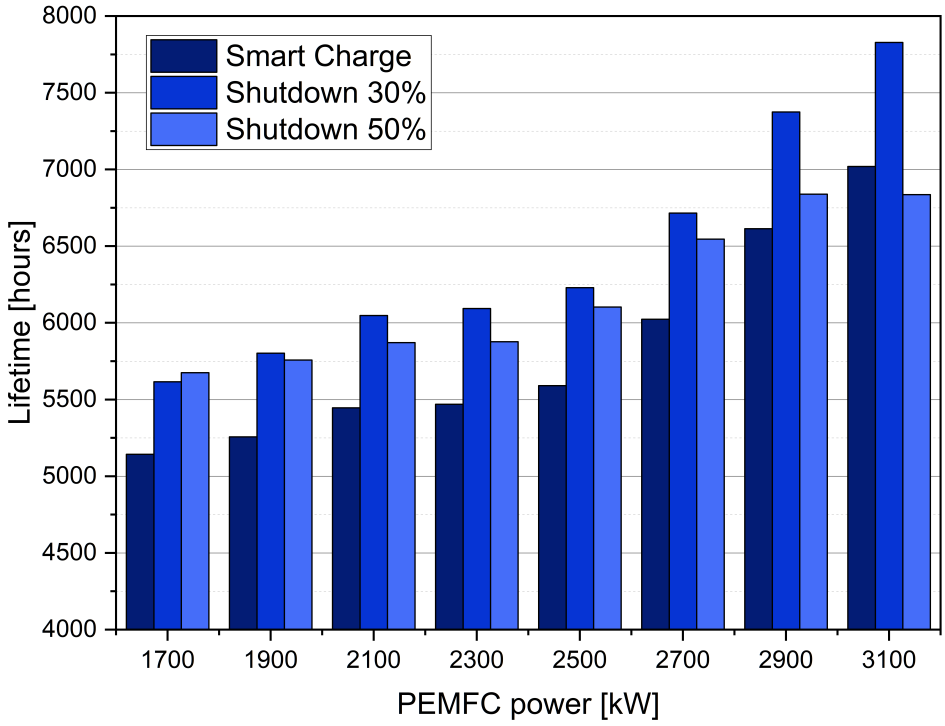

Figure A.12: PEMFC lifetime for fuel cell power / module shutdown threshold - experiment 3

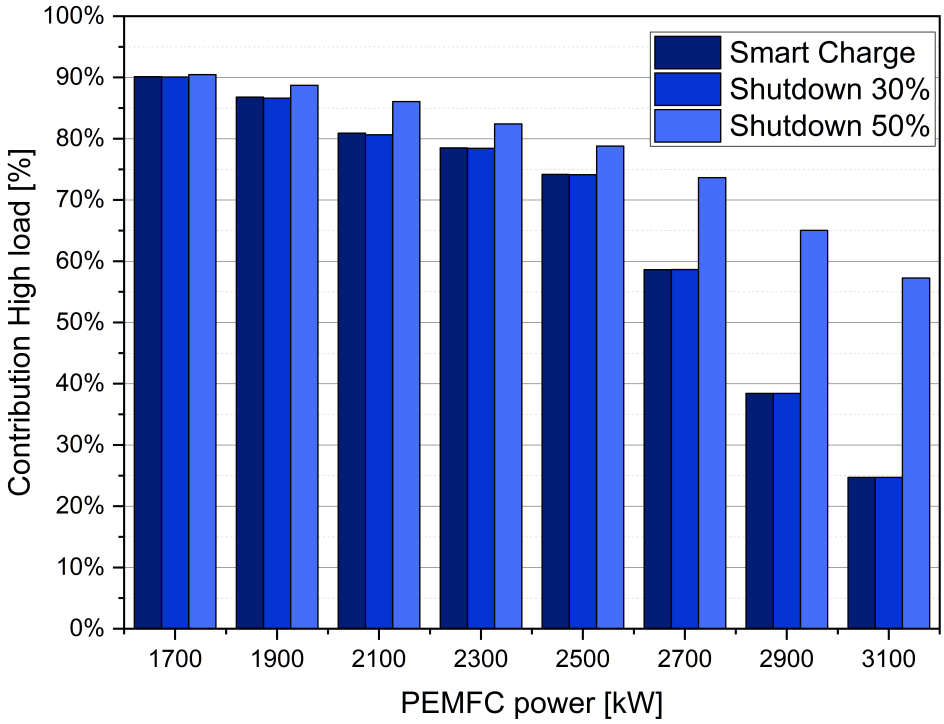

Figure A.13: Contribution High load condition for fuel cell power / module shutdown threshold - experiment 3

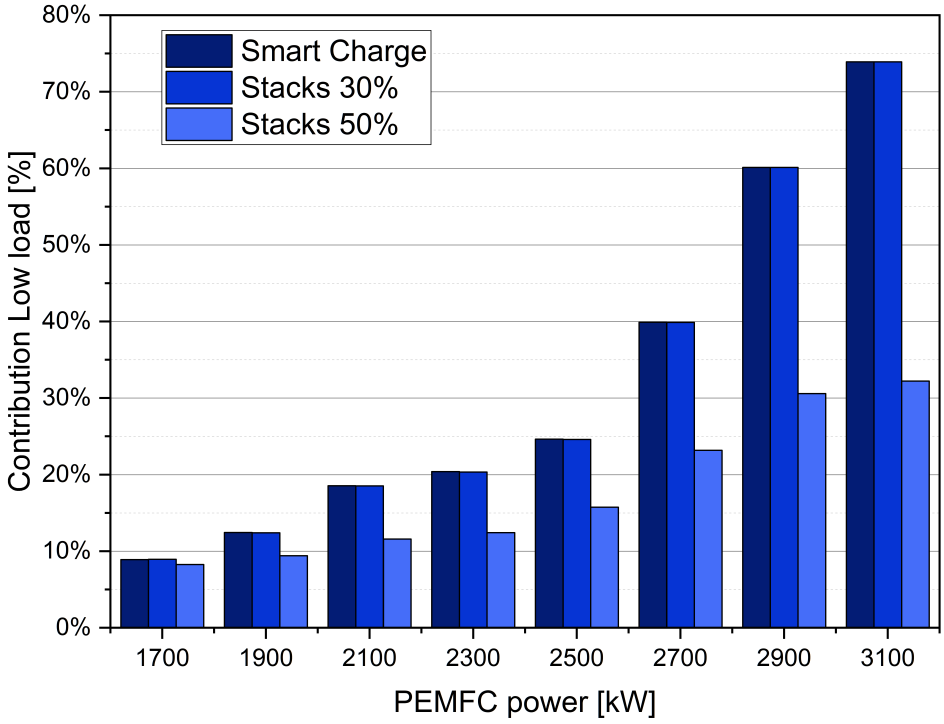

Figure A.14: Contribution Low load condition for fuel cell power / module shutdown threshold - experiment 3

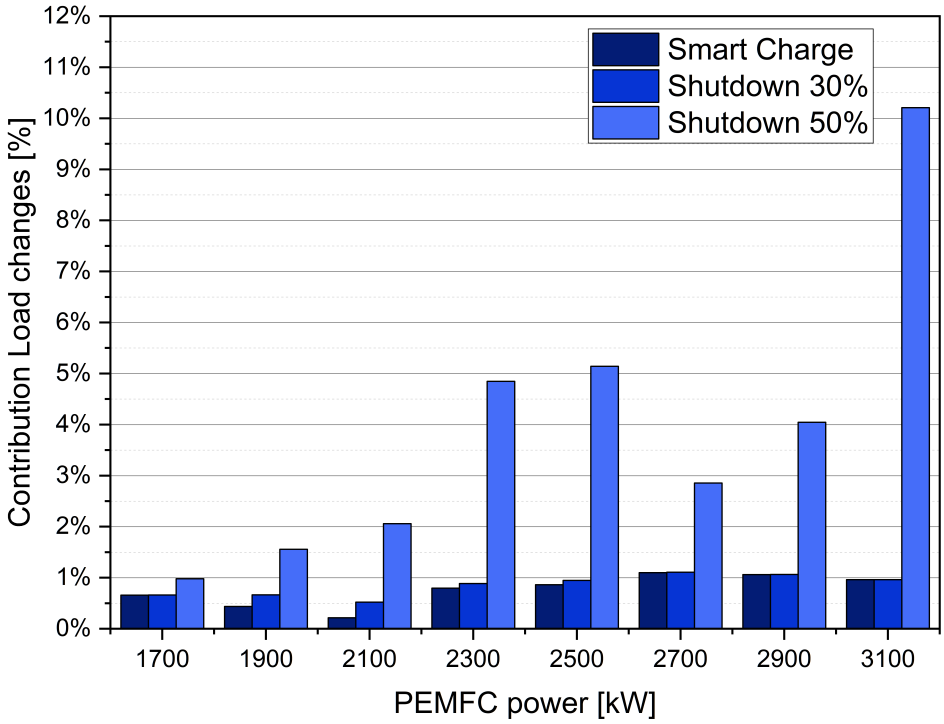

Figure A.15: Contribution Load changes condition for fuel cell power / module shutdown threshold - experiment 3

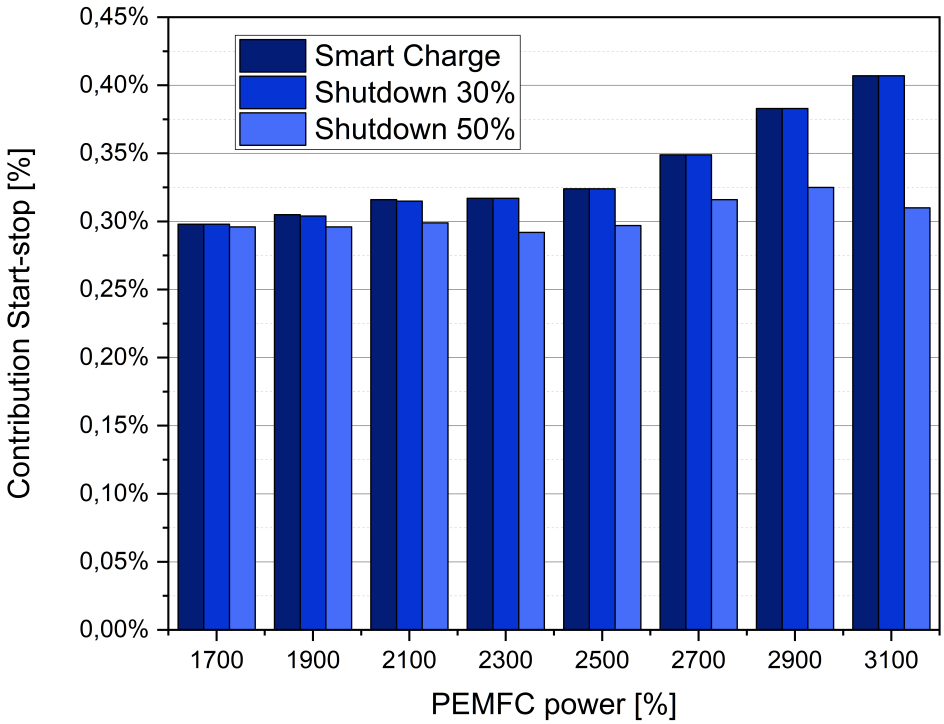

Figure A.16: Contribution Start-stop condition for fuel cell power / module shutdown threshold - experiment 3

A.4 Experiment 4

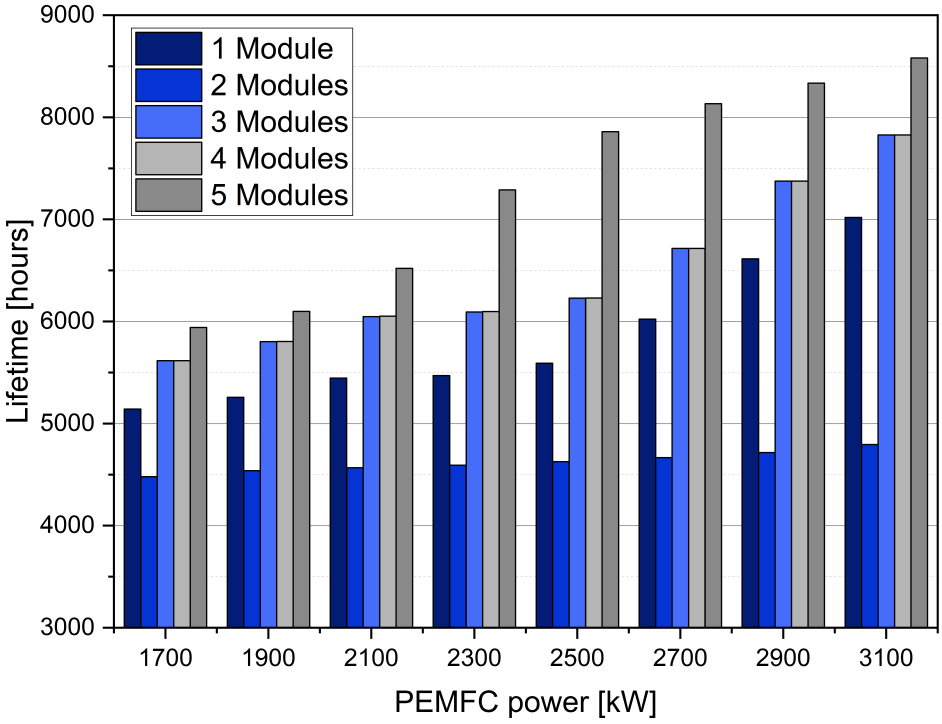

Figure A.17: PEMFC lifetime for fuel cell power / number of modules - experiment 4

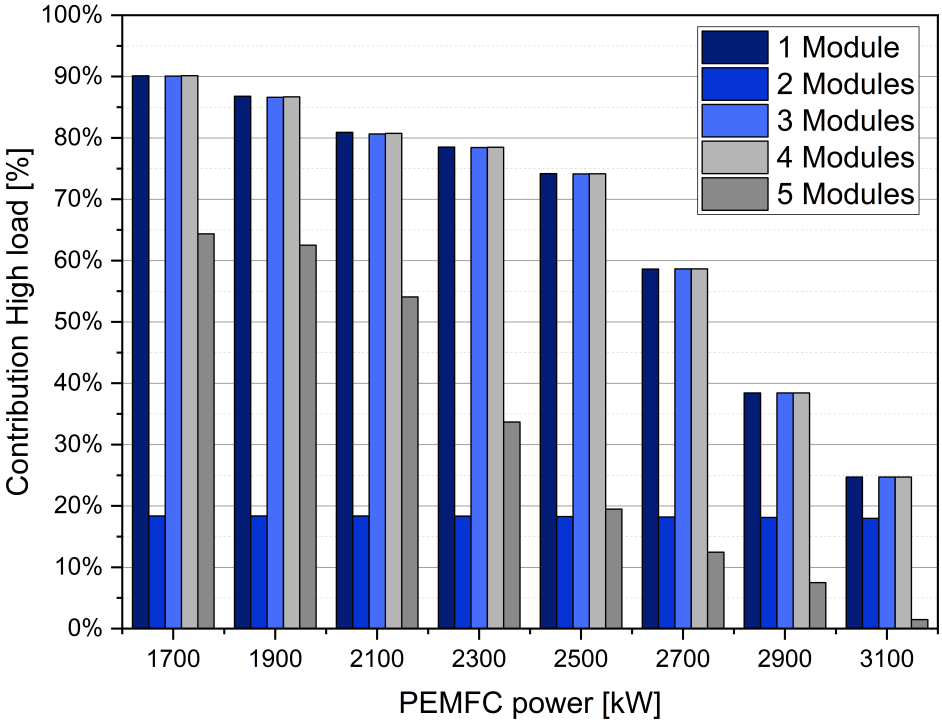

Figure A.18: Contribution High load condition for fuel cell power / number of modules - experiment 4

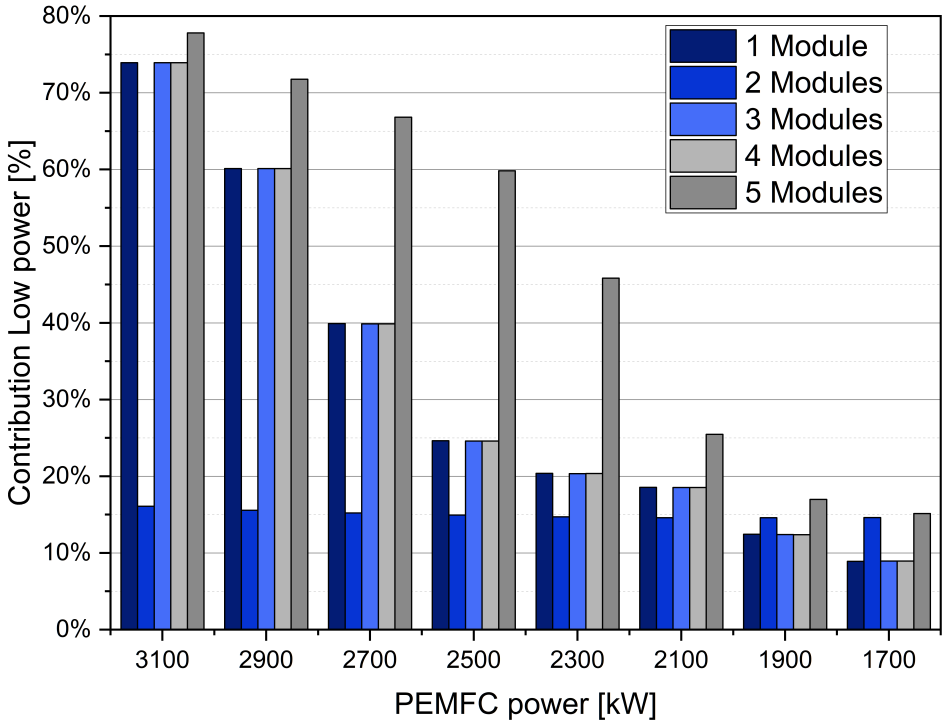

Figure A.19: Contribution Low load condition for fuel cell power / number of modules - experiment 4

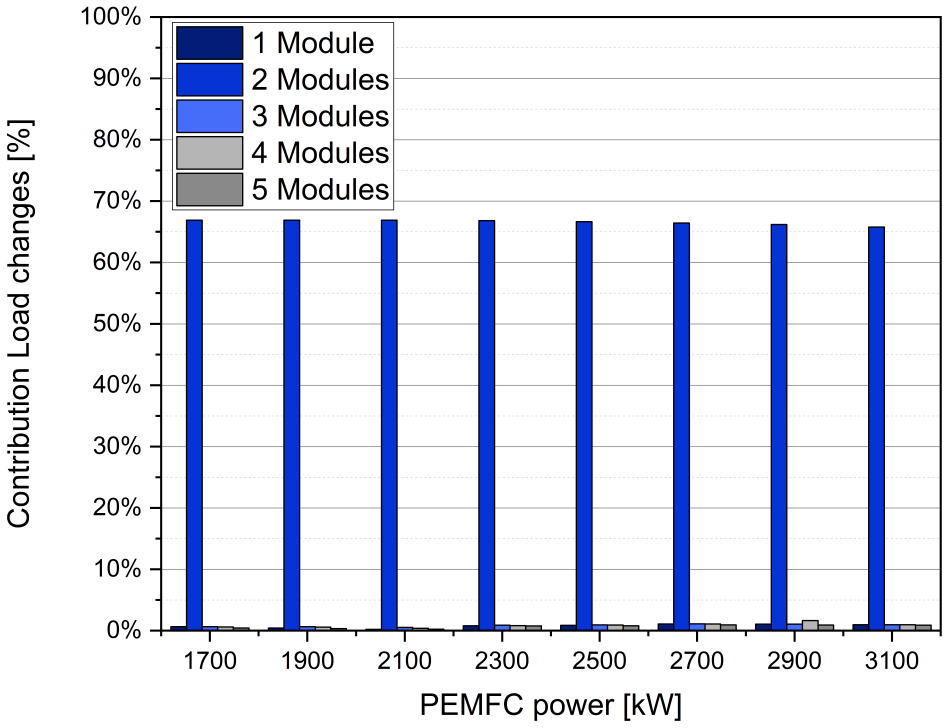

Figure A.20: Contribution Load changes condition for fuel cell power / number of modules - experiment 4

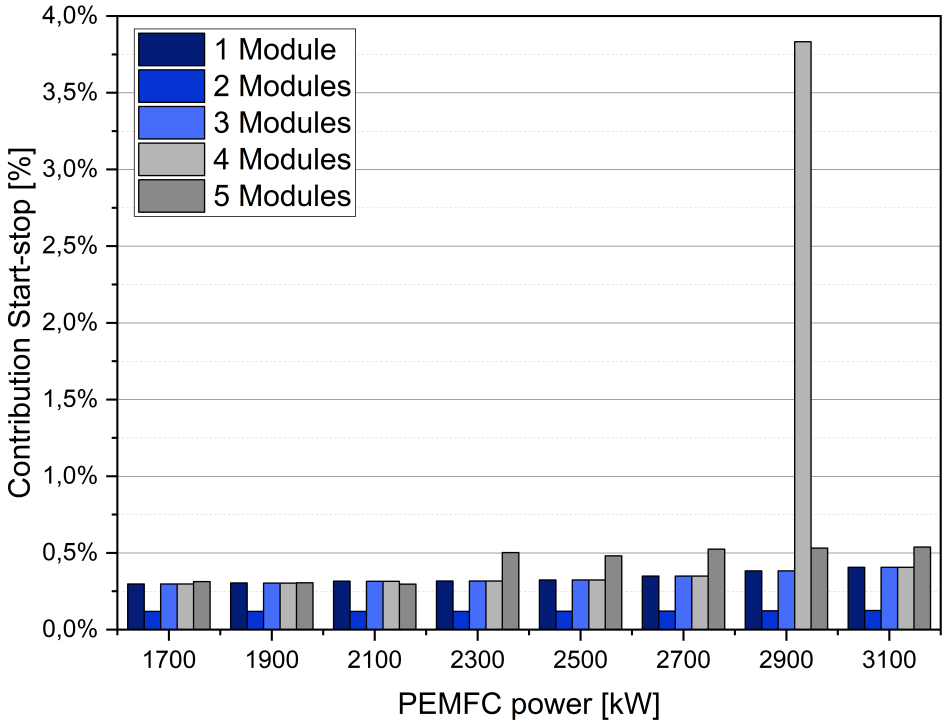

Figure A.21: Contribution Start-stop condition for fuel cell power / number of modules - experiment 4

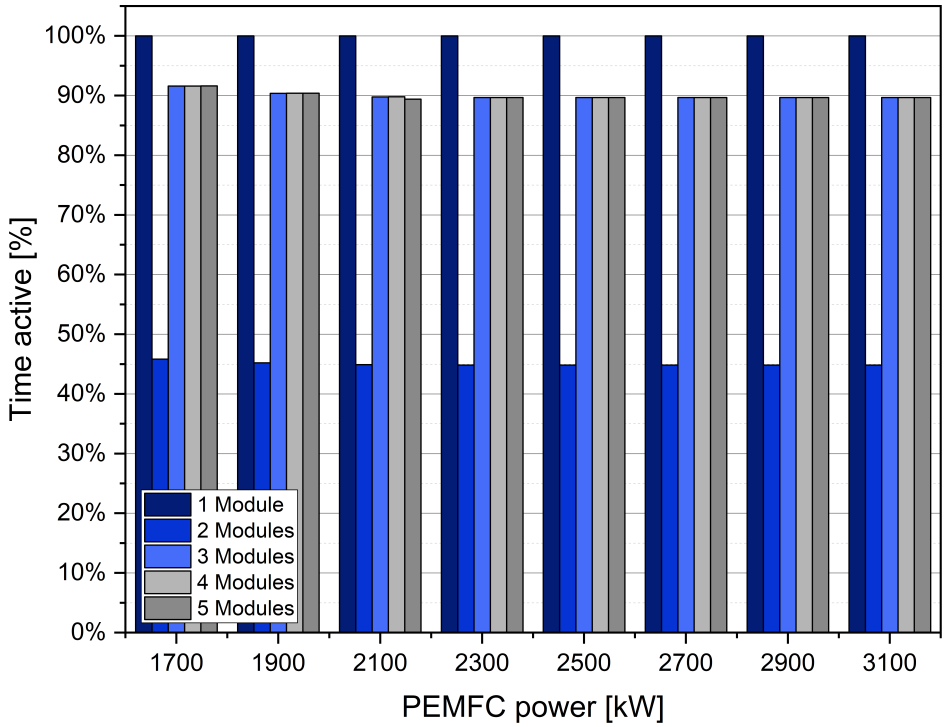

Figure A.22: Time active for fuel cell power / number of modules - experiment 4

A.5 Additional results

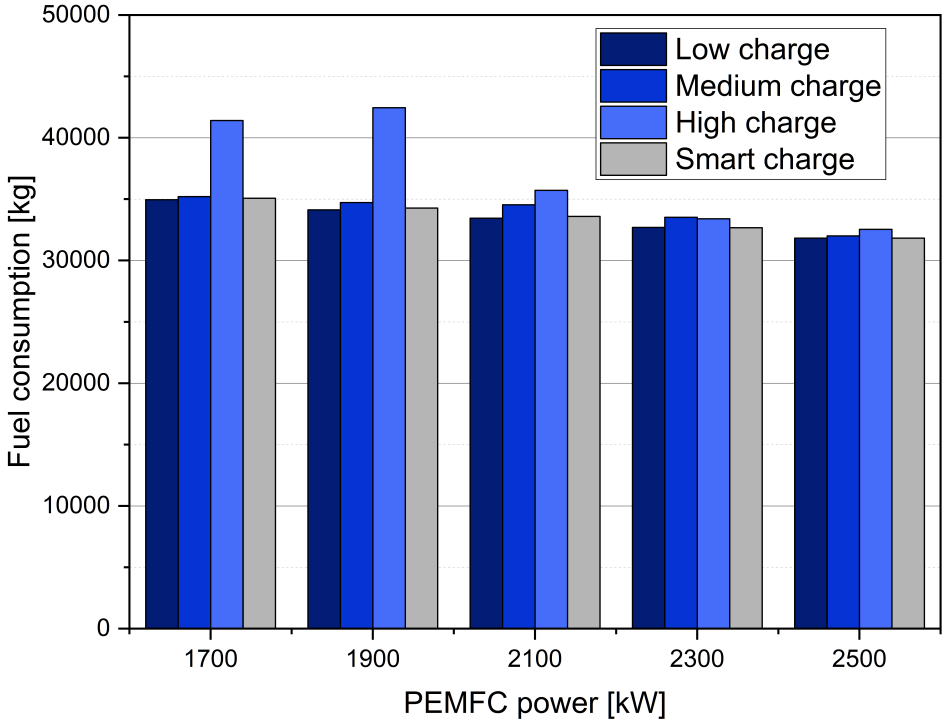

Figure A.23: Fuel consumption for fuel cell power / energy management strategy combinations - experiment 1&2

B. Appendix B: Results overview

	Low charge		Medium Charge		High charge		Smart charge		
	Capacity	600	*Capacity*	600	*Capacity*	600	*Capacity*	600	*kWh*
	Fuel	31830	*Fuel*	32010	*Fuel*	32540	*Fuel*	31830	*kg*
	Lifetime	5591	*Lifetime*	5548	*Lifetime*	5497	*Lifetime*	5591	*hrs*
	Load change	0.008615	*Load change*	0.01109	*Load change*	0.02514	*Load change*	0.00862	*ratio*
2500 kW	*Start-Stop*	0.003241	*Start-Stop*	0.00322	*Start-Stop*	0.003186	*Start-Stop*	0.00324	*ratio*
	High power	0.7418	*High power*	0.7501	*High power*	0.7298	*High power*	0.7418	*ratio*
	Low power	0.2464	*Low power*	0.2356	*Low power*	0.2418	*Low power*	0.2464	*ratio*
	Capacity	900	*Capacity*	700	*Capacity*	700	*Capacity*	700	*kWh*
	Fuel	32700	*Fuel*	33520	*Fuel*		*Fuel*	32680	*kg*
	Lifetime	5503	*Lifetime*	5170	*Lifetime*	5338	*Lifetime*	5470	*hrs*
	Load change	0.003307	*Load change*	0.04103	*Load change*	0.03193	*Load change*	0.00796	*ratio*
2300 kW	*Start-Stop*	0.003189	*Start-Stop*	0.003	*Start-Stop*	0.003094	*Start-Stop*	0.00317	*ratio*
	High power	0.7865	*High power*	0.7997	*High power*	0.7663	*High power*	0.7851	*ratio*
	Low power	0.207	*Low power*	0.1563	*Low power*	0.1987	*Low power*	0.2039	*ratio*
	Capacity	4800	*Capacity*	2800	*Capacity*	2700	*Capacity*	3700	*kWh*
	Fuel	33450	*Fuel*	34540	*Fuel*	35720	*Fuel*	33600	*kg*
	Lifetime	5442	*Lifetime*	5059	*Lifetime*	5175	*Lifetime*	5446	*hrs*
	Load change	0.006887	*Load change*	0.01897	*Load change*	0.04809	*Load change*	0.00216	*ratio*
2100 kW	*Start-Stop*	0.003154	*Start-Stop*	0.00293	*Start-Stop*	0.003	*Start-Stop*	0.00316	*ratio*
	High power	0.7978	*High power*	0.897	*High power*	0.7788	*High power*	0.8092	*ratio*
	Low power	0.1922	*Low power*	0.08109	*Low power*	0.1701	*Low power*	0.1855	*ratio*
	Capacity	16300	*Capacity*	15000	*Capacity*	11100	*Capacity*	15400	*kWh*
	Fuel	34130	*Fuel*	34730	*Fuel*	42450	*Fuel*	34280	*kg*
	Lifetime	5256	*Lifetime*	5075	*Lifetime*	5055	*Lifetime*	5257	*hrs*
	Load change	0.007895	*Load change*	0.01257	*Load change*	0.02639	*Load change*	0.00437	*ratio*
1900 kW	*Start-Stop*	0.003046	*Start-Stop*	0.00294	*Start-Stop*	0.00293	*Start-Stop*	0.00305	*ratio*
	High power	0.8591	*High power*	0.9088	*High power*	0.8784	*High power*	0.8681	*ratio*
	Low power	0.1299	*Low power*	0.07564	*Low power*	0.09232	*Low power*	0.1244	*ratio*
	Capacity	36400	*Capacity*	35100	*Capacity*	32300	*Capacity*	35400	*kWh*
	Fuel	34950	*Fuel*	35210	*Fuel*	41410	*Fuel*	35080	*kg*
	Lifetime	5144	*Lifetime*	5083	*Lifetime*	4799	*Lifetime*	5143	*hrs*
	Load change	0.009582	*Load change*	0.0192	*Load change*	0. 06639	*Load change*	0.00659	*ratio*
1700 kW	*Start-Stop*	0.002982	*Start-Stop*	0.00295	*Start-Stop*	0.002781	*Start-Stop*	0.00298	*ratio*
	High power	0.893	*High power*	0.9105	*High power*	0.859	*High power*	0.9013	*ratio*
	Low power	0.09444	*Low power*	0.07565	*Low power*	0.07179	*Low power*	0.08911	*ratio*

Figure B.1: Tabular overview of the results of experiment 1 and 2

	Smart charge		30 % threshold		operational lifetime	% active	50% threshold		operational lifetime	% active
	Capacity	200	*Capacity*	200			*Capacity*	200		
	Fuel	30180	*Fuel*	30180			*Fuel*	30880		
3100 kW	*Lifetime*	7020	*Lifetime*	7020	7827.832293	0.8968	*Lifetime*	5353	6836.235154	0.783033333
	Load change	0.00963	*Load change*	0.00963			*Load change*	0.1021		
	Start-Stop	0.00407	*Start-Stop*	0.00407			*Start-Stop*	0.0031		
	High power	0.2471	*High power*	0.2471			*High power*	0.5726		
	Low power	0.7392	*Low power*	0.7392			*Low power*	0.3223		
	Capacity	300	*Capacity*	300			*Capacity*	300		
	Fuel	30620	*Fuel*	30620			*Fuel*	31030		
2900 kW	*Lifetime*	6614	*Lifetime*	6614	7375.111508	0.8968	*Lifetime*	5608	6839.580454	0.819933333
	Load change	0.01063	*Load change*	0.01065			*Load change*	0.04047		
	Start-Stop	0.00383	*Start-Stop*	0.00383			*Start-Stop*	0.00325		
	High power	0.3843	*High power*	0.3843			*High power*	0.6504		
	Low power	0.6013	*Low power*	0.06012			*Low power*	0.3059		
	Capacity	400	*Capacity*	400			*Capacity*	400		
	Fuel	31140	*Fuel*	31140			*Fuel*	31470		
2700 kW	*Lifetime*	6024	*Lifetime*	6023	6716.101695	0.8968	*Lifetime*	5451	6545.651043	0.832766667
	Load change	0.011	*Load change*	0.01108			*Load change*	0.02855		
	Start-Stop	0.00349	*Start-Stop*	0.00349			*Start-Stop*	0.00316		
	High power	0.5864	*High power*	0.5866			*High power*	0.7365		
	Low power	0.3991	*Low power*	0.3988			*Low power*	0.2318		
	Capacity	600	*Capacity*	600			*Capacity*	600		
	Fuel	31830	*Fuel*	31840			*Fuel*	31250		
2500 kW	*Lifetime*	5591	*Lifetime*	5586	6229.276634	0.896733333	*Lifetime*	5122	6103.67428	0.839166667
	Load change	0.00862	*Load change*	0.009477			*Load change*	0.05143		
	Start-Stop	0.00324	*Start-Stop*	0.003237			*Start-Stop*	0.002969		
	High power	0.7418	*High power*	0.7414			*High power*	0.7881		
	Low power	0.2464	*Low power*	0.2459			*Low power*	0.1575		
	Capacity	700	*Capacity*	700			*Capacity*	700		
	Fuel	32680	*Fuel*	32690			*Fuel*	32910		
2300 kW	*Lifetime*	5470	*Lifetime*	5465	6094.115898	0.896766667	*Lifetime*	5040	5877.094103	0.857566667
	Load change	0.00796	*Load change*	0.008871			*Load change*	0.04847		
	Start-Stop	0.00317	*Start-Stop*	0.003167			*Start-Stop*	0.002921		
	High power	0.7851	*High power*	0.7845			*High power*	0.8243		
	Low power	0.2039	*Low power*	0.2035			*Low power*	0.1243		
	Capacity	3700	*Capacity*	3700			*Capacity*	3700		
	Fuel	33600	*Fuel*	33600			*Fuel*	33770		
2100 kW	*Lifetime*	5446	*Lifetime*	5430	6047.668548	0.89786667	*Lifetime*	5152	5871.225071	0.8775
	Load change	0.00216	*Load change*	0.00523			*Load change*	0.02059		
	Start-Stop	0.00316	*Start-Stop*	0.00315			*Start-Stop*	0.00299		
	High power	0.8092	*High power*	0.8064			*High power*	0.8606		
	Low power	0.1855	*Low power*	0.1853			*Low power*	0.1158		
	Capacity	15400	*Capacity*	15400			*Capacity*	15400		
	Fuel	34280	*Fuel*	34270			*Fuel*	34390		
1900 kW	*Lifetime*	5257	*Lifetime*	5245	5802.847028	0.90386667	*Lifetime*	5114	5757.496153	0.888233333
	Load change	0.00437	*Load change*	0.00665			*Load change*	0.01559		
	Start-Stop	0.00305	*Start-Stop*	0.00304			*Start-Stop*	0.00296		
	High power	0.8681	*High power*	0.8663			*High power*	0.8873		
	Low power	0.1244	*Low power*	0.124			*Low power*	0.09416		
	Capacity	35400	*Capacity*	35400			*Capacity*	35400		
	Fuel	35080	*Fuel*	35070			*Fuel*	35160		
1700 kW	*Lifetime*	5143	*Lifetime*	5144	5615.924888	0.91596667	*Lifetime*	5109	5675	0.900266667
	Load change	0.00659	*Load change*	0.00661			*Load change*	0.0098		
	Start-Stop	0.00298	*Start-Stop*	0.00298			*Start-Stop*	0.00296		
	High power	0.9013	*High power*	0.9009			*High power*	0.9046		
	Low power	0.08911	*Low power*	0.08953			*Low power*	0.08269		

Figure B.2: Tabular overview of the results of experiment 3

	1 Module		2 Modules		operational lifetime	% active	3 Modules		operational lifetime	% active	4 Modules		operational lifetime	% active	5 Modules		operational lifetime	% active
	Capacity	200	*Capacity*	200			*Capacity*	200			*Capacity*	200			*Capacity*	200		
	Fuel	30180	*Fuel*	30187			*Fuel*	30180			*Fuel*	30180			*Fuel*	30180		
3100	*Lifetime*	7020	*Lifetime*	2150	**4795.360767**	0.44835	*Lifetime*	7020	**7827.832293**	0.8968	*Lifetime*	7020	**7827.832293**	0.8968	*Lifetime*	7696	**8581.62355**	0.8968
	Load chan	1%	*Load change*	66%			*Load change*	1%			*Load change*	1%			*Load change*	1%		
	Start-Stop	0%	*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	1%		
	High powe	25%	*High power*	18%			*High power*	25%			*High power*	25%			*High power*	1%		
	Low power	74%	*Low power*	16%			*Low power*	74%			*Low power*	74%			*Low power*	78%		
	Capacity	300	*Capacity*	300			*Capacity*	300			*Capacity*	300			*Capacity*	300		
2900	*Fuel*	30620	*Fuel*	31460			*Fuel*	30620			*Fuel*	30620			*Fuel*	30620		
	Lifetime	6614	*Lifetime*	2115	**4716.77074**	0.4484	*Lifetime*	6614	**7375.111508**	0.8968	*Lifetime*	6614	**7375.111508**	0.8968	*Lifetime*	7475	**8335.191793**	0.8968
	Load chan	1%	*Load change*	66%			*Load change*	1%			*Load change*	2%			*Load change*	1%		
	Start-Stop	0%	*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	1%		
	High powe	38%	*High power*	18%			*High power*	38%			*High power*	38%			*High power*	8%		
	Low power	60%	*Low power*	16%			*Low power*	60%			*Low power*	60%			*Low power*	72%		
	Capacity	400	*Capacity*	400			*Capacity*	400			*Capacity*	400			*Capacity*	400		
2700	*Fuel*	31140	*Fuel*	41450			*Fuel*	31140			*Fuel*	31140			*Fuel*	31140		
	Lifetime	6024	*Lifetime*	2093	**4667.186977**	0.44845	*Lifetime*	6023	**6716.101695**	0.8968	*Lifetime*	6023	**6716.101695**	0.8968	*Lifetime*	7294	**8133.363069**	0.8968
	Load chan	1%	*Load change*	66%			*Load change*	1%			*Load change*	1%			*Load change*	1%		
	Start-Stop	0%	*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	1%		
	High powe	59%	*High power*	18%			*High power*	59%			*High power*	59%			*High power*	12%		
	Low power	40%	*Low power*	15%			*Low power*	40%			*Low power*	40%			*Low power*	67%		
	Capacity	600	*Capacity*	600			*Capacity*	600			*Capacity*	600			*Capacity*	600		
2500	*Fuel*	31830	*Fuel*	39980			*Fuel*	31840			*Fuel*	31830			*Fuel*	31830		
	Lifetime	5591	*Lifetime*	2075	**4626.53287**	0.4485	*Lifetime*	5586	**6729.276634**	0.89673333	*Lifetime*	5587	**6729.928635**	0.8968	*Lifetime*	7048	**7859.054416**	0.8968
	Load chan	1%	*Load change*	67%			*Load change*	1%			*Load change*	1%			*Load change*	1%		
	Start-Stop	0%	*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%		
	High powe	74%	*High power*	18%			*High power*	74%			*High power*	74%			*High power*	20%		
	Low power	25%	*Low power*	15%			*Low power*	25%			*Low power*	25%			*Low power*	60%		
	Capacity	700	*Capacity*	700			*Capacity*	700			*Capacity*	700			*Capacity*	700		
2300	*Fuel*	32680	*Fuel*	36220			*Fuel*	32690			*Fuel*	32680			*Fuel*	32680		
	Lifetime	5470	*Lifetime*	2060	**4593.088071**	0.4485	*Lifetime*	5465	**6094.115898**	0.89676667	*Lifetime*	5468	**6097.064645**	0.896825	*Lifetime*	6537	**7288.763018**	0.89686
	Load chan	1%	*Load change*	67%			*Load change*	1%			*Load change*	1%			*Load change*	1%		
	Start-Stop	0%	*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	1%		
	High powe	79%	*High power*	18%			*High power*	78%			*High power*	78%			*High power*	34%		
	Low power	20%	*Low power*	15%			*Low power*	20%			*Low power*	20%			*Low power*	46%		
	Capacity	3700	*Capacity*	3700			*Capacity*	3700			*Capacity*	3700			*Capacity*	3700		
2100	*Fuel*	33600	*Fuel*	29970			*Fuel*	33600			*Fuel*	33590			*Fuel*	33590		
	Lifetime	5446	*Lifetime*	2052	**4568.121104**	0.4492	*Lifetime*	5430	**6047.668548**	0.8978667	*Lifetime*	5436	**6053.452116**	0.898	*Lifetime*	5830	**6521.252796**	0.894
	Load chan	0%	*Load change*	67%			*Load change*	1%			*Load change*	0%			*Load change*	0%		
	Start-Stop	0%	*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%		
	High powe	81%	*High power*	18%			*High power*	81%			*High power*	81%			*High power*	54%		
	Low power	19%	*Low power*	15%			*Low power*	19%			*Low power*	19%			*Low power*	25%		
	Capacity	15400	*Capacity*	15400			*Capacity*	15400			*Capacity*	15400			*Capacity*	15400		
1900	*Fuel*	34280	*Fuel*	22590			*Fuel*	34270			*Fuel*	34260			*Fuel*	34260		
	Lifetime	5257	*Lifetime*	2052	**4537.815126**	0.4522	*Lifetime*	5245	**5802.847028**	0.9038667	*Lifetime*	5248	**5805.309735**	0.904	*Lifetime*	5514	**6099.017786**	0.90408
	Load chan	0%	*Load change*	67%			*Load change*	1%			*Load change*	1%			*Load change*	0%		
	Start-Stop	0%	*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%		
	High powe	87%	*High power*	18%			*High power*	87%			*High power*	87%			*High power*	63%		
	Low power	12%	*Low power*	15%			*Low power*	12%			*Low power*	12%			*Low power*	17%		
	Capacity	35400	*Capacity*	35400			*Capacity*	35400			*Capacity*	35400			*Capacity*	35400		
1700	*Fuel*	35080	*Fuel*	16340			*Fuel*	35070			*Fuel*	35060			*Fuel*	35060		
	Lifetime	5143	*Lifetime*	2053	**4479.598516**	0.4583	*Lifetime*	5144	**5615.924888**	0.9159667	*Lifetime*	5146	**5617**	0.916075	*Lifetime*	5443	**5941**	0.91618
	Load chan	1%	*Load change*	67%			*Load change*	1%			*Load change*	1%			*Load change*	0%		
	Start-Stop	0%	*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%			*Start-Stop*	0%		
	High powe	90%	*High power*	18%			*High power*	90%			*High power*	90%			*High power*	64%		
	Low power	9%	*Low power*	15%			*Low power*	9%			*Low power*	9%			*Low power*	15%		

Figure B.3: Tabular overview of the results of experiment 4