

The effect of a ripple wave power supply on PEM electrolysis efficiency

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EXECUTIVE SUMMARY

The two matured water electrolysis technologies commercially available today are Alkaline water electrolysis and Proton exchange membrane water electrolysis (PEMWE). Although alkaline water electrolysis is in a more mature stage of development, PEMWE holds a few advantages over this technology. These advantages include minimum mass transport limitations, the compact cell design which results in rapid response times, the simplicity of the cell design, the high current density capabilities, the ability to discharge hydrogen gas at high pressures and the high purity hydrogen gas produced. However, PEMWE is still a relatively new technology compared to Alkaline water electrolysis and consequently has the highest need for research and development to reduce the cost and improve the efficiency of this technology.

Past research and development in this field focused mainly on material science of the electrolyser components and the operating conditions such as temperature and pressure to improve the efficiency and reduce the cost of this technology. Water electrolyzers are usually supplied with a steady DC current, and it is common to use the electrical characteristics (i.e. voltage, current density, and impedance) as a measure of the electrolyser's performance. Unfortunately, very little research is available on the effect that specific electrical characteristics of the power supplied to the PEM electrolyser (i.e. ripple current) have on the performance and efficiency of the cell. In the little literature that is available, the main focus was on the efficiency of the converters used and the effect that different converter topologies have on the efficiency of a PEM electrolyser.

Much more literature is however available on the effect of electrical characteristics, such as a fluctuating current or voltage, on the cell efficiency of alkaline water electrolyzers. These studies indicated that electrical characteristics such as the ripple factor, frequency, and waveform of the applied electrical power affect the hydrogen production rate as well as the power consumption rate of the electrolyser. Although some respectable information was obtained from the literature, all the studies made use of alkaline water electrolysis systems and the effects of a ripple current on PEMWE are still unknown.

This study aims to determine how the efficiency of a PEM electrolyser is affected by a ripple current. The primary objective was determining how the ripple current frequency, ripple factor, and waveform affects the hydrogen production, power consumption, efficiency and durability of a PEM electrolyser. Electrochemical impedance spectroscopy (EIS) was used to characterise the PEM electrolyser after which the impedance data were used to develop an equivalent electrical circuit (EEC) model. The EEC model was then used to simulate the effects of different ripple currents on the voltage response and power consumption of the cell. An active laboratory sized PEM electrolysis system was used to further investigate the impact of varying ripple currents on the efficiency of the system and to verify and validate the simulation results.

Keywords: Proton exchange membrane, Electrolyser, Ripple Current, Efficiency

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LIST OF ACRONYMS AND ABBREVIATIONS

AC	Alternating current
AEM	Anion exchange membrane
AFC	Alkaline fuel cells
AWE	Alkaline water electrolysis
BoL	Beginning of life
CAPEX	Capital expenditure
CPE	Constant phase element
DC	Direct current
EEC	Equivalent electric circuit
EIS	Electrochemical impedance spectroscopy
EoL	End of life
GDL	Gas diffusion layer
HHV	Higher heating value
Hz	Hertz
LHV	Lower heating value
MCFC	Molten carbonate fuel cells
MEA	Membrane electrode assembly
nL	Normal Litres
nLPM	Normal Litres per minute
OPEX	Operational expenditure
PAFC	Phosphoric acid fuel cells
PEM	Proton exchange membrane
PEMWE	Proton exchange membrane water electrolysis
PFSA	Perfluorosulfonic acid polymer
RF	Ripple factor
RMS	Root mean square
SOE	Solid oxide electrolysis
SOFC	Solid oxide fuel cells
SPICE	Simulation program with integrated circuit emphasis

LIST OF SYMBOLS

Greek symbols

η	Overpotential
η_{act}	Activation overpotential
η_{ohm}	Ohmic overpotential

LIST OF SYMBOLS

η_{con}	Concentration overpotential
α	Transfer coefficient
ε_{cell}^{HHV}	Cell efficiency
ε_V^{HHV}	Voltage efficiency
ε_I	Faradaic efficiency
ω	Angular frequency

Roman Letters

C_1	Gas concentration current condition
C_0	Reference gas concentration
C_{dl}	Double-layer capacitance
E^0	Open circuit/ Nerquist potential
E_{rev}	Reversible potential
E_{rev}^0	Reversible potential at standard conditions
E_{th}^0	Thermoneutral potential at standard conditions
E_{cell}	Cell Potential
f	Frequency
F	Faraday's constant
G	Gibbs free energy
H	Enthalpy
H_R	Reaction Enthalpy
H_f	Formation Enthalpy
I	Current
I_{rms}	RMS current
I_{DC}	Current DC component
i	Current AC component
i_{rms}	RMS of current AC component
i_0	Exchange current density
i_f	Forward reaction rate
i_b	Backward reaction rate
n	Number of electrons
$\dot{n}_{H_2}$	Hydrogen molar flow rate
P_{avg}	Average Power consumption
$P_{measured}$	Measured power consumption
P_{theor}	Theoretical power consumption
Q_{H_2}	Hydrogen volumetric flow rate
R	Universal gas constant
R_{ohmic}	Ohmic resistance
R_{elec}	Electrode resistance

LIST OF SYMBOLS

R_{pl}	Bipolar plate resistance
R_{mem}	Membrane resistance
S	Entropy
S_R	Reaction Entropy
T	Absolute temperature
U_{DC}	Voltage DC component
U_{cell}	Measured cell voltage
U_{rms}	RMS voltage
Z_R	Resistor impedance
Z_C	Capacitor impedance
Z_L	Inductor impedance
Z_Q	CPE impedance
Z_W	Warburg impedance

CHAPTER 1: INTRODUCTION

The first chapter of this dissertation gives an overview of the research project with the title “The effect of a ripple wave power supply on PEM electrolysis efficiency”. This chapter discusses background theory on hydrogen production as well as hydrogen as an energy carrier for renewable energy. Chapter 1 also gives some background on the specific research problem and shortcomings in the existing research, the problem statement as well as the aim and scope of this research project. The scope of the project includes the primary objective, secondary objectives, and key research questions. Next, the used research methodology is discussed, and finally, the chapter closes with a dissertation overview to explain the structure of this document.

1.1 Background

The energy challenges the world is currently facing are more significant and more concerning than ever before. The world’s energy demand increases every year and has been doing so for the past few decades. The amount of energy consumed worldwide grew with 2.9% in 2018, while the average annual growth from 2007 to 2017 was only 1.5% [1]. Fossil fuels are still the world’s primary energy resource, and for most of the world’s population, the only form of energy they have access to [2]. Unfortunately, the current methods of energy generation through the combustion of fossil fuels produce vast amounts of carbon dioxide and other greenhouse gasses which many believe to be the primary contributor to global warming [3]. The increase in the world population, energy requirements, and global warming forces us to find alternative energy resources. Renewable energy is a promising alternative to fossil fuels, but storage and transport of renewable energy remain a problem. Renewable energy sources like solar, wind, and hydropower, only provide power at specific periods of the day as it continually fluctuates due to weather conditions.

Currently, a great deal of research and development is directed towards the hypothesis that hydrogen is the energy carrier of the future [4-6]. Due to the lack of hydrogen occurring in gas form on earth, we use hydrogen as an energy carrier rather than an energy source. The processes used to separate and reform hydrogen-containing compounds include Thermal, Electrolytic and Photolytic processes [4]. The most favourable of these processes to use in a pollution-free hydrogen energy system is water electrolysis since the energy required can be obtained from a renewable energy source. Water electrolysis is the process where water is split into two gasses known as hydrogen and oxygen by applying electrical energy to an electrolytic cell. The three primary water electrolysis processes used in the industry to produce hydrogen are Alkaline water electrolysis, PEM water electrolysis and Solid oxide electrolysis [7, 8].

Currently an ample amount of research and development is being done on PEM water electrolysis as this method of hydrogen production holds a few advantages over other water electrolysis technologies. Some of the benefits include a thin solid electrolyte allowing minimum mass transport limitations and separation of hydrogen and oxygen, a thin electrode architecture coated directly on to the solid electrolyte allowing a zero-gap design, the compact cell design which results in rapid response times, the simplicity of the cell and system design, the low impact it has on the environment, the high current density capabilities and the purity of hydrogen gas produced [8, 9]. These advantages make PEM water electrolysis the most appealing form of water electrolysis for the future. This technology is also relatively new compared to Alkaline water electrolysis and consequently has the highest need for research and development to address cost reduction and efficiency improvement.

Although hydrogen, produced from renewable energy, may seem like the perfect energy carrier, the efficiency and high cost of hydrogen production through water electrolysis remains a concern. Figure 1-1 illustrates that globally only about 4% of hydrogen production is through water electrolysis. The remainder of the hydrogen is produced through processes like steam-methane reforming, oil gasification and coal gasification [10]. The result is that more than 95% of all current hydrogen production uses fossil fuels as an energy source.

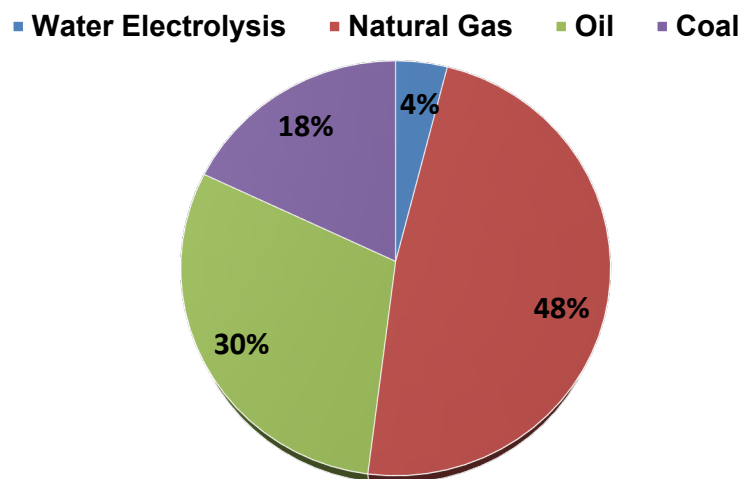


Figure 1-1: Global hydrogen production (adapted from [10]).

One of the main reasons for the low amount of hydrogen produced through water electrolysis is the high capital expenditure (CAPEX) and operating expense (OPEX) of these systems. An improvement in the CAPEX, OPEX and efficiency of water electrolysis systems is required for this process to be commercially competitive with the fossil fuel driven alternatives. The OPEX of a water electrolysis system depends on the cost of electricity while the CAPEX depends on the capacity factor or utilization of the electrolyser. The use of renewable energy sources lowers the electricity cost per unit of hydrogen gas produced, which results in a lower OPEX.

However, a lower OPEX due to the use of renewable energy sources also result in a lower capacity factor and a higher CAPEX since the electrolyser is only utilized at certain periods when the renewable energy is available [11]. The overall cost of hydrogen production through water electrolysis thus depends on the initial capital cost, capacity factor, electricity cost and efficiency of the system. Current research and development tend to focus on material science and manufacturing to improve the efficiency and lower the overall cost of PEM water electrolyzers [12, 13]. In contrast, very little research is done on the electrical characteristics of the power supplied to such a system. An electrolyser requires a DC supply which is generally provided by a network of converters, connected to power sources, as illustrated by Figure 1-2 below. The DC supply is thus supplied by an AC-DC converter where AC power sources are used and a DC-DC converter where DC power sources are used.

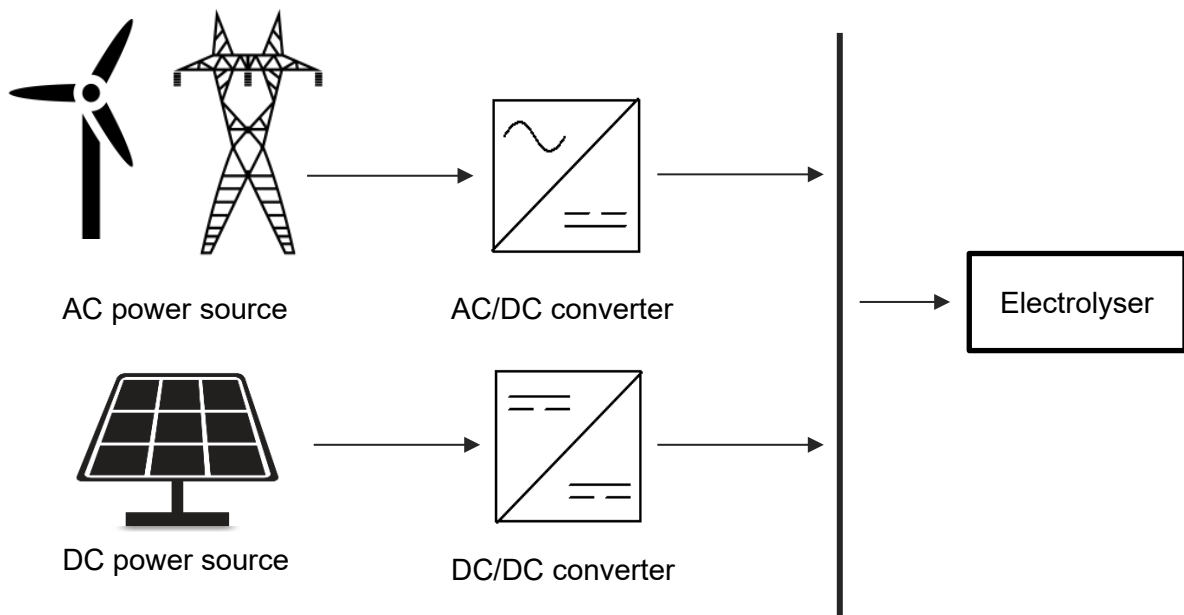


Figure 1-2: Electrolyser power supply system (adapted from [14]).

Based on the topologies used in industrial applications, these converters may generate a significant ripple on the output [15]. An AC-DC converter uses a transformer to transform the voltage supplied by the power source to the desired level. The alternating current output on the secondary side of the transformer is then converted to direct current with the use of a rectifier and a filter. These converters are conventionally thyristor-based to accommodate for the high current density requirements of the electrolyzers [16]. Although thyristor-based converters can accommodate higher current densities, the generated ripple is much higher than in transistor-based converters [17]. The ripple is induced by the switching of these devices according to the frequency of the applied AC waveform as illustrated by Figure 1-3 below.

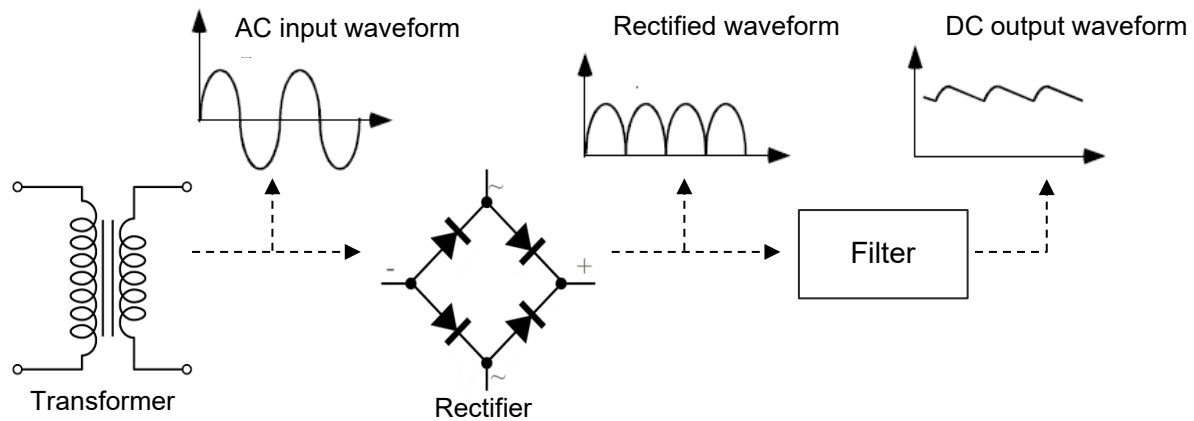


Figure 1-3: Rectified output waveforms.

A ripple is thus present in the DC power supplied to an electrolyser and the effect of the ripple on the efficiency of the electrolyser is not yet fully understood [15],[18]. Although experiments and studies on the electrical characteristics of the power supplied to a water electrolysis system are uncommon to find, some studies showed that a power supply ripple has an impact on the hydrogen production and energy consumption rates [15, 17-22]. An inadequacy of these studies is research and experiments on PEM electrolysers as most of the studies done were on alkaline water electrolysers. The focus of this research is thus on analysing the effects that different ripple currents have on the efficiency of a PEM electrolyser.

1.2 Purpose of Research

1.2.1 Problem Statement

Some research has been done on the effect that current and voltage fluctuation or the power supply ripple have on the efficiency of water electrolysis systems. The literature shows that electrical characteristics such as the waveform, frequency, AC amplitude and DC offset of the ripple power supplied to the electrolyser affects the power consumption and gas production rate [15, 20]. Some of the studies indicate that a specific and controlled power supply ripple or deviation from a steady DC supply, such as a pulse potential, could have a positive effect on the efficiency of the electrolyser [19]. The literature indicated that an increase in efficiency is possible due to an enhancement in the mass transport of hydrogen and oxygen that forms on the electrodes. The improvement in the mass transport is caused by the pumping effect that the ripple power supply induces. An increase in the mass transport will reduce the electrode surface resistance and in return, lower the energy consumption. Other studies showed that a power supply ripple, or any deviation from a steady DC supply, has a negative impact on the efficiency with the efficiency loss directly proportional to the magnitude of the ripple [15, 20].

The discrepancy in the literature indicates that the effect of a ripple power supply is not consistent between different systems and water electrolysis technologies. Whether the effect of a ripple power supply is positive or negative, the prevailing trend is that a ripple power supply does affect the performance of an electrolyser. The electrical characteristics of the applied power are thus known to have a considerable influence on the efficiency of an electrolysis system [17, 18]. Still, most of the literature focused only on alkaline electrolysis systems. Little to no research is available for PEMWE systems, and the purpose of this research is to fill this gap.

1.2.2 Aim

This study aimed to determine if a power supply ripple have a positive or negative effect on the efficiency of a PEM electrolyser. Regardless of the efficiency, the effects that different power supply ripple characteristics, such as frequency and amplitude, have on the hydrogen production and power consumption were investigated. Furthermore, this study aimed to determine the effect of a power supply ripple on the degradation rate of a PEM electrolyser.

1.3 Scope of Project

The sections below discuss the scope of this research project is discussed in the subsections below, which includes the primary objective, secondary objectives and key research questions. The purpose of this section is thus to highlight the focus areas and set the limitations of this project.

1.3.1 Primary Objective

The primary objective of the research was to determine the effects of a power supply ripple, at various waveform, frequency, AC amplitude and DC offset settings, on the efficiency of a PEM electrolyser.

1.3.2 Exclusions and Limitations

The study excludes and was limited by the following:

- Investigations on operating variables, other than the electrical characteristics of the power supply, such as temperature, pressure and water inlet flow rate were excluded.
- The design of the PEM electrolyser cell and the investigation of other cell designs and components were excluded, except for the component trade-offs in section 3.4.3.
- The ranges of the frequency, AC amplitude and DC offset settings were limited to the specifications and limitations of the power supply, other apparatus and the PEM electrolyser that were available for this study as outlined in sections 3.4.2 and 3.4.3.

- The experimental tests were limited to one single cell PEM electrolyser with an active area of 25 A/cm^2 .
- The maximum applied current or DC offset was limited to 25 A (1 A/cm^2) to stay within the allowed cell voltage range and avoid damage to any of the limited cell components that were available for this study.

1.3.3 Secondary Objectives

The aim and primary objective of this study was achieved by completing the next mentioned secondary objectives:

- a) Since the energy requirement, cell voltage and efficiency are crucial elements in this research project, the electrochemical fundamentals of a PEM water electrolysis system needed to be researched. The conducted research included the thermodynamics, cell potential, reaction kinetics and efficiency calculations of a PEM electrolyser. Further important research done include methods available to characterise and model a PEM electrolyser with the focus on the electrical characteristics of the electrolyser.
- b) The above mention research was then used to characterise the PEM electrolyser and to develop simulation models which represent the dynamic behaviour of the cell. These models were used to simulate the frequency response, voltage response, impedance and hydrogen flow rate of the PEM electrolyser at various operating conditions.
- c) The results obtained from characterising, modelling and simulating the PEM electrolyser were used to develop the experimental procedure, parameter ranges and setup. The experimental setup was used to measure the hydrogen production, power consumption and voltage response for different applied ripple current settings at various waveforms, frequencies, AC amplitudes and DC offsets as outlined in the experimental design chapter.

1.3.4 Key Research Questions

The key research questions were formulated from the research objectives. By the completion of this study, these questions should be answered successfully.

1. Does a ripple power supply have a positive or negative effect on the efficiency of a PEM electrolyser?
2. How does ripple currents, at various waveform, frequency, AC amplitude and DC offset settings, influence the hydrogen production rate as well as the energy consumption rate of a PEM electrolyser?

-
3. Will applying a ripple current to a PEM electrolyser accelerate the degradation rate?

These questions are discussed and answered in section 6.2 of the final chapter of this dissertation.

1.4 Research Methodology

The methodology is the step by step process that was followed to complete this research project and achieve the desired outcome. It was critical to follow this methodology to ensure that the research is of value to the scientific and engineering society and to guarantee the aim of this study is achieved. The following points define the methodology that was followed: 1) Problem Identification, 2) Literature Review, 3) Design, 4) Experiment system setup, 5) Characterisation, Modelling and Simulation, 6) Experimental Measurements, 7) Results Analysis, Conclusion and Recommendations, 8) Verification and Validation.

1.4.1 Problem Identification

The first step of this study was to formulate a problem statement together with project objectives to ensure that the problem being addressed as well as the desired outcomes of the research project are fully understood. This includes the problem statement, aim, objectives as well as the key research questions.

1.4.2 Literature Review

After the problem and aim of the research were fully defined, an in-depth literature study on the relevant topics of the research project was carried out. The literature review includes a study of existing research publications and textbooks which focus on topics relevant to this study. The literature study ensured that the rest of the study and experiments were done with a sufficient amount of knowledge on the research problem, the shortcomings of previous studies and the experimental methods available. Attaining a good theoretical understanding of the electrochemical fundamentals and electrical characteristics of a PEMWE system was a crucial part of the literature study.

1.4.3 Design

A detailed design of the experimental process was developed after the completion of the literature review. The experimental design includes defining the experimental specification, developing the experimental procedure, variable and parameter selection as well as component and apparatus selection and integration. All equipment specifications and industry standards were taken into account during the design process to ensure the value of the results obtained from the experimental tests.

1.4.4 Experiment system setup

As soon as the experimental design and specifications were defined all of the sub-systems were integrated to form the system on which the experiments were executed. The main integrated sub-systems include the PEM electrolyser, test station, potentiostat, power supply and control software. In the integrated system, the PEM electrolyser is the main component and consists of several smaller components that were selected and combined according to the requirements and specifications of this project. The system is constructed to adhere to the relevant safety standards to avoid any possible harm to the environment or civilians.

1.4.5 Characterisation, Modelling and Simulation

In this step, the PEM electrolyser was characterised, modelled and simulated with the help of simulation and modelling software. The PEM electrolyser cell was first characterised using techniques such as electrochemical impedance spectroscopy (EIS), polarisation curves (PC) and galvanostatic hold tests. The data was then used to develop an equivalent electrical circuit (EEC) model of the electrolyser with the help of Gamry's Echem Analyst® software. Using the EEC model, the frequency response of the PEM electrolyser were investigated in electrical simulation software LTSpice®. The hydrogen flow rate and voltage response of the system were also modelled and simulated in mathematical software MATLAB® and Simulink®.

1.4.6 Experimental Measurements

Ripple currents with various frequencies, AC amplitudes, DC offsets and waveforms were applied to a PEM electrolyser. These settings were changed in each experiment while the response of the cell to the specific ripple current was measured. The measurements included the applied current, the voltage response, the power consumption and the hydrogen flow rate. The results were then used to calculate the efficiency of the cell and compare the effects of different ripple current settings. Furthermore, a few selected ripple currents were applied to the PEM electrolyser over a more extended period to determine if the cell's degradation rate is affected. All experimental tests and measurement were done as outlined by the experimental specifications, parameter ranges and procedures in the design phase.

1.4.7 Analysis, Conclusion and Recommendations

The next step was to analyse the data obtained from the simulations and experiments and compare them to each other and the baseline data collected from the characterisation of the PEM electrolyser. From this analysis, a conclusion and some recommendations were formulated.

1.4.8 Validation and Verification

Validation is a process used to ensure that the results obtained during a specific process, is the correct results according to the requirements for the process. Validation is thus to ensure the value of the results to the relevant problem or desired outcome. Verification is used to ensure that the correct methods are used to obtain the results. Verification is thus to ensure that the results obtained are accurate and justified. The Verification and Validation process is essential to this research project and were performed throughout the design, simulation and experimental phases. A graphical illustration of the complete research methodology described in this section is illustrated in Figure 1-4.

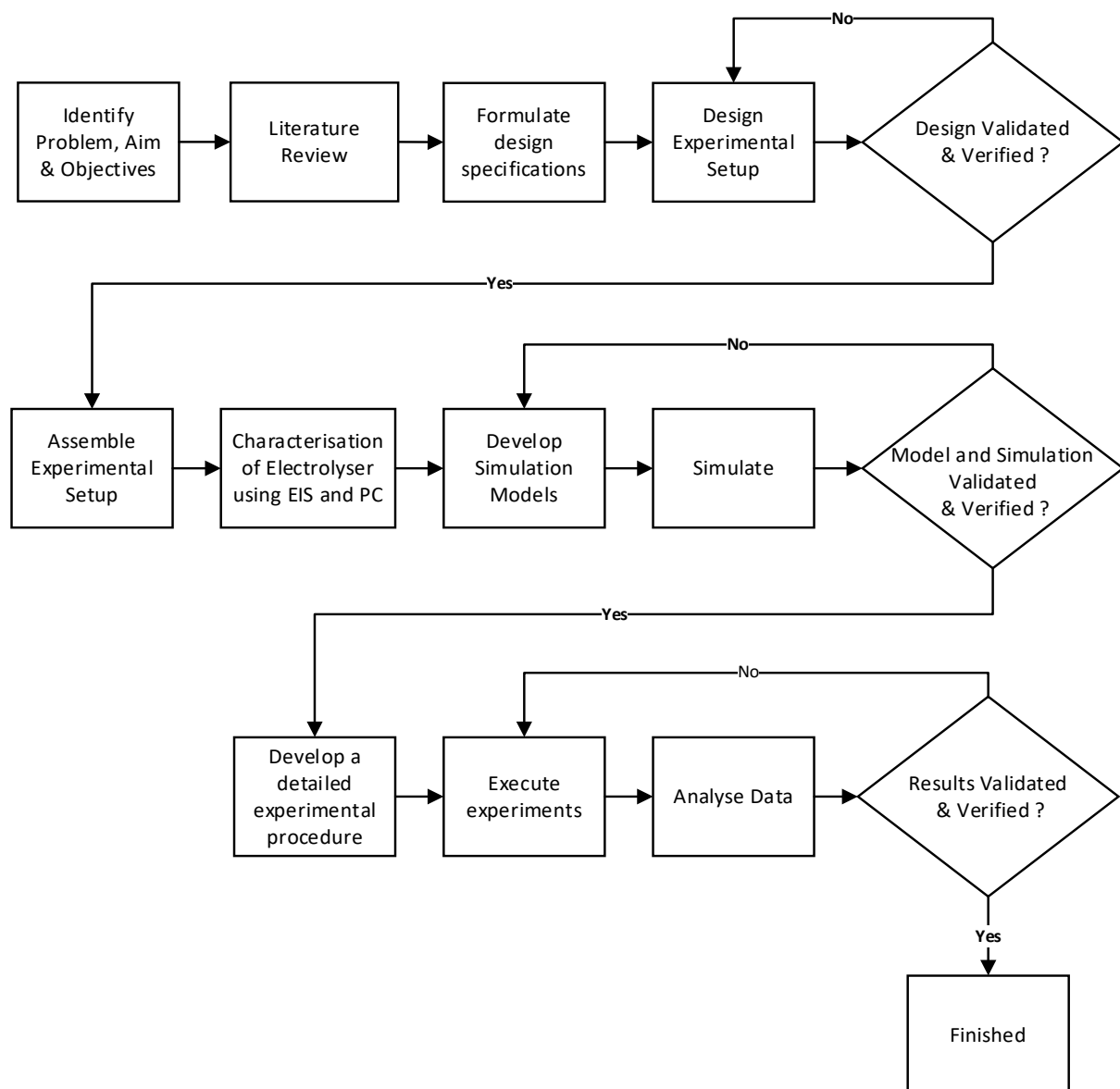


Figure 1-4: Research Methodology.

1.5 Publications and peer reviews

This study was summarised in a journal article, which has been submitted and pending peer review. The details as well as the abstract of the paper is shown below, and the complete article is presented in Appendix B.

Articles submitted and pending peer review:

- H.P.C. Buitendach, R. Gouws, C.A. Martinson, C. Minnaar and D. Bessarabov, “Effect of a ripple current on the efficiency of a PEM electrolyser”

Article Abstract

The aim of this study was to determine how the efficiency of a proton exchange membrane (PEM) electrolyser is affected by an electric ripple current and the different characteristics of the ripple current (frequency, amplitude and waveform). This paper presents simulated and experimentally measured results, used to analyse the effect of ripple currents at various frequencies, ripple factors and waveforms on the hydrogen production, power consumption and efficiency of a PEM electrolyser. An equivalent electrical circuit model was developed from electrochemical impedance spectroscopy then utilised as a simulation model. An active laboratory-size PEM electrolysis system was used to investigate the impact of various ripple currents on the efficiency of the system and to verify the simulation results. Results revealed that the average power consumption increases as the ripple factor increases and decreases as the frequency of the ripple increases, while the waveform of the applied current has no effect. Furthermore, the average hydrogen flow rate is unaffected by the ripple factor, frequency or waveform of the applied ripple current.

1.6 Dissertation Overview

The first chapter of the dissertation includes background on the research project, the problem statement, aims and objectives, key research questions as well as a discussion on the research methodology used. Chapter 2 contain the literature study on all topics required for the rest of the research project. The topics discussed include the PEMWE operation and alternatives, electrochemical fundamentals, characterisation methods, equivalent electrical circuit models and power supply ripple characteristics. Several case studies on similar projects were also reviewed and included. The information presented in this chapter provides the foundation on which the following chapters were built. In Chapter 3, the experimental design is illustrated. This chapter includes a conceptual design, a detailed setup design as well as the experimental procedure that is followed. Chapter 4 presents the characterisation, modelling and simulation of the PEM electrolyser used in this study.

The purpose of this chapter is to formulate an accurate model of the PEM electrolyser and simulate the possible effects of a power supply ripple on the efficiency of the electrolyser. In Chapter 5 the experimental results are presented and analysed. In this chapter the effect of a fluctuating or ripple current on the power consumption, hydrogen production rate, efficiency and degradation rate of a PEM electrolyser are discussed. Chapter 6 is the final and closing chapter of this dissertation in which an overview of the study is presented. In this chapter the key research questions are answered, a summary of the verification and validation processes is given, a conclusion is drawn and some recommendations for future work are made.

1.7 Conclusion

The purpose of the first chapter was to give an overview of the research project and where the focus of this project lays. Background on the research problem is provided in Section 1.1, after which the purpose of the research including the problem statement, aims and objectives as well as the key research questions are discussed. Section 1.4 is a description of the research methodology that was followed to successfully complete the project, which is also illustrated in Figure 1-4.

The following chapter (Chapter 2) is the literature review chapter in which existing research and textbooks focusing on the main topics of this research project are reviewed. The literature study is required to ensure the correct methods are used to obtain accurate and useful results and subsequently answer the key research questions.

CHAPTER 2: LITERATURE STUDY

2.1 Introduction

This chapter contains an in-depth study on all principals, procedures, components and technologies that were necessary to complete this research project successfully. The literature reviewed in this chapter served as a foundation for the rest of the study and the chapters that follow. Figure 2-1 is a summary of all topics that were reviewed in the literature study and served as the literature review plan. Each block in the literature review plan is addressed and discussed in this chapter concerning existing research publications and textbooks.

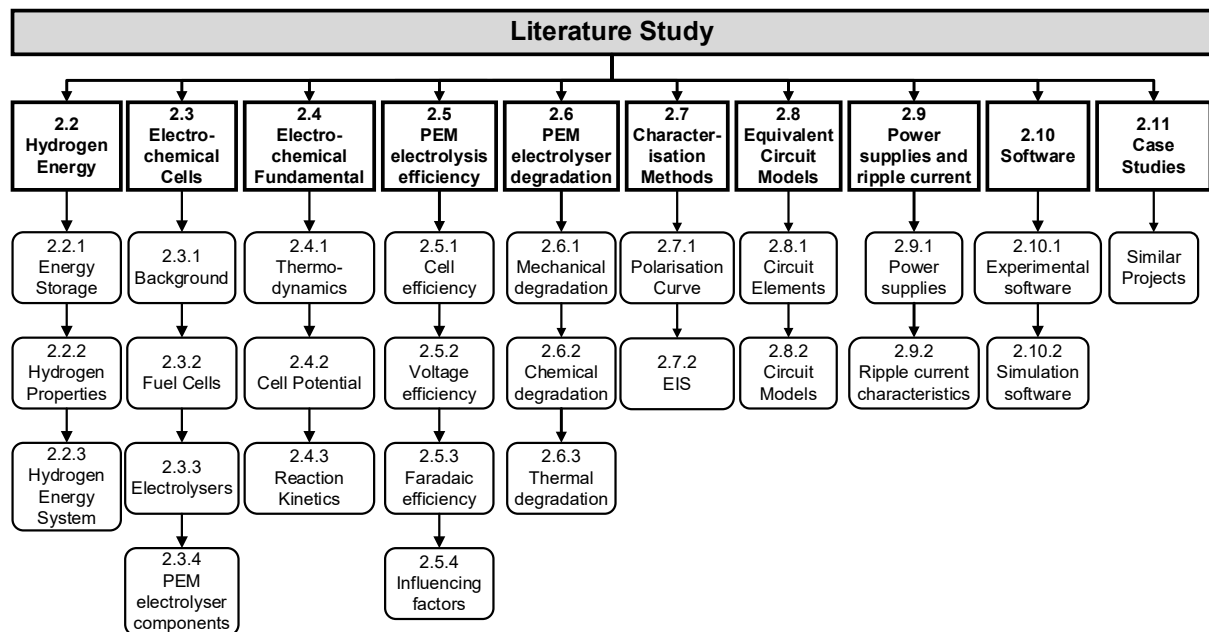


Figure 2-1: Overview diagram of Literature Study.

2.2 Hydrogen energy

The popularity of hydrogen as an energy carrier is increasing, and the purpose of this section is to highlight the reasons for the appeal. Topics reviewed in this section includes a comparison between possible energy storage mediums, the general properties of hydrogen as well as an introduction on hydrogen energy systems.

2.2.1 Energy Storage

Renewable energy is one of the fastest growing industries in the energy sector and could be the solution to the world's increasing energy demand and limited fossil fuel resources.

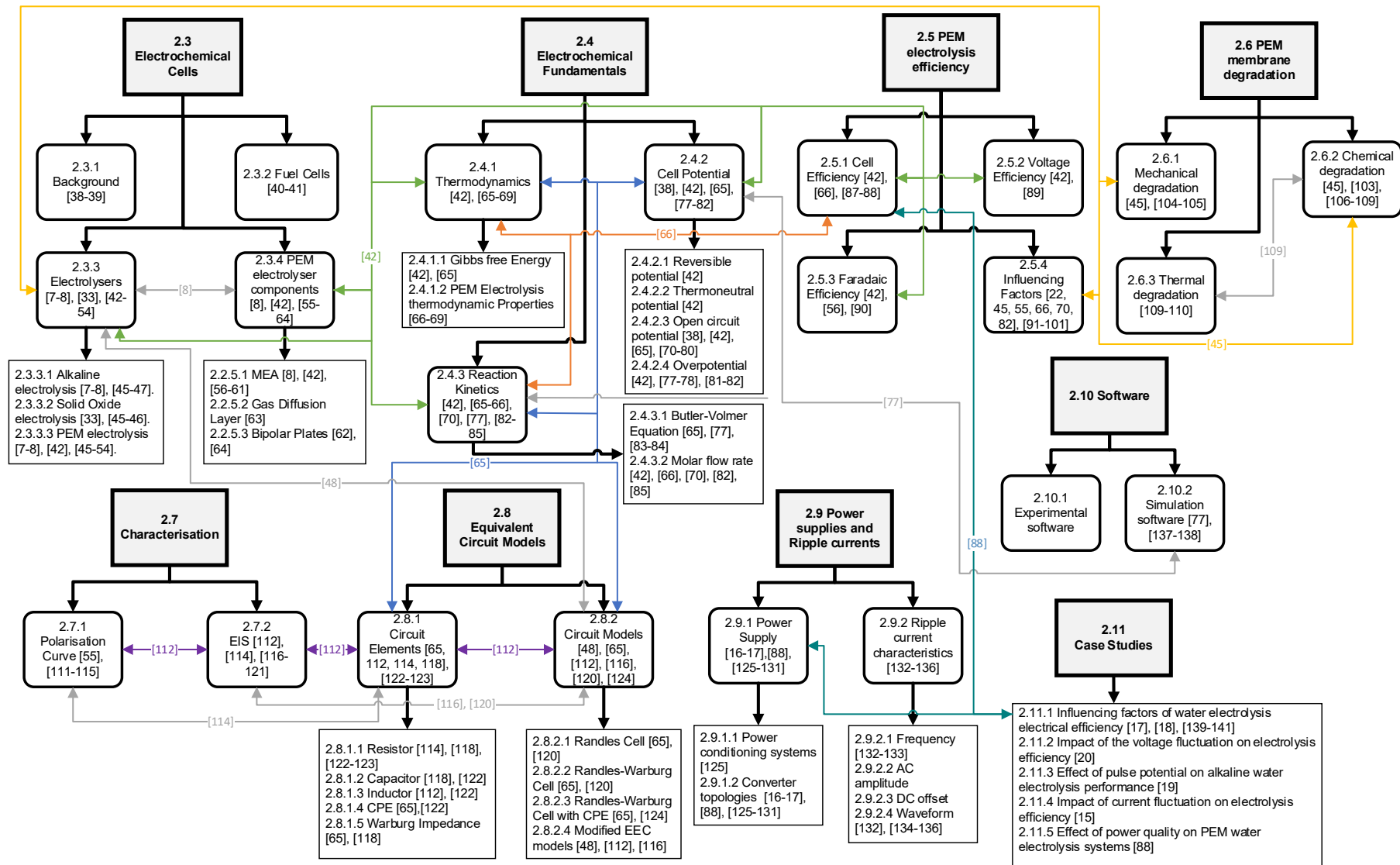


Figure 2-2: Detailed diagram of Literature study.

According to the International Renewable Energy Agency (IRENA), the global capacity for renewable energy generation reached a record increase of 167 GW in 2017 and stood at a total of 2179 GW globally in 2018 [23]. The average growth from 2011 to 2017 is around 8.3% per year according to statistics released by IRENA in March 2018 [24]. The main concern with renewable energy is the constant fluctuation in the energy supply due to the large dependency on weather conditions. Energy storage is thus essential to utilization renewable energy on a large scale and replaces the current methods of energy generation. Energy can be stored using several different storage mediums and Figure 2-3 illustrates the advantages and disadvantages of each storage type in terms of its discharge time and storage capabilities. The most promising energy storage technologies in terms of storage capacity are hydrogen, pumped-hydro and compressed air energy. Although pumped-hydro and compressed air energy are worthy alternatives to hydrogen energy, these methods of energy storage are largely subjected to geographical conditions [25]. Many thus believe that hydrogen is the energy carrier of the future and that hydrogen energy also has the most substantial potential for storage capacity improvement [4-6]. The potential storage capacity of hydrogen is even larger than the scale of Figure 2-3 and can be achieved by liquid hydrogen or compressed hydrogen gas storage [25].

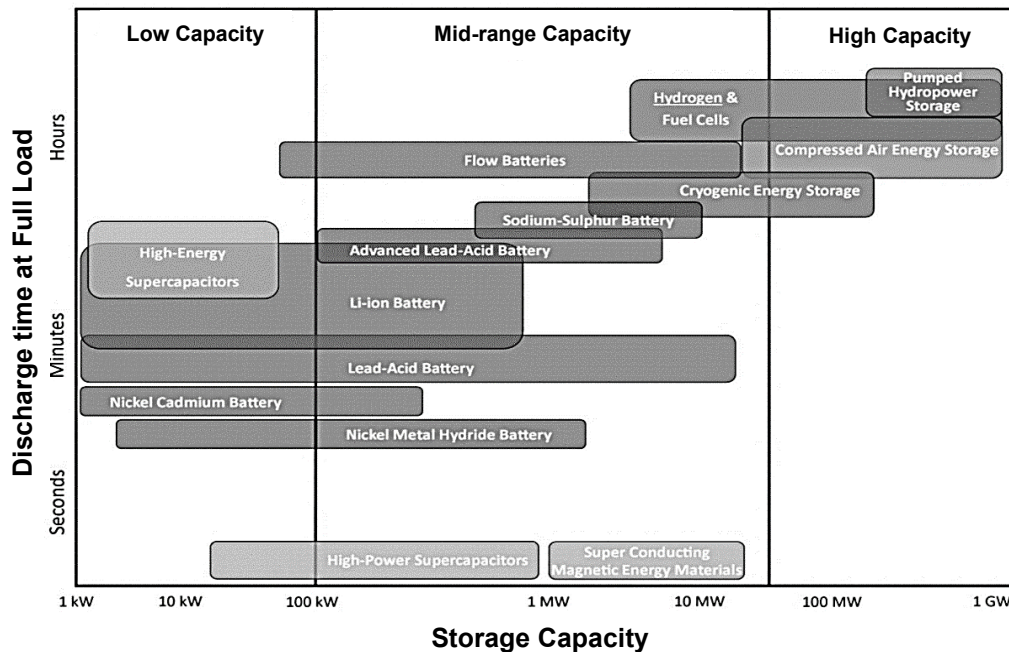


Figure 2-3: Comparison of energy storage technologies (adapted from [25]).

2.2.2 Hydrogen Properties

Hydrogen was already unknowingly discovered in the early stages of the 16th century by physician Theophrastus Paracelsus when he dissolved iron in sulphuric acid which reacted to produce an unknown gas [26].

However, he did not receive credit for the discovery since the gas he observed was not classified and formally described. More than two centuries later, in 1766 Henry Cavendish received credit for the discovery after he described some of the characteristics of hydrogen and recognized hydrogen as an element [26, 27]. However, the name hydrogen did not come from Cavendish who simply referred to hydrogen as “inflammable gas”. Later it was discovered that hydrogen gas is not an element but a molecule that can be simplified into hydrogen atoms. Hydrogen is known to be the most abundant element in the universe, with more than 90% of all atoms being hydrogen and these atoms contributing up to 75% of the total mass of the universe [28]. Hydrogen can be found on earth, primarily combined with oxygen to form water, but is also present in a lot of other compounds such as biomass (plants, animals, etc.) and fossil fuels (coal, oil, etc.). Hydrogen molecules are made up of two hydrogen atoms and are a colourless and also odourless gas [29]. This gas is the lightest of all gases with a density of only $0.08988 \text{ g} \cdot \text{L}^{-1}$, which makes hydrogen the fuel with the highest energy to mass ratio available [30]. This property enables large amounts of energy to be stored in smaller packages than possible with other fuels and energy storage mediums available. Table 2-1 show the basic properties of hydrogen as an atom and molecule.

Table 2-1: Hydrogen properties (combined from [28], [29], [31], [32]).

Hydrogen Atom	
Atomic Number	1
Atomic Symbol	H
Atomic Weight	[1.00784; 1.00811]
Electron Configuration	1
Hydrogen Molecule	
Molecule Formula	H ₂
Chemical Structure	H-H
Molecular weight	2.01588 g
Gas Density	0.08988 g.L ⁻¹ (at 273.15 K and 1 atm)
Electrical energy per kg	39.4 kWh (HHV), 33.3 kWh (LHV)

2.2.3 Hydrogen energy system

Ball *et al.* (2009) [6], Veneri (2011) [4], Wang *et al.* (2014) [33], Møller *et al.* (2017) [25], Dincer *et al.* (2018) [5] and many more all describe hydrogen as the energy carrier of the future provided that sustainable energy sources are used for its production. However, the International Renewable Energy Agency (IRENA) reported that more than 95% of all current hydrogen production uses fossil fuels as an energy source [10], which means that only a very small percentage of the current hydrogen production systems use sustainable energy sources.

In order to build a clean and sustainable hydrogen energy system for the future, it is thus essential to use renewable energy sources (RES) such as solar, wind and hydro energy. When using a fluctuating RES, such as wind or solar, to produce hydrogen the excess energy supply can be stored as hydrogen gas, eliminating the need for additional energy storage systems such as batteries. A clean hydrogen energy system, using water as a material source and renewable energy as an energy source is illustrated by Figure 2-4 below. The first stage of the hydrogen energy system presented in the figure below is the hydrogen production. The hydrogen is produced making use of an electrolyser, which splits water into hydrogen and oxygen gas using the electrical energy supplied by the RES. Next, the hydrogen gas can either be injected into the pipelines of an existing gas network [7] or transported via super tankers tot the end user [34]. The stored hydrogen can then be used for transportation applications such as hydrogen-powered vehicles [35], as an alternative/replacement for natural gas [36], [37] or reconverted to electricity using a fuel cell. The only emissions from all of the above-mentioned applications are either water or steam [34]. The main advantages of hydrogen as an energy carrier are the capability of hydrogen to be store on a large scale, the level of flexibility hydrogen provides and the low negative impact on the environment (if produced using RES).

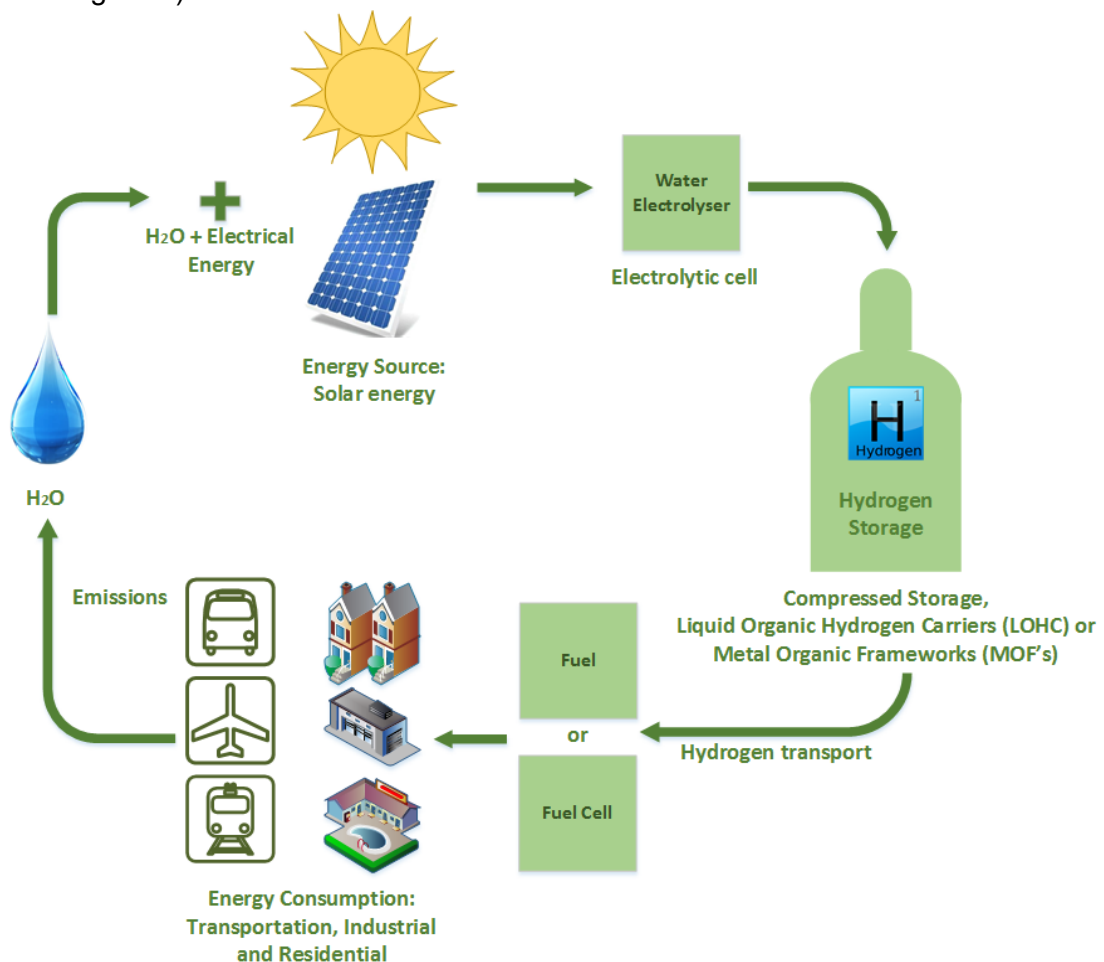


Figure 2-4: Hydrogen Energy System (adapted from [34]).

2.3 Electrochemical Cells

This section of the literature study is thus devoted to the investigation of the electrochemical cells used in a hydrogen energy system. The research included reviewing different electrochemical cells, alternatives to PEMWE as well as an in-depth review on the operation, components and characteristics of a PEM electrolyser.

2.3.1 Background

Electrochemical cells are the devices that initiate an electrochemical process to takes place and are made up of two electrodes and an electrolyte. The electrodes, known as the anode and cathode, are responsible for the conduction of electrons, while the electrolyte is the ionic conductor which separates the anode and cathode. There are two types of electrochemical cells used in a hydrogen energy system. The first is a Galvanic cell which is used to transform chemical energy into electrical energy and the second an Electrolytic cell which is used to convert electrical energy into chemical energy [38].

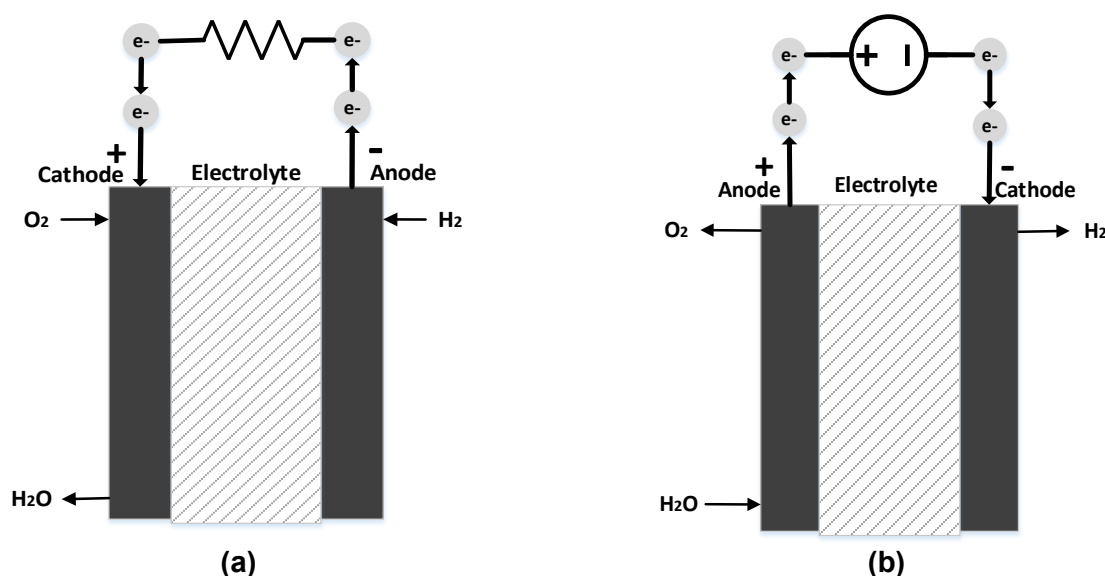
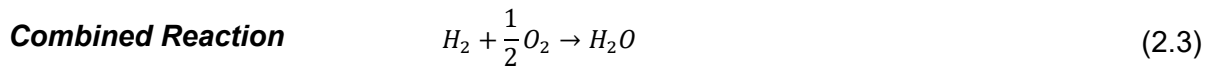
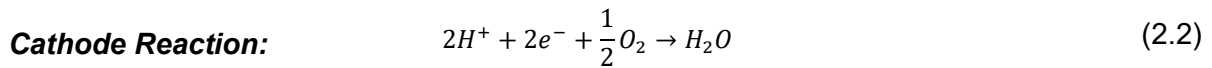
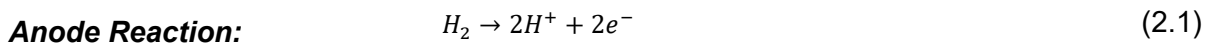


Figure 2-5: Electrochemical (a) Galvanic cell (b) Electrolytic cell (adapted from [39]).

2.3.2 Fuel Cells

Figure 2-5 (a) above is a representation of a Galvanic cell. A galvanic cell consumes chemical energy in the form of hydrogen and oxygen gas and transforms the energy captured in these gases to electrical energy. These cells are commonly known as fuel cells and are used to generate electricity and utilize the stored energy in a hydrogen system. Fuel cells have many advantages over conventional forms of electricity generation through combustion of fossil fuels.

These advantages include a relatively good efficiency compared to combustion-based electricity generation (up to 60%), high current density capabilities, pollution free operation and the only by-products, which are water and heat, can potentially be reused or reallocate [40]. Figure 2-5 (a) illustrates that hydrogen gas is supplied to the anode side of the fuel cell where it is oxidized and in effect releases electrons and hydrogen ions as per equation (2.1) [41]. The electrons generated at the anode are transferred to the cathode through an external circuit to which an electric load can be connected. The oxygen supply, as well as the electrons generated, are reduced to O_2^{2-} ions at the cathode side of the fuel cell. The H^+ ions then migrate through the electrolyte to the cathode and combine with the O_2^{2-} ions to form water as illustrated by equation (2.3) [41].



There are several different types of fuel cells available that can be used over a wide range of applications such as portable electricity generation (<100 W), stationary electricity generation (up to 1 MW) or in automotive vehicles. The characteristics of the most common fuel cell technologies are compared in Table 2-2 below.

Table 2-2: Fuel cell comparison (adapted from [40]).

Fuel Cell	PEM	AFC	PAFC	MCFC	SOFC
Electrolyte	Perfluoro sulfonic acid	Potassium hydroxide	Phosphoric acid	Molten lithium, sodium, and potassium carbonates	Ytria stabilized zirconia
Operational Temp.	<120 °C	<100 °C	150-200 °C	600-700 °C	500-1000 °C
Sack size	1 - 100 kW	1 -100 kW	5 - 400 kW	300 kW – 3 MW	1 kW – 2 MW
Efficiency (LHV)	≤ 60%	≤ 60%	≤ 40%	≤ 50%	≤ 60%

2.3.3 Electrolysers

Figure 2-5 (b) illustrates an electrolytic cell, which uses an electric current to produce hydrogen and oxygen gas by splitting water. The electrochemical process that takes place to split water into hydrogen and oxygen by passing an electric current through the electrodes of an electrolyser is known as water electrolysis [42]. Hydrogen production through water electrolysis is a pollution free process if renewable energy sources are used and consequently considered the cleanest technique to produce hydrogen [7].

However, fuel processing hydrogen production techniques such as steam-methane reforming, oil gasification and coal gasification currently contribute more than 95% to the total hydrogen production. The reason is that even though water electrolysis is better for the environment, it is much more expensive than fossil fuel-based hydrogen production techniques. If hydrogen is considered a fuel that needs to be produced in the most economical way possible, water electrolysis is not the solution. However, if hydrogen is regarded as an energy storage medium for the growing renewable energy sector, water electrolysis shows excellent potential. Electrolysis also enables hydrogen end users to produce hydrogen on site which eliminates transportation costs and possibly become less expensive than other forms of hydrogen production [43]. Experts in the water electrolysis industry believe that research and development on water electrolysis processes can reduce the initial capital investment by as much as 24% with the possibility of an additional 30% cost reduction through a production scale-up [44]. As is the case with fuel cells, there are different types of water electrolysis technologies, with the primary difference the electrolyte used. The most widely used technology is alkaline water electrolysis (AWE) with solid oxide electrolysis (SOE), anion-exchange membrane electrolysis (AEWE) and proton exchange membrane water electrolysis (PEMWE) the fastest developing technologies [43]. The focus of this study is on PEM electrolysis, but before this technology is reviewed in detail, the alternative technologies namely Alkaline electrolysis and Solid oxide electrolysis are discussed.

2.3.3.1 Alkaline Electrolysis

AWE is the oldest electrolysis technology used for hydrogen production; this technology is thus the most developed and the economical of the above-mentioned electrolysis types. AWE is more than 100 years old and one of the simplest and advanced methods used for hydrogen production. An AWE system operates at low temperatures of between 40 °C and 90 °C and the electrolyte used is a liquid alkaline solution containing sodium hydroxide (NaOH) or potassium hydroxide (KOH) [8]. The advantages of AWE include the low cost, mature stage of development and long durability while disadvantages such as the low hydrogen gas purity and low operational current densities remain the primary concerns [8]. In an alkaline water electrolyser, the water is decomposed to form H_2 and OH^- at the cathode side of the electrolyser. This reduction is caused by the electrons that are gained from the power supply connected to the electrolyser. The charge carrier is OH^- which migrates to the anode, through the electrolyte, where it is oxidised and O_2 are formed. The chemical reactions that take place at the cathode and anode of an alkaline electrolyser are expressed by equations (2.4) [45] and (2.5) [45], a schematic of a typical AWE cell is illustrated in Figure 2-6 and the general characteristics of the cell can be seen in Table 2-3.

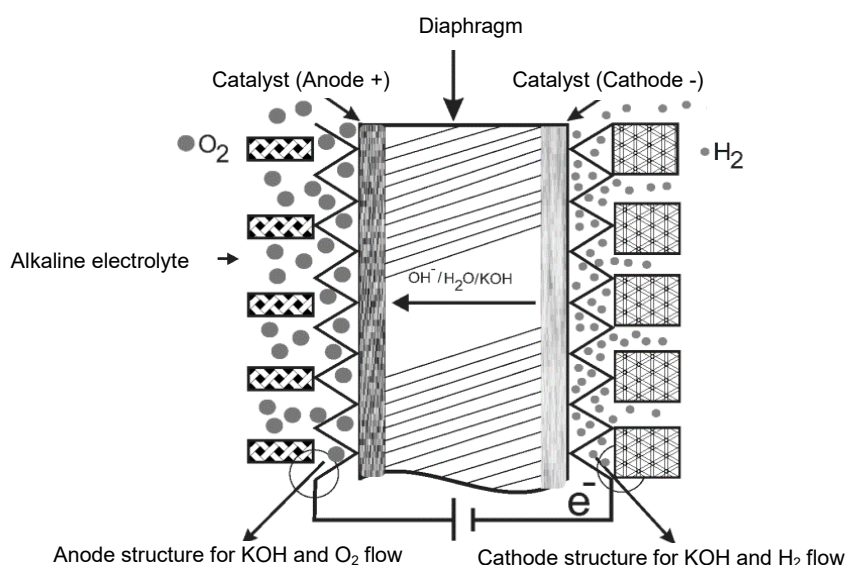
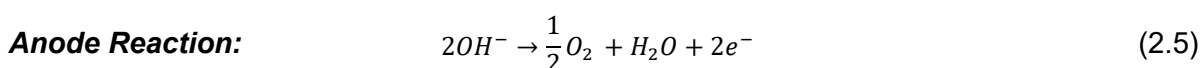
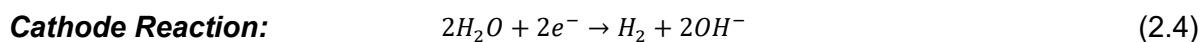


Figure 2-6: AWE cell schematic (adapted from [46]).

Table 2-3: Alkaline water electrolysis characteristics (combined from [45] and [46]).

Characteristics	
Operating temperature	40-90 °C
Operating Cell Voltage	1.8-2.4 V [47]
Operating Current Density	0.2 – 0.5 A/cm ²
Efficiency HHV	60% - 77%
Discharge pressure	2-30 bar
Hydrogen purity	99.5% - 99.9998%
System lifetime	20-30 Years [7],[47]
Electrolyte	NaOH/KOH
OER Electrode	Ni/Co/Fe
HER Electrode	Ni
Charge carrier	OH ⁻

A solid polymer electrolyte such as an anion-exchange membrane (AEM) can also be used in AWE instead of the liquid electrolyte discussed above. In an AEM-based water electrolysis cell, the same half reactions take place as were expressed by equations (2.4) and (2.5). However, a much lower concentration alkaline solution is required, and no corrosive liquid electrolyte is used. It has also been reported that AEM-based water electrolysis cells have the potential to meet the high performance capabilities of PEM water electrolysis cells, but at a fraction of the cost [46].

2.3.3.2 Solid Oxide Electrolysis

SOE is an electrolysis process that takes place at high temperatures of between 700 °C and 1000 °C. The electrolyte used for this technology is conventionally a Zirconium dioxide (ZrO_2) doped with Yttrium oxide (Y_2O_3) solid ceramic electrolyte. High temperature electrolysis is appealing due to the electrical power efficiency of such a system. The electrical energy demand of the system, as well as the decomposing voltage of water, decreases as the system temperature increases; this relation is illustrated in Figure 2-7.

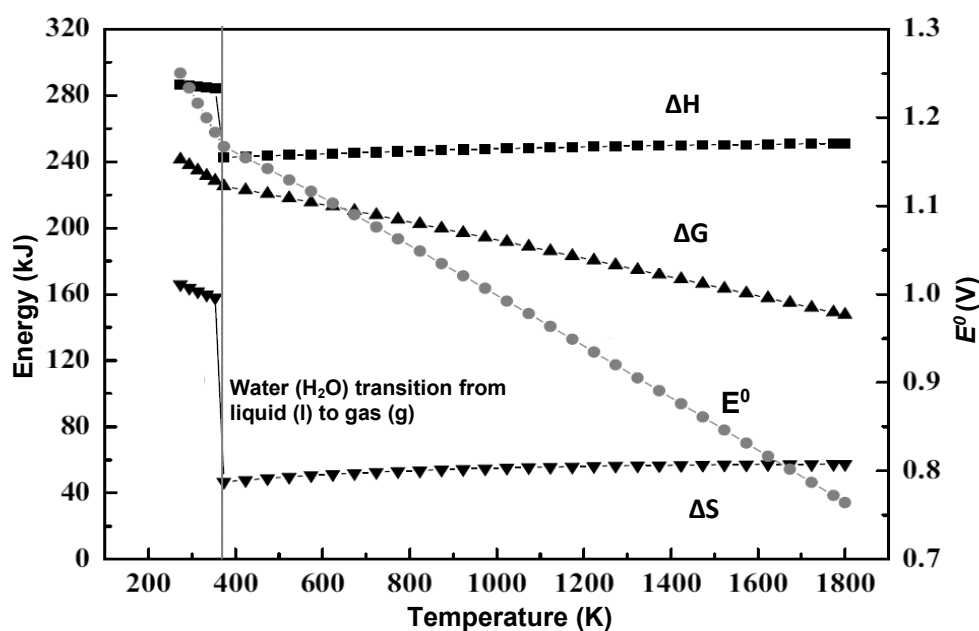


Figure 2-7: Thermodynamics of water electrolysis (adapted from [33]).

At standard conditions which are at 25 °C and 1 atm, the theoretical electrical energy demand of a water electrolysis system is 474 kJ.mol⁻¹ and the theoretical decomposing voltage of water is 1.23 V. If the same calculation is to be done at a temperature of 900 °C, the electrical energy demand and decomposing voltage would decrease to 366 kJ.mol⁻¹ and 0.95 V respectively [33]. In addition to the drop in the decomposing voltage of water, overpotentials also decrease as the temperature increases. Although high temperature electrolysis has many advantages, some of the drawbacks that are experienced are the size of the system and the low durability of the system due to the high temperature under which it operates. In a solid oxide electrolyser, the water supply, H_2O , is reduced to H_2 and O^{2-} at the cathode side of the electrolyser due to an electron gain. The charge carrier, O^{2-} , then migrates through the electrolyte to the anode side of the electrolyser where it is oxidised to form O_2 . The anode and cathode half reactions are expressed in equations (2.7) [45] and (2.6) [45] and the general characteristics of solid oxide electrolysis are shown in Table 2-4.

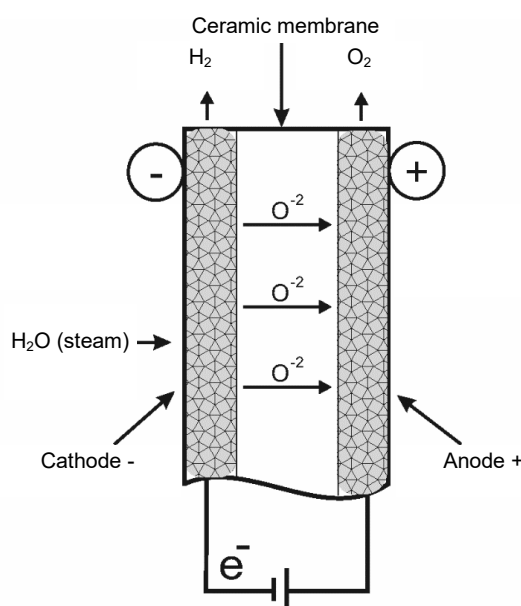
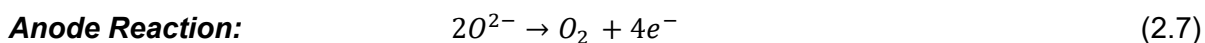
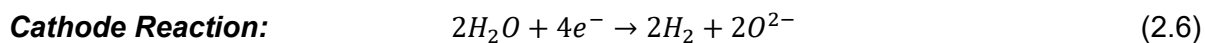


Figure 2-8: SOE cell schematic (adapted from [46]).

Table 2-4: Solid Oxide electrolysis characteristics (combined from [45] and [46]).

Characteristics	
Operating temperature	700-1000 °C
Operating Current Density	0.5 – 1 A/cm ²
Efficiency HHV	Up to 89%
Discharge pressure	10-40 bar
System lifetime	Up to 1 Year
Electrolyte	Ceramic membrane
Electrode	Ni-cement
Charge carrier	O ²⁻

2.3.3.3 PEM Electrolysis

As previously stated, this study is focused on PEMWE since this technology holds many advantages, which will be discussed in the following two sections, over other water electrolysis technologies. Figure 2-9 is a schematic that illustrates the basic operation and the main components in a single cell PEM electrolyser. The essential components include a solid polymer electrolyte called a Proton Exchange Membrane (PEM), catalyst layers or electrodes; gas diffusion layers (GDL) and flow fields. A complete description of these components is provided in section 2.3.4

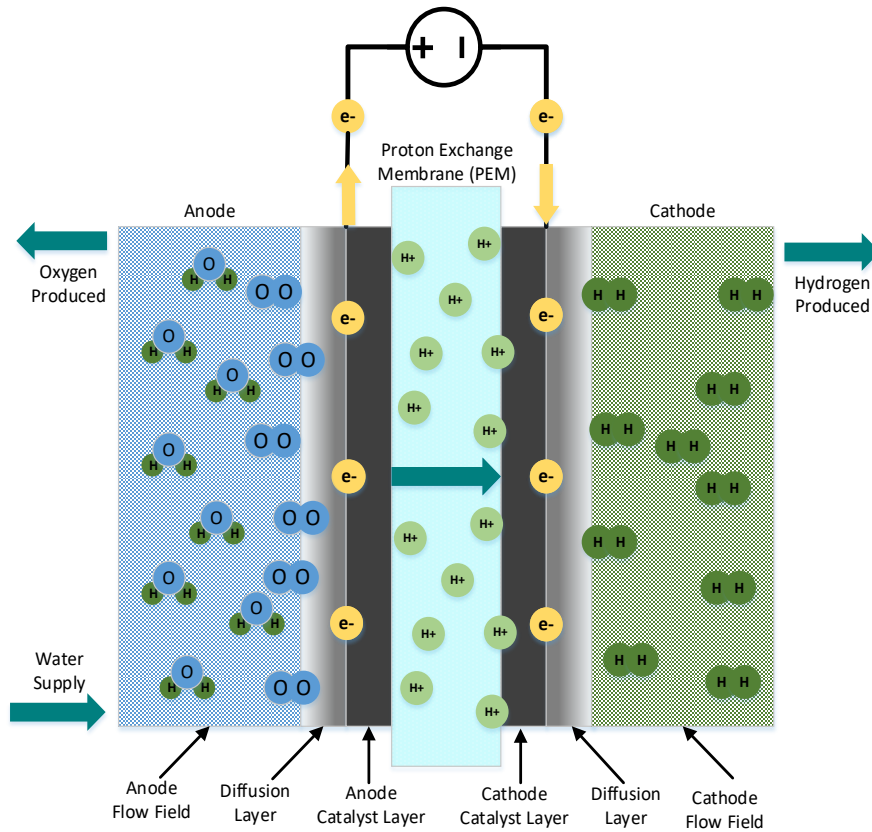
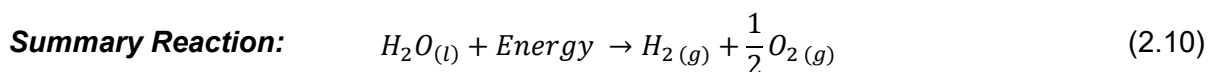
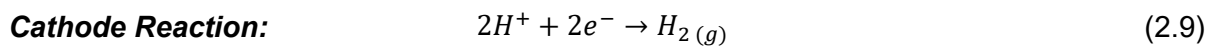
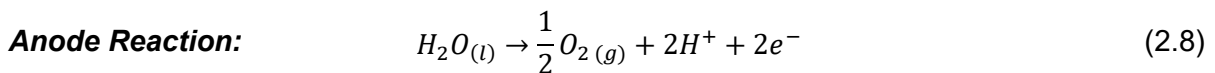


Figure 2-9: PEM Electrolyser (adapted from [48-50]).

When an electrical current is applied to the electrolyser, electrons are released at the anode side of the system and the water supplied to the anode is oxidised to form oxygen (O_2) and hydrogen ions or protons (H^+) [8, 51]. The ion-conducting membrane then transfers the hydrogen ions H^+ from the anode to the cathode. The electrons released at the anode side are transferred to the cathode side through the electrical power supply. The hydrogen ions then gain electrons at the cathode side of the system and are reduced to hydrogen in gas form (H_2) [8, 51]. The anode, cathode as well as the summary reactions taking place during hydrogen production through PEM water electrolysis is illustrated in equations (2.8), (2.9) and (2.10) [8, 51].



The operating conditions of a PEM electrolysis system can vary a great deal depending on the size of the system and the design used by electrolyser manufacturers such as ITM Power, Hydrogenics, Giner, Proton OnSite, Siemens, AREVA H₂Gen and H-TEC System [7], [52].

The typical operating conditions and characteristics of a PEM electrolyser, illustrated in Table 2-5, is thus only a guideline as reported by several authors who researched PEM electrolysis. Literature shows that most of the existing PEM electrolysis systems generate hydrogen at a pressure of up to 30 bar, but the possibility exists to significantly increase the operating pressure in the future (up to 350 bar) [7, 45, 47]. The high pressure operating capabilities of a PEM electrolyser is one of the most considerable advantages since it reduces the energy required for hydrogen gas pressurization [7, 47, 53]. PEM electrolysers are typically operated at temperatures between 50 and 90 °C and a cell voltage between 1.8 and 2.2 V [47]. The temperature and voltage range are very similar to that of an alkaline electrolyser with the current density being the property that differs the most. A PEM electrolyser can operate at current densities of more than 2 A/cm² in ideal conditions which is much higher than the capability of an alkaline electrolyser which typically only operate at current densities up to 0.5 A/cm² [45, 47, 54]. The higher current density capabilities of a PEM electrolyser result in a lower operational cost which can possibly reduce the overall cost of hydrogen production through water electrolysis [47]. The thin and solid electrolyte (membrane) also allows for a high proton conductivity and ion transfer which lowers the ohmic losses when compared to alkaline water electrolysers [7, 42, 47, 53]. Another property of PEM electrolysis that stands out above other forms of electrolysis is the high purity of the hydrogen gas produced. Most of the disadvantages, when compared to the other water electrolysis technologies, have to do with the cost and durability of a PEM water electrolyser. The PFSA membrane is more expensive than the liquid electrolyte used by alkaline water electrolysis and the thin membrane is sensitive to mechanical damage and chemical degradation [42, 46].

Table 2-5: PEM Electrolysis characteristics (combined from [45] and [46]).

Characteristics	
Cell temperature	50-90 °C
Cell Voltage	1.8-2.2 V [47]
Current Density	0.6-2.5 A/cm ²
Efficiency HHV	40-65%
Maximum pressure	15-50 bar (potentially up to 350 bar)
Hydrogen purity	99.999%
System lifetime	Up to 5 Years
Electrolyte	Perfluorosulfonic acid polymer membrane
OER Electrode	Ir/IrOx/Ru
HER Electrode	Pt
Charge carrier	H ⁺

2.3.3.4 Electrolysis technology comparison

Since this study is focusing only on PEMWE, the positives and negatives of this technology compared to AWE and SOWE are reviewed. Comparing the stage of development in each of the above-mentioned electrolysis technologies, it is clear that alkaline water electrolysis is the most established water electrolysis technology to produce hydrogen. For more than 100 years alkaline water electrolysis has been used and improved in many different industrial applications. Even though alkaline electrolysis is the most widely used electrolysis technology, the advantages of PEM electrolysis have increased the appeal to this relatively new technology over the past few years. The benefits of PEM water electrolysis are also superior to the advantages obtained from high temperature water electrolysis such as solid oxide electrolysis since this technology shows low durability and are still in an immature stage. The main advantages and disadvantages of Alkaline, PEM and Solid oxide electrolysis were obtained from several research publications and textbooks and are presented in Table 2-6 below.

Table 2-6: Advantages and disadvantages of different electrolysis technologies (combined from [7], [42], [47], [53], [46]).

Alkaline electrolysis	PEM electrolysis	Solid oxide electrolysis
Advantages	Advantages	Advantages
Established and proven technology	Higher current densities (up to 2.5 A/cm ²)	High efficiency (Up to 89%)
Low cost of components	Rapid response time	High operating pressure (up to 40 bar)
Large stack size (MW-scale)	High voltage efficiencies	
High proven durability (up to 30 years)	High hydrogen gas purity	
	High operating pressure (potentially up to 350 bar)	
Disadvantages	Disadvantages	Disadvantages
Low current densities (up to 0.5 A/cm ²)	High cost of components	Low proven durability (up to 1 year)
Low operating pressure (up to 30 bar)	Low proven durability (up to 5 years)	Immature technology
	Limited stack size (currently only small-scale use)	Limited load flexibility

2.3.4 PEM Electrolyser components

Although the design of the PEM electrolyser used during the experimental procedure is not covered in this project, the main components were investigated to understand the general operation of the cell fully.

Knowledge on the components of a PEM electrolyser was essential to ensure the correct components were selected for this study. The main components of a PEM electrolyser include a membrane electrode assembly (MEA), gas diffusion layers (GDL's) and bipolar plates which also contains the flow fields [8, 42, 55]. The location and commonly used materials for each component in a PEM electrolysis cell are illustrated in Figure 2-10.

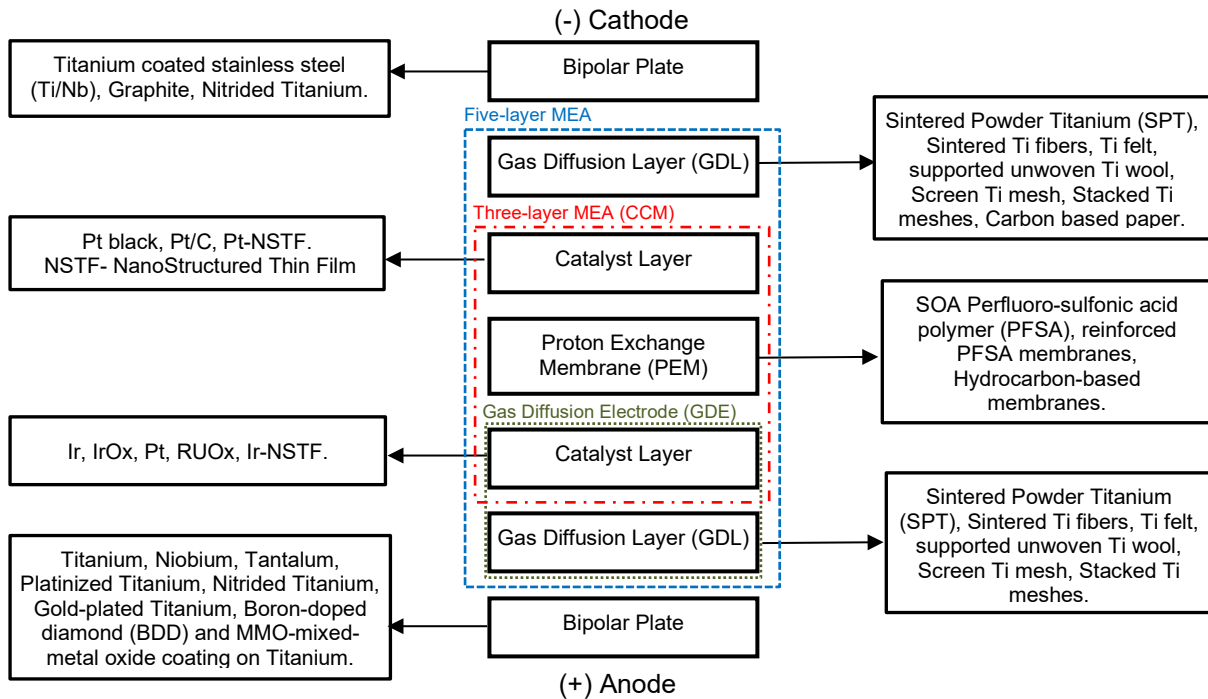


Figure 2-10: PEM electrolyser component materials and terminology (adapted from [46]).

2.3.4.1 Membrane Electrode Assembly

A three-layer MEA consists of a proton exchange membrane positioned between the anode and cathode electrodes (catalyst layers). In a three-layer MEA the electrodes (catalyst layers) are coated directly onto the membrane, in which case the membrane can also be referred to as the catalyst coated membrane (CCM) [42], [56]. A five-layer MEA on the other hand consists of a proton exchange membrane, the anode and cathode electrodes (catalyst layers) and two GDL's. In a five-layer MEA the catalyst layers can either be coated to the membrane or to the GDL's, in which case the GDL's are called the gas diffusion electrodes (GDE).

Membrane

In a PEM electrolyser, the membrane or PEM is a solid polymer electrolyte, positioned between the cell electrodes (catalyst layers) and is between 50 μm and 250 μm thick [57]. The membrane is responsible for the conduction of hydrogen ions and also serves as a separation between the hydrogen and oxygen in the cell. The membrane used in PEM electrolyzers is required to be in possession of certain properties.

Considering the critical role a membrane plays in a PEM electrolyser, the membrane properties have a significant influence on the performance and durability of the cell. Essential membrane properties include high proton conductivity, small gas permeability, mechanical strength, oxidative and reductive stability as well as durability [8, 57, 58]. The perfluorosulfonic acid polymers (PFSA) that possess the required properties and can be used in a PEM electrolyser includes Nafion[®], Flemion[®], Fumapem[®] and Aciplex[®], with Nafion[®] being the most commonly used one [8, 57]. Nafion[®] is the brand name used by the manufacturer, DuPont, for this sulfonated tetrafluoroethylene based fluoropolymer [59].

Anode and Cathode electrode

The electrodes form part of the MEA in the form of a catalyst layers coated on each side of the solid electrolyte or onto the GDL's. Several different methods are available for coating the electrodes in the form of catalyst layers directly onto the membrane to form a CCM or onto the GDL's to form GDE's. The most commonly used methods include spray coating, screen printing and electro-depositing [60, 61]. The catalyst layers are key components in a PEM electrolyser since all of the electrochemical reactions take place on the surface of the electrodes [61]. Oxidation takes place at the anode catalyst layer while reduction occurs at the cathode catalyst layer. The archetypal material used for the anode catalyst is iridium oxide while platinum is used for the cathode catalyst [62].

2.3.4.2 Gas diffusion Layer

The gas diffusion layers are positioned on the outsides of the three-layer MEA between the catalyst layers and the flow fields of the bipolar plates. These GDL's should consist of specific porous properties as to allow the transportation of gas from the catalyst layers to the flow channels, while also providing an electrically conductive path between the catalyst layers and the bipolar plates [63]. The GDL's have a significant impact on the performance of a PEM electrolyser since slow gas transportation and a meagre conductive path will increase the cell resistance.

2.3.4.3 Bipolar plates

In an electrolyser system, a specific number of electrolytic cells are combined to generate a sufficient amount of hydrogen gas for the required application. These cells are combined in a series configuration and typically known as electrolyser stacks. Bipolar plates are the components in an electrolyser that connects these cells to form stacks [62]. One of the functions of the bipolar plate in an electrolyser cell stack is to create an electrical connection between the series connected cells. Additionally, the bipolar plates also serve as a barrier between the oxygen formed at the anode of one cell and the hydrogen formed at the cathode of the next cell in the stack. The bipolar plates also contain flow field structures to improve the flow of water, hydrogen and oxygen to and from the electrodes [62].

These plates are thus sometimes referred to only as the flow fields. Figure 2-11 below is an illustration of a PEM electrolyser stack with two bipolar plates combining three PEM electrolyser cells. The stack is held together by the end plates which are positioned on the sides of the stack and contain only of one flow field each.

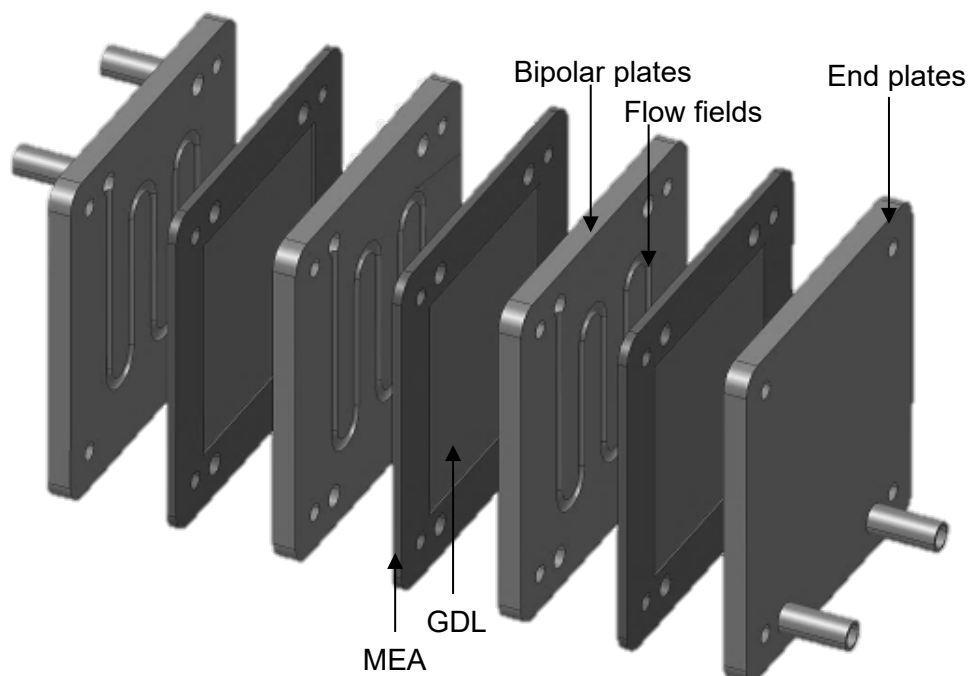


Figure 2-11: PEM Electrolyser stack (adapted from [64]).

2.4 Electrochemical Fundamentals

In this section of the literature study, the electrochemical fundamentals of a PEM water electrolyser are discussed. The fundamentals explained include thermodynamics, reaction kinetics, overpotential, efficiency and degradation. The focus of this section is on the mathematical models used to represent the reaction speeds, energy required, losses and efficiency of a PEM electrolysis cell.

2.4.1 Thermodynamics

In a PEM water electrolysis system, the primary purpose is to decompose water into oxygen and hydrogen. The energy that is required to break or form bonds in a chemical reaction is referred to as the reaction enthalpy ΔH . The reaction enthalpy can be defined as the sum of the products enthalpies of formation $\Delta H_{f,prod}$, minus the sum of the reactants enthalpies of formation $\Delta H_{f,rcf}$ [42]. In the case of water electrolysis under ambient conditions, the products of the reaction are hydrogen and oxygen gas while water is the only reactant. Since the products of the reaction exits in molecule form and no further bond breaking occurs, their enthalpy of formation is zero [42].

The reaction enthalpy for water electrolysis is thus determined only by the enthalpy of formation of the water reactant. The decomposing of water in a water electrolysis reaction is activated by two forms of energy, namely thermal and electrical energy. The change in enthalpy ΔH can be written as the sum of the electrical and thermal energy required as illustrated by equation (2.11), where ΔG is the change in Gibbs free energy, ΔS is the change in entropy and T the system temperature [42, 65]. The entropy term $T\Delta S$ gives the thermal energy required while the change in Gibbs free energy ΔG represents the electrical energy required. The relation between these thermodynamic terms and how they are affected by temperature are illustrated in Figure 2-7 discussed in section 0 above.

$$\Delta H = \Delta G + T\Delta S \quad (2.11)$$

2.4.1.1 Gibbs free energy

The Gibbs free energy is a thermodynamic quantity that is used to determine if the reaction will occur spontaneously without the addition of an external energy source. Equation (2.12) defines the change in Gibbs free energy, where ΔH is the change in enthalpy, ΔS is the change in entropy and T the system temperature [42, 65].

$$\Delta G_R = \Delta H_R - T\Delta S_R \quad (2.12)$$

If $\Delta G < 0$ the reaction does not need the addition of energy and will spontaneously take place, while if $\Delta G > 0$ the reaction is nonspontaneous and needs an external energy supply, which is true in the case of water electrolysis. In a water electrolysis reaction, the Gibbs free energy is supplied to the system in the form of an electrical energy source.

2.4.1.2 Thermodynamic properties of PEM water electrolysis

The change in Gibbs free energy (ΔG_R^0), the change in enthalpy (ΔH_R^0) and the change in entropy (ΔS_R^0) for a water electrolysis process under standard conditions can be determined, using the values given in Table 2-7 together with the general chemical reaction of water electrolysis, expressed by equation (2.13) below [42].



Table 2-7 gives the thermodynamic properties for the reactants and products of water electrolysis under standard conditions ($p = 1$ atm and $T = 298.15$ K). Included in the table is the enthalpy of formation (ΔH_f^0) and the entropy of formation (S_R^0) values for each product and reactant presented in equation (2.13).

Table 2-7: Thermodynamic properties (combined from [66-68]).

Substance	Molecular weight (g. mol ⁻¹)	ΔH_f^0 (kJ. mol ⁻¹)	S_R^0 (J. mol ⁻¹ K ⁻¹)
Liquid Water $H_2O_{(l)}$	18.01528	-285.830	69.942
Hydrogen Gas $H_{2(g)}$	2.01588	0.000	130.681
Oxygen Gas $O_{2(g)}$	31.99880	0.000	205.149

The change in reaction entropy (ΔS_R^0) which is defined as the reaction entropy difference between the product and the reactants can be calculated as illustrated by equation (2.14) [69]. The change in the reaction enthalpy (ΔH_R^0) is defined as the difference between the enthalpies of formation of the reactants and the products as shown by equation (2.15) [69]. After obtaining the change in entropy and the change in enthalpy, the change in Gibbs free energy (ΔG_R^0) under standard conditions can be calculated using equation (2.16) [69]. The change in enthalpy (ΔH_R^0) can also be referred to as the higher heating value (HHV) while the Gibbs free energy (ΔG_R^0) can be referred to as the lower heating value (LHV) [69].

$$\Delta S_R^0 = S_{R,prod}^0(H_2) + \frac{1}{2} S_{R,prod}^0(O_2) - S_{R,rcr}^0(H_2O) = 0.1633135 \text{ kJ. mol}^{-1} \text{ K}^{-1} \quad (2.14)$$

$$\Delta H_R^0 = \Delta H_{f,prod}^0(H_2) + \frac{1}{2} \Delta H_{f,prod}^0(O_2) - \Delta H_{f,rcr}^0(H_2O) = 285.83 \text{ kJ. mol}^{-1} \quad (2.15)$$

$$\Delta G_R^0 = \Delta H_R^0 - T \Delta S_R^0 = 285.83 - 298(0.1633135) = 237.16 \text{ kJ. mol}^{-1} \quad (2.16)$$

2.4.2 Cell potential

Water electrolysis is a nonspontaneous electrochemical reaction that requires an energy source to take place. The required energy is obtained from an electrical power source which supplies a constant current to the electrolyser, causing a potential difference between the electrodes. Current is defined as the rate at which electric charge flows past a point in the circuit, while the cell potential is a measure of the work done per unit charge. Since the current supply is constant, the cell potential is a good indication of the electrical efficiency of an electrolyser.

2.4.2.1 Reversible potential

The reversible potential of an electrolyser can be defined as the minimum theoretical potential required to decompose water at standard conditions ($p = 1 \text{ atm}$ and $T = 298.15 \text{ K}$). The potential of an electrolyser operating in reversible condition, that is in conditions without losses, can be expressed as a function of Gibbs free energy ΔG_R^0 or the LHV as illustrated by equation (2.17) [42].

The Gibbs free energy, ΔG_R^0 , is divided by the product of Faraday's constant, F , and the electrons, n , transferred during the chemical reaction [42]. The minimum theoretical potential required to decompose water at standard condition is thus 1.23 V.

$$E_{rev}^0 = \frac{\Delta G_R^0}{nF} = 1.23 \text{ V} \quad (2.17)$$

2.4.2.2 Thermoneutral potential

In conditions where there is no source of thermal energy ($T\Delta S$), all energy required for the reaction to occur should be obtained from the electrical energy source. The voltage required to decompose water under standard conditions without a thermal energy source is obtained using the reaction enthalpy ΔH_R^0 or the HHV rather than the Gibbs free energy ΔG_R^0 . This voltage is referred to as the thermoneutral potential and expressed by equation (2.18) [42]. If the thermal energy required is supplied by the electrical energy source, the minimum theoretical potential required to decompose water at standard condition is 1.48 V.

$$E_{th}^0 = \frac{\Delta H_R^0}{nF} = 1.48 \text{ V} \quad (2.18)$$

2.4.2.3 Open circuit potential

The Nernst equation was developed to determine the electrode potential of an electrochemical cell which operates at non-standard temperature and pressure conditions. Since chemical reactions are temperature and pressure dependant the electrode potential of an electrochemical cell is also affected by temperature and pressure. The chemical reaction that takes place in an electrochemical cell can be represented in terms of reduction (R) and oxidation (O), where oxidation is the loss of electrons (e^-) and reduction the gain of electrons. This chemical reaction is illustrated by equation (2.19) [38].



The Gibbs free energy can also be expressed in terms of the reduction and oxidation that take place in an electrochemical cell as shown in equation (2.20) below, where ΔG^0 is the Gibbs free energy under standard conditions, R the universal gas constant, T the temperature, and $[R]$ and $[O]$ are the activities of the product (R) and reactant (O) respectively [38, 65].

$$\Delta G = \Delta G^0 + RT \ln \frac{[R]}{[O]} \quad (2.20)$$

Since the Gibbs free energy represents the electrical energy in the electrochemical reaction, it can also be expressed in terms of the electrode potential as per equation (2.21), where n is the number of electrons in the reaction, F is Faraday's constant and E the electrode potential [38, 65].

$$\Delta G = -nFE \quad (2.21)$$

Equation (2.22), derived from the equations above, gives the general Nernst equation for a water electrolysis reaction where E^0 is the open circuit voltage, E_{rev} the reversible potential, a_{H_2O} the water vapour concentration, a_{H_2} the hydrogen gas concentration and a_{O_2} the oxygen gas concentration [42, 70].

$$E^0 = E_{rev} - \frac{RT}{nF} \ln \frac{a_{H_2O}}{a_{H_2} \cdot a_{O_2}} \quad (2.22)$$

The Nernst equation can be expressed in terms of pressure by replacing the reactant and products concentrations with the partial pressures p_{H_2O} , p_{H_2} and p_{O_2} as illustrated by equation (2.23) below. This equation or some version of this equation are used by many different authors to model and simulate the open circuit voltage of a PEM electrolyser [71-75].

$$E^0 = E_{rev} - \frac{RT}{nF} \ln \left(\frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{1/2}} \right) \quad (2.23)$$

The equation above is the commonly used equation for the open circuit voltage of a PEM electrolyser. In many of the reported work authors use a value 1.23 V for E_{rev} since this is the standard reversible potential (at $p = 1$ atm and $T = 298.15$ K). However, other authors use a temperature dependant expression for the reversible potential as illustrated by equation (2.24) below [76-79].

$$E_{rev} = 1.229 - 0.9 \times 10^{-3}(T - 298.15) \quad (2.24)$$

Although many authors use equation (2.24), few of them give a clear explanation for this equation. The following equations illustrate how equation (2.24) can be obtained. The first step is to substitute the standard Gibbs free energy term in the reversible potential equation, with the change in enthalpy equation [80].

$$E_{rev} = \frac{\Delta G_R}{nF} = \frac{\Delta H_R - T\Delta S_R}{nF} \quad (2.25)$$

Now assuming ΔH and ΔS are constant, equation (2.25) can be modified to equation (2.26) and then to equation (2.27) as illustrated below [80].

$$E_{rev} = \frac{(\Delta G_R^0 + 298.15 \cdot \Delta S_R^0) - T\Delta S_R^0}{nF} \quad (2.26)$$

$$E_{rev} = \frac{\Delta G_R^0}{nF} - \frac{\Delta S_R^0}{nF} (T - 298.15) \quad (2.27)$$

A unique open circuit voltage definition containing a temperature dependant expression for the reversible potential is expressed in equation (2.28) below [80].

$$E^0 = \frac{\Delta G_R^0}{nF} - \frac{\Delta S_R^0}{nF} (T - 298.15) - \frac{RT}{nF} \ln \left(\frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{1/2}} \right) \quad (2.28)$$

The equations above show that the open circuit voltage (E^0) of a PEM electrolyser, which is the theoretical voltage at which water decompose, is affected by both the operating temperature and pressure.

2.4.2.4 Overpotential

The electrochemical parameter known as overpotential is defined as the potential difference between the theoretical decomposing voltage of water (E_{rev}^0), or at non-standard conditions the open circuit potential (E^0), and the actual voltage required to activate the chemical reaction. Overpotential is caused by kinetic losses such as activation losses, ohmic losses and concentration losses in the PEM electrolyser.

Equation (2.29) is an expression of the overpotential η , where E_{cell} is the total cell voltage and E^0 the Nernst or open circuit voltage as determined by Nernst's equation.

$$\eta = E_{cell} - E^0 \quad (2.29)$$

The cell voltage of the electrolyser can be described as the sum of the open circuit potential (E^0), the activation overpotential (η_{act}), the ohmic overpotential (η_{ohm}) and the concentration overpotential (η_{con}) as per equation (2.30) below [78].

$$E_{cell} = E^0 + \eta_{act} + \eta_{ohm} + \eta_{con} \quad (2.30)$$

Figure 2-12 illustrates the contribution of each overpotential to the total cell potential (E_{cell}) at different current densities by mean of a polarisation curve (PC). This figure shows that in the low current density region, the activation overpotential contribute the most to the cell potential, and as the current density increase, the ohmic overpotential becomes dominant. Polarisation curves as a characterisation technique are further discussed in section 2.7.1.

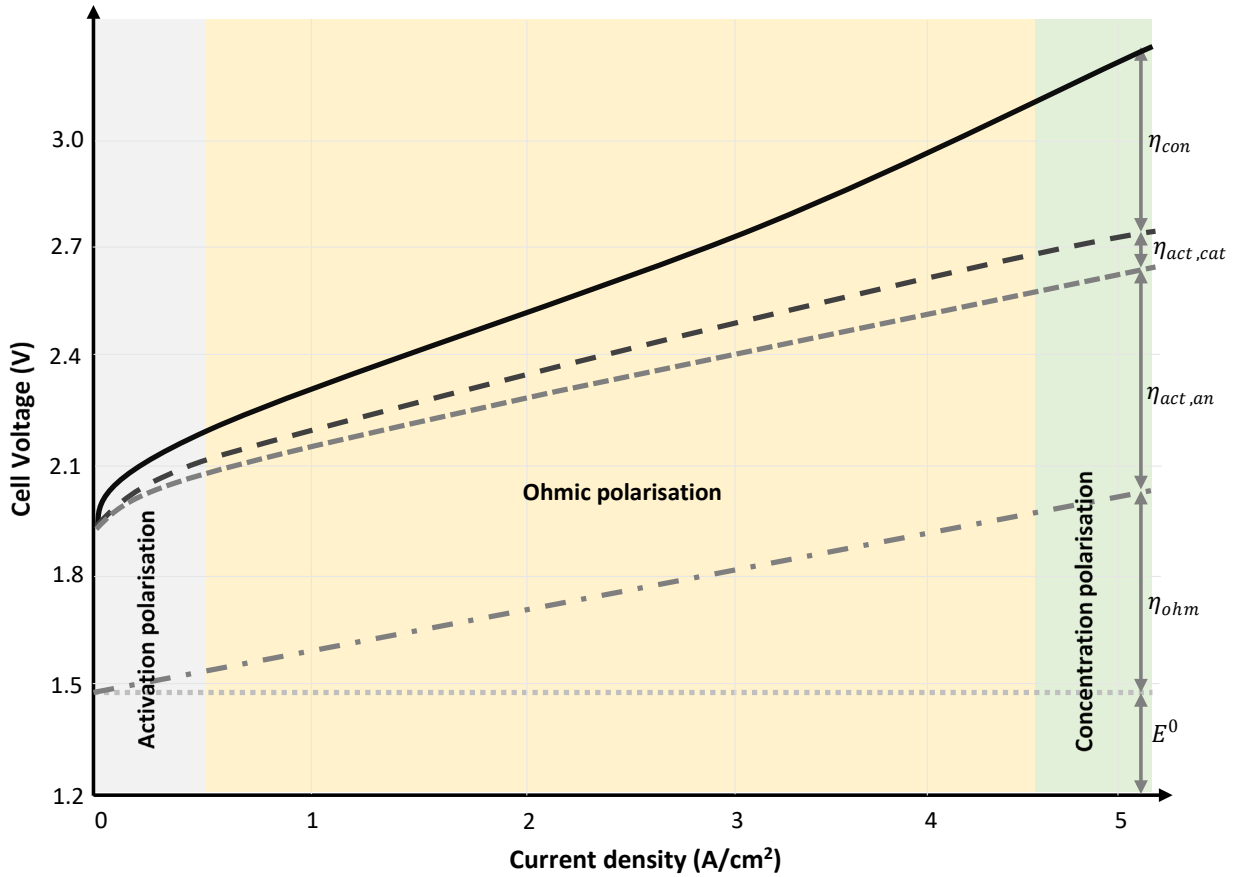


Figure 2-12: Overpotential contributions to total cell voltage (adapted from [42]).

2.4.2.4.1 Activation overpotential

Activation overpotential is the potential added to the reversible potential to produce sufficient current to accommodate the activation energy required by the electrolyser cell. The activation energy required for the electrochemical reaction to take place is caused by a resistance against electron flow at the electrode surface and are present at the anode as well as the cathode catalysts layers. The resistance against electron flow is called the charge transfer resistance. The activation overpotential illustrates the rate at which reactions takes place at the electron surface and thus represents the electrochemical kinetic rate or reaction rate. The activation overpotential can be expressed by equation (2.31), where R is the universal gas constant, T the temperature, α the transfer coefficient, F Faraday's constant, i the current density, and i_0 the exchange current density [78, 81]. The activation overvoltage, caused by the activation losses, is most noticeable in the low current density region.

$$\eta_{act} = \frac{RT}{\alpha_{an}F} \operatorname{arcsinh} \left(\frac{i}{2i_{0,an}} \right) + \frac{RT}{\alpha_{cat}F} \operatorname{arcsinh} \left(\frac{i}{2i_{0,cat}} \right) \quad (2.31)$$

2.4.2.4.2 Ohmic overpotential

The ohmic overpotential is caused by the ohmic resistance against the flow of electrons through the cell electrodes and bipolar plates as well as the flow of ions through the membrane. The resistance for each of these components depends on the characteristics of the materials used. The ohmic overpotential can be expressed using Ohms law and is thus directly proportional to the current as illustrated in equation (2.32) and (2.33), where R_{ohmic} is the total ohmic resistance, R_{elec} the electrode resistance, R_{pl} the bipolar plate resistance, R_{mem} the proton exchange membrane resistance and I the current [77, 78]. The ohmic overpotential caused by the cell ohmic resistance, does not change with a fluctuating current density and is thus linear across all current density regions.

$$\eta_{ohm} = R_{ohmic}I \quad (2.32)$$

$$\eta_{ohm} = (R_{elec} + R_{pl} + R_{mem})I \quad (2.33)$$

2.4.2.4.3 Concentration overpotential

The concentration overpotential is caused by losses that occur at the catalyst layers due to a change in the amount of reactant reaching the electrode surface. At high current densities, there is an increase in the reaction speed of the electrolyser, which causes a high concentration of oxygen gas to form at the anode surface.

The oxygen gas formed at the anode restricts the water supplied to the electrolyser to reach the anode surface and thus changes the concentration of the reactant at the point of reaction. The concentration overpotential can be obtained using a form of the Nernst equation in terms of the modular concentration of the products, where C_1 is the gas concentration at the electrode for the current condition and C_0 the reference gas concentration for a working condition as per equation (2.34) [77, 78, 82].

$$\eta_{con} = E_1 - E_0 = \left(E^0 + \frac{RT}{zF} \ln C_1 \right) - \left(E^0 + \frac{RT}{zF} \ln C_0 \right) = \frac{RT}{zF} \ln \frac{C_1}{C_0} \quad (2.34)$$

2.4.3 Reaction Kinetics

The thermodynamics of water electrolysis systems were reviewed in section 2.4.1 to comprehend the energy requirements of the reaction; however, no information on the reaction speed was obtained. Reaction kinetics is an investigation of the rate at which chemical reactions take place. The reaction kinetics of water electrolysis is largely dependent on the amount of current supplied to the electrolyser as illustrated in this section.

2.4.3.1 Butler–Volmer equation

The Butler-Volmer equation is used to describe the relationship between the rate at which the chemical reaction takes place, or the current density, and the electrode potential. The Butler-Volmer equation is thus an essential concept in electrochemical kinetics. The forward reaction rate or current density (i_f) for a charge-transfer reaction is,

$$i_f = i_0 \exp\left(-\frac{\alpha_{an} F \eta_{act}}{RT}\right) \quad (2.35)$$

and the backwards reaction rate or current density (i_b) is,

$$i_b = i_0 \exp\left(\frac{\alpha_{cat} F \eta_{act}}{RT}\right) \quad (2.36)$$

where i_f is the forward reaction rate (current density), i_b the backward reaction rate (current density), η_{act} the activation overpotential, R the universal gas constant, F Faraday's constant, α_{an} the anodic charge transfer coefficient and α_{cat} the cathodic charge transfer coefficient [65]. The transfer coefficient is defined by the IUPAC (International Union of Pure and Applied Chemistry) [83], as the portion of the electric potential energy that influences the reduction rate of a reaction at an electrode. The combined reaction rate or current density for the reaction is expressed as the difference between the forward and the backwards reaction rates,

$$i = i_f - i_b = i_0 \left(\exp\left(\frac{\alpha_{an} F \eta_{act}}{RT}\right) - \exp\left(\frac{\alpha_{cat} F \eta_{act}}{RT}\right) \right) \quad (2.37)$$

where i_0 is the exchange current density [65, 77, 84]. The exchange current density can be defined as the current density that occurs at equilibrium where the forward reaction current density is equal to the backwards reaction current density. There is thus no remaining current flowing into or out of the system.

2.4.3.2 Molar flow rate

Faraday's law shows that the rate at which reactions in an electrolyser take place are dependant and directly proportional to the electrical current supplied to the cell [66]. Equation (2.38) define Faraday's law, with Q being the total charge, n the number of moles, z the number of charges (electrons) and F Faraday's constant. The total charge can be defined as $q = \int_0^t I(t).dt$ with I the being the total current, which can also be expressed in terms of the current density and cell area, i.e. $I = iA$ [42].

$$q = nzF \quad (2.38)$$

From equation (2.38) the molar flow rate of the water consumed by a PEM electrolyser as well as the hydrogen and oxygen generated by the electrolyser can be written respectively as [70, 82, 85]:

$$\dot{n}_{H_2} = \frac{I}{2F} \varepsilon_I \quad (2.39)$$

$$\dot{n}_{O_2} = \frac{I}{4F} \varepsilon_I \quad (2.40)$$

$$\dot{n}_{H_2O} = 1.25 \frac{I}{2F} \varepsilon_I \quad (2.41)$$

The Faraday's efficiency ε_I added to each of the above terms is to account for the current losses in the PEM electrolyser and is discussed in section 2.5.3.

2.5 PEM electrolysis efficiency

This section of the literature study is dedicated to defining the different definitions used for the efficiency of an electrolysis system. The lack of consistent use of the term “efficiency” in the literature makes it difficult to compare the efficiencies obtained by different authors. An accurate and constant definition for efficiency is described by Lamy *et al.* [86] as a critical concept that is needed to determine the true cost of hydrogen production through electrolytic processes.

2.5.1 Cell Efficiency

Water electrolysis is considered to be a power to gas energy conversion system used to store electrical energy in the form of hydrogen gas. The efficiency of such a system is defined as the ratio between the useful energy output and the required energy input. For water electrolysis processes that occur at low temperatures, the useful energy output is hydrogen gas, while the energy input is electrical energy. The energy efficiency can thus be defined as the hydrogen energy output per unit of electrical energy input.

This definition is based on the following assumptions [42]:

- Electrical energy is the only form of energy input to the system with operating temperatures under 100 °C.
- Only the hydrogen produced is considered as an energy output.
- The water is supplied to the system is in a liquid state.

The literature shows three methods to determine the cell efficiency of an electrolyser. These methods are discussed below.

2.5.1.1 Method 1

The efficiency of a PEM electrolyser is defined as the product of the hydrogen molar flow rate $\dot{n}_{H_2}$ and either the higher heating value HHV or, the lower heating value LHV, divided by the electrical power supplied to the cell P_{avg} . Cell efficiency based on the HHV is preferred over the LHV when liquid water is used since the enthalpy of evaporation needs to be provided by the electrolyser [42]. The cell efficiency can thus be expressed by equation (2.42) below, where ΔH_R^0 is the change in enthalpy under standard conditions, also known as the HHV, I_{cell} is the cell current and U_{cell} the cell voltage [42, 66].

$$\varepsilon_{cell}^{HHV} = \frac{\Delta H_R^0 \cdot \dot{n}_{H_2}}{I_{cell} \cdot U_{cell}} = \frac{HHV \cdot \dot{n}_{H_2}}{P_{avg}} \quad (2.42)$$

2.5.1.2 Method 2

Equation (2.42) in method one above makes use of average hydrogen flow and power values to determine the efficiency of the cell. If the hydrogen flow rate is not measured, but the total amount of hydrogen produced is known, the efficiency can also be calculated determining the ratio between the total energy output (hydrogen gas) and the total energy input (electrical energy). To determine the amount of energy stored in the hydrogen, the number of moles in the hydrogen is determined by using the molecular weight of hydrogen as shown in Table 2-7. The chemical energy of the hydrogen produced is then calculated using the HHV and the number of moles in the hydrogen produced as per equations (2.43) and (2.44) [87].

$$\text{Number of moles} = \frac{\text{Total Weight}}{\text{Molecular Weight}} \quad (2.43)$$

$$\text{Chemical Energy (J)} = \text{moles of hydrogen produced} \cdot \text{HHV} \quad (2.44)$$

After the electrical energy unit is converted to Joules, as per equation (2.45) [87], and both the input and output energy values have the same unit, the cell efficiency can be calculated as illustrated by equation (2.46) [87].

$$\text{Electrical Energy (J)} = \text{Electrical Energy (kWh)} \times (3.6 \times 10^6) \quad (2.45)$$

$$\varepsilon_{cell}^{HHV} = \frac{\text{Chemical Energy (J)}}{\text{Electrical Energy (J)}} \quad (2.46)$$

2.5.1.3 Method 3

The total cell efficiency ε_{cell}^{HHV} can also be defined as the product of the voltage efficiency ε_V^{HHV} and the Faraday's efficiency ε_I as illustrated by equation (2.47) below [42], [88].

The terms voltage efficiency and Faraday's efficiency are discussed in the following sections 2.5.2 and 2.5.3.

$$\varepsilon_{cell}^{HHV} = \varepsilon_V^{HHV} \times \varepsilon_I \quad (2.47)$$

Although all of the methods mentioned above appear different, the electrochemical fundamentals are the same, and all of the calculations would provide the same efficiency value.

2.5.2 Voltage Efficiency

The efficiency of an electrolyser can also be simplified by using only voltage values to indicate the losses in the cell. This is known as the voltage efficiency of the cell ε_V and defined as the ratio between the thermoneutral voltage $E_{th}(T)$ at a specific temperature and the actual cell voltage U_{cell} at a specific temperature [89]. Although this is the commonly used definition, more often the voltage efficiency ε_V^{HHV} is calculated using the thermoneutral voltage E_{th}^0 at standard conditions. The voltage efficiency ε_V^{HHV} can thus be expressed as [42]:

$$\varepsilon_V^{HHV} = \frac{E_{th}^0}{U_{cell}} \quad (2.48)$$

This definition is based on the assumption that all of the electrical current supplied to the electrolyser is converted into chemical energy used only for the water splitting reaction. This will never be the case practically since there are some unintentional reactions, stray current and gas leakage inside the electrolyser cell. These losses can be accounted for by calculating the Faradaic or current efficiency.

2.5.3 Faradaic Efficiency (Current)

The Faradaic efficiency of an electrolyser can be defined as a ratio between the actual and theoretical hydrogen gas produced [42]. The actual hydrogen gas produced is a measured value while the theoretical hydrogen gas produced can be calculated making use of Faraday's law and ideal gas law. Faraday's law is defined by equation (2.38) [42],

$$n = \frac{q}{z \cdot F} = \frac{I \cdot t}{z \cdot F} \quad (2.49)$$

and the ideal gas law is defined by equation (2.50),

$$PV = nRT \quad (2.50)$$

where P is the pressure (1 atm or 101.325 kPa), V is the volume (litres), n the number of moles, R the ideal gas constant (0.082057 L.atm.mol⁻¹.K⁻¹ or 8.3145 m³.Pa.mol⁻¹.K⁻¹ or 8.3145 L.kPa.mol⁻¹.K⁻¹) and T the temperature (Kelvin).

By substituting equation (2.49) into the ideal gas law, equation (2.51) is obtained, with $Q_{H_2,theor}$ being the theoretical volumetric flow rate in cubic meter per second ($m^3 \cdot s^{-1}$) [90].

$$Q_{H_2,theor} = \frac{V}{t} = \frac{I \cdot R \cdot T}{2 \cdot F \cdot P} \quad (2.51)$$

The Faradaic efficiency of a cell can then be determined by measuring the actual flow rate and obtaining the ratio between the theoretical and measure values. Equation (2.52) represents the Faradaic efficiency, where $Q_{H_2,actual}$ is the measured flow rate and $Q_{H_2,theor}$ the theoretical calculated flow rate [42].

$$\varepsilon_I = \frac{Q_{H_2,actual}}{Q_{H_2,theor}} \quad (2.52)$$

The Faradaic efficiency indicates the electrons in the external circuit which are successfully transported to the electrode surface to be used in the electrochemical reaction [56]. All of the efficiency definitions mentioned above are summarized and compared in Table 2-8 below.

Table 2-8: Efficiency definitions comparison (combined from [42, 66]).

	Voltage efficiency	Faradic efficiency	Cell efficiency
Equation	$\varepsilon_V^{HHV} = \frac{E_{th}^0}{U_{cell}}$	$\varepsilon_I = \frac{Q_{H_2,actual}}{Q_{H_2,theor}}$	$\varepsilon_{cell}^{HHV} = \frac{HHV \cdot \dot{n}_{H_2}}{P_{avg}}$
Used to measure	Cell voltage losses.	Cell current losses.	Cell input energy losses.
Losses/Inputs accounted for	Activation, ohmic and concentration overpotentials.	Stray current, crossover gasses and gas leakages.	Overpotentials, stray current, crossover gasses and gas leakages.
Assumptions	All the applied current is converted to chemical reaction.	No voltage losses.	No external heat source.

2.5.4 Influencing Factors

In this section, the major operating conditions that affect the efficiency of a PEM electrolyser such as temperature and pressure are discussed. It is widely known that temperature is one of the operational conditions with the largest impact on the efficiency of an electrolysis process. The efficiency of an electrolysis process increases as the operating temperature is increased since the amount of electrical energy required to decompose water decreases [22].

Recent experimental studies which focused on the effects of temperature on the performance of a PEM electrolyser also showed that an increased operational temperature lowers the activation, ohmic and concentration losses of the cell. An example of such a study is the research conducted by Liso *et al.* (2018) [70], who used modelling and experimental techniques to determine the effect of different operating temperatures, ranging from 50 °C to 80 °C, on a PEM electrolyser. Their study showed that an increase in the operating temperature would lower the Gibbs free energy of the electrolysis process and in effect lower the open circuit voltage of the cell. The results also illustrate that increasing the temperature will improve the ionic conductivity of the membrane, which results in a lower ohmic overpotential. In another study conducted by Toghyani *et al.* (2018) [55], a performance assessment on high temperature PEM electrolysis also showed a decrease in cell voltage as the temperature is increased. They showed that the voltage drop at increased temperatures is caused by an improved electron flow to and from the electrode surfaces, resulting in a lower charge transfer resistance and activation overpotential. Also, an increase in the operational temperature will increase the kinetic reaction rate, which results in a lower concentration overpotential. Similar trends are also seen in larger PEM electrolyser stacks as illustrated by the research of Dale *et al.* (2008) [91]. They studied the performance of a 6 kW PEM electrolyser stack and determined that the exchange current densities increase, the membrane conductivity increase and the reversible potential decrease when increasing the operational temperature. In addition to the efficiency of an electrolyser, the efficiency of a fuel cell also increases at high temperature operation. The efficiency increase in fuel cells is caused by increased reaction kinetics and a higher tolerance to impurities in the supplied hydrogen gas [92]. A higher operational temperature thus results in higher electrolyser efficiency; however, an increase in temperature also has a negative impact on the degradation rate of the MEA. The thermal degradation that occurs at raised temperatures is believed to result from an increased sulfonic acid release by the perfluorosulfonic acid membrane [45]. It has also been reported that the FRR and MEA thinning drastically rise as the operating temperature is increased [45].

Pressure is another factor that influences the efficiency of a PEM electrolyser. Equation (2.23) in section 2.4.2 shows that the theoretical decomposing voltage of water increases as the operating pressure increases. The voltage increase will cause the efficiency of the electrolyser to be lower at higher pressures. In a study conducted by Nafchi *et al.* (2018) [93], they described the higher cell voltage at increased pressures to be instigated by a decrease in proton diffusion through the membrane. The authors also expressed that high pressure at the cathode can cause an opposite migration of hydrogen protons which in effect decrease the efficiency of the electrolyser.

Marangio *et al.* (2009) [82], Selamet *et al.* (2013) [94] and Roy *et al.* (2006) [95] also concluded in their studies that an increase in the operating pressure results in a higher cell voltage and a lower electrolyser efficiency. However, the relation between the operating pressure and the change in the electrolyser voltage is not linear. In a predictive study conducted by Onda *et al.* (2004) [96], they determined that an increase in the operational pressure up to 100 atm would have a substantial effect on the cell voltage, but with a further increase in pressure, the effect would become relatively small. An increased operating pressure could however have a positive effect on the efficiency of the complete electrolysis system. In an electrolysis system, the generated hydrogen gas is usually compressed with the use of an external gas compressor for more efficient storage. By increasing the operating pressure of the electrolyser, the amount of external pressurisation required is reduced. The energy required to increase the operating pressure with the use of a high pressure water pump is far less than the energy required to externally pressurise the hydrogen gas generated [42, 93]. However, to fully understand the effect on the efficiency of an electrolysis system, the power consumption of the high pressure water pump and external compressor should be accounted for [97]. Producing compressed hydrogen gas by pressurising the water supply can be referred to as “symmetric pressure electrolysis” since both the anode and cathode are under high pressure [98]. In a PEM electrolysis system, electrochemical compressed hydrogen can also be generated by keeping the cathode side of the electrolyser under pressure while the anode side and water supply operate at standard pressure (1 atm). This process can be referred to as “asymmetric pressure electrolysis” and the advantage of this process is that the need for a high pressure water pump and external compressor are eliminated [98]. However, the safety of these systems remains a significant drawback; the high pressure cathode chamber increases the hydrogen diffusion through the membrane to the anode side, which can form an explosive gas (hydrogen and oxygen mixture) [99].

Although the design of the PEM electrolyser does not form part of this study, the electrolyser components and assembly are also known to have a significant effect on the efficiency of an electrolysis system. Some other factors that are proven to influence the efficiency of a PEM electrolysis system as determined by Siracusano *et al.* (2011) [100], Zhang *et al.* (2012) [66] and Tomas-Garcia *et al.* (2017) [101] are the membrane (PEM) thickness, effectiveness of the heat exchangers used, inlet water flow rate, compression pressure of the electrolyser and the catalyst loading. Many studies also showed that the electrical characteristics of the applied power signal have an impact on the hydrogen production and energy consumption rates of an electrolyser. The effect of ripple currents, power quality and converter topologies are discussed in sections 2.8.2.4 and 2.11 of this chapter.

2.6 PEM membrane degradation

The membrane is the key component of a PEM electrolyser assembly and is responsible for proton transfer, separating the hydrogen and oxygen products and supporting the anode and the cathode catalyst layers. It is thus crucial for the membrane to have a high proton conductivity, a small gas permeability, great mechanical strength as well as excellent chemical and thermal stability in order for the PEM electrolyser to perform optimally. However, the membrane has been reported as the weakest component of a PEM electrolyser assembly and will over time degrade and cause decay in the electrolyser performance [102]. The degradation of the membrane is thus one of the most extensive challenges researchers and developers have to face in order to improve the durability of PEM water electrolyzers. According to Feng *et al.* (2017) [45], the mechanisms that will cause a membrane to degrade can be categorised into three groups: mechanical, thermal, and chemical degradation. These three degradation mechanisms are classified as irreversible degradation processes, which can accelerate ageing, cause membrane thinning or pinhole formation and ultimately lead to failure of the electrolyser [103].

2.6.1 Mechanical degradation

The failure of a PEM electrolyser at an early stage (less than 1000 hours of operation) is most likely caused by mechanical degradation [45]. Cracks, tears and punctures in the membrane, formed during manufacturing of the MEA (application of catalyst layers to the membrane) or during operation under high mechanical stress can cause mechanical degradation. The presence of dust or any micro object on the membrane when the catalyst layers are applied can initiate a small crack that will propagate once the membrane is introduced to mechanical stress. Siracusano *et al.* [104] determined that the process used to apply the catalyst layers to the membrane also affects the durability of the MEA. Propagating tears and cracks, initiated during the manufacturing of the MEA, will significantly decay the membrane's life expectancy, causing mechanical degradation and early failure. In an electrolyser stack assembly, the membranes are exposed to high compressive forces induced by the bipolar plates. These forces in conjunction with the sharp edges on the flow fields and uneven GDL's can cause cracks or punctures that would spread during operation and cause mechanical degradation [45], [105]. It has also been reported that punctures created in the membrane by the GDL's is one of the main reasons for the increase in hydrogen crossover when the cell compression is increased [105]. High compressive forces will also cause deformation in the membrane, which will decay the ion transfer and possibly cause physical damage to the membrane.

Severe mechanical degradation can result in the anode and cathode catalyst layers to come in contact with each other causing an internal short which will result in a cell failure [45]. The degradation rate of the membrane can be followed by electrochemical impedance spectroscopy (EIS) which are thoroughly discussed in section 2.7.2.

2.6.2 Chemical degradation

Chemical degradation is a degradation of the membrane material which can be hydrocarbon, partially fluorinated, or perfluorinated ionomers [106]. Perfluorosulfonic acid is the most widely used ionomer and consists of a perfluorinated polymeric backbone with a sulfonic acid side chain [107], [108]. During PEM water electrolysis, hydrogen peroxide (H_2O_2) can be formed by the two electrode oxidation-reduction reaction at the catalyst surfaces ($\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2\text{O}_2$) [45, 103, 109]. The reaction is caused by hydrogen and oxygen crossover gasses and can occur in the membrane or at the cathode side of the cell [103]. After the diffusion of H_2O_2 into the membrane, radical species such as hydroperoxyl (HO_2) and hydroxyl (HO) can be formed in the presence of ferrous ions [103, 109]. These species attack the perfluorosulfonic acid ionomer resulting in membrane thinning and a fluoride and sulfur release. The chemical degradation rate can thus be determined by measuring the fluoride release rate (FRR), sulfur emission rate (SER) and by comparing the membrane thickness at the beginning and end of the concerned period [45, 109]. Chandesris *et al.* (2015) [109] showed that the current density effects the rate at which chemical degradation takes place. Their study showed an increase in the degradation rate as the current density is increase, until a maximum degradation rate is reached at a relatively low current density, after which the degradation rate decreases again.

2.6.3 Thermal degradation

PEM electrolyzers generally operate at raised temperatures of between 50 and 90 °C in order to achieve the required energy to split water into hydrogen and oxygen while still staying within the allowed voltage range of the electrolyser. Although an increase in temperature promotes the electrolytic efficiency (as discussed in section 2.5.4), it has a negative impact on the degradation rate of the MEA. LaConti *et al.* (2006) [110] as well as Chandesris *et al.* (2015) [109] reported a sharp increase in the FRR and therefore the degradation rate when the operating temperature of the PEM electrolyser is increased. Chandesris *et al.* (2015) [109] also investigated the influence of the operating temperature on the membrane thinning rate and reported that at 60 °C the membrane thickness reached 50% of its initial value after 38 500 hours while at 80 °C it took only 8 700 hours. A temperature increase of just 20 °C can thus reduce the life span of the membrane with more than 75%.

2.7 Characterisation

Individual characterisation of components such as the solid polymer electrolyte, electrode catalysts, GDL's and end plates can easily be achieved by manufactures when no external components are present. However, when all these components are combined by consumers to form an electrolytic cell, characterisation is much more challenging. The main challenge is not to characterise the cell, but to obtain properties of individual components within the complete unit. The characterisation techniques available to achieve this is an integral part of this study since it is used to determine the effect of different ripple currents on the performance of the cell and the individual components within the cell. These techniques are also used to determine the degradation caused by a ripple current.

2.7.1 Polarisation curve

Polarisation curve (PC) measurements are the standard and most widely used technique to characterise an electrolyser. Almost all experimental test protocols on electrochemical cells start with a beginning of life (BoL) PC measurement and end with another end of life (EoL) PC measurement. A PC is a plot of the cell voltage vs. current density at constant operating conditions (temperature and pressure). This plot can be obtained by operating the cell over a range of current densities and measuring the cell voltage at each current density (galvanostatic mode) or by measuring the current density as a function of the cell voltage (potentiostatic mode) [111].

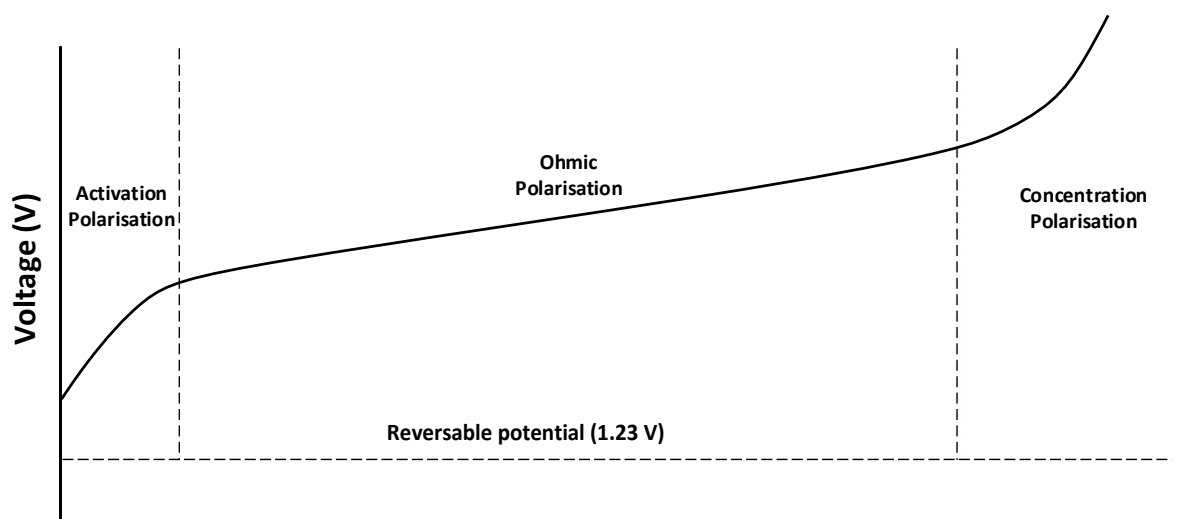


Figure 2-13: Polarisation Curve (adapted from [112]).

This technique can provide electrochemical characteristics such as the cell charge transfer resistance, ohmic resistance and mass transport resistance. The results of a PC measurement can also be used to determine the power consumption or efficiency of an electrolyser [113].

In addition to the performance information that can be obtained, the BoL and EoL PC's can be compared and used to obtain information on the degradation of the electrolyser. The cell voltage of an electrolyser with good performance should be relatively low and would not increase significantly at high current densities [114]. The magnitude and slope are indications of the cell losses, and the difference between the BoL and EoL PC's an indication of the durability of the cell. There are three regions present in a polarisation curve, as illustrated by Figure 2-13 above, which are the activation, ohmic and concentration polarisation regions [114]. The activation polarisation region is the low current densities region and the losses in this region are due to slow reaction kinetics. The charge transfer resistance is large in this region when compared with the small ohmic resistance. The large charge transfer resistance, which resembles the resistance against the flow of electrons at the electrode surfaces, cause the voltage-current relationship to have a logarithmic form [115]. In the second region, called the ohmic polarisation region, the resistance that exists against the flow of ions is the main contributor to the losses present [114]. Ohmic resistance is thus the largest resistance present in the intermediate current density region. Here the charge transfer resistances are left out since the anode and cathode surfaces have received enough energy to activate the reaction and start electron flow. The voltage-current relationship is linear in this current density range [115]. The concentration polarisation region is initiated in the high current density range of the polarisation curve, and the losses that occur here are due to the mass transfer effects [114]. This characterisation technique is commonly used by researchers and developers to analyse the performance of an electrolyser as a unit.

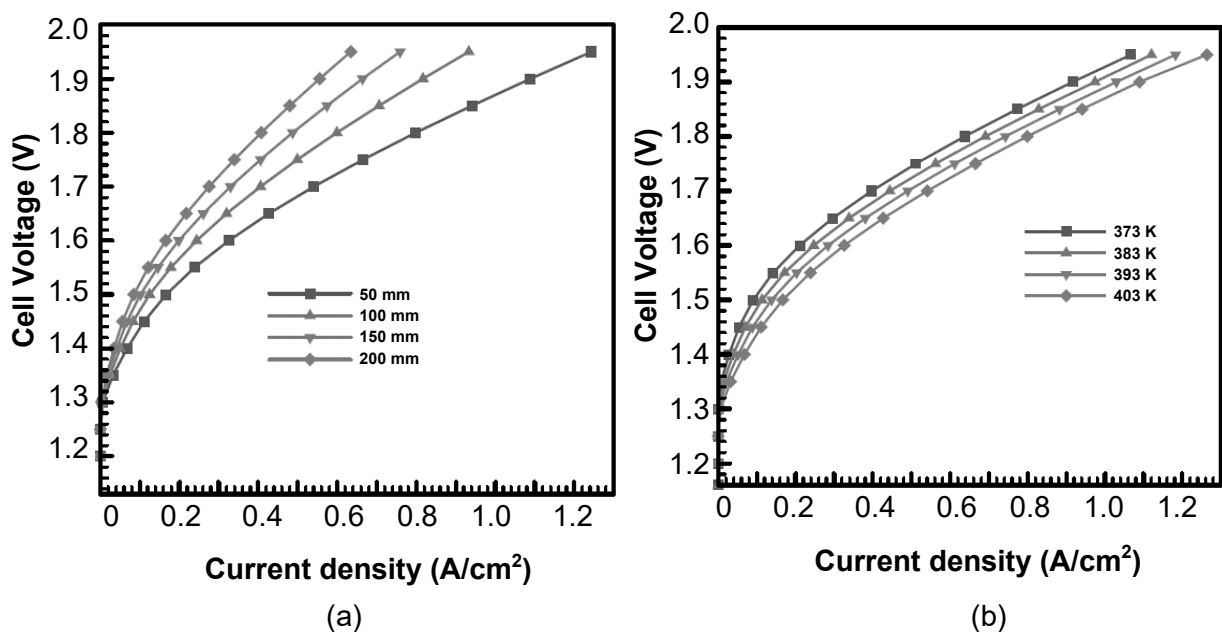


Figure 2-14: Polarisation curve characterisation at (a) different membrane thicknesses, and (b) different temperatures (adapted from [55]).

Polarisation curves are often used to investigate the effect of different operating conditions, such as temperature and pressure, on the cell performance in the pursuit of optimising the efficiency. The effects of individual cell component and the parameters of these components, such as the thickness or type of membrane, can also be analysed using PC measurements as illustrated by Toghyani et al. (2018) [55]. Figure 2-14 above illustrates how polarisation curves can be used to investigate the performance of an electrolyser at different operating conditions and component selections. Figure 2-14 (a) shows the effect of the membrane thickness on the performance of the electrolyser, while Figure 2-14 (b) shows the effect of the operating temperature.

2.7.2 Electrochemical impedance spectroscopy

The second electrochemical characterisation technique that is widely used by researchers and developers is electrochemical impedance spectroscopy (EIS). EIS is an analysis technique used to characterise an electrochemical cell by obtaining the impedance of the cell as a function of frequency. The obtained impedance values can be used to determine the electrical characteristics and degradation rate of a PEM electrolyser [116]. EIS measurements can also be used to determine the losses associated with specific components in the cell [117]. This technique is carried out by applying a small AC current or voltage signal to the electrochemical cell at a steady state and measuring the cell's response [118]. The response of the electrochemical cell will thus be the voltage signal when a current signal is applied (galvanostatic mode) and the current signal in the case where a voltage signal is applied (potentiostatic mode). The impedance can then be obtained by calculating the ratio of the applied and the response signals as per ohms law [114, 118]. If an EIS test is done in potentiostatic mode, a small sinusoidal voltage signal is applied to the cell. The form of the signal is expressed by equation (2.53), where $v(t)$ is the potential as a function of time, V_{max} is the amplitude and ω is the radial frequency. The cell's current response $i(t)$ is then measured which can be expressed by equation (2.54), where the response signal has shifted in phase ϕ and have a different amplitude I_{max} .

$$v(t) = V_{max} \sin(\omega t) \quad (2.53)$$

$$i(t) = I_{max} \sin(\omega t + \phi) \quad (2.54)$$

The impedance of an electrochemical cell is a measure of the opposition presented to an alternating current, due to the combination of ohmic resistance and reactance. The impedance $Z(j\omega)$ is a function of frequency and can be determined by making use of ohms law as illustrated by equation (2.55), where $\mathcal{F}\{v(t)\}$ and $\mathcal{F}\{i(t)\}$ are the Fourier transforms of the applied voltage and current response signals [119].

The Fourier transform is the method used to transform the signals from the time domain to the frequency domain. The impedance expressed as a complex value, in terms of its real and imaginary parts, is illustrated by equation (2.56), (2.57) and (2.58) [119]. The ohmic resistance is referred to as the real part while the reactance is known as the imaginary part.

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{\mathcal{F}\{v(t)\}}{\mathcal{F}\{i(t)\}} \quad (2.55)$$

Complex Impedance $Z(\omega) = |Z|(\cos \phi + j\sin \phi)$ (2.56)

Real Part $Re(Z) = |Z| \cos \phi$ (2.57)

Imaginary Part $Im(Z) = |Z| \sin \phi$ (2.58)

EIS is a characterisation technique that presents the data measured from an electrochemical cell as functions of frequency and not time, as is the case in numerous other techniques [120]. To obtain the cell impedance as a function of frequency, the process of applying an AC signal to the cell has to be repeated for various frequencies across the frequency band that is investigated [119]. The impedances that are collected by using the EIS method at various frequencies are graphically illustrated making use of a Nyquist plot. The real part of the impedance is designated to the x-axis and the imaginary part to the y-axis. The high frequency impedances are towards the left of the graph and the lower frequency impedances towards the right. Figure 2-15 shows a simple Nyquist plot on which the complex impedance is presented as a function of the absolute impedance $|Z|$, the phase shift ϕ and the frequency ω .

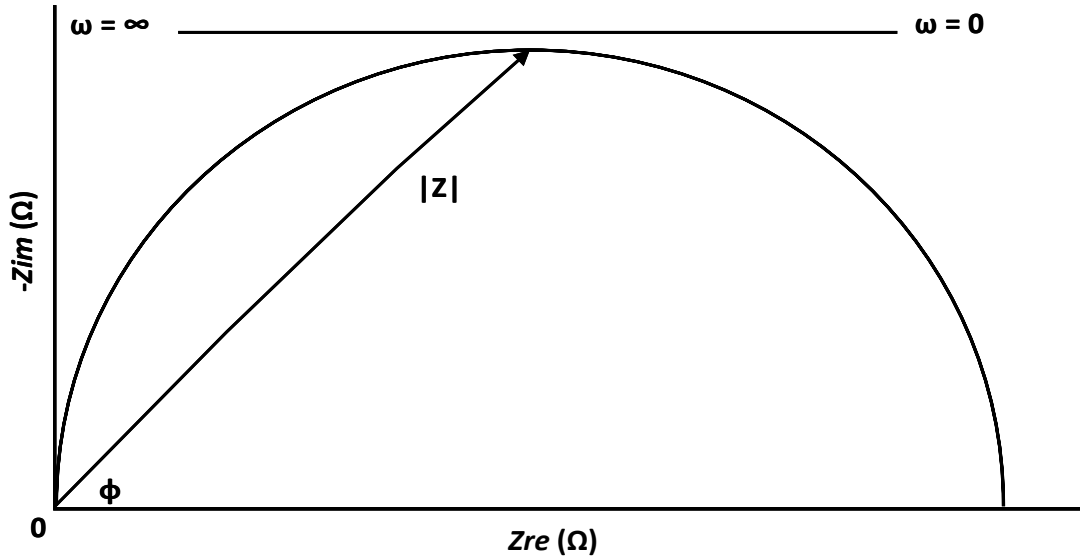


Figure 2-15: Nyquist plot (adapted from [121]).

One of the main applications of the EIS technique in the electrochemical industry is to develop an equivalent electrical circuit (EEC) model of an electrochemical cell.

Van der Merwe *et al.* (2013) [112] reported that the EIS technique could be applied to a PEM electrolyser to identify three loss regions, namely activation, ohmic and concentration losses. Van der Merwe showed that each of these loss regions represents a specific process in the electrolyser and can be represented by an electrical component in an EEC model. Figure 2-16 illustrates which part of a Nyquist plot represents each of these loss regions. The intercept with the real axis at the high frequency side of the plot is the ohmic resistance value while the intercept at the low frequency side is the sum of the ohmic and charge transfer or activation resistance. The difference between the two intercepts is therefore equal to the charge transfer or activation resistance value. Different EEC models and their corresponding Nyquist plots are discussed in section 2.8.

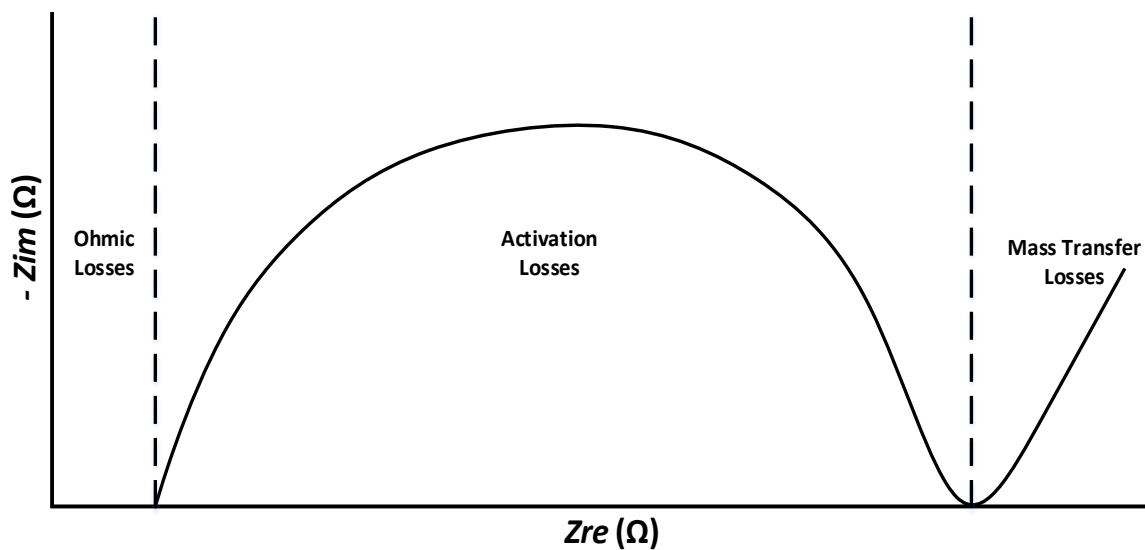


Figure 2-16: Nyquist plot loss regions (adapted from [114]).

2.8 Equivalent Circuit Models

The impedance data obtained from applying the EIS technique to an electrochemical cell can be used to develop an equivalent electrical circuit (EEC) model of the cell. This section of the literature study focusses on circuit elements used in EEC models as well as the typical EEC models used to represent electrochemical cells such as PEM electrolyzers and fuel cells.

2.8.1 Equivalent circuit elements

The circuit model can consist of resistors, capacitors, inductors, and some specialized electrochemical elements [65]. Each element in an EEC model represents a specific process or characteristic of the electrochemical cell. An EEC model is thus a method used to model the impedance response of an electrochemical cell with the use of the lumped or common electrical elements. The individual impedance of some typical elements present in EEC models is shown in Table 2-9 below.

Table 2-9: Equivalent circuit elements (combined from [65, 122]).

Element	Symbol	Impedance
Resistor	R	$Z_R = R$
Capacitor	C	$Z_C = \frac{1}{j\omega C}$
Inductor	L	$Z_L = j\omega L$
Constant phase element (CPE)	Q	$Z_Q = q^{-1}(j\omega)^{-n}$
Warburg element	W	$Z_W = \sigma\omega^{-\frac{1}{2}} - j\left(\sigma\omega^{-\frac{1}{2}}\right)$

2.8.1.1 Resistor

The impedance of a resistor only contains a real part and is thus not dependent on the frequency of the applied voltage or current waveform. The current that passes through a resistor is in phase with the voltage applied to the resistor due to the absence of an imaginary impedance component [118], [122]. The impedance response of a PEM water electrolyser contains two key resistances namely the ohmic/membrane resistance and activation resistance [123]. Each of these resistances is represented by a resistor in an EEC model.

(a) Membrane resistor (Ohmic losses)

The membrane resistor R_m , represents the ohmic resistance of the PEM electrolyser in an EEC model. Although the ohmic resistance of a PEM electrolyser consists of the internal resistance between the components, the membrane resistance, as well as the catalyst layer resistance, the membrane resistance is the main contributor [114]. The membrane resistance is directly proportional to the resistivity ρ , and the thickness d , of the membrane [123].

(b) Charge transfer resistor (Activation losses)

The second resistor that is present in a typical EEC model of a PEM electrochemical cell is the charge transfer resistor R_{ct} . This resistor represents the resistance against electron flow to and from the electrode surfaces and is present at both the anode and cathode catalysts layers. The charge transfer resistor, which is also sometimes referred to as the activation resistor, thus represents the cell's charge-transfer kinetics and activation losses [114].

2.8.1.2 Capacitor

The impedance of a capacitor contains only an imaginary part and has a negative value. The impedance is thus dependant on the frequency of the applied voltage waveform and the magnitude decreases as the frequency of the applied voltage increases [122]. The current response of the capacitor is 90° out of phase with the applied voltage [118]. The primary capacitive characteristic present in a PEM water electrolyser is the double-layer capacitance which can be represented by a capacitor in an EEC model.

(a) Double-layer capacitor

The electrochemical double layer is formed when ions form a layer on the electrode surface and as a result, separates the charged electrodes from the charged ions. A capacitor can thus represent the double layer in an equivalent electrical circuit since a capacitor is an element which separates charges by an insulator [118]. The capacitor used to represent the double layer in an EEC model is known as the Double layer capacitor C_{dl} .

2.8.1.3 Inductors

The impedance of an inductor also contains only an imaginary part, but in contrast to the impedance of a capacitor, has a positive value. The impedance is thus also dependent on frequency, but the relationship between the impedance and frequency is opposite to that of a capacitor. For an inductor, the magnitude of the impedance increases as the frequency of the applied voltage increases [122]. The current response of the inductor is -90° out of phase with the applied voltage. Van der Merwe (2013) [112] used an inductor in the EEC model of a single cell PEM electrolyser to represent the inductance related to the power supply conductors.

2.8.1.4 Constant phase element (CPE)

Common or lumped elements like resistors, capacitors and inductors are sufficient to represent ideal systems, but the use of only these elements to represent a practical system is not adequate. Some specialized electrochemical elements, such as the constant phase element (CPE) were developed to more accurately represent a practical system. The CPE can be associated with the uneven surfaces of catalyst layers, uneven current distribution and a non-uniform reaction rate which prevents the system from responding as pure resistors, capacitors and inductors [122]. Table 2-9 shows that the impedance of a CPE can be expressed as,

$$Z_Q = q^{-1}(j\omega)^{-n} \quad (2.59)$$

where q is a proportional factor of the magnitude, while n represents the phase shift [122]. In an ideal system, the values of n would be ($n = 0, 1, -1$) for the CPE to represent a pure resistor, capacitor and inductor respectively [65, 122]. Table 2-10 below illustrates the different elements that can be represented by the CPE and show the values of n and q for each of these elements.

Table 2-10: Constant phase element (adapted from [65]).

CPE Designation	n	q
Capacitance	1	C
Resistance	0	R^{-1}
Inductance	-1	L^{-1}
Warburg impedance	0.5	σ^{-1}

2.8.1.5 Warburg impedance

The Warburg impedance represents the mass transfer or concentration losses in an electrochemical cell [65]. The Warburg impedance consists of a real as well as an imaginary part and is thus dependent on frequency. The imaginary part has a negative value (capacitive); thus, the impedance becomes smaller as the frequency gets higher [118]. The current response of a Warburg element is 45° out of phase with the applied voltage [118]. The Warburg impedance can be expressed by,

$$Z_W = \sigma \omega^{-\frac{1}{2}} - j \left(\sigma \omega^{-\frac{1}{2}} \right) \quad (2.60)$$

which is considered to be a resistor $R = \sigma \omega^{-\frac{1}{2}}$ connected in series with a capacitor $C = \sigma \omega^{-\frac{1}{2}}$ [65]. The real and imaginary part of the Warburg impedance is thus equal in value and can be represented as a 45° line on the Nyquist plot.

2.8.2 Circuit Models

EEC models play an essential role in this study since they are used to simulate the cell's response to different input signals. The focus of this study is on the electrical characteristics of a PEM electrolyser and how these characteristics are affected by different voltage or current ripples. In this section, a few widely used EEC models, such as the Randles cell and Randles-Warburg cell, are reviewed.

2.8.2.1 Randles cell

The Randles cell is a standard equivalent circuit model that consists of two resistors (R_m and R_{ct}) and a capacitor (C_{dl}). The Randles cell is used as a basic model and then further developed to represent the investigated electrochemical cell accurately. Figure 2-17 (a) represents an EEC model of an electrochemical cell in the form of a Randles cell. The impedance of the Randles cell can be expressed as,

$$Z(\omega) = R_m + \frac{1}{R_{ct}^{-1} + j\omega C_{dl}} \quad (2.61)$$

where R_m and R_{ct} is the membrane and charge transfer resistances and C_{dl} the double layer capacitance [65, 120]. The representative Nyquist plot of a Randles cell is a semicircle as illustrated by Figure 2-17 (b).

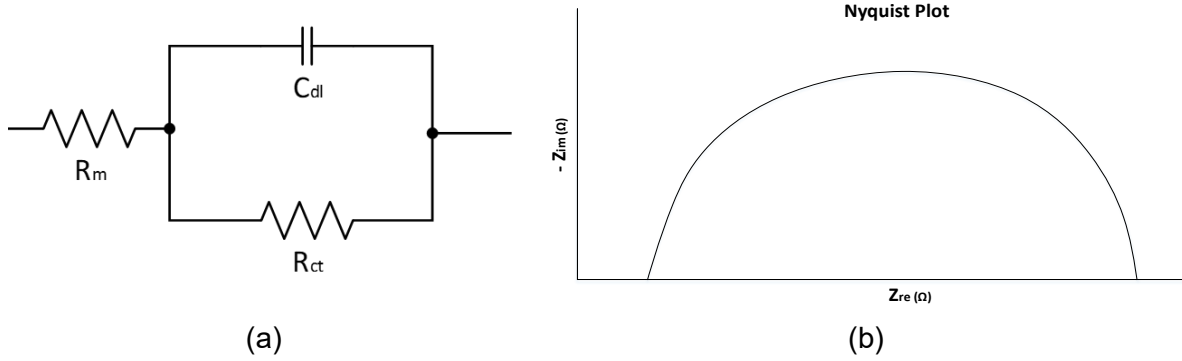


Figure 2-17: Randles Cell (a) EEC model and (b) Nyquist Plot (adapted from [65]).

2.8.2.2 Randles-Warburg cell

The Randles-Warburg cell is a Randles cell that has been modified to accommodate for the mass transfer losses that occur in an electrochemical cell. The Warburg impedance Z_w is thus added to the Randles cell, in series with the charge transfer resistance and in parallel with the double layer capacitance. Figure 2-18 (a) represents an EEC model of an electrochemical cell in the form of a Randles-Warburg cell. The impedance of the Randles-Warburg cell can be expressed as,

$$Z(\omega) = R_m + \frac{1}{j\omega C_{dl} + (R_{ct} + Z_w)^{-1}} \quad (2.62)$$

where Z_w is the Warburg impedance [65, 120]. The representative Nyquist plot of a Randles-Warburg cell is a semicircle as illustrated by Figure 2-18 (b).

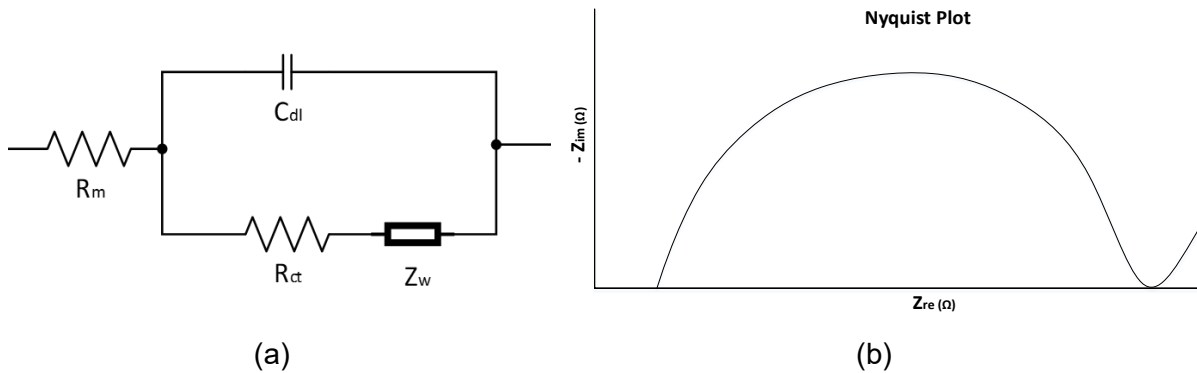


Figure 2-18: Randles-Warburg Cell (a) EEC model and (b) Nyquist Plot (adapted from [65]).

2.8.2.3 Randles-Warburg cell with CPE

The double-layer capacitance that represents the ion layer formed on the electrode surfaces cannot represent the effects of this ion layer accurately. Since the electrodes are porous and have uneven surfaces, the effects of the ion layers cannot be represented as pure capacitors. As a result, the semicircle shown in a Nyquist plot is typically not centred on the real axis.

The double-layer capacitance of a Randles-Warburg cell is therefore replaced with a CPE to account for the semicircle centre being below the real axis. Figure 2-19 (a) represents an EEC model of an electrochemical cell in the form of a Randles-Warburg cell containing a CPE. The impedance of the Randles-Warburg cell with a CPE can be expressed as,

$$Z(\omega) = R_m + \frac{1}{Z_Q^{-1} + (R_{ct} + Z_W)^{-1}} \quad (2.63)$$

where Z_Q is the CPE impedance as defined in section 2.8.1.4 [124]. The representative Nyquist plot of the cell is a semicircle as illustrated by Figure 2-19 (b).

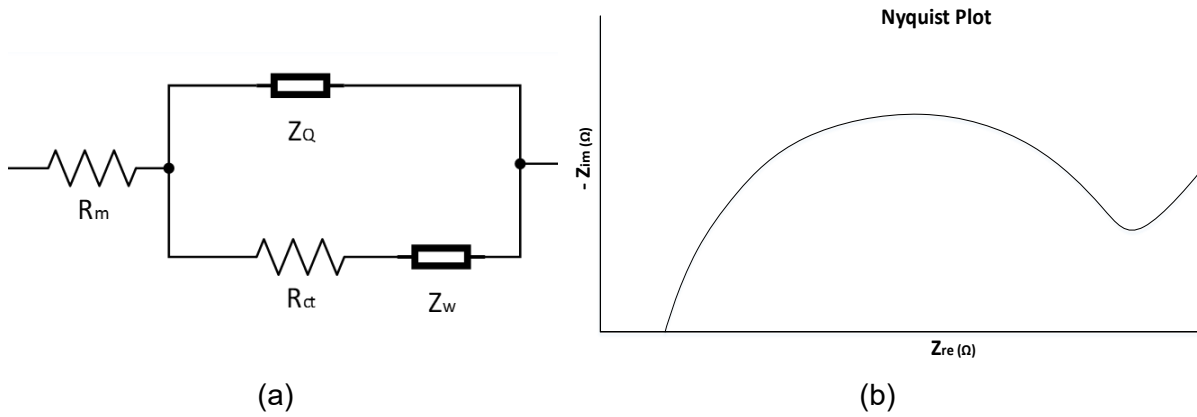


Figure 2-19: Randles-Warburg Cell with CPE (a) EEC model and (b) Nyquist Plot (adapted from [65]).

2.8.2.4 Modified EEC models

The models described above are very basic and usually only used as a starting point to model an EEC that accurately represent an electrochemical cell. A few more complex and accurate EEC models developed specifically for a PEM electrolyser were reviewed and are presented in the figures below. Figure 2-20 shows the EEC model developed by Van der Merwe *et al.* (2013) [112] for a single cell PEM electrolyser, using the EIS characterisation technique. The proposed model is similar to the Randles-Warburg cell discussed above, with the only difference being the addition of an inductor. The inductance of the power supply conductors is represented by L , the ohmic resistance of the cell by R_{ohmic} , the activation resistance by R_{act} , the double layer capacitance by the CPE and the mass transport losses by the Warburg impedance.

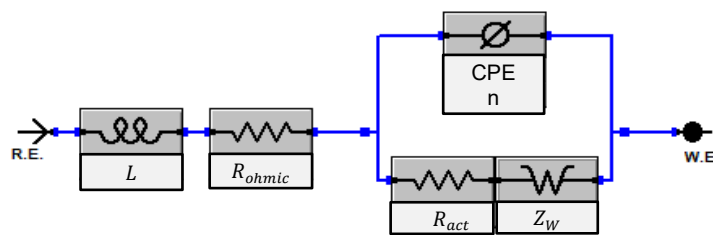


Figure 2-20: EEC model used by Van der Merwe [112].

Figure 2-21 shows the EEC model used by Martinson *et al.* (2014) [48] to characterise a PEM electrolyser using the current interrupt method. Martinson started with a Randle-Warburg cell, but used an impedance transfer function, given by equation (2.69), to approximate the Warburg impedance [112].

$$Z_W(s) = R_d \left(\frac{r_1}{(r_1 c_1 R_d C_d)s + 1} + \frac{r_2}{(r_2 c_2 R_d C_d)s + 1} \right) \quad (2.64)$$

The mass transport losses are represented by $r_1 R_d$, $r_2 R_d$, $c_1 C_d$ and $c_2 C_d$ (r_1 , c_1 , r_2 and c_2 are the Warburg coefficients), the membrane resistance by R_m , the charge transfer resistance by R_{ct} and the double layer capacitance by C_{dl} .

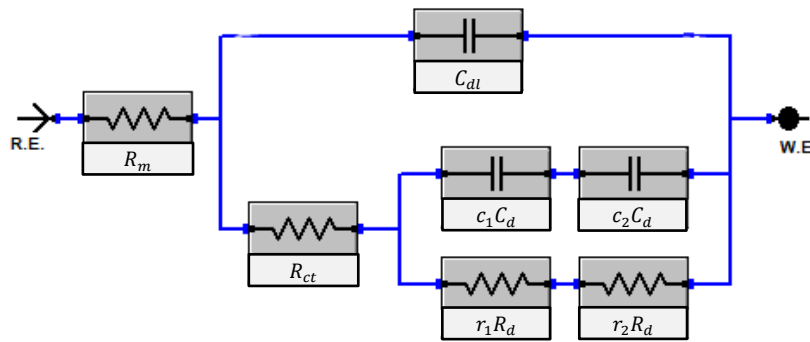


Figure 2-21: EEC model used by Martinson [48].

Figure 2-22 shows the EEC model proposed by Rozain *et al.* (2014) [116] in their study, which focused on the electrochemical characterization of PEM electrolyzers. In the proposed EEC model, each charge transfer interface (anode and cathode catalyst layers) in the PEM electrolyser are represented by a polarization resistance (R_{ct_c} and R_{ct_a}) connected in parallel with a CPE (CPE_c and CPE_a). The cathode and anode diffusion impedances (Z_c and Z_a), the cathode and anode ohmic or electronic resistances (R_{ohmic_c} and R_{ohmic_a}), as well as the resistance of the solid polymer electrolyte (R_{el}) are then all connected in series to the parallel connection.

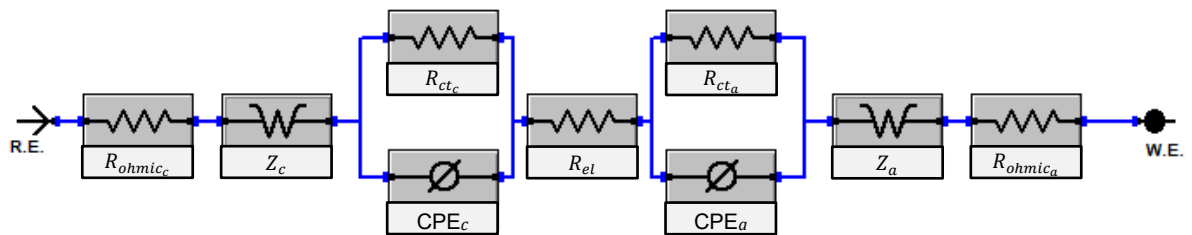


Figure 2-22: EEC model used by Rozain [116].

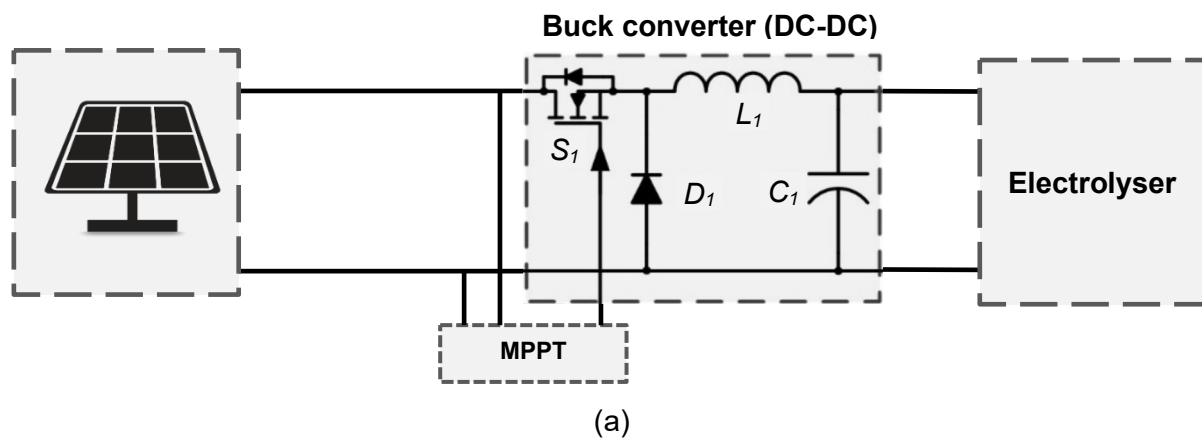
2.9 Power supplies and Ripple currents

In a water electrolysis system, the electrolyser stack is not the only component affecting the efficiency of the system. As previously discussed, an electrolyser requires a DC power source which is generally provided by a power conditioning system which can include AC-DC and DC-DC converters. Depending on the power conditioning system and the topology of the converter, a significant current and voltage ripple occur on the output side of the converter. In this section, the different power supplies used for water electrolysis systems and the electrical characteristics of the induced ripple current, which may affect the efficiency of an electrolyser are reviewed.

2.9.1 Power supply

2.9.1.1 Power conditioning systems

The type of power conditioning system used for a water electrolyser depends on the energy source, which can be solar energy, wind energy or grid power. Figure 2-23 below is an illustration diagram of the different types of power conditioning systems used for different power sources. Figure 2-23 (a) shows an electrolysis system supplied by solar energy. The system consists of photovoltaic panels followed by a step-down buck converter (DC-DC converter), controlled by a maximum power point algorithm. Next, Figure 2-23 (b) illustrates an electrolysis system supplied by wind energy. The system consists of a three-phase generator driven by wind energy followed by a three-phase diode rectifier (AC-DC converter) and a step-down buck converter (DC-DC converter). Finally, Figure 2-23 (c) shows an electrolysis system supplied with grid power. The system consists of a three-phase transformer connected to the grid, followed by a three-phase thyristor bridge rectifier (AC-DC converter).



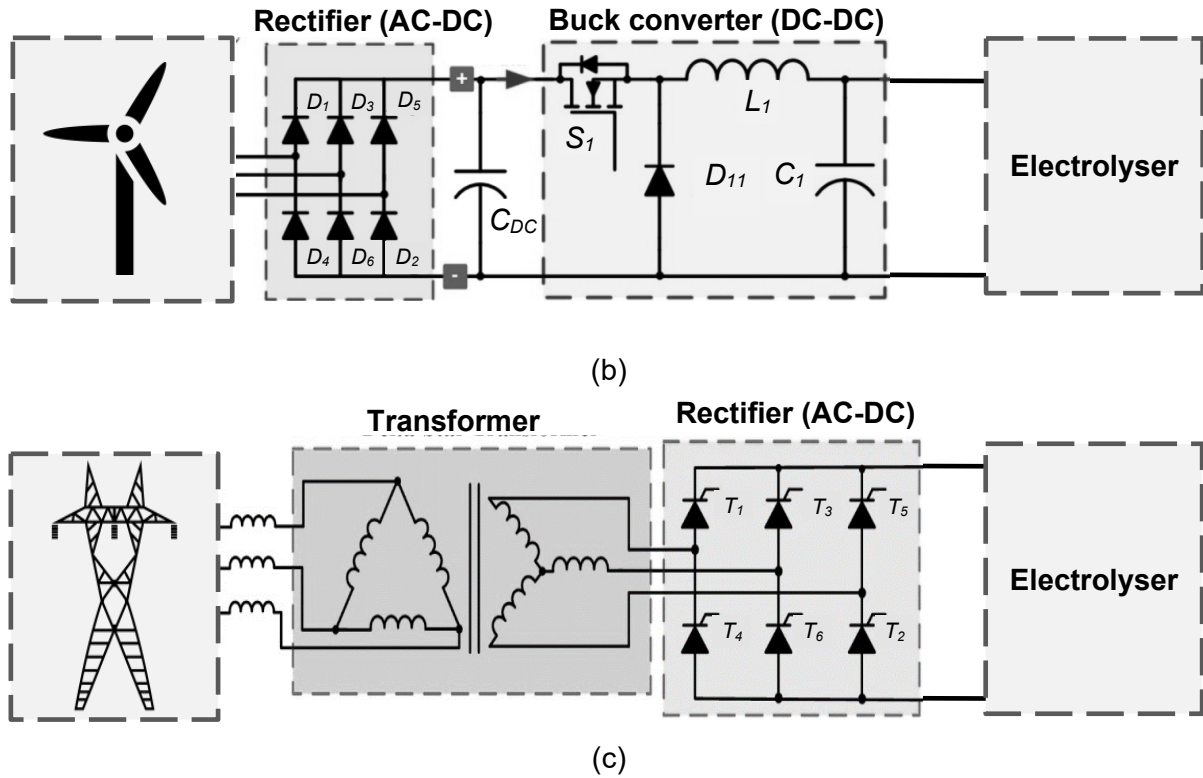


Figure 2-23: Power conditioning system for an electrolyser supplied by (a) solar energy, (b) grid power and (c) wind energy (adapted from [125]).

2.9.1.2 Converter topologies

In this section, the different converters used in the power conditioning systems of different power supplies are reviewed. The section is divided into two subsections, one for the DC-DC converter topologies and the second for AC-DC converter topologies.

2.9.1.2.1 DC-DC converters

In recent years a lot of research and development is directed towards the use of water electrolysis systems to produce hydrogen gas from renewable energy sources like solar and wind energy. Figure 2-23 (a) and (b) above shows that the power conditioning systems used for solar and wind energy requires a DC-DC converter to supply the electrolyser with the low DC voltage needed to produce hydrogen gas. Due to the simplicity and low cost of buck converters, this DC-DC topology is usually used to achieve the required voltage for water electrolyzers. Although the simplicity and low cost of buck converters make this topology desirable, recent studies showed that buck converters are far from ideal in terms of the output current ripple, energy efficiency and reliability. In a literature review by Guilbert *et al.* (2017) [126], they showed several other topologies such as half-bridge, full-bridge and interleaved buck converters (IBC) are better suited candidates for water electrolysis processes. These topologies showed a lower output current ripple, higher energy efficiency and higher reliability than the classic buck converter.

Some basic schematic diagrams for a buck converter, full-bridge converter, and interleaved buck converter are presented in Figure 2-24 below. A few of the topologies discussed in [126] are compared in Table 2-11 in terms of the fundamental requirements of a DC-DC converter used in a water electrolysis process. The output ripple current should be as low as possible, the energy efficiency as high as possible, voltage ratio as high as possible and the cost as low as possible.

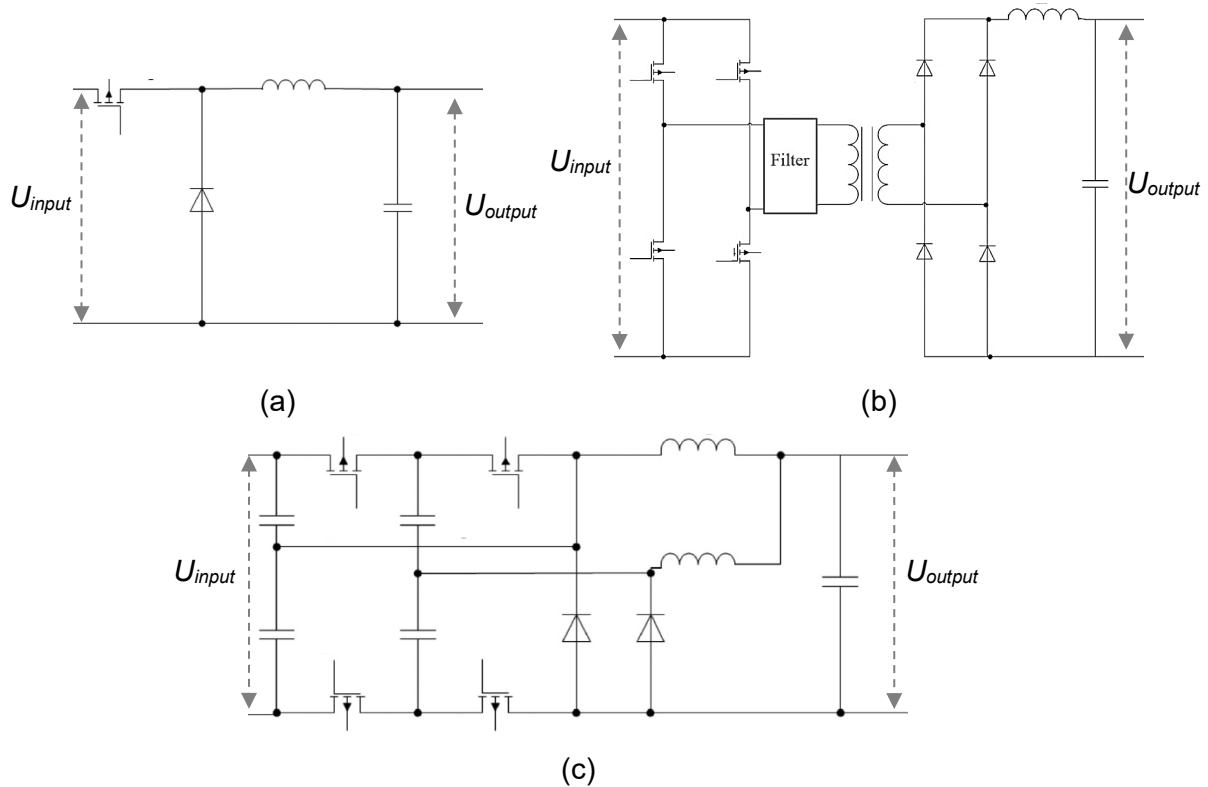


Figure 2-24: Common DC-DC converter topologies: (a) Classic buck converter, (b) Full-bridge converter and (c) IBC (adapted from [126])

Table 2-11: DC-DC converter topology comparison (combined from [126]).

	Buck converter	Interleaved buck converter	Half-bridge converter	Full-bridge converter
Output current ripple	High	Low	Low	Medium
Energy efficiency	Low	High	High	High
Voltage ratio	Low	High	High	Medium
Reliability	No	Yes	No	Yes
Cost	Low	High	High	High

2.9.1.2.2 AC-DC converters

Although water electrolysis systems should ideally use renewable energy sources, most often utility grid power is used in these systems. Figure 2-23 (c) in the preceding section showed that when grid power is used for water electrolysis, the power conditioning system consists of two main parts, a transformer and an AC-DC converter.

Since grid connected power supplies are ordinarily used, a relatively large amount of literature is available on the influence that AC-DC converters have on the performance and efficiency of a water electrolysis system.

Koponen *et al.* (2019) [16] conducted a study to determine the effect that different convertor topologies have on the energy consumption of a water electrolysis process. The energy consumption of an electrolyser stack connected to a practical power supply using a transistor-based converter, 6-pulse thyristor-based rectifier and 12-pulse thyristor-based rectifier were compared to the theoretical energy consumption of an ideal DC power supply. They found that by using a transistor-based rectifier, the energy consumption of an electrolyser stack can be between 9 and 14% lower than when a thyristor-based rectifier is used. They stated that although transistor-based rectifiers are more efficient, the rectifiers used in industrial converters are conventionally thyristor-based to accommodate for the high current density requirements of water electrolyzers [16]. In a supplementary study, discussed in section 2.11.5, Koponen *et al.* (2020) [88] focus specifically on the negative effect of a 12-pulse thyristor-based rectifier on the energy consumption of a PEM electrolyser.

In another study by Ursúa *et al.* (2009) [17], similar experimental tests were done on a 1 Nm³/h commercial water electrolyser. Their results show an energy consumption of 4995 Wh/Nm³ with a thyristor-based converter and 4560 Wh/Nm³ with a transistor-based converter. The energy consumption of the electrolyser stack was thus 9% lower with the use of a transistor-based converter. The generated ripple of thyristor-based rectifiers is much higher than in transistor-based converters, thus causing thyristor-based converters to have higher energy consumption [17].

As previously stated, although thyristor-based rectifiers have a lower efficiency than transistor-based converters, industrial converters are conventionally thyristor-based to accommodate for the high current density requirements. One of the most widely used semi-controllable thyristor rectifier topologies is a three phase, 6-pulse thyristor rectifier bridge, as illustrated in Figure 2-25 (a). A 6-pulse thyristor bridge rectifier has six pairs of thyristors which will conduct in turn every 60°. Consequently, the output DC current will contain a ripple with a frequency six times the AC grid frequency (300 Hz for a grid frequency of 50 Hz). Another widely used topology is a 12-pulse thyristor bridge rectifier as illustrated in Figure 2-25 (c). A 12-pulse thyristor bridge rectifier is formed by connecting two 6-pulse thyristor bridge rectifiers in series. The two 6-pulse thyristor bridge rectifiers are connected to an AC transformer which produces a 30° phase shift between the supply of each bridge. A transformer with a star-delta configuration produces this phase shift. The output DC current will contain a ripple with a frequency twelve times the AC grid frequency (600 Hz for a grid frequency of 50 Hz).

Lastly, Figure 2-25 (b) illustrates a fully controllable transistor-based converter, which consists of a 6 or 12 pulse uncontrollable diode bridge followed by a controllable step-down converter, such as a buck converter. Due to the high switching frequency (kHz range) of these converters, the output current ripple would be notably smaller compared to thyristor-based rectifiers.

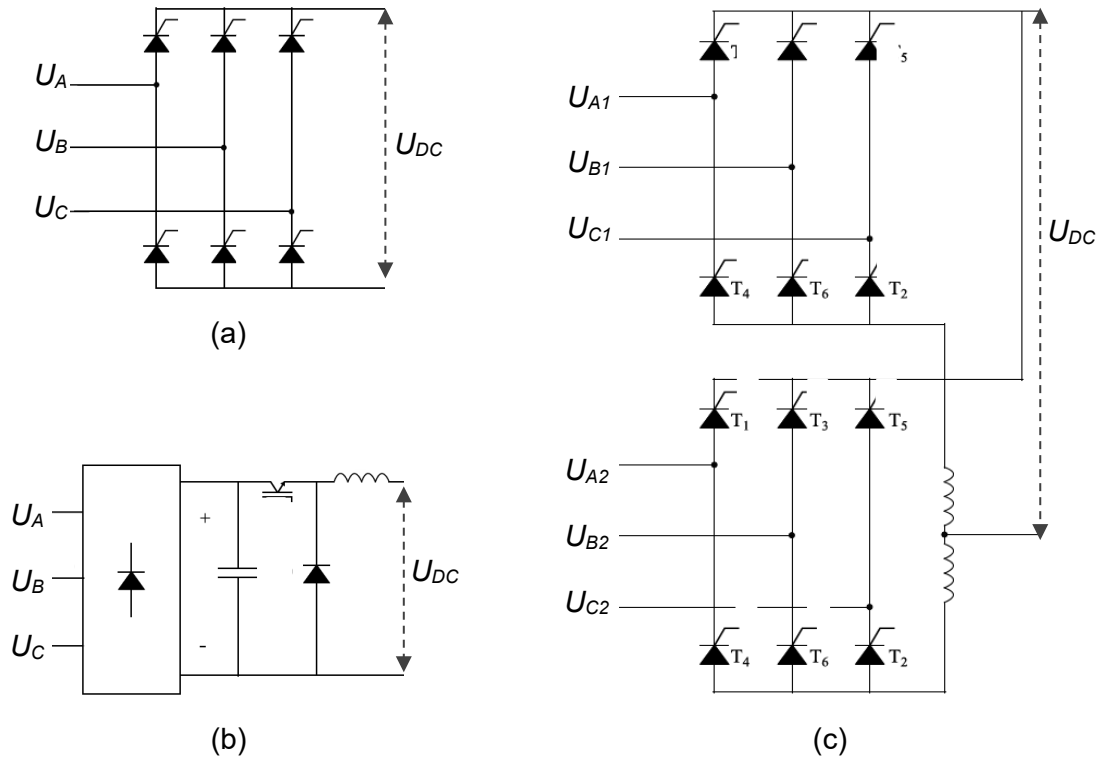


Figure 2-25: Common AC-DC converter topologies: (a) 6-pulse thyristor bridge rectifier, (b) diode bridge followed by a transistor-based converter and (c) 12-pulse thyristor bridge rectifier (adapted from [127]).

In addition to the topology used, the converter control strategy also affects the performance of a water electrolysis system. Yodwong *et al.* (2020) [125] conducted a study on different modelling techniques that are being used for the power electronics control of PEM electrolysis systems. According to their study, the efficiency of a water electrolysis system could be improved if the dynamic behaviour of both the electrolyser and the renewable energy source is taken into account in the design of the power converter's control strategy. Literature by [16, 17, 125, 126, 128-131] show that the topology and control strategy used in power conditioning systems, have a significant effect on the quality of the power supplied to the electrolysis system. Although the literature shows the effect of different converters on the power quality, little insight is provided on the effect of characteristics such as frequency and ripple factor on the performance of electrolyser.

2.9.2 Ripple current Characteristics

A ripple current can be defined as an alternating current, added or present, in a direct current signal. The current is still defined as DC as it moves in one direction but contains a periodic variation. This characteristic is seen as an imperfection of the power supply and one of the main contributors to the energy losses in the supplied system. As determined by [18, 20] as well as several other studies that will be discussed in section 2.11, the electrical characteristics and quality of a DC power supplied to a water electrolyser, influence the efficiency of the system. The characteristics of a current ripple, such as the waveform, frequency, AC amplitude and DC offset are discussed in this section.

2.9.2.1 Frequency

Frequency is the number of cycles a varying wave completes in one second. Frequency can be described by equation (2.65), where f is the frequency, measured in hertz, and T the time, measured in seconds, it takes for one complete cycle or osculation, referred to as the period [132].

$$f(Hz) = \frac{1}{T(s)}, \quad (2.65)$$

The number of cycles a function completes each second can also be represented by angular frequency ω . The angular frequency of a function can be defined by equation (2.66), where ω is measured in radians per second [132].

$$\omega(rad/s) = 2\pi f = \frac{2\pi}{T(s)}. \quad (2.66)$$

In section 2.8, it was presented that an electrolyser contains some inductive and capacitive characteristics which cause the cell to be frequency dependant. The resonance frequency will occur at the point where the inductive and capacitive reactance's are equal.

The resonance frequency will thus be the frequency at which the cell shows maximum conductivity or in other words, minimum impedance. Mazloomi *et al.* (2013) [133] analysed the frequency response of an electrolyser and illustrated that a resonance frequency, which is the frequency at which the electrolyser's impedance reaches a minimum, can be obtained using essential laboratory equipment such as a signal generator and oscilloscope. One of the objectives of this study is to determine the frequency range where a PEM electrolyser shows minimum impedance since this information can be valuable in the design of power conditioning systems and converters.

2.9.2.2 AC amplitude

AC amplitude is defined as the peak value of the AC voltage or current waveform present in a ripple wave. The AC amplitude is thus the maximum magnitude a varying voltage or current wave reaches, measured from the DC offset.

The AC amplitude of the applied current waveform can potentially be a useful tool to increase the maximum applied current to the electrolyser without the risk of irreversible degradation. The peak value of the ripple current will only be applied for a short time before it decreases again as the waveform oscillates. The root mean square (RMS) of the waveform would thus be lower than the applied peak amplitude. The RMS of an AC signal is the equivalent DC value at which the same amount of power is dissipated in a resistive load. The RMS value of an AC current or voltage waveform can thus also be referred to as the effective value of the waveform. The ratio between the peak or AC amplitude and the effective or RMS values of an AC waveform is called the crest factor. The RMS value of an AC waveform can thus be calculated by dividing the AC amplitude with the waveform's crest factor. Table 2-12 illustrates the RMS values for some common waveforms as a function of the AC amplitude (A).

Table 2-12: RMS values of common waveforms (adapted from [15]).

Waveform	Crest factor	RMS value
Sinusoidal wave	$\sqrt{2}$	$RMS = \frac{A}{Crest\ factor} = \frac{A}{\sqrt{2}}$
Rectified sinusoidal wave	$\sqrt{2}$	$RMS = \frac{A}{Crest\ factor} = \frac{A}{\sqrt{2}}$
Triangular wave	$\sqrt{3}$	$RMS = \frac{A}{Crest\ factor} = \frac{A}{\sqrt{3}}$
Square wave	1	$RMS = \frac{A}{Crest\ factor} = \frac{A}{1}$

2.9.2.3 DC offset

A waveform without a DC offset has a mean amplitude of zero. The voltage or current waveform thus oscillates around the zero point. When a DC offset is added to the waveform, the mean amplitude of the wave will no longer be zero as the wave will oscillate around another point known as the DC offset. The DC offset of a waveform can be defined as the average value of the AC waveform. The DC offset for this study should be chosen to ensure maximum performance but without the risk of degradation in the PEM electrolyser membrane.

2.9.2.4 Waveform

Different waveform represents different means by which a wave varies with time. Some of the most generally used waveforms include sine, square and triangular waves. The shape of these waves differs as they oscillate around a centre point as illustrated by Figure 2-26 below. *Saleet et al.* (2017) [134] showed in their study that the voltage or current waveform applied to an electrolysis system influences the hydrogen and oxygen production rate of the system. From their study, it is also clear that the waveform with the best performance at a specific voltage or current does not necessarily have the best performance at a different voltage or current.

It is thus essential to test each of the waveforms several times across a specific range to ensure comparability between the waveforms.

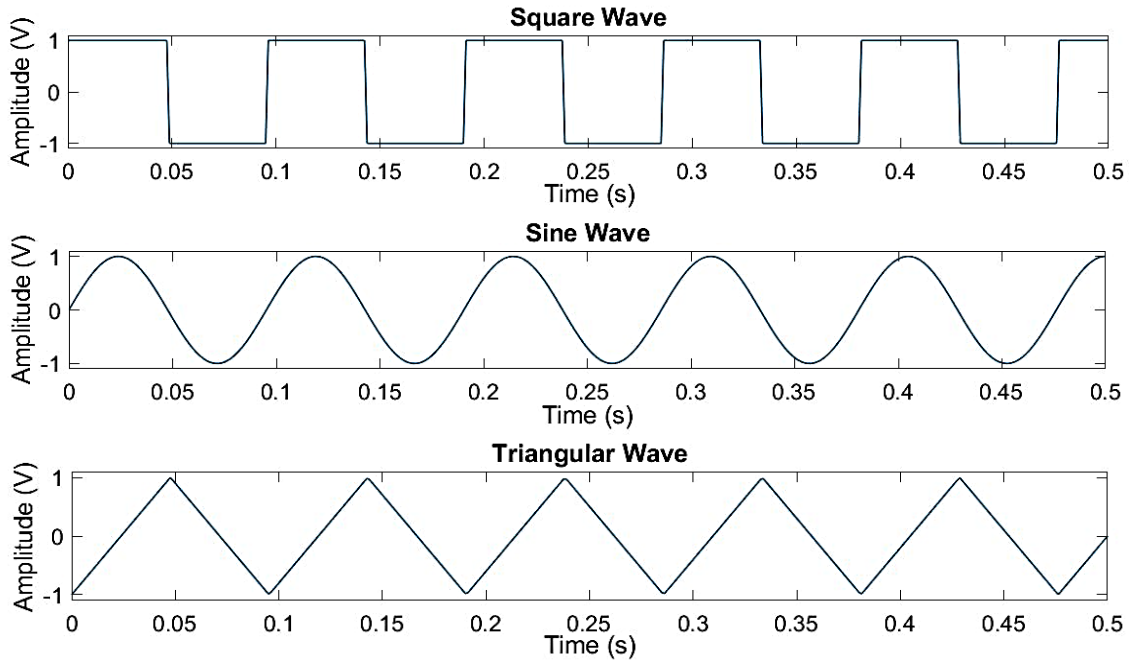


Figure 2-26: Ripple waveforms (adapted from [132]).

The triangular and square waveforms mentioned above can be described as a power series with a power series having the form,

$$P(t) = a_0 + a_1t + a_2t^2 + a_3t^3 + \dots, \quad (2.67)$$

where a_0, a_1, a_2, a_3 etc. are constants [135]. These waveforms can however also be described by an infinite sum of harmonically related sine and cosine terms [132]. A function representing a periodic function by making use of trigonometric terms is called a Fourier series. The advantages of using a Fourier series to represent a waveform include the presents of only one representative frequency in each term. A Fourier series can thus be used to describe a system response to a periodic input where the system is dependent on the frequency of the input signal [135]. The waveforms discussed can be expressed by equations (2.68) to (2.70), where A is the AC amplitude, B the DC offset and ω_0 the fundamental frequency [132], [136].

Sinusoidal Wave	$f(t) = A \sin(\omega_0 t) + B$	(2.68)
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Triangular Wave	$f(t) = \frac{8A}{\pi^2} \sum_{n=1,3,5}^{\infty} \left[\frac{1}{n^2} \sin\left(\frac{n\pi}{2}\right) \right] \sin(n\omega_0 t) + B$	(2.69)
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Square Wave	$f(t) = \frac{4A}{\pi} \sum_{n=1,3,5}^{\infty} \frac{1}{n} \sin(n\omega_0 t) + B$	(2.70)
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2.10 Software

During this study, some simulation software would be needed to simulate the effects of different ripple currents on the impedance, voltage response, power consumption and hydrogen production rate of a PEM electrolyser. The required simulation software includes electrical as well as mathematical simulation software, both of which are discussed in this section. In addition to the simulation software, other software packages that would be used during the experimental tests are also discussed.

2.10.1 Experimental software

The experimental test and the characterisation of the PEM electrolyser planned for this study would require control and measurement software. All of the experimental tests would be done on a test station manufactured by Greenlight Innovation and controlled by Greenlight Innovation's Emerald[®] control and automation software. This software provides the user with a graphical user interface to control the system, write scripts to automate the experiment and log the measured data. This software package allows the user to control multiple devices such as a DC power supply, potentiostat/galvanostat, cooling/heating module and supply pump from one computer. The Emerald[™] control and automation software would thus form a crucial part of this study. Although the Emerald[®] control and automation software is able to control a DC power supply, additional software will be required for the power supply used in this study. The software discussed above only allows the user to control the DC current/voltage value and since this study is focused on the effect of a ripple current, the AC amplitude, frequency and waveform of the power supply also needs to be controlled. To achieve this level of control, Elektro-Automatics EA Power Control[®] software needs to be used. The software enables the user to display and control the DC offset, AC amplitude, frequency and waveform of the DC power supply's output. The measured data can then also be logged by making use of the software's semi-automatic data acquisition features.

2.10.2 Simulation Software

In Section 2.8 equivalent electrical circuits (EEC) that can be used to simulate the response of an electrochemical cell were discussed. The EEC models can be simulated making use of electrical simulation software such as LTspice[®]. LTspice[®] is a free SPICE (Simulation Program with Integrated Circuit Emphasis) software package that was developed by Linear Technologies which manufactures a wide range of integrated circuits. Linear Technologies, now owned by Analog Devices, Inc., use LTspice[®] to design and simulate all the integrated circuits that are developed and manufactured by them.

Analog Devices, Inc. [137] describes LTspice® as a “high performance SPICE simulation software, schematic capture and waveform viewer with enhancements and models for easing the simulation of analog circuits”. LTspice® offer a wide range of functions such as transient, AC analysis, DC sweep, noise and DC transfer simulations which attracts users from many different disciplines. The built-in schematic capture enables users to generate new circuits while the waveform viewer allows the user to control the way the data is presented.

In section 2.4 of this literature study, some electrochemical fundamentals and the mathematical models linked to each of them were discussed. To be able to simulate these mathematical models, it is required to make use of mathematical simulation software such as MATLAB® and Simulink®. MATLAB® and Simulink® are mathematical computing software, developed by The MathWorks, that can be used to prepare Model based system designs and simulations without the use of C, C++, and HDL code [138]. MATLAB® which is an acronym for matrix laboratory is a programming language used to develop algorithms, analyse and visualise data, and numerically calculate complex mathematical problems [138]. Simulink® is a graphical computing platform that can be used to develop multi-domain models and simulations [138]. MATLAB® and Simulink® can be used together, combining the numerical and graphical platforms. Abdin *et al.* (2015) [77] developed mathematical models in terms of material parameters for the anode, cathode and membrane of a PEM electrolyser cell. These models were then combined into a single model which was simulated using Simulink®. Their experimental results were then used to validate their mathematical and simulation models. Making use of platforms such as MATLAB® and Simulink® can thus be crucial for the validation and verification processes.

2.11 Case Studies

In this section of the literature, case studies related to this study are listed and reviewed. The purpose of this section is to evaluate the different methods used, results obtained and shortcomings of each of the reviewed studies. The case studies will also be used to verify and validate the results obtained in this research project.

2.11.1 Influencing factors of water electrolysis electrical efficiency

Mazloomi and Sulaiman (2012) [18] studied the key factors that have an influence on the electrical efficiency of an electrolysis system. The focus of this study was to determine how to enhance the efficiency of water electrolysis by reducing the electrical power consumption. From their study, they determined that the electrolyte quality, electrolyte resistance, electrode material, separator material, operational temperature, operational pressure, and the applied voltage waveform all have an influence on the electrical efficiency of a water electrolysis system.

Most of the influencing factors have to do with the design and construction of the electrochemical cell and will thus not be discussed for the purpose of this study (as per section 3.3.5). The applied waveform however in one of the parameters that will be considered in this study since it is an electrical parameter affected by the power supply. They reviewed studies done by Shimizu *et al.* (2005) [139], Ursúa *et al.* (2009) [17], Brad (1980) [140] and Armstrong *et al.* (1972) [141] to determine how the applied voltage waveform affects the efficiency of a water electrolyser. The studies did not focus solely on the electrical parameters of the applied voltage waveform and a conclusion as to what the effect of the applied voltage waveform is could not be made. This study showed that a further investigation of the effects of different voltage and current waveforms applied to a water electrolyser are required.

2.11.2 Impact of the voltage fluctuation on electrolysis efficiency

Dobó and Palotás (2016) [20] conducted a study to determine the impact that different voltage fluctuations in the power supplied to an electrolysis system have on the efficiency of the system. They determined that a fluctuation in the voltage supplied to an electrolyser have a dynamic influence on the performance of the electrolyser. They conducted a series of experiments to determine what the influences are. The variables for the experiments were the AC amplitude, frequency and DC-offset of the power supplied to the cell, while the applied signal waveform was constant. The electrolyser's response to different voltage fluctuations was determined by measuring the cell voltage, cell current and the cell pressure, or in other words, the hydrogen production rate since the pressure growth is directly proportional to the hydrogen gas flow rate. The power supply variable ranges and constants they used are given in Table 2-13 below [20].

Table 2-13: Experimental parameters (adapted from [20]).

Parameter	Range
AC amplitude	0.0 V – 2.0 V (0.2 V steps)
DC offset	1.4 V – 2.8 V (0.2 V steps)
Frequency	1 Hz – 97 Hz (4 Hz steps) and 200 Hz – 5000 Hz (100 Hz steps)
Waveform	Sinusoidal signal

A total of 6512 measurements, where each measurement had different parameter values, were obtained and analysed during this study. From the measurements obtained, they determined that the gas production increases at the low end of the frequency range and the high end of the AC amplitude range. Although the hydrogen production rate increased at lower frequencies and higher AC amplitudes, the power consumption of the cell also increased, resulting in a decrease in the overall efficiency [20].

Although this study is a good indication of how a fluctuating voltage affects the efficiency of an electrolyser, some shortcomings were observed. The first is that the experimental tests were done using only one waveform and the second is that the experiment was done only on an alkaline water electrolyser. This study thus also showed that a further investigation of the effects of different voltage and current waveforms applied to a water electrolyser are required.

2.11.3 Effect of pulse potential on alkaline water electrolysis performance

Demir *et al.* (2018) [19] conducted a study to determine the effect of a pulse potential power supply on the energy consumption of an alkaline water electrolysis system. The study showed that by applying a pulse potential to an alkaline water electrolyser, the mass transfer losses that occur on the electrodes could be reduced. The alkaline water electrolyser used in this experiment consisted of a 200 ml KOH solution as the electrolyte and two cylindrical electrodes made from Pt and placed 10 mm from each other in the electrolyte bath. The experiment also included a MOSFET driver circuit, used to generate a square wave signal with an adjustable duty cycle, frequency and amplitude. The parameter ranges of the pulse potentials applied to the alkaline electrolyser are given in Table 2-14 below [19].

Table 2-14: Experimental parameters (adapted from [19]).

Parameter	Range
Waveform	Square wave
Peak Voltage	6 V – 10 V
Frequency	0.1 Hz – 1.2 MHz
Duty Cycle	10% – 100%

The study showed that by applying a pulse potential with a specific duty cycle and frequency, the mass transport of hydrogen and oxygen bubbles that forms on the electrodes could be improved. The improvement of the mass transport results in lower mass transport losses and in effect a lower power consumption. Demir *et al.* (2018) [19] concluded that a 20-25% improvement on the power consumption could be achieved when a pulse potential with a peak voltage of 6 V, a duty cycle of 50% and a frequency of up to 1200 kHz is applied to an alkaline water electrolysis system. As with the previous studies discussed, the main shortcoming of this study is that the experiments were done on alkaline water electrolysis and the effect of pulse potential on PEM water electrolysis was not investigated.

2.11.4 Impact of current fluctuation on electrolysis efficiency

Dobó and Palotás (2017) [15] studied the impact that a fluctuating current has on the efficiency of an alkaline water electrolysis system.

The results of this study showed that the ripple factor, frequency and current density of the applied current ripple have an impact on the efficiency of the electrolyser. To determine the impact of a fluctuating current on a water electrolysis system, various current waveforms (sinusoidal, triangular, square and sawtooth), frequencies, AC amplitudes and DC offsets were applied to a lab scale alkaline water electrolyser. An automatic experimental system was developed to automatically apply different ripple currents to the electrolyser and generate a large number of experimental measurements (4620 different parameter settings). The measurements included the voltage, current and pressure of the cell. The data obtained from these measurements were used to calculate the power consumption, the gas flow rate and the efficiency of the electrolyser using equation (2.71),

$$\varepsilon = 100Q \left[\frac{V_m P}{U^0 F} \left(\frac{1}{z_{H_2}} + \frac{1}{z_{O_2}} \right) \right]^{-1} \quad (2.71)$$

where Q is the gas flow rate, V_m the volume of an ideal gas, U^0 the theoretical decomposing voltage, F Faraday's number and z the charge number [15]. The experiments showed that the efficiency of the electrolysis cell is influenced by three parameters of the fluctuating current which includes the ripple factor, the frequency and the current density. The waveform of the fluctuating current did not affect the efficiency of the electrolysis system. The results showed a decrease in efficiency as the ripple factor increased and an increase in efficiency as the frequency increased. The highest frequency tested was 10 kHz, but Dobó and Palotás (2017) [15] expects the efficiency to increase further if the frequency is further increased. Although a higher frequency resulted in a higher efficiency, any deviation from a steady DC current lowered the overall efficiency of the cell. This is caused by an increase in the power consumption, without an increase in the hydrogen production rate. This study covered all the electrical characteristics of a ripple current and the only shortcoming is the absence of experiments on a PEM water electrolyser.

2.11.5 Effect of power quality on PEM water electrolysis systems

Koponen *et al.* (2020) [88] studied the effect of power quality on the energy consumption of a PEM electrolyser cell. In order to determine the effect of power quality, they developed a semi-empirical model of a single cell PEM electrolyser with a Nafion 117 membrane. The model was developed, and the model specific parameter values were obtained from polarisation curve and anode hydrogen content measurements. All experimental measurements were conducted at an operating temperature of 75 °C and a pressure of 1 atm. The semi-empirical cell model was then used to simulate the energy consumption of the PEM electrolyser for two different ripple current scenarios.

The first simulation was for a sinusoidal ripple current with a frequency of 300 Hz and a ripple amplitude up to 100 % of the DC current value while the second simulation was for a ripple induced by a 12-pulse thyristor bridge. Their simulation results showed that with the use of a 12-pulse thyristor bridge rectifier, the active area of the PEM electrolyser should be up to five times larger to achieve the same specific energy consumption ($\text{kWh}_{\text{electrical}}/\text{kgH}_2$) as with the use of an ideal DC power supply. They concluded that the power quality has a large effect on the specific energy consumption of a PEM electrolyser and highlighted the importance of minimising the current ripple supplied to PEM electrolyzers. Although this study delivers great insights on the possible effect of a ripple current on the efficiency of a PEM electrolyser, the findings were based on simulation results that need to be verified with experimental measurements.

2.12 Conclusion

In the opening section of this chapter, background on hydrogen as an energy storage medium and carrier were presented which were followed by a review on the electrochemical cells that are used in a hydrogen energy system. Although different water electrolysis technologies were reviewed, the focus of these opening sections was on hydrogen production through PEM water electrolysis which included the components and characteristics of a PEM electrolyser.

After a review on the general operation of electrochemical cells, the electrochemical fundamentals of PEM electrolysis were studied. This study includes the thermodynamics, overpotential, reaction kinetics, efficiency and degradation of a PEM electrolysis system. The literature study also covered the methods available to characterise an electrolyser and the equivalent electrical circuit models that can be used to represent and simulate an electrochemical cell. The final sections of Chapter 2 were devoted to the electrical characteristics of the power supplied to an electrolysis system, the possible effects it has on the efficiency of the system as well as a review on previous studies regarding this matter. Chapter 2 provides the necessary background theory to design an experimental procedure and setup to obtain the required information that would be of value to the scientific and engineering industries.

This chapter also formed a crucial part of the verification and validation procedures used in this study. The literature reviewed in sections 2.4 and 2.5 provided the necessary knowledge to verify and validate that the experimental system and procedure would deliver the correct measurements to determine the effect of a ripple current on the efficiency of a PEM electrolyser. Next, the literature presented in sections 2.7, 2.8 and 2.10 were used to verify and validate the characterisation techniques and the developed simulation models.

Lastly, sections 2.8.2.4 and 2.11 were used to verify and validate the parameter ranges and setting of the ripple currents that should be tested. The following chapter (Chapter 3) presents the experimental design, which includes the conceptual design, design specifications, detail design and experimental procedures.

CHAPTER 3: EXPERIMENTAL DESIGN

3.1 Introduction

Once the literature review was complete, the experimental specifications, conceptual design and detailed design were formulated, and are discussed in this chapter. This includes the identification and design of the experiment requirements, experimental processes, experimental apparatus, as well as the setup of the experimental test station. Verification and validation are also included to ensure the reliability and repeatability of the experimental tests conducted on the system. All the topics which are presented in Chapter 3 are outlined by the chapter structure in Figure 3-1.

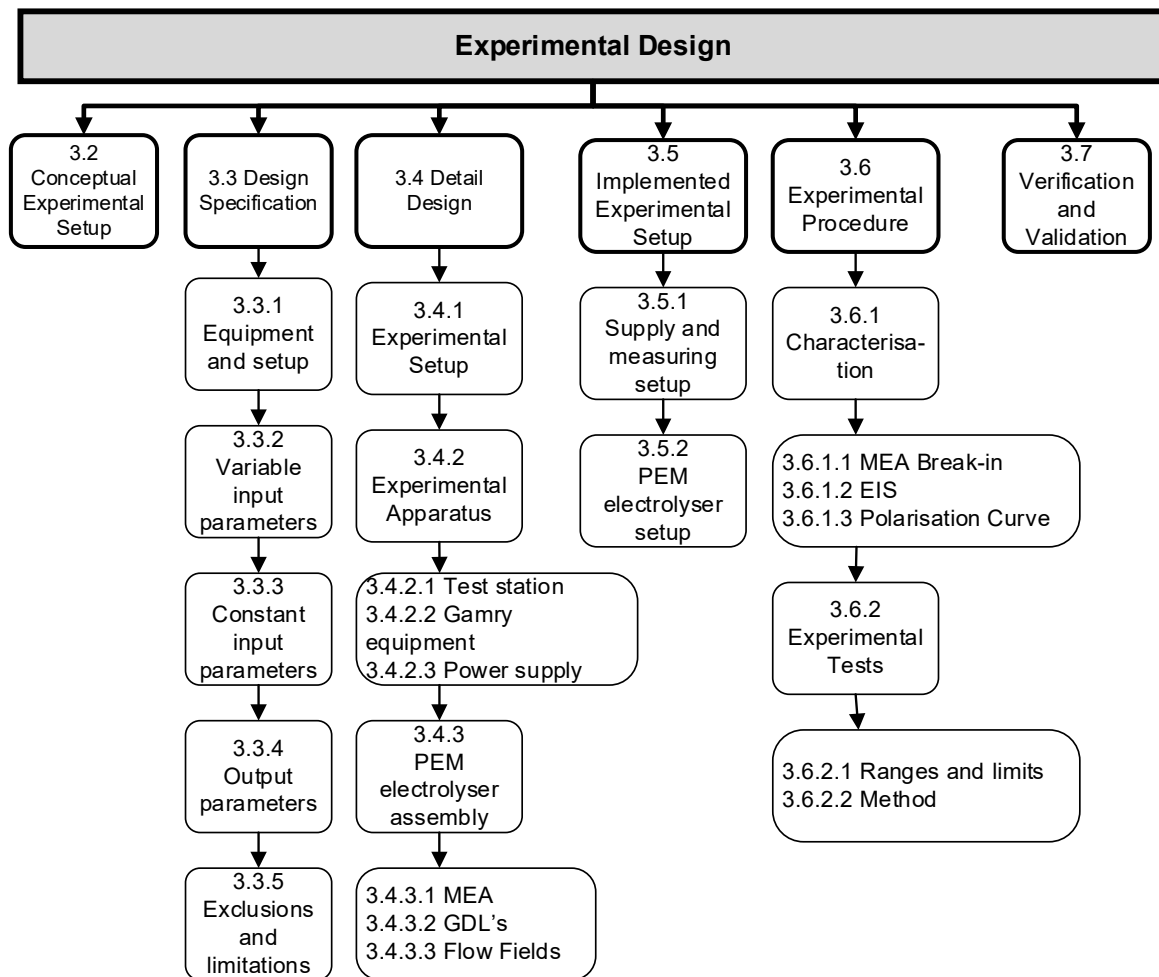


Figure 3-1: Overview diagram of Chapter 3 structure.

3.2 Conceptual Experimental Setup

Figure 3-2 is a diagram of the conceptual experimental setup used during this study. The diagram presents the main apparatus required for the experiments, which includes the PEM electrolyser, power supply, water supply, computer and measuring instrumentation.

The thick solid lines represent the power flow in the system while the thin solid lines represent the flow of liquid and gas. The dashed lines represent the transfer of data within the system, either for control or measurements. The heat exchanger, water pump and power supply are the apparatus that is controlled, while the voltage, current and hydrogen flow are the main measurements required from the system. This conceptual experimental setup was used as a baseline during the detail design, presented in section 3.4, to stay within the scope of the research project.

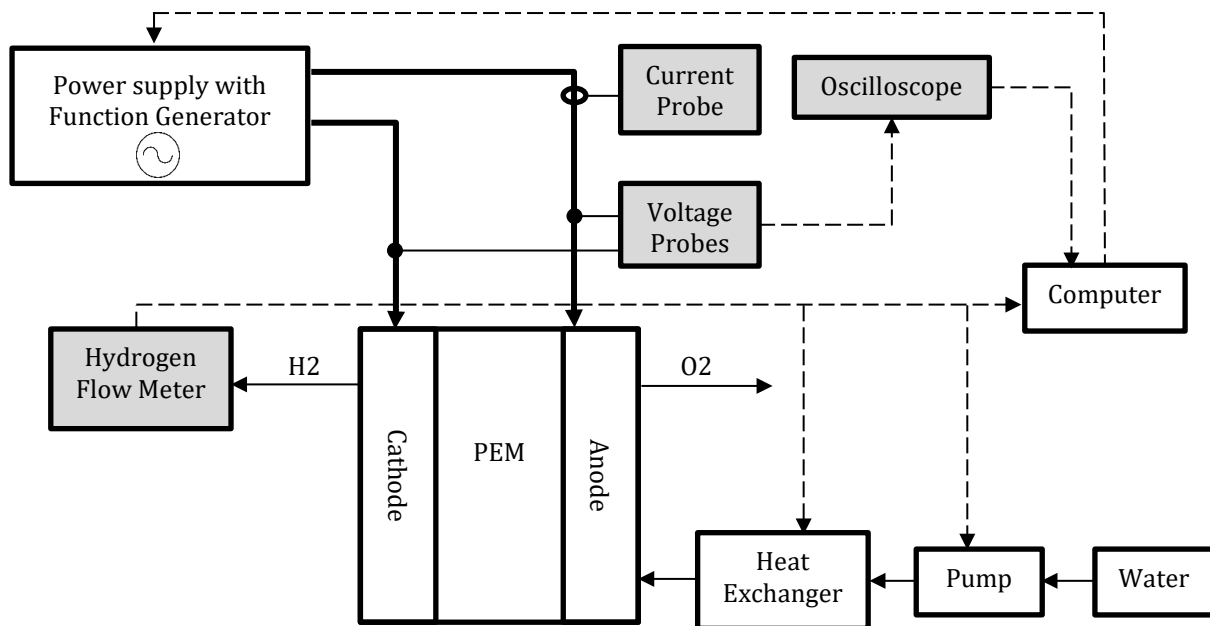


Figure 3-2: Conceptual experimental setup.

3.3 Design specifications

This project aims to determine what effect ripple currents have on the efficiency of a PEM electrolysis system. To achieve this outcome, some experimental test should be done on a laboratory sized system to derive an educated conclusion on the possible effects of a ripple current on a superior system. The specifications of this study were based on reports issued by the publication's office of the European Union for testing of water electrolysis cells. Since the characterisation methods used in this study are Polarisation curves and EIS, the two reports used to set-up the specifications are:

- EU harmonised polarisation curve test method for low-temperature water electrolysis, EUR 29182 EN, [142], and
- EU harmonised test procedure: electrochemical impedance spectroscopy for water electrolysis cells, EUR 29267 EN, [117].

In addition to the protocols published by the European Union, other industry standards for the design and testing of PEM water electrolysis cells were also considered [49], [101], [100], [143]. The experimental requirements are divided into four sections, namely the test equipment and setup, variable input parameters, constant input parameters and output parameters.

3.3.1 Equipment and setup

The experimental test system should consist of the following physical requirements, as determined by the industry standards mentioned above:

- A single cell PEM electrolyser assembly, with relatively easy access to the cell components such as the MEA, GDL's and flow fields. Replacement or inspection of the MEA and GDL's should be possible without damaging the rest of the system.
- MEA, GDL's and flow fields which allow the cell to have a stable performance are required. A stable cell performance can be used as a baseline for the experimental tests and ensures that all tests are comparable.
- A supply system to supply the PEM electrolyser with the required electrical power, heat and water. This system thus includes a power supply, water supply and heat exchanger. The above-mentioned supply system should also be controllable.
- A measurement system to monitor and log the required data from the system. Measurements to determine the cell performance and efficiency are required.
- A test station which combines the supply and measuring system and applies to the relevant safety standards for testing of hydrogen systems.

The equipment requirements for the experimental set-up to test the PEM electrolyser are illustrated in Table 3-1. These specifications will be used to validate the design and set-up of the experimental system.

Table 3-1: Equipment required (adapted from [142], [117]).

Equipment	Range/Specification	Quantity
Hydrogen pressure sensor	Determined by applied pressure	1
Oxygen pressure sensor	Determined by applied pressure	1
Hydrogen temperature sensor	15-100 °C	2
Oxygen temperature sensor	15-100 °C	2
Hydrogen flow meter	Determined by predicted flow	1
Oxygen flow meter	Determined by predicted flow	1
Cell temperature sensor	15-100 °C	1
Gas liquid separator	As required	2
Cell heating and cooling device	Ambient to 100 °C	1

Equipment	Range/Specification	Quantity
Water circulation pump	Determined by the applied current	1
Water treatment device	As required	1
Water conductivity meter	0.1-10 ⁻⁶ S.cm	1
DC power supply	Galvanostatic control: $\geq 2\text{ A/cm}^2$ Potentiostatic control: $\geq 2\text{ V/cell}$	1
Control and data-acquisition HW and SW	As required by I/O parameters	1
Sine waveform generator (EIS)	10 ⁻² -10 ⁺⁶ Hz	1
Galvanostat to amplify AC signals (EIS)	0.5% – 5% of I_{DC}	1

3.3.2 Variable input parameters

The variable input parameters are the parameters that are required to be changed during the experimental tests. The essential variable input parameters required to test the performance of an electrolyser are shown in Table 3-2. These parameters are the standardised parameters required to do EIS and polarisation cure tests on any electrolyser as documented by the European Union in [142] and [117]. To test the effect that ripple currents have of the efficiency of a PEM electrolyser, some additional variables as shown in Table 3-3 are required. These variable input parameters were selected based on the aim and objectives of this study, as outlined in Chapter 1, as well the parameters used in the case studies reviewed in section 2.11.

Table 3-2: Variable input parameter requirements (adapted from [142], [117]).

Variable Input Parameter	Symbol	Accuracy
Current density (galvanostatic control)	j	$\pm 2\%$ for $j < 0.1\text{ A/cm}^2$ $\pm 1\%$ for $j \geq 0.1\text{ A/cm}^2$
Voltage (potentiostatic control)	U	$\pm 1\text{ mV}$
Water inlet temperature	T	$\pm 2\text{ }^\circ\text{C}$

Table 3-3: Variable input parameter requirements for ripple wave.

Variable Input Parameter (Ripple wave)	Symbol	Accuracy
Waveform	-	-
DC offset	I_{DC}/V_{DC}	$\pm 1\%$ of the full range
AC amplitude	I_{AC}/V_{AC}	$\pm 1\%$ of the full range
Frequency	f	0.1 Hz

3.3.3 Constant input parameters

Some of the experimental parameters should be kept constant for all the tests that would be carried out. This is to ensure that the only variable that is able to affect the performance of the cell is the applied ripple current. The constant input requirements are presented in Table 3-4.

Table 3-4: Constant input parameter requirements (adapted from [142], [117]).

Static Input Parameter	Symbol	Accuracy
Water inlet pressure	p_{water}	$\pm 2\%$
Water inlet volumetric flow rate	Q_v	$\pm 1\%$ of full scale
Cell Temperature	T_c	$\pm 2\text{ }^\circ\text{C}$
Number of points per decade (Required for EIS)	PPD	Minimum of 3
Range of frequencies (Required for EIS)	f	10^{-2} – 10^{+6} Hz
Current peak-peak amplitude (Required for EIS)	I_{AC}	0.5% – 5% of I_{DC}

Other aspects of the experimental set-up that should be kept constant include:

- The MEA and GDL's type and quality. If it is necessary to change the MEA or the GDL's during the course of the experiments, the new component should be the same as the first component and of equal quality (no damage).
- Flow fields, current collectors and endplates. These components would not be exchanged or replaced during this study.
- The experimental setup, testing station and measuring equipment.

3.3.4 Output parameters

To determine if the efficiency improves or declines with the application of a ripple current, certain parameters need to be measured during the tests. The measured data would also be used to characterise the electrolyser and determine the degradation rate of the MEA as a result of the ripple current. The required output parameters are shown in Table 3-5.

Table 3-5: Output parameter requirements (adapted from [142], [117]).

Output Parameter	Symbol	Unit
Current density (potentiostatic control)	j	A/cm ²
Voltage (galvanostatic control)	U	V
Electric power density	P_d	W/cm ²
Hydrogen flow rate	Q_{H_2}	nLPM
Oxygen flow rate	Q_{O_2}	nLPM
Imaginary part of impedance as a function of frequency	$Z_{Im}(f)$	Ω or $\Omega\cdot\text{cm}^2$
Real part of impedance as a function of frequency	$Z_{Re}(f)$	Ω or $\Omega\cdot\text{cm}^2$
Impedance magnitude as a function of frequency	$ Z (f)$	Ω or $\Omega\cdot\text{cm}^2$
Impedance phase as a function of frequency	$\Theta(f)$	$^\circ$

3.3.5 Exclusions and Limitations

PEM water electrolysis is a complex process which requires an ample amount of chemical, mechanical and electrical knowledge to master. In order to complete this study without the risk of focussing on too many characteristics, some exclusions and limitations are listed below.

- Investigations on variables other than the electrical characteristics of the power supply are excluded.
- The design of the PEM electrolyser cell components is excluded.
- The experimental tests were limited to one PEM electrolyser cell.
- The experimental tests were limited by ranges of the available apparatus and the specifications of the PEM electrolyser.

3.4 Detail Experimental Design

In this section, the detailed experimental design is presented, which includes detailed information on the experimental setup, the apparatus used in the setup as well as the PEM electrolyser assembly and component selection.

3.4.1 Experimental Setup

The experimental setup is a crucial part of the detail design since the value of the experimental results relies hugely on the accuracy of the integrated system. The equipment selection and integration were based on the specifications and requirements of this project as outlined in section 3.3. The conceptual design of the experimental setup presented in section 3.2 was developed into a detailed design as shown in Figure 3-3. The solid black lines represent the electrical connection and the flow of power in the system, which includes the connections between the PEM electrolyser, the power supply and the Gamry Interface 1000. The solid red lines represent the flow of liquid and gas in the system, while the dashed blue lines show the control and measurement data flow. The PEM electrolyser assembly and the individual components included in the assembly are presented in section 3.4.3, while the rest of the apparatus used in the setup are discussed in section 3.4.2. The experimental setup includes the following equipment:

- The PEM electrolyser cell.
- Greenlight innovation[®] electrolysis test station (incl. Hydrogen flow meter, Water supply pump, Water temperature and flow control systems, Hydrogen and Oxygen gas separators and Emerald[®] Control and Automation software)
- Gamry[®] Interface 1000. (incl. Gamry EIS software)
- Elektro-Automatic[®] EA-PSI 9080-170 Power supply (incl. EA Power Control[®] software)

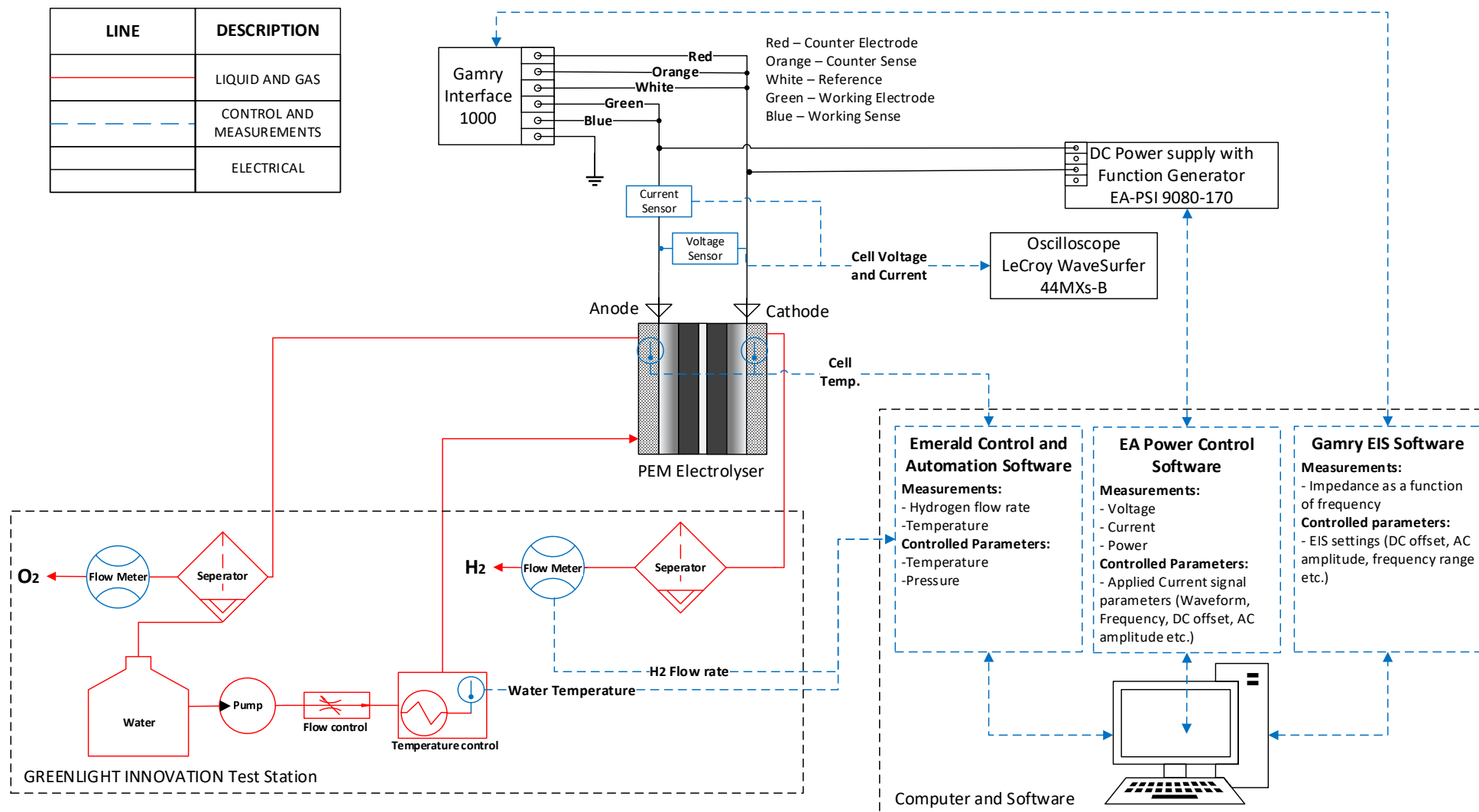


Figure 3-3: Detailed experimental setup.

3.4.2 Experimental Apparatus

In this section, the main apparatus used in the experimental setup, as illustrated by Figure 3-3 are presented. The apparatus presented includes the Greenlight Innovation® test station, the Gamry® Interface 1000 and the Elektro-Automatic® power supply. A short description, the task for which it is used and the specifications of each piece of equipment are included.

3.4.2.1 Test Station

The Greenlight innovation test station, shown in Figure 3-4, provides the user with a fully automated and extremely accurate platform for research and development on PEM cells. The test station is imbedded with all hardware required to do various test and experiments on PEM electrolyzers, including the water supply, temperature control, gas separation and measurement systems. The test station is controlled by Greenlight Innovation's Emerald® control and automation software. This software provides the user with a graphical user interface to control the system, write scripts to automate the experiment and log the measured data. For the purpose of this study, the Greenlight innovation test station is used to supply the PEM electrolyser with water, control the water supply flow and temperature and measure the produced hydrogen flow rate. The main components imbedded in the test station and used during this study, are illustrated in Table 3-6.



Figure 3-4: Greenlight Innovation test station.

Table 3-6: Test station components and specifications (combined from [144-147]).

COMPONENT	RANGE	ACCURACY
Mass Flow meter (EL-FLOW F-111B-5K0)	0.042 – 6.5 nLPM (H ₂)	± 1% of range
Thermocouples (Type T)	-27 – 300 °C	± 1 °C
Temperature controller (AKT7 series)	-205 – 400 °C	0.2% of range/ ± 1 °C
Supply Pump (0.12kW Y-2951)	12 l/min	–

3.4.2.2 Gamry® equipment

Potentiostats and Galvanostats are used in experiments where the responses of an electrochemical cell to specific potentials or currents are required. When the instrument is operated in potentiostatic mode, the potential between the working and reference electrodes of the electrochemical cell is controlled while the current flow between the electrodes is measured [148]. In galvanostatic mode the current applied to the cell is controlled while voltage response is measured. One of the leading names in electrochemical testing equipment is Gamry Instruments®, manufacturer of the Interface 1000, which can be operated as a potentiostat, galvanostat or ZRA. Some useful specifications of the Interface 1000 are given in Table 3-7 below [149].

Table 3-7: Interface 1000 Specifications (adapted from [149]).

SYSTEM	
Control Modes	Pstat, Gstat, ZRA
Connections Options	2, 3 and 4 electrode
Maximum Current	±1 A
Minimum Current Resolution	3.3 fA
Maximum Voltage	±12 V
Minimum Voltage Resolution	1 µV
EIS MEASUREMENT	
Frequency Range	10 µHz – 1 MHz
Max AC Amplitude	2330 mV RMS
Min AC Amplitude	17.8 µV RMS

The EIS software offered by Gamry® can be used together with the Interface 1000 to perform EIS tests on electrochemical cells. This software is able to analyse the measured data and present it in the form of a Nyquist or a bode plot. This software is also used to fit the measured impedance over a specific frequency range to an EEC model. The Gamry equipment and software was thus selected to use in this study to characterise the PEM electrolyser through EIS and develop an EEC model of the cell.

3.4.2.3 Elektro-Automatic® DC Power Supply

The EA-PSI 9080-170 is a programmable power supply that can operate in four different modes where either the voltage, current, power or resistance is regulated. This power supply can be controlled either through the human interface on the power supply or by making use of the EA Power Control® software. The software enables the user to display and control the actual voltage, current and power values of the DC power supply remotely. The measured data can then also be logged by making use of the software's semi-automatic data acquisition features. The DC power supply was selected for this study mainly because of the function generator it includes. The function generator can apply various pre-defined functions either to the output voltage or current of the power supply. The EA Power Control® software controls the function generator. Table 3-8 below shows the specifications of the Elektro-Automatics® DC power supply.

Table 3-8: DC power supply specifications (adapted from [150]).

EA-PSI 9080-170 POWER SUPPLY	
Rated Voltage	0 – 80 V
Rated Current	0 – 170 A
Rated Power	0 – 5 kW
Voltage Resolution	≤4 mV
Current Resolution	≤7 mA
Features	- Voltage, current, power or resistance control - Semi-automatic data acquisition - Function Generator - Control Software

3.4.3 PEM Electrolysis cell

The main apparatus used in this study is the PEM electrolyser and each component of the electrolyser thus needs to be carefully considered. Figure 3-5 below gives an overview of the PEM electrolyser assembly as well as the different components included in the assembly. The electrolyser components consist of end plates, current collectors, flow fields, gas diffusion layers, gaskets and an MEA sealed in the middle of the assembly.

3.4.3.1 Membrane Electrode Assembly

In any PEM electrolyser assembly, similar to the one presented in Figure 3-5, the MEA has the most significant influence on the performance and stability of the cell. The MEA selection was thus a crucial part of the design process and needed to be carefully considered.

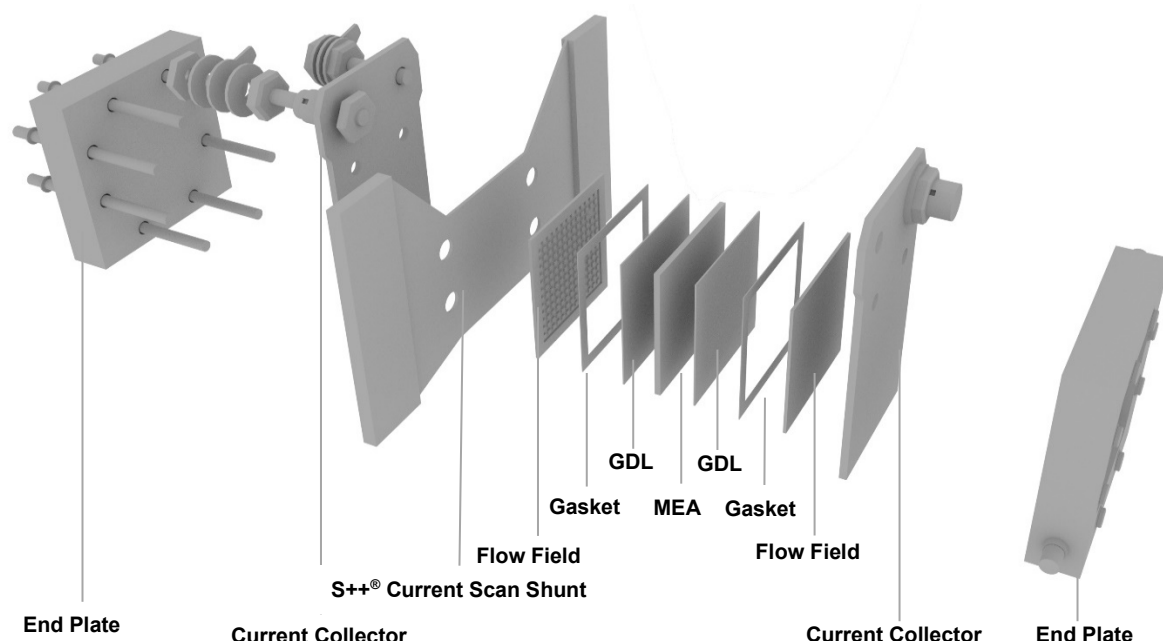


Figure 3-5: PEM Electrolyser Assembly (adapted from [151]).

The selection was not based on performance alone, but rather on the MEA's compliance with the requirements of this research project. An MEA was selected based on the specifications as defined in section 3.3.1, with main requirements being the membrane resistance as well as the stability of the cell voltage. The EIS, Polarisation curve and galvanostatic hold characterisation tests were used to characterise different MEA's and select the most suitable one. All tests were done at a cell temperature of 70 °C and standard pressure (1 atm). Four different MEA's, each from a different supplier was considered and compared to each other. The results of the EIS and Polarisation curve characterisation are shown in Figure 3-6 and Figure 3-7 below; these figures were used to analyse the ohmic and activation losses of each MEA.

Figure 3-6 contains a PC for each of the four MEA's and is obtained by increasing the current density in increments of 0.04 A/cm² while measuring the voltage response. Polarisation curves represent the voltage to current relation in electrochemical cells and were used to determine the performance of each of the four MEA's. The PC's indicates that the MEA produced by supplier B has the lowest overpotential while the MEA by supplier C has the highest overpotential. The overpotentials present included activation overpotential in the low current density region, ohmic overpotential in the intermediate current density region and concentration overpotential in the high current density region. Figure 3-7 shows the Nyquist plot for each MEA, which were obtained by applying the EIS technique with the use of the Gamry® Interface 1000.

The Nyquist plot represents the relation between the real and imaginary impedance in electrochemical cells and was used to identify two loss regions namely the activation and ohmic losses in each of the four MEA's. The intercept with the real axis at the high frequency side of the plot is the ohmic resistance value while the intercept at the low frequency side is the sum of the ohmic and charge transfer resistance. The difference between the two intercepts is therefore equal to the charge transfer or activation resistance value. The Nyquist plots indicated that the MEA from supplier C has the smallest ohmic resistance and also the largest activation resistance. In contrast to supplier C, the MEA by supplier A has the smallest activation resistance and the largest ohmic resistance.

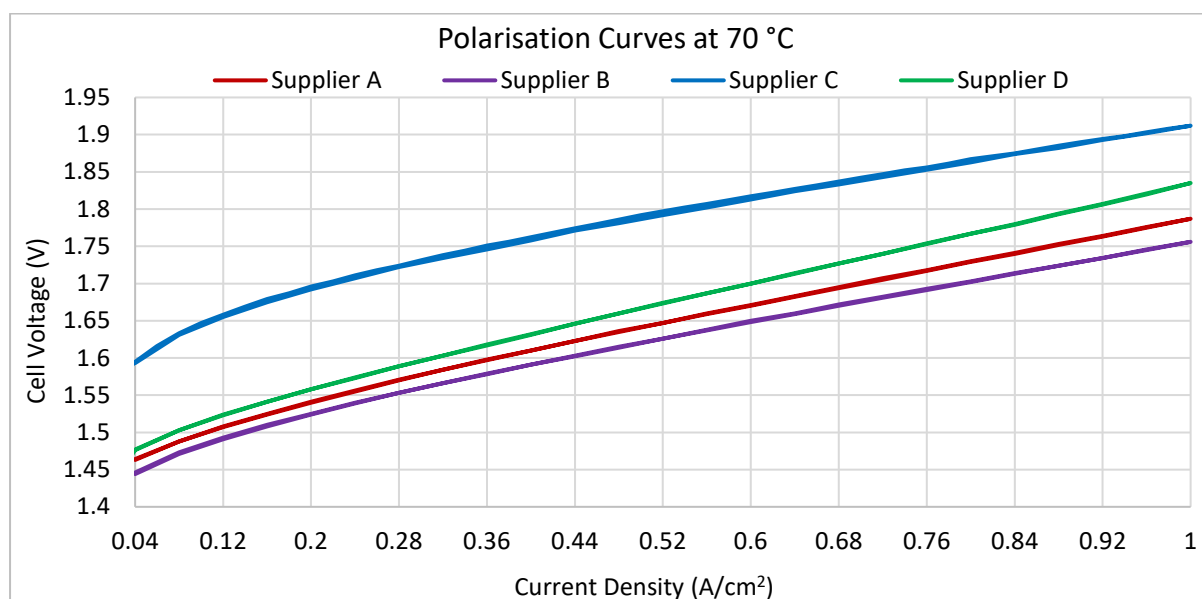


Figure 3-6: Polarisation curve of four different suppliers.

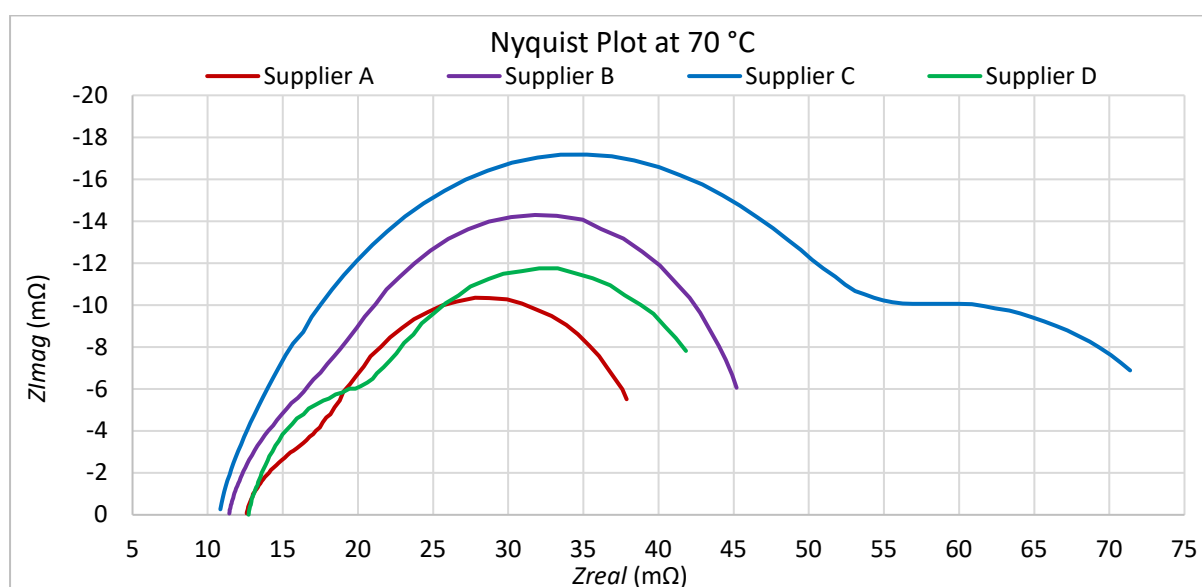


Figure 3-7: Nyquist plot of four different suppliers.

Ohmic and Activation resistance

The ohmic overpotential is caused by the ohmic resistance, which is the resistance against the flow of ions through the membrane. The slope of the PC in the intermediate current density region is one of the measures used to determine the size of the ohmic resistance of an electrolyser. A higher ohmic resistance will cause the PC to have a greater slope, indicating an inferior performance. The ohmic resistance can also be obtained from the high frequency intercept with the real axis on the Nyquist plot shown in Figure 3-7. The Nyquist plots show that the MEA from supplier C has the lowest ohmic resistance while supplier D has the highest ohmic resistance. This is verified with the PC since the MEA from supplier C resulted in the smallest slope while the MEA from supplier D resulted in the largest slope.

The activation overpotential is caused by the charge transfer resistance, which is the resistance against electron flow at the electrode surface. The charge transfer resistance is defined as the difference between the low and high frequency intercepts with the real axis on the Nyquist plot shown in Figure 3-7. The slope of the PC in the low current density region is also a measure of the electrolyser's activation resistance since the activation resistance is the main contributor to the cell losses in this region. The Nyquist plots show that the MEA produced by supplier A has the lowest activation losses, while the MEA by supplier C has the highest. The EIS and PC characterization results were verified by comparing the slopes obtained from polarisation curve with the resistances obtained from the Nyquist plot. The comparison shown in Table 3-9 below verifies these methods since the results obtained from both shows similar trends in resistance variances between the different MEA's.

Table 3-9: Polarisation curve and EIS results.

Supplier	PC Ohmic Resistance (mΩ)	EIS Ohmic Resistance (mΩ)	PC Activation Resistance (mΩ)	EIS Activation Resistance (mΩ)
A	11.8	12.597	21.5	25.283
B	11	11.439	27	33.755
C	10	10.845	46	60.537
D	13.6	12.723	23	30.104

Degradation rate

The galvanostatic hold test was used to determine the stability of the electrolyser for each of the considered MEA's, by calculating the voltage drift after running the cell for at least 50 hours. The first 50 hours of the test is considered to be the break-in period and was not used in the calculation. The electrolyser was operated at a constant current density of 1 A/cm², a temperature of 70 °C and a pressure of 1 atm for each of the four tests.

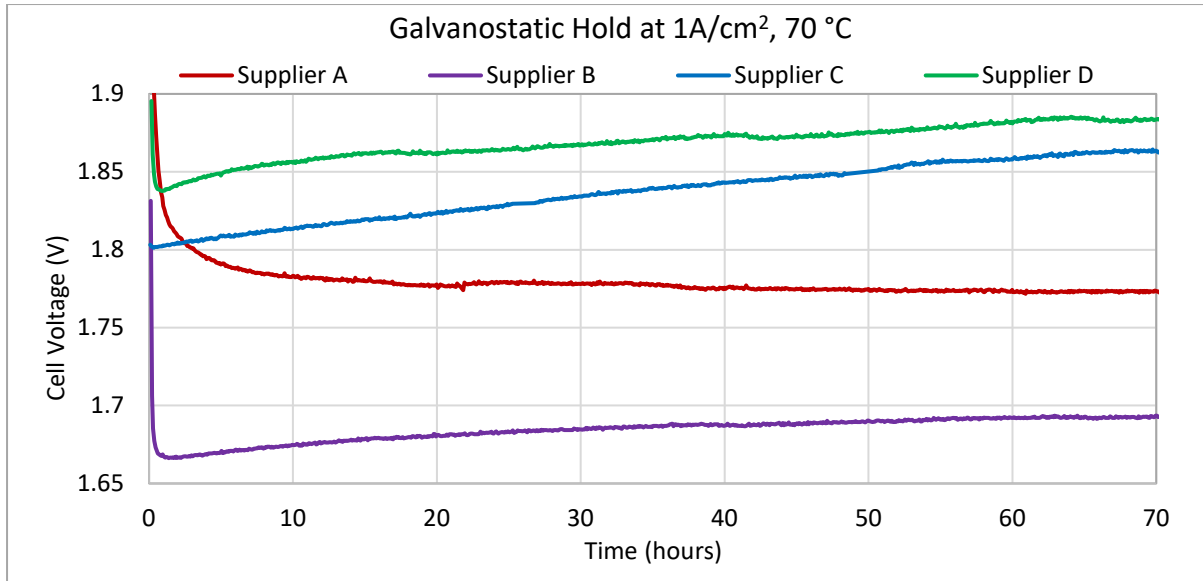


Figure 3-8: Galvanostatic hold of four different suppliers.

The results of the galvanostatic hold test, shown in Figure 3-8, were used to determine the stability of the cell voltage. Any voltage drift after the break-in period is caused by membrane degradation which will result in the electrolyser performing inconsistently. The voltage drift was calculated using equation (3.1) and the results are presented in Table 3-10.

$$\frac{V_{50h} - V_{70h}}{\Delta 20h} \quad (3.1)$$

The membrane degradation or voltage drift was verified by measuring the fluoride content (ppm) in the cathode return water since fluoride loss is one of the main contributors to membrane degradation

Table 3-10: Membrane degradation results.

Supplier	Voltage Drift (mV/h)	Fluoride loss (ppm)
A	0	0.0590
B	0.13	0.0783
C	0.65	0.4010
D	0.420	0.149

MEA selection

The MEA selected to use for this research project is the MEA produced by supplier A. The tests described above show that this MEA is stable and no degradation is measured under normal operating conditions. The activation resistance for this MEA is also the lowest, thus having the best performance in terms of linearity. Table 3-11 below gives the specifications and characteristics of the selected MEA.

Table 3-11: Selected MEA specifications.

PEM Electrolyser specifications	
Supplier	A
Membrane area	25 cm ²
PFSA Membrane material	Long side chain (LSC)
Membrane thickness (dry)	120µm
Membrane thickness (wet)	130µm
Catalyst loading (Anode)	2.2 mg/cm ² Iridium oxide
Catalyst loading (Cathode)	0.65 mg/cm ² Platinum

3.4.3.2 Gas Diffusion Layers

The gas diffusion layers (GDL's) considered for this study are 0.3 mm thick sintered titanium fibres plated with gold and sintered titanium fibres plated with platinum. A close-up view of the gold-plated mesh can be seen in Figure 3-9 (a) and of the platinum-plated mesh in Figure 3-9 (b), where the uniformity of the gold and platinum covering was investigated. Gold plated GDL's were chosen for this study since they are the most stable GDL's available with the smallest chance of degradation. As with the MEA, the stability of the GDL's was crucial to determine the effect of a ripple current on the performance of the PEM electrolyser without risking a change in performance due to normal degradation.

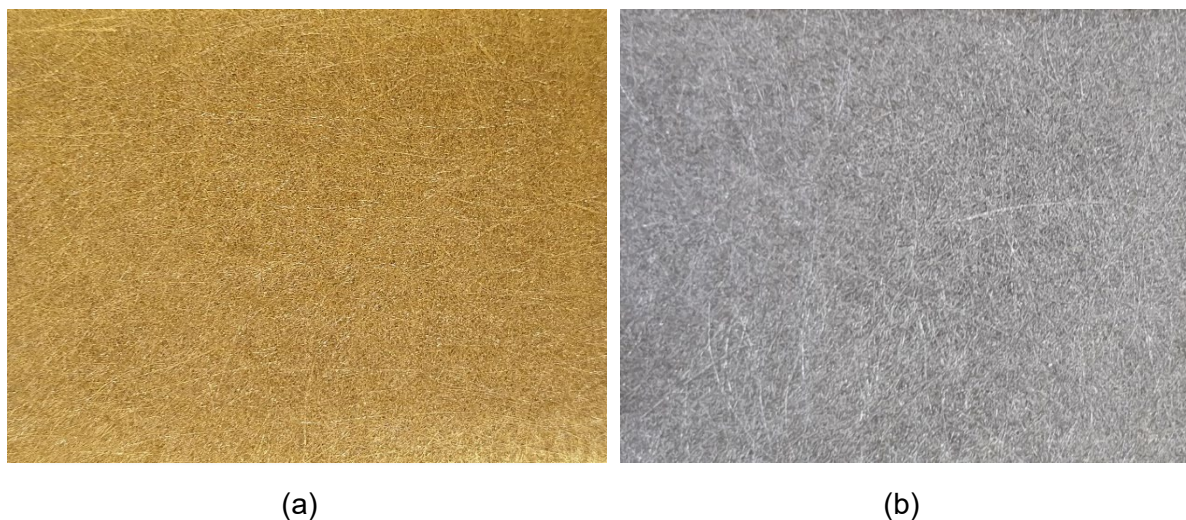


Figure 3-9: Gas diffusion layers: (a) Gold-plated (b) Platinum-plated.

3.4.3.3 Flow fields

A titanium plate, covered with square shaped pins, is the flow field design selected for this study. The pins have an area of 3.17 mm² with 1.78 mm channels between them. HySA Infrastructure manufactured and tested various flow field designs and found that the square shaped pin-type flow field design has the most equally distributed current density [152].

This design also showed the most uniform heat distribution, which eliminates the risk of temperature hot-spot formation. The results presented in [152] were verified by measuring the current and temperature distribution of this flow field design. Figure 3-10 illustrates the flow field design and Figure 3-11 the current and temperature distribution across the flow field. The current and temperature distribution were measured using a current scan shunt, produced by S++[®], which is included in the PEM electrolyser assembly as shown in Figure 3-5.

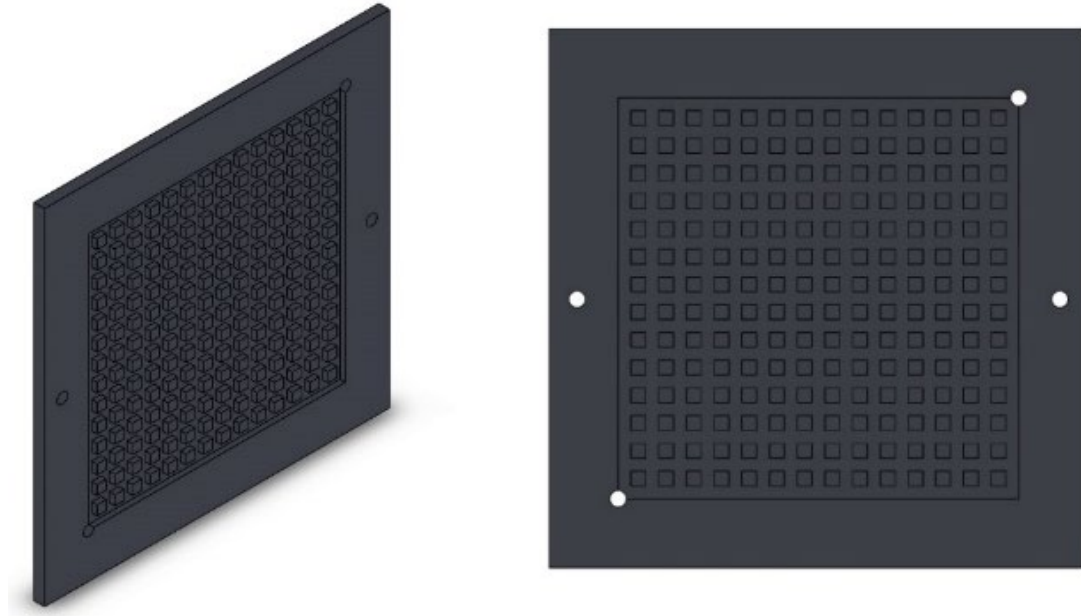


Figure 3-10: Stainless-steel square pin flow field design.

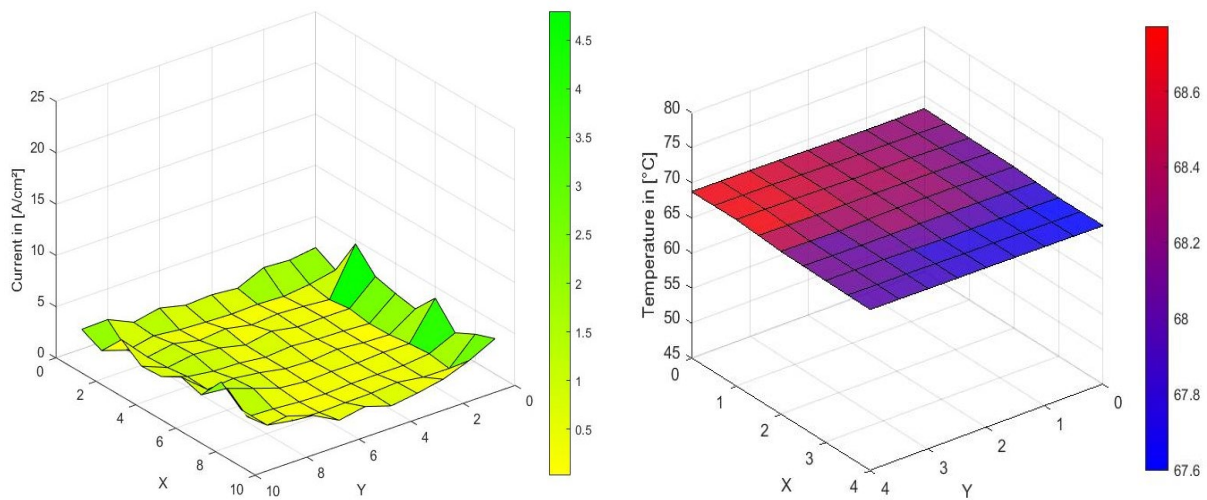


Figure 3-11: Current and Temperature distribution.

3.5 Implemented Experimental Setup

Upon completion of the detailed setup design, as presented in section 3.4, the design was implemented. The figures below show the actual experimental setup which includes all the required apparatus as well as the PEM electrolyser assembly. This setup would be used for the PEM electrolyser characterisation as well as the ripple current tests.

3.5.1 Supply and measuring setup

Figure 3-12 shows the Greenlight Innovation® test station, Gamry® Interface 1000 and the PEM electrolyser, while Figure 3-13 shows the power supply and the oscilloscope that were used.

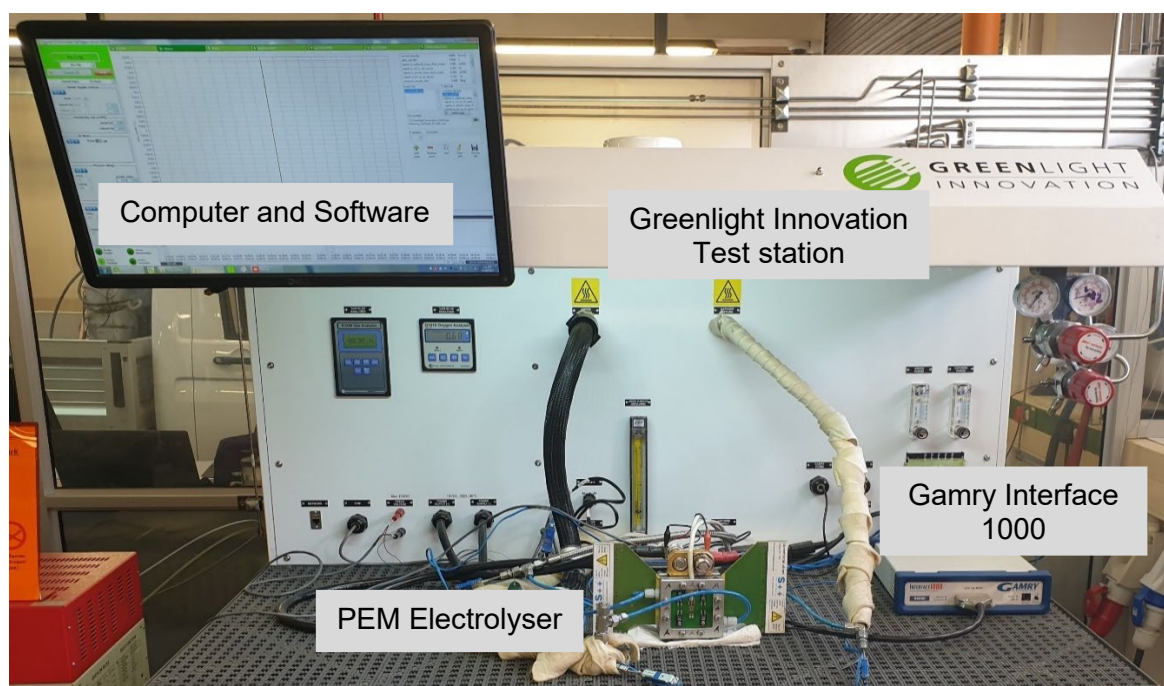


Figure 3-12: Implemented Test station arrangement.

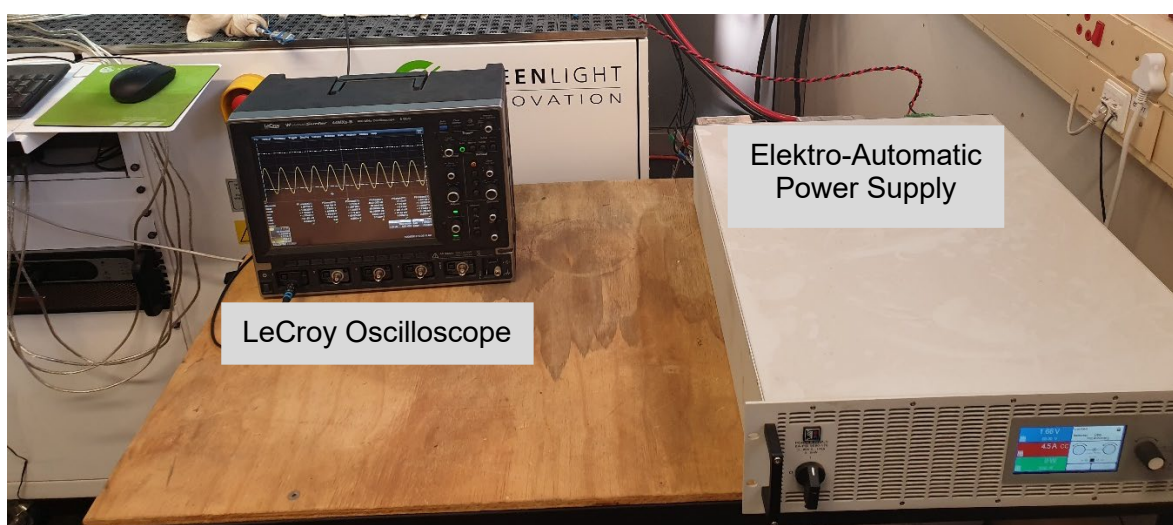


Figure 3-13: Implemented Test station arrangement.

3.5.2 PEM electrolyser setup

The PEM electrolyser assembly and connections are shown in Figure 3-14 below. The figure shows the anode supply which supplies the electrolyser with temperature controlled deionised water, the anode return which transports the oxygen gas produced and the cathode return which transports the hydrogen gas produced. The power supply's power and sensing cable connections as well as the S++[®] current scan shunt is also shown. The right-hand side of the figure shows part of the PEM electrolyser assembly to illustrate how the different components of the assembly such as the current collectors, flow fields and end plates were combined to form the electrolyser.

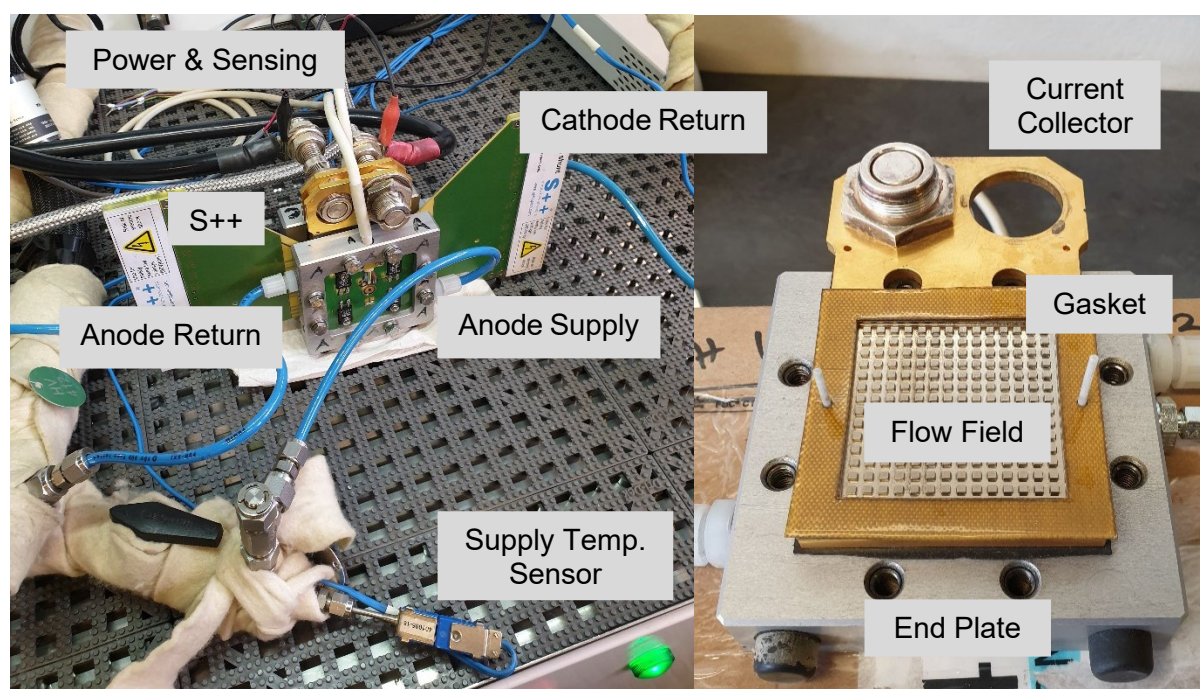


Figure 3-14: Implemented PEM electrolyser assembly.

3.6 Experimental Procedure

This section describes the experimental process that was followed to obtain the required data to answer the key research questions presented in section 1.3.4. The experimental procedure can be divided into two main categories, namely characterisation and experimental tests. The PEM electrolyser characterisation was used as a baseline for the rest of the study and is presented in section 3.6.1. The experimental tests were the next step in the experimental procedure and are presented in section 3.6.2.

3.6.1 Characterisation

The first step of the experimental process was to characterise the PEM electrolysis cell. Characterisation refers to the process where the cell performance and electrochemical characteristics at different operating conditions are identified.

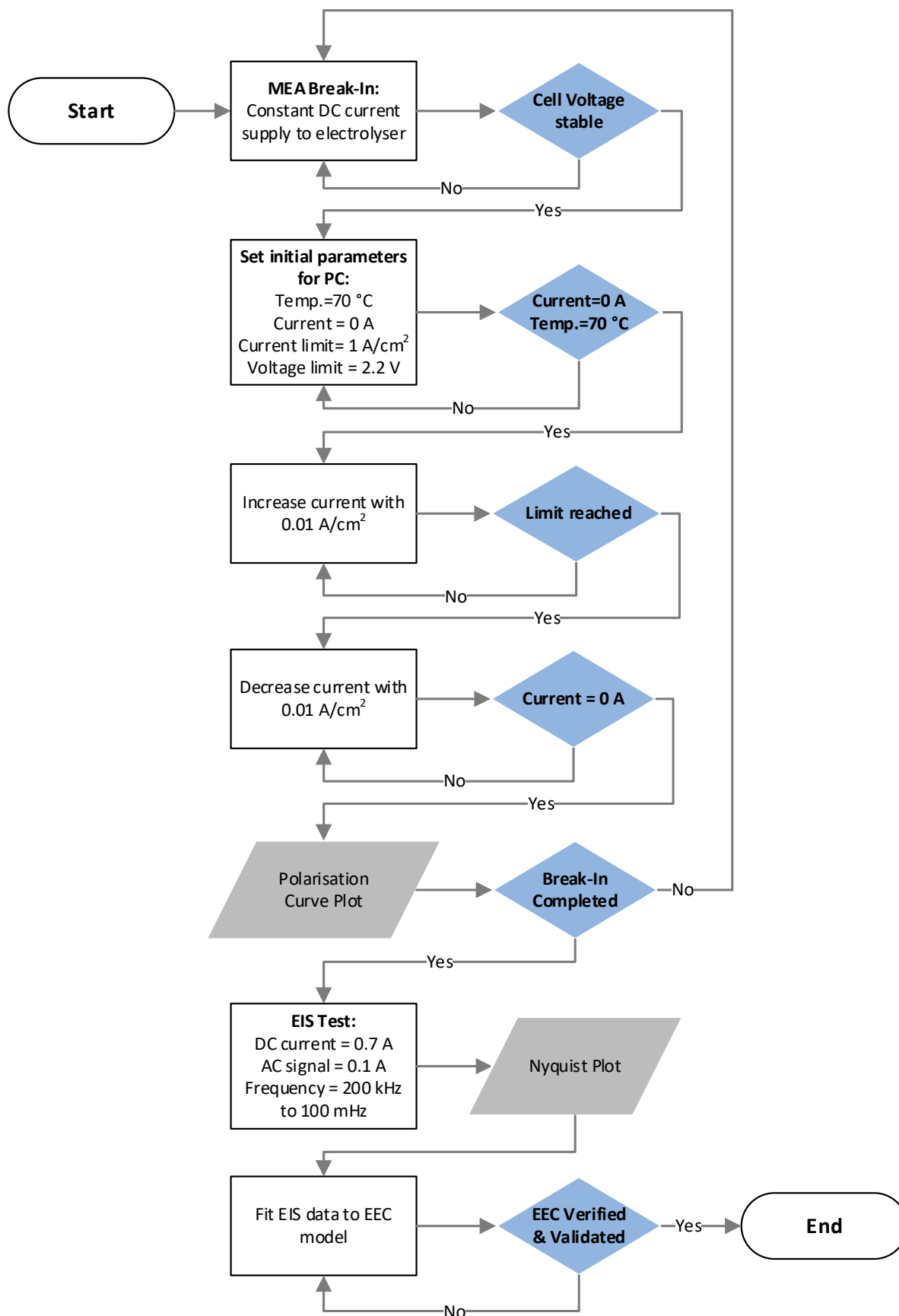


Figure 3-15: Characterisation flow diagram.

This data was used as the baseline for normal operation under DC conditions and compared to the performance of the cell when a ripple containing power supply is used. The characteristics of the cell were also used to model and simulate the cell's impedance and voltage response at different operating conditions. This process was one of the most important parts of this study since the experimental parameters were determined during this phase of the study. The process followed to characterise the PEM electrolyser is described in this section and Figure 3-15 is a flow diagram of the followed process. The first step would be to break in the membrane to achieve a stable cell voltage after which the characterisation process could start. The two characterisation techniques used is a polarisation curve to determine the cell voltage at different current densities and an EIS test to determine the beginning of life impedance of the cell. The polarisation curves would also be used to determine if the membrane break-in process is complete.

3.6.1.1 MEA Break-In

Before the characterisation process can start, the membrane needs to run for a break-in period. The break-in period refers to the operation of a PEM electrolyser for a specific time at a voltage, current or load within its normal operating range. The break-in of an MEA ensure an even spreading of phosphoric acid, removes the impurities in the catalyst layers and in effect improves the conductivity of the MEA. In this study, the cell was operated in galvanostatic hold mode for several hours in order to break-in the MEA. The cell was connected to a power supply with a constant DC current output while the cell voltage was measured. Next, the cell voltage was plotted against time to investigate the stability of the cell and determine the progress of the MEA break-in process.

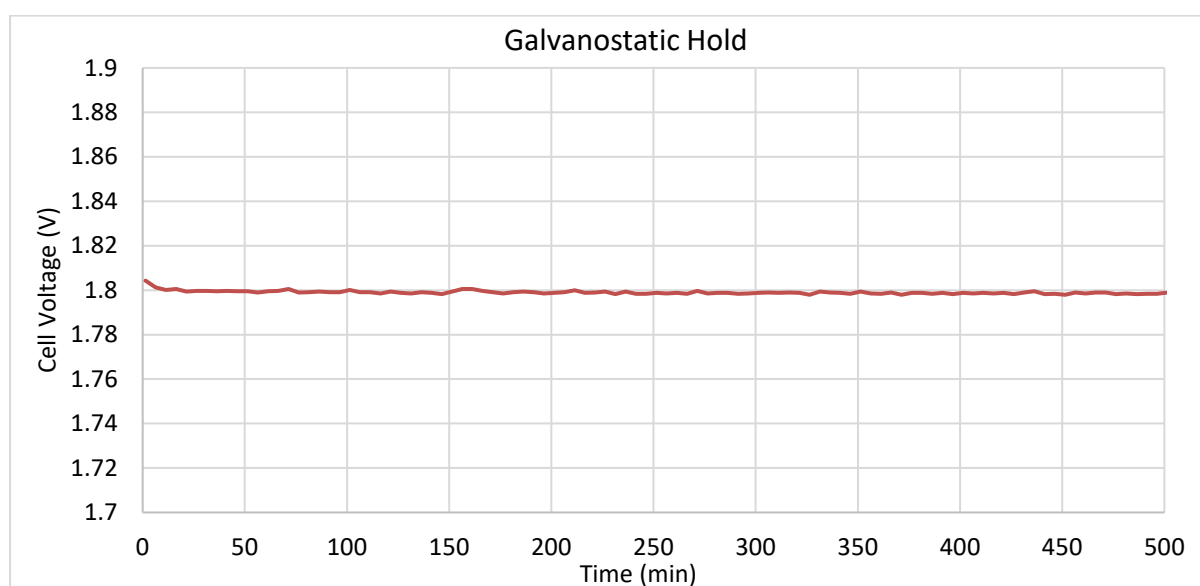


Figure 3-16: MEA break-in verification.

A stable cell is an indication that the MEA break-in process is complete. The cell is considered to be stable if the cell voltage does not significantly increase or decrease over time. Small fluctuations in the cell voltage were expected as these fluctuations can be caused by various external factors such as varying temperature, humidity, current, water supply and pressure. Figure 3-16 above is a plot of the cell voltage at the end of the break-in period.

To verify that the break-in process of the MEA in the PEM electrolyser was complete, a polarisation-curve test was used. The current density applied to the electrolyser cell was incrementally increased until the maximum cell potential or current density was reached, while the cell potential was measured. The cell potential was plotted against the applied current density on a polarisation curve. At the time when the current density could not be increased any further, the current density was incrementally decreased and plotted on the same graph. The forward and backwards polarisation curve should be close to identical with an offset of no more than 10 mV at each current density point. While the galvanostatic hold test was a measure of the cell's stability over a large period of time, the PC is a measure of the cell's stability at different current densities. Figure 3-17 below shows that the MEA break-in process was successfully completed as the forward and backward PC was close to identical. The maximum offset occurred at the lower current densities, with a value not exceeding 5mV.

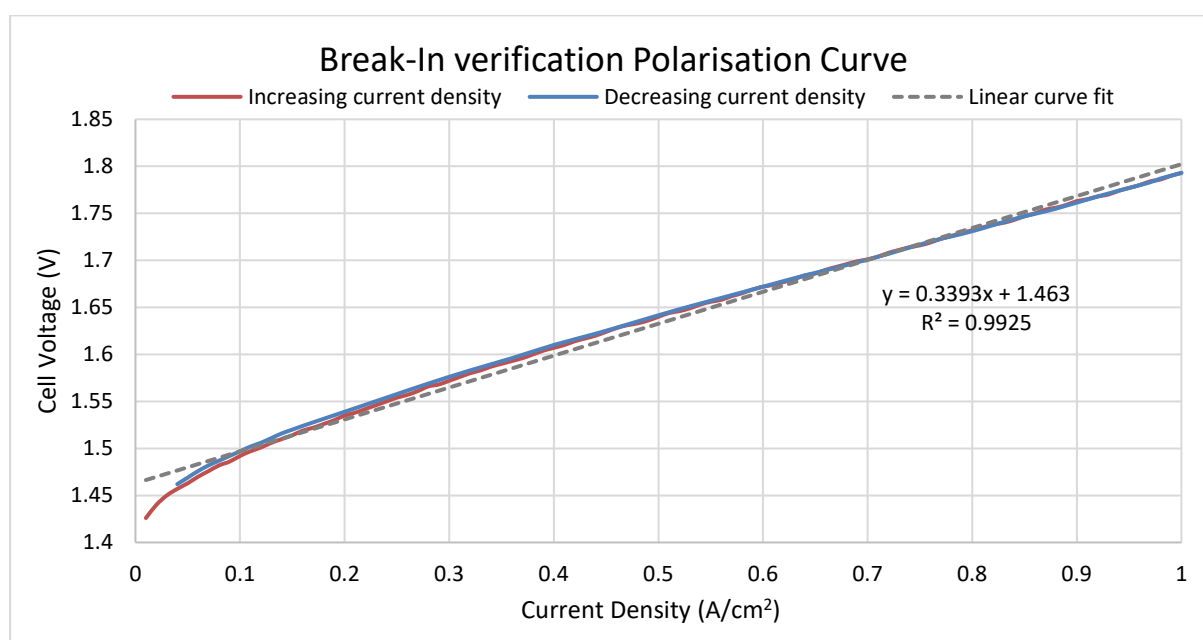


Figure 3-17: MEA break-in verification.

3.6.1.2 EIS Characterisation

Two characterisation techniques were used to obtain the performance parameters of the PEM electrolysis cell. The first technique that was used is the EIS technique from which the ohmic, activation and mass transfer losses can be obtained and fitted to an EEC model.

The EIS technique was thus used to obtain certain electrical characteristics of the PEM electrolyser, which were used to model the cell electrically. The apparatus used for the EIS characterisation process includes the Interface 1000 potentiostat/galvanostat, the EIS software, the test station and the PEM electrolyser cell. The Interface 1000, controlled by the EIS software, was operated in galvanostatic mode. A small AC current signal was applied to the PEM electrolyser while the cell's voltage response signal was measured. The electrolyser was operated at normal steady state conditions, with the addition of a sinusoidal signal to the DC current. The amplitude of the applied AC signal was approximately 15% of the DC current at which the cell operates in steady state conditions. The AC signal was applied at various frequencies in the selected frequency range to determine the impedance response of the cell in the frequency domain. The test conditions and parameters for the EIS measurements are presented in Table 3-12 below, which were selected to meet the project requirements and specifications as outlined in section 3.3.

Table 3-12: EIS test conditions.

Selected parameters for EIS test	
DC current offset	0.7 A
AC signal amplitude	0.1 A
Initial frequency	200 kHz
Final frequency	100 mHz

3.6.1.3 Polarisation Curve Characterisation

The second technique is the polarisation curve technique which was used to determine the relationship between the electrolysis cell current and voltage. This relationship was used to determine the change in the PEM electrolyser's performance due to the applied ripple currents. The polarisation curve of the PEM electrolyser was obtained by controlling and applying a range of current densities to the cell and measuring the cell's voltage at each of the applied current densities. The Volmer-Butler equation discussed in section 2.4.3.1, shows that the current density will increase exponentially as a function of the overpotential present in the cell. Thus, to obtain an accurate polarisation curve of the electrolyser, the applied current values needed to be selected to capture this exponential increase. This exponential increase is present in the low current density region after which the ohmic resistance of the electrolyser will increase to be the significant resistance present. The voltage-current relationship will then take on a linear form according to ohms law. A large number of low current density measurements were thus reserved for the exponential increase in voltage after which the number of measurements was decreased as the current density increases into the linear range.

The apparatus used for the polarisation curve characterisation process included a DC power supply, the test station and the PEM electrolyser cell. The DC power supply was used to apply each current density point for two minutes before the cell potential was measured. This was to allow for the electrolyser to become stable at each current density condition.

3.6.2 Experimental Tests

The main objective of the experimental study is to determine the effect of a ripple current on the efficiency of a PEM electrolyser, while all other operational conditions are kept constant. The investigated characteristics include the frequency, AC amplitude, DC offset and waveform. The purpose of this section of the design was to plan the tests that would be executed and determine the suitable test range for each of the above-mentioned characteristics.

3.6.2.1 Ripple current ranges

The first step is to decide on the magnitude of the ripple currents to apply to the PEM electrolyser. This entails investigating the data obtained from the electrolyser characterisation as well as industry standards to determine the voltage and current limits, which will under normal operating conditions not damage the cell. The PC characterisation shows that the supplied current can be increased up to 1 A/cm^2 without reaching the voltage limit of 2 V specified in the design specification. A maximum applied mean current of 1 A/cm^2 was thus selected to ensure the cell operates below the voltage limit even if the voltage increases due to the applied ripple. Since the ripple currents applied to the electrolyser are not pure DC, the RMS values of the ripple currents would be used as a measure of the effective magnitude. RMS current is defined as the effective value of the current or in other words, the DC value that would supply the same amount of power to a given resistive load.

The two characteristics of a ripple current that determines the effective magnitude or RMS are the DC offset and the AC amplitude. The DC offset would not exceed 1 A/cm^2 (25 A) and the AC amplitudes would range from 0 A/cm^2 (0 A) to 1 A/cm^2 (25 A). Since measurements need to be much more accurate at lower current densities, the AC amplitude range is divided into two parts. The first is the low current density region which ranges from 0 A to 5 A and would be changed in increments of 1 A; the second is part covers the rest of the range and would be changed in increments of 5 A. Since the impedance of an electrolyser is frequency dependant, the applied ripple current frequency is expected to be a key parameter affecting the efficiency of the electrolyser. The bode plot of the developed EEC model, which will be discussed in Chapter 4, was used to select the frequency range that should be tested. The bode plot indicated the frequency range in which the impedance of the PEM electrolyser changes the most.

Theoretically, the frequency at which the impedance is the lowest should be the frequency at which the efficiency of the cell is the best, but due to the absence of studies on this matter, several different frequencies would be tested. By testing a variety of frequencies, an accurate conclusion on the effect of the ripple frequency can be made. The selected frequency range for the ripple current tests is from 1 Hz to 1 kHz since the impedance has the highest change in this range. During the ripple current test, the frequency would be increased exponentially using $f = 10^x$, where x would be changed from 0 to 3 in increments of 1.

Table 3-13: Ripple current parameter ranges

Ripple Current Characteristic	Range
AC amplitude	0 A – 5 A (1 A steps), 5 A – 25 A (5 A steps)
DC offset	0 A – 25 A (1 A/cm ²)
Frequency	1 Hz – 1 kHz ($f = 10^x, x = 0,1,2,3$)
Waveform	Sinusoidal, Triangular and Square

3.6.2.2 Method

The method to be used during the ripple current tests is illustrated by the flow diagram in Figure 3-18 below. The experiment would start by selecting the initial parameter setting, which is an AC amplitude of 0 A, a DC offset of 25 A, a frequency of 1 Hz and a sinusoidal waveform. The ripple current would then be generated and applied to the PEM electrolyser. The average hydrogen flow rate would be measured using the hydrogen flow meter in the Green Innovation test station while the cell voltage, current and average power consumption of the electrolyser are measured using an oscilloscope.

After the first measurements, the AC amplitude setting would be changed to the next value in the range. This process would be repeated until an AC amplitude value of 25 A is reached. At this point, one full range of AC amplitude measurement would be complete. The next step would be to repeat a range of AC amplitude measurements at the following frequency setting. This process would then again be repeated until all AC amplitude settings are measured for the complete frequency range. All of the above would then be done for each of the selected waveforms.

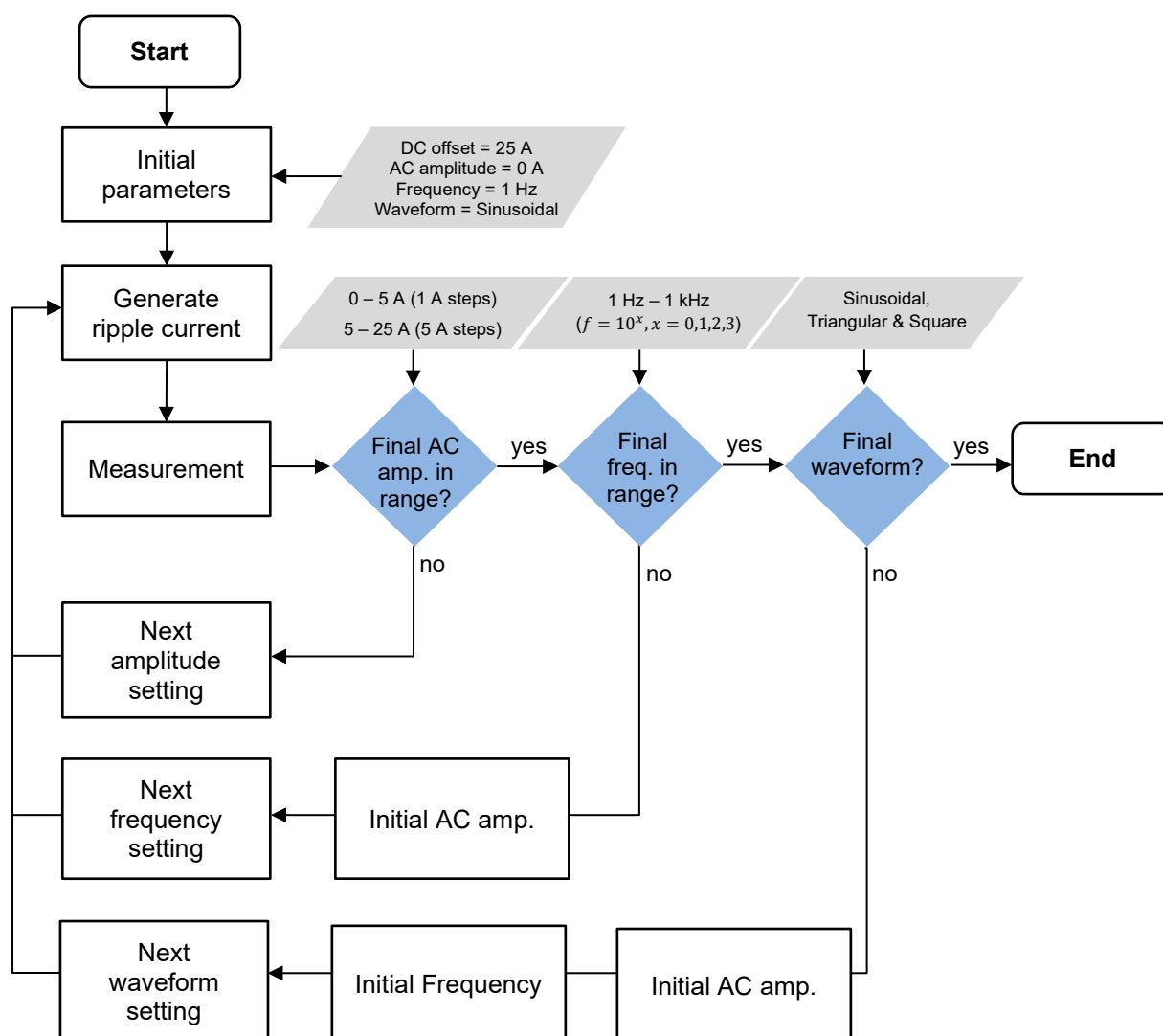


Figure 3-18: Ripple current experiment method

3.7 Verification and Validation

In section 3.3 of this chapter, the specification and requirements for the testing and characterisation of an electrolyser were defined. The specifications were validated against industry standards for the testing of water electrolysis cells as outlined in reports EUR 29182 EN [142] and EUR 29267 EN [117] issued by the publication's office of the European Union. The design of the experimental setup and procedures, presented in sections 3.4, 3.5 and 3.6, were also validated against the test protocols and procedures presented in [142] and [117]. This validation was crucial to ensuring that the specifications and requirements were fulfilled, and the study objectives could be met. This validation process also included validating the design and the manufacturer's specifications of each piece of apparatus against similar experiments and industry standards for the design and testing of PEM water electrolysis cells and experimental systems [49], [100], [101], [143].

One of the focus areas of the design discussed in this chapter was the selection of the MEA and the various characterisation methods used to choose an MEA for this research project. The selection was based on the results obtained from electrochemical characterisations methods such as EIS, polarisation curves and galvanostatic hold tests. The EIS results were verified and confirmed with the data obtained from the polarisation curves as presented in Table 3-9. The results obtained from the galvanostatic hold test, used to determine the membrane degradation or voltage drift, were verified by measuring the MEA's fluoride release rate (FRR). The measured FRR confirmed the results obtained from the galvanostatic hold test and are presented in Table 3-10. The verification of the EIS, polarisation curves and galvanostatic hold tests are also presented in Figure 3-19 and Figure 3-20 below. A second important component selection in the PEM electrolyser assembly was the flow field design. The selection was based on the results presented by Minnaar *et al.* (2019) [152] which were verified by measuring the temperature and current distribution of the selected flow field design.

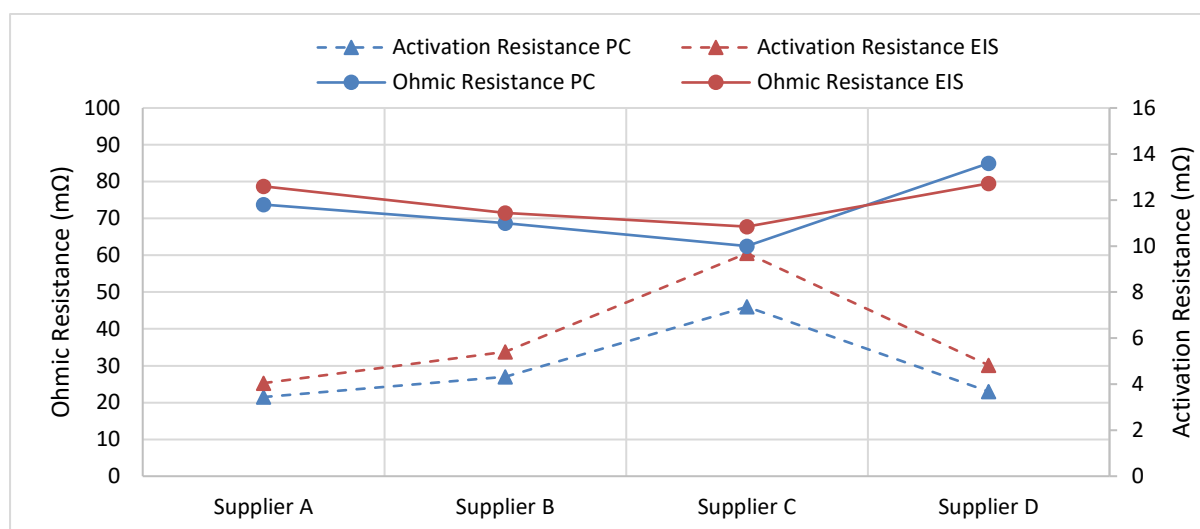


Figure 3-19: EIS and polarisation curve tests verification.

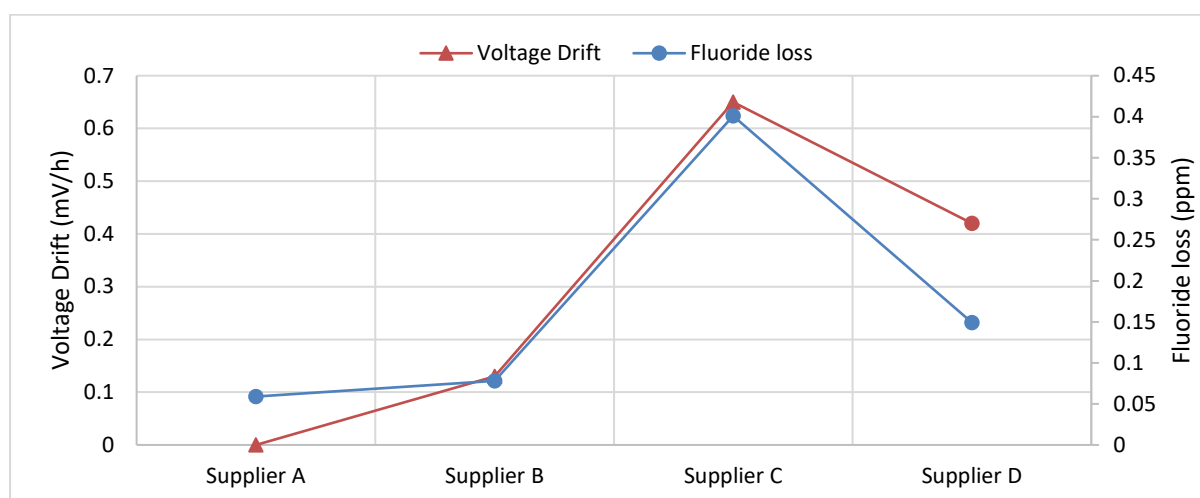


Figure 3-20: Galvanostatic hold test verification.

3.8 Conclusion

The design chapter opened with a conceptual design of the experimental setup, followed by the design specifications in section 3.3. The design specifications included the equipment and setup requirements, the system input requirements, the system output requirements as well as the exclusions and limitations of this research project. The design specifications were followed by the detail experimental design, presented in section 3.4.

Included in the detail experimental design were the experimental setup, the PEM electrolyser assembly as well as the experimental apparatus. In this section, the PEM electrolyser component selection, as well as the selection of the required apparatus, were presented. The design of the final setup and equipment integration were also included. The experimental procedures were then presented in section 3.6, which were divided into two subsections. The first of the subsections presented the characterisation methods while the focus of the second subsection was on the ripple current tests. The design verification and validation methods used were discussed in the final section of the chapter.

The characterisation, modelling and simulation of the PEM electrolyser are shown in the next chapter (Chapter 4).

CHAPTER 4: CHARACTERISATION, MODELLING AND SIMULATION

4.1 Introduction

Upon completion of the design and the experimental setup implementation, the PEM electrolyser was characterised as illustrated in the opening section of this chapter. The data obtained from the characterisation were then used to develop both electrical and mathematical models and simulate the response of the electrochemical cell. The final sections of Chapter 4 include a verification and validation section which is followed by a conclusion at the end. The chapter structure is presented in Figure 4-1 below.

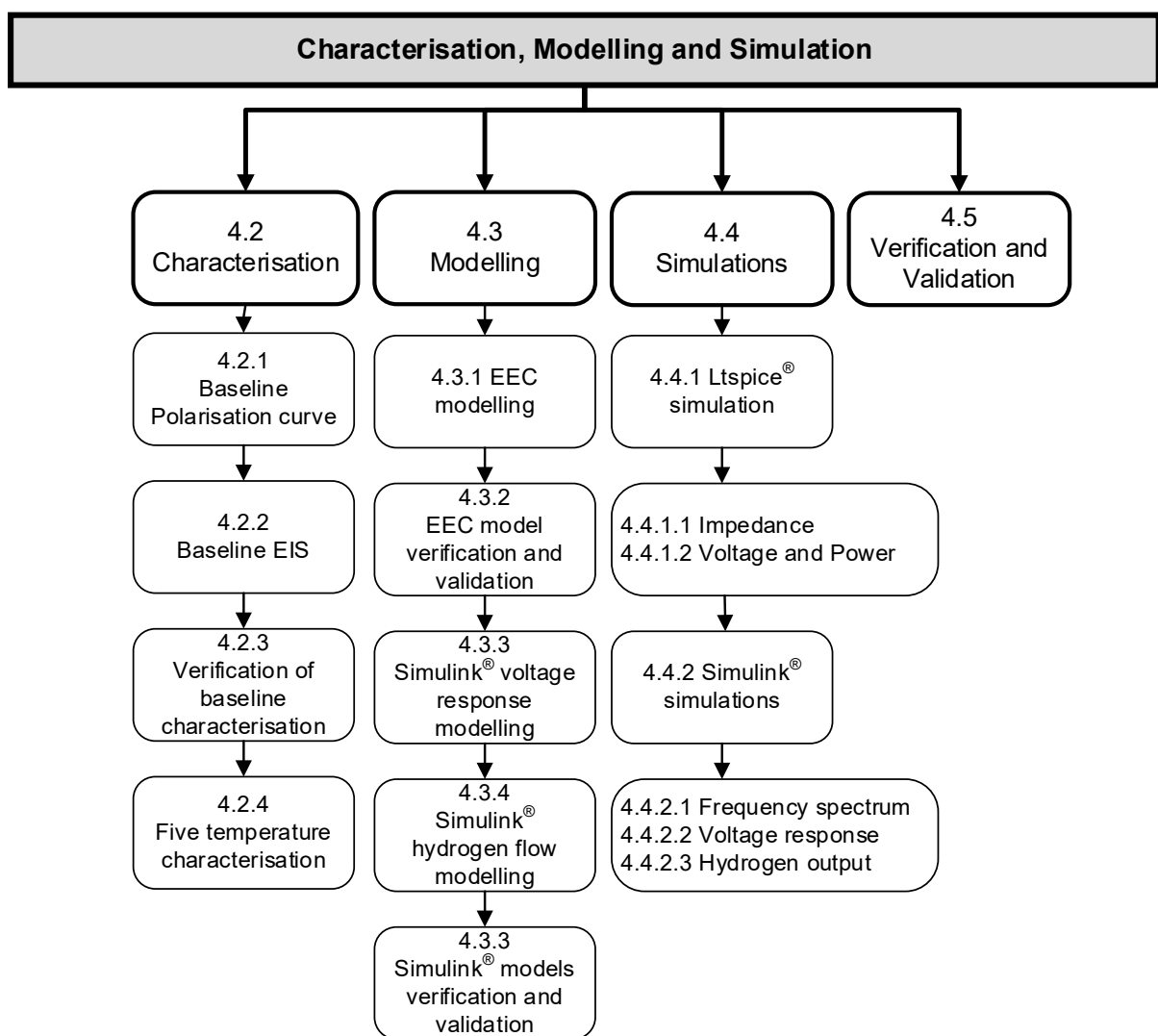


Figure 4-1: Overview diagram of Chapter 4 structure.

4.2 Characterisation

In order to truly understand the effects of ripple currents on a PEM electrolyser, some baseline data on the performance of the electrolyser under normal conditions (DC supply) is required. This section of Chapter 4 presents the PEM electrolyser characterisation that was used as a baseline to measure the effect of ripple currents against. The PEM electrolyser illustrated in section 3.4.3, which use the MEA from Supplier A, was used for the characterisation.

4.2.1 Baseline Polarisation Curve

The first test was the baseline polarisation curve test, used to determine the voltage response of the PEM electrolyser supplied with a steady DC power supply. During this test, the voltage response was measured over a range of steady current densities. The applied current densities ranged from 0 to 1 A/cm² and were applied in 0.01 A/cm² increments. The duration between each current adjustment was 5 minutes to allow the cell to stabilize at the specific current. The voltage measurements were then taken at the end of each 5-minute interval. This test was done at an operating temperature of 70 °C since this is the temperature at which the ripple current tests would be done. Table 4-1 presents the test parameters, and Figure 4-2 illustrates the results. The PC shows the voltage response of the PEM electrolyser under normal operating conditions. The PC shows that the water electrolysis process starts at a cell voltage of 1.43 V and increases to 1.79 V at a current density of 1 A/cm².

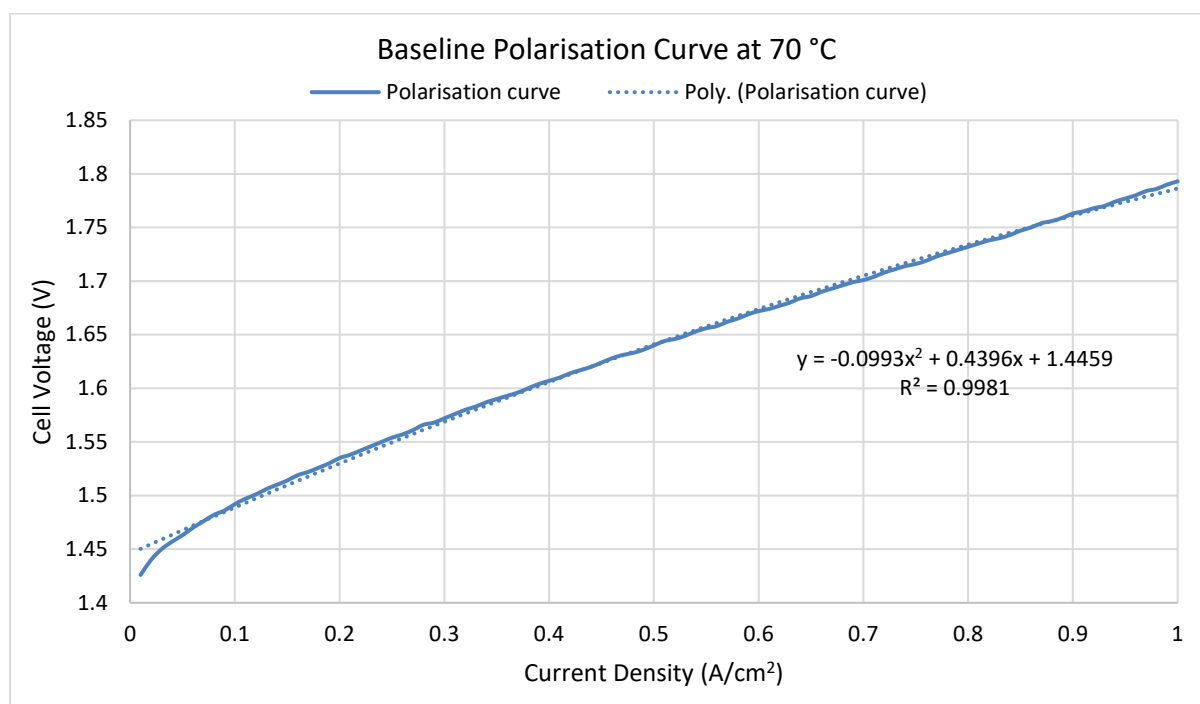


Figure 4-2: Baseline Polarisation curve at 70 °C

Table 4-1: Baseline PC test parameters.

Parameter	Specification
Applied current type	Steady DC
Current range	0 A/cm ² – 1 A/cm ² (0A – 25A)
Step size	0.01 A/cm ²
Step duration	5 minutes
Amount of measurements	250
Temperature	70 °C
Pressure	1 atm (Standard pressure)
PEM Electrolyser MEA	Supplier A

4.2.2 Baseline EIS

The next test was the baseline EIS test, used to characterise the impedance of the PEM electrolyser. A small AC signal with a DC offset of 0.7 A and an amplitude of 0.1 A was applied to the PEM electrolyser over a frequency range of 100 mHz to 200 kHz. The cell's voltage response signal was measured at each frequency and used to calculate the impedance response. This test was also done at an operating temperature of 70 °C. Figure 4-3 below illustrates the impedance of the PEM electrolyser in the form of a Nyquist plot. The point at which the Nyquist plot intercept with the real axis at the high frequency side shows that the PEM electrolyser has ohmic resistance of 12.6 mΩ. The difference between the low frequency intercept, or in this case the point at which the plot stops, and the high frequency intercept is equal to a charge transfer or activation resistance value of 25.3 mΩ.

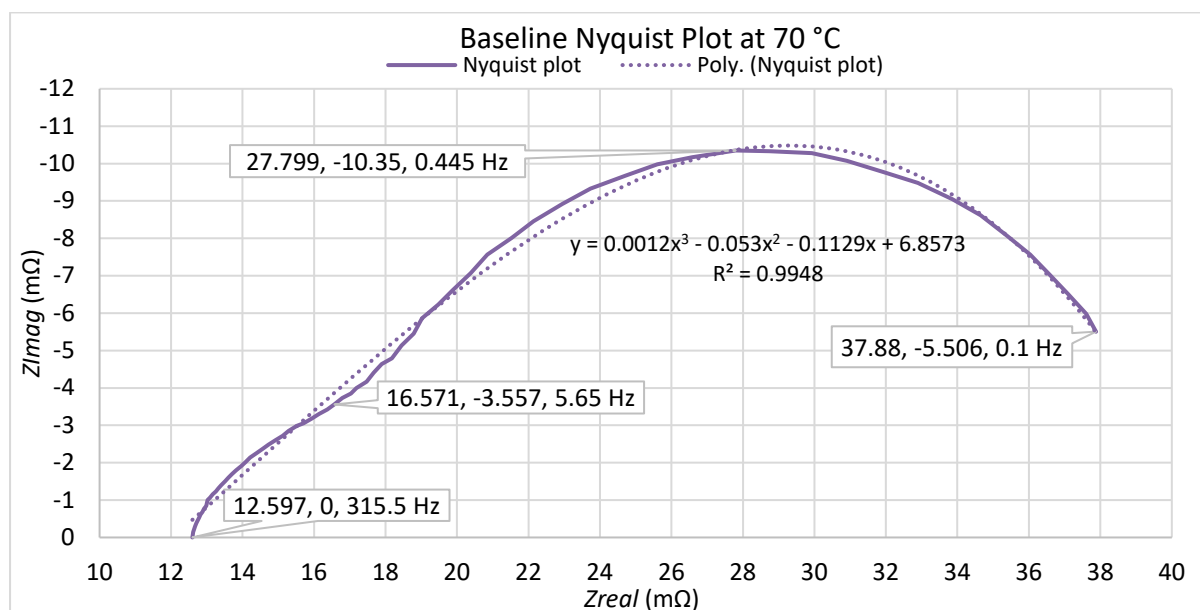
**Figure 4-3:** Baseline Nyquist plot at 70 °C.

Table 4-2: Baseline EIS test parameters.

Parameter	Specification
DC current offset	0.7 A
AC signal amplitude	0.1 A
Initial frequency	200 kHz
Final frequency	100 mHz
Temperature	70 °C
Pressure	1 atm (Standard pressure)
PEM Electrolyser MEA	Supplier A

4.2.3 Verification of baseline characterisation

The PC and EIS test results were verified by comparing the results obtained from both characterisation methods with each other. The Nyquist plot and the PC each present different characteristics of the PEM electrolyser which cannot easily be compared. However, specific characteristics such as the ohmic resistance can be obtained from both these techniques and used for verification. Since Figure 4-3 is a plot of the electrolyser's impedance, the ohmic resistance can be obtained directly from the plot. The Nyquist plot shows that the electrolyser has an ohmic resistance of 12.6 mΩ, which is the value of the high frequency intercept with the real axis. The ohmic resistance can also be obtained from the ohmic polarisation region on the PC. The ohmic polarisation region is the mid current density region, where the resistance that exists against the flow of ions is the main contributor to the losses. The ohmic resistance can be obtained by calculating the PC slope in this region as per equation (4.1) below, which verifies the accuracy of the Nyquist plot.

$$\begin{aligned}
 R_{ohmic} &= \frac{\text{Voltage difference}}{\text{Current Density difference} \cdot \text{Area}} \\
 &= \frac{1.76 \text{ V} - 1.54 \text{ V}}{(0.9 \text{ A} \cdot \text{cm}^{-2} - 0.2 \text{ A} \cdot \text{cm}^{-2}) \cdot 25 \text{ cm}^2} \\
 &= 12.57 \text{ m}\Omega
 \end{aligned}
 \tag{4.1}$$

The PC and Nyquist plots, shown in Figure 4-2 and Figure 4-3, were also verified by repeating the tests several times. By repeating the tests, the maximum deviation in the results due to uncontrollable external factors such as a varying temperature, humidity, water supply and pressure are determined. Although the cell temperature is regulated at 70 °C, a ± 1 °C variation in the temperature is possible due to a change in the ambient temperature. Figure 4-4 and Figure 4-5 below respectively show the results of the repeated PC and EIS tests.

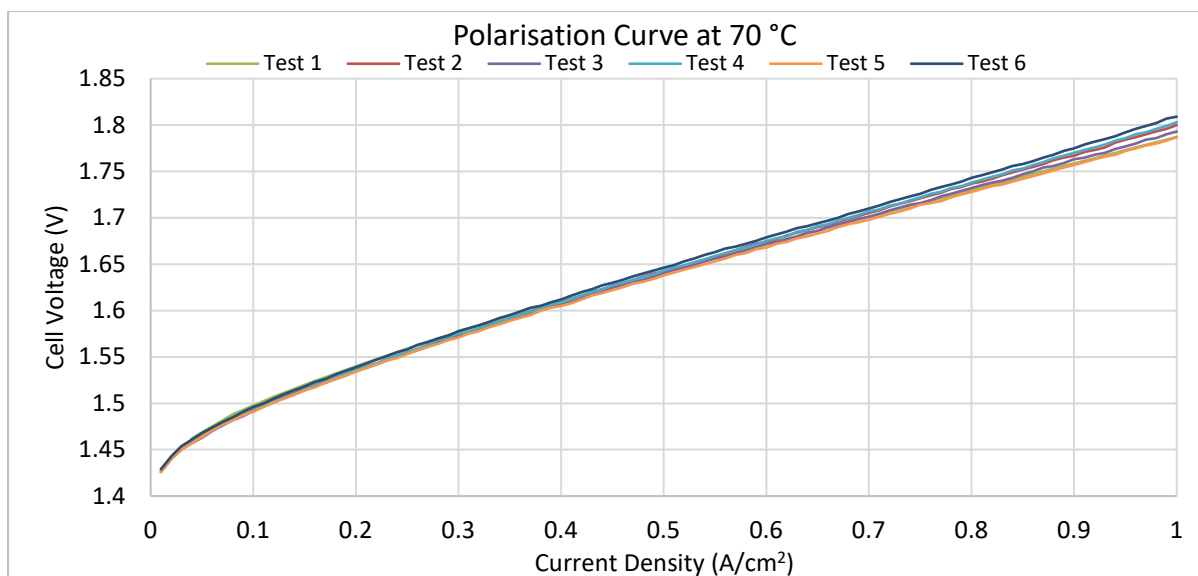


Figure 4-4: Baseline Polarisation curve verification.

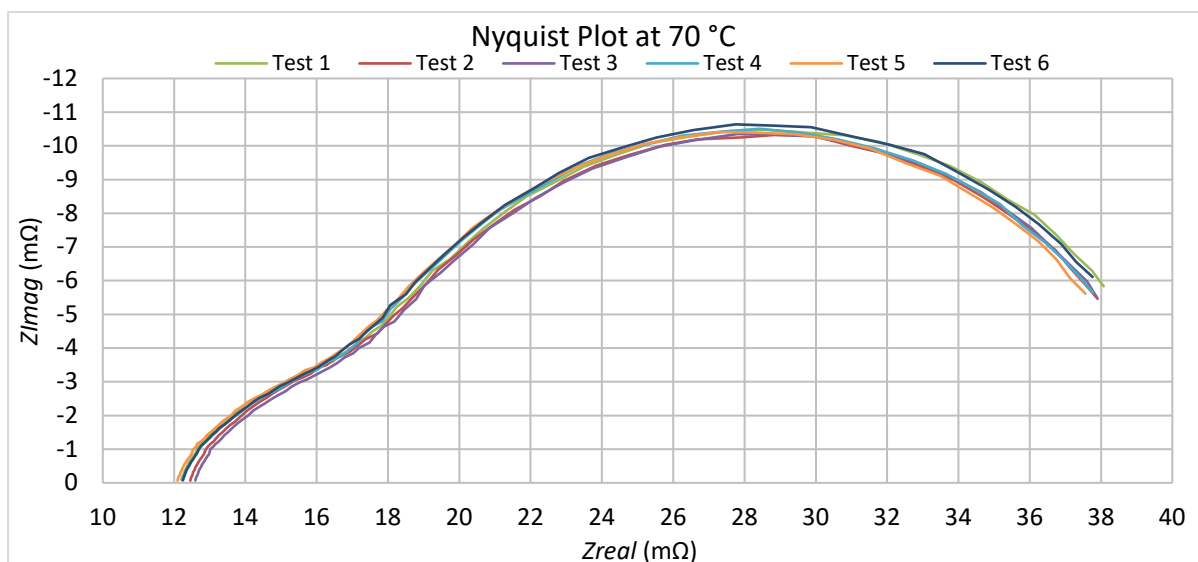


Figure 4-5: Baseline Nyquist plot verification.

4.2.4 Five Temperature

As indicated in section 2.4.1 of the literature review, operating conditions have a significant impact on the performance of an electrochemical cell. One such operating condition is the temperature which affects the internal resistance of an electrolyser and in effect the amount of electrical energy required to decompose water. The precise effect of the operating temperature on the selected PEM electrolyser was determined by characterising the electrolyser at five different temperatures within its standard operating range as outlined in section 2.3.3.3. The minimum and maximum achievable temperatures of the single cell PEM electrolyser and the equipment at disposal for this study were close to 40 °C and 80 °C respectively. The characterisation tests were thus conducted for five different temperatures

ranging from 40 °C to 80 °C, in 10 °C increments. The characterisation includes both PC and EIS measurements which are presented in Figure 4-6 and Figure 4-7 below.

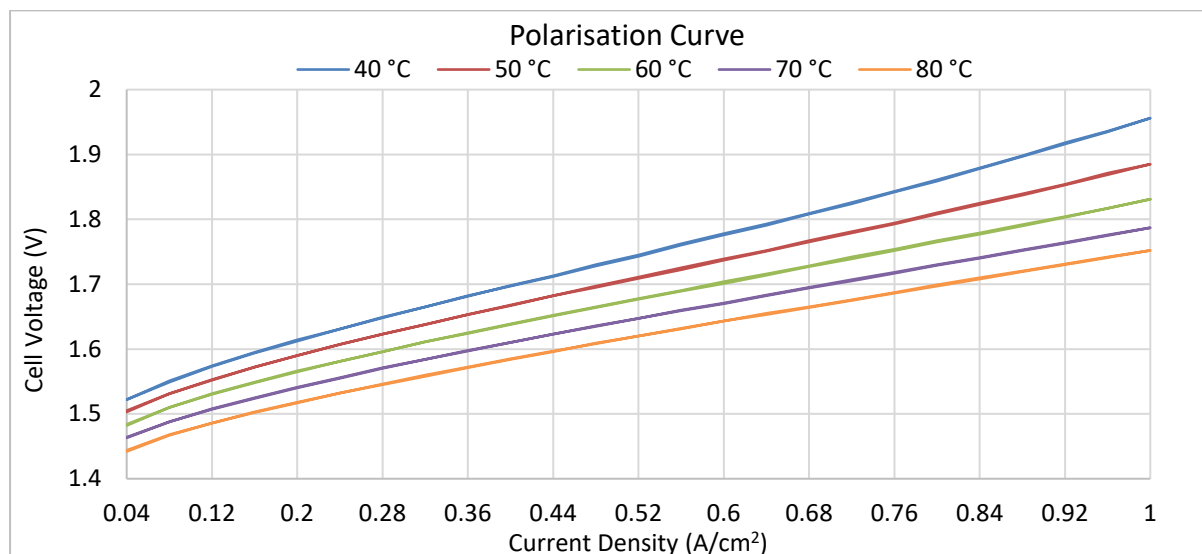


Figure 4-6: Five temperature Polarisation curve.

The polarisation curves were plotted for five different temperatures ranging from 40 °C to 80 °C, in 10 °C increments. The PC confirms that the performance of the PEM electrolyser is affected by the temperature at which it is operated since it is clear that the voltage efficiency increases as the temperature increases. Another observation made from the PC plots is that the effect that temperature has on the voltage efficiency is not constant at all current densities. In the low current density region, the difference in voltage efficiency between the different temperatures is relatively small but increases as the current density increases.

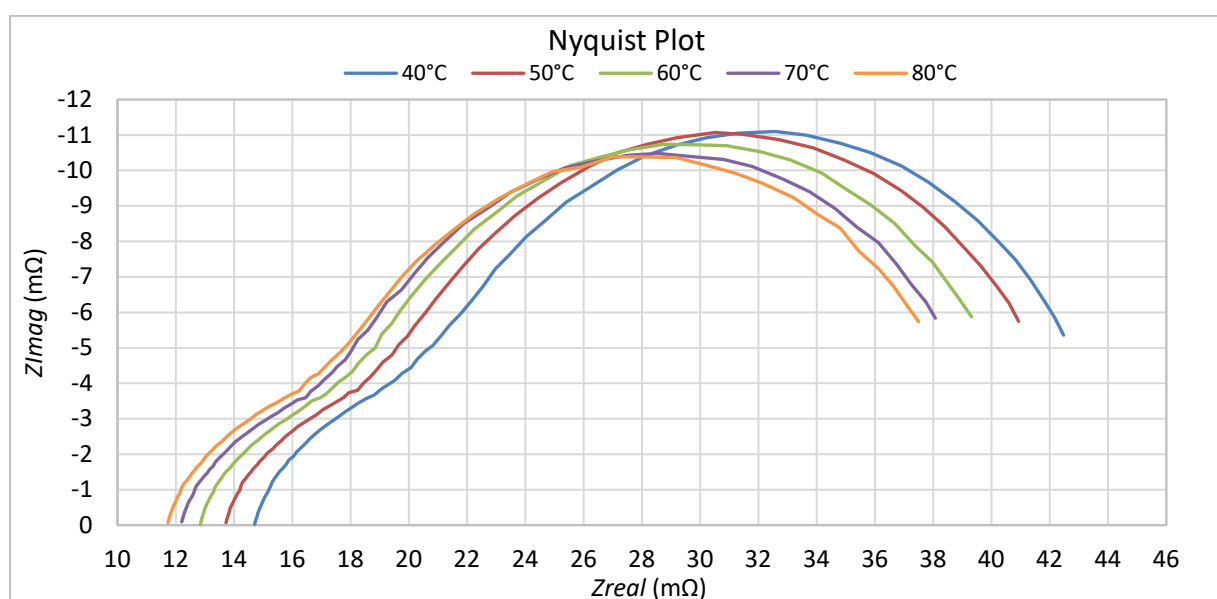


Figure 4-7: Five temperature Nyquist plot.

EIS measurements were also taken at five different temperatures and presented as a Nyquist plot in the figure above. The Nyquist plot is an illustration of the electrolyser's impedance as a function of frequency, where the high frequency region is on the left and the low frequency region on the right. The ohmic resistance of the electrolyser can be obtained from the high frequency intercept with the real axis while the activation resistance is the difference between the low and high frequency intercepts with the real axis. The Nyquist plot shows that both the ohmic and activation resistances of the electrolyser are affected by the operating temperature. A higher temperature shows a decrease in the resistance and overall impedance of the PEM electrolyser. The increased performance of the PEM electrolyser at higher temperatures is thus confirmed by the EIS measurements, which show a decrease in impedance as the operating temperature is increased.

4.3 Modelling

Upon completion of the PEM electrolyser characterisation, the results were used to develop two models that can accurately represent these characteristics. These models mainly focus on the electrical characteristics of the cell in order to determine the possible effects that a ripple current would have on the performance (power consumption, voltage efficiency, H_2 production rate and Faradaic efficiency) of the electrolyser. The first model is an EEC model that was developed in the Echem Analyst[®] platform, while the second model is a voltage response model developed in the Simulink[®] platform.

4.3.1 EEC modelling

The goal of the EEC modelling process was to model an EEC model that can represent the dynamic voltage and impedance behaviour of the PEM electrolyser by making use of electrical elements. Section 2.8.1 of the literature study presented the different electrical elements used in such a model. The primary purpose of this section is to develop an EEC model that can represent the impedance of the selected PEM electrolyser. The development of an EEC model is an intuitive process since a relationship between electrical elements, and electrochemical processes need to be recognized. Fortunately, some work has been done on this subject matter and can be used as a starting point. Section 2.8.2 in the literature study shows various models that are used by the electrochemical industry to represent electrochemical cells. After the development of the EEC model, to the measured EIS data presented in section 4.2.2 was fitted to the model. The impedance fit was done with the use of a non-linear least squares (NLLS) fitting program which minimises the difference between the value of the model and the measured data. Echem Analyst[®] form part of the Gamry[®] software and include two NLLS fitting algorithms, namely the Simplex and the Levenberg-Marquardt algorithm.

Nelder and Mead developed the Simplex algorithm while Marquardt and Levenberg developed the Levenberg-Marquardt algorithm [153]. The simplex algorithm was used for this project since this method only requires function evaluations and no derivatives. This algorithm is illustrated by equation (4.2) [153],

$$\chi^2 = \sum_{i=1}^N W_i^2 \left[\left(Z_{measured_{real}} - Z_{fit_{real}} \right)^2 + \left(Z_{measured_{imag}} - Z_{fit_{imag}} \right)^2 \right] \quad (4.2)$$

where χ^2 is Chi-squared, W_i the weighting parameter calculated according to user input, $Z_{measured}$ the measured impedances and Z_{fit} the EEC model impedances [2, 154, 155]. The value of Chi-squared indicates the proportion variance of the model fit and is equal to the sum of the weighted residuals. This algorithm was used in the Echem Analyst® platform to obtain the parameter values of the EEC model at which a minimum Chi-squared (goodness of fit) value is reached.

4.3.1.1 Starting EEC model (Model 1)

The modelling process started with a Randles-Warburg cell which includes a CPE ($Z_Q = q(j\omega)^n$), Warburg impedance (Z_w) and two resistors (R_{mem} and R_{act}) as illustrated in Figure 4-8. The membrane resistor (R_{mem}) represents the ohmic resistance, the activation resistor (R_{act}) represents the charge transfer resistance, the CPE (Z_Q) represent the double layer impedance and the Warburg impedance (Z_w) represent the mass transfer or concentration losses. The impedance of the model is given by equation (4.3) below.

$$Z(\omega) = R_{mem} + \{q(j\omega)^n + [R_{act} + Z_w]^{-1}\}^{-1} \quad (4.3)$$

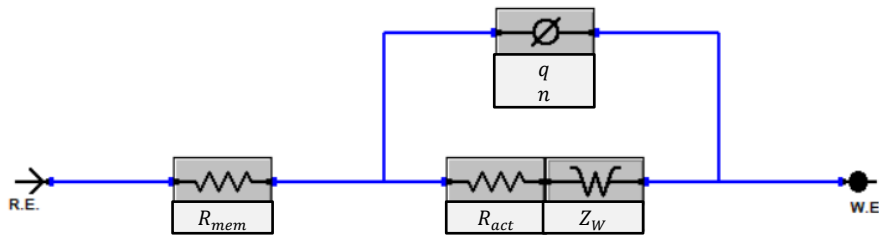


Figure 4-8: Randles-Warburg cell with CPE (Model 1).

The result of the impedance fit, illustrated in Figure 4-9 below, shows that the model is not able to represent the two semicircles of the Nyquist plot accurately.

In this model, as well as several models discussed in the literature, the impedance of the anode and cathode sides is modelled as one. Although this is ideal, in certain cases the anode and cathode reactions need to be modelled separately. The first of the two semicircles (small semicircle) is caused by the hydrogen evolution reaction (HER) at the cathode while the second semicircle is caused by the oxygen evolution reaction (OER) at the anode. Further work on the model is thus required.

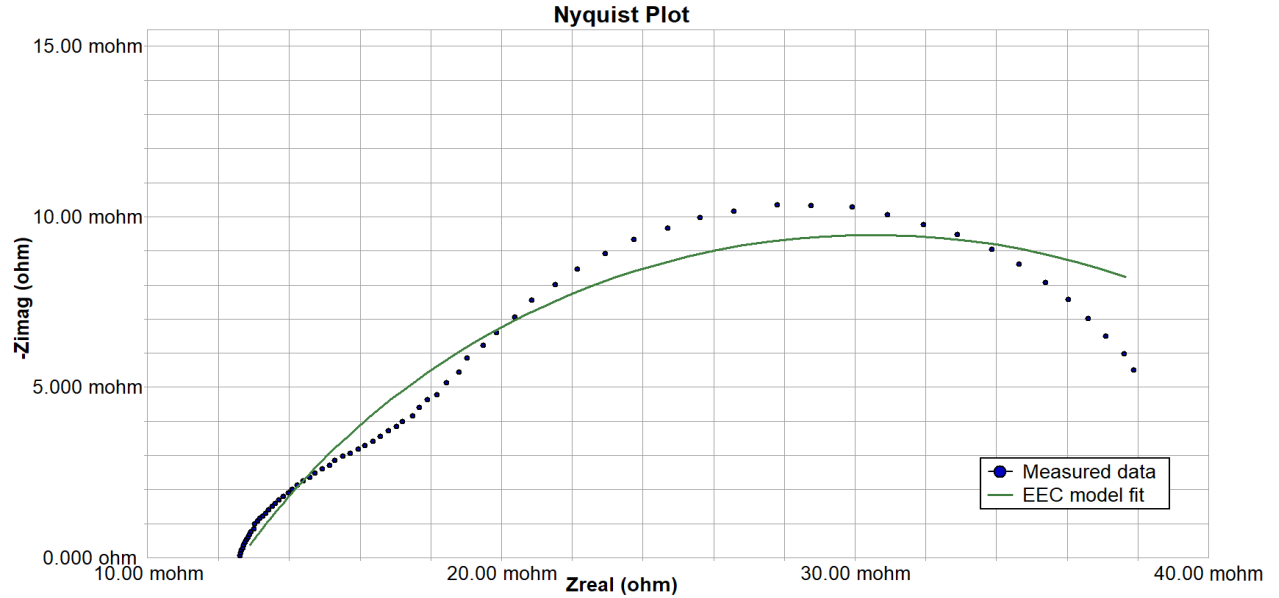


Figure 4-9: Supplier A Nyquist plot EEC Model 1.

4.3.1.2 EEC model for the anode and cathode (Model 2)

The EEC model was therefore modified to represent the losses at the anode and cathode of the PEM electrolyser separately. The resulting EEC is shown in Figure 4-10 which includes two CPE's (Z_{Qa} and Z_{Qc}), two Warburg impedances (Z_{wa} and Z_{wc}) and three resistors (R_{mem} , R_{acta} and R_{actc}). Each element in the circuit above, except for the membrane resistance (R_{mem}), were thus divided into two separate elements to represent the process at the anode and cathode respectively. The membrane resistor (R_{mem}) represents the ohmic resistance while the activation resistors (R_{acta} and R_{actc}) represents the charge transfer resistances of both electrodes respectively. The two CPE's (Z_{Qa} and Z_{Qc}) are used to accurately represent the double layer impedances present at both the anode and the cathode side of the electrolyser while the Warburg impedance (Z_{wa} and Z_{wc}) represent the mass transfer or concentration losses. Equation (4.4) below gives the impedance of the model.

$$Z(\omega) = \left\{ q_a(j\omega)^{n_a} + [R_{act_a} + Z_{w_a}]^{-1} \right\}^{-1} + R_{mem} + \left\{ q_c(j\omega)^{n_c} + [R_{act_c} + Z_{w_c}]^{-1} \right\}^{-1} \quad (4.4)$$

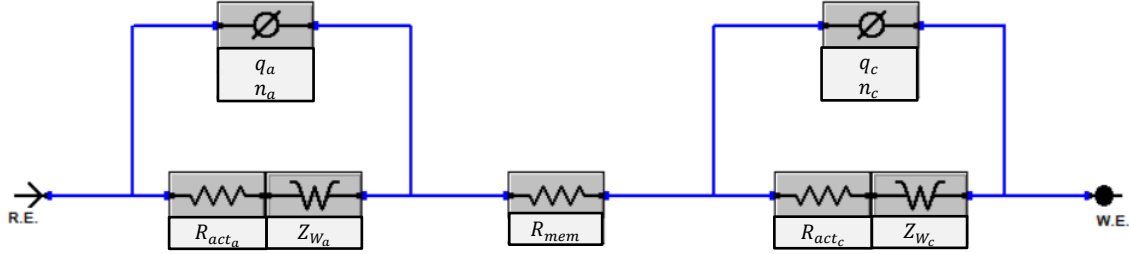


Figure 4-10: Model for the anode and cathode (Model 2).

EIS data (section 4.2.2) was also fitted to the modified model, and the resulting parameter values are shown in Table 4-3 while the Nyquist plot is shown in Figure 4-11 below. The figure shows an enormous improvement on the fit as a result of the two parts, representing the HER at the cathode and the OER at the anode separately.

Table 4-3: EEC model 2 parameters.

	Value	Unit		Value	Unit
<i>Racta</i>	4.283×10^{-17}	Ω	<i>q_a</i>	342.5	$S \cdot s^n$
<i>Rmem</i>	12.10	m Ω	<i>n_a</i>	-0.337	-
<i>Ractc</i>	25.35	m Ω	<i>Zw_a</i>	31.74	$S \cdot s^{0.5}$
<i>q_c</i>	15.75	$S \cdot s^n$	<i>Zw_c</i>	1135	$S \cdot s^{0.5}$
<i>n_c</i>	0.935	-	<i>χ²</i>	1.096×10^{-4}	-

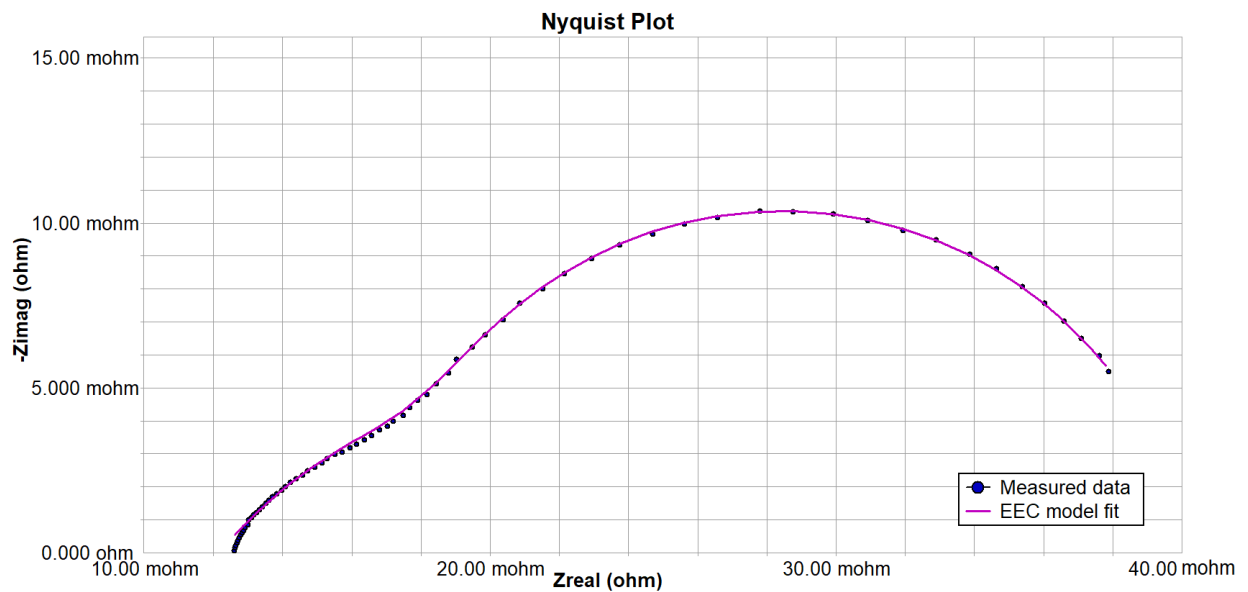


Figure 4-11: Supplier A Nyquist plot EEC Model 2.

4.3.1.3 Final EEC model (Model 3)

Although the model above shows an almost perfect fit to the measured EIS data, the model was further modified, as shown in Figure 4-12 below. The purpose of this modification was to replace all the specialized electrochemical elements such as the CPE's and Warburg impedances with common elements like resistors and capacitors. The reason for the replacements is to develop a model that can be simulated in LTspice® since these specialized electrochemical elements are not included in the LTspice® platform. Each CPE (Z_{Qa} and Z_{Qc}) were replaced with a resistor and capacitor connected in series, while the effect of the Warburg impedance was mimicked by connecting a capacitor in parallel with each activation resistor. Equation (4.5) gives the impedance of this model.

$$Z(\omega) = \left[\left(R_{qa} + \frac{1}{j\omega C_{qa}} \right)^{-1} + (R_{acta}^{-1} + j\omega C_{wa})^{-1} \right]^{-1} + R_{mem} + \left[\left(R_{qc} + \frac{1}{j\omega C_{qc}} \right)^{-1} + (R_{actc}^{-1} + j\omega C_{wc})^{-1} \right]^{-1} \quad (4.5)$$

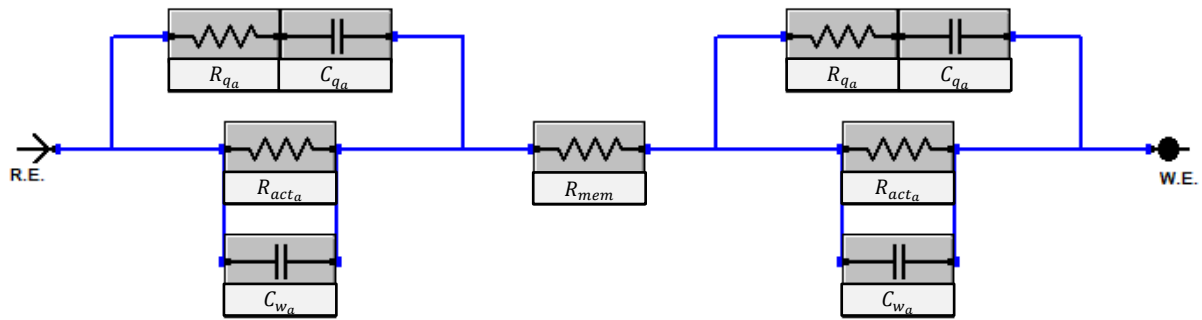


Figure 4-12: Final EEC model (Model 3).

The model above was fitted to the EIS data (section 4.2.2) and the results are shown in Figure 4-13 below. The results verify the replacements of the specialized electrochemical elements since this model can also deliver an almost perfect fit to the measured data.

Table 4-4: Final EEC model parameters.

	Value	Unit		Value	Unit
R_{acta}	12.53	mΩ	C_{qa}	32.29	F
R_{mem}	12.74	mΩ	R_{qa}	6.115	mΩ
R_{actc}	14.48	mΩ	C_{wc}	2.341	F
C_{qc}	14.84	F	C_{wa}	6.445	F
R_{qc}	2.613	mΩ	χ^2	0.301×10^{-4}	-

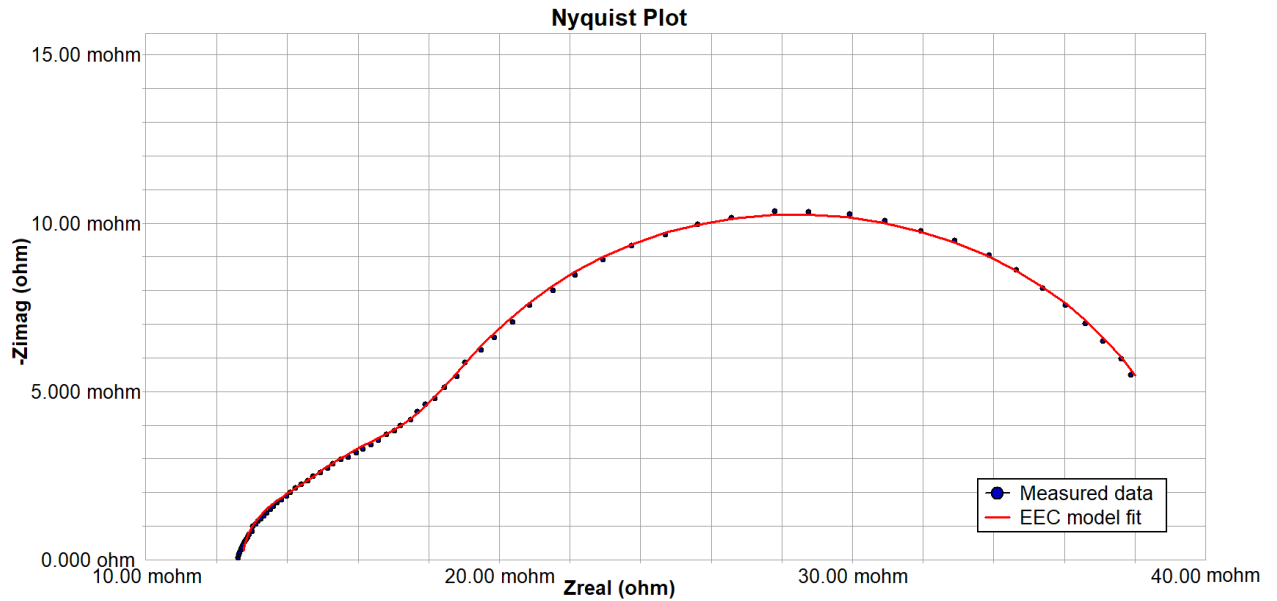


Figure 4-13: Supplier A Nyquist plot EEC Model 3.

4.3.2 EEC model verification and validation

Section 4.3.1.3 above shows that the EEC model can accurately represent a PEM electrolyser which uses the specific MEA selected for this study. Although this was the goal, the EEC model should also be able to represent a variety of other PEM electrolyser assemblies in order to be effective. The EEC model, as well as the data fitting method, was validated by fitting the model to the EIS data of the other MEA's considered for this study as presented in section 3.4.3.1 (Supplier B, C & D). This was done to ensure that the EEC model used for simulations is correctly implemented and capable of accurately representing different PEM electrolysers. The results are illustrated by the Nyquist plots in Figure 4-14, Figure 4-15 and Figure 4-16 below.

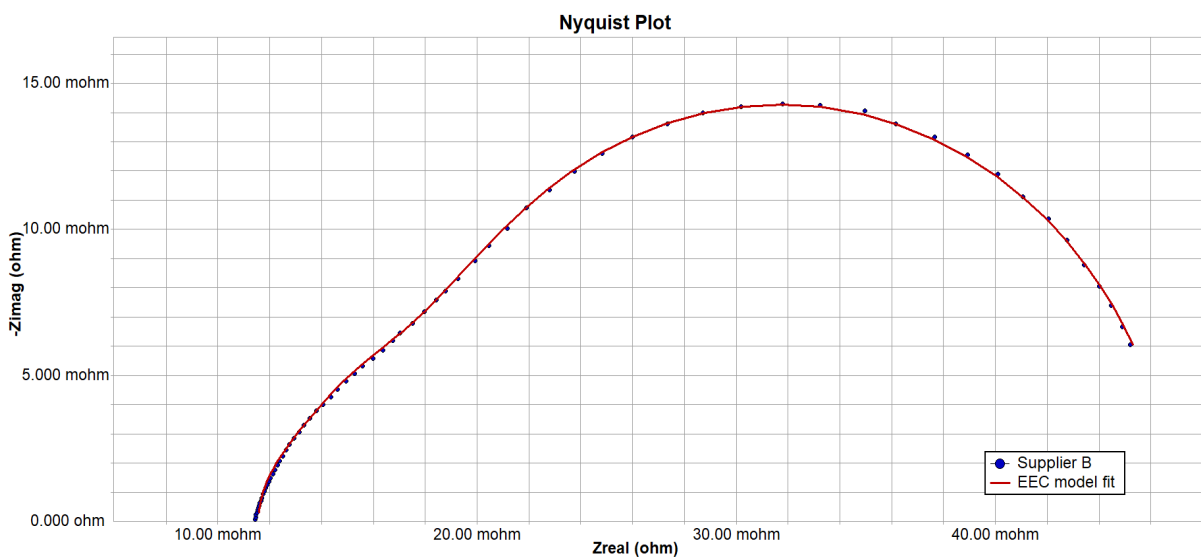


Figure 4-14: Supplier B Nyquist plot EEC Model 3.

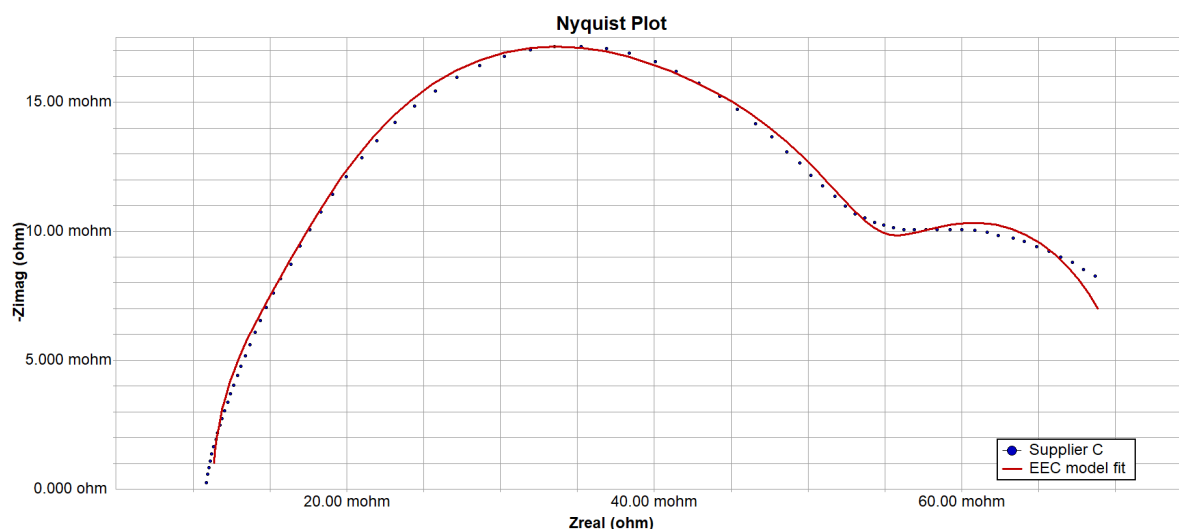


Figure 4-15: Supplier C Nyquist plot EEC Model 3.

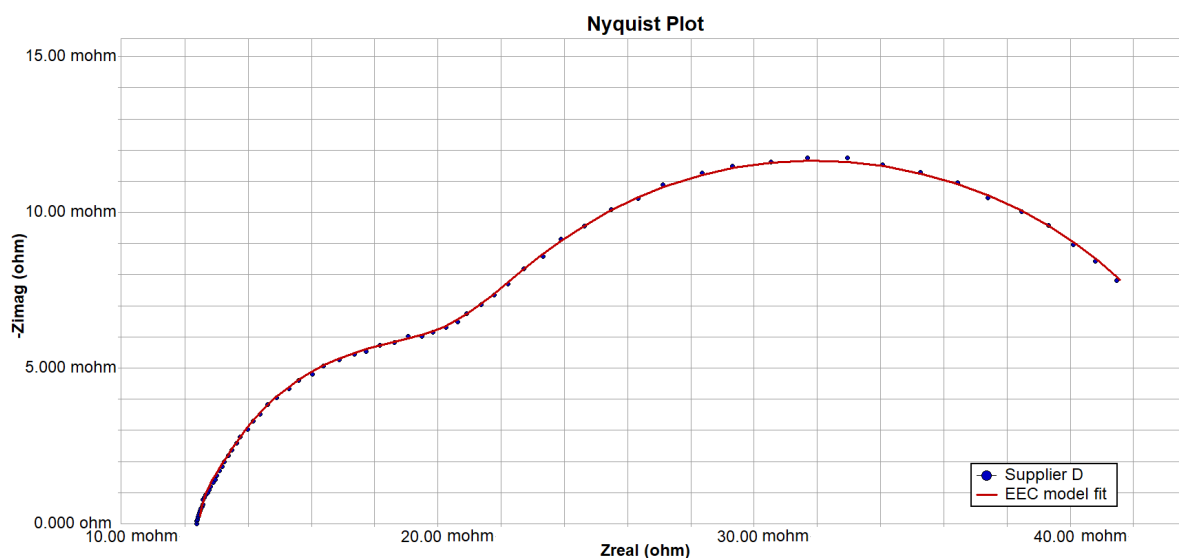


Figure 4-16: Supplier D Nyquist plot EEC Model 3.

The Nyquist plots above show that this EEC model can also be used to represent PEM electrolyser with different MEA's. This is accomplished by changing the values of the electrical elements in the EEC model to fit the electrochemical characteristics of the PEM electrolyser. Table 4-5 illustrates how these values vary between the different MEA's.

The EEC model also needed to be validated to ensure that the model accurately represents a real-world system. The EEC model parameter values, presented in Table 4-5, are validated by comparing these values to the actual measured values obtained during the MEA selection phase in section 3.4.3.1. The actual and modelled membrane resistances, as well as the actual and modelled activation resistances, are compared in Table 4-6 below.

Table 4-5: Final EEC model parameters.

EEC Parameters	Supplier A	Supplier B	Supplier C	Supplier D	Unit
R_{act_a}	12.53	9.118	30.78	24.21	mΩ
R_{mem}	12.74	11.57	11.27	12.47	mΩ
R_{act_c}	14.48	26.09	29.60	8.319	mΩ
CQ_c	14.84	6.955	0.086	1.208	F
RQ_c	2.613	3.260	26.37	7.010	mΩ
CQ_a	32.29	24.67	4.817	4.060	F
RQ_a	6.115	14.67	35.80	204.1	mΩ
CW_c	2.341	2.849	0.1302	2.564	F
CW_a	6.445	5.327	1.854	21.64	F
χ^2 (Goodness of Fit)	0.301×10^{-4}	0.364×10^{-4}	3.208×10^{-4}	0.267×10^{-4}	-

The activation resistances (R_{act}) displayed in the table are the total activation resistance, which is equal to the sum of the cathode activation resistance (R_{act_c}) and the anode activation resistance (R_{act_a}). Also included in the table is a percentage error for each parameter, calculated with the following formula:

$$\%Error = \frac{\text{Measured resistance} - \text{Modelled resistance}}{\text{Measured resistance}} \times 100 \quad (4.6)$$

The calculated error percentages validate the EEC model as well as the fitting method used to determine the parameter values are accurate.

Table 4-6: Polarisation curve and EIS results.

Supplier	Measured R_{mem} (mΩ)	Modelled R_{mem} (mΩ)	% Error	Measured R_{act} (mΩ)	Modelled R_{act} (mΩ)	% Error
A	12.60	12.74	1.11%	25.28	27.01	6.84%
B	11.44	11.57	1.14%	33.76	35.21	4.30%
C	10.85	11.27	3.87%	60.54	60.38	0.26%
D	12.37	12.47	0.81%	30.10	32.53	8.07%

4.3.3 Simulink® voltage response modelling

A voltage response model was developed for the PEM electrolyser making use of the literature reviewed in Chapter 2 of this document. As discussed in section 2.4.2.4 the operational voltage or cell voltage of a PEM electrolyser can be expressed as the summation of the Nernst potential or open circuit voltage, E^0 , and the overpotentials. Equation (4.7) illustrates this relation.

$$E_{cell} = E^0 + \eta_{total} \quad (4.7)$$

4.3.3.1 Open circuit voltage

The open circuit voltage of an electrolyser is dependent on the operating temperature and pressure of the system. As discussed in section 2.4.2.3 of the literature study, the Nernst equation can be used to calculate the open circuit potential of an electrolyser at non-standard temperature and pressure conditions. At standard temperature and pressure, the voltage would be equal to the reversible voltage at standard conditions, E_{rev}^0 , which is 1.229 V. Since the PEM electrolyser used in this study is operated at an elevated temperature of 70 °C, the open circuit potential would not be equal to 1.229 V. The open circuit voltage at non-standard temperature is calculated using the Nernst equation presented in equation (4.8) below [77] [95].

$$E^0 = E_{rev} - \frac{RT}{nF} \ln \left(\frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{1/2}} \right) \quad (4.8)$$

The first part of the model is the calculation of the reversible cell voltage, E_{rev} , at a nonstandard operational temperature with the use of equation (2.27), discussed in section 2.4.2.3 of the literature study. The calculation is carried out by first calculating the Gibbs free energy at the specific temperature which is then divided by the product of Faraday's constant and the number of electrons transferred during the reaction as shown in Figure 4-17. The value of reversible cell voltage, E_{rev} , is then used in the open circuit voltage model illustrated in Figure 4-18.

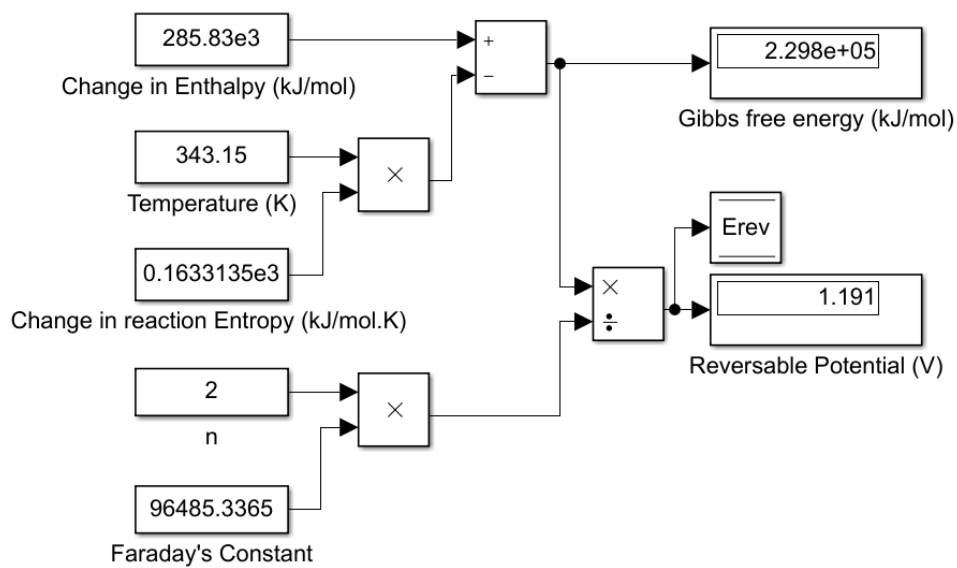


Figure 4-17: Reversible cell voltage Simulink® model.

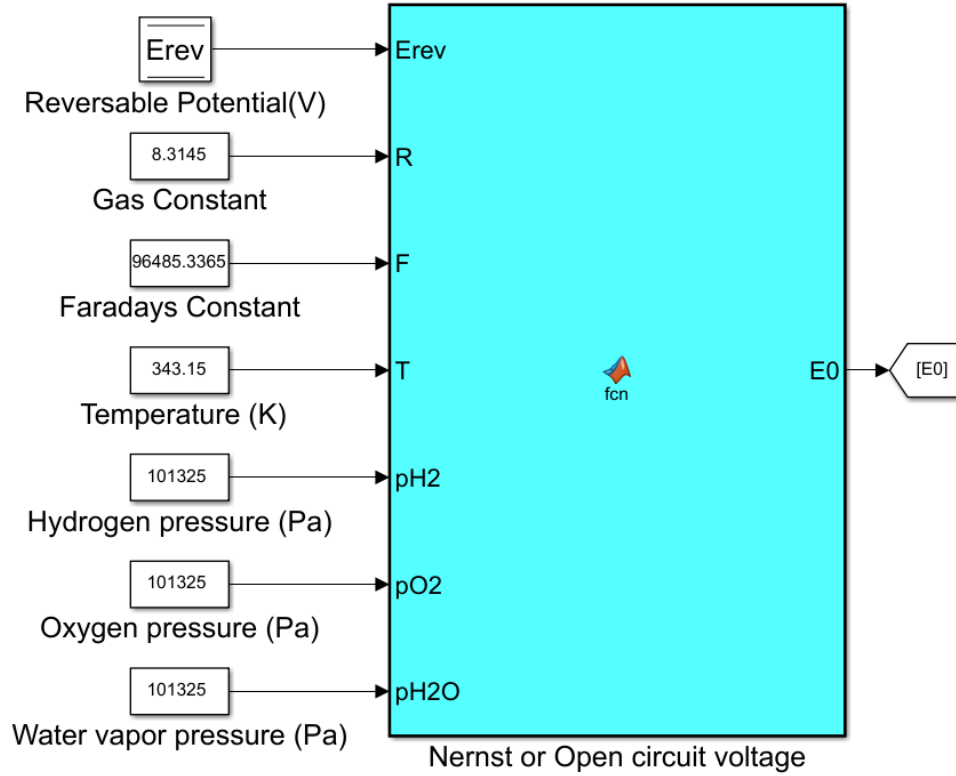


Figure 4-18: Open circuit voltage Simulink® model.

4.3.3.2 Overpotentials

The baseline PC of the PEM electrolyser, discussed in section 4.2.1, shows that the two main overpotentials affecting the performance of this PEM electrolyser, in the specific current density range investigated, are the activation and ohmic overpotentials. The activation overpotential can be expressed by inverting the Butler-Volmer equation which gives equation (4.9), where R is the universal gas constant, T the temperature, α the transfer coefficient, F Faraday's constant, i the current density, and i_0 the exchange current density [78, 81].

$$\eta_{act} = \frac{RT}{\alpha_{an}F} \operatorname{arcsinh}\left(\frac{i}{2i_{0,an}}\right) + \frac{RT}{\alpha_{cat}F} \operatorname{arcsinh}\left(\frac{i}{2i_{0,cat}}\right) \quad (4.9)$$

The ohmic overpotential is the other main contributing overpotential and is linearly proportional to the current density and can be expressed by equation (4.10) below, where R_{mem} is the membrane resistance, i the current density and A the area of the cell.

$$\eta_{ohm} = R_{mem} \cdot i \cdot A \quad (4.10)$$

The parameters for the model was selected based on the information obtained from characterising the PEM electrolyser, as presented in section 4.2, as well as various literature sources, as illustrated in Table 4-7. The selected parameters used in this study are provided in Table 4-8, and the Simulink® model for the total overpotential is presented in Figure 4-19 below.

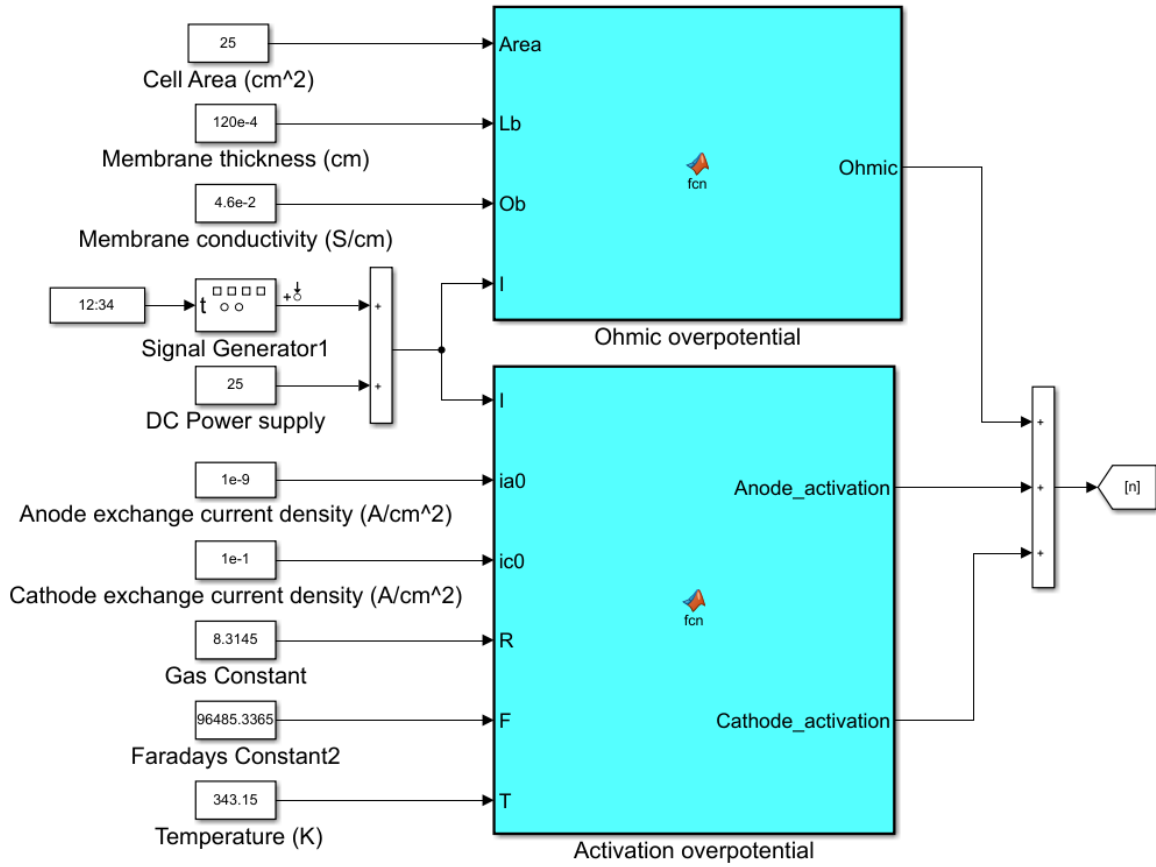
Table 4-7: Reported values for exchange current densities and charge transfer coefficients.

$i_{0,an}$	$i_{0,cat}$	α_{an}	α_{cat}	Reference
1×10^{-7}	1×10^{-1}	0.8	0.25	Abdin <i>et al.</i> [77]
1×10^{-12} ^a , 1×10^{-7} ^b	1×10^{-3} ^a	0.5	0.5	Choi <i>et al.</i> [156]
2×10^{-7}	2×10^{-3}	2	0.5	Yigit <i>et al.</i> [74]
1×10^{-9} ^b	1×10^{-3} ^a	0.835 ^c , 0.921 ^d	0.209 ^c , 0.230 ^d	Tijani <i>et al.</i> [157]

^a Pt based catalyst, ^b Pt-Ir based catalyst, ^c 20 °C, ^d 50 °C

Table 4-8: Model parameters for PEM electrolyser voltage response simulation.

Parameter	Values	Unit
$i_{0,an}$	1×10^{-9}	A/cm ²
$i_{0,cat}$	1×10^{-1}	A/cm ²
α_{an}	0.5	-
α_{cat}	0.5	-
L_B	120×10^{-4}	cm
σ_B	4.6×10^{-2}	S/cm

**Figure 4-19:** Overpotential Simulink® model.

4.3.4 Simulink® hydrogen flow rate modelling

The hydrogen flow rate model is based on the theoretical flow rate which can be calculated to obtain either the molar flow rate (mol per second) or the volumetric flow rate (cubic meter per second) as illustrated by equations (4.11) and (4.12) below.

$$\dot{n}_{H_2} = \frac{I}{zF} \text{ (mol.s}^{-1}\text{)} \quad (4.11)$$

$$\dot{V}_{H_2} = \frac{I}{zF} \times \frac{RT}{P} \text{ (m}^3\text{.s}^{-1}\text{)} \quad (4.12)$$

The equations show that the hydrogen flow rate is dependent on the operating current, temperature and pressure of the electrolysis system. The volumetric flow rate is however often normalised to obtain the flow rate in nLPM which is a unit used to define what the flow rate would be at a pressure of 1 atm (101.325 kPa) and temperature of 0 °C (273.15 K). Since the hydrogen flow was measured in nLPM during the experimental tests, this normalisation was used for this model as well. Equation (4.13) gives the theoretical volumetric hydrogen flow rate in nLPM.

$$\dot{V}_{H_2} = \frac{I}{zF} \times \frac{R \cdot 273.15 \text{ K}}{101.325 \text{ kPa}} \times 1000 \text{ dm}^3\text{.s}^{-1} \times 60 \text{ s (nLPM)} \quad (4.13)$$

The hydrogen flow rate Simulink® model used to determine the theoretical molar flow rate, volumetric flow rate and total hydrogen gas produced, is illustrated in Figure 4-20 below.

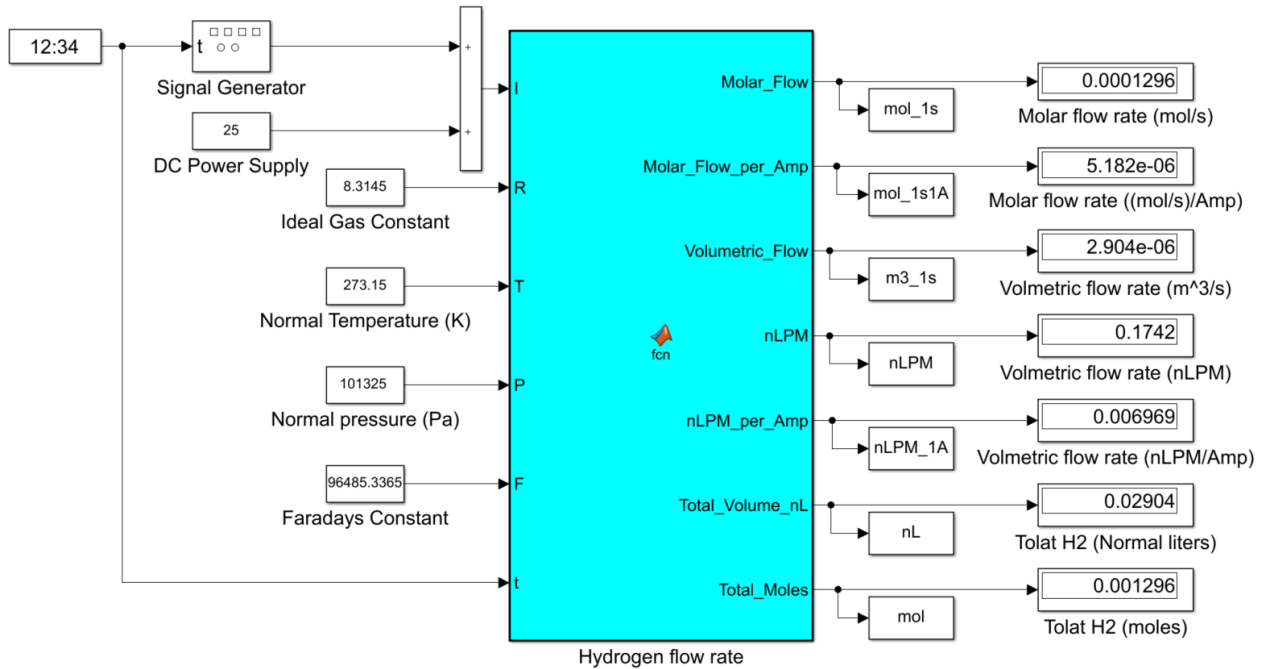


Figure 4-20: Hydrogen flow rate Simulink® model.

4.3.5 Simulink® models verification and validation

The Simulink® models were verified by comparing these models to PEM electrolyser models developed by other authors. Several of these authors used Simulink® [74, 77, 158], which validates the use of this simulation platform for modelling PEM electrolyzers. The functions used in the Simulink® models were verified against functions used in models developed by several other authors who focused on PEM electrolyzers. Table 4-9 below illustrates the studies used for verifying the model functions. The model parameters were also verified by comparing the parameters chosen for this study to the parameters used by authors in similar models as previously illustrated in Table 4-7 and Table 4-8.

Table 4-9: Voltage response and hydrogen flow verification.

Model functions		References
Open circuit voltage	$E_0 = E_{rev,T}^0 - \frac{RT}{nF} \ln \left(\frac{p_{H_2O}}{p_{H_2} \sqrt{p_{O_2}}} \right)$	[76-79]
Overpotential	$\eta_{act} = \frac{RT}{\alpha_{an}F} \operatorname{arcsinh} \left(\frac{i}{2i_{0,an}} \right) + \frac{RT}{\alpha_{cat}F} \operatorname{arcsinh} \left(\frac{i}{2i_{0,cat}} \right)$ $\eta_{ohm} = R_{mem} \cdot i \cdot A$	[74, 76, 77, 79, 82, 98, 159, 160]
Hydrogen flow rate	$\dot{n}_{H_2} = \frac{I}{zF}$	[70, 82, 85]

4.4 Simulation

The simulation section of the PEM electrolyser was divided into two main subsections, namely LTspice® simulations and Matlab®/Simulink® simulations. In the LTspice® section, the developed EEC model was used to simulate the effect of different electrical operating conditions on the impedance and voltage response of the PEM electrolyser as a complete unit. In the Matlab®/ Simulink® section, the developed mathematical models were used to simulate the effect of operating conditions on the open circuit voltage, overpotentials and hydrogen flow.

4.4.1 LTspice® simulation

The developed EEC model was used to simulate the response of the PEM electrolyser in LTspice® by using the schematic diagram shown in Figure 4-21, and the parameter values in Table 4-4. This simulation platform was chosen to simulate the electrical characteristics of the PEM electrolyser, rather than Matlab®/ Simulink®, due to the wide range of predefined and verified transient and AC analysis simulation tools as discussed in section 2.10.2. The purpose of the LTspice® simulations is to determine the possible effects of a current ripple and the characteristics of the ripple on the impedance and voltage response of the PEM electrolyser.

This section of the simulations focus only on the voltage efficiency and electrical power consumption of the cell since the Faradaic efficiency and energy output are dependent on the hydrogen flow rate which cannot be simulated in LTspice®.

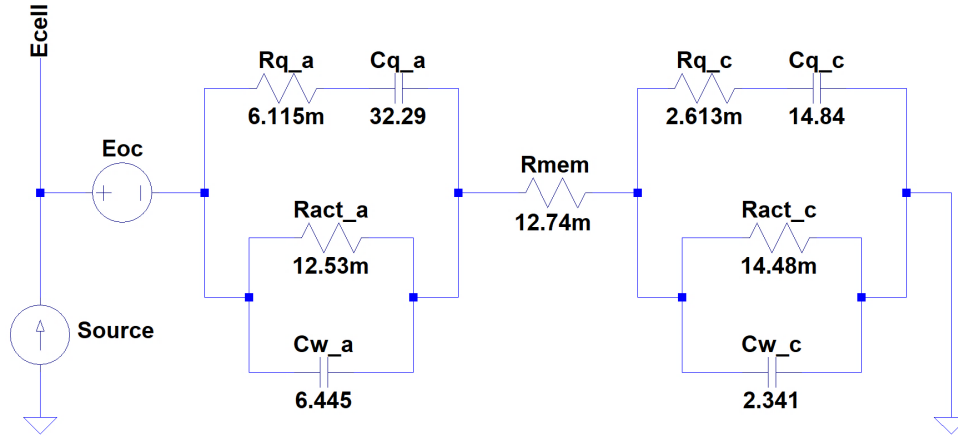


Figure 4-21: LTspice® schematic of EEC model.

4.4.1.1 Impedance

Figure 4-22 below is the simulated bode diagram of the PEM electrolyser's impedance. The bode diagram is a plot of the magnitude and phase of the electrolyser's impedance as a function of frequency. The bode plot shows a decrease in the impedance as the operating frequency is increased up to approximately 1 kHz; Thereafter, the change in the impedance is negligible. The magnitude is close to static while the phase approaches 0° at frequencies higher than 1 kHz. The effect of frequency is thus significant in the low frequency range (below 1 kHz) and can be neglected in the high frequency range (above 1 kHz).

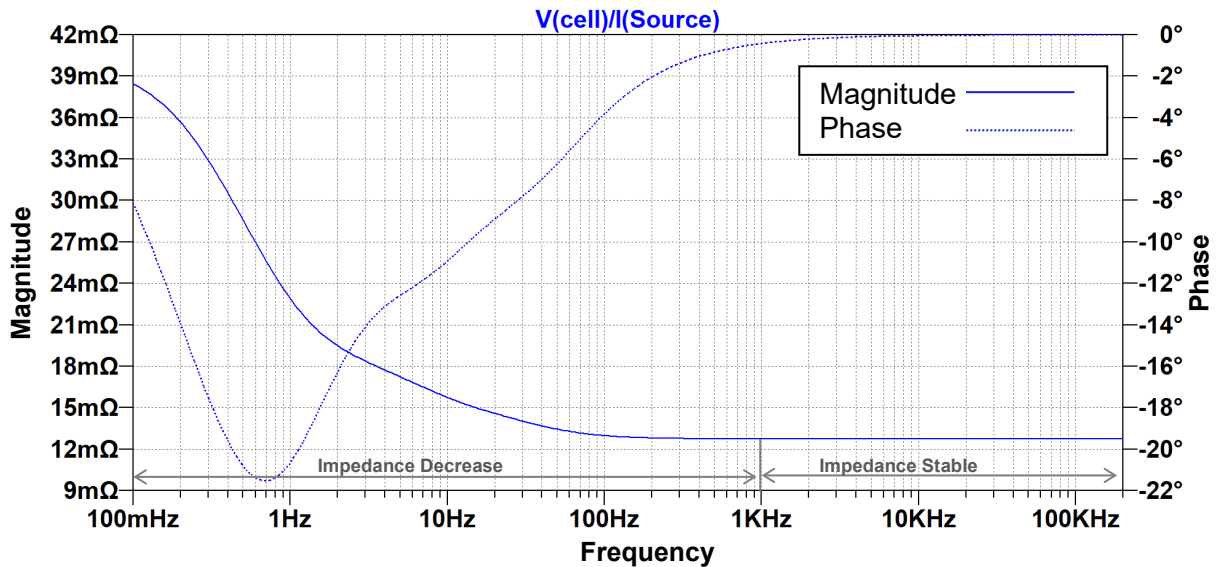


Figure 4-22: Simulated PEM electrolyser impedance bode plot.

The effect of frequency on the impedance of the PEM electrolyser can also be illustrated with a Nyquist plot. Figure 4-23 below shows the simulated Nyquist plot of the PEM electrolyser. The plot shows that the magnitude of the resistance (real part of impedance) decrease as the frequency increase. The minimum resistance of 12.74 mΩ is observed at frequencies above 1 kHz. The values of the electrolyser's impedance at a few selected frequencies are shown in Table 4-10 in both Cartesian and polar form. The bode and Nyquist plots are clear indicators that the frequency of a ripple current would affect the performance of an electrolyser. Presented in the next section is the effect of frequency on the voltage response.

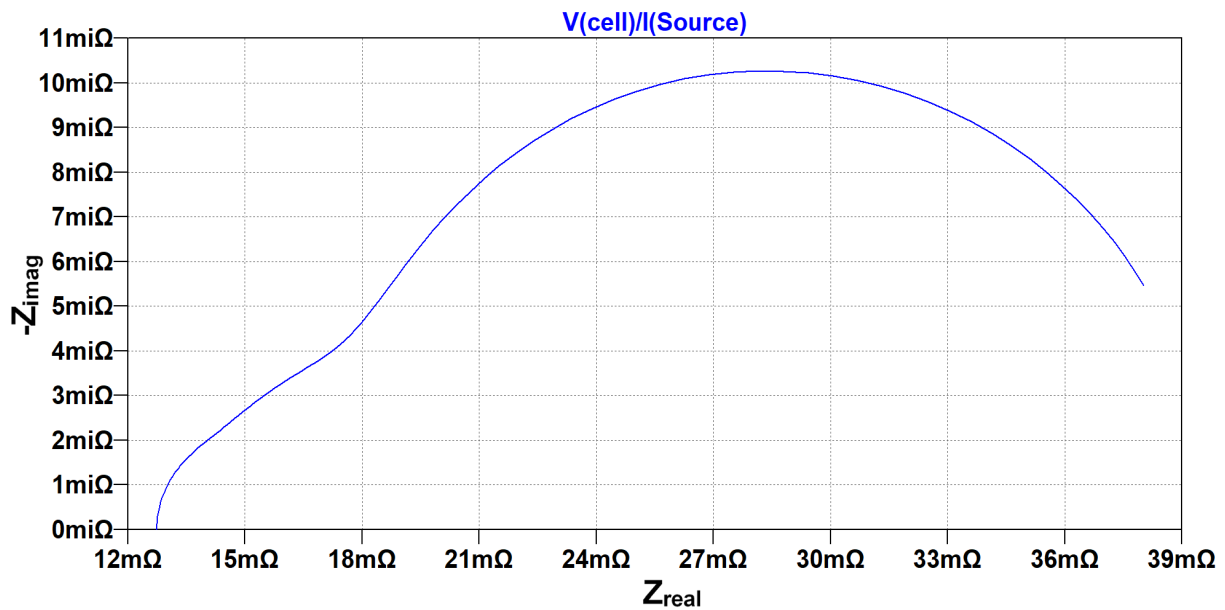


Figure 4-23: Simulated PEM electrolyser impedance Nyquist plot.

Table 4-10: Impedance at different frequencies.

Frequency (Hz)	Cartesian form		Polar form	
	Z_{real} (mΩ)	Z_{imag} (mΩ)	$ Z $ (mΩ)	ϕ (deg)
0.1	38.0284	-5.4643	38.419	-8.18
0.8	22.8520	-8.9507	24.542	-21.39
1.6	19.343	-6.189	20.310	-17.74
3.2	17.6995	-4.3614	18.229	-13.84
9.7	15.5092	-3.0157	15.800	-11.00
19.4	14.449	-2.283	14.628	-8.98
38.8	13.616	-1.686	13.720	-7.06
102.4	12.9332	-0.8444	12.961	-3.74
204.8	12.792	-0.444	12.800	-1.99
409.6	12.753	-0.225	12.755	-1.01
1008.6	12.7422	-0.0918	12.743	-0.41
6553.6	12.7400	-0.014	12.740	-0.06
200000.0	12.7400	-0.0005	12.740	0.00

4.4.1.2 Voltage response and power consumption

Various ripple currents waveforms were applied to the EEC model in LTspice® to simulate the effect of the ripple amplitude, frequency and waveform on the voltage response and power consumption of a PEM electrolyser. The simulated waveforms include sinusoidal, triangular and square waves since these waveforms are the most commonly found in power electronic converters. Each waveform was simulated at a constant DC offset value of 25 A, AC amplitude values that range from 0 to 25 A and frequency values that range from 1 to 1000 Hz. The simulated current (I) and voltage (U) can be expressed by equations (4.14) and (4.15), where I_{DC} and U_{DC} is the DC offset or average values while i and u is the AC components [15].

$$I = I_{DC} + i \quad (4.14)$$

$$U = U_{DC} + u \quad (4.15)$$

The simulated voltage response results for each of the considered waveforms are illustrated on a plot of the RMS current (I_{rms}) and RMS voltage (U_{rms}) as a function of the ripple amplitude at different frequencies. The RMS value of a fluctuating current or voltage is the effective value or the equivalent DC value that dissipates an equal amount of power in a resistive load. The RMS value of the current can be expressed by equation (4.10), where I_{DC} is the DC offset or average value and i_{rms} is the RMS value of the AC component (i) [15].

$$I_{rms} = \sqrt{I_{DC}^2 + i_{rms}^2} \quad (4.16)$$

A parallel equation for the cell RMS voltage can be expressed by equation (4.17), where U_{DC} is the DC offset or average value and u_{rms} is the RMS value of the AC component (u) [15].

$$U_{rms} = \sqrt{U_{DC}^2 + u_{rms}^2} \quad (4.17)$$

Furthermore, the simulated power consumption results for each of the considered waveforms are shown as a function of the ripple amplitude at different frequencies in the following sections. The average power consumption can be illustrated by equation (4.12) below [15].

$$P_{avg} = \frac{1}{T} \int_0^T UI \cdot dt \quad (4.18)$$

The parameter ranges and values that were simulated are shown in Table 4-11 below while Figure 4-24 shows one of the applied current ripples to illustrate the process that was followed to obtain the results that follow. Simulations similar to the one shown in Figure 4-24 below were carried out for all waveforms, AC amplitude and frequency settings and the results are presented and discussed in the following sections.

The results are divided into four sections, with one section for each of the three waveforms and a comparison section in which the different waveforms are compared.

Table 4-11: LTspice® simulation parameters.

Ripple Current Characteristic	Range
Waveform	Sinusoidal wave, Triangular wave and Square wave
DC offset (I_{DC})	25 A (1 A/cm ²)
AC amplitude (i amplitude)	0 – 25 A
Frequency	1 – 1000 Hz

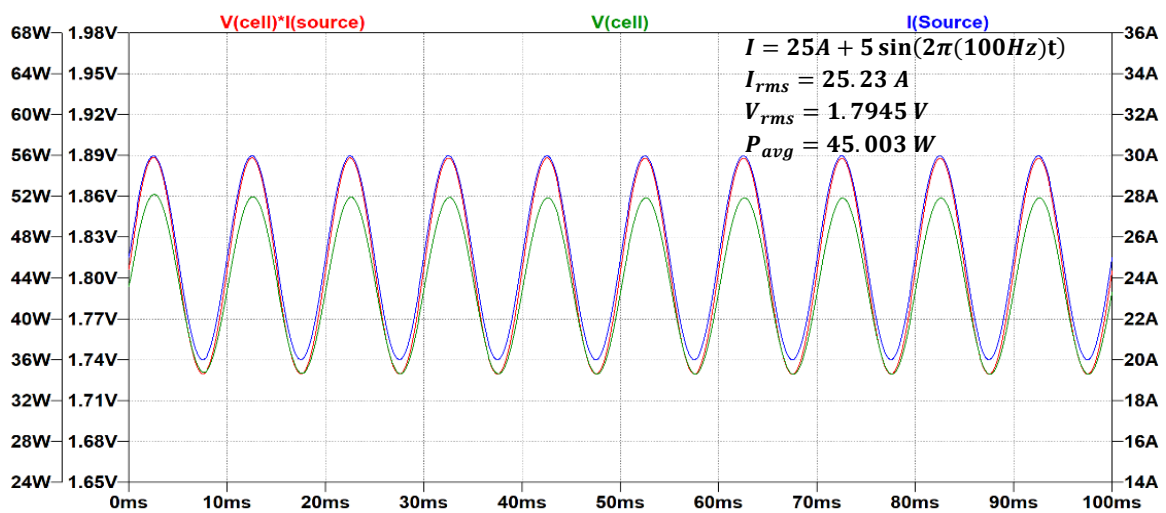


Figure 4-24: Sine wave current ripple with a DC offset of 25 A, AC amplitude of 5 A and a frequency of 100 Hz.

A further explanation of the processes followed to simulate the different waveforms in LTspice® is presented in Appendix A, section A.2

4.4.1.2.1 Sinusoidal Wave

The simulated effect of the ripple amplitude and frequency is illustrated by Figure 4-25 and Figure 4-26 below. In Figure 4-25 the RMS voltage and current are plotted against the ripple amplitude at various frequencies while in Figure 4-26 the average power is plotted at the same parameters. The plots illustrate that the RMS voltage and current increase, which cause an increase in the power consumption, as the ripple amplitude is increased. It is also shown that the effect of the ripple amplitude is lower at higher frequencies. If a sinusoidal ripple is applied to the PEM electrolyser, the maximum voltage efficiency and minimum power consumption would therefore be observed at the lowest possible ripple amplitude and the highest possible frequency.

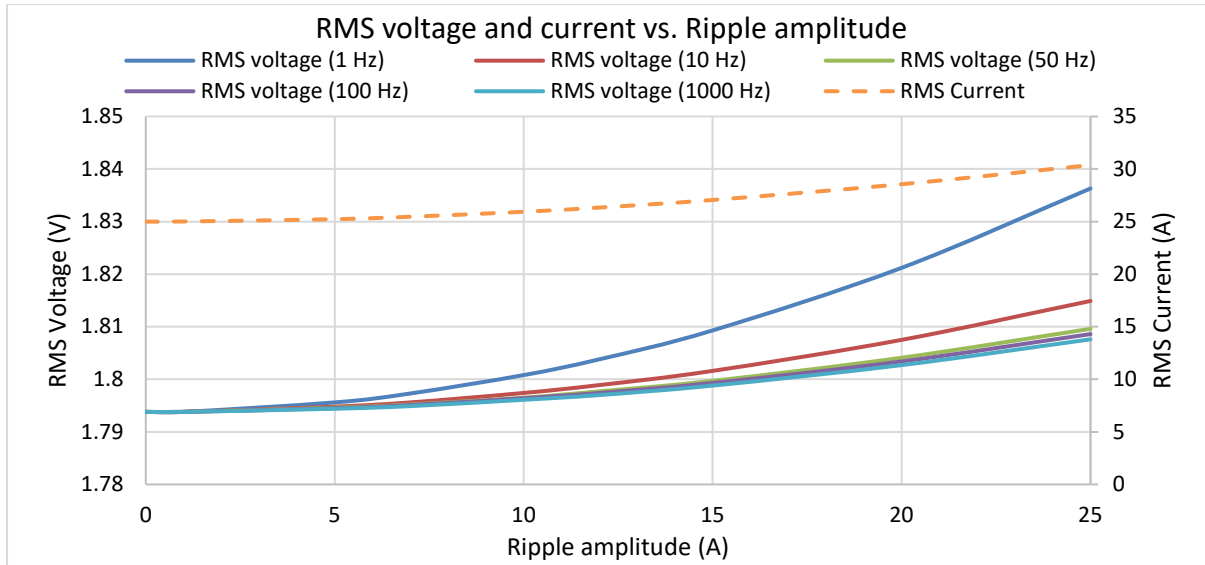


Figure 4-25: Sine wave RMS voltage and current vs. ripple amplitude.

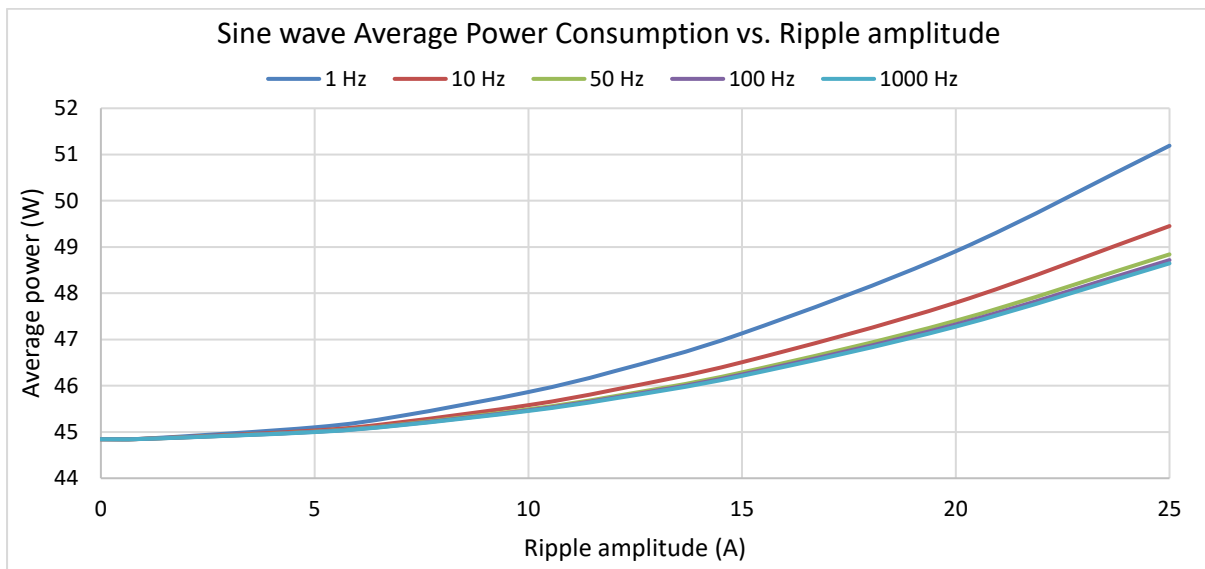


Figure 4-26: Sine wave average power consumption vs. ripple amplitude.

4.4.1.2.2 Triangular Wave

The simulated effect of the ripple amplitude and frequency on the RMS voltage and current of a PEM electrolyser, for a triangular ripple current, is shown in Figure 4-27 while the average power is shown in Figure 4-28 below. As with the sinusoidal wave, the RMS voltage and current values, as well as the power consumption increases as the ripple amplitude is increased. However, the effect of frequency when a triangular ripple current is used, is inconsistent and different than the results obtained from the sinusoidal wave simulations. The simulated results show that if a triangular ripple is applied to the PEM electrolyser, the maximum voltage efficiency would be observed at the lowest possible ripple amplitude and a frequency between 10 and 100 Hz.

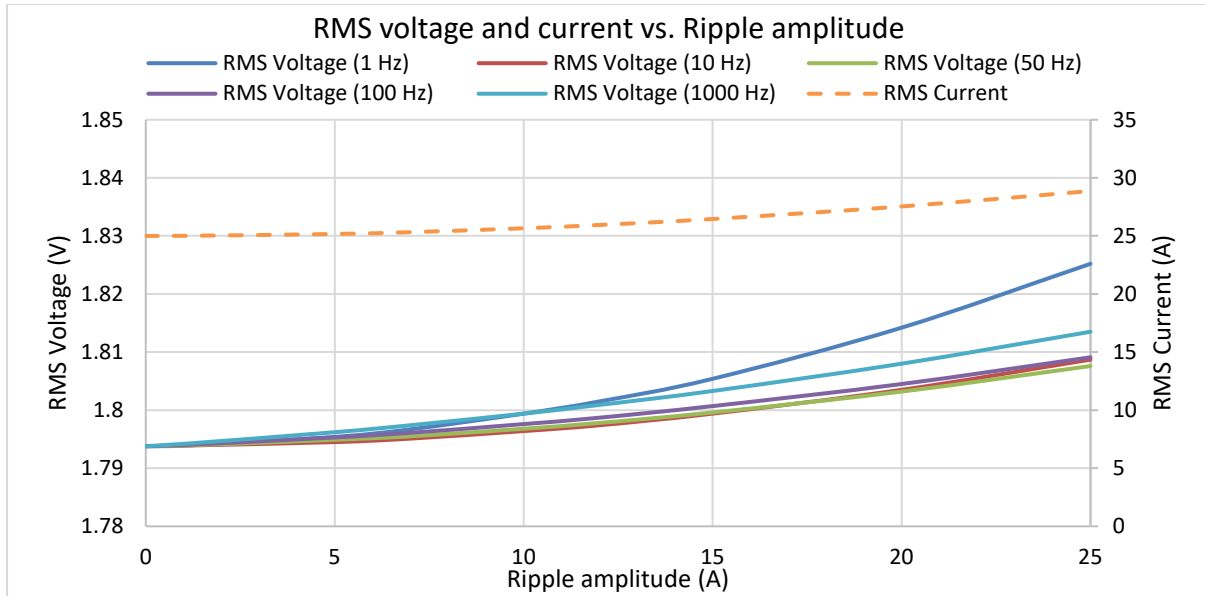


Figure 4-27: Triangular wave RMS voltage and current vs. ripple amplitude.

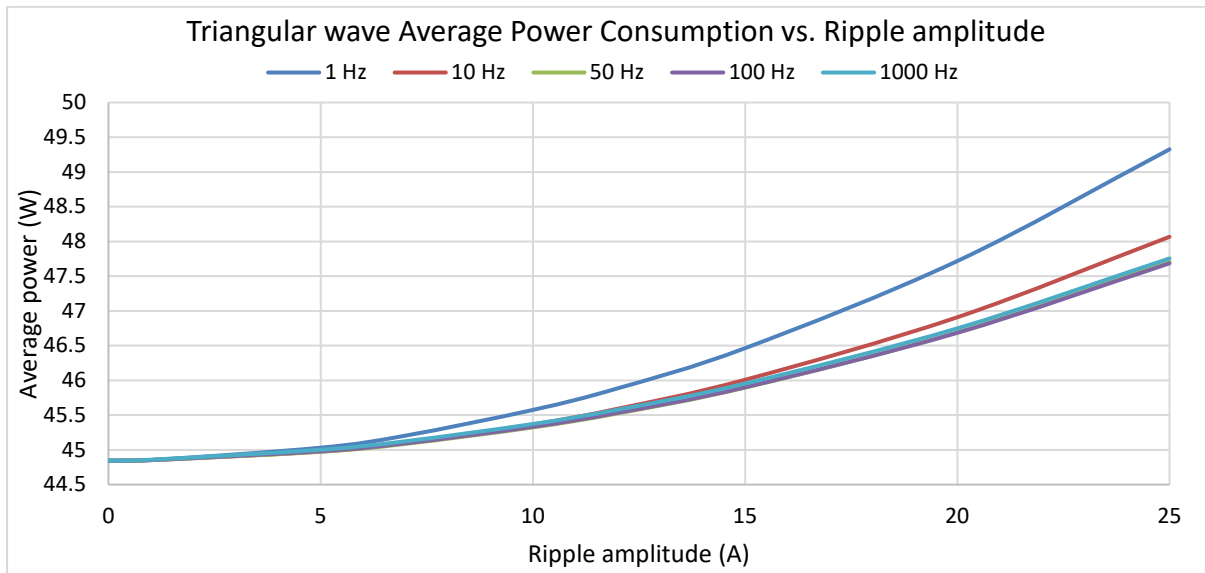


Figure 4-28: Triangular wave average power consumption vs. ripple amplitude.

4.4.1.2.3 Square Wave

The simulated effect of the ripple amplitude and frequency on the RMS voltage and current as well as the power consumption of a PEM electrolyser, for a square wave ripple current, are shown in Figure 4-29 and Figure 4-30 below. As with the sinusoidal and triangular wave, the RMS voltage, RMS current and average power consumption increases as the ripple amplitude is increased. The simulated results show that if a square wave ripple is applied to the PEM electrolyser, the maximum voltage efficiency would be observed at the lowest possible ripple amplitude and a frequency between 50 and 100 Hz.

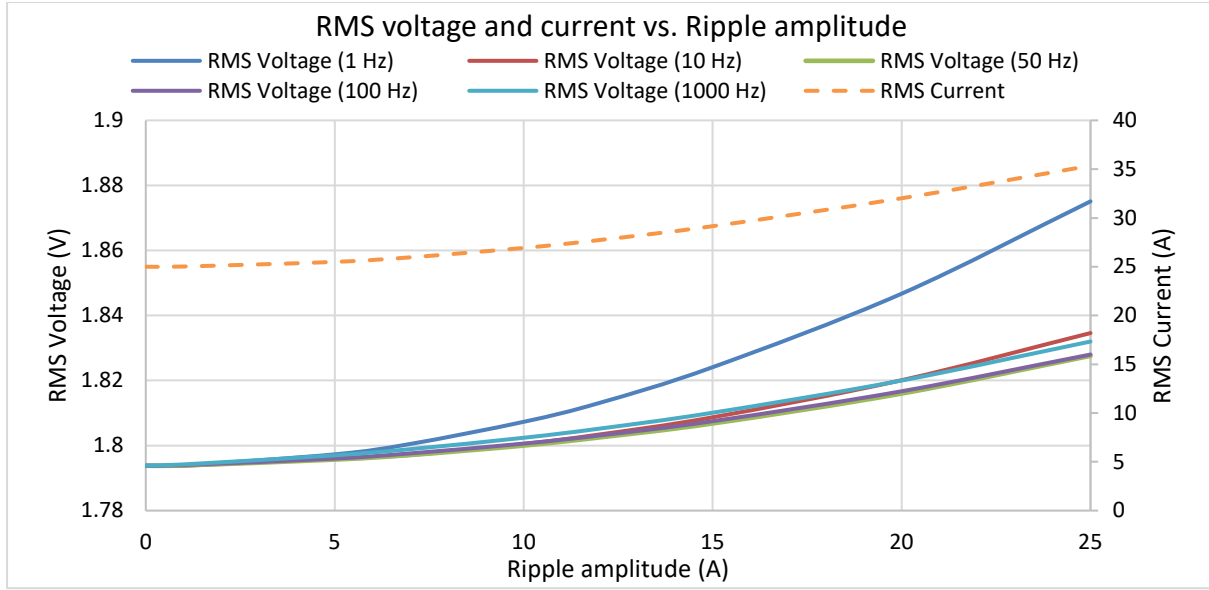


Figure 4-29: Square wave voltage efficiency vs. ripple amplitude.

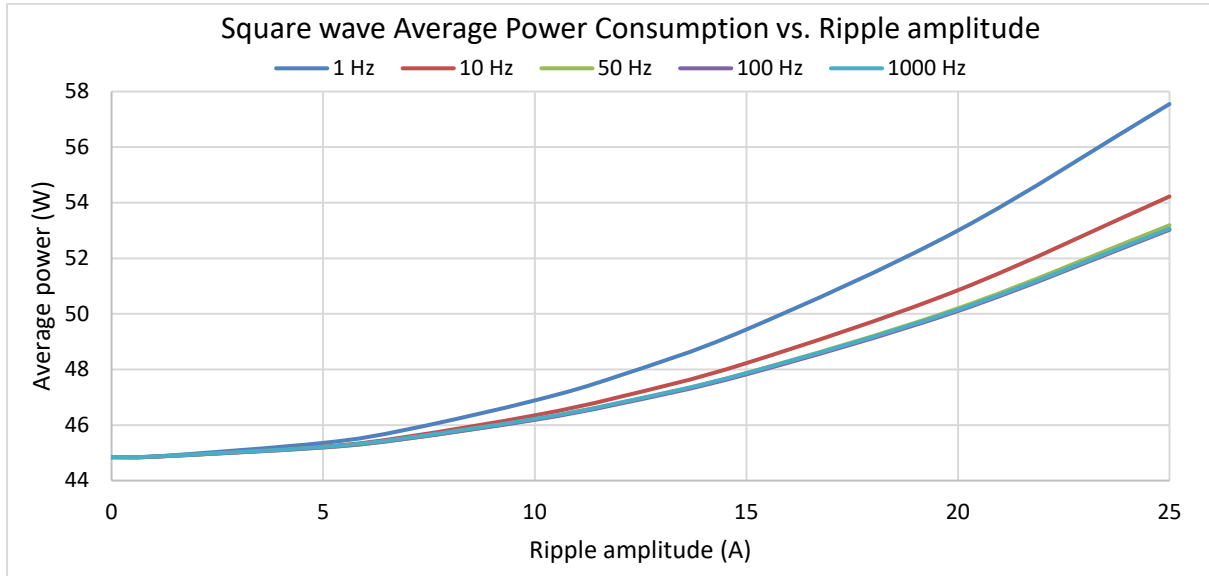


Figure 4-30: Square wave average power consumption vs. ripple amplitude.

4.4.1.2.4 Comparison

The simulation results shown in the sections above illustrates that the AC amplitude of a ripple current would have a large impact on the voltage efficiency and the average power consumption of a PEM electrolyser. However, Table 2-12 in the literature study shows that the same AC amplitude setting results in different RMS values for different waveforms. In order to effectively compare the results obtained from the different waveforms, the ripple factor (RF) was used. The ripple factor can be calculated using equation (4.19), where i_{rms} is the RMS value of the AC component of the ripple current and I_{DC} the DC offset value [15].

The maximum achievable ripple factor as well as the crest factor and a simple RMS calculation for each waveform used in this study are presented in Table 4-12.

$$RF = 100 \frac{i_{rms}}{I_{DC}} \quad (4.19)$$

Table 4-12: Maximum achievable ripple factor for each of the waveforms.

Waveform	Crest factor	i_{rms}	Maximum ripple factor (RF)
Sinusoidal	$\sqrt{2}$	$\frac{A}{\sqrt{2}}$	70.7%
Triangular	$\sqrt{3}$	$\frac{A}{\sqrt{3}}$	57.7%
Square	1	A	100%

The simulated average power consumption of the PEM electrolyser for the different waveforms, at a constant DC offset and frequency, are illustrated as a function of the ripple amplitude in Figure 4-31 and as a function of the ripple factor in Figure 4-32.

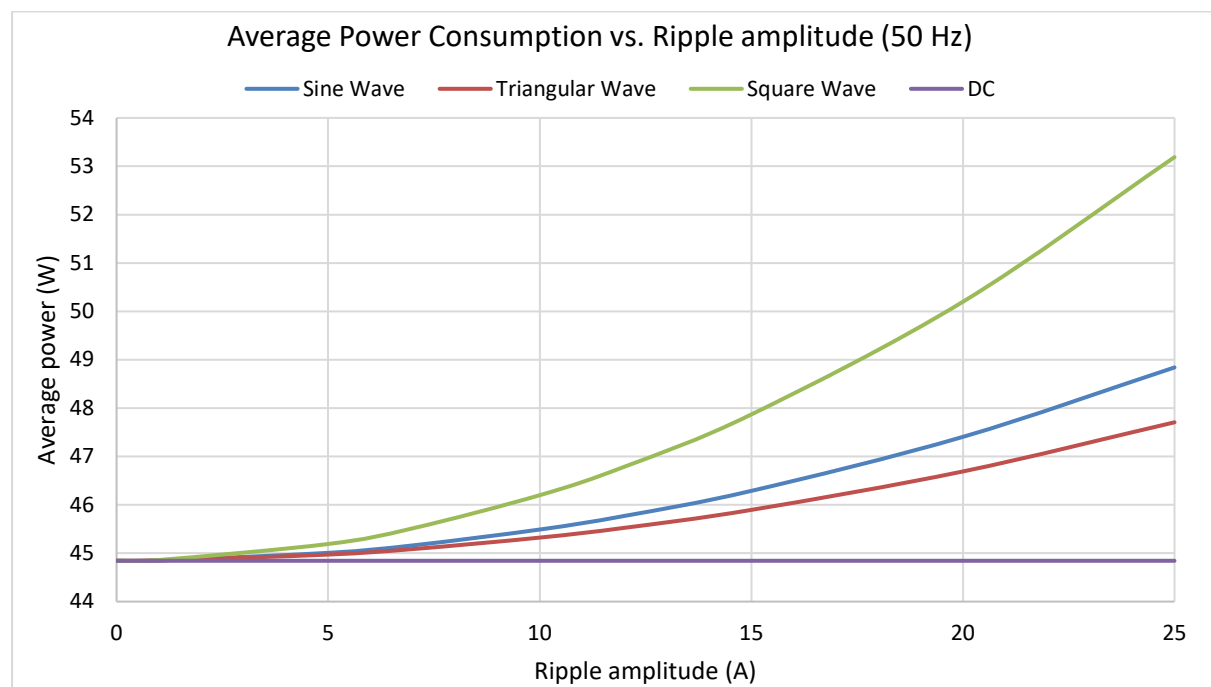


Figure 4-31: Average power consumption as a function of ripple amplitude at a constant frequency.

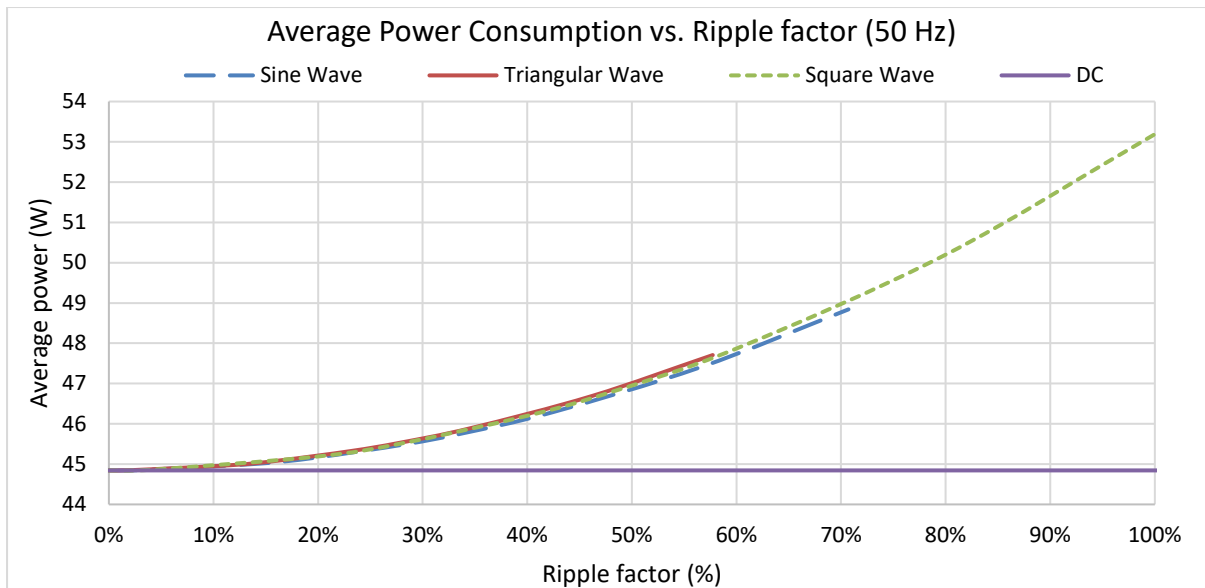


Figure 4-32: Average power consumption as a function of ripple factor at a constant frequency.

Although the maximum achievable ripple factor with each waveform is different as illustrated in Table 4-12 above, Figure 4-32 demonstrate that a similar change in the average power consumption occurs when the ripple factor is changed in each of the simulated waveforms. Figure 4-32 shows that the ripple factor would have a substantial effect on the power consumption of a PEM electrolyser while the effect of the waveform is relatively small. A similar trend is observed in the figures below where the average power consumption is plotted as a function of frequency at a constant ripple amplitude in Figure 4-33 and a constant ripple factor in Figure 4-34. Although small differences occur between the different waveforms, Figure 4-34 shows that that primary influencing parameter is the frequency and not the waveform.

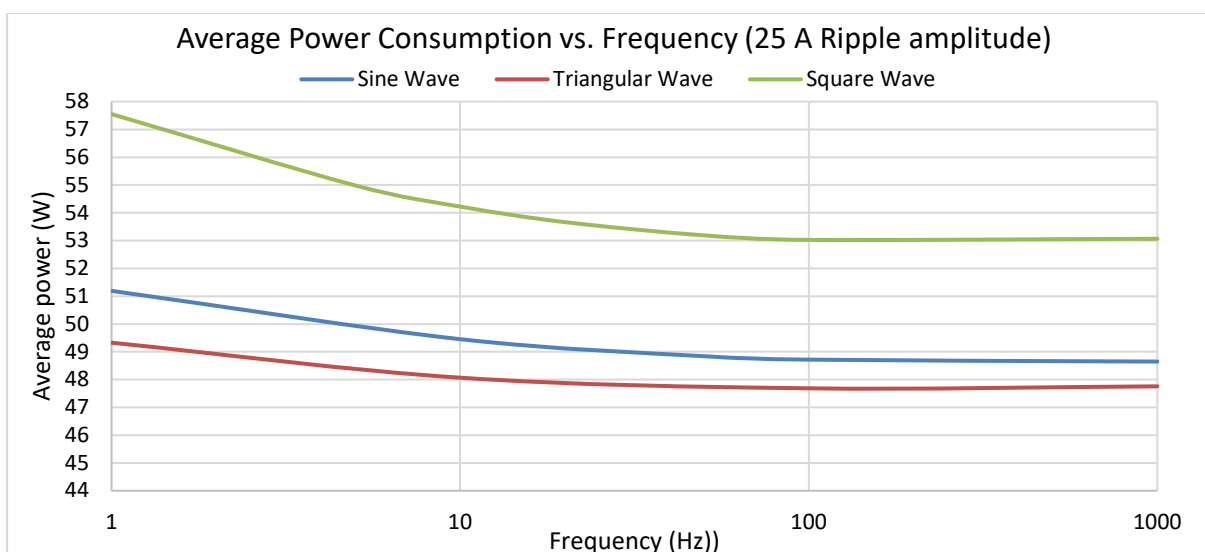


Figure 4-33: Average power consumption as a function of frequency at a constant ripple amplitude.

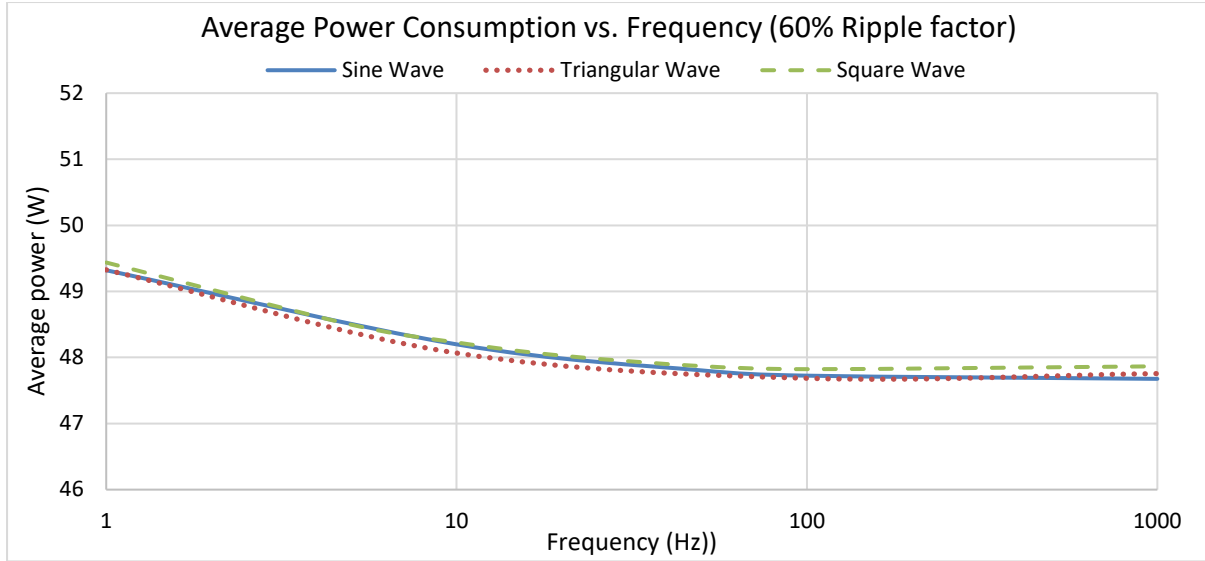


Figure 4-34: Average power consumption as a function of frequency at a constant ripple factor.

All of the results obtained from the LTspice® simulations are summarized in Table 4-13 below. The table shows the ripple factor (RF), RMS current (I_{rms}), RMS voltage (U_{rms}), voltage efficiency (ε_V^{HHV}) and average power (P_{avg}) results for various different frequencies, AC amplitude and waveform settings. Equation (4.20) below was used to calculate the voltage efficiency [42].

$$\varepsilon_V^{HHV} = \frac{E_{th}^0}{U_{rms}} \quad (4.20)$$

As were expected, the simulation results show that an increase in the ripple factor would also increase the power consumption of the PEM electrolyser. On the other hand, the results show that if a ripple is present in the current supplied to the electrolyser, the power consumption decreases as the frequency of the applied ripple current increase. By comparison, the waveform type does not seem to have a large effect on the power consumption, provided that the DC offset, ripple factor and frequency are constant. The results presented by the LTspice® simulations also validated the parameter ranges selected for the experimental tests in Table 3-12. Certain ranges and setting, such as the AC amplitude and DC offset, were chosen not to damage the PEM electrolyser but others such as the frequency and waveform types were selected based only on the little available literature. The LTspice® simulations showed that the effect of frequency is the largest in the low frequency range (below 100 Hz), thus validating the selected frequency range of 1 Hz to 1 kHz. The selected waveforms were also validated since the simulations showed that the effect of the waveform type is insignificant.

Table 4-13: LTspice® simulation results.

Freq (Hz)	AC Amp (A)	Sinusoidal wave					Triangular wave					Square wave				
		RF	I_{rms} (A)	U_{rms} (V)	ε_V^{HHV}	P_{avg} (W)	RF	I_{rms} (A)	U_{rms} (V)	ε_V^{HHV}	P_{avg} (W)	RF	I_{rms} (A)	U_{rms} (V)	ε_V^{HHV}	P_{avg} (W)
0	0	0.0%	25	1.7938	82.5%	44.844	0.0%	25	1.7938	82.5%	44.844	0%	25	1.7938	82.5%	44.844
1	5	14.1%	25.23	1.7956	82.4%	45.101	11.5%	25.166	1.7954	82.4%	45.031	20%	25.495	1.7973	82.3%	45.357
1	10	28.3%	25.935	1.8008	82.2%	45.864	23.1%	25.658	1.7994	82.2%	45.575	40%	26.926	1.8073	81.9%	46.885
1	15	42.4%	27.058	1.8093	81.8%	47.133	34.6%	26.457	1.8054	82.0%	46.464	60%	29.155	1.8241	81.1%	49.437
1	20	56.6%	28.557	1.8212	81.3%	48.909	46.2%	27.537	1.8142	81.6%	47.718	80%	32.016	1.8467	80.1%	52.999
1	25	70.7%	30.375	1.8363	80.6%	51.191	57.7%	28.867	1.8252	81.1%	49.326	100%	35.355	1.8751	78.9%	57.552
10	5	14.1%	25.23	1.7948	82.5%	45.032	11.5%	25.166	1.7945	82.5%	44.976	20%	25.495	1.796	82.4%	45.221
10	10	28.3%	25.935	1.7974	82.3%	45.58	23.1%	25.658	1.7964	82.4%	45.365	40%	26.926	1.8005	82.2%	46.348
10	15	42.4%	27.058	1.8016	82.1%	46.509	34.6%	26.457	1.7994	82.2%	46.009	60%	29.155	1.8087	81.8%	48.227
10	20	56.6%	28.557	1.8075	81.9%	47.797	46.2%	27.537	1.8035	82.1%	46.909	80%	32.016	1.8201	81.3%	50.851
10	25	70.7%	30.375	1.8149	81.5%	49.453	57.7%	28.867	1.8087	81.8%	48.067	100%	35.355	1.8346	80.7%	54.225
50	5	14.1%	25.23	1.7946	82.5%	45.008	11.5%	25.166	1.7949	82.5%	44.972	20%	25.495	1.7957	82.4%	45.191
50	10	28.3%	25.935	1.7965	82.4%	45.49	23.1%	25.658	1.7968	82.4%	45.323	40%	26.926	1.8	82.2%	46.2
50	15	42.4%	27.058	1.7997	82.2%	46.289	34.6%	26.457	1.7996	82.2%	45.896	60%	29.155	1.8068	81.9%	47.869
50	20	56.6%	28.557	1.8041	82.0%	47.406	46.2%	27.537	1.8032	82.1%	46.691	80%	32.016	1.816	81.5%	50.199
50	25	70.7%	30.375	1.8096	81.8%	48.841	57.7%	28.867	1.8076	81.9%	47.707	100%	35.355	1.8276	81.0%	53.189
100	5	14.1%	25.23	1.7945	82.5%	45.003	11.5%	25.166	1.7953	82.4%	44.98	20%	25.495	1.796	82.4%	45.194
100	10	28.3%	25.935	1.7964	82.4%	45.469	23.1%	25.657	1.7976	82.3%	45.332	40%	26.926	1.8006	82.2%	46.187
100	15	42.4%	27.058	1.7993	82.3%	46.244	34.6%	26.456	1.8007	82.2%	45.901	60%	29.155	1.8075	81.9%	47.823
100	20	56.6%	28.557	1.8034	82.1%	47.327	46.2%	27.535	1.8045	82.0%	46.685	80%	32.016	1.8167	81.5%	50.103
100	25	70.7%	30.375	1.8086	81.8%	48.717	57.7%	28.864	1.8091	81.8%	47.685	100%	35.355	1.828	81.0%	53.025
1000	5	14.1%	25.23	1.7944	82.5%	44.998	11.5%	25.166	1.7962	82.4%	45.002	20%	25.495	1.797	82.4%	45.214
1000	10	28.3%	25.935	1.7961	82.4%	45.455	23.1%	25.657	1.7994	82.2%	45.372	40%	26.926	1.8024	82.1%	46.221
1000	15	42.4%	27.058	1.7988	82.3%	46.215	34.6%	26.456	1.8033	82.1%	45.954	60%	29.155	1.8101	81.8%	47.866
1000	20	56.6%	28.557	1.8027	82.1%	47.279	46.2%	27.535	1.808	81.9%	46.749	80%	32.016	1.82	81.3%	50.147
1000	25	70.7%	30.375	1.8076	81.9%	48.647	57.7%	28.864	1.8135	81.6%	47.756	100%	35.355	1.832	80.8%	53.066

4.4.2 Simulink® simulation

The developed Simulink® models, presented in sections 4.3.3 and 4.3.4, were used to simulate the PEM electrolyser response to different electrical, temperature and pressure operating conditions. Included in the simulations are the effects of these operating conditions on the open circuit voltage, overpotential and hydrogen flow rate. In addition, the frequency spectrum of each of the considered waveforms was analysed using MATLAB®'s Fast Fourier Transform (FFT) function.

4.4.2.1 Frequency Spectrum

The LTspice® simulations showed a small difference in the effect of frequency on the response of a PEM electrolyser for each of the different waveforms considered. The reason is that the frequency spectrum for each of these waveforms is different. To analyse the frequency spectrum of each waveform, the Fourier Transform (FT) was used to decompose the waveform into a series of sinusoidal frequency components. By applying the FT to each waveform, it was observed that a sine wave consists of only one frequency which is called the fundamental frequency, while the frequency spectrum of a triangular or square wave contains both the fundamental frequency as well as harmonic frequencies.

The fundamental frequency can be defined as the lowest or base frequency of the signal, while harmonic frequencies are higher frequencies superimposed on the fundamental frequency. Numerous frequencies are thus present in the frequency spectrum of triangular and square waves since these functions consist of a combination of sinusoidal functions, as shown in section 2.9.2.4 of the literature study. The frequency spectrum of each waveform was simulated in MATLAB® by using the FFT function. The parameters are shown in Table 4-14 below, and the frequency spectrums in the figures that follow. The results show that even at the same fundamental frequency, the frequency spectrum is dependent on the waveform and the effect of frequency on an inductive and capacitive load would thus be different.

Table 4-14: Matlab® simulation parameters.

Ripple Current Characteristic	Range
Waveform	Sinusoidal wave, Triangular wave and Square wave
Offset (DC component)	25 A
Amplitude (AC component)	10 A
Fundamental frequency	100 Hz
Frequency spectrum	0 – 1000 Hz

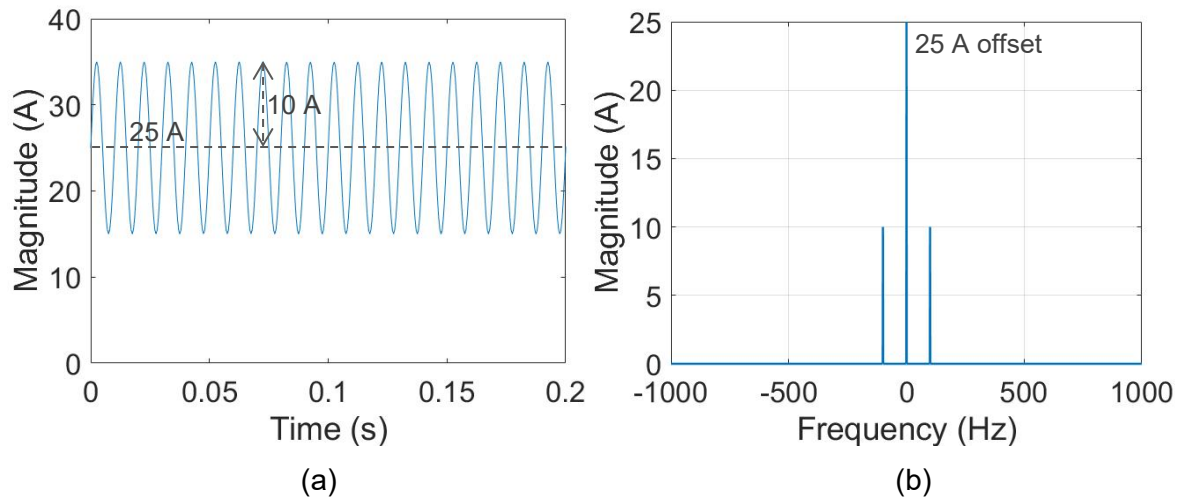


Figure 4-35: Sine wave at a fundamental frequency of 100 Hz (a) waveform (b) FFT.

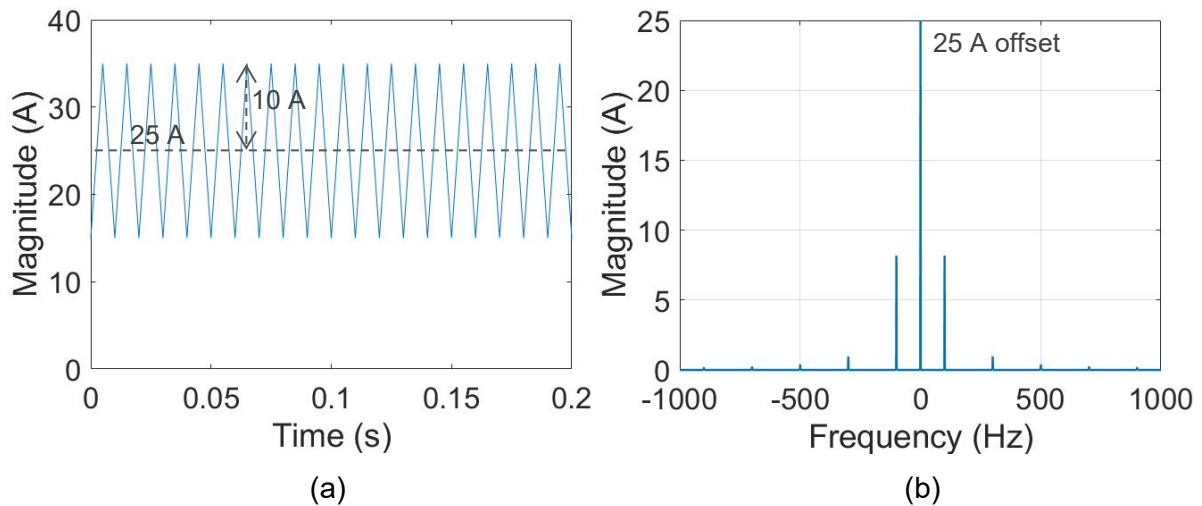


Figure 4-36: Triangular wave at a fundamental frequency of 100 Hz (a) waveform (b) FFT.

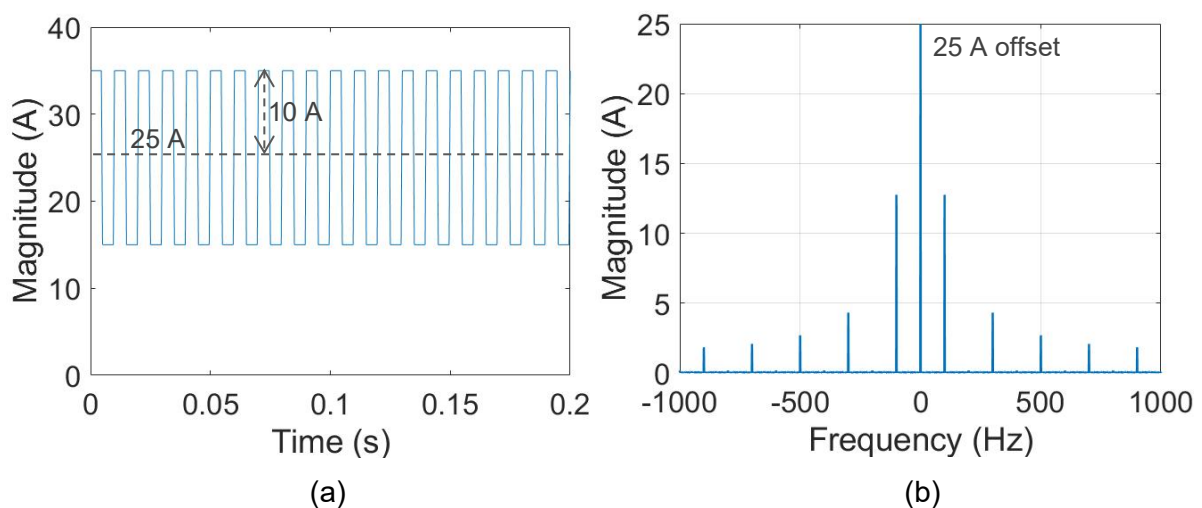


Figure 4-37: Square wave at a fundamental frequency of 100 Hz (a) waveform (b) FFT.

4.4.2.2 Voltage response

The open circuit voltage is the cell voltage when no external electric current flows through the cell, while the overpotential is the voltage losses that occur when current flow is initiated. From the literature, we know that temperature and pressure are the main operating conditions affecting the open circuit voltage while the overpotential is also affected by the electrical characteristics of the applied current. The PEM electrolyser's open circuit voltage was thus simulated at different operating temperatures and pressures, while the overpotential was simulated at different electrical operating conditions.

4.4.2.2.1 Open circuit voltage

The Simulink® model, presented in section 4.3.3.1, was used to simulate the open circuit voltage of the PEM electrolyser at different operating conditions. In Figure 4-38 below, the theoretical open circuit voltage is plotted, at seven different temperatures ranging from 0 °C to 70 °C (273.15 K to 343.15 K), as a function of the operating pressure. It can be seen on the figure that the open circuit voltage at standard conditions (25 °C and 0.101325 MPa) is 1.23 V.

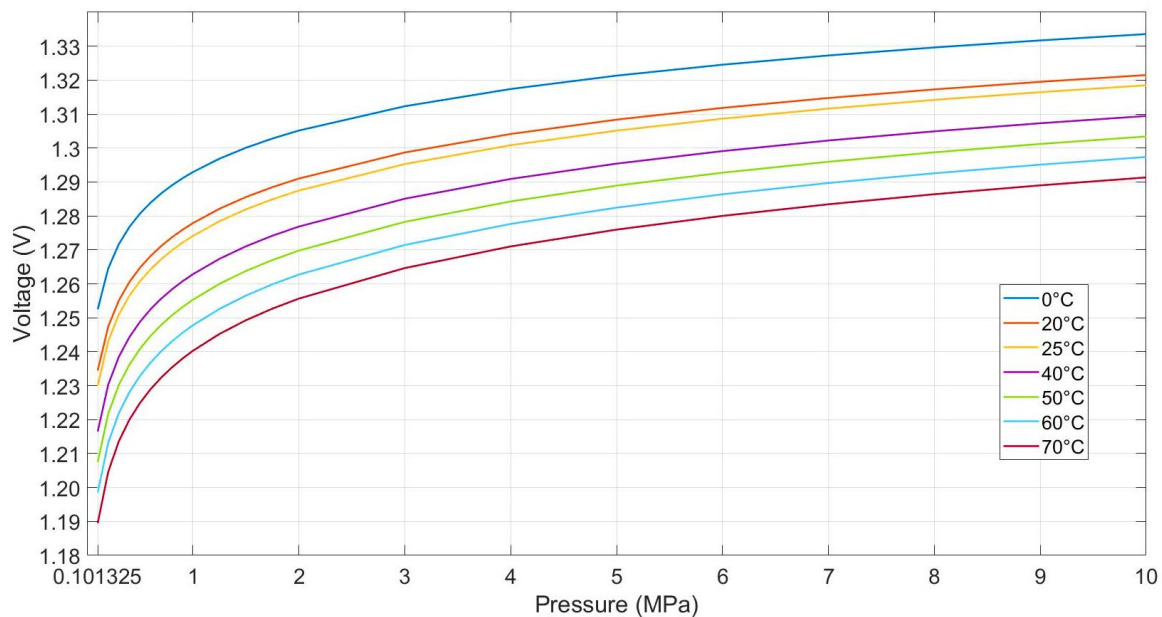


Figure 4-38: Theoretical open circuit voltage as a function of the operating pressure at seven different temperatures (0-70 °C).

The figure above thus indicates that the open circuit voltage of the PEM electrolyser is affected by both the operating temperature and pressure conditions. Figure 4-39 is a plot of the open circuit potential as a function of both temperature and pressure. The figure illustrates that the minimum open circuit potential, and in effect the maximum voltage efficiency, would be achieved at the maximum operational temperature and the minimum operational pressure, which is standard pressure (0.101325 MPa or 1 atm).

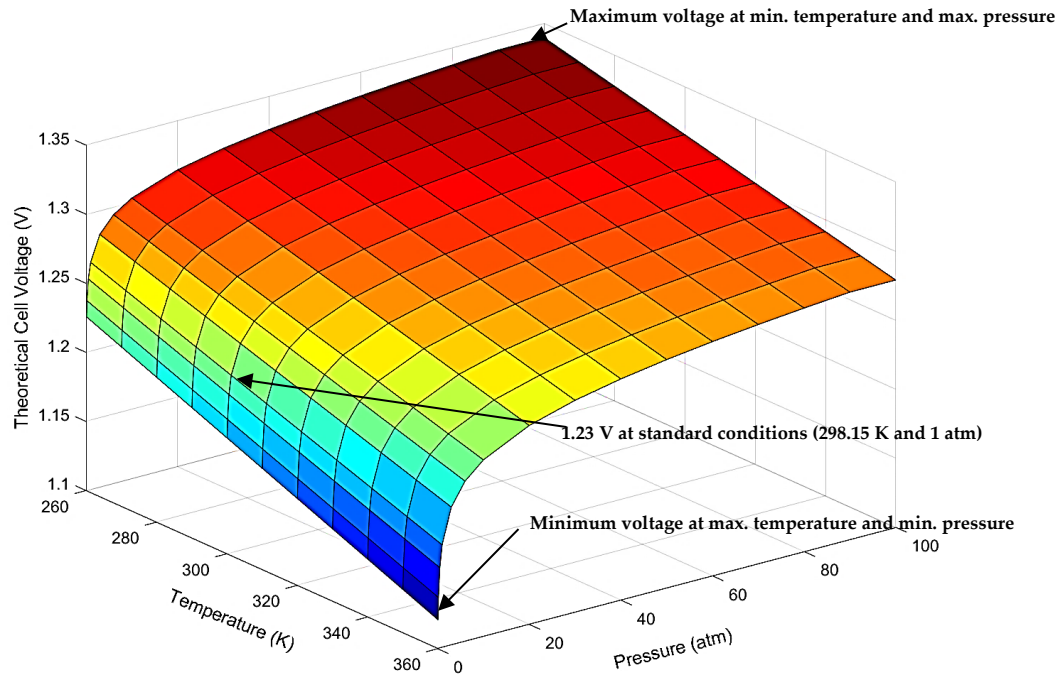


Figure 4-39: Theoretical open circuit voltage as a function of the operating temperature and pressure.

4.4.2.2.2 Overpotential

The Simulink® model, as illustrated in section 4.3.3.2, was used to simulate the overpotential of a PEM electrolyser. In Figure 4-40 the simulated anode activation, cathode activation and ohmic overpotentials are plotted as a function of the applied current density.

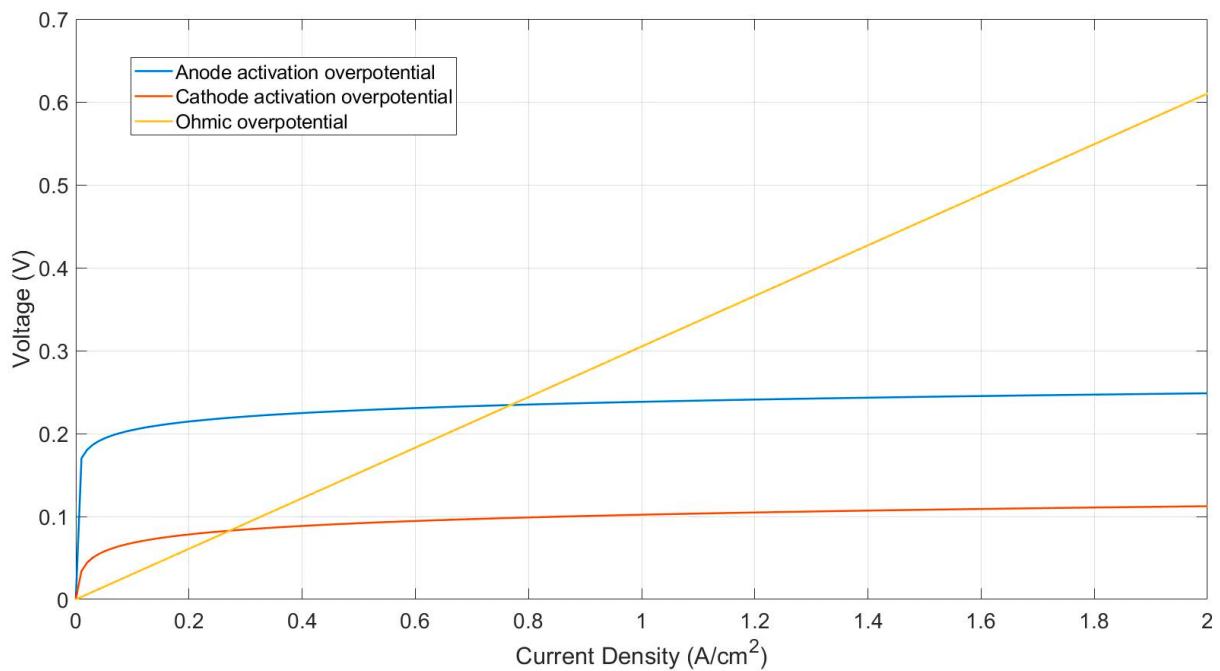


Figure 4-40: Theoretical overpotential as a function of the current density.

Figure 4-41 below illustrates the simulated cell voltage as a function of the current density and illustrates the contribution of the open circuit voltage and each overpotential. Each of the voltages shown accumulates to obtain the total cell voltage.

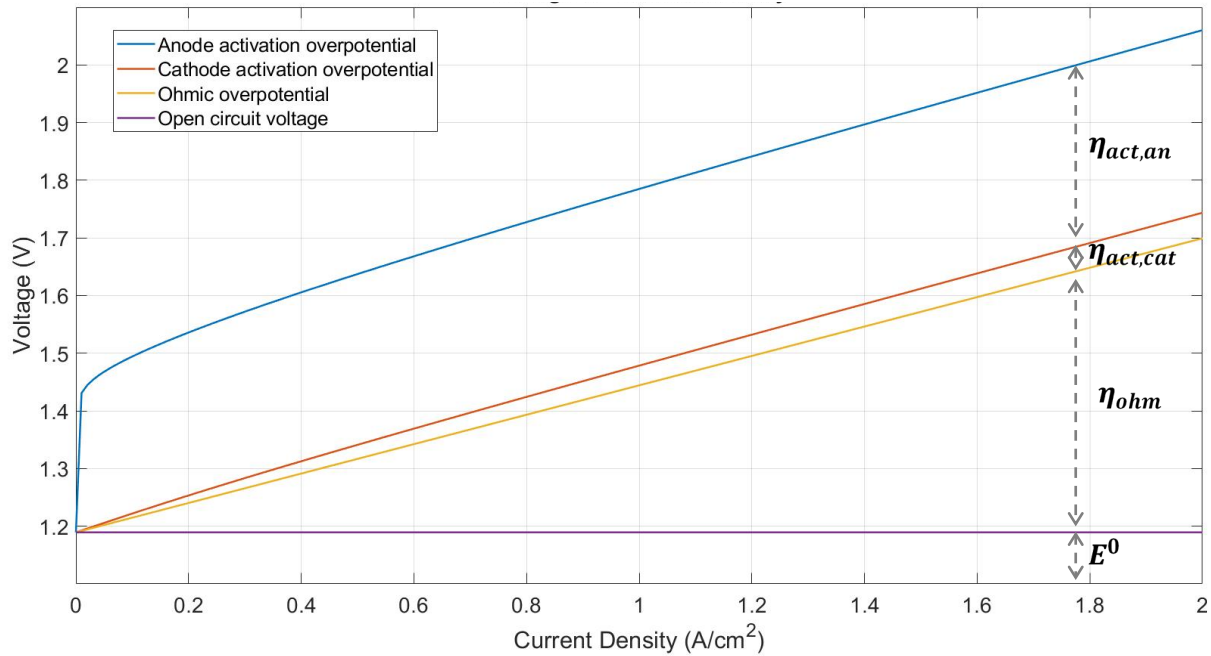


Figure 4-41: Simulation of the total cell voltage vs. current density illustrating the contribution of the open circuit potential as well as each overpotential.

The figures above show that the activation overpotential is the main contributing overpotential to the total cell voltage at current densities below 1.2 A/cm²; Thereafter, the ohmic overpotential becomes the most significant contributor. The figures also illustrate that the activation overpotentials rise rapidly in the low current density region and then becomes close to constant at higher current densities. The ohmic overpotential, on the other hand, is linear and increases as the current density increases.

4.4.2.3 Hydrogen output

The hydrogen flow rate model, as illustrated in section 4.3.4, was used to simulate the flow rate of the hydrogen and oxygen gas produced by the PEM electrolyser. All simulations, unless otherwise illustrated, were carried out at a pressure of 101.325 kPa and a temperature of 273 K (normal conditions) since the flow meters used in the experimental tests give the readings in normal litres per minute. Figure 4-42 below illustrates the simulated theoretical hydrogen and oxygen flow rates as a function of the current density or DC offset of the 25 cm² PEM electrolyser. The figure shows that both the hydrogen and oxygen flow rates increase linearly as the current density increases.

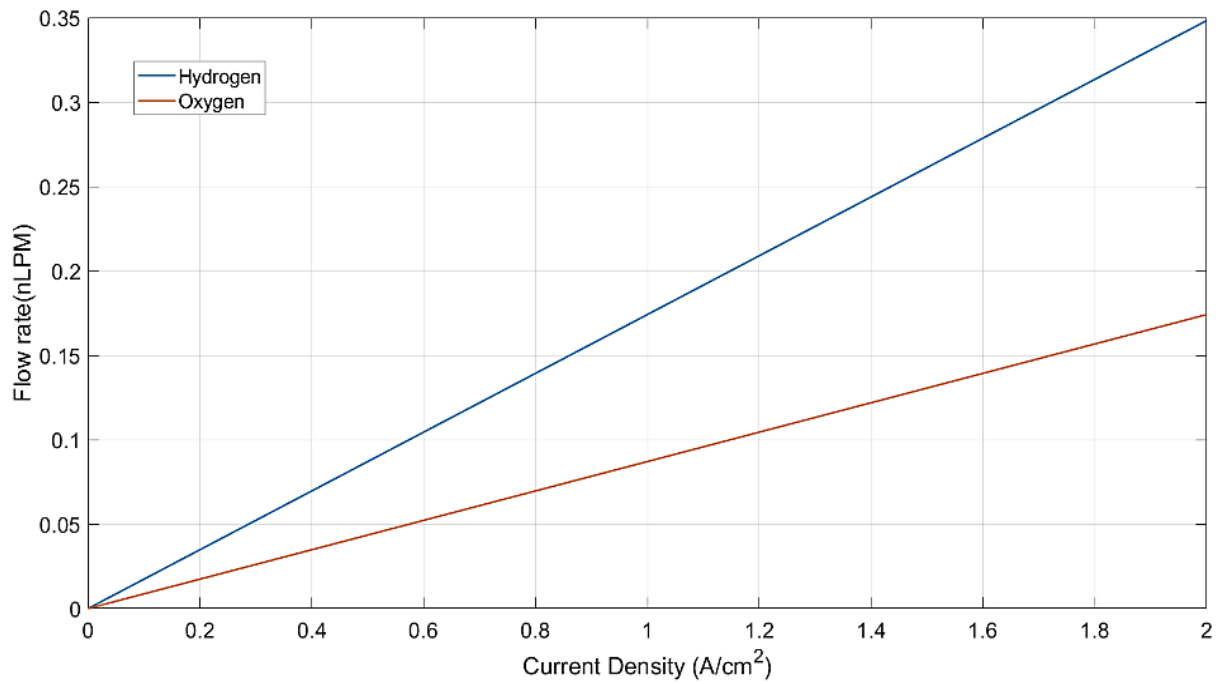


Figure 4-42: Theoretical hydrogen and oxygen flow rates as a function of the current density.

In Figure 4-43 it is also shown that the average hydrogen and oxygen gas flow rates are not affected by the ripple factor of the applied ripple current. The average flow rates are dependant only on the average current applied to the cell and thus stay constant at a constant DC offset.

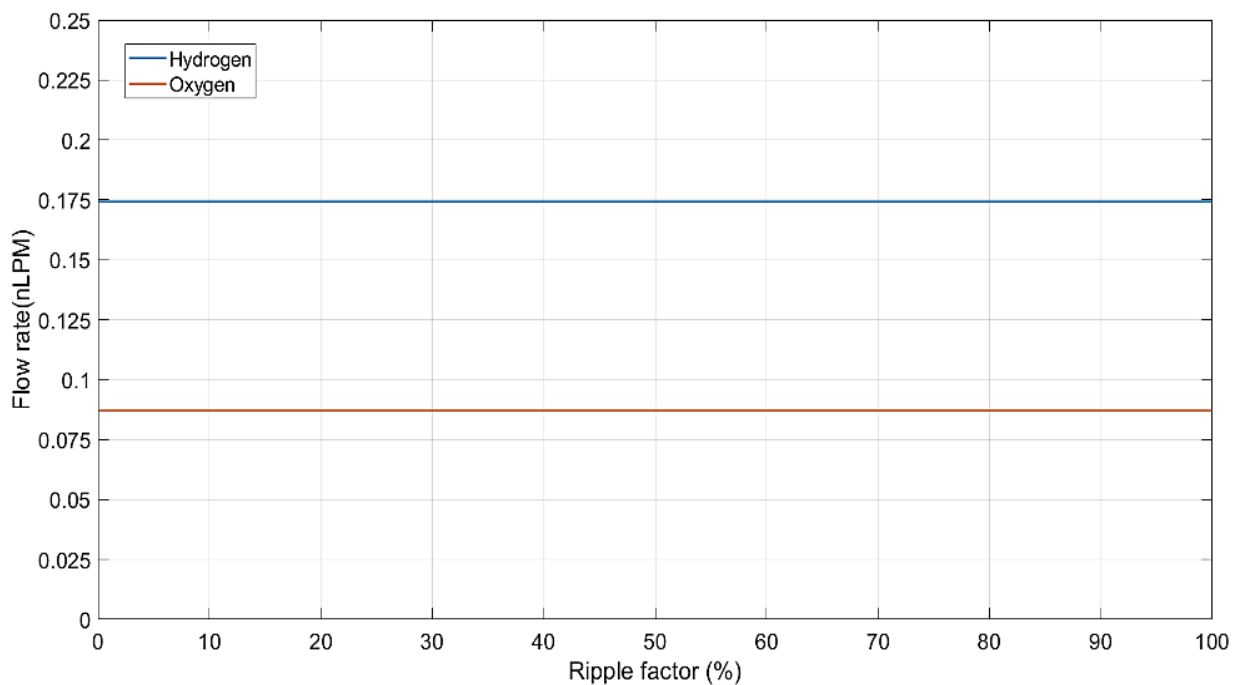


Figure 4-43: Simulation of the average hydrogen and oxygen flow rates vs. ripple factor.

Figure 4-44 below illustrates the simulated or theoretical total hydrogen flow rate of the 25 cm² PEM electrolyser as a function of the applied current offset (DC component) and the ripple factor (AC component).

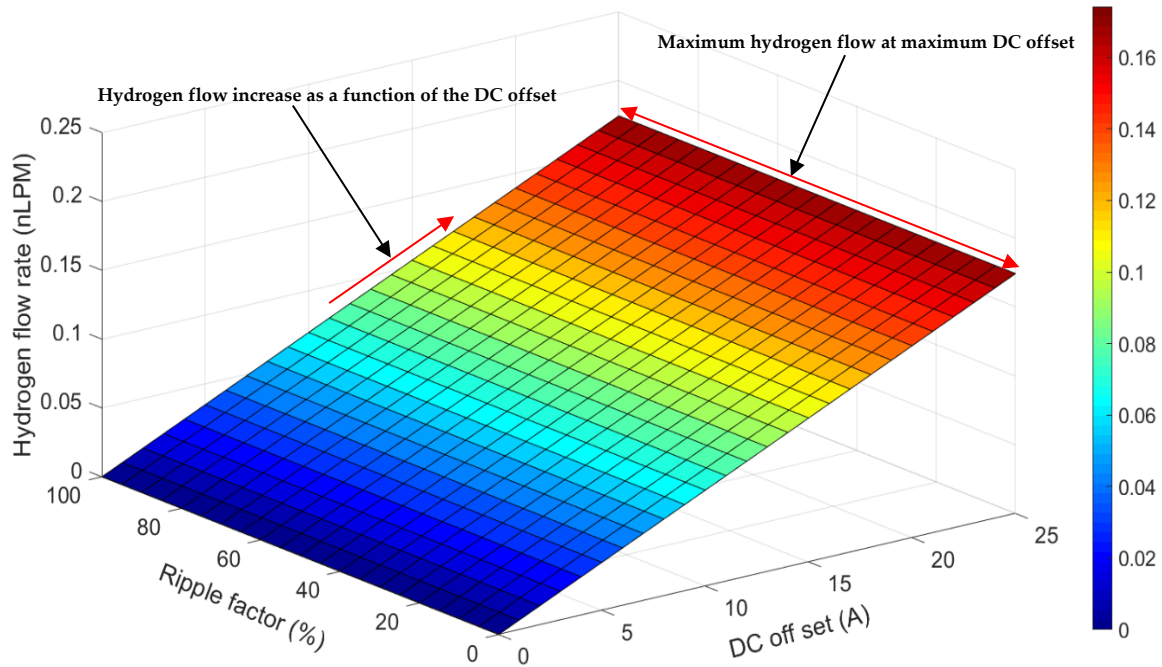
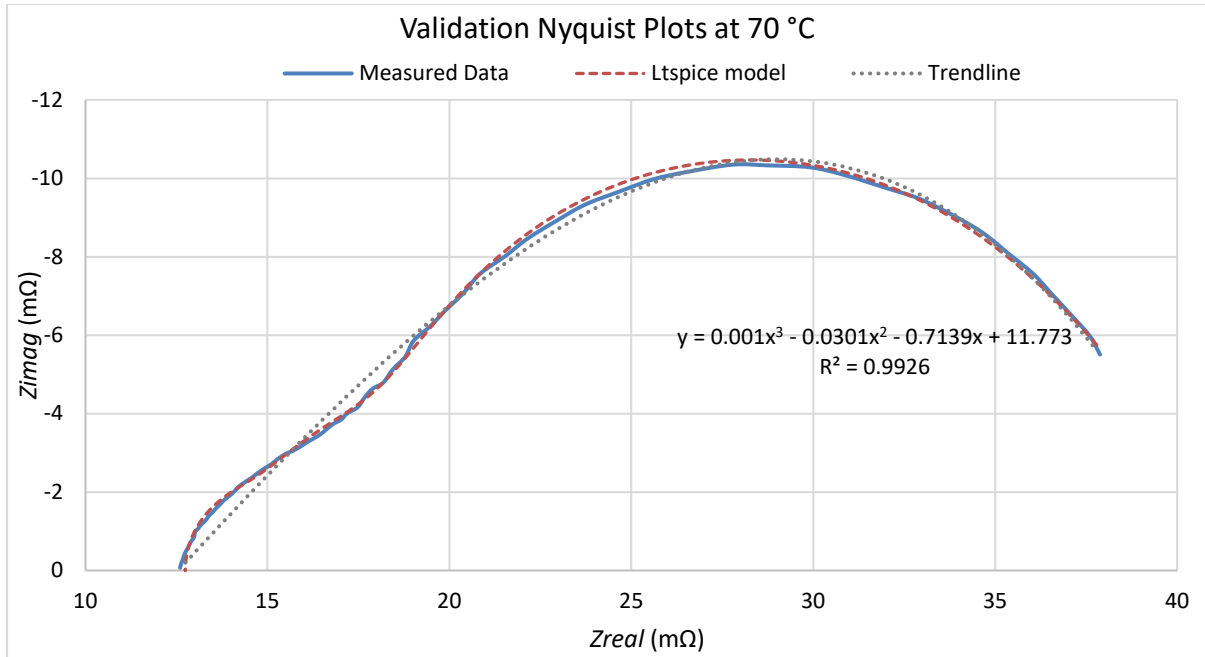
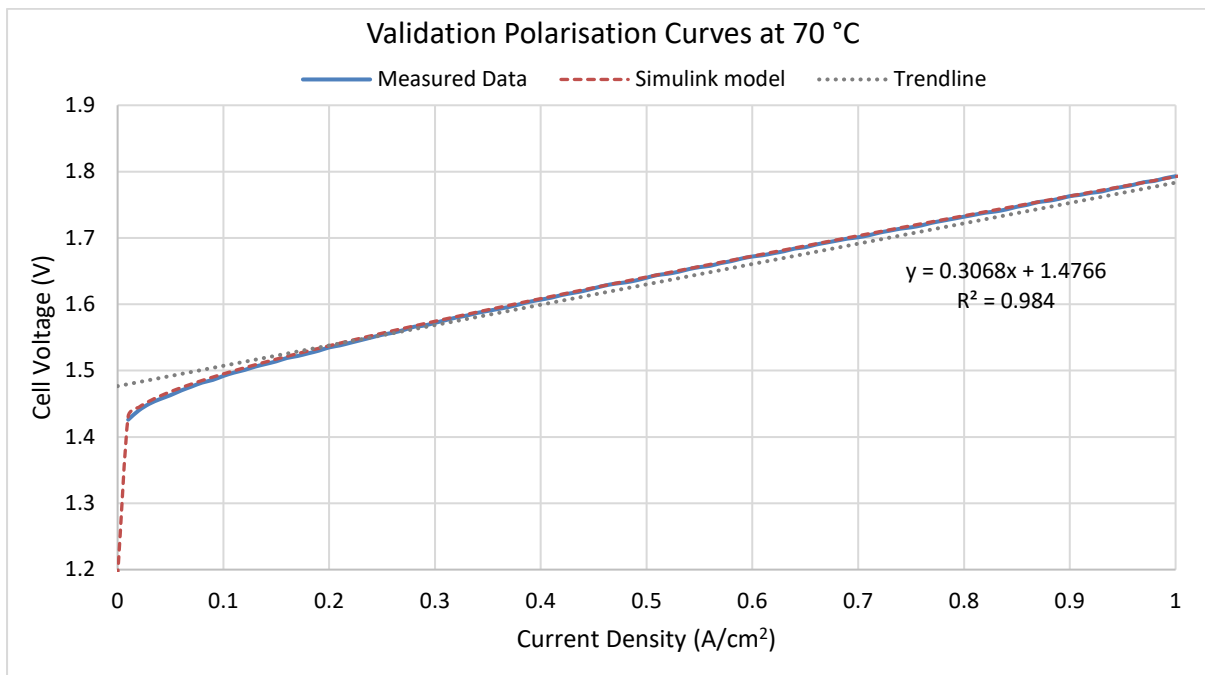


Figure 4-44: Hydrogen flow rate as a function of the ripple amplitude and DC offset.

4.5 Verification and validation

As mentioned earlier, the EEC model as well as the voltage and hydrogen prediction models used to simulate the PEM electrolyser needed to be verified in order to ensure that these models can be used to represent any PEM electrolyser. This verification and the processes used were done and thoroughly discussed in section 4.3.2 and 4.3.5. The LTspice® and Simulink® simulation were further validated by comparing the Nyquist plot and Polarisation curve obtained from the simulations to the actual data measured during the characterisation of the PEM electrolyser.

The validation of the simulation models was done to ensure that the results obtained from the simulations are an accurate representation of a real-world system. Figure 4-45 and Figure 4-46 below show the comparison between the simulated and measured results. These figures confirm that the simulation models are accurate representations of the actual PEM electrolyser. The average percentage deviation of the simulated impedance from the measured impedance values is 0.59% across the entire frequency range, while the average percentage deviation of the simulated cell voltage from the measured voltage values is 0.12% across all of the tested current densities.

**Figure 4-45:** LTspice® model validation.**Figure 4-46:** Simulink® model validation.

The simulations were further validated by comparing the results to the results obtained by Dobó and Palotás in [15]. They conducted a similar study to determine the effects of ripple current on the efficiency of a water electrolysis system; However, they used an alkaline water electrolyser in their study. The electrolyser used in their study was also much smaller in terms of the hydrogen production and power consumption rate. Figure 4-47 presents the power consumption and hydrogen flow rate they obtained as a function of the ripple frequency and ripple factor.

Their results show a decrease in power consumption as the frequency increase and increase in power consumption as the ripple factor increase. A similar trend is observed in the simulation results of this study, as illustrated in Figure 4-48 (a). In both their study results and the simulation results of this study, the average hydrogen flow rate is not affected by the frequency or ripple factor of the applied current. The simulated hydrogen flow rate for this study is presented in Figure 4-48 (b) as a function of the ripple frequency and ripple factor. However, the study conducted by Dobó and Palotás in [15] was on an alkaline water electrolyser. The simulations were therefore also validated by comparing the simulation results to the results obtained from the experimental test on the PEM electrolyser, which is discussed in the next chapter.

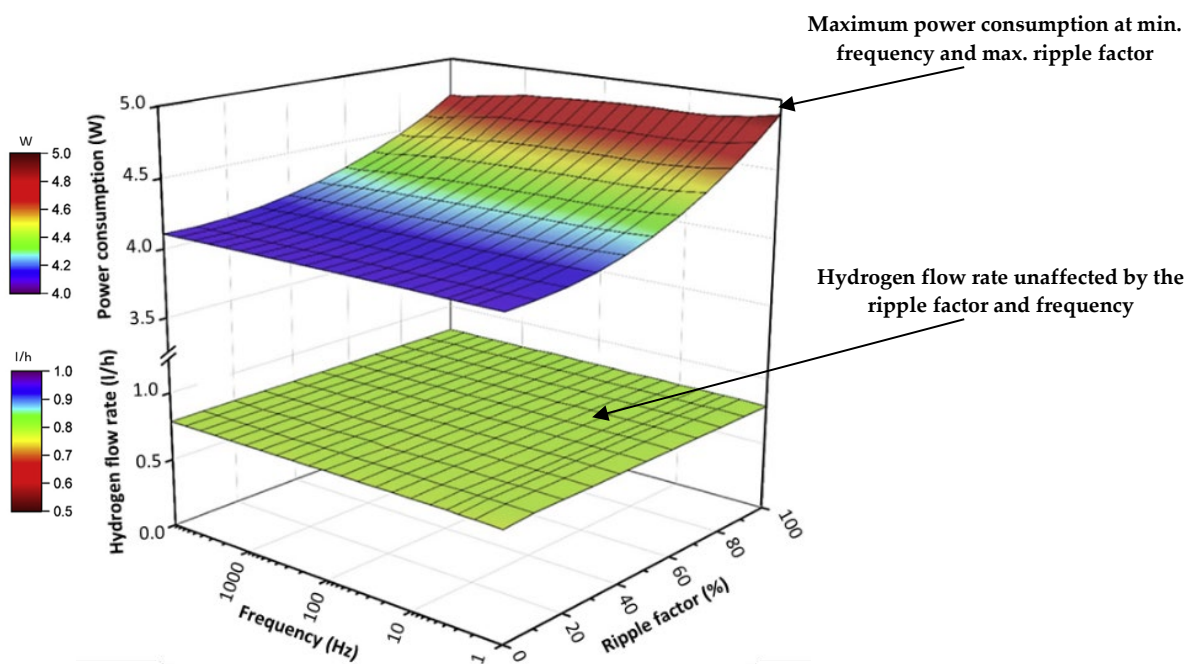


Figure 4-47: Experimental results of Dobó and Palotás (adapted from [15]).

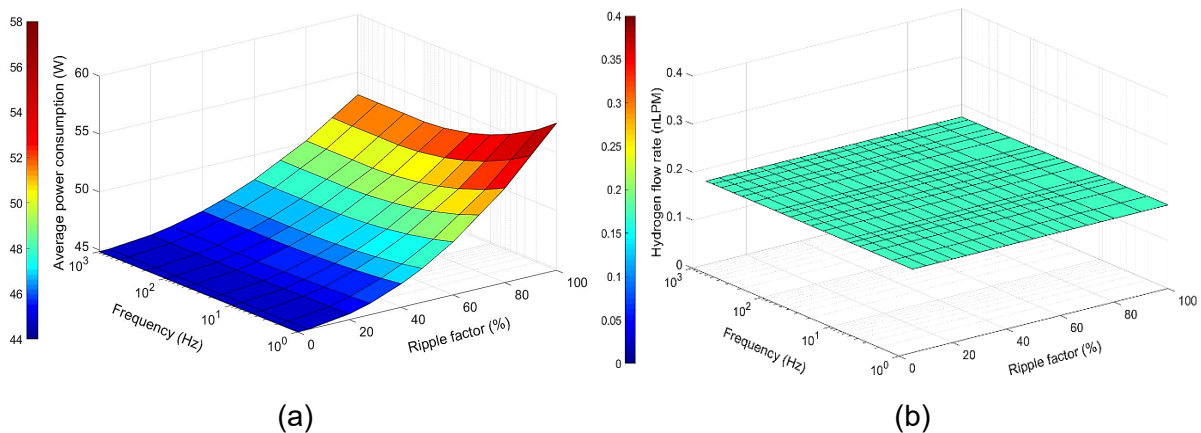


Figure 4-48: Simulation results of this study comparison to that of Dobó and Palotás.

4.6 Conclusion

This chapter opened with the characterisation of the PEM electrolyser to obtain some baseline data on the performance of the electrolyser under DC operating conditions. The characteristics obtained were then used to develop an electrical and mathematical model of the PEM electrolyser. These models were used to simulate the impedance, voltage efficiency, power consumption, open circuit voltage, overpotentials and hydrogen flow rate of the PEM electrolyser at different operating conditions. The simulation results suggest that the cell efficiency would be negatively affected when a ripple current is applied to the electrolyser. By analysing the simulation results, it was determined that the electrical characteristics with the largest effect on the efficiency are the ripple factor and the frequency of the ripple, while the waveform has a minimal effect. Summing up, the highest cell efficiency would be achieved at the lowest possible ripple factor and the highest possible ripple frequency. Furthermore, the simulation results suggest that the hydrogen flow rate is not affected by a ripple current; Therefore, the decrease in efficiency can mainly be assigned to the increase in the power consumption of the PEM electrolyser. The simulations were verified and validated against actual measured data obtained during characterisation of the PEM electrolyser as well as results obtained in previously conducted studies.

The next chapter (Chapter 5) is the results chapter and presents the results obtained during the experimental tests that were done on the PEM electrolyser.

CHAPTER 5: EXPERIMENTAL TEST RESULTS

5.1 Introduction

Having finished the characterisation of the PEM electrolyser and establishing the simulated effects that a ripple current would have on the performance of the PEM electrolyser in the previous chapter (Chapter 4), this chapter presents the results obtained from the experimental tests. The obtained results were verified and validated by comparing it to the simulation results as well as the results of similar studies as presented in the literature study. The chapter structure is presented in Figure 5-1 below.

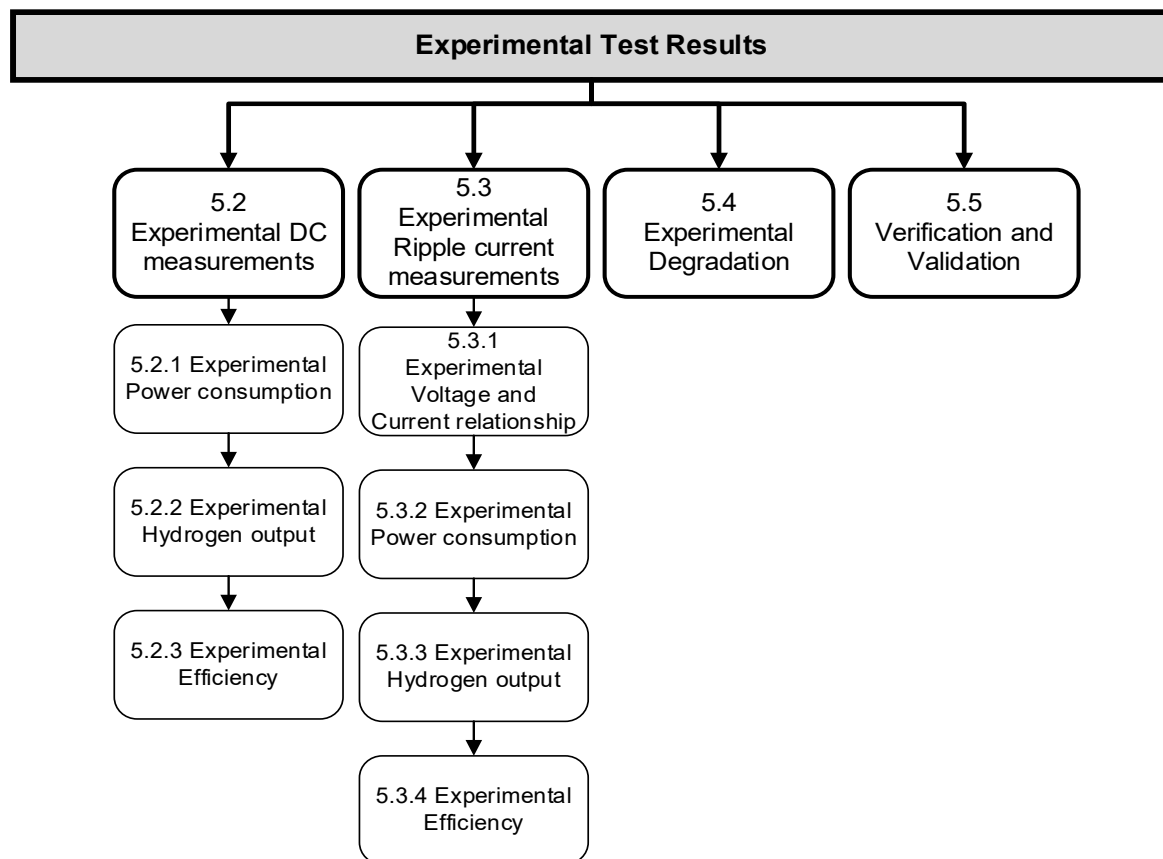


Figure 5-1: Overview diagram of Chapter 5 structure.

Chapter 3 discussed the method and parameter ranges used for the experimental ripple current tests presented in this chapter. As presented earlier, the investigated characteristics include the frequency, AC amplitude, DC offset and waveform of the applied current ripple. The investigated frequency range is from 1 Hz to 1 kHz, the AC amplitude from 0 A to 25 A and the waveforms are limited to sinusoidal, triangular and square waves. In order to analyse the influence of these parameters on the dynamic behaviour of the PEM electrolyser, the parameter values were changed while the voltage response, power consumption and hydrogen flow rate were measured at each experiment.

The main objective of this study is to determine the effect of these ripple current parameters on the efficiency of the PEM electrolyser. The efficiency of any energy conversion system, such as an electrolyser which converts electrical energy into hydrogen gas, can be defined as the ratio between the useful energy output and the required energy input. The energy input of a PEM water electrolysis cell can be defined by equation (5.1) [87] below;

$$\text{Energy input} = P_{cell} = U_{cell} \cdot I \cdot t \quad (5.1)$$

where P_{cell} is the electrical power measured in Watts or Joules per second, U_{cell} is the cell potential measured in Volts, I is the current measured in Amperes and t the time in seconds. In a water electrolysis process, only hydrogen gas is considered to be a useful energy output. Equation (2.35) gives the theoretical molar flow rate of the hydrogen gas output of a PEM water electrolysis process. However, the actual hydrogen flow rate is lower than the theoretical flow rate due to hydrogen and current losses within the cell [73, 161]. The energy output of a PEM water electrolysis cell, measured in Joules per second, can be defined by equation (5.2) [87] below;

$$\text{Energy output} = \dot{n}_{H_2,act} \cdot t \cdot HHV \quad (5.2)$$

where $\dot{n}_{H_2,act}$ is the actual hydrogen molar flow rate measured in mol per second, HHV the higher heating value in Joules per mol and t the time in seconds. Efficiency calculations using the HHV is preferred over the LHV when liquid water is used, because of the enthalpy of evaporation that needs to be provided by the electrolyser [42]. In this chapter, the energy input and output of the PEM electrolyser are discussed and analysed for each of the conducted experiments at various DC offset, frequency and AC amplitude values at three different waveforms. The experimental tests were divided into three major sections, with the first being steady DC measurements and the second the ripple current measurements and lastly the degradation measurements. All the experiments were conducted using the experimental setup presented earlier in sections 3.4 and 3.5 of the design chapter (chapter 3).

5.2 Experimental DC measurements

The effect of the DC offset on the behaviour of the PEM electrolyser was studied separately with the intention of doing the rest of the experiments using only a single DC offset value. The steady DC measurements also provided a baseline to compare the rest of the experiments against. The current density was changed from 0 A/cm² (0 A) to 1 A/cm² (25 A) in 0.02 A/cm² (0.5 A) increments while the voltage and hydrogen flow rate were measured. There was a 5-minute waiting period between each current density change to allow the electrolyser to stabilise. In the following three subsections the power consumption, hydrogen output and the efficiency of the PEM electrolyser at each of the DC offset values are illustrated and discussed.

5.2.1 Experimental Power consumption

The measured, as well as the theoretical, power consumption of the PEM electrolyser is illustrated as a function of the DC offset or current density in Figure 5-2 below. The theoretical power consumption would be the power consumed by the electrolyser if the cell operated without any voltage losses (100% Voltage efficiency). The theoretical power consumption was calculated as the product of the current applied to the cell and the thermoneutral voltage ($P_{theor} = E_{th}I$) while the measured power was calculated as the product of the current applied to the cell and the measured cell voltage ($P_{measured} = U_{cell}I$) [17]. Since the current is the controlled variable, the ratio between the measured and the theoretical power consumption gives the ratio between the cell voltage and the thermoneutral voltage which is also known as the voltage efficiency of the electrolyser. The voltage efficiency, which is also illustrated on the figure, decreases as the current density is increased. This is caused by an increase in the cell voltage at elevated current densities. Furthermore, the results show that the power consumption of the PEM electrolyser has a nonlinear response to the DC offset, which is caused by the nonlinear voltage response as shown in the polarisation curve of the cell in section 4.2.1. At a DC offset of 25 A or a current density of 1 A/cm², the measured power consumption was 44.83 W while the theoretical power consumption at the same current density is 37 W. This gives a voltage efficiency of 82.5% at a DC offset of 25 A, which is the DC offset at which the rest of the experiments were done.

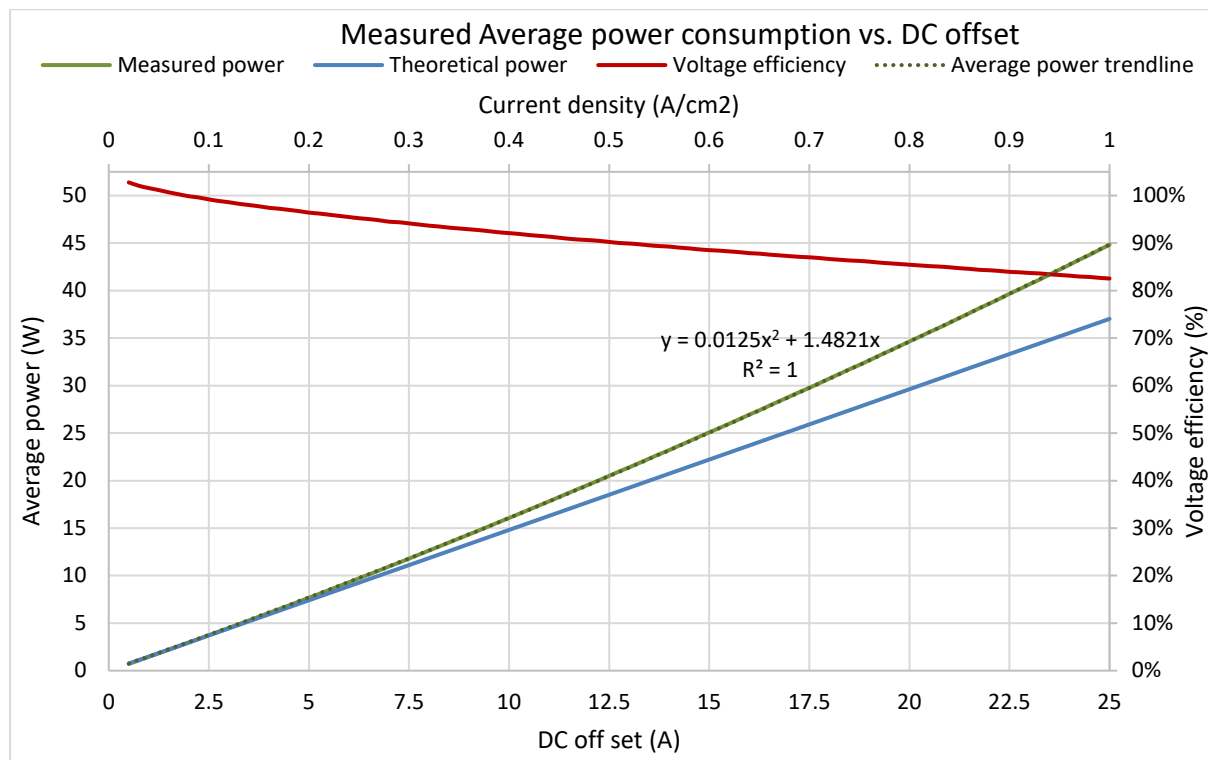


Figure 5-2: Theoretical and measured power consumption at various DC offsets or current densities.

5.2.2 Experimental Hydrogen output

The measured, as well as the theoretical hydrogen flow rates, are shown in Figure 5-3 as a function of the DC offset or current density applied to the electrolyser. The hydrogen gas formation started at a cell voltage of 1.44 V and increased linearly as the DC offset increased. The theoretical flow rate is the ideal hydrogen production rate in the absence of any current or gas losses (100% Faradaic efficiency), as discussed in section 2.4.3.2 of the literature study. The difference between the theoretical and measured hydrogen flow rate indicates that current and/or gas losses are present.

The impact of these losses can be illustrated with the Faradaic efficiency, which is the ratio between the measured and theoretical flow rates. The Faradaic efficiency, which is also plotted on the graph, shows a sharp increase up to a current density of 0.2 A/cm² where after the increase slows down. This response is in good agreement with the literature on similar experiments as presented by Tijani and Rahim in [97]. At a DC offset of 25 A or a current density of 1 A/cm², the measured hydrogen flow rate was 0.1310 nLPM while the theoretical flow rate at the same current density is 0.1742 nLPM. This gives a Faradaic efficiency of 75.2% at a DC offset of 25 A, which is the DC offset at which the rest of the experiments were done.

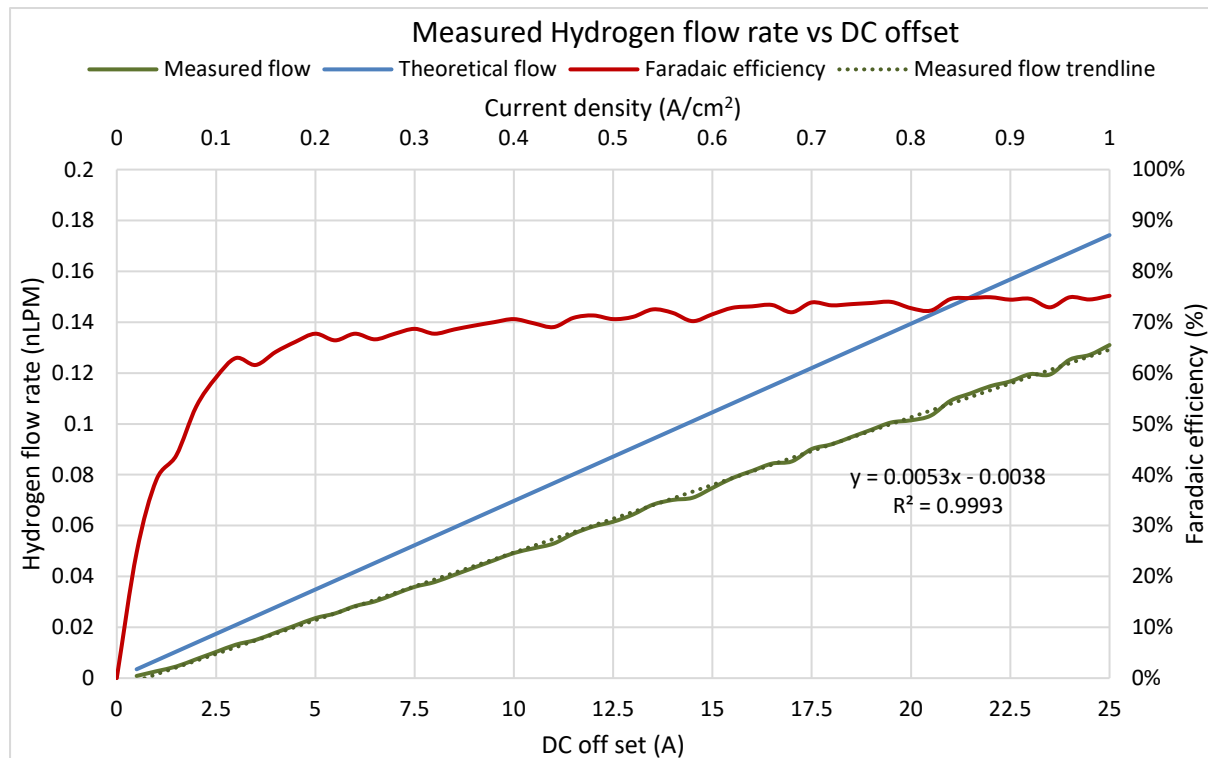


Figure 5-3: Theoretical and measured hydrogen flow rate at various DC offsets or current densities.

5.2.3 Experimental Efficiency

In the sections above the voltage and the Faradaic efficiency of the PEM electrolyser were illustrated at various DC offset values. The voltage efficiency is a measure of the cell voltage losses and the Faradaic efficiency a measure of the cell current losses. The next step is to determine the total cell efficiency, which is a measure of all input energy losses. The measured power consumption and hydrogen flow rates were used to calculate the total cell efficiency of the PEM electrolyser with the following formula [42, 66]:

$$\varepsilon_{cell}^{HHV} = \frac{HHV \cdot \dot{n}_{H_2}}{I_{cell} \cdot U_{cell}} \quad (5.3)$$

where $\dot{n}_{H_2}$ is the measured hydrogen flow rate, U_{cell} the measured cell voltage, I_{cell} the applied current and HHV is equal to 285.83 kJ.mol⁻¹. The hydrogen flow rate was measured in normal litres per minute (nLPM) while the hydrogen flow rate in equation (5.3) is the molar flow rate in moles per second (mol.s⁻¹). To convert the measured flow rate to the molar flow rate, the gas density was first calculated at normal temperature and pressure conditions (273.15K and 1 atm) using a modified form of the ideal gas law as illustrated below.

$$V = \frac{nRT}{P} \quad (5.4)$$

$$\text{with } n = \frac{m \text{ (Mass of the gas)}}{MM \text{ (Molecular mass)}} \quad (5.5)$$

$$\frac{m}{V} = \frac{MM \cdot P}{RT} = \frac{2.01588 \text{ g} \cdot \text{mol}^{-1} \cdot 1 \text{ atm}}{0.082057 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 273.15 \text{ K}} = 0.08993895478 \text{ g} \cdot \text{L}^{-1} \quad (5.6)$$

With the gas density of hydrogen under normal conditions know, the measured flowrate in nLPM was then converted to the molar flow rate in mol.s⁻¹ as demonstrated by equation (5.7).

$$\dot{n}_{H_2} = \frac{nLPM \cdot 0.08993895478 \text{ g} \cdot \text{L}^{-1}}{2.01588 \text{ g} \cdot \text{mol}^{-1} \cdot 60 \text{ s}} \quad (5.7)$$

All the measured, calculated and constant values were then substituted into equation (5.3) to calculate the efficiency of the PEM electrolyser over a range of current densities (0 A/cm² to 1 A/cm²). Figure 5-4 below shows the calculated cell efficiency results as a function of the applied DC offset or current density. It is observed that in the low current density region (0 – 0.2 A/cm²) the increase in the cell efficiency directly corresponds to the increase in the Faradaic efficiency since the cell voltage is close to the thermoneutral voltage in this region. However, as the DC offset or current density further increases the increase in the Faradaic efficiency slows down, and the decrease in the voltage efficiency becomes superior. In the high current density region (> 0.2 A/cm²), the cell efficiency thus decreases as the DC offset value is increased.

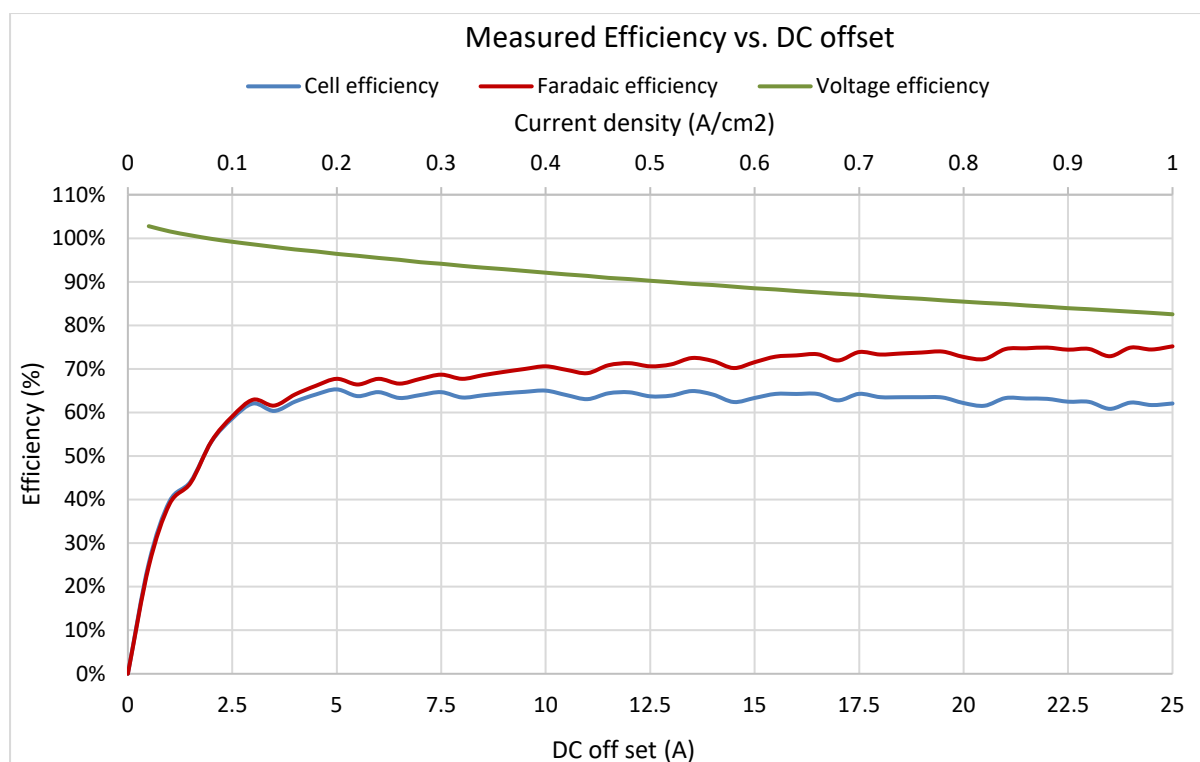


Figure 5-4: Hydrogen flow, Cell voltage and Cell efficiency at various current densities.

5.3 Experimental ripple current measurements

The second and most important part of the study was the ripple current experiments conducted on the PEM electrolyser. The purpose of these experiments was to determine how the dynamic behaviour of the PEM electrolyser is affected by different ripple current parameter settings such as the AC amplitude, frequency and waveform. In the following sections, the voltage response, power consumption, hydrogen production rate and efficiency of the PEM electrolyser are discussed for all considered parameter settings as presented in section 3.6.2.

5.3.1 Experimental Voltage and Current Relationship

This first subsection is devoted to the voltage response of the PEM electrolyser as observed at current ripples with different parameter values. In a recent study by Ruuskanen *et al.* [162], they attempted to determine the effects of ripple current on the efficiency of a PEM electrolyser by measuring the RMS and mean voltage and current of the cell. The results that they obtained showed that the RMS and mean voltage and current alone does not give an accurate estimate of the effect of a ripple current on the efficiency and power quality of the PEM electrolyser, but only an indication of the possible effects. They recommended that the voltage and current waveforms should also be measured as a function of time in order to accurately determine the effect of a current ripple on the efficiency and power quality of a water electrolyser.

5.3.1.1 Experimental Voltage and Current waveforms

In the following figures, the measured applied current and voltage response of the PEM electrolyser for a few of the conducted experiments are presented as a function of time. Figure 5-5 present the measured voltage response of a sinusoidal ripple current with a frequency of 50 Hz and a DC offset of 25 A at several different AC amplitudes. This figure illustrates the effect that the AC amplitude or ripple factor of the applied ripple current have on the voltage response of the PEM electrolyser. The main observations made from this figure is that the voltage response has the same waveform as the applied current and although the ripple factor of the voltage response increase as the ripple factor of the applied current increase, the increase observed in the cell voltage is much smaller.

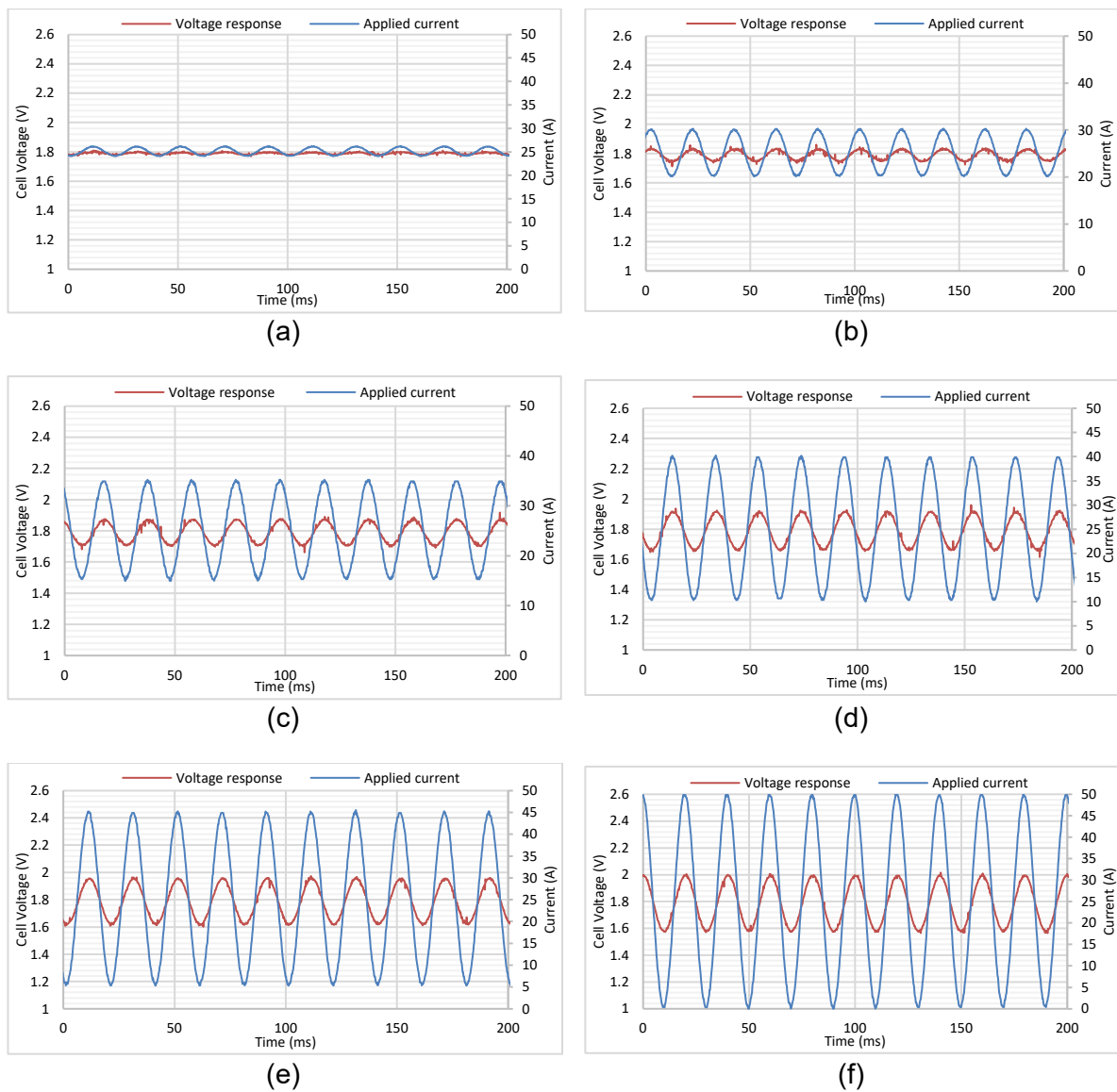


Figure 5-5: Voltage response of a sinusoidal ripple current with a frequency of 50 Hz, a DC offset of 25 A and an AC amplitude of (a) 1 A, (b) 5 A, (c) 10 A, (d) 15 A, (e) 20 A and (f) 25 A.

The next figure, Figure 5-6, present the measured voltage response of a triangular ripple current with an AC amplitude of 20 A and a DC offset of 25 A at several different ripple frequencies. The purpose of this figure is to illustrate the effect of the ripple frequency on the voltage response of the PEM electrolyser. This figure shows that the RF, and therefore the RMS value of the voltage response, is also affected by the frequency of the applied ripple current.

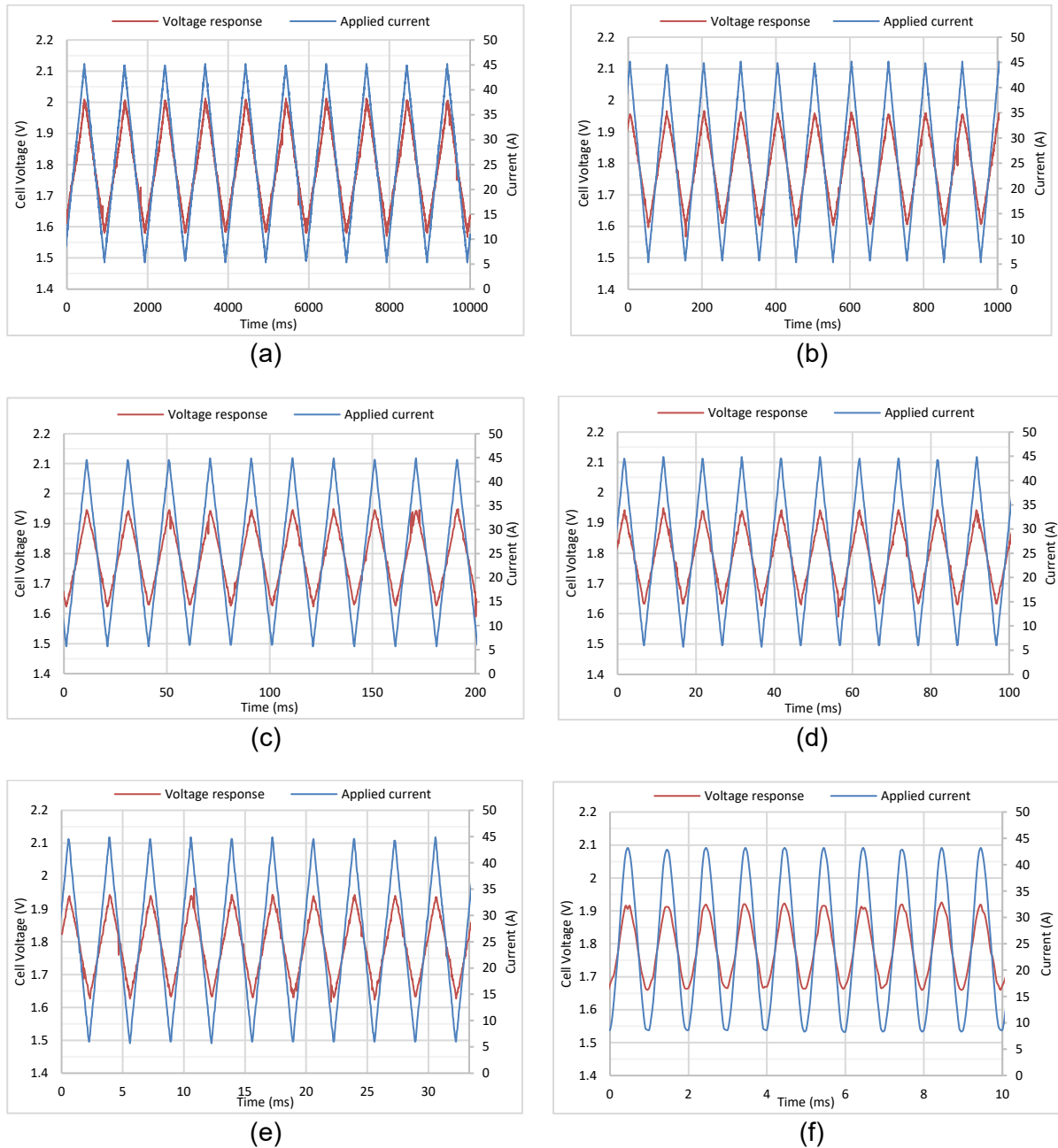
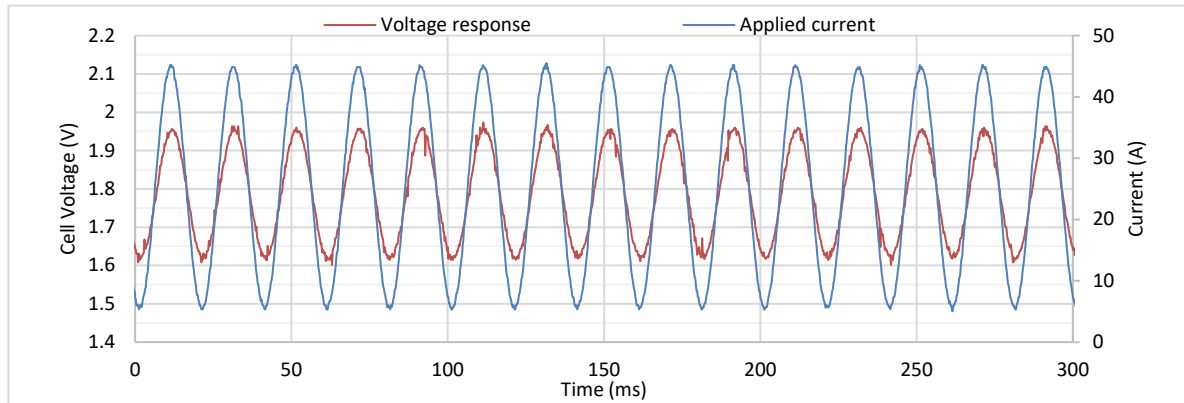
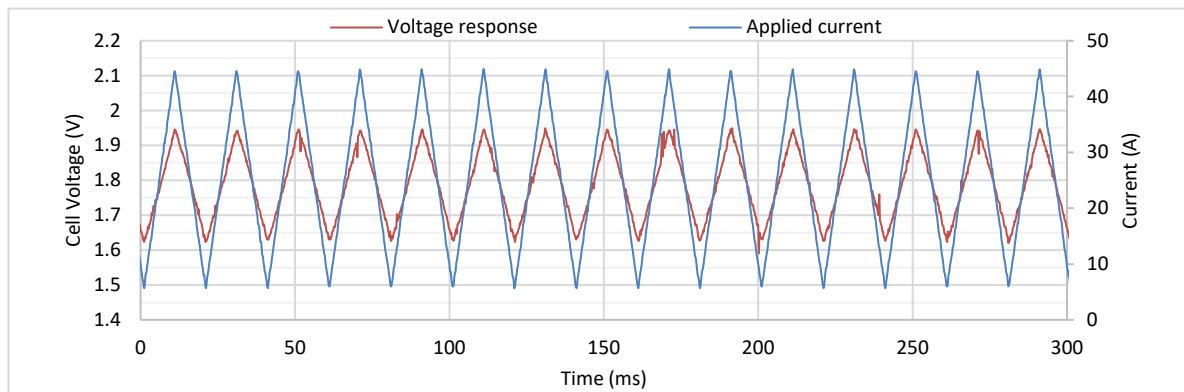


Figure 5-6: Voltage response of a triangular ripple current with a DC offset of 25 A, an AC amplitude 20 A and a frequency of (a) 1 Hz, (b) 10 Hz, (c) 50 Hz, (d) 100 Hz, (e) 300 Hz and (f) 1000 Hz.

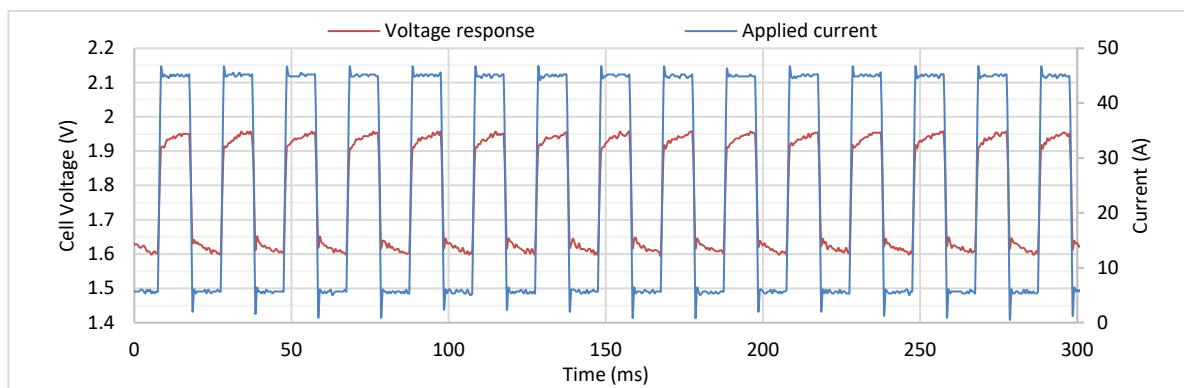
Finally, Figure 5-7 present the measured voltage response of all the considered waveforms (sinusoidal, triangular and square) for a current ripple with a frequency of 50 Hz, a DC offset of 25 A and an AC amplitude of 20 A. The purpose of this figure is to illustrate the effect of the ripple waveform type on the voltage response of the PEM electrolyser. It is observed that the DC offset and AC amplitude of the voltage response is close to the same irrespective of the waveform. However, the RMS values of the voltage response are different for each waveform since the waveforms have different crest factors.



(a)



(b)



(c)

Figure 5-7: Voltage response of a ripple current with a frequency of 50 Hz, a DC offset of 25 A, an AC amplitude of 20 A and a (a) Sine, (b) Triangular and (c) Square waveform.

5.3.1.2 Experimental Voltage and Current RMS values

As previously stated, the above figures only show the measured response of a few of the conducted experiments for illustrative purposes. Figure 5-8 to Figure 5-10 below summarise the effect of a ripple current on the voltage response of the PEM electrolyser for all of the conducted experiments. The measured results for each of the considered waveforms are illustrated respectively on a plot of the RMS current (I_{rms}) and RMS voltage (U_{rms}) as a function of the ripple factor and frequency. These figures show how the RMS voltage values are affected by the RF, frequency and waveform of the applied ripple current. The applied current is the controlled variable, and the RMS value of the current is thus unaffected by frequency. The results for a sinusoidal wave ripple current is shown in Figure 5-8, for a triangular ripple current in Figure 5-9 and for a square wave ripple current in Figure 5-10 below.

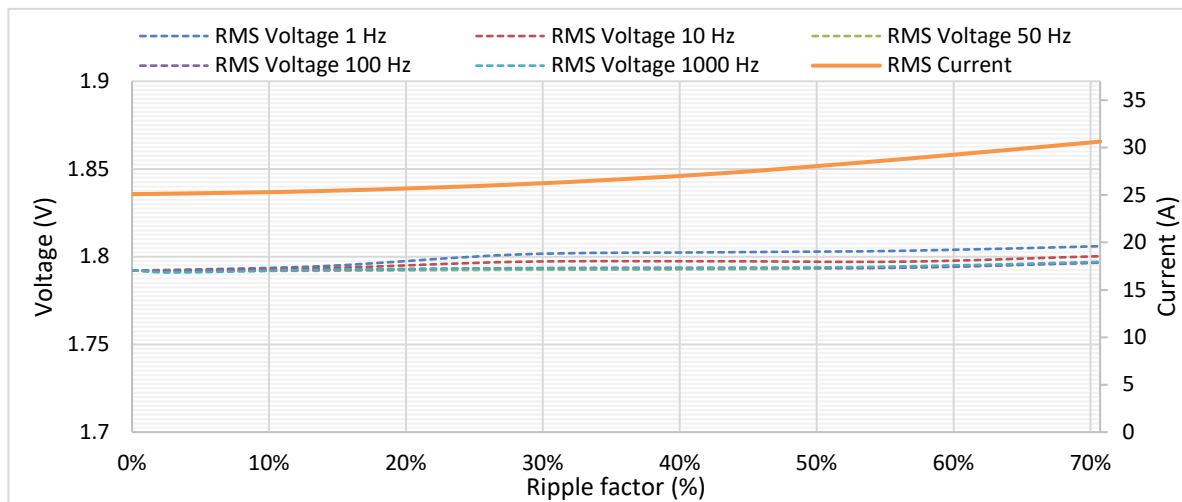


Figure 5-8: Sinusoidal wave RMS current and RMS voltage response at different ripple current parameters.

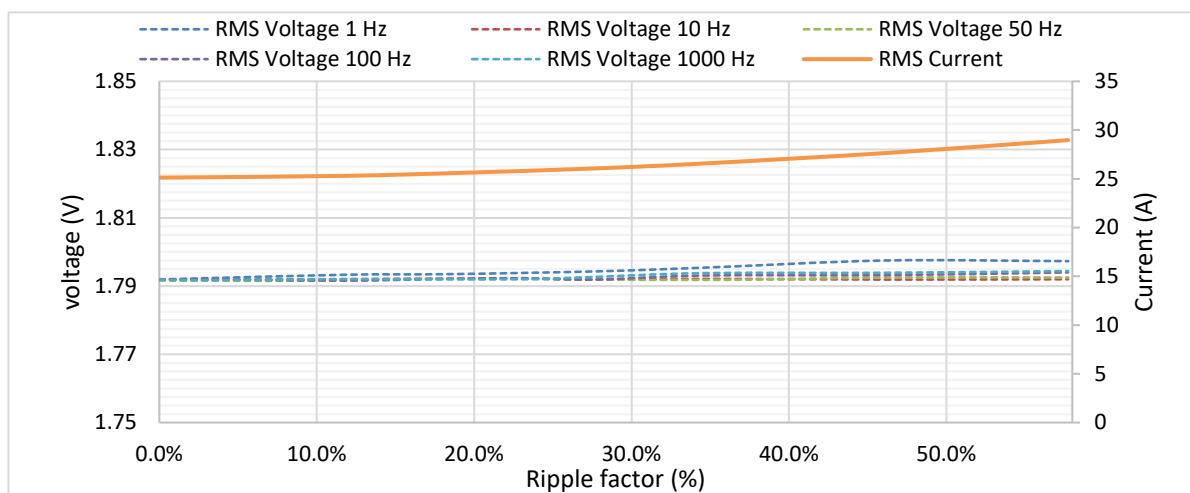


Figure 5-9: Triangular wave RMS current and RMS voltage response at different ripple current parameters.

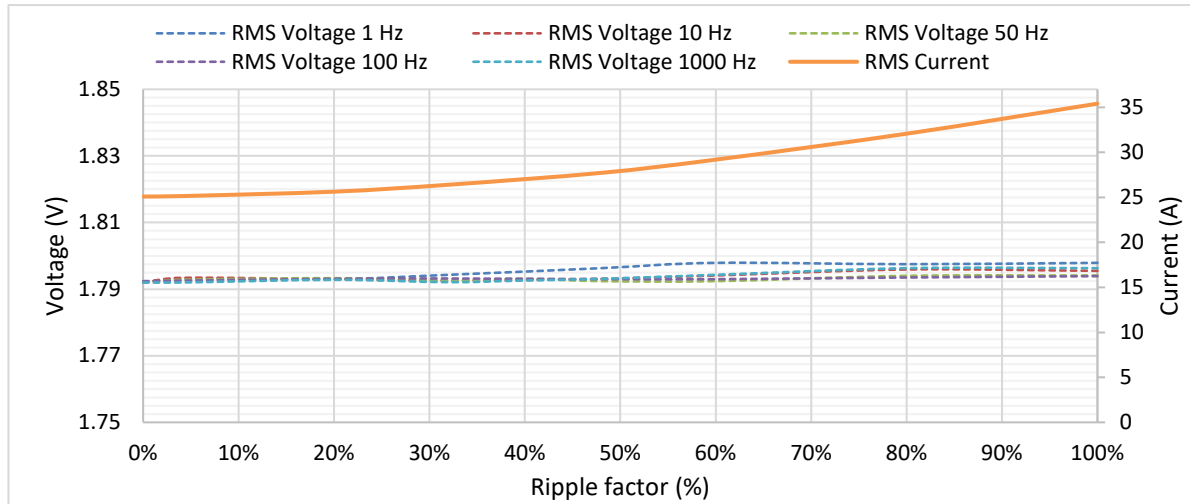


Figure 5-10: Square wave RMS current and RMS voltage response at different ripple current parameters.

It is observed that the effect that the ripple factor and frequency have on the RMS voltage of the PEM electrolyser is different for different waveforms. However, regardless of the waveform, an increase in the RMS voltage is observed as the ripple factor of the current increase. Figure 5-8 above shows that for a sine wave ripple current, the RMS voltage of the PEM electrolyser decreases as the ripple frequency increases. The RMS voltage of the electrolyser was thus the lowest for frequencies above 50 Hz. However, in the case where a triangular ripple current was applied, the RMS voltage of the electrolyser was the lowest for frequencies ranging from 10 Hz to 100 Hz. This is different for a square wave ripple current as well in which case the RMS voltage was the lowest between 50 Hz and 100 Hz. Nevertheless, the results are in good agreement with the simulation results discussed in section 4.4.1.2 of the previous chapter. The reason that the effect of frequency is different for different waveforms is due to the difference in the frequency spectrum of each waveform, as explained in section 4.4.2.1.

Although the figures above show that the RMS voltage is affected by the frequency of the applied ripple current, no clear trend is observed in the RMS voltage as a function of the RF. This is primarily due to the low voltage of the single cell electrolyser used in this study. A different approach was thus necessary to analyse the RMS current and voltage values as a function of the ripple current. In a recent study by Ruuskanen *et al.* [162] they showed that the difference between the RMS and mean voltage and current values can be used to obtain an estimate of the power quality supplied to the electrolyser. They found that the difference between the RMS and mean voltage and current values can be used as an estimation of the additional losses caused by a current ripple.

In Figure 5-11 below, the difference between the cell RMS current (I_{rms}) and mean current (I_{DC}) values is plotted as a function of the current AC and DC components. Further, the difference between the cell RMS voltage (U_{rms}) and mean voltage (U_{DC}) values are plotted as a function of the current AC and DC components in Figure 5-12. The DC component of the applied current ripple is equal to the mean current (I_{DC}) while the AC component is defined using the ripple factor (RF). A 100% ripple factor means that the RMS value of the AC component is equal to the DC component. The figures show that the current losses increase linearly as a function of the DC component while the ripple factor determines the rate of the increase. A similar trend is observed in the voltage losses, although the increase is nonlinear as an effect of the electrolyser polarisation curve. It is also observed that the current losses are significantly larger than the voltage losses, which verifies the results shown in the figures above. To illustrate the small effect of the current AC component on the RMS voltage of the cell, the measured polarisation curve at different RF's is shown in Figure 5-13.

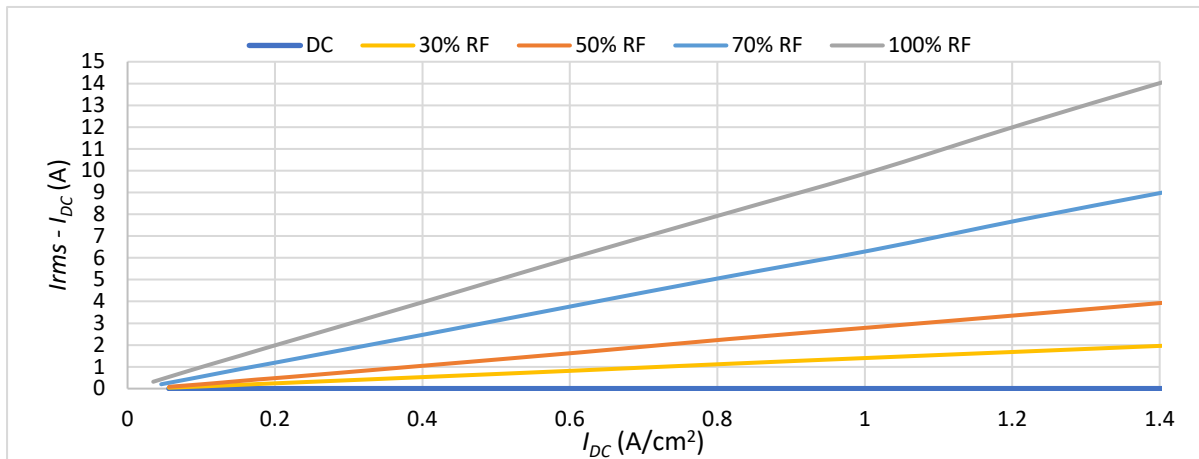


Figure 5-11: Experimental difference between the current RMS and mean values as a function of the current AC and DC components.

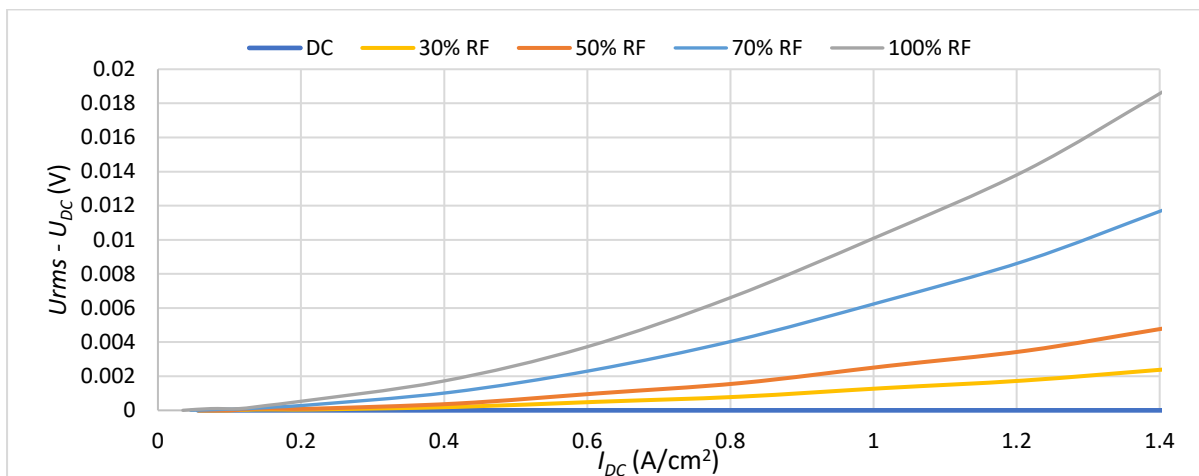


Figure 5-12: Experimental difference between the voltage RMS and mean values as a function of the current AC and DC components.

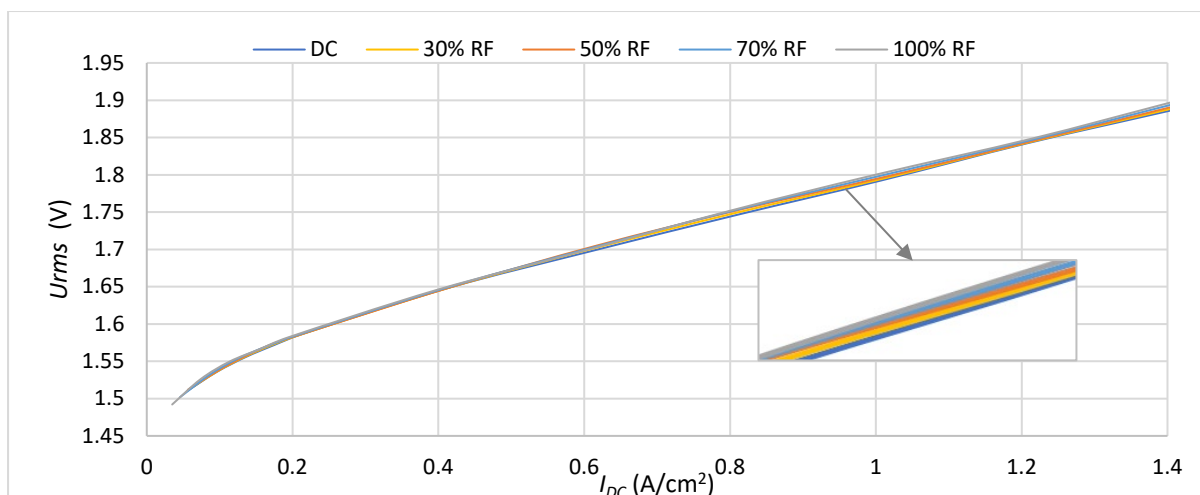


Figure 5-13: Experimental cell RMS voltage as a function of the current AC and DC components.

5.3.1.3 Experimental Voltage and Current hysteresis

Since the frequency of the ripple current is shown to affect the behaviour of the PEM electrolyser, a further investigation on this matter was required. The measured voltage and current were plotted in v-i plots to investigate the hysteresis between the voltage and current at different frequencies. Figure 5-8 shows the v-i plots for a sinusoidal wave ripple current, Figure 5-9 for a triangular wave ripple current, and Figure 5-10 for a square wave ripple current; each at various frequencies.

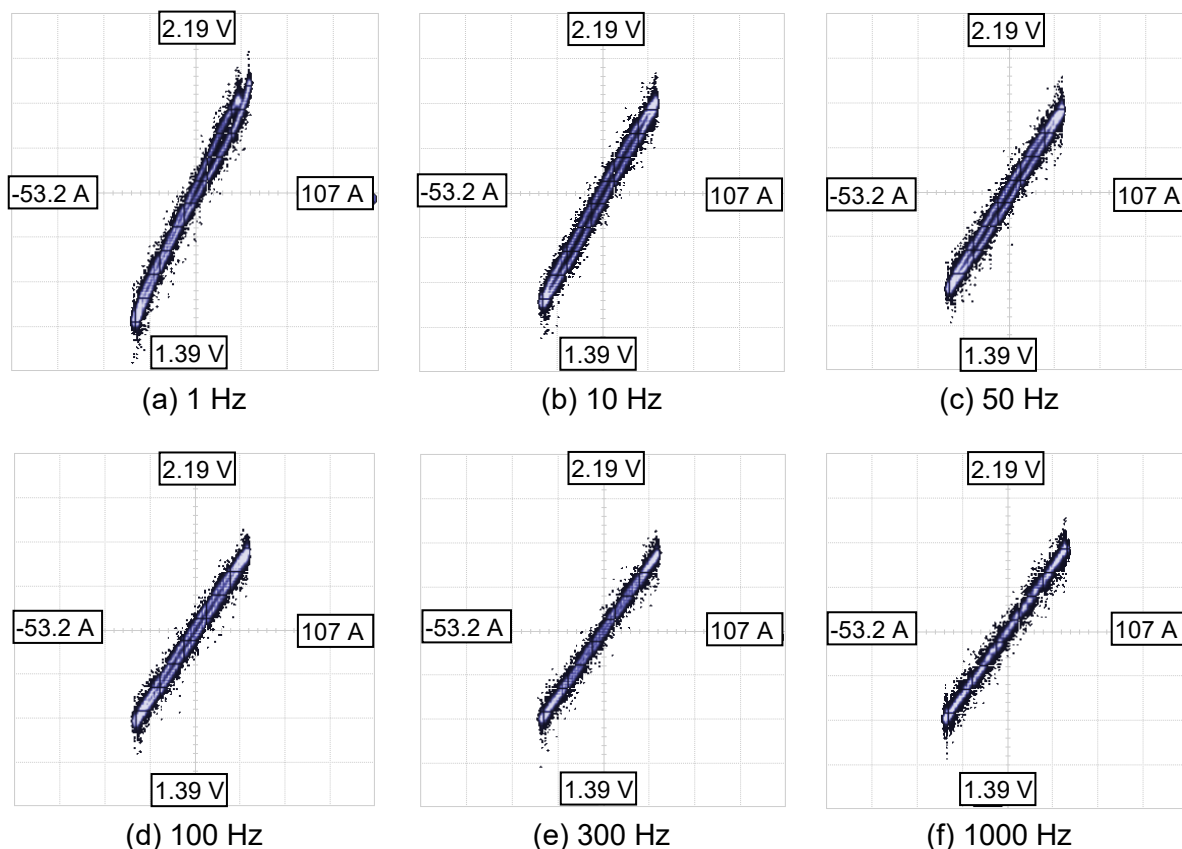


Figure 5-14: PEM electrolyser voltage and current hysteresis with sine wave ripple.

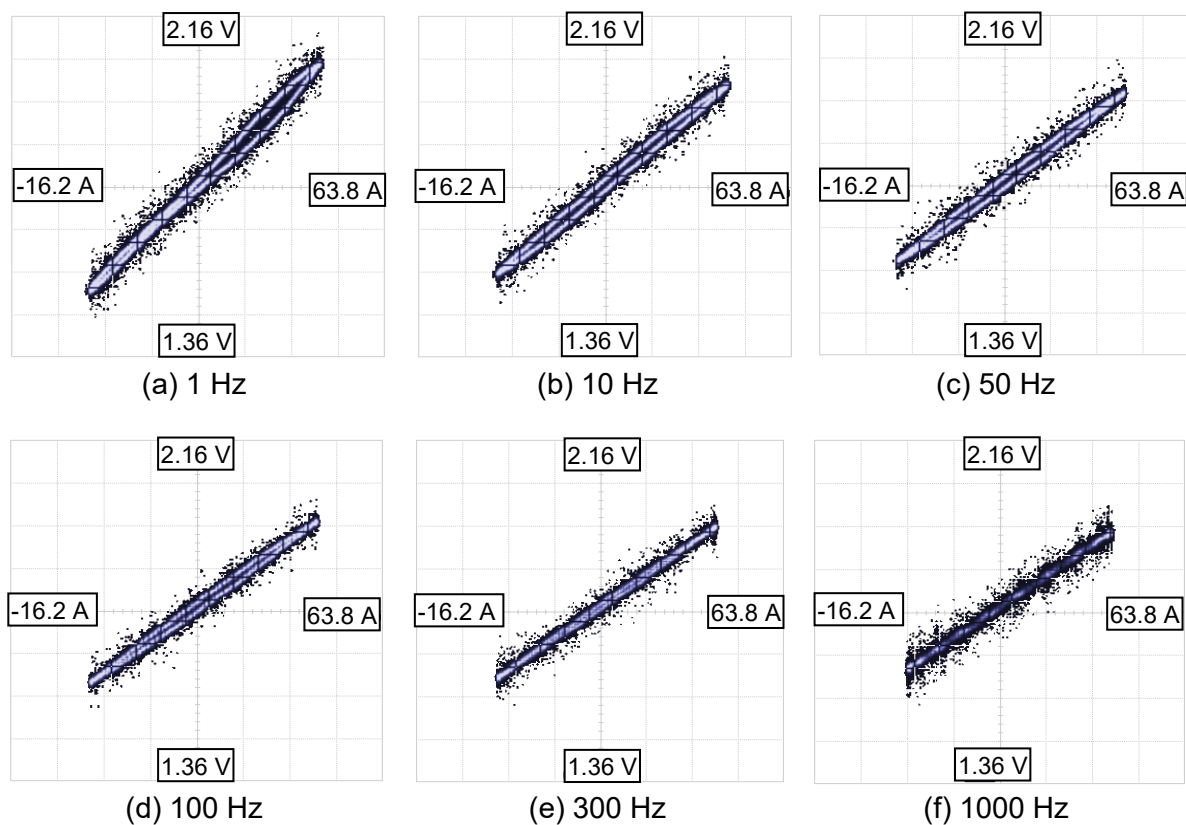


Figure 5-15: PEM electrolyser voltage and current hysteresis with triangular wave ripple.

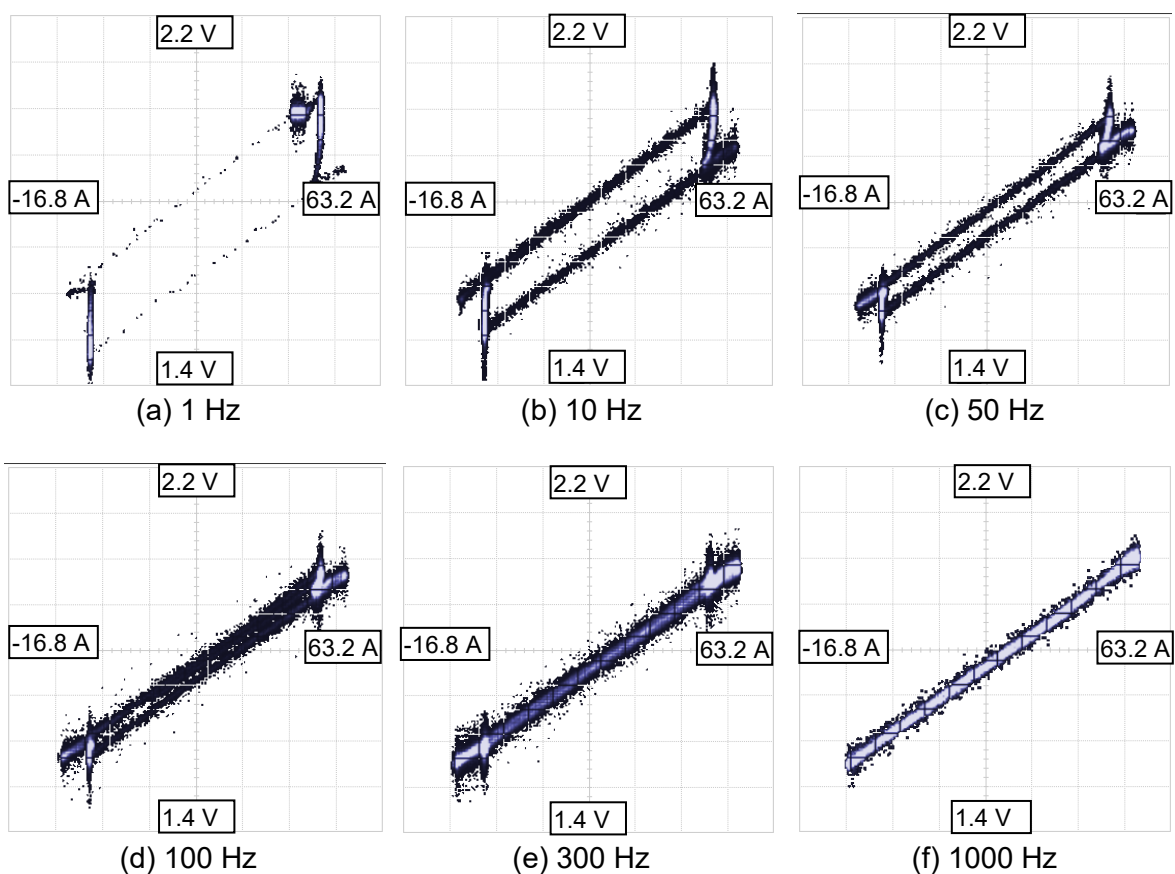


Figure 5-16: PEM electrolyser voltage and current hysteresis with square wave ripple.

It is observed that the hysteresis between the voltage and current are the largest for frequencies below 300 Hz which indicates that the voltage and current are out of phase. The hysteresis at low frequencies is due to the double layer capacitance, which is caused by ions that form a layer on the electrode surface and as a result, separates the charged electrodes from the charged ions. The effect of frequency on the hysteresis can thus be explained by the impedance related to the double layer capacitance (imaginary part) which decreases as the frequency increases and approaches 0 Ω at frequencies above 300 Hz. The relation between the impedance and frequency were illustrated by the baseline EIS test in Figure 4-3. The effect of frequency on the impedance and phase shift is also illustrated in section 4.4.1.1 of the simulation chapter through simulated Nyquist and bode plots. The hysteresis between the voltage and current fades at high frequencies since the impedance of the double layer capacitance reduces.

5.3.2 Experimental Power consumption

The results in section 5.3.1 above show that any deviation from steady DC causes additional voltage losses to occur. Although at certain parameter values the change in voltage is arguably negligible, when the ripple factor of the applied current increases the RMS value of the current also increase, which would then cause the power consumption to increase. Section 5.3.1 also shows that at low frequencies, a noteworthy hysteresis exists between cell voltage and current. This occurrence indicates that the cell voltage and current are out of phase, which will cause an increase in the power consumption of the electrolyser. It is thus expected to see an increase in the power consumption as the ripple factor increase and a decrease in the power consumption as the frequency increase. The following two formulas illustrate the relation between the applied current, measured voltage and the power consumption of the cell,

$$P = UI \quad (5.5)$$

$$P_{avg} = \frac{1}{T} \int_0^T UI \cdot dt \quad (5.6)$$

where P is the instantaneous power, P_{avg} the average power, U the measured cell voltage, I the applied current and T the periodic time of the waveform [15]. Since the PEM electrolyser was operated at a temperature below 100 °C, the electrical power consumed by the cell is considered to be the only form of energy input into the system, as discussed in section 2.5.1 of the literature study. The power consumption of the cell thus plays a crucial part in the efficiency of the cell.

5.3.2.1 Measurement Procedure

A large number of experiments needed to be done in order to cover all the parameter values in the ranges set out in the design chapter. Each experiment was thus only run for a short time while current, voltage and power were measured using an oscilloscope. The oscilloscope displays the instantaneous values of the current, voltage as well as the power, which is the product of the instantaneous current and voltage as per equation (5.5). The average power, as illustrated by equation (5.6), was then determined by obtaining the mean value of the instantaneous power function. An example of a current, voltage and power measurement for one of the conducted experiments is shown in Figure 5-17 below. This figure is a screen shot of the oscilloscope's display and illustrates the different parameters that were measured with the oscilloscope and the accompanying probes.

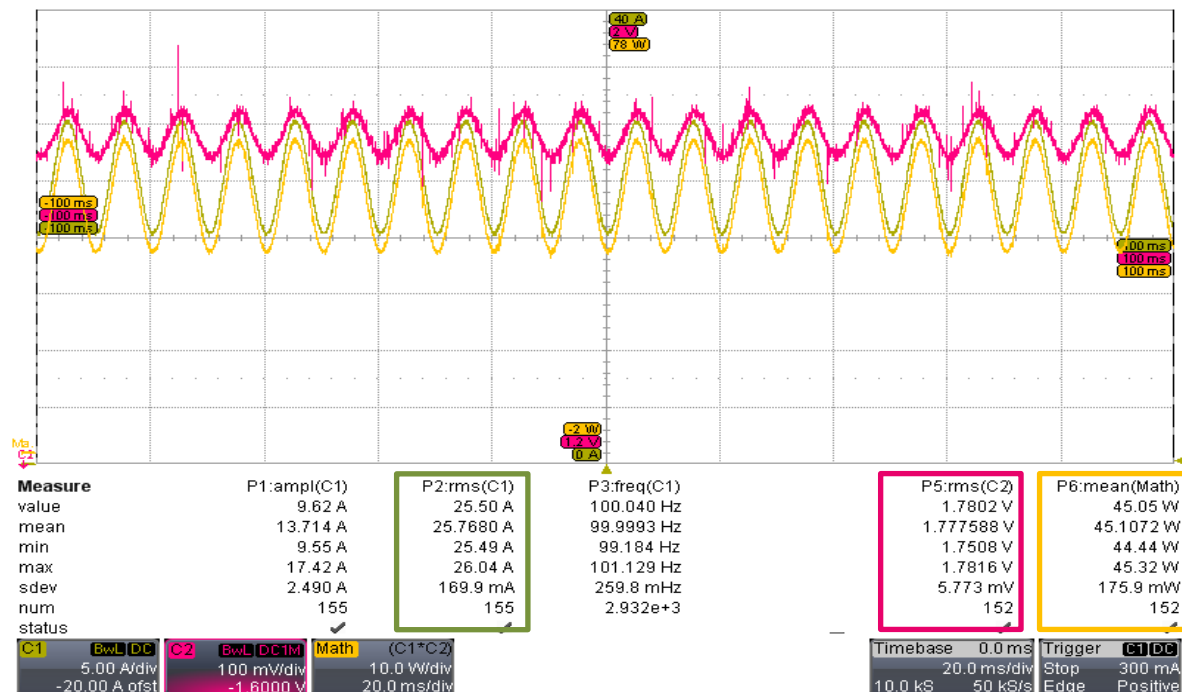


Figure 5-17: Instantaneous current (C1), voltage (C2) and power (Math).

5.3.2.2 Measurement Results

Figure 5-18 shows the average power consumption of the PEM electrolyser as a function of the ripple factor at various frequencies. The applied ripple current has a sinusoidal waveform and a DC offset of 25 A. The power consumption at a 0% RF, is about 45.1 W which is in good agreement with the DC measurements illustrated in Figure 5-2. The ripple factor was then incrementally increased to the maximum achievable ripple factor which also caused the average power consumption to increase. At a maximum frequency of 1 kHz and a ripple factor of 14.1% (AC amplitude 5 A), the power consumption is 45.3 W, at 42.4% (AC amplitude 15 A) it increases to 46.1 W and at 70.7% (AC amplitude 25 A) it further increases to 47.5 W.

The figure also shows that the effect of frequency on the power consumption is the highest at frequencies below 50 Hz which corresponds with the literature and simulation results. At a maximum ripple factor of 70.7% and a frequency of 1 Hz, the power consumption is 48.8 W, at 10 Hz it decreases to 48.2 W, and at 50 Hz it further decreases to 47.6 W. Above 50 Hz the frequency of the ripple has only a minor effect on the average power consumption. It is also evident that the effect of frequency on the power consumption increase as the ripple factor increase.

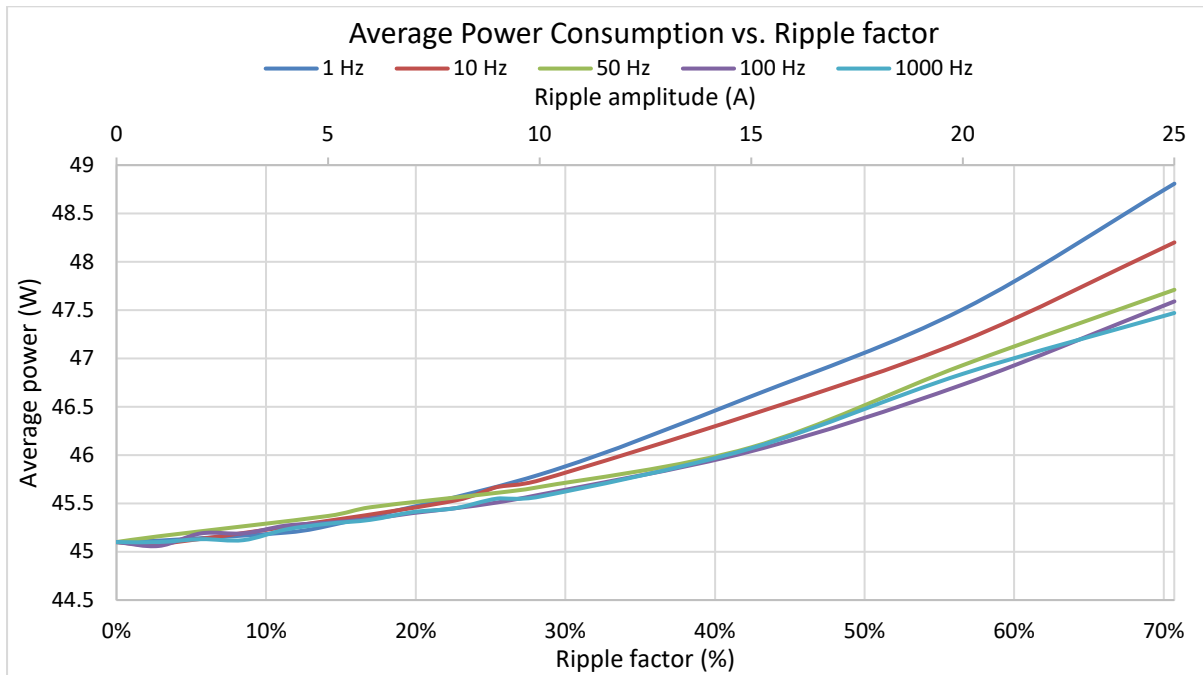


Figure 5-18: Average power consumption vs. ripple factor for a sinusoidal ripple current with a DC offset of 25A.

Similar experiments were conducted using triangular and square waveforms to compare the effect of the waveform type on the power consumption. Figure 5-19 below shows the average power consumption of the PEM electrolyser as a function of the ripple factor at various frequencies when a ripple current with a triangular waveform and a DC offset of 25 A is used. The ripple factor was increased from 0% to the maximum achievable ripple factor of 57.7% at each of the considered frequencies. As was the case with a sinusoidal ripple current, the maximum power consumption with a triangular ripple was observed at the maximum achievable ripple factor (57.7%) and the lowest frequency (1 Hz). To summarise, an increase in the ripple factor results in an increase in the power consumption while an increase in frequency has the opposite effect.

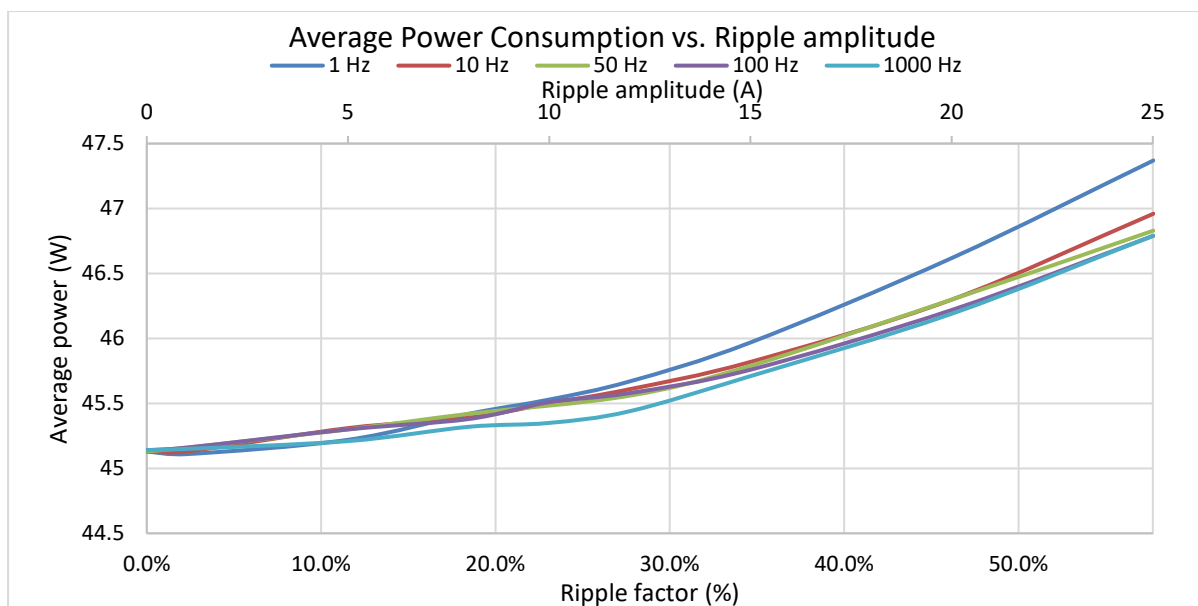


Figure 5-19: Average power consumption vs. ripple factor for a triangular ripple current with a DC offset of 25A.

Figure 5-20 shows the average power consumption of the PEM electrolyser as a function of the ripple factor at various frequencies when a ripple current with a square wave waveform and a DC offset of 25 A is used. The ripple factor was incrementally increased from 0% to the maximum achievable ripple factor of 100% at each of the considered frequencies. The results agree with the results for sinusoidal and triangular waveforms and show that an increase in the ripple factor results in an increase in the power consumption while an increase in frequency has the opposite effect.

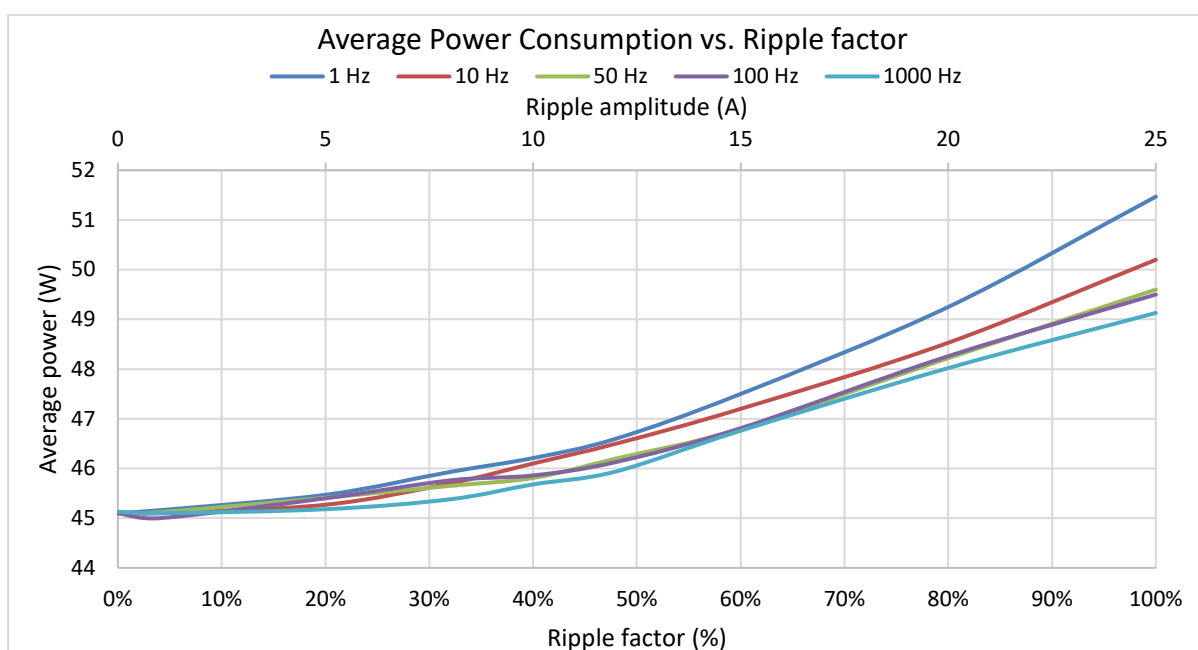
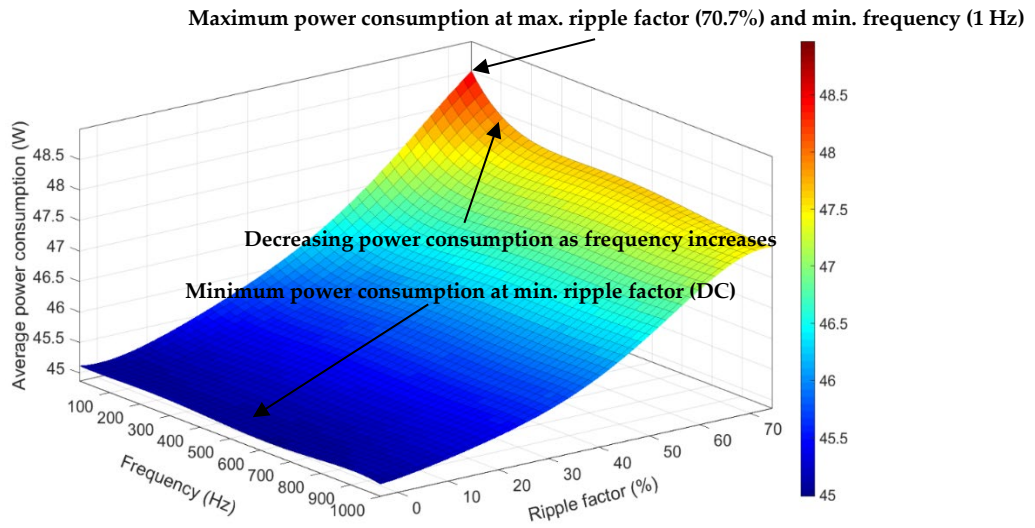


Figure 5-20: Average power consumption vs. ripple factor for a square wave ripple current with a DC offset of 25A.

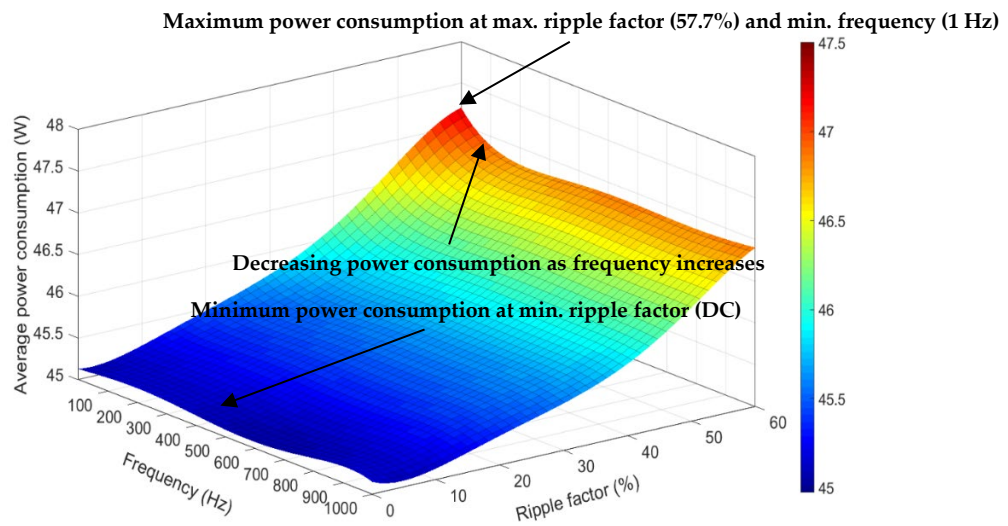
The measured results for all the considered waveforms, at parameter values with the most considerable effect on the power consumption of the PEM electrolyser, are summarised in Table 5-1 below. All of the average power measurements obtained from the experiments were also used in Matlab®'s curve fitting platform to obtain surface plots which represent the average power consumption as a function of both the ripple factor and frequency. Figure 5-21 below shows the surfaces fitted to the data points for a sinusoidal, triangular and square wave ripple current.

Table 5-1: PEM electrolyser average power consumption at different ripple current settings.

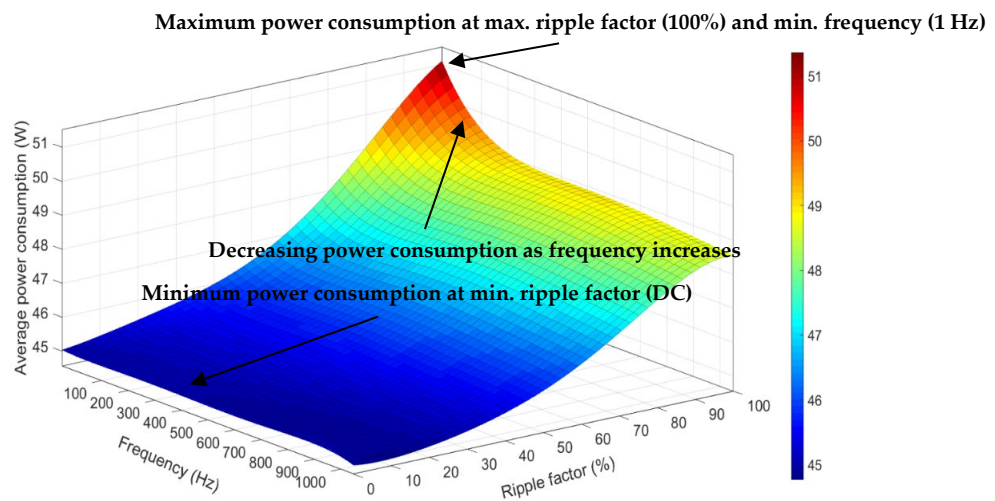
Frequency (Hz)	AC Amp. (A)	Sinusoidal wave		Triangular wave		Square wave	
		RF	P_{avg} (W)	RF	P_{avg} (W)	RF	P_{avg} (W)
0	0	0.0%	45.1	0.0%	45.1	0%	45.1
1	5	14.1%	45.268	11.5%	45.22	20%	45.47
1	10	28.3%	45.798	23.1%	45.53	40%	46.21
1	15	42.4%	46.608	34.6%	45.97	60%	47.5
1	20	56.6%	47.508	46.2%	46.62	80%	49.25
1	25	70.7%	48.808	57.7%	47.37	100%	51.47
10	5	14.1%	45.32	11.5%	45.31	20%	45.27
10	10	28.3%	45.74	23.1%	45.5	40%	46.1
10	15	42.4%	46.42	34.6%	45.82	60%	47.2
10	20	56.6%	47.18	46.2%	46.3	80%	48.53
10	25	70.7%	48.2	57.7%	46.96	100%	50.2
50	5	14.1%	45.37	11.5%	45.3	20%	45.41
50	10	28.3%	45.67	23.1%	45.5	40%	45.81
50	15	42.4%	46.08	34.6%	45.79	60%	46.8
50	20	56.6%	46.93	46.2%	46.3	80%	48.22
50	25	70.7%	47.71	57.7%	46.83	100%	49.6
100	5	14.1%	45.3	11.5%	45.3	20%	45.4
100	10	28.3%	45.59	23.1%	45.51	40%	45.86
100	15	42.4%	46.04	34.6%	45.76	60%	46.81
100	20	56.6%	46.858	46.2%	46.22	80%	48.26
100	25	70.7%	47.59	57.7%	46.79	100%	49.5
1000	5	14.1%	45.29	11.5%	45.21	20%	45.18
1000	10	28.3%	45.57	23.1%	45.35	40%	45.68
1000	15	42.4%	46.07	34.6%	45.71	60%	46.76
1000	20	56.6%	46.84	46.2%	46.19	80%	48.02
1000	25	70.7%	47.47	57.7%	46.79	100%	49.13



(a)



(b)



(c)

Figure 5-21: Average power consumption as a function of the ripple factor and frequency for a (a) Sinusoidal, (b) Triangular and (c) Square wave ripple current.

The figures discussed above as well as the values in the table illustrate that for any waveform, the power consumption increase as the ripple factor increase and decrease as the frequency of the ripple increase. This observation is in strong agreement with the simulated results as well as the results of similar studies. In this study the highest ripple frequency tested was 1 kHz and a further increase in frequency may lead to an even lower power consumption. However, the results show that the effect of frequency in this high frequency region is insignificant and not possible to accurately measure on an electrolyser as small as the one used in this study. The results show that the effect of frequency on the power consumption is the most substantial in the low frequency range (1 Hz to 50 Hz). It is typical for industrial electrolyzers to be supplied by a 6 or 12-pulse thyristor bridge rectifier, which generates a ripple with a dominating harmonic frequency of 300 Hz and 600 Hz respectively when supplied with an AC frequency of 50 Hz [163]. Practically the current supplied to an electrolyser would thus never have a ripple with a frequency in this low range (1 Hz to 50 Hz) since the rectified AC power sources used for electrolysis usually have a frequency of 50 Hz or higher. Some of these rectified AC power sources used for electrolysis include grid power and wind energy, as illustrated in section 2.8.2.4 of the literature study. The results also show that the effect of frequency is minimal and almost negligible at any ripple factor below 30%. Furthermore, these figures show that the ripple factor or AC amplitude has a significant impact on the power consumption. The ripple factor of the applied current is thus the parameter with the most considerable effect on the power consumption of a PEM electrolyser.

The power consumption measurements for a sinusoidal, triangular and square waveform show a similar trend when comparing the effect of the ripple factor and frequency. In Figure 5-22 below the average power consumption of the three considered waveforms at a frequency of 50 Hz are illustrated as a function of the ripple factor. As mentioned earlier the maximum achievable ripple factor for a sinusoidal waveform is 70.7%, for a triangular waveform 57.7% and for a square waveform 100%. The figure shows that regardless of the waveform type and the maximum achievable ripple factor of the waveform, the effect of the ripple factor on the power consumption is consistent. In Figure 5-23 below the average power consumption of each waveform, at a ripple amplitude of 25 A, is illustrated as a function of the ripple frequency. The figure shows that although the power consumption value is different for each waveform, since the ripple factor corresponding to a 25 A ripple amplitude is different, a similar trend can be observed in the effect of frequency for each of the waveforms. This means that although the behaviour of the PEM electrolyser is somewhat different with the use of different waveforms, the waveform type does not have a significant impact on the power consumption of the cell.

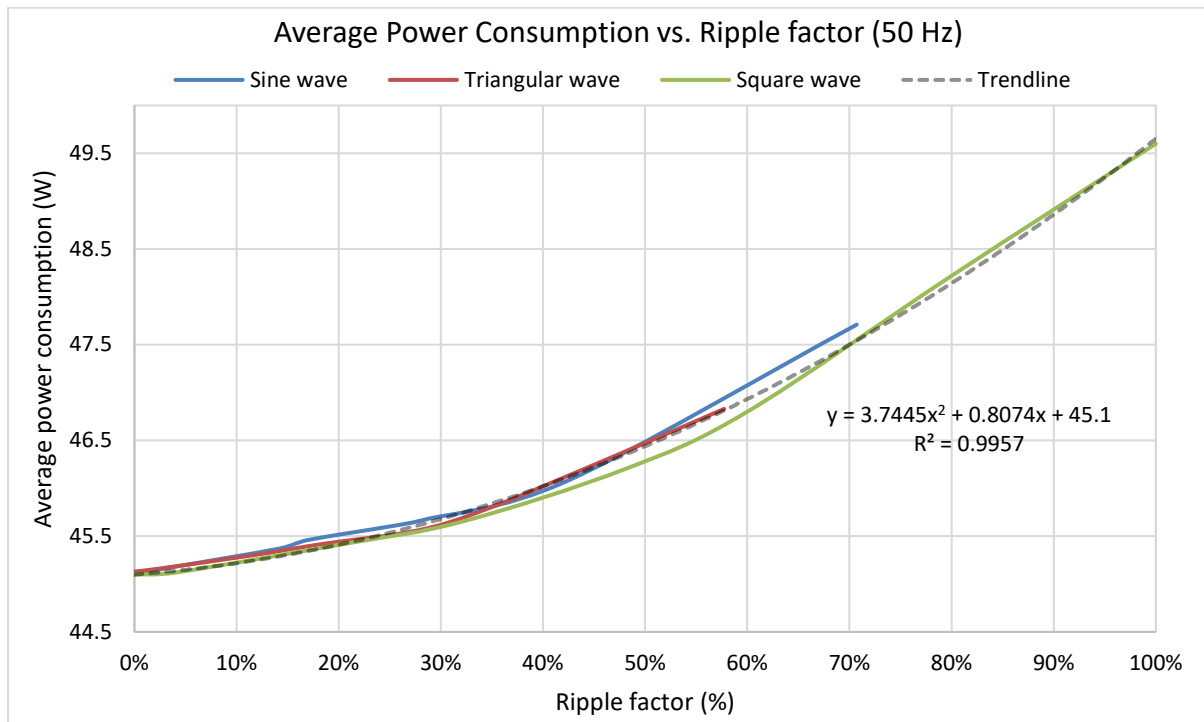


Figure 5-22: The relation between the average power consumption and the ripple factor observed at different waveforms.

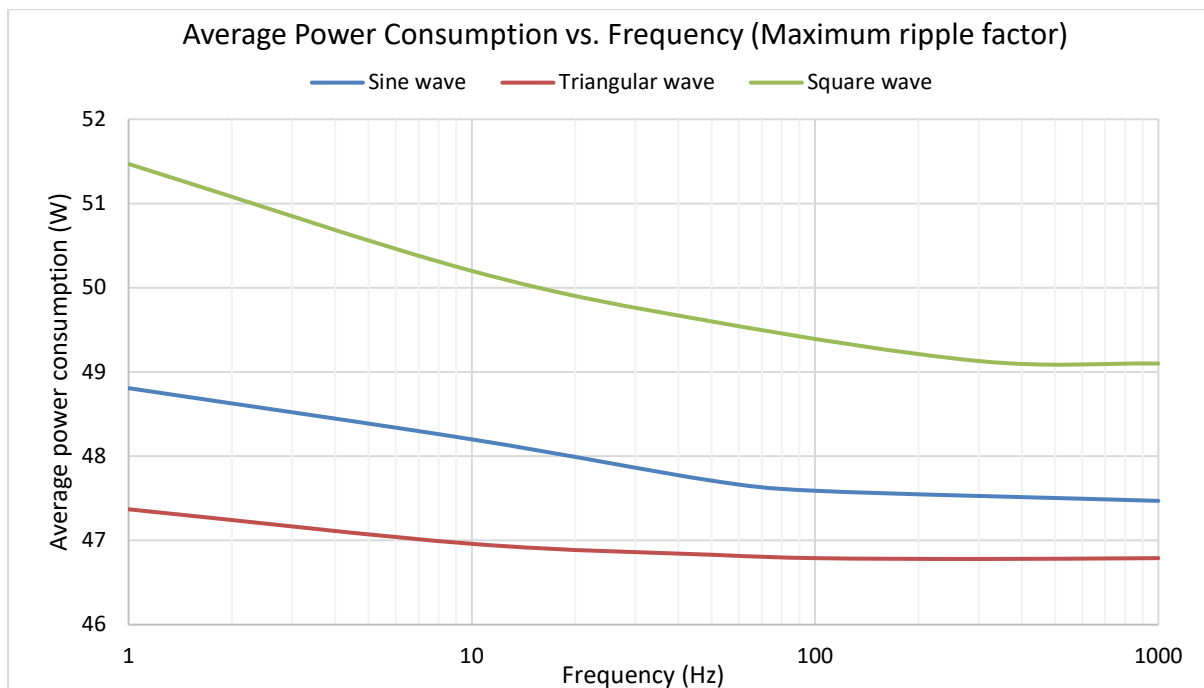


Figure 5-23: The relation between the average power consumption and the frequency observed at different waveforms.

The results discussed in this section showed that the AC component of the applied current affects the power consumption of the PEM electrolyser; however, all of these experiments were conducted only at one DC offset value.

In Figure 5-24 below, the power consumption of the electrolyser is plotted as a function of both the AC and DC components of a ripple current with a square waveform and a frequency of 300 Hz. The figure shows that the effect of the AC component is relatively small compared to the effect of the DC component. It is also observed that the effect of the AC component increases as the DC component increases.

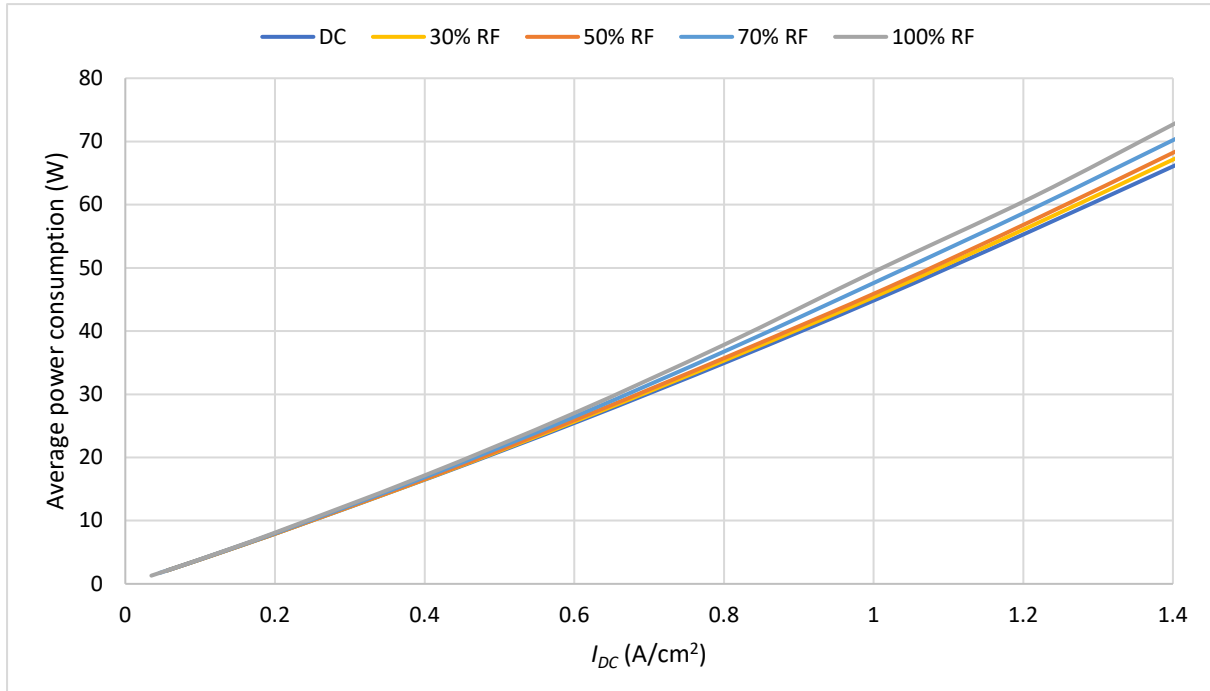


Figure 5-24: Average power consumption as a function of the current AC and DC components.

5.3.3 Experimental Hydrogen output

Hydrogen gas is considered to be the only useful energy output from the PEM electrolyser and thus play a crucial role in the efficiency of the electrolyser. In order to determine the effect of a ripple current on the efficiency of the PEM electrolyser, the hydrogen flow rates were measured for various ripple currents (different parameter settings).

5.3.3.1 Measurement Procedure

The hydrogen output was measured with a mass flow meter which gives the hydrogen flow at normal conditions (0 °C and 1 atm); all of the hydrogen flow rate measurements are thus given in normal litres per minute (nLPM). In each of the conducted experiments, the instantaneous hydrogen flow rate was measured at a log rate of 100 ms for the duration of the experiment after which the average hydrogen flow rate was determined. The figure below is an illustration of the instantaneous hydrogen flow and cell voltage, measured at a steady DC supply in Figure 5-25 (a), compared with the instantaneous hydrogen flow and cell voltage measured with a ripple current supply in Figure 5-25 (b).

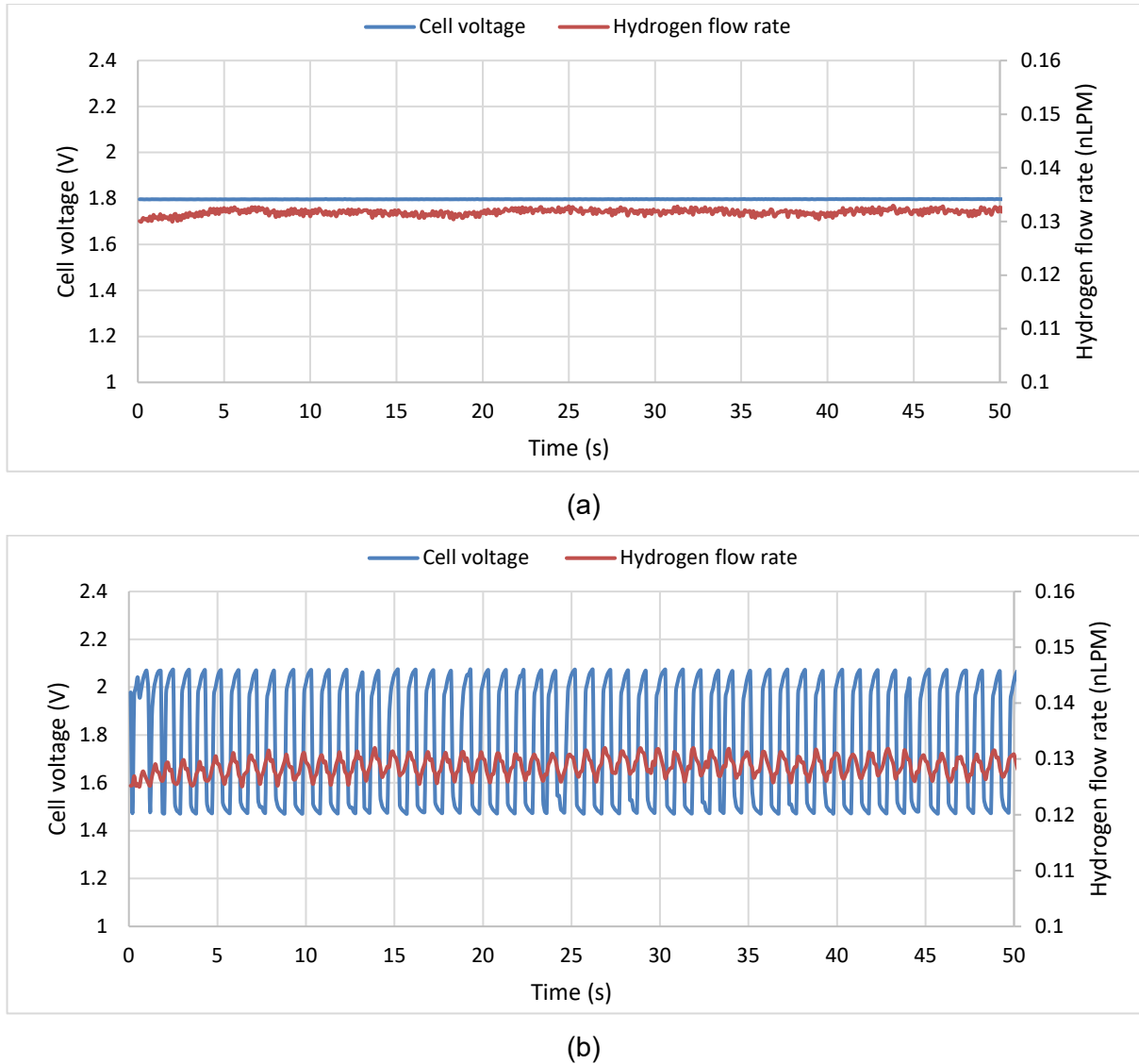


Figure 5-25: Instantaneous hydrogen flow rate at (a) a steady DC supply of 25 A and (b) a square wave with a DC offset of 25 A and a 100% ripple factor.

Since the hydrogen flow rate, voltage and power measurements were taken simultaneously, an average hydrogen flow rate was determined for each RF, frequency and waveform setting discussed in section 5.3.2 above. The average hydrogen flow rate of the PEM electrolyser was then plotted as a function of the ripple factor and frequency for each of the considered waveforms similarly as done for the power consumption.

5.3.3.2 Measurements Results

Figure 5-26 below shows the results for a sinusoidal ripple current with a DC offset of 25 A. The average hydrogen flow rate for all of the sinusoidal ripple current tests is 0.1308 nLPM with a standard deviation of 0.0008 nLPM. The maximum average flow rate observed in any of the sine wave experiments was 0.1312 nLPM and the minimum 0.1302 nLPM. The percentage difference between the maximum and minimum flow rates are thus only 0.77%.

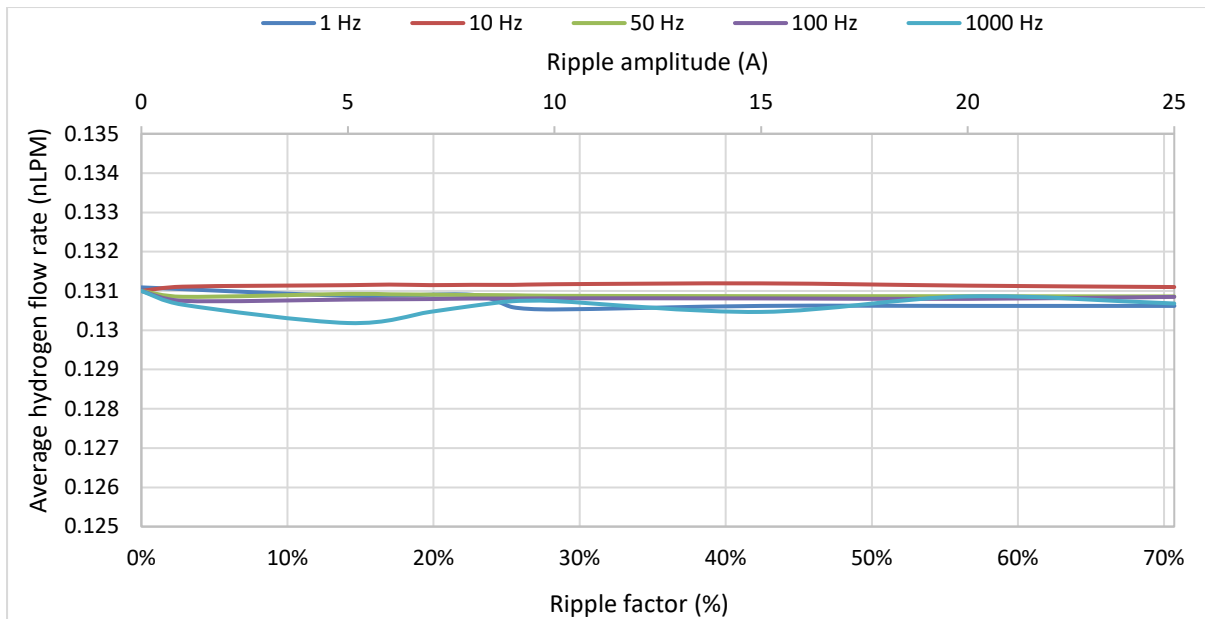


Figure 5-26: Average hydrogen flow rate vs. ripple factor for a sinusoidal ripple current with a DC offset of 25A.

Figure 5-27 below shows the average hydrogen flow rate results for a triangular ripple current with a DC offset of 25 A. Since a triangular wave is the waveform with the lowest achievable RF, the difference in the hydrogen flow rate at different parameter settings was expected to be the lowest. The average hydrogen flow rate seen in the figures is 0.1307 nLPM, with a standard deviation of 0.0004 nLPM. The maximum average flow rate observed in any of the triangular wave experiments was 0.1310 nLPM and the minimum 0.1302 nLPM. The percentage difference between the maximum and minimum flow rates are thus only 0.6%.

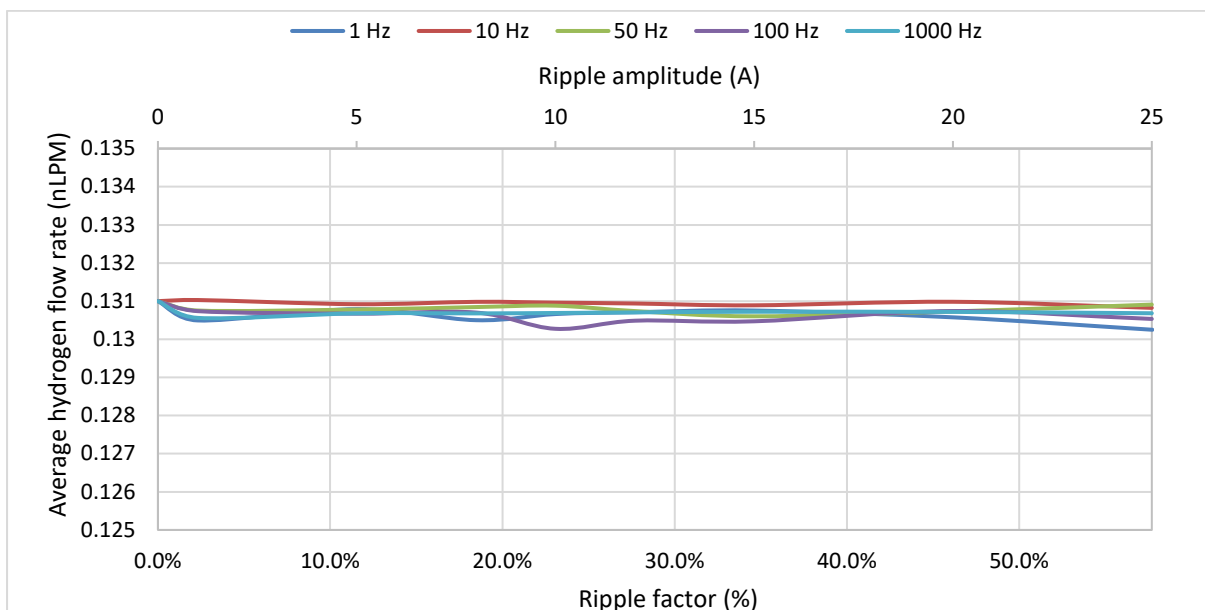


Figure 5-27: Average hydrogen flow rate vs. ripple factor for a triangular ripple current with a DC offset of 25A.

A square wave is the waveform with the highest achievable ripple factor and thus also the most likely to show a difference in the hydrogen flow rate. Figure 5-28 below illustrates the hydrogen flow rate for a square wave ripple current with a DC offset of 25 A at various ripple factor and frequency settings. The average hydrogen flow of all the data point displayed in the figures is 0.1308 nLPM with a standard deviation of 0.0005 nLPM. The maximum average flow rate observed in any of the experiments was 0.1313 nLPM, and the minimum 0.1302 nLPM. The percentage difference between the maximum and minimum flow rates are thus only 0.85%.

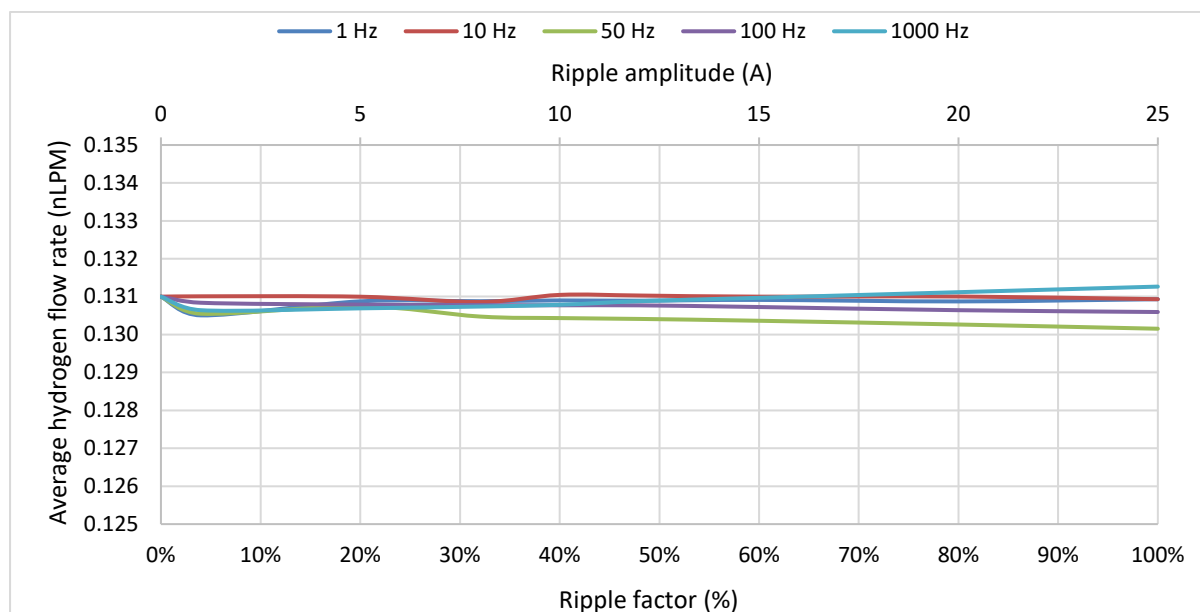


Figure 5-28: Average hydrogen flow rate vs. ripple factor for a square wave ripple current with a DC offset of 25A.

All of the average hydrogen flow rate measurements obtained from the experiments were used in Matlab®'s curve fitting platform to obtain surface plots which represent the flow rate as a function of both the ripple factor and frequency. Figure 5-29 (a), (b) and (c) below shows the surfaces fitted to the data points for a sinusoidal, triangular and square wave ripple current. The figures show that the hydrogen flow rate is not affected by the RF, frequency or waveform of the applied ripple current. The average hydrogen flow rate observed at each of the ripple current settings were very close to the 0.131 nLPM flow rate measured at a steady DC supply of 25 A. The highest difference in the flow rate was observed with a square wave ripple current, but the difference between the maximum and minimum flow rate was still below 1%.

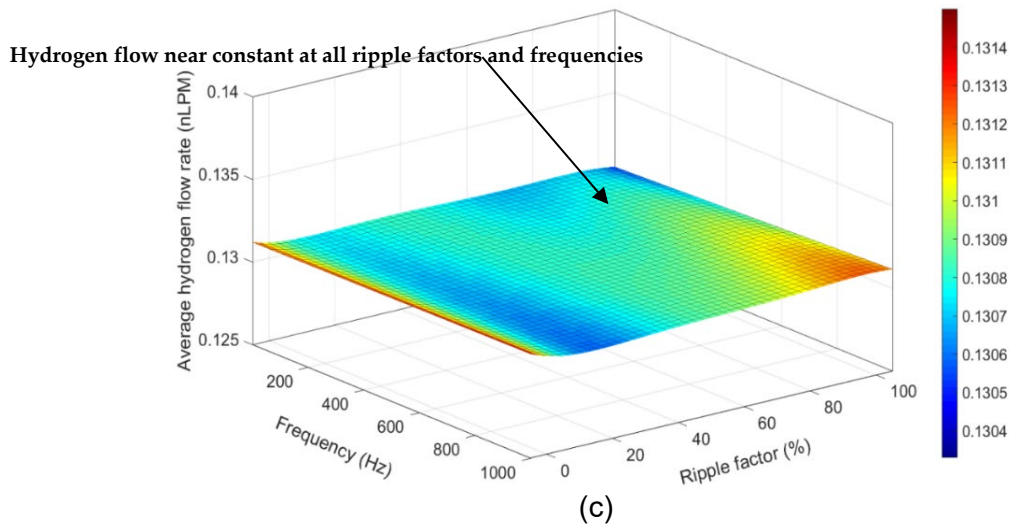
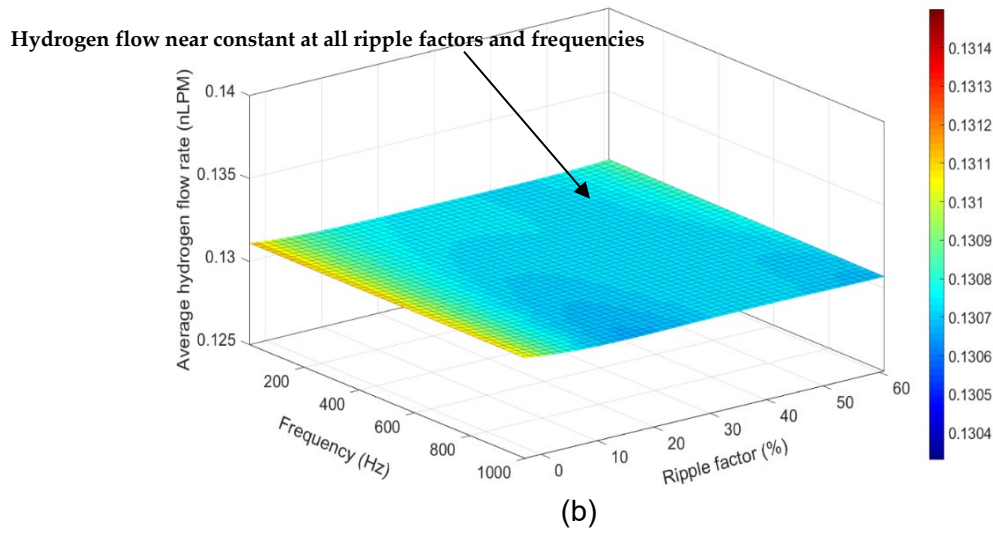
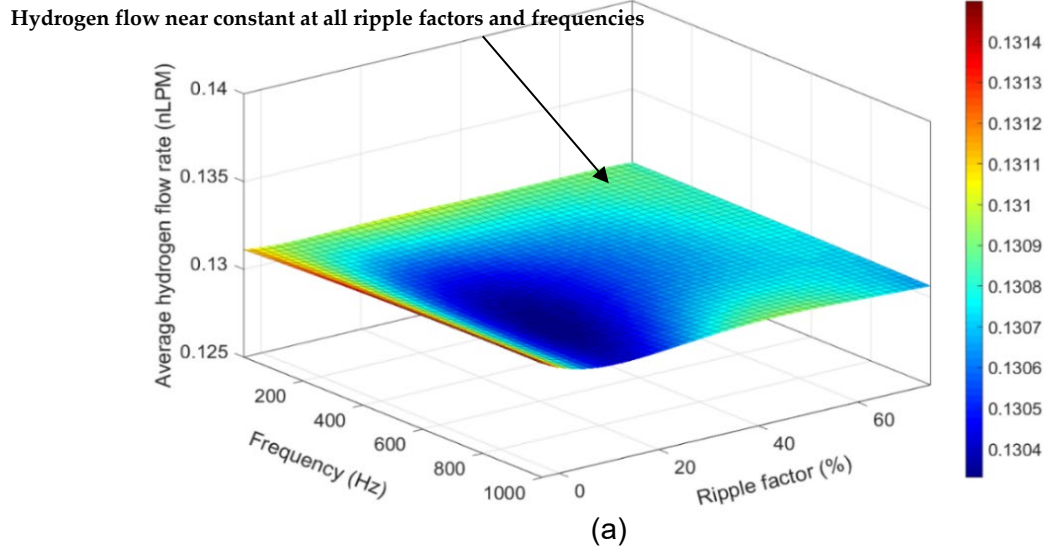


Figure 5-29: Average hydrogen flow rate as a function of frequency and ripple factor at a constant DC offset for a (a) Sinusoidal, (b) Triangular and (c) square wave ripple current.

In Figure 5-30 below, the hydrogen flow rate is plotted as a function of both the AC and DC components of a ripple current with a square waveform and a frequency of 300 Hz. The figure clearly shows that the hydrogen flow rate depends solely on the average current or the DC offset of the applied current. Since the hydrogen production rate of the PEM electrolyser does not differ at different ripple factor and frequency settings, the efficiency of the electrolyser at the different ripple factor and frequency settings is mainly affected by the power consumption.

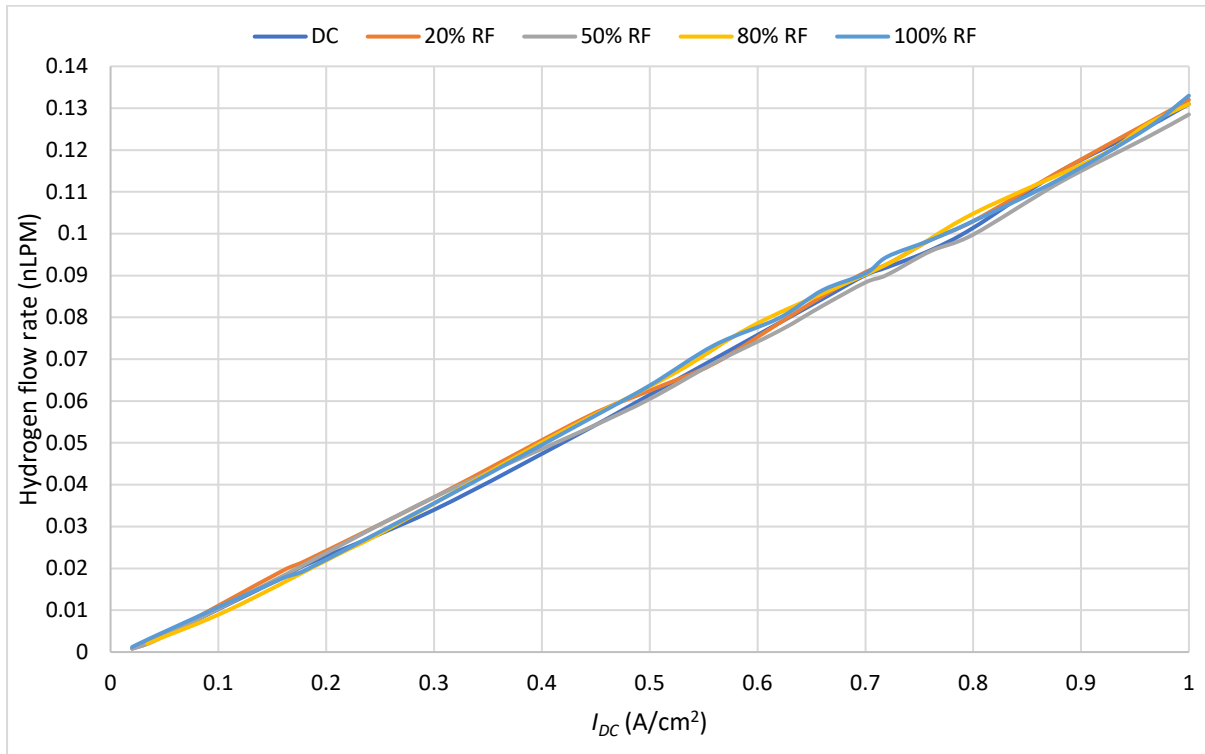


Figure 5-30: Hydrogen flow rate as a function of the current AC and DC components.

5.3.4 Experimental Efficiency

Several definitions exist to calculate the efficiency of an electrolyser as previously discussed in section 2.5 of the literature study. These definitions include the voltage efficiency, which is a measure of the cell voltage losses, the Faradaic efficiency which is a measure of the cell current losses and the cell efficiency which is a measure of all input energy losses. The cell efficiency is the most relevant of the efficiencies mentioned above since it gives the ratio between the useful energy output and energy input of the electrolyser.

5.3.4.1 Cell efficiency

The efficiency of the PEM electrolyser at different current ripples was calculated making use of equation (5.10) below where $\dot{n}_{H_2}$ is the average measured hydrogen flow rate, P_{avg} the average measured power consumption, and HHV is the higher heating value equal to 285.83 kJ.mol⁻¹ [42, 66].

$$\varepsilon_{cell}^{HHV} = \frac{HHV \cdot \dot{n}_{H_2}}{P_{avg}} \quad (5.10)$$

The figures below show the efficiency of the PEM electrolyser as a function of the ripple factor at various frequencies, measured using sinusoidal (Figure 5-31), triangular (Figure 5-32) and square waveforms (Figure 5-33). It can clearly be seen in each of the figures that a ripple current, and the settings of the ripple current, has a major impact on the efficiency of the PEM electrolyser.

The figures show that the main influencing parameter of the applied ripple current is the size of the ripple factor. An increase in the ripple factor from 0% (steady DC) to 100% (25 A AC amplitude with a square wave ripple) can lead to an efficiency decrease of 7.7% at a ripple frequency of 1 Hz. The second significant influencing parameter is the frequency of the ripple current. At a ripple factor of 100%, the difference in efficiency at the lowest frequency setting (1 Hz) and the highest frequency setting (1000 Hz) is 2.8%. The trend observed between the different waveforms is very similar, which shows that the waveform type does not play a significant role.

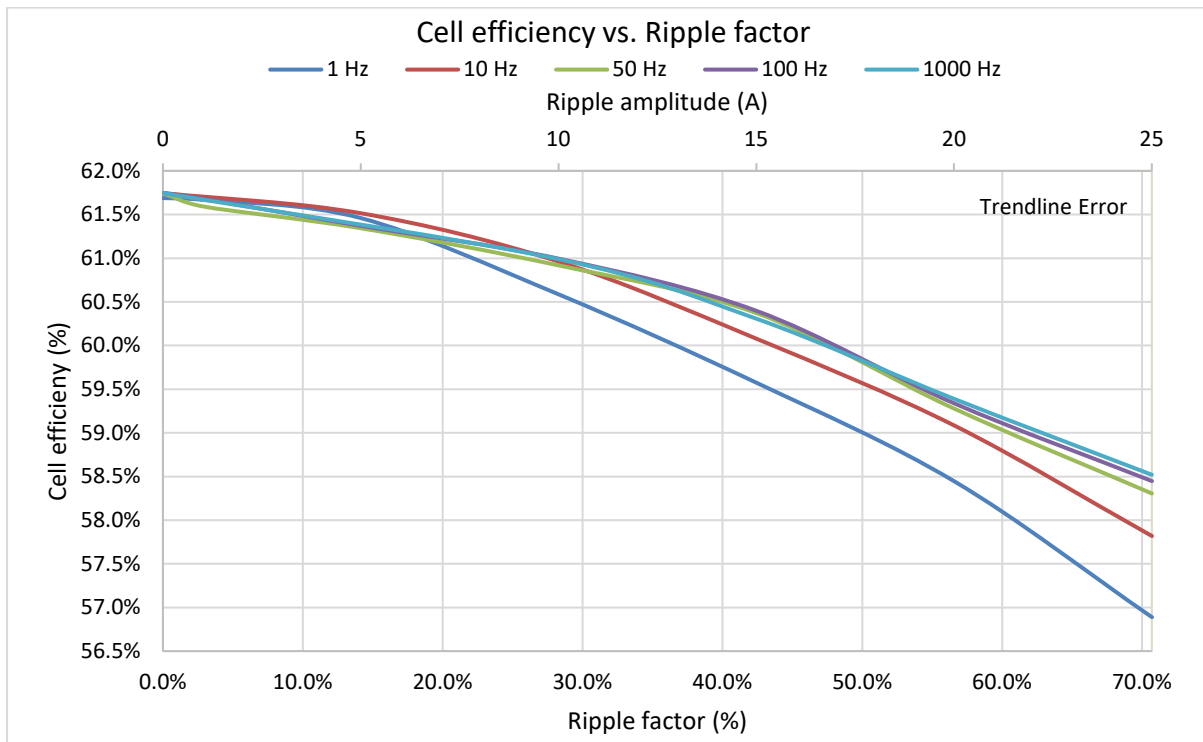


Figure 5-31: Measured cell efficiency as a function of the ripple factor of a sinusoidal ripple current with a DC offset of 25A at various frequencies.

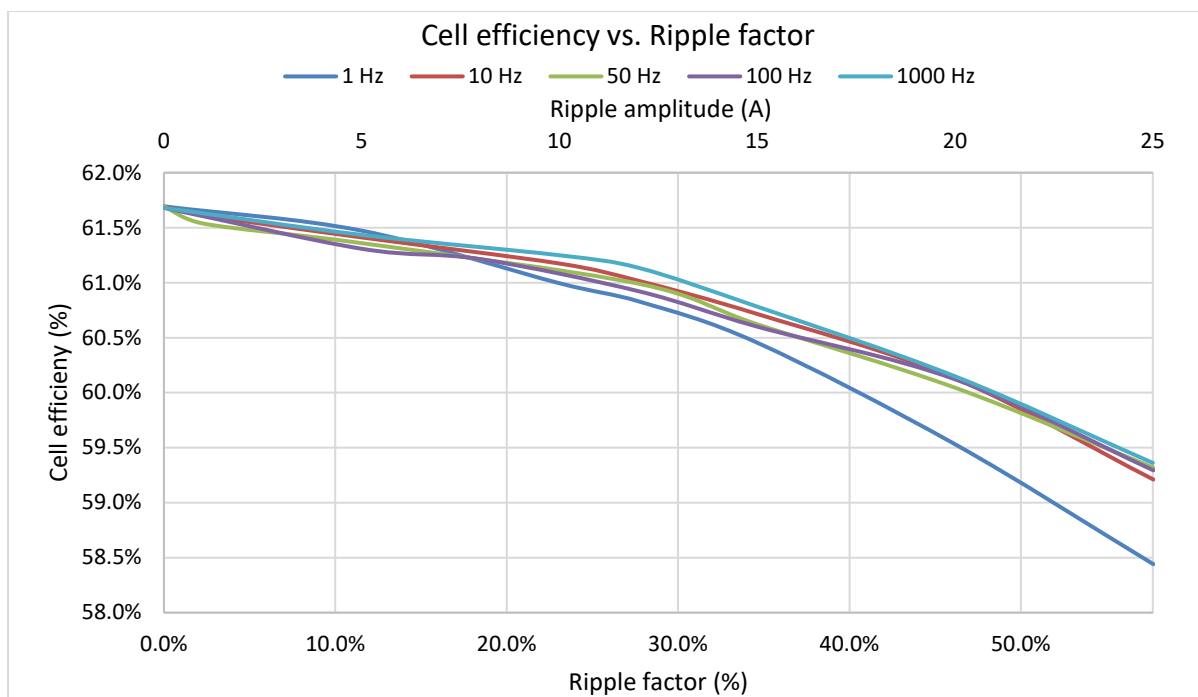


Figure 5-32: Measured cell efficiency as a function of the ripple factor of a triangular ripple current with a DC offset of 25A at various frequencies.

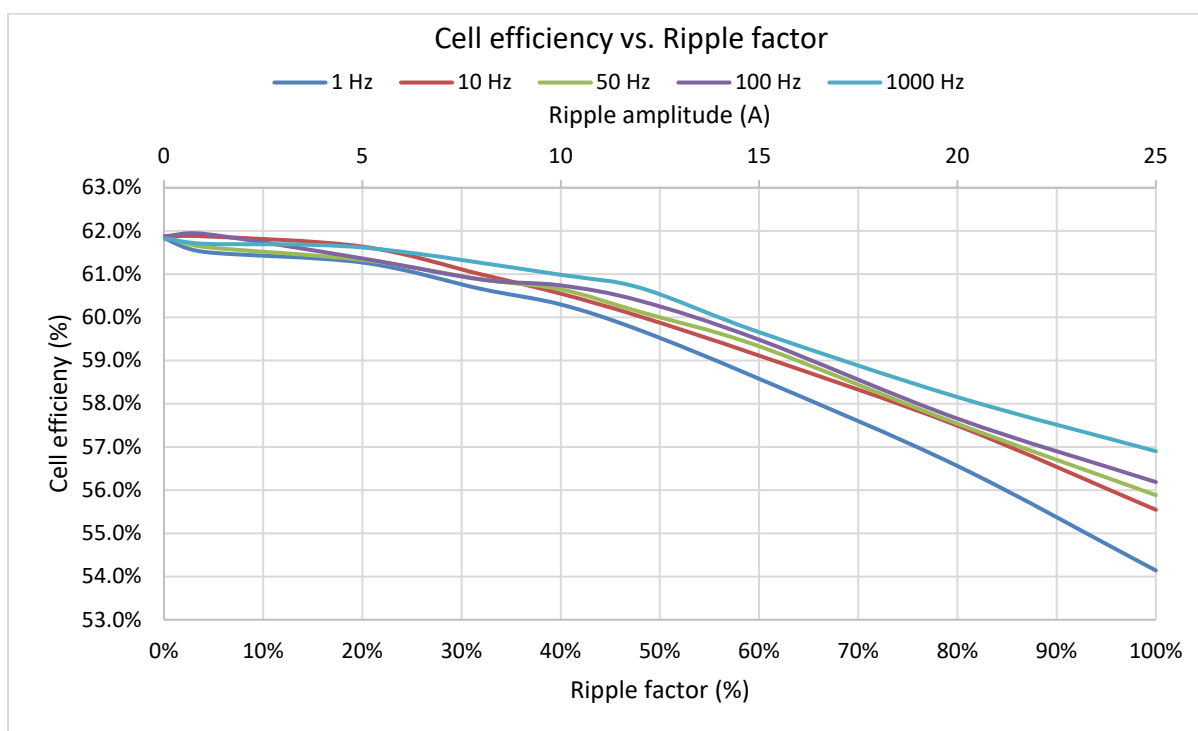


Figure 5-33: Measured cell efficiency as a function of the ripple factor of a square wave ripple current with a DC offset of 25A at various frequencies.

5.3.4.2 Voltage and Faradaic efficiency

In the previous section, it was observed that a ripple current has a substantial negative impact on the efficiency of a PEM electrolyser.

In this section, the reasons for the decrease in efficiency are discussed by investigating the effect of a ripple current on the voltage and Faradaic (current) efficiency. As previously discussed, the voltage efficiency is a measure of the cell voltage losses and is calculated using equation (5.11) where E_{th}^0 is the thermoneutral voltage at standard conditions and U_{rms} is the RMS cell voltage [42].

$$\varepsilon_V^{HHV} = \frac{E_{th}^0}{U_{rms}} \quad (5.11)$$

On the other hand, the Faradaic efficiency is a measure of the cell current losses and is calculated using equation (5.12) where $\dot{n}_{H_2,actual}$ is the actual measured hydrogen flow rate and $\dot{n}_{H_2,theor}$ the theoretical flow rate. The theoretical flow rate is calculated using equation (5.13) where F is Faraday's constant and I_{rms} is the RMS value of the applied ripple current [42].

$$\varepsilon_I = \frac{\dot{n}_{H_2,actual}}{\dot{n}_{H_2,theor}} \quad (5.12)$$

$$\dot{n}_{H_2,theor} = \frac{I_{rms}}{2F} \quad (5.13)$$

Figure 5-34 below presents and compare the Voltage, Faradaic and cell efficiency for a few different ripple current parameter settings. The efficiency analysis focuses on a ripple current with a square waveform since it is the only waveform capable of achieving a 100% ripple factor. The efficiencies for the other waveforms used in this study are however also presented in Table 5-2 below. The figure, as well as the table below, shows that the voltage efficiency of the PEM electrolyser is not largely affected by the size of the ripple current. It was also observed in section 5.3.1 that the RMS voltage of the cell does not significantly increase as the RMS current increase. Since the effect of a ripple current on the RMS cell voltage is so small, it can be concluded that the impact of the voltage losses on the cell efficiency is insignificant. On the other hand, a current ripple initiates a higher current RMS value while the hydrogen production rate is dependent only on the current mean value. The difference between the mean and RMS current values can, therefore, be defined as unused current. A current ripple thus generates additional current losses which cause a decrease in the Faradaic efficiency as well as the cell efficiency. In the previous section, it was observed that the frequency of the ripple current also affects the cell efficiency of the PEM electrolyser. However, since both the Voltage and Faradic efficiency is dependent on the RMS current and voltage values, information like the phase shift between the instantaneous current and voltage waveforms are lost. The Voltage and Faradaic efficiencies are therefore not significantly affected by the ripple frequency. The higher cell efficiency at higher frequencies is caused by a decrease in the power consumption, as discussed previously in section 5.3.2.

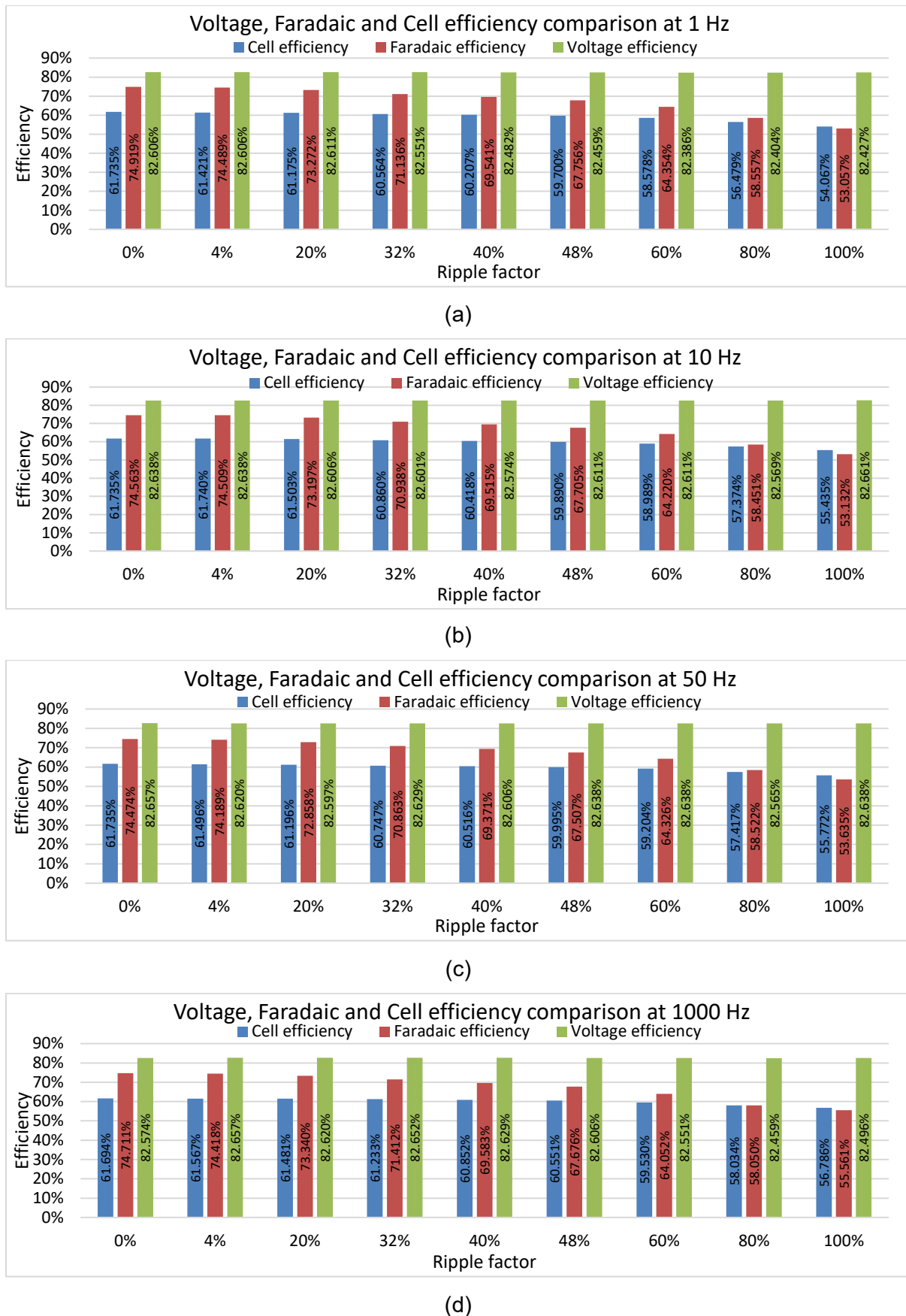


Figure 5-34: Voltage, Faradaic and Cell efficiency comparison at different ripple factors and a frequency of (a) 1 Hz, (b) 10 Hz, (c) 50 Hz and (d) 1000 Hz.

Table 5-2: Measured efficiency results.

Freq. (Hz)	AC Amp. (A)	Sinusoidal wave				Triangular wave				Square wave			
		RF	Voltage efficiency	Faradic efficiency	Cell efficiency	RF	Voltage efficiency	Faradic efficiency	Cell efficiency	RF	Voltage efficiency	Faradic efficiency	Cell efficiency
0	0	0.0%	82.65%	74.64%	61.68%	0.0%	82.65%	74.64%	61.68%	0%	82.65%	74.64%	61.68%
1	5	14.1%	82.53%	73.97%	61.45%	11.5%	82.60%	74.18%	61.47%	20%	82.61%	73.27%	61.18%
1	10	28.3%	82.23%	71.82%	60.58%	23.1%	82.55%	72.67%	60.99%	40%	82.48%	69.54%	60.21%
1	15	42.4%	82.18%	68.73%	59.56%	34.6%	82.50%	70.59%	60.45%	60%	82.39%	64.35%	58.58%
1	20	56.6%	82.13%	65.50%	58.44%	46.2%	82.40%	67.76%	59.53%	80%	82.40%	58.56%	56.48%
1	25	70.7%	82.02%	62.00%	56.88%	57.7%	82.41%	64.51%	58.44%	100%	82.43%	53.06%	54.07%
10	5	14.1%	82.59%	74.26%	61.50%	11.5%	82.66%	74.08%	61.41%	20%	82.61%	73.20%	61.50%
10	10	28.3%	82.42%	72.22%	60.95%	23.1%	82.65%	72.78%	61.17%	40%	82.57%	69.52%	60.42%
10	15	42.4%	82.41%	69.01%	60.07%	34.6%	82.65%	70.66%	60.71%	60%	82.61%	64.22%	58.99%
10	20	56.6%	82.42%	65.34%	59.07%	46.2%	82.66%	68.02%	60.13%	80%	82.57%	58.45%	57.37%
10	25	70.7%	82.28%	61.32%	57.81%	57.7%	82.69%	64.82%	59.21%	100%	82.66%	53.13%	55.43%
50	5	14.1%	82.66%	73.85%	61.33%	11.5%	82.68%	74.03%	61.36%	20%	82.60%	72.86%	61.20%
50	10	28.3%	82.63%	71.84%	60.91%	23.1%	82.69%	71.93%	60.99%	40%	82.61%	69.37%	60.52%
50	15	42.4%	82.62%	68.94%	60.36%	34.6%	82.67%	70.50%	60.62%	60%	82.64%	64.33%	59.20%
50	20	56.6%	82.57%	65.13%	59.27%	46.2%	82.63%	67.88%	60.04%	80%	82.56%	58.52%	57.42%
50	25	70.7%	82.44%	61.28%	58.30%	57.7%	82.68%	64.78%	59.32%	100%	82.64%	53.64%	55.77%
100	5	14.1%	82.63%	73.76%	61.36%	11.5%	82.68%	73.94%	61.31%	20%	82.61%	73.02%	61.23%
100	10	28.3%	82.59%	71.83%	60.98%	23.1%	82.64%	72.37%	60.84%	40%	82.58%	69.47%	60.61%
100	15	42.4%	82.58%	68.80%	60.39%	34.6%	82.61%	70.49%	60.60%	60%	82.56%	64.26%	59.36%
100	20	56.6%	82.57%	65.19%	59.33%	46.2%	82.60%	67.92%	60.12%	80%	82.48%	58.45%	57.54%
100	25	70.7%	82.45%	61.26%	58.44%	57.7%	82.56%	64.77%	59.29%	100%	82.56%	53.68%	56.07%
1000	5	14.1%	82.63%	73.31%	61.09%	11.5%	82.66%	74.00%	61.43%	20%	82.62%	73.34%	61.48%
1000	10	28.3%	82.60%	71.44%	60.98%	23.1%	82.66%	72.57%	61.25%	40%	82.63%	69.58%	60.85%
1000	15	42.4%	82.56%	68.00%	60.30%	34.6%	82.57%	70.17%	60.78%	60%	82.55%	64.05%	59.53%
1000	20	56.6%	82.50%	64.15%	59.38%	46.2%	82.57%	67.16%	60.15%	80%	82.46%	58.05%	58.03%
1000	25	70.7%	82.39%	60.20%	58.51%	57.7%	82.55%	63.87%	59.36%	100%	82.50%	55.56%	56.79%

5.4 Experimental Degradation

One of the objectives of this study was to determine if a ripple current would accelerate the degradation rate of the PEM electrolyser. The degradation rate of a PEM electrolyser is measured by investigating the increase in the cell voltage at constant current, temperature and pressure operating conditions. To achieve this goal, various ripple currents were applied to the electrolyser while the cell voltage was measured. The duration of each experiment was a minimum of 72 hours with a voltage measurement taken every minute. A minimum of 4320 data points was thus obtained from each experiment and used to determine the voltage drift, which can be defined as the increase in the mean cell voltage. The fluoride loss was also measured to verify the rate at which chemical degradation takes place in the MEA.

The experiments were done at a constant frequency to determine if the size of the ripple factor influences the degradation rate. Ripple currents with a square waveform were used (as illustrated in Figure 5-35) since this is the only waveform with which a 100% ripple factor can be achieved. The experiments were done at a ripple frequency of 300 Hz since it is the typical output frequency of a three-phase full wave rectifier using standard grid power (50 Hz). The results are illustrated in Figure 5-36 to Figure 5-40 below and were measured at a constant DC offset of 25 A while the ripple factor was increased in each experiment. The first figure shows the voltage drift at a 0% ripple factor (steady DC) while the last figure shows the voltage drift at a 100% ripple factor.

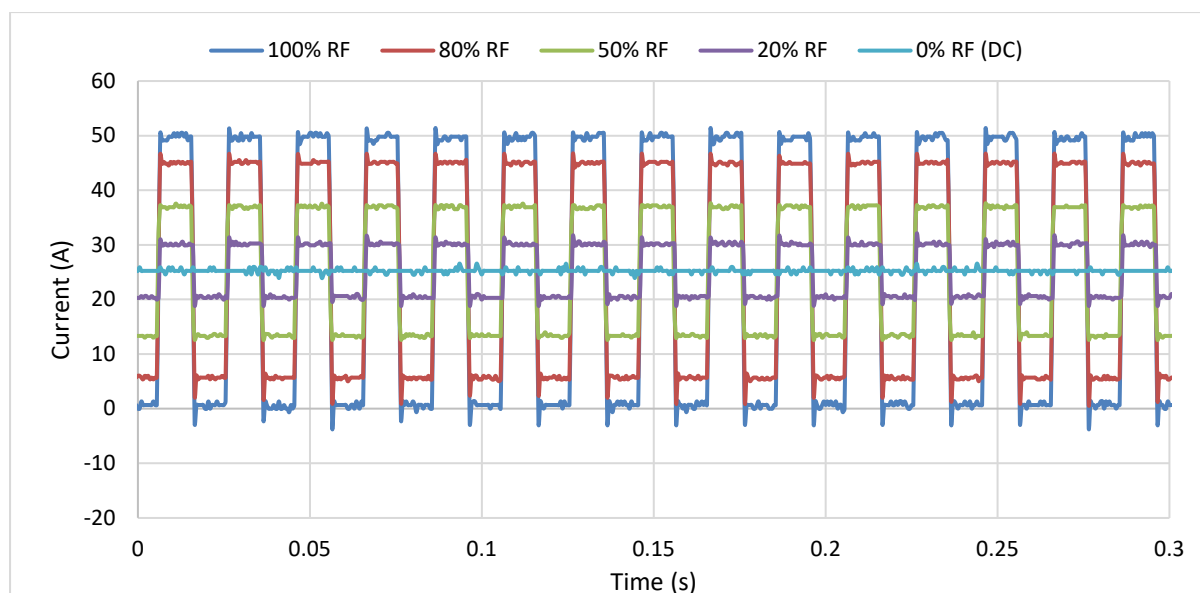


Figure 5-35: Ripple currents applied to the PEM electrolyser during the degradation tests.

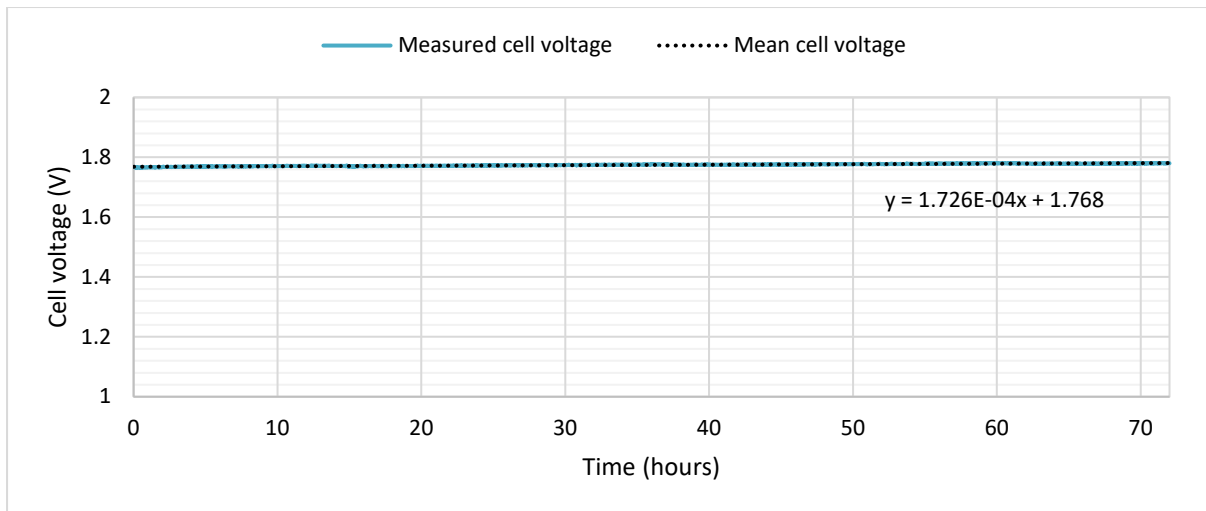


Figure 5-36: Degradation test for a steady DC current of 25 A (at a ripple factor of 0%).

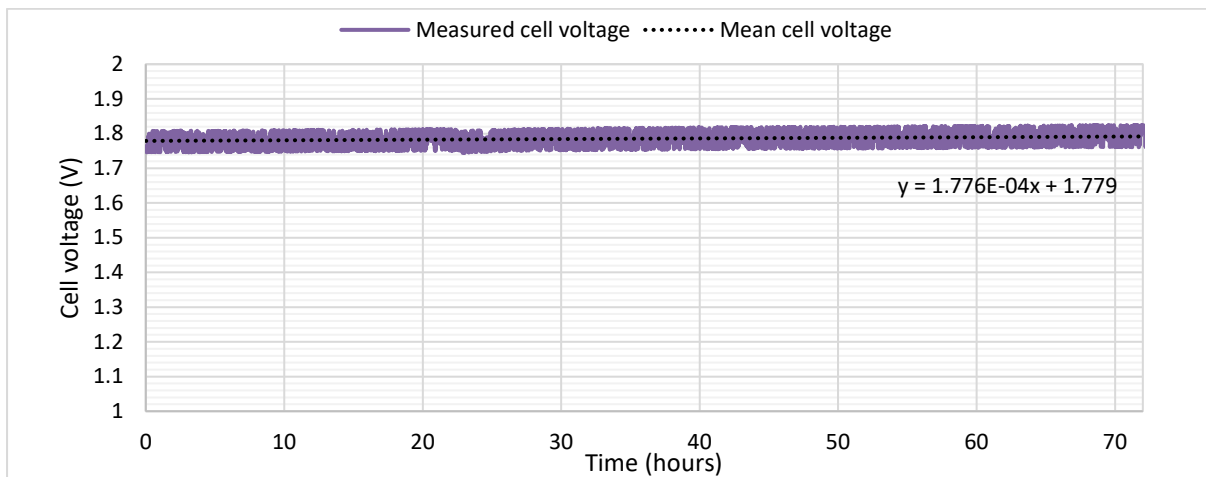


Figure 5-37: Degradation test for a square wave ripple current with a DC offset of 25 A, a frequency of 300 Hz and a ripple factor of 20%.

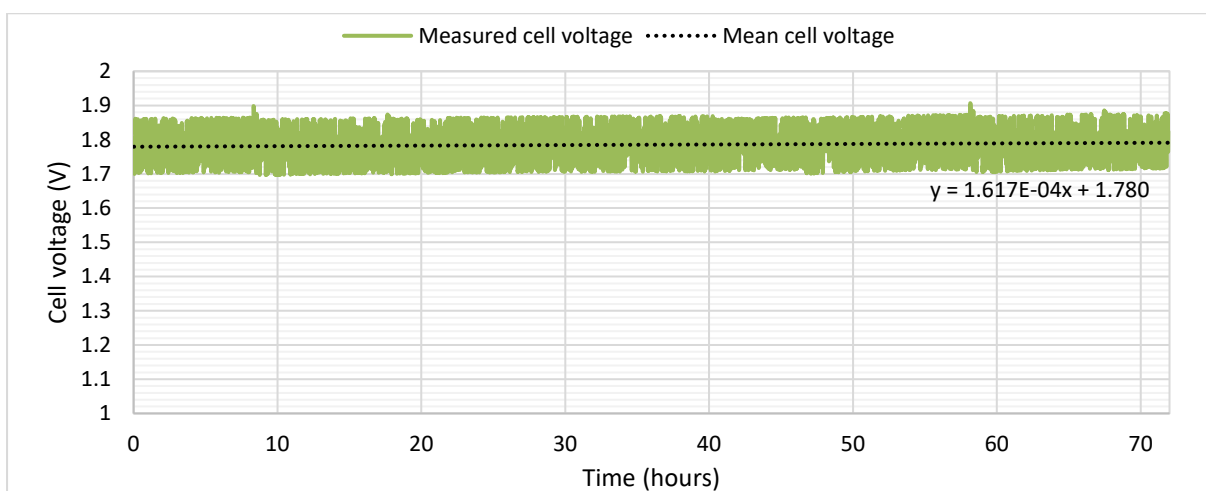


Figure 5-38: Degradation test for a square wave ripple current with a DC offset of 25 A, a frequency of 300 Hz and a ripple factor of 50%.

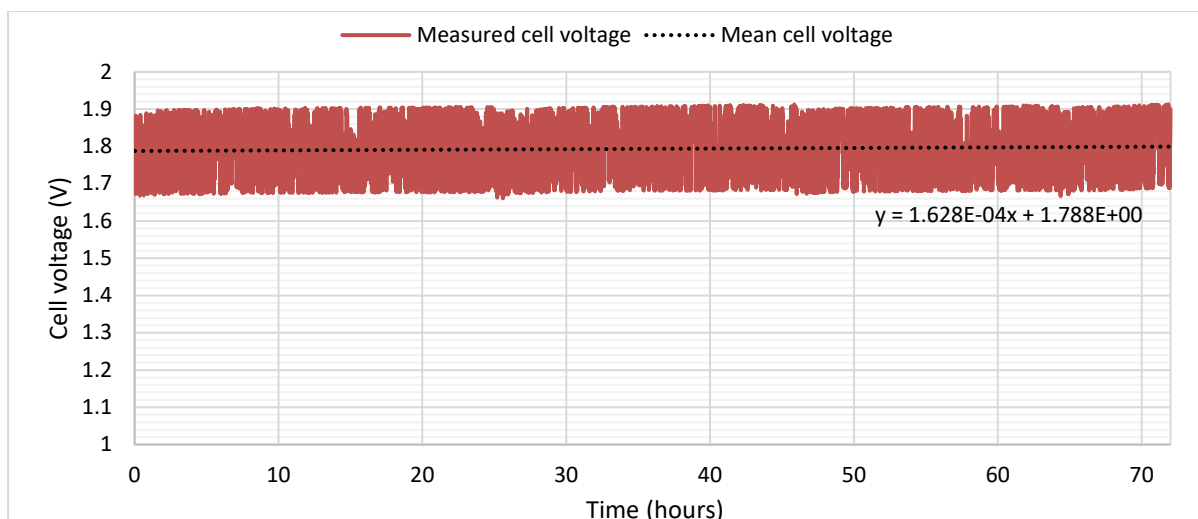


Figure 5-39: Degradation test for a square wave ripple current with a DC offset of 25 A, a frequency of 300 Hz and a ripple factor of 80%.

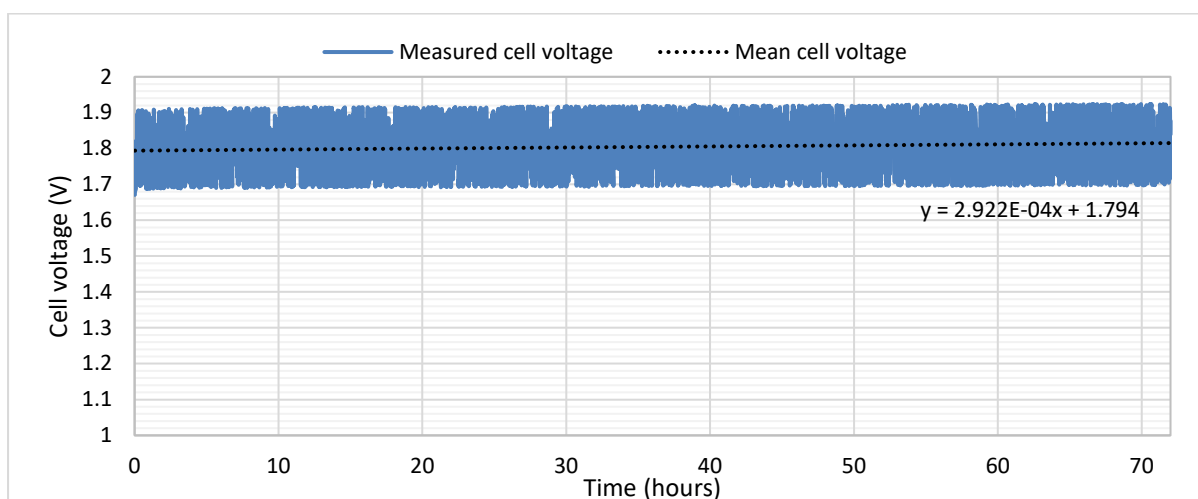
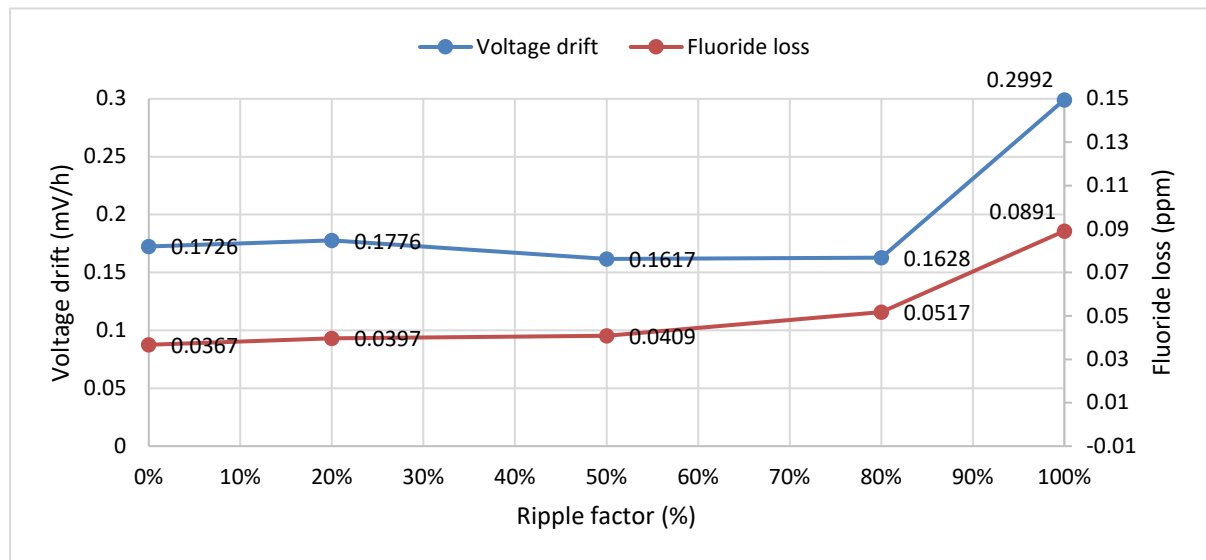


Figure 5-40: Degradation test for a square wave ripple current with a DC offset of 25 A, a frequency of 300 Hz and a ripple factor of 100%.

The results obtained from each of the above degradation tests were investigated to determine the rate at which the electrolyser degrades at different ripple factor sizes. This investigation was conducted by fitting a trendline to the measured voltage data points, which returns a linear line, illustrating the average cell voltage at each point in time. The slopes of these trendlines represent the rate at which the DC offset of the cell voltage increase. Table 5-3 and Figure 5-41 below show the voltage drift observed in each of the degradation tests, as well as the accompanying fluoride losses. The results show no indication that the voltage drift or the fluoride loss of the PEM electrolyser is affected by a ripple factor of 50% or less. Since these tests were not run simultaneously and operating conditions such as the ambient temperature could not be controlled, a slight difference between the observed voltage drifts was expected. However, when the ripple factor was increased to 100%, a definite increase in both the voltage drift and the fluoride loss were observed.

Table 5-3: Degradation test results at different ripple factors.

Ripple factor	Frequency (Hz)	Voltage Drift (mV/h)	Fluoride loss (ppm)
0%	0 (DC)	0.1726	0.0367
20%	300	0.1776	0.0397
50%	300	0.1617	0.0409
80%	300	0.1628	0.0517
100%	300	0.2922	0.0891

**Figure 5-41:** PEM electrolyser voltage drift and fluoride loss as a function of the applied ripple factor.

5.5 Verification and validation

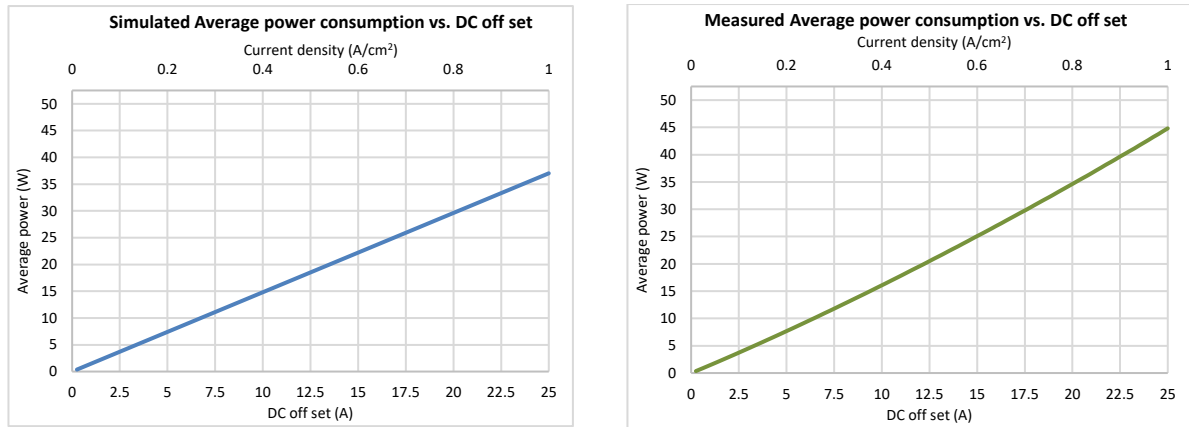
The verification and validation of the experimental results were done by comparing it to the simulation results obtained in the previous chapter (Chapter 4). As mentioned in Chapter 4, the comparison between the experimental and simulation results was also used to validate the simulation models and confirm the capability of the models to represent a practical system. The main objective of this study was to determine the effect of a ripple current, and the different parameter setting of the ripple current, on the efficiency of a PEM electrolyser. The experimental results showed that the hydrogen output of the PEM electrolyser is unaffected by the ripple factor, frequency or waveform of the applied ripple current, which is in good agreement with the simulation results. However, the ripple factor, frequency and waveform have a significant impact on the power consumption and thus the efficiency of the electrolyser.

The verification and validation were done by comparing the simulated effects of a ripple current on the average power consumption, to the measured effects. The comparison between the simulated and experimental results are illustrated in Figure 5-42 to Figure 5-44, respectively, for the effect of the DC offset, ripple factor, frequency and waveform on the power consumption.

These figures show that the simulation results accurately represent the effect of different parameter values on the power consumption of the PEM electrolyser. Both the simulated and measured results show an increase in the power consumption as the ripple factor increase, a decrease in the power consumption as the frequency increase and that the power consumption is not significantly affected by the waveform. Although the simulated and experimental data show a similar trend, the effect of the ripple factor and frequency on the power consumption is intensified in the simulation results. As discussed in section 4.2.2 the EIS data used to develop this EEC model were obtained by applying a current signal, with a DC offset of 0.7 A and an AC amplitude of 0.1 A, to the PEM electrolyser. However, the impedance of a PEM electrolyser is dependent on the kinetics of the electrochemical reactions and thus changes as the current density changes. A study done by van der Merwe *et al.* [114], shows that the activation resistance and capacitance significantly reduce at higher current densities. The actual activation resistance and capacitance values of the PEM electrolyser at a DC offset of 25 A are thus lower than the values used in the simulation model. The exact values at a current of 25 A (1 A/cm²) could however not be obtained since Interface 1000, used for the EIS tests, has a current limit of 1 A. The simulations consequently do not show the exact impedance, voltage or power consumption of the PEM electrolyser at all current densities, but rather the proportional effect of the different ripple current parameters.

Table 5-4: Percentage error between the average power consumption measured experimentally and simulated.

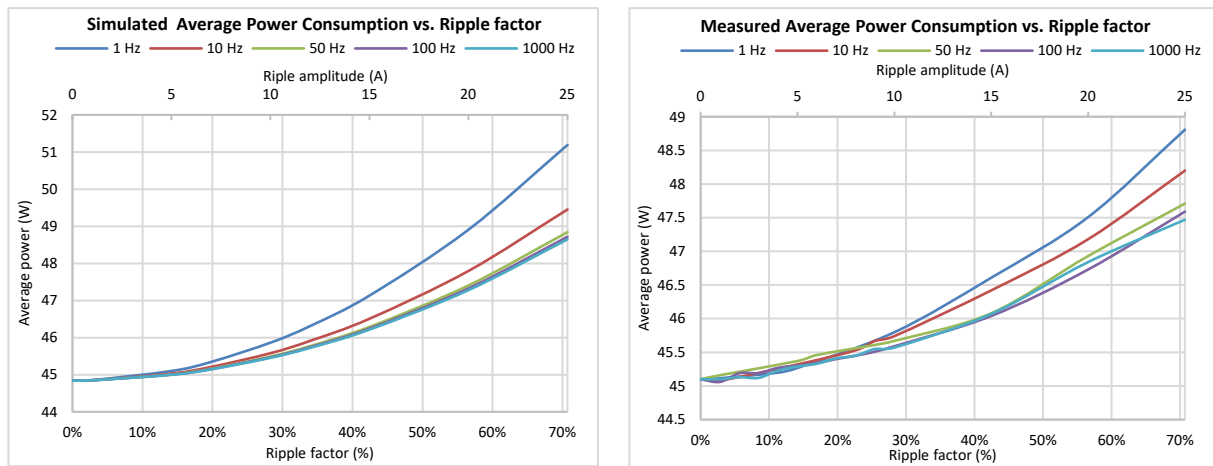
Waveform parameters			Percentage Error				
	AC Amp. (A)	Ripple factor (%)	1 Hz	10 Hz	50 Hz	100 Hz	1000 Hz
Sinusoidal	5	14.1	0.37%	0.64%	0.80%	0.66%	0.64%
	15	42.4	1.13%	0.19%	0.45%	0.44%	0.31%
	25	70.7	4.88%	2.60%	2.37%	2.37%	2.48%
Triangular	5	11.5	0.42%	0.74%	0.72%	0.71%	0.46%
	15	34.6	1.07%	0.41%	0.23%	0.31%	0.53%
	25	57.7	4.13%	2.36%	1.87%	1.91%	2.06%
Square	5	20	0.25%	0.11%	0.48%	0.45%	0.08%
	15	60	4.08%	2.18%	2.28%	2.16%	2.37%
	25	100	11.82%	8.02%	7.24%	7.12%	8.01%



(a)

(b)

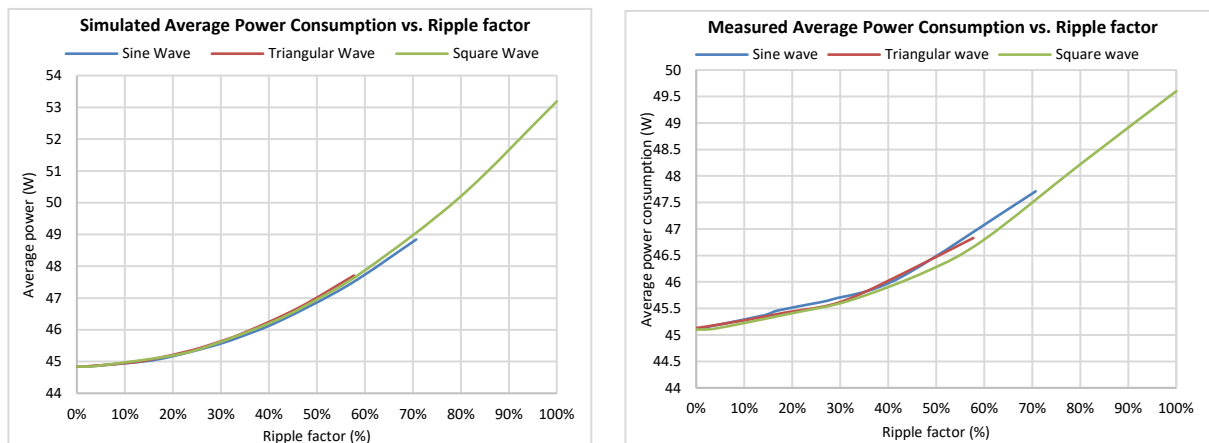
Figure 5-42: Validation of (a) Simulated/ Analytical power consumption and (b) measured power consumption at different DC offset values.



(a)

(b)

Figure 5-43: Validation of (a) Simulated/ Analytical power consumption and (b) measured power consumption at different ripple factor and frequency values.



(a)

(b)

Figure 5-44: Validation of (a) Simulated/ Analytical power consumption and (b) measured power consumption at different waveforms.

The reliability and repeatability of the experimental results and processes were verified by repeating the experiments at the same test conditions with a different membrane from a different supplier. Figure 5-45 below illustrates that the effects of the ripple factor and frequency show a similar trend, irrespective of the membrane. Figure 5-45 (a) shows the power consumption measured with a membrane from supplier A (membrane used for this study), while Figure 5-45 (b) shows the power consumption measured with a membrane from supplier B (membrane used for verification). In both cases the power consumption of the PEM electrolyser increases as the ripple factor increases and decreases as the frequency increases. The hydrogen flow rate measured with the membrane from supplier B was also unaffected by the ripple factor and frequency of the supplied current, as was the case with the membrane from supplier A.

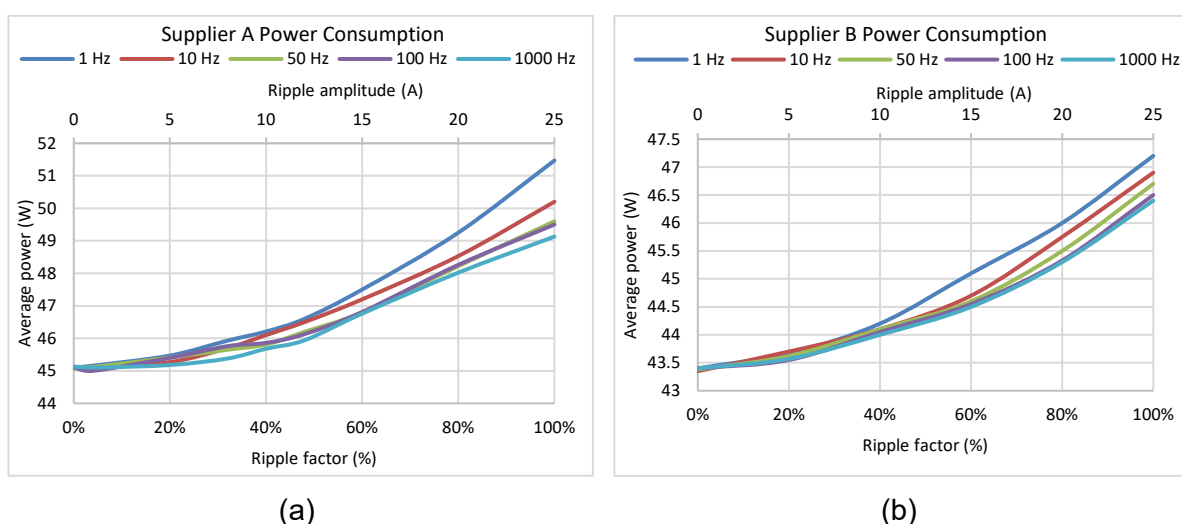


Figure 5-45: Verification of the effects of a ripple current on the power consumption of a PEM electrolyser: (a) Membrane from supplier A, (b) Membrane from supplier B.

As mentioned earlier, each experiment at different parameter settings was conducted only for a short period due to the magnitude of the different settings tested. The effect of the ripple current on the degradation rate was also not known at the time, and since a limited amount of MEA's were at disposal for this study, any damage caused by a ripple current was avoided. The degradation tests however proved that the effect of a ripple current on the degradation rate of the electrolyser is minimal and the results of these long-term test could therefore be used to validate the results obtained in the preceding ripple current tests. The two main observations made from the degradation tests, in comparison to the preceding ripple current test, are that the hydrogen flow rate is unaffected by the ripple factor and frequency of the applied current and these parameters only have a slight impact on the RMS cell voltage. These observations are in good agreement and therefore validate the ripple current measurements illustrated in section 5.3.

5.6 Conclusion

In section 5.3.2 it was illustrated that a ripple current and the ripple current settings such as the ripple factor or frequency has a major effect on the power consumption or energy input of the PEM electrolyser. On the other hand, the energy output or hydrogen output is directly proportional to the mean value of the applied ripple current and thus unaffected by the current waveform, ripple factor or frequency seeing that the DC offset is unchanged as shown in section 5.3.3. The efficiency loss caused by a ripple current is thus due to the increase in the energy consumption of the PEM electrolyser without an increase in the hydrogen output.

An increase in the ripple factor of the applied current also causes an increase in the ripple factor of the cell voltage, as illustrated in section 5.3.1. The result is thus higher RMS current and voltage values which increase the power consumption and decrease the efficiency of the cell. Although the effect of frequency is smaller than the effect of the ripple factor, an increase in the frequency causes an increase in the cell efficiency. The effect of frequency is also getting more noticeable as the ripple factor of the applied current increases. It was observed in section 5.3.1 that noticeable hysteresis exists between the cell voltage and current at low frequencies. This phase shift is due to the impedance related to the double layer capacitance (imaginary part) and cause an increase in the power consumption and a decrease in the cell efficiency.

Although the different current ripple waveforms tested on the PEM electrolyser produced different results, a similar trend in the effect of the ripple factor was observed in all of them. The effect of the ripple amplitude on the power consumption and the efficiency of the cell is however different for each waveform since the crest factor is different for each waveform. The frequency of the ripple current also affects the efficiency of the cell differently since the frequency spectrum of each waveform is different. However, for all of the tested ripple current waveforms, the cell efficiency is the highest at a frequency of 1 kHz, which is the highest frequency in this study.

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

6.1 Introduction

This chapter is the closing chapter of the dissertation and serves as the conclusion of the conducted research. Firstly, the previous chapters of the dissertation are discussed; next, the key research questions are answered; then, the verification and validation processes are summarised; and finally, some recommendations for future work are made.

6.2 Discussion

Chapter 1 presented the background information of this research project, the problem statement and aim of this study. The aim was to determine the effect of a power supply ripple on the efficiency of a PEM electrolyser. Next, the primary and secondary objectives were outlined, as well as the key research questions and limitations of the study. The primary objective was to determine how the different electrical characteristics of a ripple current such as the waveform, frequency, AC amplitude and DC offset, affects the efficiency of a PEM electrolyser. The listed secondary objectives are the objectives that needed to be achieved in order to finally achieve the primary objective. Finally, the methodology was presented which is the step by step process that was followed to complete this research project and achieve the desired outcome.

Chapter 2 contain the literature study on all topics that were required for the rest of the research project. The main topics reviewed include the electrochemical fundamentals of water electrolysis, the efficiency of a PEM electrolyser, electrochemical characterisation techniques, equivalent electrical circuit models, power supply ripple characteristics and similar studies. The information presented in Chapter 2 was crucial since it provided the foundation on which the following chapters, as well as the verification and validation processes, were built.

In Chapter 3, the design specifications, experimental setup and procedures, as well as the implementation of the setup, were presented. Included in this chapter is the input and output parameter identification and range selection, equipment and component selection and integration as well as a comprehensive explanation of the experimental method and measurement sequences.

Chapter 4 presented the characterisation, modelling and simulation of the PEM electrolyser. The purpose of the activities presented in this chapter was to characterise the PEM electrolyser and use the acquired information to formulate an accurate EEC model as well as an analytical model of the PEM electrolyser.

The models were then used to simulate the effects of a power supply ripple on the dynamic behaviour of the PEM electrolyser. The EEC model was simulated in LTspice® while Simulink® was used to simulate the analytical model. The simulation results suggested that the cell efficiency would be negatively affected when a ripple current is applied to the electrolyser since the power consumption increases without an increase in the hydrogen production rate. The simulation results show that the increase in power consumption and therefore, the decrease in cell efficiency, is directly related to the size of the applied ripple (size of AC component). Furthermore, the results showed that the waveform of the applied ripple current does not affect the behaviour of the PEM electrolyser when using the ripple factor as a measured of the ripple size rather than the AC amplitude. The ripple factor is not only affected by the AC amplitude of the ripple current but also by the crest factor of the waveform. It was also observed that an increase in the frequency of the applied ripple would reduce the effect of the ripple on the power consumption. The effect of frequency on the power consumption and voltage response of the simulated PEM electrolyser can be explained by the impedance related to the double layer capacitance (imaginary part), which decrease as the frequency increase. The chapter also presented the processes used to verify and validate the developed models and the results obtained from the simulations.

In Chapter 5, the experimental results were presented and analysed. In this chapter, the measured effect of a ripple current on the voltage and current relationship, power consumption, hydrogen production rate, efficiency and degradation rate of a PEM electrolyser were discussed. The three major sections of chapter 5 are the DC measurements, ripple current measurements and the degradation measurements. The results presented in chapter 5 illustrated that a ripple current and the electrical characteristics of the ripple current (DC offset, ripple factor, frequency) has a significant effect on the power consumption of the PEM electrolyser. In contrast, the hydrogen output is directly proportional only to the mean value of the applied ripple current and thus unaffected by the current waveform, ripple factor or frequency seeing that the DC offset is unchanged. The results were verified by comparing the measured results to the simulation results in which similar trends were observed. The chapter also presented the results of the degradation tests, which showed that a very large ripple factor (> 80%) could decrease the life expectance of the MEA and other cell components. However, the results show no clear indication that a more likely ripple factor of 50% or less, increases the degradation rate of the PEM electrolyser.

This chapter is the final and closing chapter of this dissertation in which an overview of the study is presented. Included are answers to the key research questions, a summary of the verification and validation processes and some recommendations for future work.

6.3 Key Research Questions

At the start of this study, the key research questions that had to be addressed were formulated from the research objectives, presented in sections 1.3.1 and 1.3.3. These questions, presented in section 1.3.4 of the introductory chapter, are restated and answered accordingly in this section. The purpose of the simulation and experimental tests done were to answer each question as accurately as possible within the limitations of the project, as outlined in section 1.3.2.

1. Does a ripple power supply have a positive or negative effect on the efficiency of a PEM electrolyser?

The purpose of this question was to determine if certain controlled ripple currents, supplied to a PEM electrolyser can improve the efficiency of the cell. This question comes after certain studies in the available literature showed that a pulsing DC input to alkaline electrolyzers might improve the efficiency of the cell. In contrast, other studies showed that any deviation from a continuous DC supply has a negative impact on the efficiency. The discrepancy in the literature, as well as the absence of studies on PEM electrolyzers, revealed this gap that needed to be addressed. In the course of the ripple current measurements, illustrated in section 5.3, two main observations were made. The first is that the hydrogen production rate of the PEM electrolyzers is affected only by the mean value of the supplied current and the second is that any deviation from a continuous DC supply increases the power consumption of the electrolyser. The results, therefore, show that a ripple current or a pulsing DC supply has a negative impact on the efficiency of a PEM electrolyser since the energy input is increased without increasing the energy output.

2. How does ripple currents, at various waveform, frequency, AC amplitude and DC offset settings, influence the hydrogen production rate as well as the energy consumption rate of a PEM electrolyser?

After determining that a ripple current or any deviation from a continuous DC supply lowers the efficiency of a PEM electrolyser, the next step was to determine the effect of the waveform, frequency, AC amplitude and DC offset respectively. To answer this question, a wide range of different ripple currents and pulsing DC currents were applied to the PEM electrolyser while the voltage, power consumption and hydrogen flow rate were measured. The results illustrated in section 5.3, showed that an increase in the ripple factor of the applied current causes an increase in the cell voltage and power consumption while the hydrogen flow rate is unaffected. It was also observed that if the PEM electrolyser receives a ripple current input, the power consumption decreases as the frequency increases, provided that the ripple factor remains the same.

The hydrogen production rate of the PEM electrolyser is not affected by the frequency of the applied ripple current. The waveform type does not have a significant impact on the power consumption of the cell as illustrated in section 5.3.2, and since the hydrogen production rate is only dependant on the mean value of the applied current, the waveform type does not affect the hydrogen flow rate provided that the DC offset is the same.

3. Will applying a ripple current to a PEM electrolyser accelerate the degradation rate?

Knowing that a ripple current would decrease the efficiency of the PEM electrolyser, it was also essential to establish what the effect of such a ripple current would be on the life expectancy of the cell, specifically the MEA. Several degradation tests were done in which the voltage drift, as well as the fluoride loss of the PEM electrolyser, were measured as illustrated in section 5.4. These experimental tests proved that there is no significant increase or decrease in the rate at which the MEA degrades over time if the applied ripple factor is less than 50%. However, when the ripple factor is increased to 80%, a slight increase in the fluoride loss can be observed and with a further increase up to 100% both the voltage drift and the fluoride loss significantly increase. A substantial ripple factor, therefore, accelerates the degradation rate, but there is no proof of an accelerated degradation rate when a smaller more probable ripple factor is present in the power supplied to a PEM electrolyser.

6.4 Verification and Validation

In section 1.4.8 of the introductory chapter, it was stated that the verification and validation processes are essential to ensure the accuracy and validity of this study. These processes were performed throughout the design, modelling, simulation and experimental phases as illustrated by the verification and validation chart in Figure 6-1.

The literature study presented in Chapter 2 formed a crucial part of the verification and validation procedures used in this study. The literature reviewed was used to validate the experimental specifications, the experimental setup, as well as the characterisation and test protocols presented in sections 3.3, 3.4 and 3.6 of Chapter 3. In sections 2.7 and 2.8 of the literature study different characterisation techniques and EEC models were reviewed, which were used to validate the characterisation and the developed simulation models presented in sections 4.2 and 4.3. Finally, the case studies presented in section 2.11 were used to verify and validate the simulation results listed in section 4.4.

The characterisation and modelling of the PEM electrolyser (sections 4.2 and 4.3) were verified in sections 4.2.3, 4.3.2 and 4.3.5. The verification of the characterisation was achieved by comparing the results obtained of different characterisation techniques with each other and by repeating the characterisation protocols several times to determine the accuracy of the results.

The simulation models, developed from the characterisation results, were verified by applying the models to several other PEM electrolyser cells (same assembly, different components) and by comparing the developed models to other models found in the literature. This ensured that the obtained characterisation results are repeatable and accurate while also ensuring that the developed models can be used to represent different PEM electrolyser cells accurately.

The simulation results (section 4.4) were verified by comparing the results to the results obtained from similar experiments and is presented in section 4.5. These results were further verified in section 5.5 of Chapter 5 by comparing the experimental test results to the simulated results. The experimental test results were then also further verified by repeating the test on a different PEM electrolyser cell (same assembly, different MEA) to verify that the trend observed when a ripple current is applied remains the same.

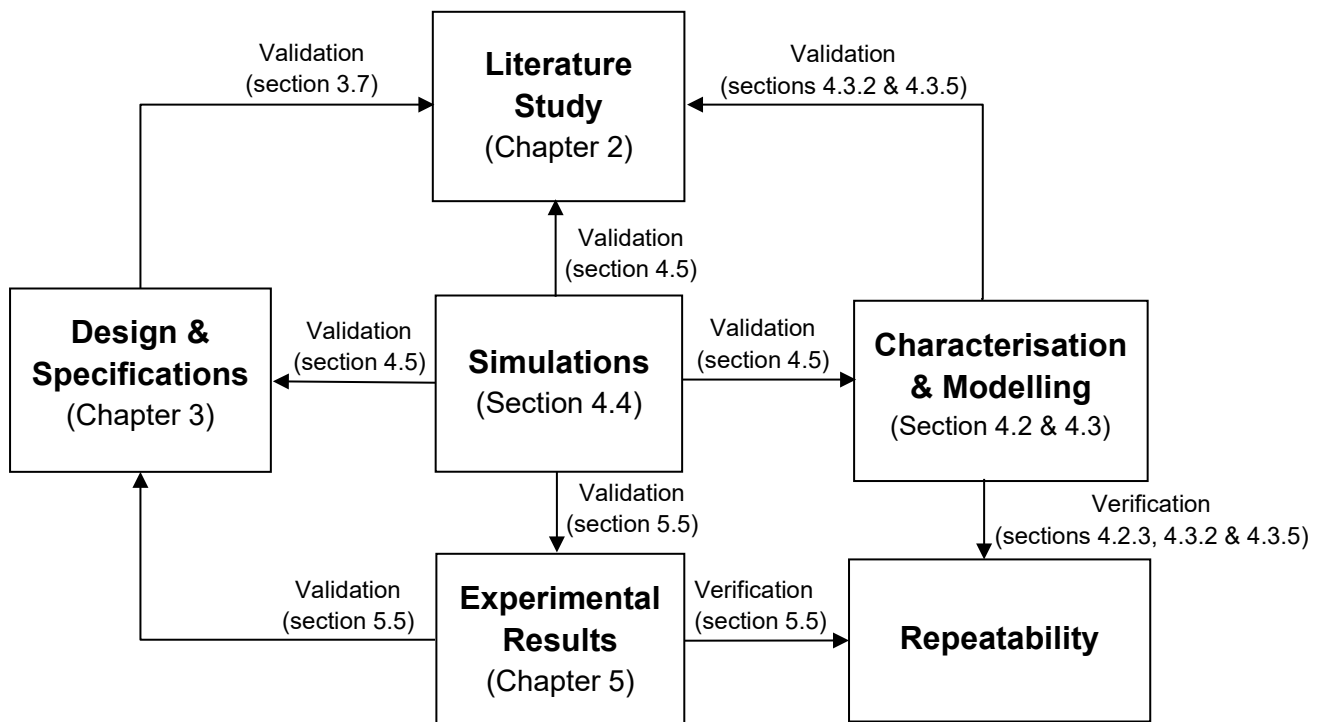


Figure 6-1: Verification and validation processes of the dissertation.

6.5 Future Work and Recommendations

The research presented in this dissertation proved that the electrical characteristics of the power supplied to a PEM electrolyser can have a significant effect on the efficiency of a water electrolysis system. In this section, recommendations are made for future research to improve and refine the current knowledge in this field.

- In this study, all experimental tests were conducted on a small 25 cm² single cell PEM electrolyser, with a maximum applied current of only 25 A. The hydrogen produced, and power consumed by the cell is thus also very small, and it is proposed that the experiments be repeated on a PEM electrolyser stack to obtain more accurate results.
- This study focused on the effect that a power ripple on the DC side of a power supply has on the power consumption and hydrogen flow rate of a PEM electrolyser. Since the reactive power on the AC side of a power supply would also be affected by a ripple on the DC side, it is proposed that the AC side power quality should be measured to accurately determine the impact of power quality on the efficiency of a PEM electrolysis system. An improvement in the power quality would not only decrease the operating expense (OPEX) of the system, but improvement in the capital expenditure (CAPEX) could possibly be achieved since the required power compensation devices would be reduced.
- The effect of a power supply ripple on the efficiency of a PEM electrolyser can be minimized by increasing the switching frequency of the converter to the frequency at which the impedance of the electrolyser is a minimum. However, this can lead to using more expensive converter topologies and in effect, increase the CAPEX. It is thus proposed that before a converter is selected for a PEM electrolysis system, a comprehensive investigation should be done to obtain the lowest overall cost based on the impedance response of the specific electrolyser. Power quality research will be especially important in the development of power converters for large-scale, low-cost hydrogen production through gigawatt scale water electrolyzers in the future.

6.6 Conclusion

In conclusion, this research was done to determine the effect of ripple currents on the efficiency of a PEM water electrolyser. Both the primary and secondary objectives have been achieved and the key research questions presented in Chapter 1 have been answered. The single cell PEM electrolyser used in this study has been characterised, modelled and simulated after which some experimental tests have been carried out on the electrolyser. The results obtained showed a decrease in the efficiency of a PEM electrolyser with an increase in the ripple factor, an increase in the efficiency with an increase in the ripple current frequency and a negligible change in the efficiency with the use of different waveforms. The study delivered a great deal of knowledge regarding the effects of power quality on the energy consumption and hydrogen production of a PEM water electrolyser which can be used to further develop this promising hydrogen production technology. Power quality research will be essential in the development of gigawatt scale PEM water electrolysis systems in the future. This dissertation is concluded with the following quote that stands true for this research.

“No research is ever quite complete. It is the glory of a good bit of work that it opens the way for something still better, and this repeatedly leads to its own eclipse.” - Mervin Gordon

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APPENDIX A: MODELING AND SIMULATION SOFTWARE

This appendix shows how the different modelling, simulation and control software packages were used during this study. The sections below illustrate the different user interfaces of each program, as well as the settings used to obtain the results discussed in the preceding chapters.

A.1 Echem Analyst®

The impedance data obtained from the EIS tests were fitted to an EEC model with the use of a non-linear least squares (NLLS) fitting algorithm included in the Echem Analyst® software package. Figure A-1 (a) shows the model editor used to develop the EEC model, Figure A-1 (b) the simplex NLLS method used to calculate the parameter values and Figure A-2 the fractional residual errors of the calculated parameter values as a function of frequency. The model editor displayed in Figure A-1 (a) contains various common electrical circuit elements such as resistors, capacitors and inductors together with some specialised electrochemical circuit elements such as CPE's and Warburg impedance blocks. The parameter values of the circuit elements selected for the created model were then calculated using the simplex NLLS method as shown in Figure A-1 (b). The parameter values are selected to minimise the difference between the impedance of the EEC model and the measured impedance of the PEM electrolyser. The residual errors of the real and imaginary parts of the model impedance are displayed in Figure A-2 as a function of frequency.

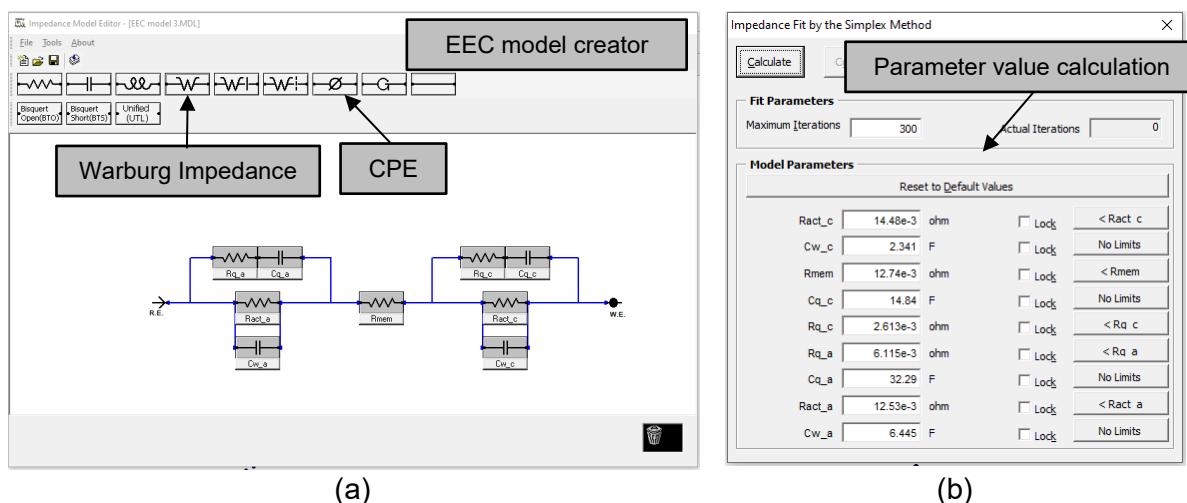


Figure A-1: Echem Analyst®: (a) Impedance model editor (b) Impedance fit by the Simplex method.

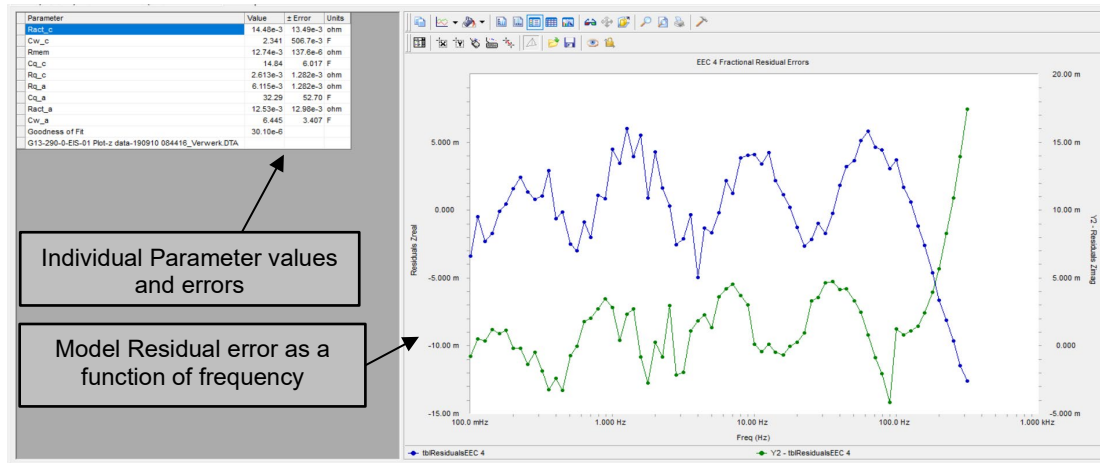


Figure A-2: Echem Analyst® impedance fit parameter values and fractional residual errors.

A.2 LTspice®

The created EEC model and the calculated parameter values described in the section above, was simulated by using the electrical simulation software LTspice®. The following figures show the impedance simulation settings and results. Figure A-3 (a) demonstrates the AC analysis settings used to simulate the impedance response of the EEC model over a frequency range of 100 mHz to 200 kHz, while Figure A-3 (b) is the output bode diagram, illustrating the magnitude and phase shift of the EEC model impedance.

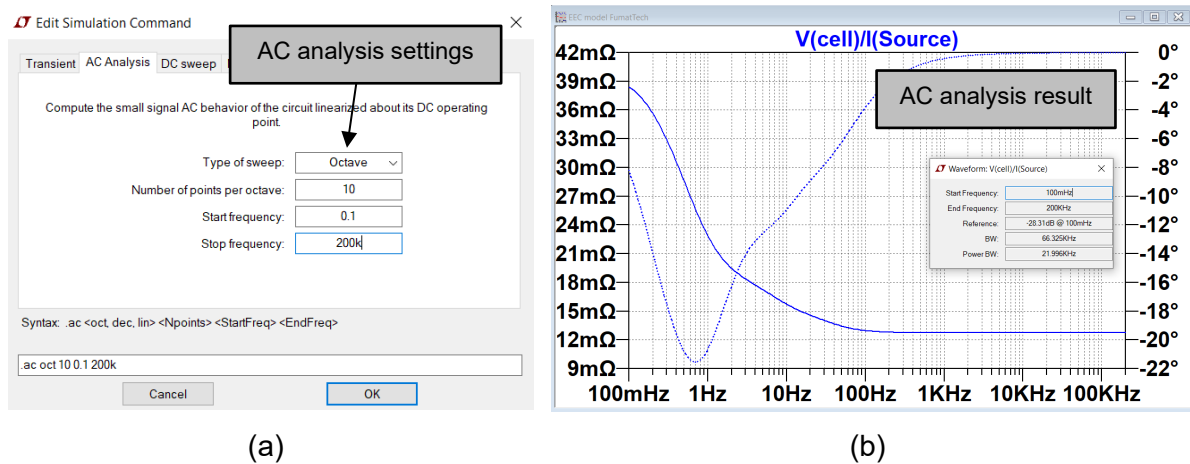


Figure A-3: LTspice® impedance simulation: (a) AC analysis settings (b) Output.

The following figures show the voltage and power consumption simulation settings and results. Figure A-4 to Figure A-6 (a) show the current source parameter settings used to simulate each of the considered waveforms (sinusoidal, triangular and square), while Figure A-4 to Figure A-6 (b) show the simulated output current, voltage and power waveforms. The ripple currents displayed in the figures, each have a DC offset of 25 A, an AC amplitude of 5 A and a ripple frequency of 100 Hz.

Using the above-mentioned settings, the average power consumption is 45.013 W for a sinusoidal ripple current as illustrated by Figure A-4 (b), 45.017 W for a triangular ripple current as illustrated by Figure A-5 (b) and 44.95 W for a square wave ripple current as illustrated by Figure A-6 (b).

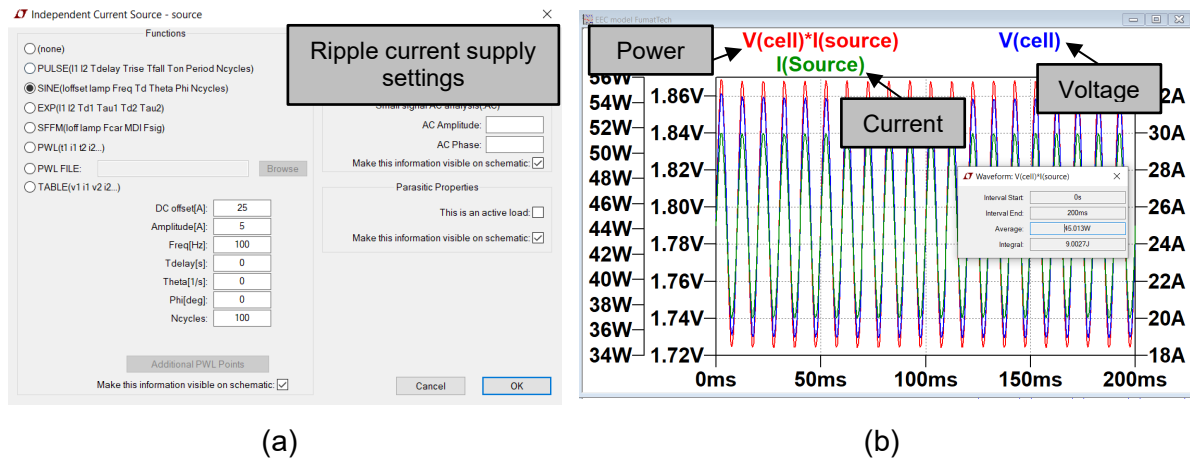


Figure A-4: LTspice® sinusoidal ripple current simulation: (a) Current source settings (b) Output.

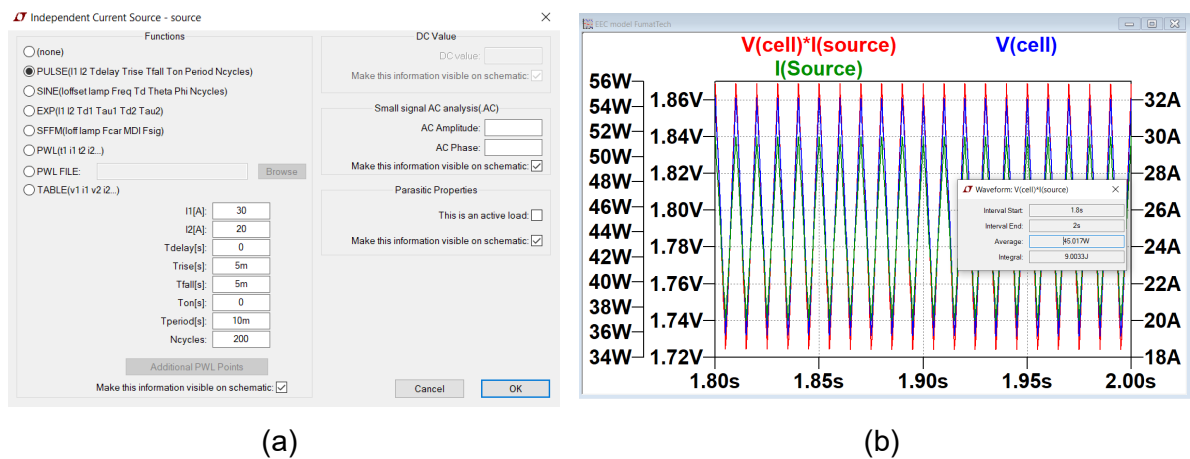


Figure A-5: LTspice® triangular ripple current simulation: (a) Current source settings (b) Output.

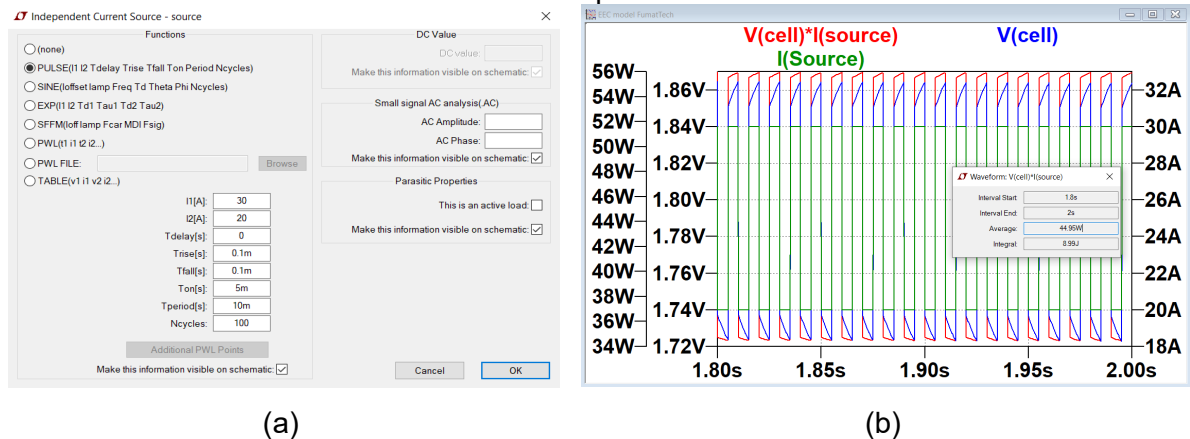


Figure A-6: LTspice® square wave ripple current simulation: (a) Current source settings (b) Output.

A.3 MATLAB® and Simulink®

The complete Simulink® model that was used to simulate the dynamic voltage response and hydrogen flow rate of the PEM electrolyser is presented in Figure A-7. The model consists of three function blocks to calculate the open circuit voltage and overpotentials of the electrolyser as well as a function block to calculate the theoretical hydrogen production rate of the system. The model allows the user to adjust several operating conditions such as the temperature, pressure as well as the electrical parameters of the power supply such as the frequency, DC offset, AC amplitude and waveform. Figure A-8 (a) and (b) show the subsystems that can be seen in the complete Simulink® model. Figure A-8 (a) is the power supply block and consist of a constant DC power supply and a signal generator to create a ripple current. The system also includes a ramp DC power supply which was used to gradually increase the current density and generate a polarisation curve. Figure A-8 (b) is the block used to calculate the reversible potential at nonstandard temperature conditions.

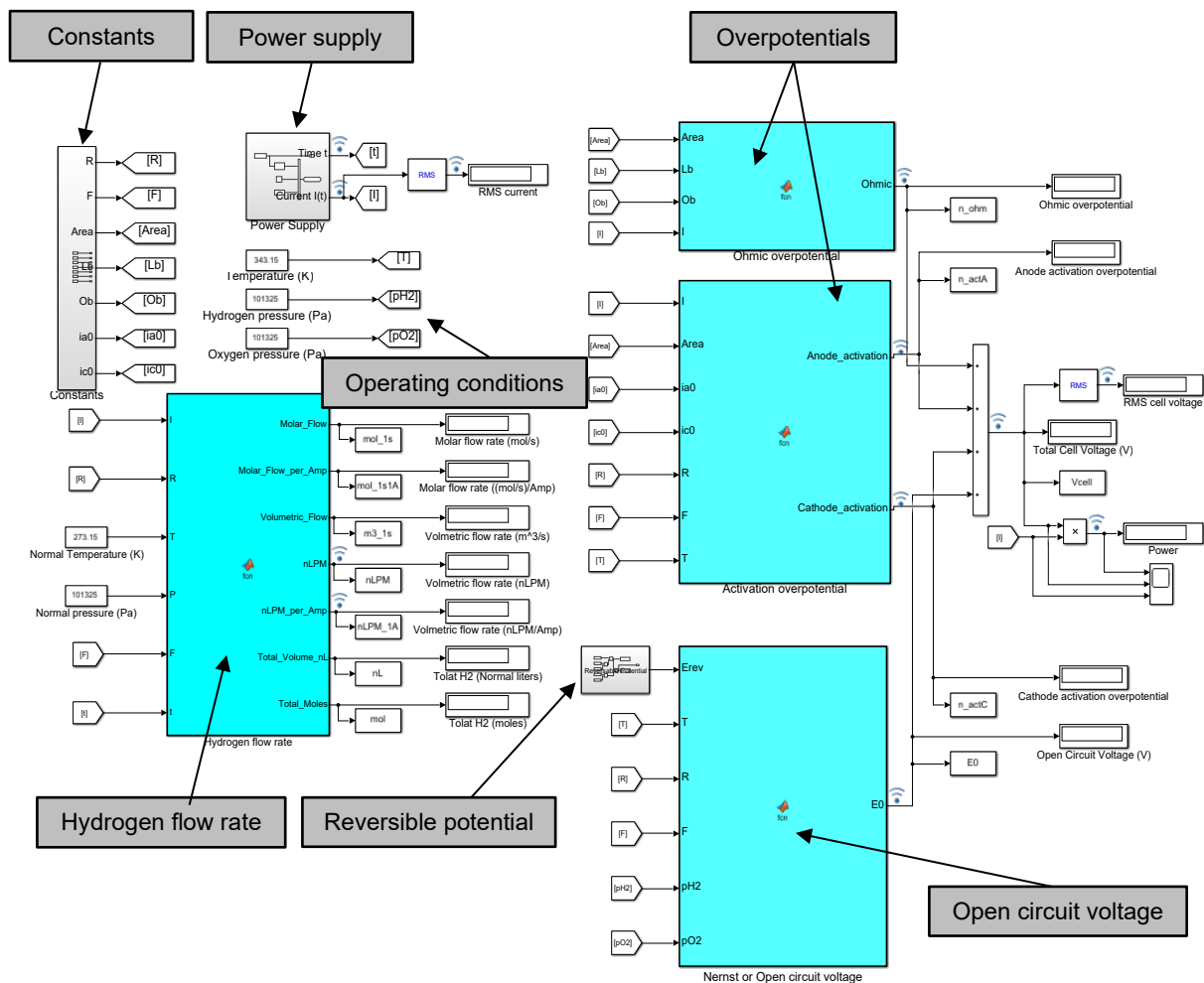


Figure A-7: Complete Simulink® simulation model.

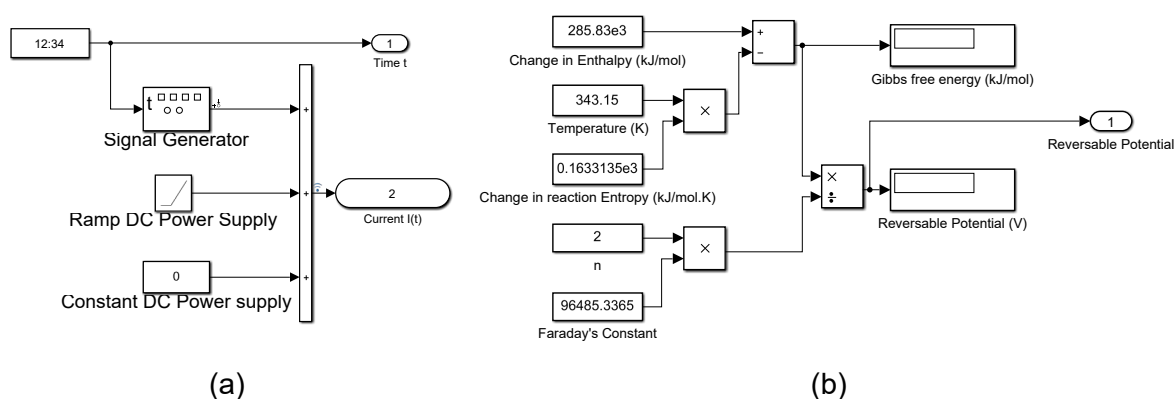


Figure A-8: Simulink® subsystems: (a) Power supply (b) Reversible potential.

The MATLAB® code of the Simulink® function blocks used to calculate the open circuit voltage, ohmic overpotential, activation overpotential and hydrogen flow as shown in Figure A-7 is presented in Figure A-9 below.

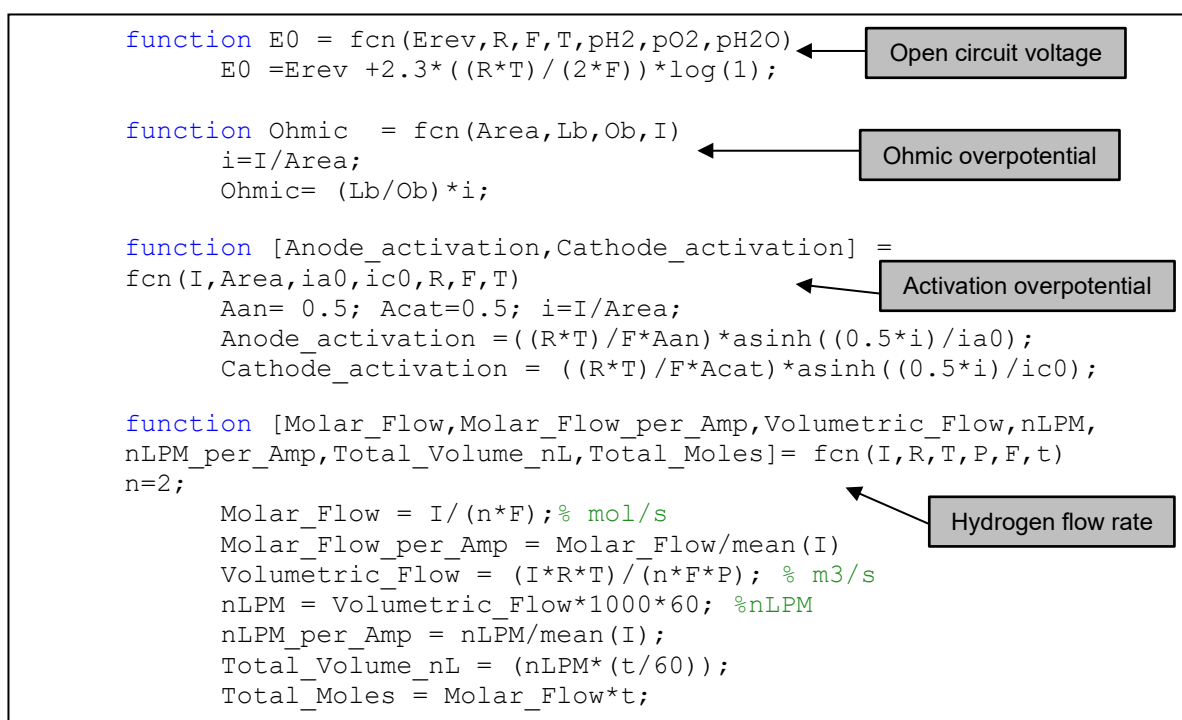


Figure A-9: MATLAB® code of the Simulink® function blocks.

A.4 EA Power Control®

EA Power Control® is the software package that was used to control the power supply and define the output current settings during the experimental tests. Figure A-9 shows the front panel that is used to changes settings such as the waveform, frequency, amplitude and DC offset. The figure displays the settings for a sinusoidal ripple current with a DC offset of 25 A, an AC amplitude of 5 A and a frequency of 10 Hz.

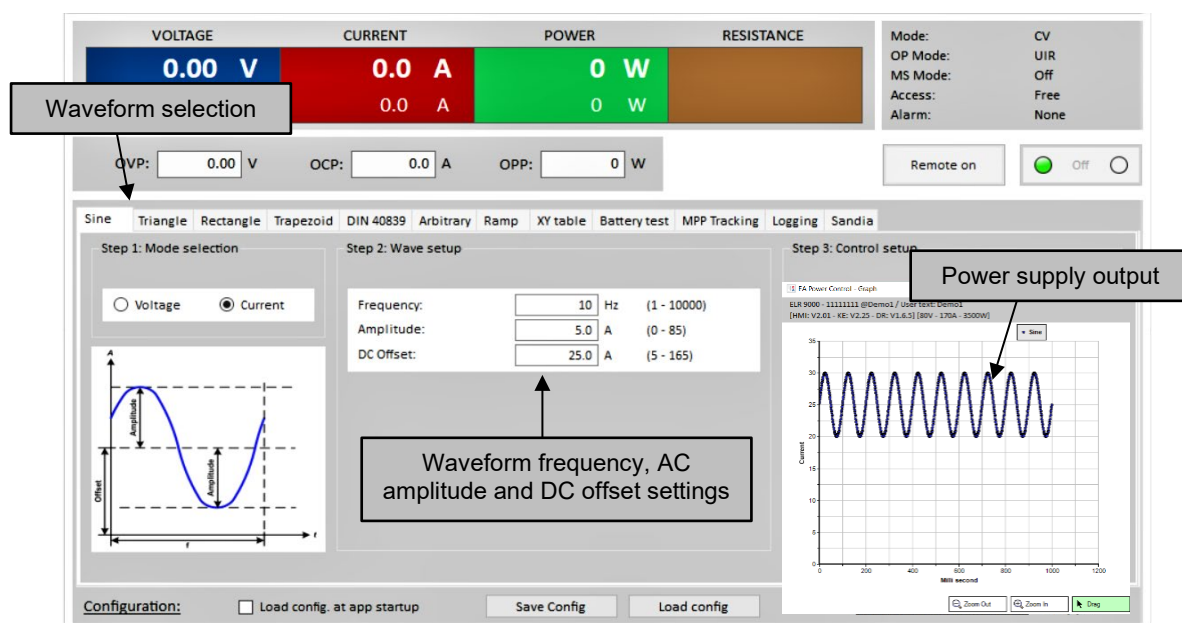


Figure A-10: EA Power Control® front panel

A.5 Emerald® Electrolyser Test System

The experimental test conditions were controlled by the electrolyser test station and accompanying software Emerald®. The front panels used to define the operational temperature and pressure, the polarisation curve and EIS settings as well as the automation sequence are shown in Figure A-11 below. Figure A-11 (a) illustrates the front panel or interface used to control the temperature and pressure of the PEM electrolyser as well as the water supply pump. In this study, the temperature and pressures conditions were kept constant as per the design specifications in section 0. The front panel presented in Figure A-11 (b) was used to select the step size as well as the current and voltage limitations of the PC measurements. The PC were then plotted in the white window in the middle and saved in the file location defined on the right hand side. Figure A-11 (c) illustrates the front panel used to define setting such as the initial and final frequency for the EIS tests. The measured impedance from the EIS tests were then plotted in the black window in the middle. Finally, the front panel presented in Figure A-11 (d) was used to set up a script for automated testing.

A.6 Conclusion

This appendix presented the modelling, simulation and control software used during the course of this study. Each of the discussed software packages played an important role in obtaining the results presented in Chapter 4 and 5 of this dissertation. The modelling software Echem Analyst® was presented in section A.1, the simulation software which include LTspice®, MATLAB® and Simulink® were then discussed in sections A.2 and A.3, and finally the control software EA Power Control® and Emerald® were presented in sections A.4 and A.5.

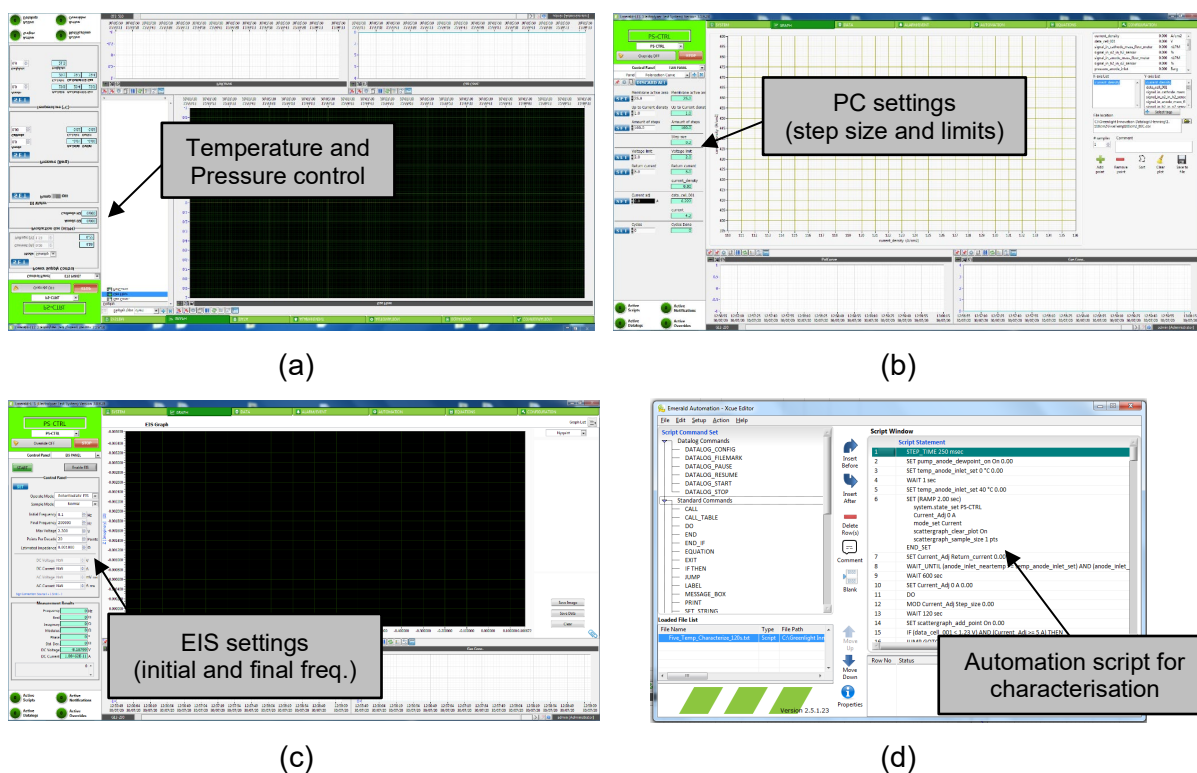


Figure A-11: Emerald® front panels: (a) Temperature and pressure control (b) Polarisation curve settings (c) EIS settings (d) Automation editor.

APPENDIX B: ARTICLES

B.1 Articles submitted and pending peer review

H.P.C. Buitendach, R. Gouws, C.A. Martinson, C. Minnaar and D. Bessarabov, "Effect of a ripple current on the efficiency of a PEM electrolyser"

Effect of a ripple current on the efficiency of a PEM electrolyser

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Abstract

The aim of this study was to determine how the efficiency of a proton exchange membrane (PEM) electrolyser is affected by an electric ripple current and the different characteristics of the ripple current (frequency, amplitude and waveform). This paper presents the experimental method and measured results, used to analyse the effect of ripple currents at various frequencies, ripple factors and waveforms on the hydrogen production, power consumption and efficiency of a PEM electrolyser. An active laboratory-size PEM electrolysis system was used to investigate the impact of various ripple currents on the efficiency of the system. The results revealed that the average power consumption increases as the ripple factor increases and decreases as the frequency of the ripple increases, while the waveform of the applied current has no effect. Furthermore, the average hydrogen flow rate is unaffected by the ripple factor, frequency or waveform of the applied ripple current.

Keywords: Proton exchange membrane, Electrolyzer, Ripple Current, Ripple factor, Efficiency

1. Introduction

As the world's population and the energy demand increase, the storage, transport and distribution of energy becomes increasingly important, along with efforts to improve the utilisation of renewable energy sources such as solar, wind and hydro power [1]. Many consider hydrogen, produced using water electrolysis and sustainable energy sources, as the potential energy carrier of the future and the solution to improving the utilisation of fluctuating renewable energy sources [1-6]. The desirability of hydrogen is mainly due to the high level of flexibility that this energy carrier offers. Stored hydrogen can be used for transportation applications, such as in fuel cell vehicles, internal combustion engine vehicles and hybrid electric vehicles [7-11]. It can be also be utilised as an alternative/replacement for natural gas used in cooking and heating applications [12, 13], or it can be reconverted to electricity using stationary fuel cells for emergency backup power, power in remote areas and applications in which highly reliable power supplies are required, such as in telecommunication applications [14, 15]. A comprehensive review of the current hydrogen usage is given in [16]. Although the flexibility, high energy density and high storage capacity potential of hydrogen is superior to other energy carriers and storage technologies [1], the International Renewable Energy Agency (IRENA) recently reported that globally only about 4% of hydrogen production is through water electrolysis [17]. The remainder of the hydrogen is produced through processes like steam-methane reforming, oil gasification and coal gasification. The result is that >95% of all current hydrogen production uses fossil fuel as a feed stock. The main reasons for the low amount of hydrogen produced through water electrolysis include the high capital expenditure (CAPEX) and operating expense (OPEX) of these systems [18-20]. Improvement in the CAPEX, OPEX and efficiency of water electrolysis systems are thus required for water electrolysis to be commercially competitive with the fossil-fuel-driven alternatives.

Nomenclature

C	Capacitance (with subscript), F
E_{th}^0	Thermoneutral potential at standard conditions, V
I	Instantaneous Current, A or A/cm ²
I_{rms}	RMS current, A
I_{DC}	Current DC component (Average Current), A
i	Current AC component, A
i_{rms}	RMS of current AC component, A
$\dot{n}_{H_2}$	Hydrogen molar flow rate, mol.s ⁻¹
P_{avg}	Average power consumption, W
$P_{measured}$	Instantaneous power consumption, W
P_{theor}	Theoretical power consumption, W
R	Resistance (with subscript), ohm
RF	Ripple factor, %
U_{cell}	Instantaneous cell voltage, V
U_{DC}	Voltage DC component (Average Voltage), V
U_{rms}	RMS voltage, V
Z	Impedance, ohm

Greek symbols

ε_{cell}^{HHV}	Cell efficiency, %
ε_V^{HHV}	Voltage efficiency, %
ε_I	Faradaic efficiency, %
χ^2	Chi-squared

Abbreviations

AC	Alternating current
AEM	Anion-exchange membrane
CAPEX	Capital expenditure
CPE	Constant phase element
DC	Direct current
EEC	Equivalent electrical circuit
EIS	Electrochemical impedance spectroscopy
GDL	Gas diffusion layer
HHV	Higher heating value
Hz	Hertz
LHV	Lower heating value
MEA	Membrane electrode assembly
nLPM	Normal Litres per minute
OPEX	Operational expenditure
PC	Polarisation curve
PFSA	Perfluorosulfonic acid polymer
PEM	Proton exchange membrane
RF	Ripple factor
RMS	Root mean square

The three primary water electrolysis technologies commercially available and being considered to improve the cost of hydrogen production through water electrolysis are alkaline water electrolysis, proton exchange membrane (PEM) water electrolysis and solid oxide electrolysis. A version of the alkaline electrolysis that can be classified as a fourth technology is known as AEM (anion-exchange membrane)–based water electrolysis [21]. Although the advantages of each of these technologies for sustainable large-scale hydrogen production are constantly debated [22–27], most experts believe that by 2030 PEM water electrolysis will be the dominant and most suitable water electrolysis technology [20]. Advantages of PEM water electrolysis include the following: rapid response times to the fluctuation of renewable energy sources, simple zero-gap cell, modular system design, high current density capabilities, high hydrogen discharge pressure and the production of high-purity hydrogen [28, 29]. To improve the efficiency and reduce the CAPEX of PEM water electrolyzers, research and development has tended to focus on topics such as the influence of the operating temperature [30–33] and pressure [34–38] [39–41] on the efficiency, reduction in the platinum group metal (PGM) content or the development of non-noble-metal electrocatalysts [42–44], the impact of component degradation mechanisms on the cell lifetime [45–51], and several other materials science challenges, such as replacement of titanium in the bipolar plates [52, 53]. Although these conventional approaches are important in the long-term development of PEM water electrolyzers, most of the studies accept the power supplied to the electrolyser to be a steady DC supply. Practically, however, this is not the case, since the power is usually supplied from a combination of AC-DC and DC-DC converters, which, based on the converter topology, may produce a noteworthy ripple [54]. Literature shows that both the topology and control strategy used in power conditioning systems have an effect on the efficiency of a water electrolysis system [7, 54–60]. Unconventional research approaches focusing on the impact of a ripple power supply as well as the different characteristics of the ripple (frequency, amplitude and waveform) could thus lead to innovative developments to improve the efficiency of water electrolysis. Power quality research will be especially important in the development of power converters for large-scale, low-cost hydrogen production through gigawatt scale water electrolyzers.

Several studies have already been carried out to address this topic—various voltage and current waveforms were used at different DC offset values, frequency and AC amplitude settings. Some studies indicate that a specific and controlled power supply ripple, such as a pulse potential, could have a positive effect on the efficiency of the electrolyser [61, 62]. According to the literature presented in [61, 62], an increase in efficiency is possible due to an enhancement in the mass transport of hydrogen and oxygen that forms on the electrode surfaces. An improvement in the rate at which gas is discharged reduces the electrode surface resistance and, in return, reduces the energy consumption. Other studies in which various frequency, waveform, DC offset and AC amplitude settings were investigated revealed that any deviation from a steady DC supply has a negative impact on the efficiency of an electrolyser [63–67]. The discrepancies evident in the literature indicates that the effect of a ripple power supply is not consistent between different systems and water electrolysis technologies.

The electrical characteristics of the applied power are thus known to have a large influence on the efficiency of an electrolysis system. Yet, to date, most of the research reported in literature has focused only on alkaline electrolysis systems. There appears to be very few report/s of research into PEM water electrolysis systems—hence, the purpose of our research is to fill this gap.

2. Materials and methods

The materials and methods used in determination of the effect of different ripple currents on the power consumption, hydrogen production and efficiency of a PEM electrolyser are now described. In Section 2.1 the experimental setup and the apparatus are discussed, in Section 2.2 the PEM electrolyser assembly is described and, finally, in Section 2.3 the experimental process that we followed is reported.

2.1 Experimental system

The experimental system, which includes a single-cell PEM electrolyser, Elektro-Automatic® programmable power supply, LeCroy® oscilloscope, Gamry® Interface 1000 potentiostat/galvanostat and a test station incorporating a water supply pump, heat exchanger, thermocouples, gas separators and flow meters, is shown in Fig. 1.

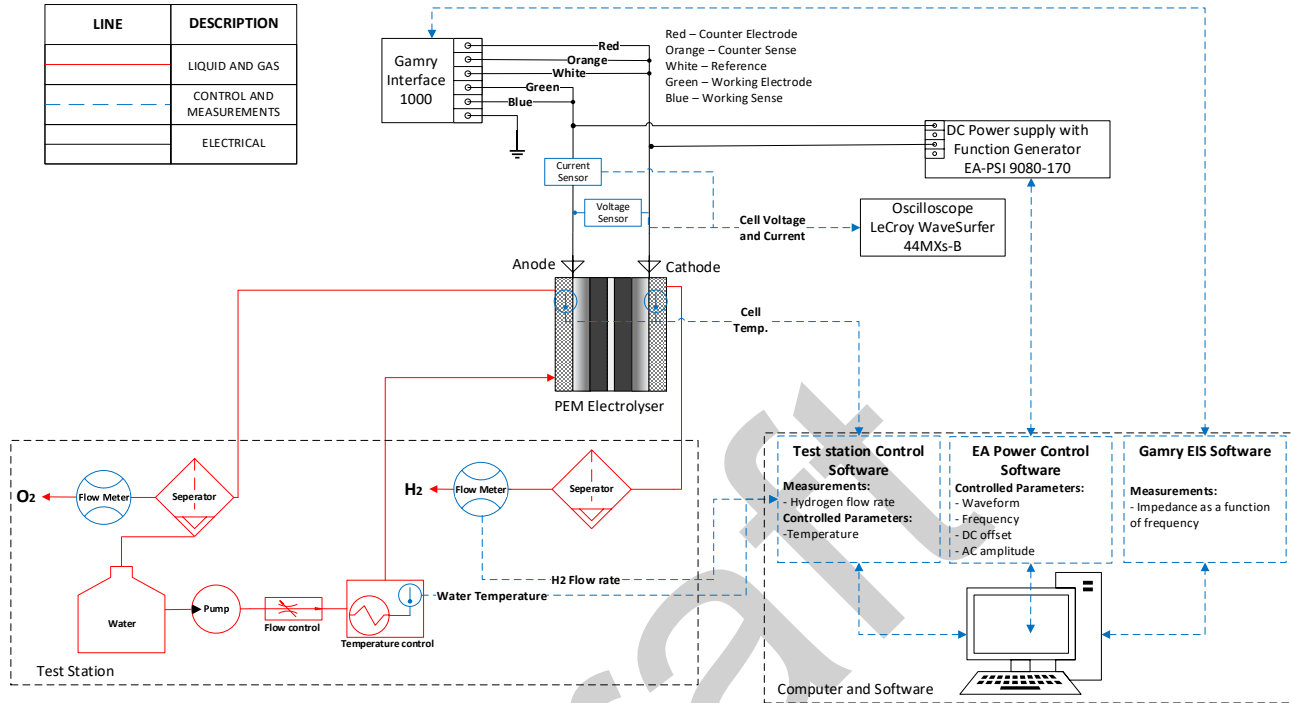


Fig. 1 - Experimental setup used for the characterisation of the single cell PEM electrolyser and for the experimental ripple current measurements.

The test station, manufacture by Greenlight Innovation®, was used to supply the PEM electrolyser assembly (shown in Fig. 2) with temperature-controlled deionised water and measure the flow rate of the hydrogen gas produced. The operating temperature was held constant at 70 °C. The hydrogen flow rate was measured in normal litres per minute (nLPM), which is the volumetric flow rate at a temperature of 273.15 K and a pressure of 1 atm. The Gamry interface 1000 was operated in galvanostatic mode. It was used to characterise the PEM electrolyser through electrochemical impedance spectroscopy (EIS) measurements. The programmable power supply, which includes a function generator with various pre-defined functions, was responsible for the generation of ripple currents with different amplitude, frequency and waveform settings to be applied to the PEM electrolyser. The current, voltage and power consumption of the electrolyser at each of the different ripple current settings were measured and logged using an oscilloscope. The ranges and limitations of the apparatus used in this study are presented in Table 1.

Table 1 – Experimental setup, apparatus and operating ranges (from refs [68-72])

Component		Range	Accuracy
Mass flow meter	(EL-FLOW F-111B-5K0)	0.042–6.5 nLPM (H ₂)	± 1% of range
Thermocouples	(Type T)	-27 – 300 °C	± 1 °C
Temperature controller	(AKT7 series)	-205 – 400 °C	0.2% of range/ ± 1 °C
Supply pump	(0.12kW Y-2951)	12 l/min	-
Power supply	(EA-PSI 9080-170)	0 – 80 V, 0 – 170 A, 0 – 5 kW	<1% of rated power
Galvanostat	(Interface 1000)	0 – 1 A, 0 – 12 V, 10 µHz – 1 MHz	1% of range
Current probe	(CP030)	0 – 30 A _{rms} , 0 – 50 A _{peak}	1% of range
Voltage probe	(PP009)	0 – 400 V	-

2.2 Single-cell PEM electrolyser

Fig. 2 shows a schematic of the single-cell PEM electrolyser used in this study. The main component in the centre of the assembly is the membrane electrode assembly (MEA), which comprises a perfluorosulfonic acid polymer (PFSA) membrane with an electrocatalyst on both sides. Gas diffusion layers (GDLs) are positioned on each side of the MEA between the electrocatalyst layer and the flow field. The assembly also includes two current collectors to evenly distribute the applied current and two end plates to hold all the components in position. The characteristics of the electrolyser components are presented in Table 2.

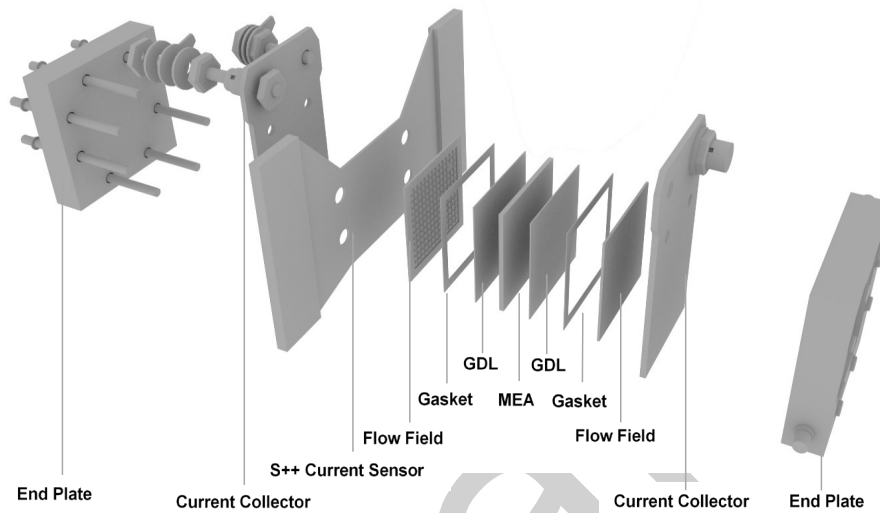


Fig. 2: Schematic of the single-cell PEM electrolyser assembly (adapted from [73]).

Table 2 – PEM electrolyser assembly characteristics and operating conditions.	
Components	Characteristics and Values
Membrane area	25 cm ²
PFSA membrane material	Long side chain
Membrane thickness	120 μ m (dry), 130 μ m (wet)
Catalyst loading (Anode)	2.2 mg/cm ² iridium oxide
Catalyst loading (Cathode)	0.65 mg/cm ² platinum
Gas diffusion layer material	Sintered titanium fibres plated with gold
Gas diffusion layer thickness	0.3 mm
Flow fields	Titanium plate with square pins (3.17 mm ²), 1.78 mm from each other
Operating pressure	1 atm
Operating temperature	70 °C

2.3 Experimental procedure

The first step in the experimental process was to characterise the PEM electrolysis cell. Here, characterisation refers to the process by which the cell performance and electrochemical phenomena such as the ohmic, activation and concentration losses are identified. Two characterisation techniques were used in this study: polarisation curve (PC) measurements and EIS. A PC is a plot of the cell voltage as a function of the current density at constant operating conditions (temperature and pressure). A PC was obtained by operating the cell over a range of current densities and measuring the cell voltage at each current density. EIS, on the other hand, is an analytical technique used to characterise an electrochemical cell by obtaining the impedance of the cell as a function of frequency. These characterisation techniques were used to obtain baseline performance data of the PEM electrolyser to determine the experimental parameters and ranges for the rest of the study.

The main objective of the experimental study was to determine the effect of a ripple current on the efficiency of a PEM electrolyser, while keeping all other operational conditions constant. Characteristics that were investigated included the ripple frequency, ripple amplitude, ripple waveform and DC offset of the applied current. A ripple current is expressed by Eq. (1) [65], where I_{DC} is the constant DC component and i the time-varying AC component. The DC component is the DC offset or average value of the applied current, while the AC component is the fluctuating waveform with a specific amplitude and frequency. The AC amplitude refers to the peak value measured from the DC offset, and the frequency is the number of cycles the waveform completes in one second.

$$I = I_{DC} + i \quad (1)$$

The effective or root mean square (RMS) value of the applied current is expressed by Eq. (2) [65], where I_{DC} is the DC component and i_{rms} is the RMS value of the AC component (i).

$$I_{rms} = \sqrt{I_{DC}^2 + i_{rms}^2} \quad (2)$$

Three different current waveforms were applied to the PEM electrolyser: sinusoidal, triangular and square waves. Since the same AC amplitude results in a different RMS values for each of the waveforms, the experimental results were analysed as a function of the ripple factor (RF) rather than the AC amplitude. The RF, which is the ratio of the RMS value of the AC component to the average value or DC component of the applied current, is calculated using Eq. (3) [65]. The maximum achievable RF, the crest factor and the RMS value of each waveform used in this study are presented in Table 3.

$$RF = 100 \frac{i_{rms}}{I_{DC}} \quad (3)$$

Table 3 – Crest factors, RMS values and maximum ripple factors of the AC components (from ref [65]).

Waveform	Crest factor	i_{rms}	Maximum ripple factor (%)
Sinusoidal	$\sqrt{2}$	$A/\sqrt{2}$	70.7
Triangular	$\sqrt{3}$	$A/\sqrt{3}$	57.7
Square	1	A	100

The ranges and values of the other ripple current characteristics that were investigated, such as the AC amplitude and frequency, are presented in Table 4. The DC offset value was limited to a maximum of 25 A or 1 A/cm², the AC amplitude values ranged from 0 to 25 A and frequency ranged from 1 to 1000 Hz.

Table 4 – Characteristics and ranges of the applied ripple currents investigated.

Characteristics	Value or range
Waveform	Sinusoidal, triangular and square
Ripple/ AC amplitude	0 A – 25 A (5 A steps)
Max. DC offset	25 A (1 A/cm ²)
Frequency	1 Hz, 10 Hz, 50 Hz, 100 Hz, 1000 Hz

The experimental investigation commenced with the selection of the initial parameter settings on the power supply: an AC amplitude of 0 A, a DC offset of 25 A, a frequency of 1 Hz and a sinusoidal waveform. By selecting an AC amplitude of 0 A, the output current is a constant DC at any given waveform or frequency setting. After an operating time of 5 min at the initial parameter settings, the AC amplitude setting was changed to the next value in the range. This process was repeated until the final value of 25 A in the AC amplitude range was reached. At this point, one full range of AC amplitude

measurement was complete for a sinusoidal ripple current with a frequency of 1 Hz. The next step was to change the frequency of the applied ripple current and repeat a full range of AC amplitude measurements at each of the frequency settings. Finally, the steps described above were repeated for a triangular and square wave ripple current. At each parameter setting, the average hydrogen flow rate was measured using the hydrogen flow meter in the test station, while the cell voltage, current and average power consumption of the electrolyser were measured using the oscilloscope. Fig. 3 is an explanatory flow chart of the experimental procedure followed.

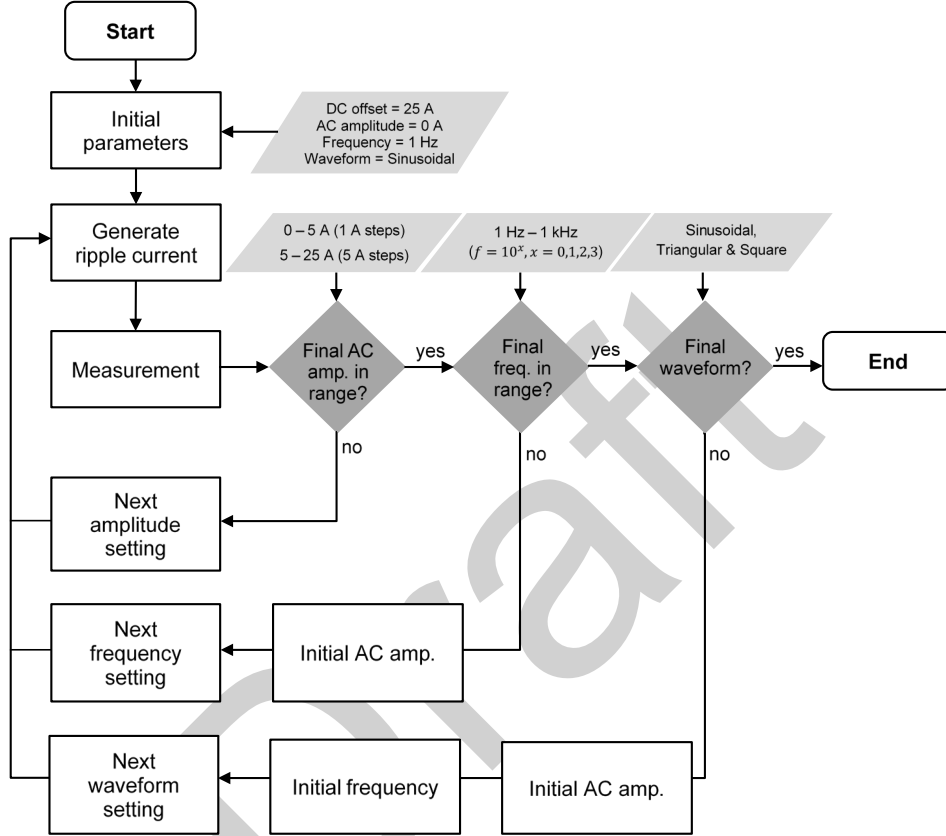


Fig. 3 – Experimental sequence used for the ripple current AC component measurements.

According to literature in [74], several different definitions are used to calculate the efficiency of water electrolysis cells. Three of the most widely used efficiency definitions are the voltage efficiency, Faradaic efficiency and cell efficiency. Voltage efficiency refers to the ratio of the thermoneutral voltage at standard conditions to the actual cell voltage, as per Eq. (4) [23]. At standard conditions, the thermoneutral voltage is calculated using the change in the reaction enthalpy ΔH_R^0 , also known as the higher heating value (HHV), as shown in Eq. (5) [23], where F is Faraday's constant and n is the number of electrons transferred during the chemical reaction. The HHV has a value of $285.83 \text{ kJ.mol}^{-1}$, the number of electrons is two and Faraday's constant is 96845 C.mol^{-1} . This definition does not account for any gas or current losses.

$$\varepsilon_V^{HHV} = \frac{E_{th}^0}{U_{cell}} \quad (4)$$

$$E_{th}^0 = \frac{\Delta H_R^0}{nF} = 1.48 \text{ V} \quad (5)$$

The gas and current losses can be measured using the Faradaic efficiency, which is defined as the ratio between the actual and theoretical hydrogen gas produced as per Eq. (6) [23].

The theoretical hydrogen flow rate is calculated using Faraday's law, and is defined by Eq. (7) [35, 75, 76], where i is the applied current, A is the surface area of the cell and F is Faraday's constant [23]. The Faradaic efficiency does not account for any voltage losses.

$$\varepsilon_I = \frac{\dot{n}_{H_2, actual}}{\dot{n}_{H_2, theor}} \quad (6)$$

$$\dot{n}_{H_2, theor} = \frac{iA}{2F} \quad (7)$$

The cell efficiency, which accounts for both the voltage and current losses of an electrolytic cell, can be defined as the ratio between the useful energy output and the required energy input. For low-temperature water electrolysis systems, such as the PEM electrolyser, the only useful energy output is considered to be hydrogen gas, while the energy input is electrical energy supplied to the electrolyser. The cell efficiency was thus calculated as the hydrogen energy output per unit of electrical energy input, as per Eq. (8)

$$\varepsilon_{cell}^{HHV} = \frac{HHV \cdot \dot{n}_{H_2}}{P_{avg}} \quad (8)$$

where $\dot{n}_{H_2}$ is the measured hydrogen molar flow rate, HHV is the higher heating value or the change in enthalpy under standard conditions and P_{avg} is the average power consumption [23, 77]. Cell efficiency based on the HHV is preferred over the lower heating value (LHV) when liquid water is used, because of the enthalpy of evaporation that needs to be provided by the electrolyser [23]. The hydrogen flow rate was measured in nLPM using the flow meter embedded in the test station, then converted to the molar flow rate from Eq. (9) [78].

$$\dot{n}_{H_2} = \frac{nLPM \cdot 0.08993895478 \text{ g} \cdot \text{L}^{-1}}{2.01588 \text{ g} \cdot \text{mol}^{-1} \cdot 60\text{s}} \quad (9)$$

The average power consumption, P_{avg} , was measured using the oscilloscope. It can be defined by Eq. (10) [65], where U is the measured cell voltage, I is the applied current and T is the periodic time of the waveform.

$$P_{avg} = \frac{1}{T} \int_0^T UI \cdot dt \quad (10)$$

3. Characterisation

The effects of ripple currents and different ripple current parameters on the performance of a PEM electrolyser can only be analysed if some baseline data, recorded under standard operating conditions (DC supply) exists. Characterisation of the single-cell PEM electrolyser that was utilised as baseline in the results comparison and to determine the impedance of the cell is now described.

3.1 Polarisation curve

First, the baseline polarisation curve test was carried out. It was used to determine the voltage response of the PEM electrolyser when a steady DC power supply is used. During this test, the voltage response was measured over a range of steady DC current densities. The applied current densities ranged from 0 to 1 A/cm² and were applied in 0.01 A/cm² increments. The duration between each current adjustment was 5 min to allow the cell to stabilise at the specific current. The voltage measurements were then taken at the end of each 5-min interval. This test was carried out at an operating temperature of 70 °C. The ripple current tests were also carried out at this temperature.

The test results are given in Fig. 4 (a), in the form of a PC that shows the voltage response of the PEM electrolyser under normal operating conditions. The PC shows that the cell voltage reached 1.79 V at a current density of 1 A/cm² and a temperature of 70 °C.

3.2 EIS

Next, the baseline EIS test was carried out. It was used to characterise the impedance of the PEM electrolyser. A small AC signal with a DC offset of 0.7 A and an amplitude of 0.1 A was applied to the PEM electrolyser over the frequency range 100 mHz to 200 kHz. The cell's voltage response signal was measured at each frequency and used to calculate the impedance response. This test was also carried out at an operating temperature of 70 °C. The impedance of the PEM electrolyser is presented in the form of a Nyquist plot in Fig. 4 (b). The point at which the Nyquist plot intercepts with the real axis at the high frequency side shows that the PEM electrolyser has an ohmic resistance of 12.6 mΩ. The difference between the low frequency intercept or, in this case, the point at which the plot stops, and the high frequency intercept, is equal to a charge transfer or activation resistance value of 25.3 mΩ.

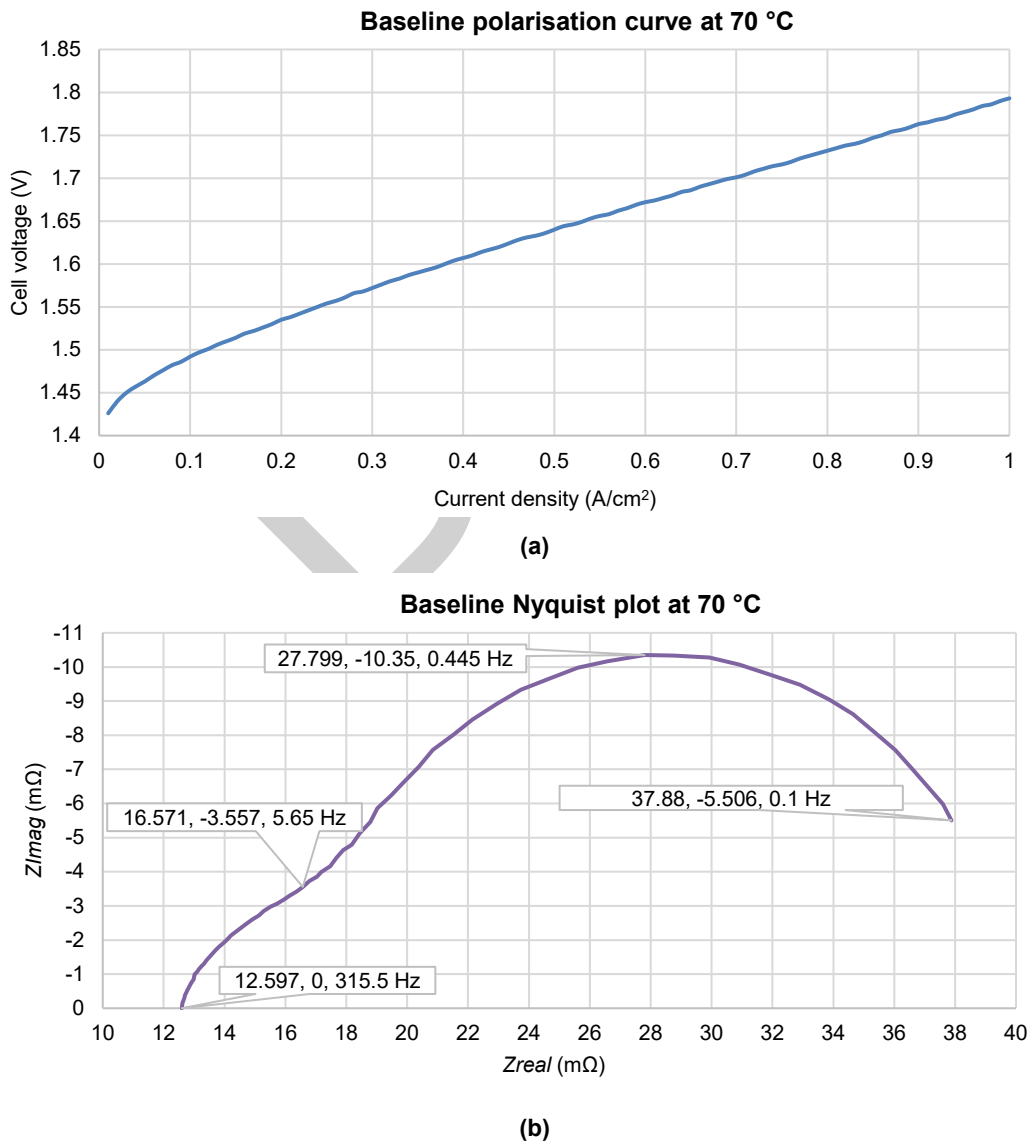


Fig. 4 – Measured characterisation results: (a) Baseline polarisation curve results and (b) Baseline EIS test results in the form of a Nyquist plot.

4. Results and discussion

According to Eq. (1), a ripple current can be expressed as the sum of a constant DC component and a time-varying AC component. During our experimental tests, the effect of the DC component as well as the AC component of the current supplied to a PEM electrolyser were investigated. Now, in Section 6.1 the effect of the DC component on the power consumption and hydrogen flow rate is analysed in the absence of a ripple or AC component, and in Section 6.2 the effect of the AC component is analysed at a constant DC offset. Furthermore, Section 6.3 addresses the combined effect of the AC and DC components on the power consumption and hydrogen flow rate. Section 6.4 addressed the effect of ripple currents on the voltage, Faradaic and cell efficiency.

4.1 Effect of a ripple current DC component

The measured and the theoretical power consumption of the PEM electrolyser as a function of the DC offset or current density are illustrated in Fig. 5 (a). The theoretical power consumption would be the power consumed by the electrolyser if the cell operated without any voltage losses (100% voltage efficiency). The theoretical power consumption was calculated as the product of the current applied to the cell and the thermoneutral voltage ($P_{theor} = E_{th}I$), while the measured power was calculated as the product of the current applied to the cell and the measured cell voltage ($P_{measured} = U_{DC}I_{DC}$) [59]. Since the current is the controlled variable, the ratio between the measured and the theoretical power consumption gives the ratio between the cell voltage and the thermoneutral voltage, which is also known as the voltage efficiency of the electrolyser. The voltage efficiency (also illustrated in the figure) decreases as the current density is increased, caused by an increase in the cell voltage. The results showed that the power consumption of the PEM electrolyser has a non-linear response to the DC offset, which is caused by the non-linear voltage response as shown in the polarisation curve of the cell presented earlier in Fig. 4 (a). At a DC offset of 25 A, or a current density of 1 A/cm², the measured power consumption was 44.83 W, while the theoretical power consumption at the same current density was 37 W. This gives a voltage efficiency of 82.5% at a DC offset of 25 A, which is the DC offset at which the rest of the experiments were carried out.

The measured and the theoretical hydrogen flow rates are shown in Fig. 5 (b) as a function of the DC offset or current density applied to the electrolyser. The hydrogen gas formation commenced at a cell voltage of 1.44 V and increased linearly as the DC offset was increased. The theoretical flow rate is the ideal hydrogen production rate in the absence of any current losses (100% Faradaic efficiency). A difference between the theoretical and measured hydrogen flow rate, as observed in Fig. 5 (b), indicates that current losses are present. The impact of these losses can be illustrated with the Faradaic efficiency, which is the ratio between the measured and theoretical flow rates. The Faradaic efficiency (also plotted on the graph) shows a sharp increase up to a current density of 0.2 A/cm², where after the increase slows down. This response is in good agreement with reports in the literature on similar experiments, as presented by Tijani and Rahim [39].

At a DC offset of 25 A, or a current density of 1 A/cm², the measured hydrogen flow rate was 0.1310 nLPM, while the theoretical flow rate at the same current density was 0.1742 nLPM. This gives a Faradaic efficiency of 75.2% at a DC offset of 25 A, which is the DC offset at which the rest of the experiments were carried out.

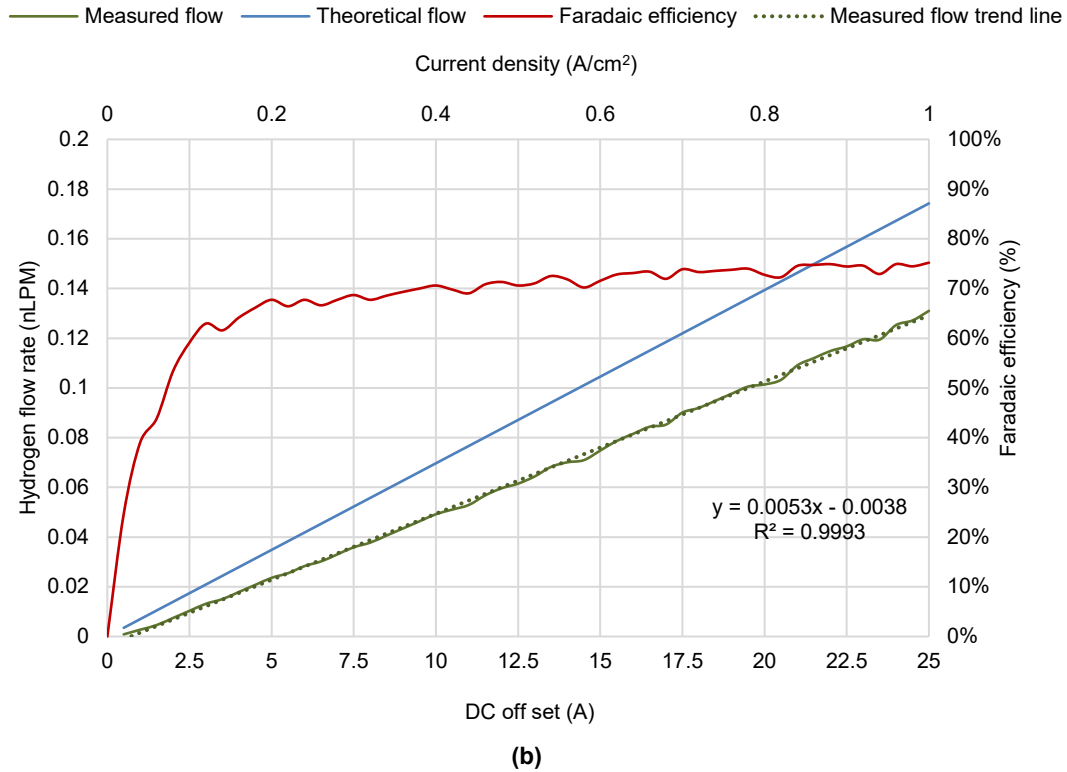
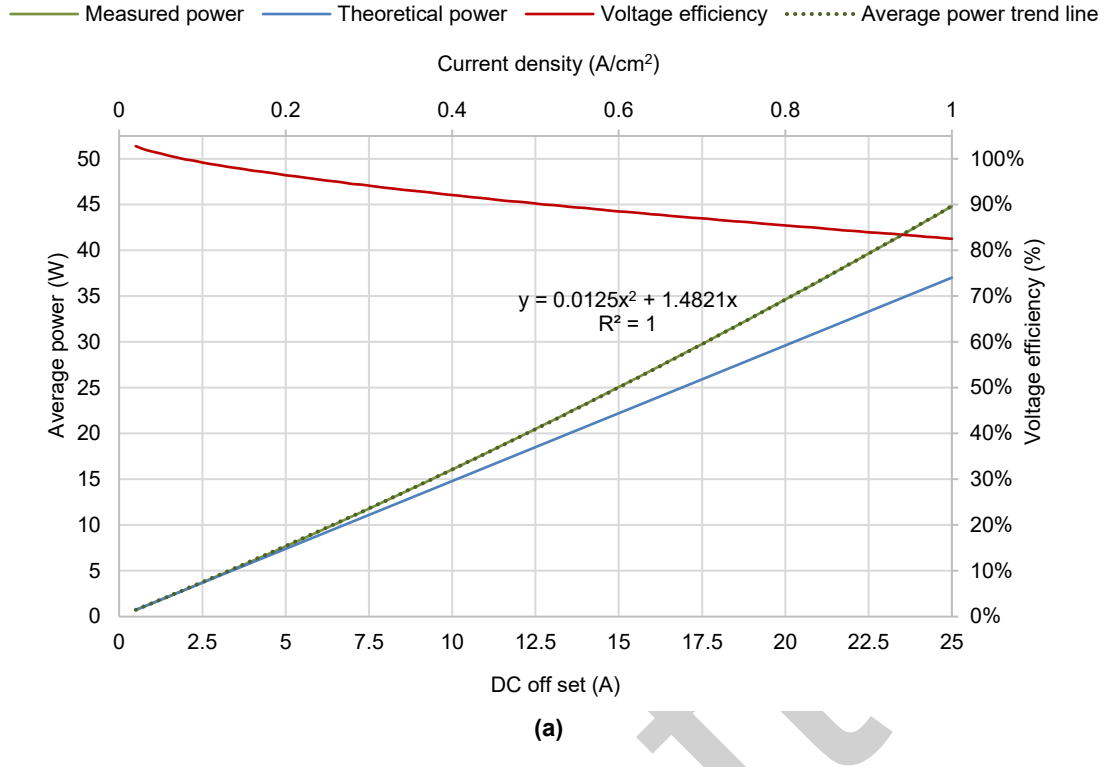


Fig. 5 – Experimental DC offset measurements: (a) power consumption and (b) hydrogen flow rate.

4.2 Effect of a ripple current AC component

Ruuskanen *et al.* [79] recently revealed that the difference between the RMS and mean voltage and current values can be used to obtain an estimate of the power quality supplied to an electrolyser. They found that the difference between the RMS and mean voltage and current values can be utilised as an

estimation of the additional losses caused by a current ripple. In Fig. 6, the difference between the cell RMS current (I_{rms}) and mean current (I_{DC}) values is plotted as a function of the current AC and DC components. Further, the difference between the cell RMS voltage (U_{rms}) and mean voltage (U_{DC}) values is also plotted as a function of the current AC and DC components on the same figure.

The results displayed are for a square wave ripple current as this is the only waveform able to achieve a 100% RF and the frequency is constant at 300 Hz since this is the dominating harmonic frequency of a commonly used 6-pulse thyristor bridge rectifier. The DC component of the applied current ripple is equal to the mean current (I_{DC}) while the AC component is defined using the RF. A 100% RF means that the RMS value of the AC component is equal to that of the DC component. The figures show that the current losses increase linearly as a function of the DC component and the rate at which the current losses increase is determined by the RF. A similar trend is observed in the voltage losses, although the increase is non-linear as an effect of the electrolyser polarisation curve. It is also observed that the current losses are significantly larger than the voltage losses.

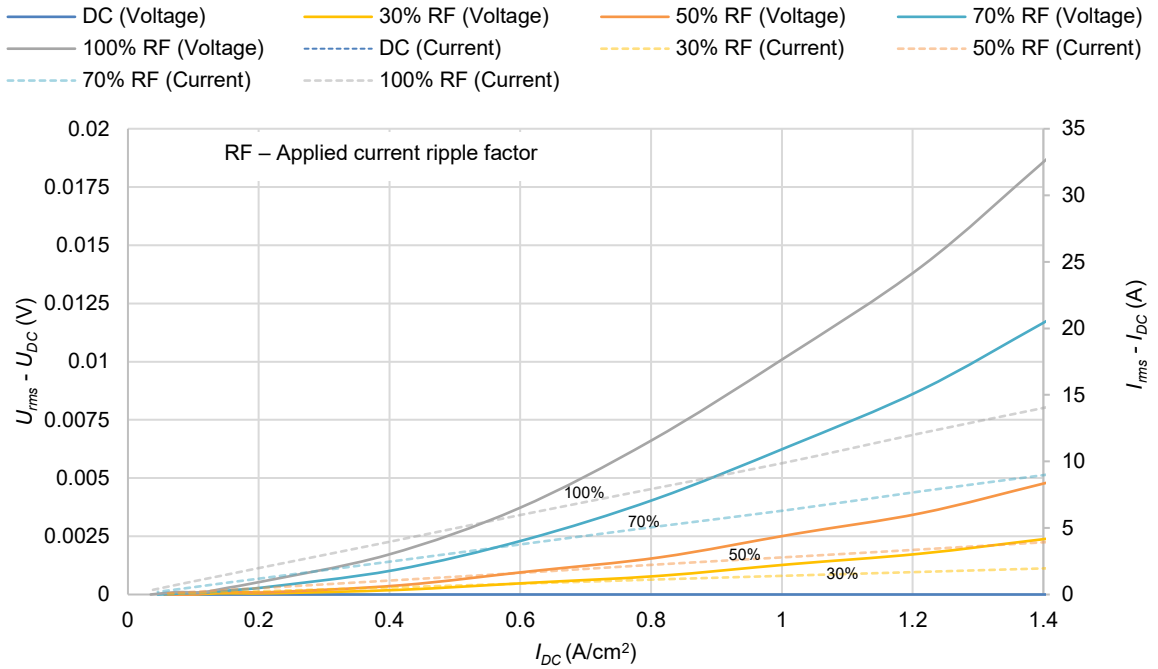


Fig. 6 – Experimental difference between the current and voltage RMS and mean values as a function of the current AC and DC components.

Fig. 7 shows the average power consumption of the PEM electrolyser as a function of the RF and the frequency for each of the considered waveforms. The DC offset of the applied ripple currents was kept constant at 25 A or 1 A/cm², while the RA, frequency and waveform settings were changed. The figures illustrate that, for any waveform, the power consumption increases as the RF increases, and decreases as the frequency of the ripple increases. This observation is in strong agreement with the simulated results as well as the results of similar studies. In the present study, the highest ripple frequency tested was 1 kHz. A further increase in frequency may lead to lower power consumption.

Nonetheless, the results showed that the effect of frequency in this high-frequency region is insignificant—it is not possible to be accurately measured on an electrolyser as small as the one used in this study. The results showed that the effect of frequency on the power consumption is the most substantial in the low frequency range (1–50 Hz). It is typical for industrial electrolyzers to be supplied by a 6- or 12-pulse thyristor bridge rectifier, which generates a ripple with a dominating harmonic

frequency of 300 Hz and 600 Hz, respectively, when supplied with an AC frequency of 50 Hz [80]. In practical terms, the current supplied to an electrolyser would thus never have a ripple with a frequency in this low range (1–50 Hz) since the rectified AC power sources used for electrolysis usually have a frequency of ≥ 50 Hz. The results also showed that the effect of frequency is minimal, and almost negligible, at any RF of $<30\%$.

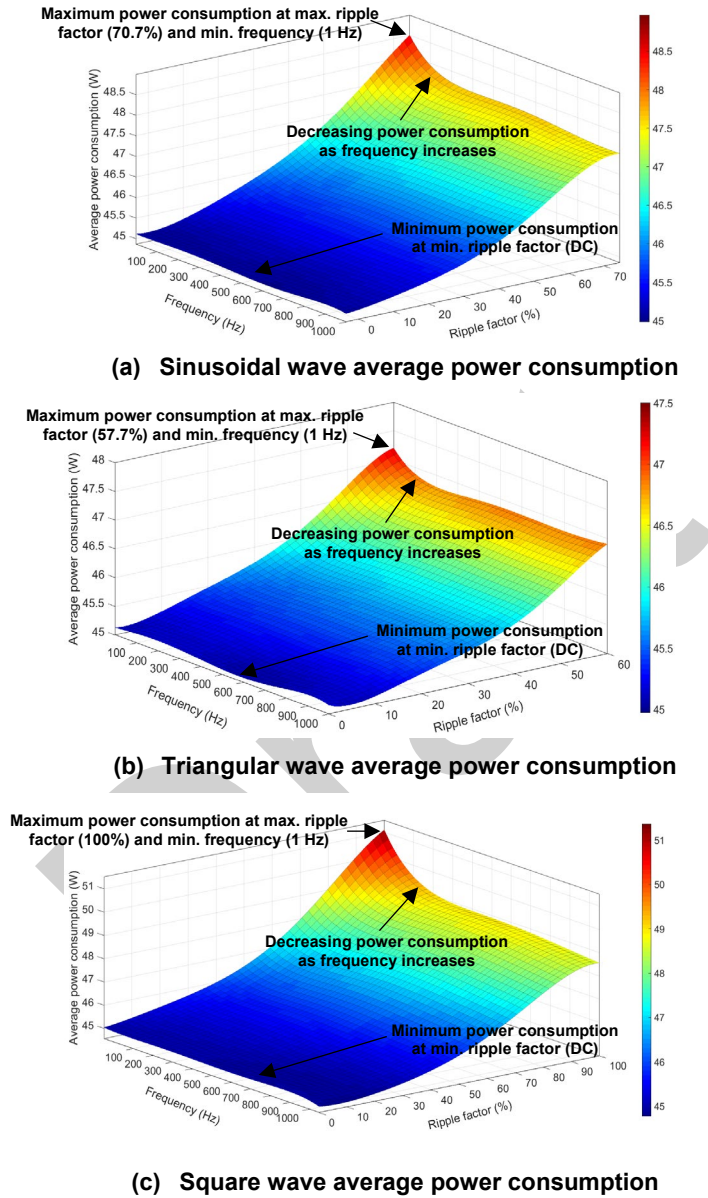
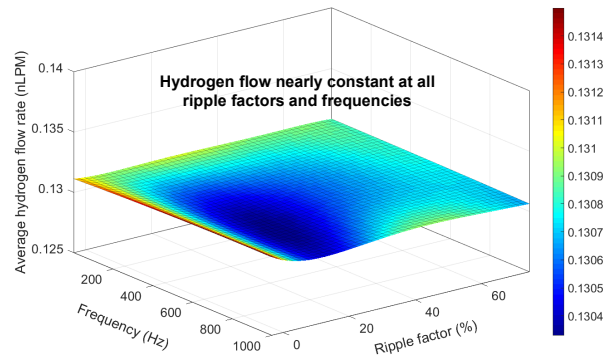
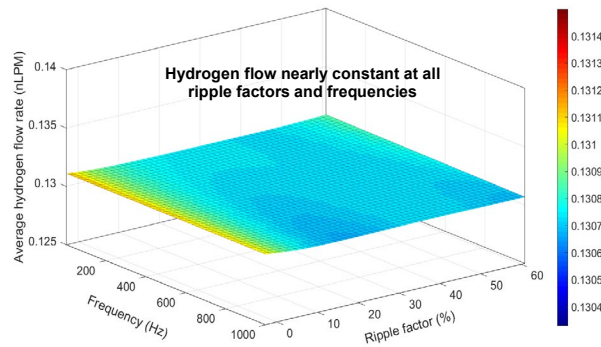


Fig. 7 – Experimental average power consumption as a function of the ripple factor, frequency and waveform: (a) sinusoidal, (b) triangular, (c) square.

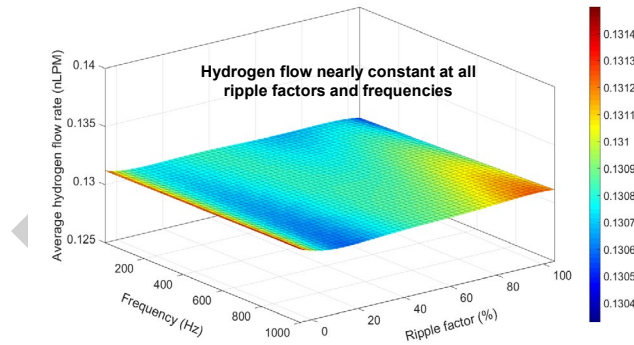
However, these figures do indicate that the RF or AC amplitude has a major impact on the power consumption at any frequency. In each of the conducted experiments, the instantaneous hydrogen flow rate was measured at a log rate of 100 ms for the duration of the experiment, after which the average hydrogen flow rate was determined. The average flow rates were then plotted, in Fig. 8, as a function of the RF and frequency for each of the considered waveforms. It is evident that the hydrogen flow rate is not affected by the RF, frequency or waveform of the applied ripple current. The average hydrogen flow rates observed at each of the ripple current settings were very close to the 0.131 nLPM flow rate measured at a steady DC current of 25 A.



(a) Sinusoidal wave hydrogen flow rate



(b) Triangular wave hydrogen flow rate



(c) Square wave hydrogen flow rate

Fig. 8 – Experimental average hydrogen flow rate as a function of the ripple factor, frequency and waveform: (a) sinusoidal, (b) triangular, (c) square.

The greatest difference in the flow rate was observed with a square wave ripple current, but the difference between the maximum and minimum flow rate remained $<1\%$. The maximum average flow rate observed in any of the experiments was 0.1313 nLPM and the minimum was 0.1302 nLPM. The results clearly showed that the hydrogen flow rate depends solely on the average current or the DC offset of the applied current. Since the hydrogen production rate of the PEM electrolyser does not differ at different RF and frequency settings, the efficiency of the electrolyser at the different RF and frequency settings is mainly affected by the power consumption.

4.3 Combined effect of DC and AC

The experimental results discussed in the previous sections reveal that the DC as well as the AC components of the applied current affects the power consumption of the PEM electrolyser respectively. Now, in this section the combined effect of the DC and AC components is investigated. In Fig. 9 (a),

the power consumption of the electrolyser is plotted as a function of both the AC and DC components of a ripple current with a square waveform and a frequency of 300 Hz. The figure shows that the effect of the AC component is relatively small compared with the effect of the DC component. Furthermore, the effect of the AC component increases as the DC component increases. On the other hand, Fig. 9 (b) shows that the hydrogen flow rate is affected only by the DC component of the applied current.

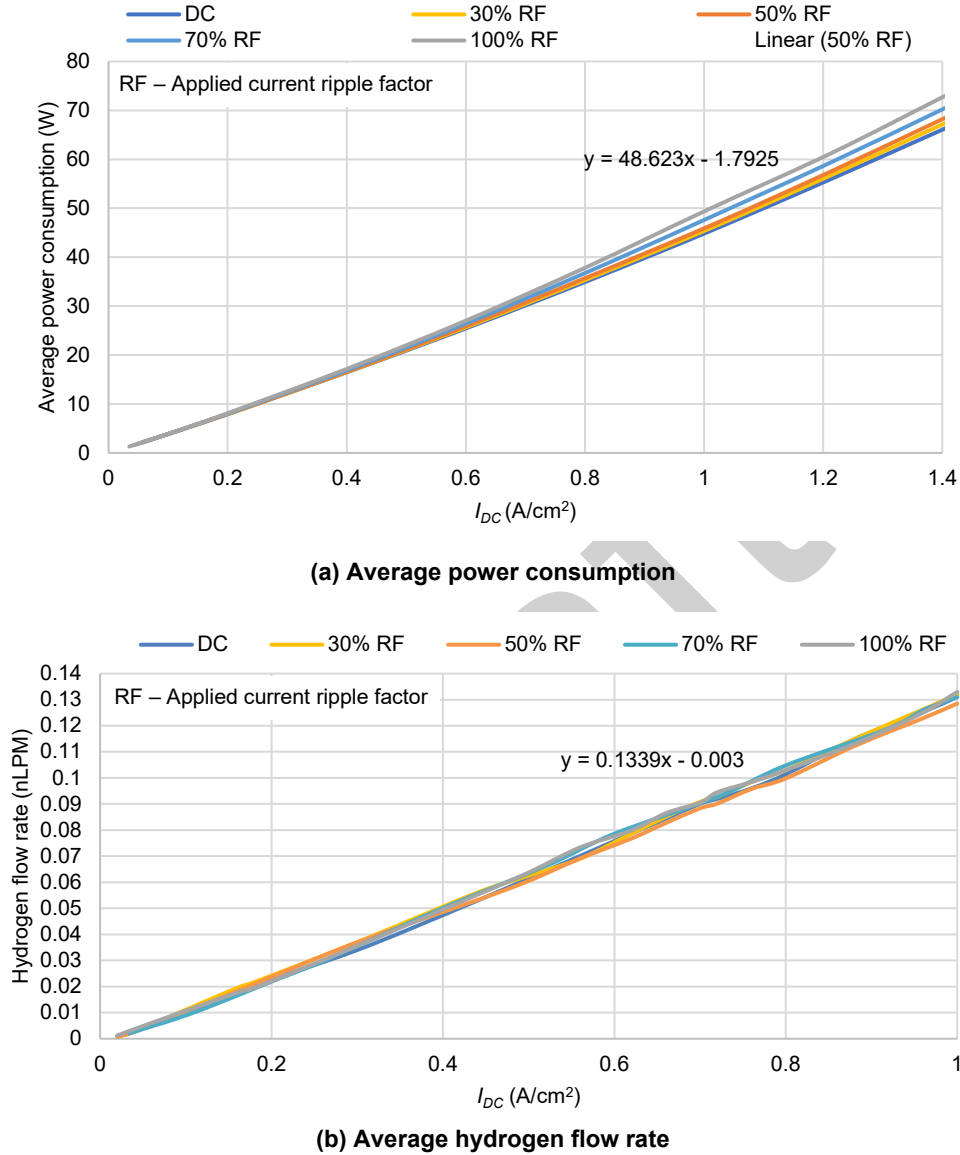
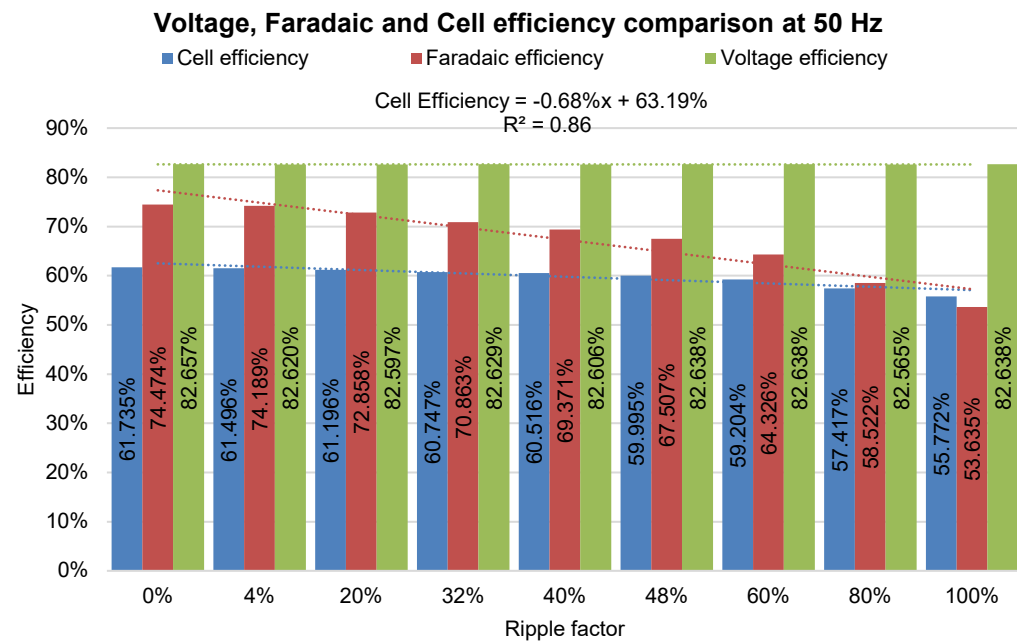


Fig. 9 – Experimentally measured results as a function of the current AC and DC components.

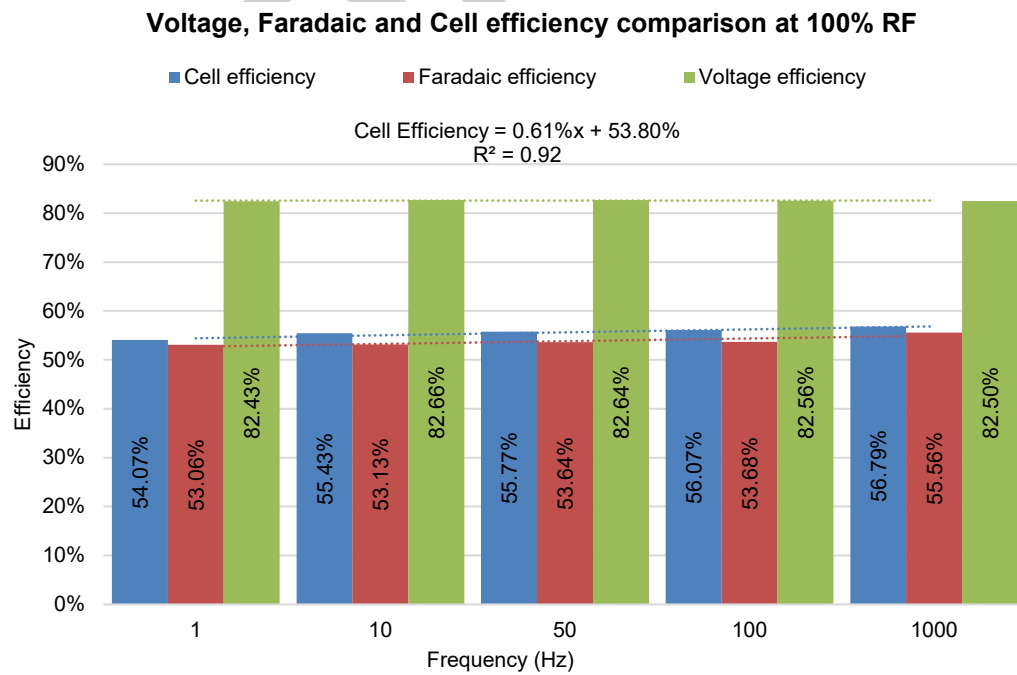
4.4 Voltage, Faradaic and cell efficiency

Fig. 10 presents, and compares, the voltage, Faradaic and cell efficiency for a few different ripple current parameter settings. The efficiency analysis focuses on a ripple current with a square waveform since it is the only waveform capable of achieving a 100% RF. However, the efficiencies for the other waveforms used in this study show a similar trend, since the waveform does not have a significant effect on the power consumption nor on the hydrogen flow rate (as determined in Sections 6.1–6.3). It was observed that the difference between the RMS and mean voltage of the cell does not significantly increase as the ripple current increases. Fig. 10 further shows that the voltage efficiency of the PEM electrolyser is thus not largely affected by the size of the ripple current. Since the effect of a ripple current on the RMS cell voltage is so small, it can be concluded that the impact of the voltage losses

on the cell efficiency is insignificant. On the other hand, a current ripple initiates a higher current RMS value, while the hydrogen production rate is dependent only on the current mean value. The difference between the mean and RMS current values can, therefore, be defined as unused current. A current ripple thus generates additional current losses, which causes a decrease in the Faradaic efficiency as well as the cell efficiency. It was observed in the measured results that the frequency of the ripple current also affects the power consumption of the PEM electrolyser. The higher cell efficiency at higher frequencies is thus caused by a decrease in the power consumption.



(a) Efficiency comparison at different ripple factors and a constant frequency (50 Hz).



(b) Efficiency comparison at different frequencies and a constant ripple factor (100%).

Fig. 10 – Experimental voltage, Faradaic and cell efficiency comparison at different ripple factors and frequencies.

5. Conclusion

The simulated and the measured results illustrated that a ripple current and the ripple current settings, such as the RF or frequency, have a major effect on the power consumption or energy input of the PEM electrolyser. On the other hand, the energy output or hydrogen output is directly proportional only to the mean value of the applied ripple current and is thus unaffected by the current waveform, RF or frequency since the DC offset is unchanged. The efficiency loss caused by a ripple current is thus due to the increase in the energy consumption of the PEM electrolyser, without an increase in the hydrogen output.

An increase in the RF of the applied current also causes an increase in the RF of the cell voltage. This results in higher RMS current and voltage values, which increase the power consumption and decrease the efficiency of the cell. Although the effect of frequency is less than the effect of the RF, an increase in the frequency causes an increase in the cell efficiency. The effect of frequency also becomes more noticeable as the RF of the applied current increases. Although the different current ripple waveforms tested on the PEM electrolyser here produced different results, a similar trend in terms of the effect of the RF was observed in all of them. The effect of the ripple/ AC amplitude on the power consumption and the efficiency of the cell is, however, different for each waveform, since the crest factor is different for each waveform. Small differences in the effect of frequency between different waveforms were observed since the frequency spectrum of each waveform is different. However, the trend is similar for all the tested ripple current waveforms and the cell efficiency is the highest at a frequency of 1 kHz, which is the highest frequency in this study.

In conclusion, this research was carried out to determine the effect of ripple currents on the efficiency of a PEM water electrolyser. The single-cell PEM electrolyser used in this study was first characterised, after which some experimental tests were carried out on the electrolyser. The results obtained showed a decrease in the efficiency of a PEM electrolyser with an increase in the RF, an increase in the efficiency with an increase in the ripple current frequency and a negligible change in the efficiency using different waveforms.

The study delivered a great deal of knowledge regarding the effects of power quality on the energy consumption and hydrogen production of a PEM water electrolyser—this could be very useful in the further development of this promising hydrogen production technology.

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7. References

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