



Current switching device development to characterise and monitor a proton exchange membrane water electrolyser

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EXECUTIVE SUMMARY

The development and of key hydrogen production techniques play an essential role in the evolution of renewable energy solutions. Numerous studies have been carried out in recent years to improve and enhance these techniques, including the proton exchange membrane water electrolysis (PEMWE) process, which has produced encouraging technological outcomes that will enable the efficient and sustainable generation of hydrogen. Furthermore, because of its high current density, higher energy efficiency compared to alkaline water electrolysis, high hydrogen discharge pressures, and smaller gas crossover, the PEMWE device is an ideal high purity hydrogen generation approach. In contrast to the alkaline water electrolysis technique, the PEMWE technology is still relatively new and has a number of intricate components and interfaces that call for particular characterisation techniques in order to get a deeper basic understanding. However, alternative cell characterisation techniques are still being investigated as to efficiently monitor and control the cell with minimal resources and response times.

The research presented in this dissertation focussed on the current interrupt (CI) method, entailing the development of a current switching (CS) approach to characterise a PEMWE cell. The CS method includes the design of a CS development board responsible for producing an attenuated and controlled perturbation signal generated via an STM32 microcontroller. This signal is responsible for the control of the cell supply current administered within a frequency range of 0.8 Hz – 20 kHz. Furthermore, the voltage and current signals measured through each experiment were recorded and analysed using Matlab® and Simulink®. However, to characterise the PEMWE cell, an equivalent electrical circuit (EEC) was designed to represent the different operational features within the cell from which a simulation model was designed within Simulink®. Numerous EEC designs were created and compared using RelaxIs®. The closest fit to the theoretical cell response resulted in the optimal EEC circuit utilised for cell characterisation. Thus, by incorporating the optimal EEC in the Simulink® simulation model, the voltage and current signals measured during each experiment could be added to the model. The measured voltage was used to generate a simulated current from the EEC, which was compared to the measured current. Utilising Response Optimizer®, the EEC parameters were calculated based on the model results by minimising the error between the simulated and measured current.

The dissertation verifies and validates that the CI method is a suitable characterisation method delivering EEC results that are closely correlated with electrochemical impedance spectroscopy (EIS) performed under similar experimental conditions.

Keywords: Current Interrupt; Electrochemical Impedance Spectroscopy; Proton Exchange Membrane; Pseudo Random Binary Sequence Signal; Water Electrolysis

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LIST OF ACRONYMS AND ABBREVIATIONS

AC	Alternating Current
AWE	Alkaline Water Electrolysis
BER	Bit Error Rate
CI	Current Interrupt
CPE	Constant Phase Element
CS	Current Switching
DC	Direct Current
DFT	Discrete Fourier Transform
EEC	Electrical Equivalent Circuit
EIS	Electrochemical Impedance Spectroscopy
EMF	Electromotive Force
GDL	Gas Diffusion Layer
GUI	Graphical User Interface
HER	Hydrogen Evolution Reaction
HySA	Hydrogen South Africa
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronics Engineers
LFSR	Linear Feedback Shift Registers
LTi	Linear Time-Invariant
MEA	Membrane Electrode Assembly
MLS	Maximum Length Sequence
NVR	Natural Voltage Response
OE	Output Error
OER	Oxygen Evolution Reaction
PC	Polarisation Curve
PCB	Printed Circuit Board
PEM	Proton Exchange Membrane
PEMWE	Proton Exchange Membrane Water Electrolysis
PRBS	Pseudo Random Binary Sequence
PSD	Power Spectral Density
PTS	Porous Transport Layer
SANS	South African National Standards
SI	System Identification
SOE	Solid Oxide Electrolysis

CHAPTER 1: INTRODUCTION

This chapter serves as an introduction highlighting the framework of this project, entailing research conducted on the development of a novel current switching device to characterise a Proton Exchange Membrane (PEM) electrolyser cell. This chapter details the significance of hydrogen technology and cell characterisation methods for Proton Exchange Membrane Water Electrolysis (PEMWE). Furthermore, Chapter 1 also discusses the background of the problem at hand, possible exclusions, limitations of the project, detailed scope accentuating the aim, primary and secondary objectives, and key research questions. The research methodology that was followed for this project, including a detailed verification and validation model used to test the feasibility and authenticity of the system models, is also discussed. Chapter 1 concludes with an overview explaining the structure and flow of the dissertation.

1.1 Background

Energy supply, responsible for the sustainable socio-development of a country, is a crucial aspect in the world of today and is significantly affecting the quality of life and infrastructural developments of communities [1, 2, 3]. According to the statistical review of world energy for 2022, the demand for primary energy has risen by 5.8% in 2021 and is much higher than the demand level of 1.3% captured in 2019 [2, 3]. However, the demand accounted for 83% of primary energy coverage being fossil fuels and the rest being renewable sources such as biofuels, solar and wind energy, and hydroelectricity generation [2, 3]. This demand caused a 5.7% increase in carbon dioxide emissions, which is slightly lower than the 5.9% of carbon emissions measured in 2019 [4]. However, the carbon dioxide emissions are still high and must be significantly reduced. Fortunately, ample research has been conducted on replacing the energy and management supply systems with green energy fuel sources such as PV, wind generation, and hydroelectric energy.

Presently, a vast amount of research is being conducted on the efficient production and utilisation of hydrogen technology, and it is currently considered a prospective energy carrier method that may contribute to national and international energy production and management strategies [5]. The demand for hydrogen used as an energy and fuel source is expected to rise continuously over the next few decades [6]. This demand has been verified after extensive research on the production, utilisation, and storage of hydrogen as fuel [7, 8]. However, research had to be done on the sustainability of hydrogen on the environment to distribute hydrogen to different industrial sectors across the world continuously. According to Hren *et al.* [5], studies found that hydrogen production through water electrolysis has a much lower greenhouse gas footprint when utilising renewable sources of electricity [9]. Water electrolysis is when electrical energy is applied to the

electrolytic cell to split water into hydrogen and oxygen [10]. The three main water electrolysis techniques include alkaline water electrolysis, proton exchange membrane (PEM) water electrolysis and solid oxide electrolysis, which have been thoroughly discussed and compared in numerous articles [9, 11, 12, 13].

During the last few years, research has been conducted on the development and amelioration of the PEM water electrolysis method. It has shown promising technological results leading to efficient and sustainable production of hydrogen. These results included the capability of successful integration with interconnected renewable energy sources responsible for supplying electricity to a community [14]. Furthermore, the PEM water electrolysis method is also considered an excellent high-purity hydrogen production technique due to its high current density, greater energy efficiency in comparison with alkaline water electrolysis, high hydrogen discharge pressures and smaller gas crossovers [15, 16, 17]. However, the PEM water electrolysis is still relatively new compared to alkaline water electrolysis, consisting of various complex parts and interfaces that require specific analysis methods for a better fundamental understanding of the cell operation. A typical illustration of a PEM water electrolyser can be seen in Figure 1.1.

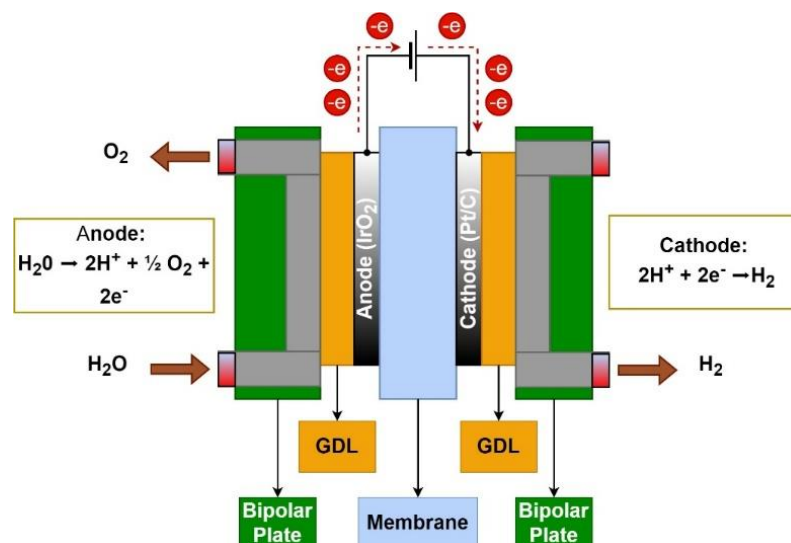


Figure 1.1: Illustration of a PEM water electrolyser (adapted from [18]).

Characterisation methods, including polarisation curves (PC), electrochemical impedance spectroscopy, and current interruption are developed to analyse the efficiency and operational stability of the PEMWE cell. PC curves are designed to monitor the performance of the cell and provide information on the ohmic, activation, and mass transport losses within the PEM water electrolyser [19]. Electrochemical Impedance Spectroscopy (EIS) is a powerful characterisation method traditionally used to determine the electrochemical information from the voltage and current response of the cell. The cell can be characterised using the generated transfer function of the system to draw the Bode and Nyquist plot used to determine the equivalent electrical circuit

(EEC) parameters of the cell [19, 20, 21, 22]. Lastly, the Current Interrupt (CI) method, consisting of both the Natural Voltage Response (NVR) method and Current Switching method (CS), is used to characterise the cell by analysing the interrupted voltage and current response to determine important EEC parameters of the cell [19].

The testing and implementation of the CI method is evident from the research project of Martinson *et al.* [19], which entailed a detailed study on characterising a PEM electrolyser by analysing, verifying, and validating the current interrupt method. Within this project, the NVR and CS methods were used to determine the electrical parameters of an equivalent electrical circuit model designed to characterise the PEM electrolyser. The equivalent electrical circuit models utilised included the Randles cell, which used the NVR method for electrical parameter calculation, and the Randles-Warburg cell, which used the CS to determine the respective EEC parameters. Both EEC models were used to determine the electrochemical characteristics of the PEMWE cell, including the ohmic, activation, and concentration losses. The Randles Warburg cell is similar to that of the Randles cell [23], clearly explained in [19], but contains an extra frequency-dependant component, namely the Warburg impedance (Z_{wbg}). The Warburg impedance can be represented by the steady increase in impedance with a decrease in frequency due to the diffusion of finite or semi-finite electroactive species in the electrolyte. This steady increase, in turn, causes less current to flow with the same applied voltage [24]. A typical equivalent electrical circuit model of the Randles Warburg cell can be seen in Figure 1.2.

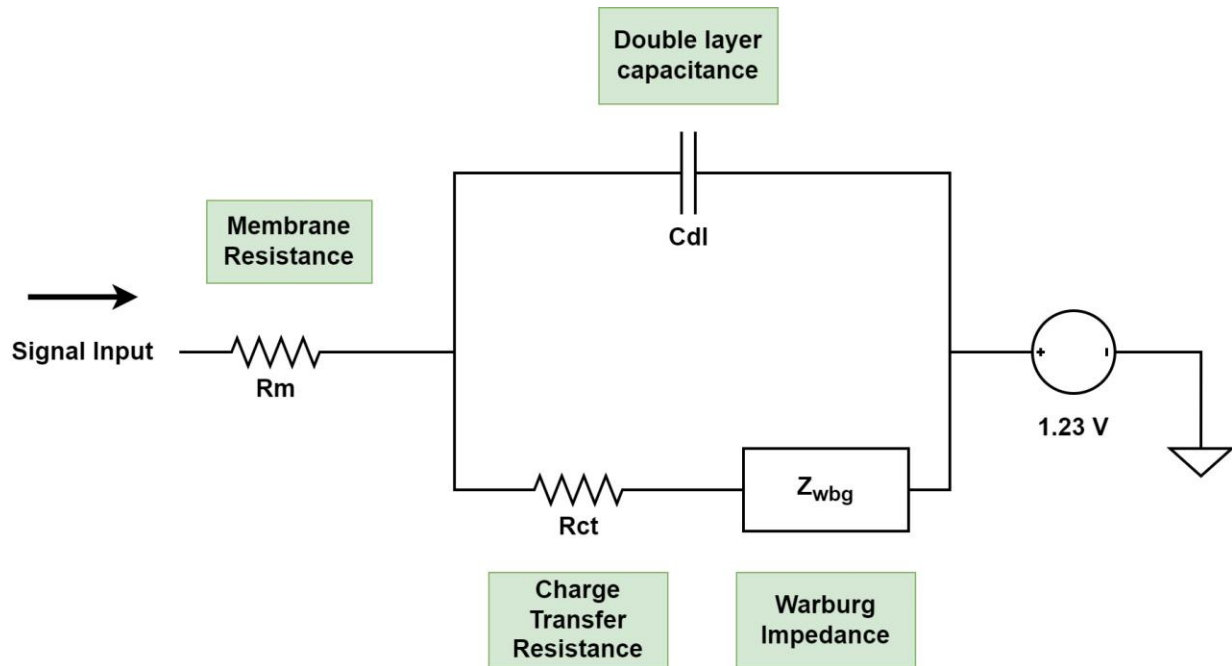


Figure 1.2: Equivalent circuit model for the Randles Warburg cell (adapted from [25]).

The equivalent electrical circuit model parameters, as seen in Figure 1.2, was successfully determined using the CS method. This approach combined multiple techniques to characterize

the electrical behaviour of the PEM electrolyser. The CS method comprised of the NVR method to accurately calculate the membrane resistance of the cell (R_m) and specifically designed pseudo random binary sequence (PRBS) signals in conjunction with System Identification (SI) techniques to determine the rest of the electrical parameters. These techniques enabled a detailed analysis of the electrolyser's electrochemical properties, such as ohmic and activation losses. After the calculation of these electrical parameters, simulations and experiments had to be performed to test the model's accuracy. Although the model was successfully verified, only the membrane resistance (R_m) was completely validated against existing literature [19]. As for the other electrical parameters, extensive errors between the simulated results and the practical measured results were obtained. The results of Martinson *et al.* [19] obtained via the CS method to determine the electrical parameters of the equivalent Randles Warburg model can be seen in Table 1.1.

Table 1.1: Adapted from [18] showing the error results obtained during the validation of the Randles Warburg model.

Experiments	Validation of practical results: Error [%] – Measured response versus simulated response	Experiments	Validation of simulated results: Error [%] – Simulated response errors
1	17.020	1	0.026
2	12.910	2	0.017
3	12.090	3	0.014
4	17.550	4	0.010
5	13.770	5	0.012
6	11.460	6	0.007
7	19.310	7	0.005
8	15.450	8	0.005
9	13.120		

It can be seen from Table 1.1 that the errors obtained for all the experiments during the practical validation are relatively high in comparison to that of the simulated response errors. Thus, it is important to ameliorate and refine the existing model to minimise the practical validation errors and eliminate certain fallacies that render the model inaccurate. This left room for another research project focussing on the rectification and refinement of the existing PEM characterisation model that will deliver results that closely correlate to traditional characterisation methods such as EIS. Thus, for this project, the Randles EEC model was used as a starting point due to its intuitive method for representing a PEMWE electrode electrically. It assists in modelling the

important electrochemical characteristics of the PEMWE cell and the easy interpretation of EEC parameters in a Nyquist plot.

1.2 Purpose of research

This section pertains to the problem statement and aim of the research project and gives a clear indication of why the research problem is deemed important and where it fits into the hydrogen roadmap.

1.2.1 Problem statement

The PEM electrolysis technology was idealised and developed as early as 1960 by Thomas Grubb and has been a revolutionary discovery with ongoing research and enhancements ever since [26, 27]. This method was developed as an augmentative model that will replace the drawbacks of the alkaline water electrolysis technique [26]. However, after much research and refinements, advanced electrocatalysts were developed for the PEMWE, resulting in higher production costs compared to alkaline water electrolysis. Still, the PEM water electrolysis technique is most favourable due to its high current density, greater energy efficiency, etc. [26, 28].

As the research and interest in PEM water electrolysis advanced, proper characterisation methods had to be implemented to determine the characteristics of the PEM electrolyser accurately. One of these traditional characterisation methods includes EIS. However, the accuracy of this method is highly dependent on the experimental setup of system equipment, measurements and mathematical models used during characterisation. This method also requires special equipment and software for accurate measurements, making it quite expensive and complex [29]. A possible alternative to EIS, the current interrupt method, was investigated by Martinson *et al.* [19] to refine and develop a working model to characterise the PEMWE cell by analysing its electrochemical data. However, this model still posed some significant deviations compared to the EIS method as discussed in [19]. Proving that the existing model needs to be updated and refined. The model must be able to successfully characterise the PEM electrolyser that will deliver results that are close to the results obtained via EIS.

1.2.2 Aim

The aim of the project was to gain competence in the analysis and design of a suitable current interrupt characterisation model that will successfully characterise the designed PEM electrolyser cell. The model was designed, built, and tested on the Greenlight® test station, utilising the necessary equipment for the model's experimental setup. To test its accuracy and precision, the model was verified and validated against EIS.

1.3 Scope of study

This section discusses the primary and secondary objectives that must be met for the successful completion of this research project. Furthermore, the project exclusions, limitations, and key research questions that highlight key focus areas within this project is also clearly shown.

1.3.1 Primary objectives

A PEMWE cell and experimental setup with detailed requirements and specifications were designed. The goal of this study was to investigate the current interrupt method as an alternative method to characterise the PEM electrolyser cell. To monitor the cell reaction rate, the current supplied to the cell was controlled utilising a current switching development board. The board was responsible for attenuating a designed PRBS signal to control the electronic switch, ensuring precise control of the current flowing to the cell. Thereafter, system identification was required to analyse electrolyser cell output, calculate the equivalent circuit parameters, and draw up a Nyquist plot to represent the stability of the system. The data obtained was then validated using EIS by performing different experiments under the same conditions for both EIS and CI. For this implementation, data precision and accuracy were required during system identification.

1.3.2 Secondary objectives

To ensure that the primary objectives listed for this project were met, the following secondary objectives had to be met:

1. Since the electrolyser's characterisation results mainly depend on the perturbation signals, a perturbation signal generator that manually allocates the bits to the desired registers was required. This generator assisted the user in more flexible perturbation signal alterations since updating the signal generator algorithm is easy. It also took up less space since a signal generator can be quite bulky compared to an Arduino. Thus, to generate the desired perturbation signals successfully, it was important to investigate and discuss new methods for shift register allocation to generate PRBS signals.
2. Since the PEMWE cell had to be characterised by calculating the electrical parameters of the EEC model, a current switching board was required to control the flow of current to the cell. By manipulating the current flow to the cell, the behaviour of the cell could be studied under different operating conditions. Thus, specific attention had to be given to switching losses, signal aliasing, simulation time, and noise generation on the output signal supplied to the cell.
3. A suitable EEC circuit representing the PEMWE cell in simulation environment needed to be designed and implemented. The EEC was properly tested and verified using real-time data measured via EIS as possible fittings to the EEC circuit. A similar EEC was implemented in the CI model for parameter comparisons between EIS and CI.
4. Voltage and current sensors were required to record the cell output. The output was then received and analysed using a designed system identification algorithm that calculated the

electrical parameters of the EEC model. The results were then compared to EIS to validate the designed CI model.

1.3.3 Exclusions and limitations

This section pertains to all the exclusions and limitations for this research project, including the:

1. Construction of the PEM electrolyser cell used for practical implementation was not done. However, pressure paper tests were conducted during cell assembly to ensure proper pressure distribution across the active area of the cell.
2. The PEMWE cell was only tested at low current densities ($0.1 - 0.3 \text{ A/cm}^2$) to analyse the intrinsic activity of the catalyst and electrode kinetics of the cell without major influences from mass transport effects.

1.3.4 Key research questions

This section entails the key research questions that were used to conduct a detailed literature study and assisted in the completion of this project.

1. What are the key parameters and performance indicators that need to be monitored in a PEMWE cell?
2. What are the critical design considerations for developing a high-speed, high-precision current switching device for PEMWE characterisation?
3. What are the key electrochemical parameters that can be extracted from the electrolyser's voltage and current response during CS?
4. What are the optimal frequency ranges of the PRBS signal for effective system identification without introducing unwanted disturbances in electrolyser performance?
5. How does the PRBS-based current switching method compare to conventional EIS in characterising PEMWE dynamics?

1.4 Research methodology

To ensure that the research project was conducted as efficiently as possible, a specific procedure was followed to ensure the success of the project's outcome. This project includes topics such as problem identification, literature study, detailed design of the system and experimental setup, simulation and subsystem testing, system integration, practical experimental setup implementation and final tests on the system setup. For a proper literature study, the research problem first needed to be identified. After the problem was identified, it was easier to distinguish between the relevance of research topics of interest. These topics were then discussed in detail, giving more insight into the detailed design of the system and experimental setup that followed. The design was then tested and simulated to determine the feasibility of the system. After the system was deemed feasible, the subsystems were developed and integrated, and the

experimental setup was practically implemented. Thereafter, the system was verified and validated to see if the project is working as intended.

1.4.1 Problem identification

The problem identification section is critical since it forms the basis of the research project and shapes the scope of the topic. From this, the literature study was conducted on topics relevant to the problem at hand.

1.4.2 Technology and literature review

For this project, a proper literature study was conducted on the relevant topics that led to its success. The literature study ensured the feasibility of the system solution and determined if the proposed solution was the most efficient option. Chapter 2 shows a detailed literature study diagram highlighting all the key factors that were analysed and discussed. Each topic within Figure 2.2 was discussed in depth so that a proper trade-off analysis could be conducted. A literature survey was implemented and included journal articles and conference proceedings relevant to each topic discussed. Furthermore, pertinent case studies were also discussed to see how a similar problem had been approached previously.

1.4.3 Conceptual design, detailed design, and simulations

After a detailed literature study, the key system components were designed and modelled. This section starts with the conceptual design, which consists of a trade-off analysis that was used to decide which components were best suited for the system application. Key components were juxtaposed based on predefined criteria from which the most suitable components were selected. Thereafter, the detailed design of the current switching board and perturbation signal generator were discussed. Furthermore, a unique algorithm responsible for current control were designed and tested before physical implementation was possible. Thereafter, all the components, as stipulated by the detailed design, were ordered so that the prototypes could be built.

1.4.4 System implementation and integration

Once the simulations had been successfully tested and the components acquired, the physical subsystems were built, tested, and integrated. The system was properly tested to see if its response was in close correlation to that of the desired response.

1.4.5 Analysis, conclusion, and recommendations

The results obtained from the experimental setup were properly analysed and discussed. Based on the success factors of the system, conclusions and recommendations were drawn.

1.4.6 Verification and validation

The accuracy of the verification and validation process is extremely important and was required to successfully complete this thesis. These two processes complement each other and specifically examined certain parts of the design process. Verification refers to whether a system is built right

while, validation refers to whether the right system is built. The verification and validation process that were followed can be seen in Figure 1.3.

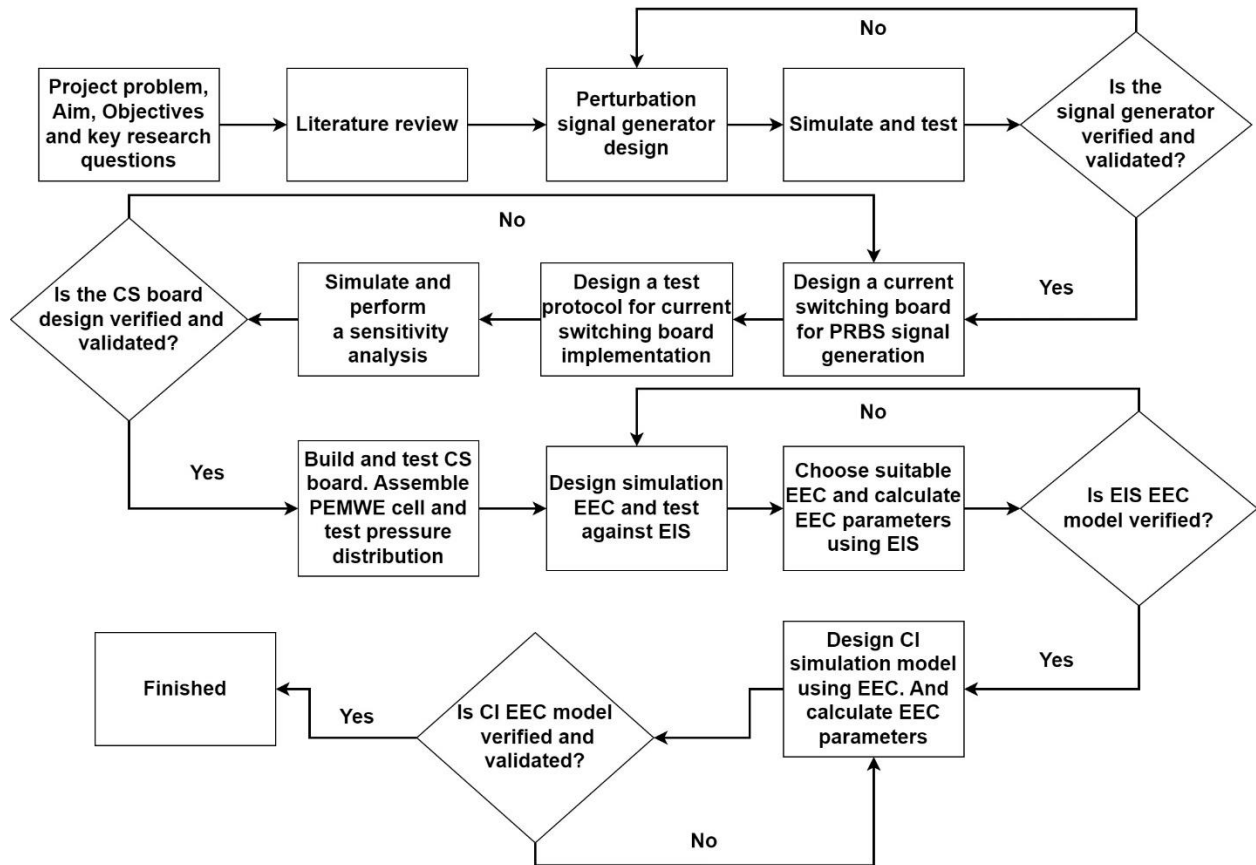


Figure 1.3: Model Verification and Validation process.

1.5 Publications and peer reviews

During the research period of this project two attempts were made to gain insight into the validity of the project as a whole. These include one research article that has been submitted but is still under review and a project conference presented at the 4th International Conference on Electrolysis, held at Sun City, South Africa, in 2023 and hosted by HySA Infrastructure Centre of Competence.

1. M. Bornman, G. Kruger, C.A. Martinson, A. Pushkarev, S.P. du Preez, D.G. Bessarabov and R. Gouws, "A novel current switching device for proton exchange membrane electrolyser characterisation and monitoring", in International Journal of Hydrogen Energy (2025) Elsevier, pp. 1-23. **[Accepted]**

"The study focusses on the development of a novel current switching (CS) device utilised to characterise and monitor a proton exchange membrane (PEM) electrolyser. The cell is modelled using an equivalent electrical circuit (EEC) responsible for evaluating the dynamic behaviour of the cell. By analysing the voltage and current response during controlled CS, critical parameters such as membrane resistance and double layer capacitance are extracted. The proposed method offers a cost-effective and simpler alternative to that of a more traditional method including electrochemical impedance spectroscopy (EIS). The accuracy and validity of the CS approach

are verified by comparing the extracted parameters with those obtained from EIS. The compared results demonstrate a high correlation enhancing the efficacy of the CS method to deliver accurate results. The enhanced characterisation method further provides real-time, non-disruptive monitoring of voltage and current responses ensuring rapid and precise cell testing and characterisation during cell operation.”

Sections of dissertation contributed to article: 1.1, 2.5.2, 2.5.3, 2.5.4, 2.6.1, 3.2.1, 3.2.2, 3.3, 4.1.1, 4.1.2, 4.1.3, 4.2, 4.3, 5.4

2. M.L. Bornman, R. Gouws, C.A. Martinson, G. Kruger, D. Bessarabov, “Current switching device development to characterise and monitor a proton exchange membrane water electrolyser”, 4th International Conference on Electrolysis, pp. 199, 2023, [Online]. Available: https://engineering.nwu.ac.za/sites/engineering.nwu.ac.za/files/files/hysa/ICE2023_abstract_book_online.pdf

“High hydrogen purity, low gas cross overs, high product efficiencies and accelerated load response times has been the incentive for escalating interests and research conducted on proton exchange membrane (PEM) water electrolysis. It is regarded as one of the most prominent methods for hydrogen production during integration with zero-carbon electricity sources. Furthermore, meticulous characterisation techniques have been developed to provide intricate insight on the analysis of the physical, chemical, and electrochemical processes that occurs during operation. This research project will focus on two of these techniques namely electrochemical impedance spectroscopy (EIS) and the current interrupt (CI) method. EIS is a powerful tool that measures the relationship between the current and applied voltage across a specified range of frequencies. It provides sufficient information on the individual contributions towards the total impedance within an electrochemical system being monitored. However, this method utilises quite complex and bulky testing equipment and analysis software that makes the technique quite expensive to use. Thus, it is imperative to implement a method that utilises less expensive and complex testing- and analyses equipment that will successfully characterise a PEM water electrolyser delivering results that is in close correlation to that of EIS. Therefore, the CI method is further investigated by designing, modelling, and implementing a PEM water electrolyser system that will imitate the CI technique both in the simulation and practical environment. The successful implementation of the CI method will later assist HySA Infrastructure in the characterisation of PEM electrolyser short stacks which can lead to great market related impacts. The specific focus areas of this research project entail:

- *Test bench station design and implementation for practical PEM water electrolyser testing.*
- *Design and model a PEM electrolyser system in simulation.*
- *Build a current switching board for current interrupt method practical implementation.*

- *Build monitoring circuit board and algorithm for PEM water electrolyser cell online monitoring.*”

Sections of dissertation contributed to article: 1.1, 2.5.2, 2.5.3, 2.5.4, 2.6.1, 3.2.1, 3.2.2

1.6 Dissertation overview

The dissertation starts off with the first chapter highlighting key research project topics such as the project background, problem statement, aim and objectives, key research questions and research methodology. The chapter ends by emphasising how the different models designed during this research project were verified and validated, as seen in Figure 1.3. Chapter 2 contains the literature study, which sets the foundation for this project by analysing and discussing relevant topics to gain sufficient insight into the problem. Topics discussed during this chapter include hydrogen technology, electrochemical cells and fundamentals, system identification and software, etc. Relevant case studies were also discussed as a guide to modelling and design parameters and results. The next chapter includes the conceptual and detailed design of the key system components of the current interrupt method. Chapter 4 discusses the experimental setup and implementation of the key components and integration with the system algorithm. Furthermore, it also includes the experimental results of the physical implementation and integration of the key system components with the designed test bench station.

After implementation, the key system components were verified and validated against EIS to test the validity of the CI model. However, the EIS model used for CI validation was first designed and verified against the literature. Lastly, the dissertation closes with an overall thesis summary, conclusion, and recommendations. In Chapter 5, emphasis is also placed on answering the key research questions, as well as a detailed summary of the validation and verification process used during this dissertation.

1.7 Conclusion

This chapter served as an introduction towards the rest of the dissertation by highlighting the key focus areas of this project. Background on the research problem was discussed in detail within section 1.1, from which the problem statement, aim, primary and secondary objectives, as well as key research questions were derived. Section 4 discussed the methodology that was followed for the rest of this project and ended by giving a detailed diagram of the model verification and validation process. The next chapter (Chapter 2) is the literature review chapter, which gives more insight and a better understanding of the key focus points of the problem. These key focus points are further analysed and discussed to generate a solution towards the problem effectively.

CHAPTER 2: LITERATURE STUDY

This chapter pertains to a detailed literature study conducted on all the major topics relevant to the successful outcomes of this project. Each of these topics, clearly outlined in Figure 2.1, is approached systematically by discussing each topic according to principle, operation, background, specifications, procedures, and technologies through relevant published documents as a reference. Furthermore, links between some topics have been established as seen in Figure 2.2. The figure gives more information on what is discussed under each topic, how the research fits into the final solution, and how model verification and validation were conducted.

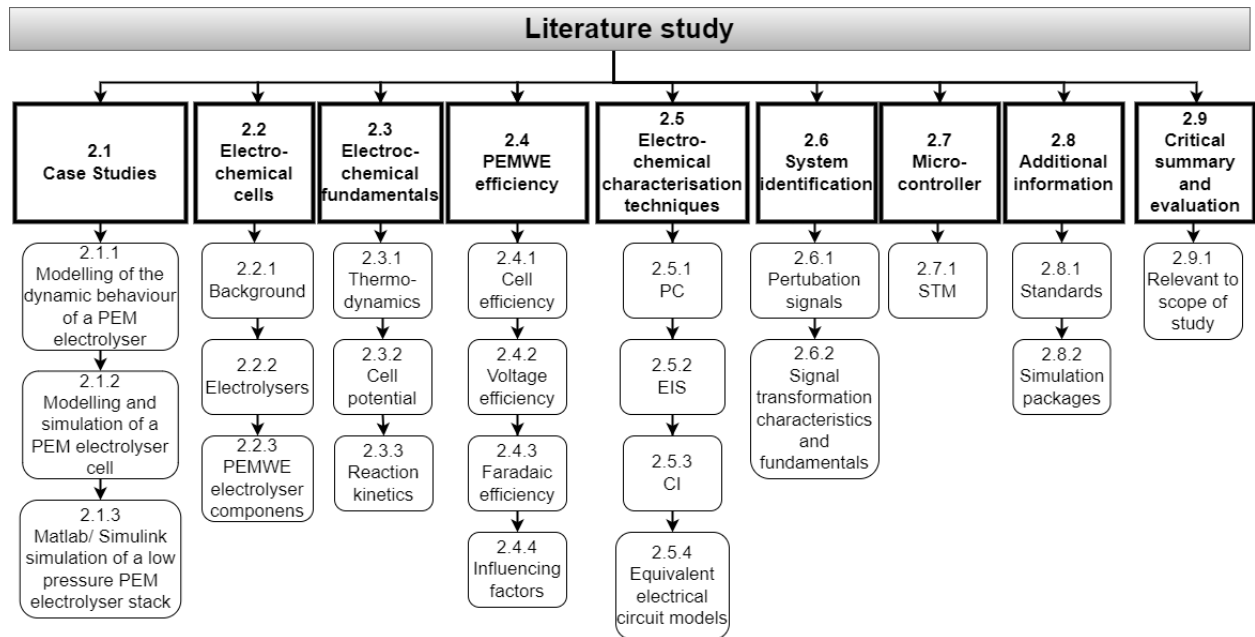
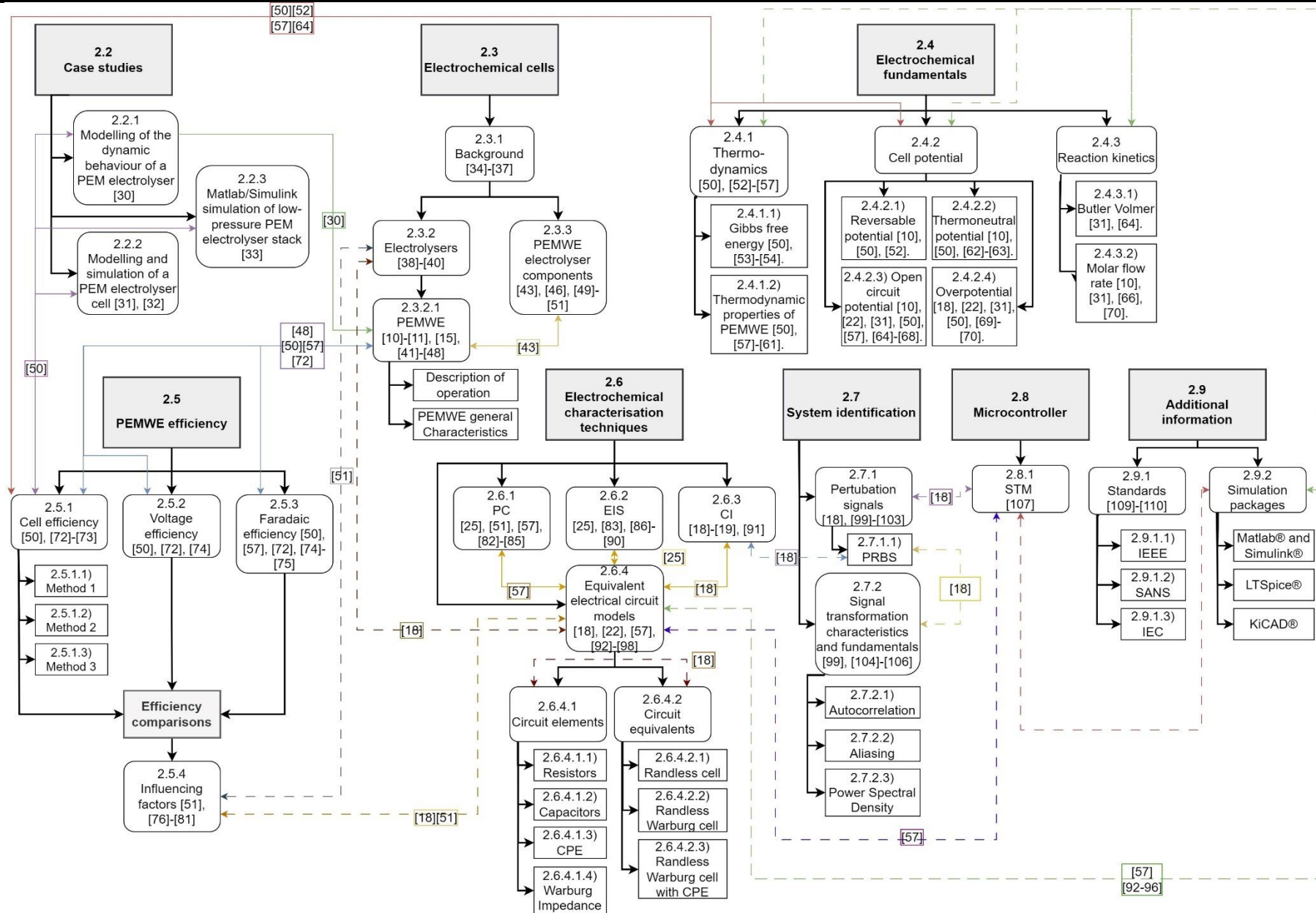


Figure 2.1: Conceptual literature review plan.

2.1 Case Studies

The credibility of results is of utmost importance in this dissertation, specifically focussing on the simulation model representing the PEMWE setup (Discussed in more detail in Chapters 3 and 4). In this thesis, we focus on assessing the credibility of results obtained from a PEMWE simulation model compared to those of a similar experimental setup. The PEMWE is a critical component in various applications, including hydrogen production, energy storage, and fuel cells. An accurate and reliable simulation model is essential for representing the operational results and performance of the cell. The objective of this literature study is to evaluate the credibility of the simulation model used in calculating the electrochemical characteristics of the cell. By conducting a thorough assessment, the study aims to determine the accuracy, reliability, and validity of the model's predictions.



This assessment will provide valuable insights into the simulation model's robustness, its limitations, and the potential impact of uncertainties and assumptions on the obtained results. The study begins with a comprehensive literature review, to establish a solid foundation for the credibility assessment. This review focusses on previous research related to simulation models for PEMWE models, highlighting the key assumptions, limitations, and uncertainties associated with these models. By understanding the existing knowledge and research in the field, the study can effectively evaluate the credibility of the proposed simulation model. Case studies explaining the internal design and mathematical modelling are also briefly discussed.

2.1.1 Current Interrupt Technique to Fully Characterize PEMWE Cells

Krenz *et al.* [30] published an article focussing on an enhanced current interrupt technique to characterise a PEMWE cell. The study investigated the limitations of traditional characterisation techniques, including EIS and Tafel analysis. A limitation identified includes using expensive and complex laboratory-scale equipment for the electrochemical analysis of the cell. However, Krenz *et al.* [30] proposed that the modified CI method, based on Martinson *et al.* [19], provides a simple, intuitive characterisation method to determine the EEC parameters of the PEMWE cell, including the ohmic resistance, charge transfer resistance, and double layer capacitance. This method further proposed the use of a non-linear activation resistance instead of the charge transfer resistance (Constant value). Thus, the activation resistance value, representing the real system, changes dynamically based on the applied current and voltage to the cell. Krenz *et al.* [30] found that the use of a non-linear function in the CI method aligns the EEC parameters calculated via the CI method well with those of EIS and Tafel analysis. However, based on the results, only the ohmic resistance, double layer capacitance, and Tafel Parameters were verified and validated against EIS, showing good correlation between the two methods. However, further validation is required to ensure the accuracy of the other EEC parameters. The use of non-linear activation resistance in the reliability of the EEC results is still in question. Hence, using a constant phase element (CPE) to model the double layer capacitance is also a possible solution that needs to be investigated.

2.1.2 Modelling of the dynamic behaviour of a PEM electrolyser

Guilbert *et al.* [31] published a conference focussing on the dynamic behaviour of PEM electrolyser models under different operating conditions. The paper investigates different simulation models that can predict the response of a PEM electrolyser. Guilbert *et al.* [31] looked at EEC modelling. However, they argued from the literature that although the models are designed to represent both electrodes with first-order time constants, the simulations cannot reflect the real-time behaviour of the PEMWE system. Furthermore, the literature dictated a black-box approach analysing the transfer function between the voltage and the current of the PEMWE at specific dynamic operating conditions, making the control of the system much easier. Thus, the focus of

the paper was to analyse and discuss different dynamic models of a PEM electrolyser that match different operating conditions. Therefore, the input and output of the PEMWE system (represented in terms of a test bench setup) have been monitored by supplying a PRBS signal (current) to the electrolyser cell and recording the voltage response of the cell. The voltage response was analysed by using a discrete-time-transfer function. However, to compensate for modelling error in system identification, two different methods were used to verify and validate the accuracy of the modelling results, namely Autoregressive exogenous (ARX) and Output Error (OE). It was found that the OE modelling of the PEM electrolyser model delivered better results when looking at the modelling errors. Guilbert *et al.* [31] concluded that the operating conditions of a PEMWE model are critical and that standard equivalent RC electrical circuits representing both electrodes of the PEM electrolyser are not enough to capture the dynamics present in real operations.

2.1.3 Modelling and simulation of a proton exchange membrane (PEM) electrolyser cell

Abdin *et al.* [32] presented an improved PEM electrolyser model utilising mathematically derived models for the electrolyser components. The modelling of both the electrodes and the membrane was crucial to understand the contributions of these components to the cell voltage when predicting overall equilibrium cell performance. A detailed model of a PEM electrolyser cell was developed and tested against multiple experimental studies (output was tested in the form of polarisation curves against the work of Marangio *et al.* [33]), considering the water transport through the PEM electrolyser as well as the resistances of the electrodes, flow field plates and the PEM. The steady state model was set up based on the characteristic properties of a specific PEM electrolyser cell, which is similar to the case of this dissertation. The main focus was on the anode, cathode and membrane modelling and mathematical design, as well as the voltage analysis, looking specifically into the influences of overpotentials on the PEM electrolyser's output. For the voltage analysis, a polarisation curve was modelling a variable voltage dependant on input current, cell area, cell temperature, electrode pressures and several internal parameters was used. The parameter assumptions were made as follows:

- Internal cell temperature was modelled as similar on both the anode and cathode.
- Anode pressure was approximately maintained at ambient pressure.
- Cathode pressure was varied up to a pressure of 90 bar.
- The membrane was completely hydrated, resulting in only a function of temperature.

The fitted parameters as well as fixed parameters, can be seen in [32] in conjunction with close-correlating polarisation curves between Abdin *et al.* [32] and Marangio *et al.* [33] output voltage analysis.

2.1.4 Matlab®/Simulink® simulation of low-pressure PEM electrolyser stack

Brezak *et al.* [34] designed a mathematical model with the primary focus on predicting the behaviour of a 1 kW PEMWE stack and its time-dependent output parameters consisting of 15 cells connected in series. The model was specifically designed to incorporate system losses such as diffusion losses due to gas and water transport. However, to simplify the mathematical procedures, a few assumptions were made, such as:

- The Gibbs free energy is directly proportional to the cell voltage with no losses.
- The reaction and product flow pressures were neglected.
- Hydrogen and oxygen gases are assumed to be ideal and do not penetrate the membrane.
- Uniform temperature, exchange current density, and reactant distribution across the electrolyser and active surfaces.
- The dissolution of gases in deionised water was neglected.
- Ideal water pump with pressure and water leaks.

The parameters and mathematical procedures are explained in detail by Brezak *et al.* [34]. The model accuracy was extensively tested against commercially available electrolyser parameters and simulation results. The model was shown to be sufficient for predicting electrolyte stack behaviour with an error margin between 2.2% and 7.4%. It was also seen that the anode and cathode charge transfer coefficients and current densities change linearly with temperature and can be easily compared to different parameter scenarios. However, further research is required on the geometry of temperature distribution over time, as well as hydraulic losses caused by improperly sized valves, etc.

2.2 Electrochemical cells

This section focusses on investigating different electrochemical cell technologies contributing towards developing and utilising hydrogen energy. The research conducted includes discussions regarding different electrolyser technologies with emphasis on the PEM water electrolyser's operation characteristics, characterisation methods, experimental setup, and components. The aim of this section is to develop a perspicuous understanding of how hydrogen energy is produced, utilised, and stored by focussing specifically on the PEMWE technique.

2.2.1 Background

An electrochemical cell utilises the redox reaction process to convert chemical energy into electrical energy. This type of cell is made up of two electrodes, a cathode and an anode, which are immersed in an electrolyte solution. The electrodes are typically made of different metals or materials, allowing for electron flow between them. The cathode is the electrode where reduction occurs and gains electrons, while the anode is where oxidation occurs and loses electrons. The electrolyte solution serves as a medium for the flow of charged particles, allowing the transfer of

electrons from the anode to the cathode. Together, these components make up the basic structure of an electrochemical cell [35]. Furthermore, these cells can be classified into two types: galvanic (voltaic) and electrolytic, depending on their mode of operation as shown in Figure 2.3. Galvanic cells generate electrical energy spontaneously through a chemical reaction, while electrolytic cells drive a non-spontaneous reaction through an external power source [35].

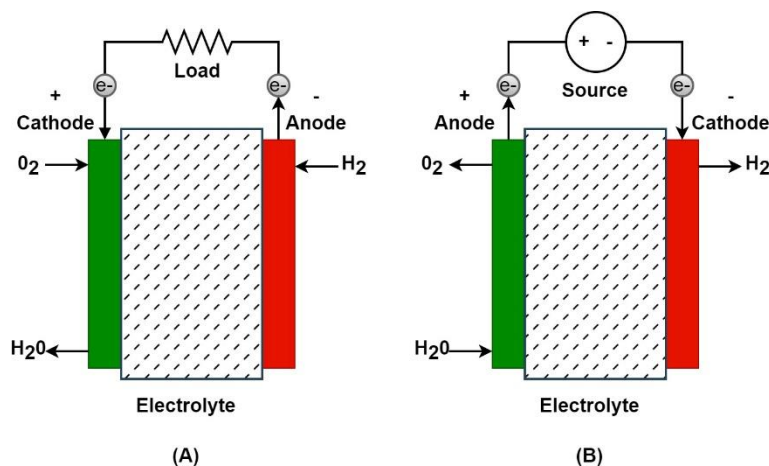


Figure 2.3: Electrochemical cells: (A) Galvanic cell and (B) Electrolytic cell (adapted from [36]).

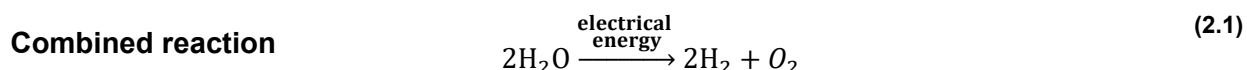
Electrochemical cells play a significant role in developing hydrogen energy technologies, particularly in the context of electrolyzers and fuel cells. Fuel cells (a typical example of a galvanic cell) are electrochemical cells that convert the chemical energy of hydrogen fuel directly into electrical energy, with water as the only by-product. This conversion makes them highly efficient and environmentally friendly energy sources. Electrolyzers are a type of electrolytic cell that use electrical energy to split water molecules into hydrogen and oxygen gas. The resulting hydrogen can then be used as a fuel source for fuel cells, which generate electricity by reacting hydrogen with oxygen. Furthermore, recent research has focused on improving the performance, efficiency, durability, proton conductivity and cost-effectiveness of electrochemical cells for hydrogen applications [37, 38].

2.2.2 Electrolyzers

Though various electrolysis technologies exist, e.g. alkaline water electrolysis (AWE), Anion-exchange membrane water electrolysis (AEM), solid oxide electrolysis (SOE), of importance here is proton exchange membrane water electrolysis (PEMWE). The operational principle of PEMWE was thus used as the example water electrolysis (WE) technology here.

An electrolyser is a device that uses electrical energy to split water into hydrogen and oxygen gas through a process called electrolysis. The process of electrolysis and charge carriers, represented by the electrolytic cell shown in Figure 2.3, vary depending on the specific technology. In PEM water electrolysis the primary charge carriers are protons (H^+).

In PEM water electrolysis an electrical energy source is required across the two electrodes, namely the positively charged anode and the negatively charged cathode. When an electric current passes through the device, the positively charged ions (usually hydrogen ions or protons i.e., H^+) migrates through the PEM towards the negative cathode where they combine with electrons to form hydrogen gas. Hydrogen produced from electrolysis can be used as a clean, carbon-free fuel for transportation, heating, and industrial applications, making it a promising energy carrier for the future due to its significant potential to serve as a key component in the transition to a sustainable, low-carbon society [39, 40]. The basic combined chemical reaction can be represented in reaction 2.1 [39, 40]:



One of the main significances of water electrolysis is that it can be integrated with renewable energy sources (responsible for supplying electrical energy as input to the electrolyser) to produce high purity hydrogen gas. Moreover, oxygen is the only important by-product of producing hydrogen from electrolysis, which is a valuable resource for many industries. Another important application of water electrolysis is in energy storage. With the growth of renewable energy sources like wind and solar, there is a need for large-scale energy storage technologies to ensure that the electricity generated can be used when it is needed. One such solution is to use excess renewable energy to produce hydrogen through electrolysis, which can then be stored and used to generate electricity when demand is high, via fuel cells. Water electrolysis technology also has the potential to help address global warming [41]. For instance, excess carbon dioxide can be captured from industrial processes and combined with hydrogen produced from water electrolysis to create synthetic fuels.

2.2.2.1 Proton exchange membrane water electrolyzers

As mentioned earlier, PEMWE technology is the focus of this research topic. The project incorporates a specifically designed PEMWE cell, which will be scrupulously tested and analysed using the CI method. A generalised schematic of the PEMWE cell is illustrated by Figure 2.4. Thus, it is of paramount importance to clearly discuss the PEMWE operation, characteristics, and component assembly to gain a comprehensive understanding on the significance of this method. More details on the physical component assembly and the significance of each layer will follow within section 2.2.3. The PEMWE technology was developed by Russel *et al.* in the 1960s [9, 42] and has been an ongoing research marathon ever since due to its significant qualities. These qualities include high purity hydrogen production in comparison to other water electrolysis methods, high current densities, dynamic operation, etc [15, 42].

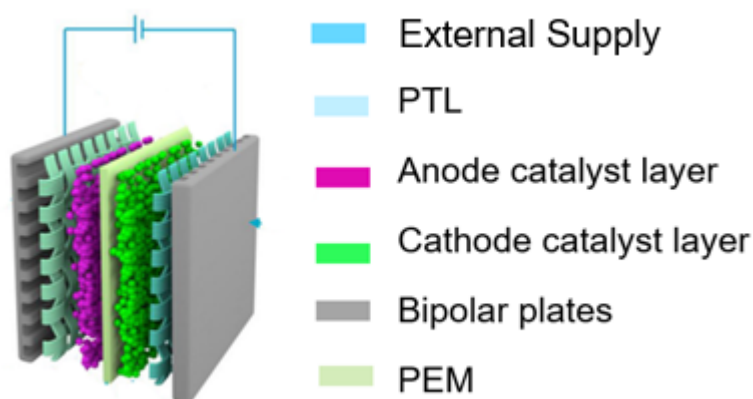
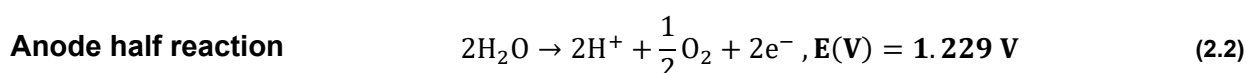
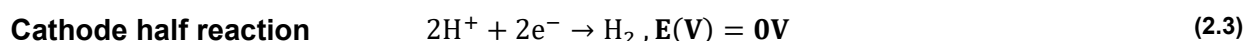


Figure 2.4: General schematic of a PEMWE cell (adapted from [43]).

PEMWE is a process that uses an electrochemical cell to split water into hydrogen gas (H_2) and oxygen gas (O_2) using an electrical energy source. The current applied to the electrolyser determines the rate of hydrogen and oxygen production [18]. The key component of PEMWE is the proton conducting membrane, which separates the anode and cathode and transports the in-situ generated H^+ from the anode to the cathode side. The anode and cathode catalyst layers comprise of an iridium and platinum-based catalyst, respectively. It is important that the supplied water is pure and free from impurities to prevent degradation of the membrane and catalysts [18]. Furthermore, PEMWE requires careful water management to maintain optimal performance. The reaction where water molecules are oxidised at the anode, releasing oxygen gas and positively charged ions (i.e., H^+), is called the anodic half-reaction (Occurring at 1.229 V [44]), as can be seen in equation (2.2) [11, 45, 46].



The released oxygen gas is collected at the anode while the protons move through the proton exchange membrane [26, 18]. This is due to the proton exchange membrane that only allows protons to pass through, blocking the passage of electrons. This selective permeability enables the separation of the anode and cathode compartments, enabling protons to migrate to the cathode, where they combine with electrons supplied from the external circuit to form hydrogen gas [26, 18]. This reaction is called the cathodic half-reaction (occurring at 0 V [44]), as can be seen in equation (2.3) [11, 45, 46].



The overall result of this process, illustrated by equation (2.4), is the production of hydrogen gas collected at the cathode and oxygen gas collected at the anode [18]. However, this electrolysis

process generates heat, which needs to be dissipated to prevent overheating. Cooling systems, such as water or air, are used to maintain an optimal operating temperature [47].

PEMWE offers numerous characteristics and advantages that make it an attractive method for hydrogen production. One advantage is higher energy conversion efficiency compared to other electrolysis methods. Its efficiency stems from using a solid polymer electrolyte membrane allowing the selective transport of protons [44, 47, 48]. This characteristic minimises energy losses associated with side reactions and enables a more efficient conversion of electrical energy into chemical energy. PEMWE also exhibits rapid response times, allowing for quick start-up and shutdown. The solid polymer electrolyte membrane facilitates the rapid transport of protons, enabling the system to reach stable operating conditions within seconds. This feature makes PEMWE suitable for applications requiring intermittent or on-demand hydrogen production.

Furthermore, PEMWE can operate at high current densities, making it suitable for high-volume hydrogen production. The proton exchange membrane, along with efficient catalyst materials such as platinum, enables the efficient transport of protons and electrons, facilitating high rates of hydrogen gas generation [44, 47, 48]. PEMWE systems are typically compact designs, making them suitable for numerous hydrogen applications. The use of a solid polymer electrolyte eliminates the need for a liquid electrolyte, simplifying system design and reducing the overall weight and size of the electrolysis unit. Additional characteristics of PEMWE in general can be seen in Table 2.1.

Table 2.1: PEMWE general characteristics (combined from [15, 18, 44, 45, 47]).

PEMWE characteristics	
Electrolyte	PEM (e.g., Nafion®; perfluoro-sulfonic acid)
Cathode catalyst material	Pt-based
Anode catalyst material	Ir-based
Typical operating current density	0.6-2 A/cm ²
Operating cell voltage	1.8-2.2 V
Operating temperature	40-90 °C
Operating pressure	1-200 bars
Hydrogen purity	99.9-99.99%
System response	Immediate response [47]

PEMWE is considered a safe hydrogen production method due to its low operating temperatures and pressures. The absence of corrosive and hazardous chemicals in the electrolysis process enhances operational safety. Additionally, this process produces hydrogen gas without any greenhouse gas emissions (if the electrolyser is powered with renewable energy sources),

contributing to a cleaner and more sustainable energy future. PEMWE can also be seamlessly integrated with renewable energy sources [9]. As these energy sources are intermittent, the fast response and dynamic operation of PEMWE allow it to adapt to fluctuations in power supply efficiently. This enables hydrogen production using excess renewable energy during periods of low demand or high generation, thus promoting the storage and utilisation of renewable energy [44, 47, 48]. PEMWE technology has the advantage of scalability, allowing hydrogen production at various scales, from small-scale applications to large industrial installations. This scalability makes PEM electrolysis adaptable to different hydrogen demand scenarios, ranging from transportation and energy storage to industrial processes. Thus, with all this in mind, continued research and development efforts in PEMWE hold the potential to enhance its performance further and reduce costs, paving the way for widespread adoption and utilisation of hydrogen as a clean and versatile energy carrier.

2.2.3 PEMWE electrolyser components

As previously mentioned, the operation of the PEM electrolyser is crucial to successfully designing a working prototype that will be able to efficiently characterise the PEMWE cell. Thus, in this section, the different components of the PEM electrolyser are analysed to gain a knowledgeable understanding of their significance within the hydrogen production process. Figure 2.5 shows a detailed diagram of the different component layers and materials within a typical PEM electrolyser cell.

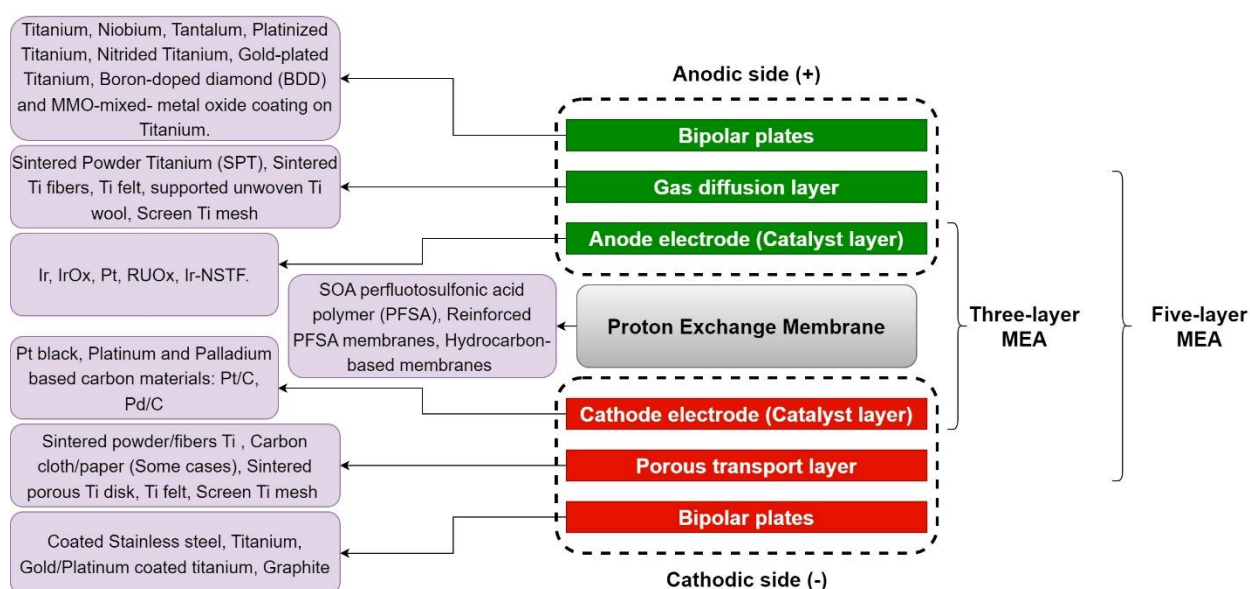


Figure 2.5: PEM electrolyser component layers and materials (adapted from [18, 46]).

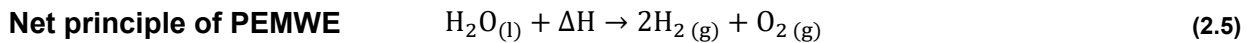
The discussion will include the membrane electrode assembly (MEA), the porous transport layer (PTL), as well as the bipolar plates containing the flow fields that improve the flow of water, oxygen, and hydrogen within the cell [49, 50, 51].

2.3 Electrochemical fundamentals

This section discusses the electrochemical fundamentals of the PEMWE to gain insight into its mathematical, chemical, and electrical characteristics. The fundamentals include detailed discussions of the thermodynamics, cell potential, reaction kinetics, electrolyser efficiency and component degradation of the PEMWE cell.

2.3.1 Thermodynamics

The thermodynamics of a PEM electrolyser involve understanding the energy changes and equilibrium conditions during the electrolysis process. In PEM electrolysis, water is split into hydrogen and oxygen gases using an electrical source. However, to successfully drive this water splitting process, the theoretical energy required by the electrolytic hydrogen production process to successfully break or build up chemical bonds needs to be calculated. It is given by the change in reaction enthalpy, ΔH . The reaction enthalpy represents the thermodynamic potential of the system and cannot be measured directly. It also has no significance during heat analysis within the water splitting process. However, the change in reaction enthalpy is more useful and can be easily calculated by using the summation product of the enthalpies of formation of the products, $\Delta H_{f,pdt}$, minus the summation product of the enthalpies of formation of the reactants $\Delta H_{f,rct}$ [50]. Based on the net general principle of water electrolysis, shown in equation (2.5) [50], during ambient temperatures water is fed though to the system as a liquid reactant (since water is operated underneath boiling point) from which hydrogen and oxygen (existing in molecular format) is then produced (equation (2.5) [51])



However, since both oxygen and hydrogen (products of the reaction) do not undergo further bond breaking, their enthalpy of formation is zero, leaving only the enthalpy of formation of the water reactant (representing the reaction enthalpy of water electrolysis). Furthermore, during the water splitting process, electrical and thermal energy are required to drive the process successfully [50, 52]. Thus, ΔH can be rewritten as shown by equation (2.6) [50, 53].

$$\Delta H = \Delta G + T\Delta S \quad (2.6)$$

Where ΔG , known as the Gibbs free energy, represents the electrical energy required, and $T\Delta S$ represents the thermal energy required [50, 54, 55, 56]. T is known as the system temperature measured in Kelvin, and ΔS as the change of entropy representing the level of disorder within a thermodynamic system. The change in entropy can also be easily calculated by using the summation product of the enthalpies of formation of the products ($\Delta S_{f,pdt}$) minus the summation product of the enthalpies of formation of the reactants ($\Delta S_{f,rct}$) [50]. The thermal energy ($T\Delta S$) is the entropy term representing the thermal energy input required to split water.

2.3.1.1 Gibbs free energy

The Gibbs free energy change is a measure of the spontaneity or feasibility of a reaction without the presence of an external energy source. The change in Gibbs free energy can be represented by equation (2.7), where ΔH_R represents the change in reaction enthalpy, T represents the system temperature, and ΔS_R represents the change in entropy [50, 53, 54].

$$\Delta G_R = \Delta H_R - T\Delta S_R \quad (2.7)$$

After calculating the change in Gibbs free energy, the resulting answer shows if the reaction occurred spontaneously without adding an external energy source. Thus, if ΔG_R is negative, the reaction occurs spontaneously and does not require an external energy source. However, if ΔG_R is positive, the reaction occurs non-spontaneously and does require an external energy source. In the case of PEM water electrolysis, the overall Gibbs free energy change is positive, indicating that the reaction requires an input of energy to proceed [50]. This energy is supplied by an external power source, typically an electrical energy source.

2.3.1.2 Thermodynamic properties of PEMWE

Now to efficiently calculate the change in Gibbs free energy (ΔG_R^0), the change in reaction enthalpy (ΔH_R^0), and the change in entropy (ΔS_R^0) at standard state ($p = 1$ atm and $T = 298.15$ K) [50], the values for the liquid reactant (H_2O) and the gaseous products (H_2 and O_2), summarised in Table 2.2, can be used (equation (2.1) [51]). The thermodynamic properties listed in Table 2.2 are obtained under standard state conditions and give the standard molecular weight, the enthalpy of formation, the entropy of formation, as well as the Gibbs free energy of reaction for each substance present within equation (2.1). Using the values listed in Table 2.2, the change in entropy at standard state can be determined using equation (2.8) [57], consisting of the summation of the entropy of formation of the products minus the entropy of formation of the reactant. The change in enthalpy at standard state can be determined using equation (2.9) [57], consisting of the summation of the enthalpy of formation of the products minus the enthalpy of formation of the reactant. From the change in enthalpy at standard state the Gibbs free energy can be calculated under standard conditions using equation (2.10) [57]. Furthermore, the change in enthalpy under standard conditions is known as the higher heating value, whilst the Gibbs free energy is known as the lower heating value [58].

$$S_R^0 = S_{R,pdt}^0(H_2) + \frac{1}{2}S_{R,pdt}^0(O_2) - S_{R,rcr}^0(H_2O) = 0.16 \text{ kJ} \cdot \text{mol}^{-1} \text{K}^{-1} \quad (2.8)$$

$$\Delta H_R^0 = H_{R,pdt}^0(H_2) + \frac{1}{2}H_{R,pdt}^0(O_2) - H_{R,rcr}^0(H_2O) = 285.83 \text{ kJ} \cdot \text{mol}^{-1} \quad (2.9)$$

$$\Delta G_R^0 = \Delta H_R^0 - T\Delta S_R^0 = 237.16 \text{ kJ} \cdot \text{mol}^{-1} \quad (2.10)$$

Table 2.2: Thermodynamic properties of water electrolysis (combined from [50, 59, 60, 61]).

Substance	Molecular Weight (g. mol ⁻¹)	ΔH_R^0 (kJ. mol ⁻¹)	ΔS_R^0 (kJ. mol ⁻¹ K ⁻¹)	ΔG_R^0 (kJ. mol ⁻¹)
Liquid H ₂ O	18.02	-285.83	69.94	236.48
H ₂ Gas	2.06	0.00	130.68	0.00
O ₂ Gas	32.00	0.00	205.15	0.00

2.3.2 Cell potential

The cell potential, also known as the voltage or electromotive force (EMF), is a crucial component in PEM water electrolysis. It represents the applied electrical potential difference between the anode and cathode required to drive the non-spontaneous electrolysis reaction, splitting water into hydrogen and oxygen gases. Since the reaction in a PEM electrolysis cell occurs non-spontaneously, the cell potential is applied externally to drive the electrolysis reaction, splitting water into hydrogen and oxygen gases. The cell potential required for electrolysis depends on various factors, including the desired hydrogen production rate, cell design, operating temperature, and catalyst activity. Typically, a voltage higher than the standard cell potential is applied to overcome the overpotential and other losses associated with the electrolysis process.

2.3.2.1 Reversible potential

The reversible potential, also known as the standard potential or standard cell potential, is the potential difference between the anode and cathode of a PEM electrolyser cell under standard conditions ($p = 1$ atm and $T = 298.15$ K). It represents the thermodynamic potential of the electrochemical reaction occurring within the electrolyser cell. Thus, in a PEM electrolyser, the reversible potential is the voltage required to drive the electrolysis reaction, splitting water into hydrogen and oxygen gases [11, 50]. The minimum theoretical standard potential of a PEM electrolyser can be approximated as 1.23 V at 25 °C. However, in an electrolyser, an external energy source is applied to exceed this reversible potential and drive the reaction whilst overcoming system losses. Thus, the reversible potential of a PEM electrolyser cell can be expressed in terms of the standard Gibbs free energy ($\Delta G_R^0 = 236.48$ kJ. mol⁻¹) [52], illustrated by equation (2.11), where F refers to the Faraday's constant ($\approx 96\,485$ C. mol⁻¹) [11] and n refers to the number of electrons transferred per reaction ($n = 2$, due to equation (2.1)) [11]. Thus, by substituting the values for the standard Gibbs free energy, Faraday's law, as well as the number of electrons per reaction, the reversible potential at standard conditions can be calculated as 1.23 V.

$$E_{Rev}^0 = \frac{\Delta G_R^0}{nF} = \frac{236.483 \times 10^3}{(2)(96485)} \cong 1.23 \text{ V} \quad (2.11)$$

It is important to note that the reversible potential is the ideal potential at which the reaction would occur under ideal, equilibrium conditions. In practice, due to various factors such as activation overpotential, concentration overpotential, and resistance losses, the actual cell potential required for the reactions in PEM electrolyzers is higher than the reversible potential and will be explained within the following few sections. Thus, understanding the reversible potential is crucial for assessing the thermodynamic feasibility and efficiency of the electrochemical reactions in PEM electrolyzers. It provides a baseline to evaluate the performance and optimise the operating conditions of these devices.

2.3.2.2 Thermo-neutral potential

At the standard reversible voltage, calculated in section 2.3.2.1 as 1.23 V, the reaction occurring within the PEM electrolyser cell is inherently endothermic ($\Delta H > 0$) [62, 63] requiring a net energy input. In general, when the cell voltage is below the thermoneutral voltage E_{th}^0 the electrolysis process operates endothermically, absorbing heat from the environment or an external source. Conversely, when the cell voltage exceeds, the process operates exothermically, producing excess heat due to the additional electrical energy input. For an endothermic reaction without an external thermal source for $T\Delta S$, the heat can alternatively be generated internally by applying an overvoltage from the electrical energy source. Thus, to sustain the reaction without net heat absorption from the environment, an additional overvoltage is required. Otherwise, the reaction will only extract continuous heat from the environment until the reaction reaches equilibrium. Thus, the thermo-neutral voltage E_{th}^0 for this endothermic reaction, which is higher than the standard reverse voltage, represents the total energy required to sustain the electrolysis process shown in equation (2.12) [50, 62, 63].

$$E_{th}^0 = \frac{(\Delta H_R^0)}{nF} = \frac{(285.5 \times 10^3 \text{ J.mol}^{-1})}{(2 \text{ mol})(96485 \text{ C.mol}^{-1})} \cong 1.48 \text{ V} \quad (2.12)$$

Where $\Delta H_R^0 = 285.5 \text{ kJ.mol}^{-1}$ [62] is the standard reaction enthalpy of formation, F refers to Faraday's constant ($\approx 96485 \text{ C.mol}^{-1}$) [11], and n refers to the number of electrons transferred per reaction ($n = 2$) [11]. Thus, substituting the values for the standard reaction enthalpy of formation, Faraday's law, as well as the number of electrons per reaction, the reversible potential at standard conditions can be calculated as 1.48 V. The thermo-neutral potential is influenced by several factors, including temperature and reactant concentrations. As temperature increases, the thermo-neutral potential generally decreases, indicating a lower energy requirement for the electrolysis reaction. Similarly, higher reactant concentrations or more active catalysts can also lower the thermo-neutral potential.

Furthermore, the actual cell potential required for PEM electrolysis is typically higher than the thermo-neutral potential due to various factors such as activation overpotential, concentration overpotential, and resistance losses in the system. These factors cause deviations from ideal thermodynamic behaviour and result in an increased cell potential requirement to drive the electrolysis reaction. Thus, a knowledgeable understanding of the thermo-neutral potential is useful for evaluating the energy efficiency and feasibility of the PEM electrolysis process. By operating the electrolyser close to the thermoneutral potential, the need for external heat input can be minimized, improving energy efficiency. Furthermore, practical operation typically requires higher voltages due to overpotentials and losses, necessitating optimization of cell design and operating conditions to maximize hydrogen production efficiency.

2.3.2.3 Open circuit potential

The Nernst equation allows us to calculate the cell potential E under non-standard conditions, considering the effect of concentration changes and temperature on the cell potential. It demonstrates the relationship between the cell potential and the driving force for the electrochemical reaction. The electrochemical reaction can be represented by equation (2.13), where R refers to reduction (electron gain) and O refers to oxidation (loss of electrons) [22] [64].



From this, the Gibbs free energy can be expressed by incorporating the electron reduction and electron oxidation reactions, as illustrated within equation (2.14), where (ΔG^0) represents the Gibbs free energy obtained under standard conditions. The R represents the universal gas constant, T the temperature in Kelvin, $[R]$ the reaction product activities, and $[O]$ the reaction reactants activities [58, 64].

$$\Delta G = \Delta G^0 + RT \ln \frac{[R]}{[O]} \quad (2.14)$$

However, the Gibbs free energy can also be represented in terms of the electrical work done using the electrode potential represented by equation (2.15), where n refers to the number of electrons transferred per reaction, F refers to Faraday's constant ($96\,485 \text{ C.mol}^{-1}$) [11], and E refers to the electrode potential. The negative sign indicates that the system is doing work on its surroundings [58, 64].

$$G = -nFE \quad (2.15)$$

Now using equation (2.15), the Nernst equation for water electrolysis can be derived as represented by equation (2.16), where E^0 is the standard open circuit voltage (thermodynamic potential) and E_{rev} is the standard reversible potential [58, 64].

$$E^0 = E_{rev} - \frac{RT}{nF} \ln \frac{[R]}{[O]} \quad (2.16)$$

However, based on equations (2.2) and (2.3) showing the anode and cathode half-reactions of the PEM water electrolyser, respectively, the potential at the anode and cathode can be used to generate equation (2.17) in the case of water vapour as the educt. Therefore, a_{H_2O} refers to the water vapour concentration, a_{H_2} the hydrogen gas concentration, and a_{O_2} the oxygen gas concentration [50, 58].

$$E^0 = E_{rev} - \frac{RT}{nF} \ln \frac{a_{H_2O}}{(a_{H_2})(a_{O_2})} \quad (2.17)$$

The Nernst equation, represented by equation (2.17), can be further updated by substituting the concentration of the products and the reactants with the partial pressures of each substance, respectively (p_{H_2O} , p_{H_2} and p_{O_2}), illustrated in equation (2.18) [50, 58].

$$E^0 = E_{rev} - \frac{RT}{nF} \ln \frac{p_{H_2O}}{(p_{H_2})(p_{O_2})^{\frac{1}{2}}} \quad (2.18)$$

Furthermore, much debate exists on the value of the standard reversible potential of PEM water electrolysis. Some authors make use of 1.23 V as the standard reversible potential, while others use equation (2.19) [32, 65, 66, 67].

$$E_{rev} = 1.229 - (0.9 \times 10^{-3})(T - 298.15) \quad (2.19)$$

Based on research conducted, equation (2.19) is favoured by most authors [32, 65, 66, 67]. The reason for this is that $E_{rev} = 1.23$ V is only true under standard conditions, that is $p = 1$ atm and $T = 298.15$ K. However, equation (2.19) can be used under a range of temperatures making it more viable in practice since standard conditions are difficult to maintain. Now to efficiently represent the open circuit voltage in terms of the temperature-dependant expression obtained in equation (2.19), equation (2.7) can firstly be substituted into equation (2.11), generating equation (2.20) [68].

$$E_{Rev}^0 = \frac{\Delta H_R - T\Delta S_R}{nF} \quad (2.20)$$

If the assumption is made that ΔH_R and ΔS_R are constant, equations (2.21) and (2.22) can be produced [68].

$$E_{Rev}^0 = \frac{(\Delta G_R^0 + 298.15\Delta S_R^0) - T\Delta S_R^0}{nF} \quad (2.21)$$

$$E_{Rev}^0 = \frac{\Delta G_R^0}{nF} - \frac{\Delta S_R^0}{nF} (T - 298.15) \quad (2.22)$$

By substituting equation (2.18) into equation (2.22), the open circuit voltage in terms of a temperature dependant expression can be obtained and is illustrated by equation (2.23) [68].

$$E^0 = \frac{\Delta G_R^0}{nF} - \frac{\Delta S_R^0}{nF} (T - 298.15) - \frac{RT}{nF} \ln \frac{p_{H_2O}}{(p_{H_2})(p_{O_2})^{\frac{1}{2}}} \quad (2.23)$$

Therefore, equation (2.23) clearly shows that the open circuit voltage E^0 is affected by both operating temperature and pressure.

2.3.2.4 Overpotential

In PEM electrolysis, overpotential, also known as polarisation, refers to the additional energy or voltage required to drive an electrochemical reaction at an electrode compared to the thermodynamic potential of the reaction. It represents the energy losses or inefficiencies associated with the electrochemical process, such as activation losses (due to reaction kinetics), ohmic losses (due to cell component resistances) and concentration losses (due to limitations of mass transport). In an electrochemical cell, the desired reaction occurs at the electrode surfaces.

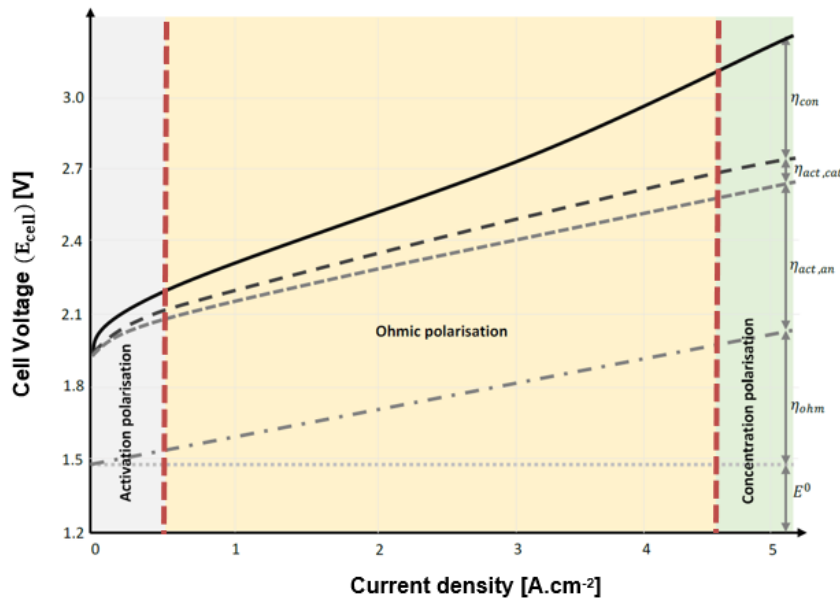


Figure 2.6: Contribution of overpotentials on the overall cell polarisation (adapted from [19, 22, 50]).

However, due to various factors, the actual potential required to drive the reaction is higher than the ideal or thermodynamic potential. This additional potential is known as overpotential. The overpotential can be represented in terms of the cell voltage E_{cell} and the open circuit voltage E_0 as illustrated by equation (2.24).

$$\eta = E_{cell} - E_0 \quad (2.24)$$

Furthermore, the cell voltage E_{cell} can be expressed as the summation of the open circuit voltage E_0 and the kinetic losses such as activation losses η_{act} , ohmic losses η_{ohm} , and concentration losses η_{con} . From Figure 2.6, it is evident how the different overpotentials influence the total cell voltage E_{cell} as the current density varies. Figure 2.6 illustrates that the activation overpotential has the highest contribution in kinetic losses during low current densities (indicated through the contribution length on the right-hand side of the figure), whereas in higher current densities, the ohmic losses become the governing contributor.

Ohmic overpotential

In a PEM water electrolyser, the flow of current is accompanied by the movement of charged ions through the PEM and electrons through the cell electrodes and the bipolar plates. However, this movement is impeded by the resistance of the electrolyte and the electrode materials. This resistance leads to a voltage drop along the conductive path, resulting in an additional potential requirement to sustain the desired electrochemical reaction. The ohmic overpotential can be quantified using Ohm's law [32, 69]. In the context of an electrochemical cell, the current passing through the cell is typically related to the rate of the electrochemical reaction [32, 69]. Therefore, the ohmic overpotential η_{ohm} can be expressed using equation (2.25) [32, 69].

$$\eta_{ohm} = IR_{Ohmic} \quad (2.25)$$

The resistance R_{Ohmic} in this case includes the summation of the electrode resistance R_{elec} , the bipolar plate resistance R_{bp} , as well as the proton exchange membrane resistance R_{pem} , illustrated by equation (2.26) and I refers to the current passing through the PEM [32, 69].

$$\eta_{ohm} = I(R_{elec} + R_{bp} + R_{pem}) \quad (2.26)$$

Ohmic overpotential can significantly impact the overall efficiency and performance of an electrochemical cell. Higher resistance leads to larger ohmic overpotential and increased energy losses.

Activation overpotential

In PEM water electrolysis, activation overpotential refers to the additional potential required to drive the desired electrochemical reactions at the electrode surfaces. It represents the energy losses or inefficiencies associated with the kinetics of the electrochemical process in a PEM electrolyser. From section 2.2.3, it is known that in PEM electrolysis, water is split into hydrogen and oxygen gases through two half-reactions. This includes the oxygen evolution reaction (OER) occurring at the anode of the cell and the hydrogen evolution reaction (HER) at the cathode. These reactions involve the transfer of protons H^+ and electrons e^- across the electrode and electrolyte interfaces. Thus, activation overpotential in PEM electrolysis can be attributed to the sluggish kinetics of these half-reactions. The electrochemical reaction at the electrodes must overcome an activation energy barrier for the desired reactions to occur. This barrier is influenced by factors such as the nature of the reactants, the presence of catalysts, and the temperature. Equation (2.27) is used to describe the activation overpotential as the rate at which reactions take place, where R is the universal gas constant, T is the temperature, α is the transfer coefficient, F is Faraday's constant, I is the current, and i_0 is the exchange current [32, 69].

$$\eta_{act} = \frac{RT}{\alpha_{an}F} \sinh^{-1} \left(\frac{i}{2i_{0,an}} \right) + \frac{RT}{\alpha_{cat}F} \sinh^{-1} \left(\frac{i}{2i_{0,cat}} \right) \quad (2.27)$$

To minimise activation overpotential in PEM electrolysis, efficient catalysts are typically used to facilitate the reactions and lower the activation energy. These catalysts, often based on precious metals such as platinum, enhance the reaction kinetics and reduce the activation overpotential. Additionally, optimising the operating conditions of the PEM electrolyser, such as temperature and reactant concentration, can also help reduce activation overpotential. Higher temperatures generally increase the reaction rates and decrease the activation overpotential. Similarly, maintaining sufficient reactant concentrations can improve kinetics and reduce the activation overpotential.

Concentration (mass transport) overpotential

Concentration overpotential, also known as mass transport losses (diffusion overpotential), is a phenomenon that occurs in electrochemical cells when there is a concentration gradient (difference in concentration with respect to the desired concentration) of reactants or products near the electrode surfaces. It refers to the additional potential required to drive the desired electrochemical reaction at the electrodes due to this concentration gradient [32, 69]. This type of overpotential arises when the internal electrical current is so high as to slow down the reaction rate by overpopulating the membrane surface (anode surface side) with oxygen gas bubbles [32, 69]. Usually, this phenomenon is observed at moderate current densities of approximately 1.3 A/cm² [69].

Furthermore, the concentration overpotential arises from two main factors: diffusion limitations and inadequate reactant or product supply. Diffusion is the process by which reactant species move from areas of high concentration to areas of low concentration. In an electrochemical cell, the movement of reactants or products is often impeded by the presence of a boundary layer or stagnant layer near the electrode surface [70]. This layer can be caused by the slow diffusion of species through the electrolyte or by the accumulation of products near the electrode. The concentration gradient across this boundary layer results in concentration overpotential. Concentration overpotential can also occur when there is a limited supply of reactants or inadequate removal of products near the electrode surface. If the reactant supply is limited, the concentration of reactants near the electrode may be lower than desired, leading to concentration overpotential. Similarly, if the products of the reaction are not efficiently removed, their concentration near the electrode may increase, resulting in concentration overpotential. Taking this into account, the concentration overpotential can be estimated using the Nernst equation as shown by equation (2.28) [70].

$$\eta_{con} = E_1 - E_0 = \left(E^0 + \frac{RT}{nF} \ln C_1 \right) - \left(E^0 + \frac{RT}{nF} \ln C_0 \right) = \frac{RT}{nF} \ln \frac{C_1}{C_0} \quad (2.28)$$

Where C_1 and C_0 refer to the gas concentration at the electrode and the reference gas concentration for a working condition, respectively. Concentration overpotential can significantly affect the performance and efficiency of electrochemical cells. It can increase the energy losses and decrease the reaction rate, decreasing overall cell efficiency.

2.3.3 Reaction kinetics

The reaction kinetics of a PEM electrolyser refers to the rate at which the desired electrochemical reactions occur at the electrode surfaces. These reactions include the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode. It involves the comprehension of mechanisms and factors that influence the speed and efficiency of these reactions. Furthermore, it is crucial to understand the reaction kinetics for optimising the performance of PEM electrolysers by studying the kinetics to optimise catalyst materials and loading and designing more efficient electrode structures (highlighted in section 2.3.2.4.2). The reaction kinetics of the PEM electrolyser cell is highly dependent on the total current supplied to the electrolyser as will be discussed during sections 2.3.3.1 and 2.3.3.2.

2.3.3.1 Butler Volmer

The Butler-Volmer equation is a fundamental equation used to describe the kinetics of an electrochemical reaction at an electrode-electrolyte interface. It provides a mathematical relationship between the current density i and the overpotential η , represented as the difference between the applied and thermodynamic potential for the given reaction [71]. The general equation can be expressed as the difference between the forward current density i_f and the backwards current density i_b from equation (2.29) [71].

$$i = i_f - i_b = i_0 \left(\exp \left(\frac{\alpha_{an} F \alpha_{act}}{RT} \right) - \exp \left(\frac{\alpha_{cat} F \alpha_{act}}{RT} \right) \right) \quad (2.29)$$

Where i is the current density measured in A/m², i_0 is the exchange current density, which represents the current density at zero overpotential, α_{an} and α_{cat} are the anodic and cathodic transfer coefficients, respectively, representing the fraction of electrons involved in the anodic and cathodic reactions, and η is the overpotential in volts [32, 64].

Furthermore, the Butler-Volmer equation describes the relationship between the reaction rate and the overpotential. It shows that the current density is exponentially dependent on the overpotential, with the forward reaction (anodic) term and the backward reaction (cathodic) term contributing to the overall current density. The exchange current density i_0 is a measure of the intrinsic kinetics of the reaction and is influenced by factors such as the nature of the reactants, the presence of catalysts, and the temperature. It represents the current density at equilibrium, where the forward and backward reaction rates are equal. The transfer coefficients α_{an} and α_{cat} reflect the degree of charge transfer involved in the anodic and cathodic reactions [32, 64]. They

are usually between 0 and 1, with values closer to 1 indicating a more complete charge transfer. The Butler-Volmer equation is commonly used in electrochemical studies to analyse and model the kinetics of reactions occurring at electrode surfaces. It provides insights into the dependence of the reaction rate on the applied potential and can be used to evaluate the performance and efficiency of electrochemical systems, including PEM electrolyzers.

2.3.3.2 Molar flow rate

In PEM electrolysis, the molar flow rate refers to the rate at which reactants or products are transported through the electrolyte in terms of the number of moles per unit time. It provides a measure of the quantity of reactants consumed or products generated during the electrolysis process. Faraday's law, illustrated from equation (2.30), can be used as a starting point for determining the equation for the molar flow rate [32, 64].

$$q = nzF \quad (2.30)$$

Where q is the total charge, n the number of moles, z the number of electrons and F the Faraday's constant ($\approx 96485 \text{ C.mol}^{-1}$) [11]. Now, using equation (2.30), the molar flow rates of the PEM water electrolyser reactant and products can be illustrated by equations (2.31), (2.32) and (2.33) [32, 66, 70].

$$\dot{n}_{H_2} = \frac{I}{2F} \varepsilon_I \quad (2.31)$$

$$\dot{n}_{O_2} = \frac{I}{4F} \varepsilon_I \quad (2.32)$$

$$\dot{n}_{H_2O} = 1.25 \frac{I}{2F} \varepsilon_I \quad (2.33)$$

Where $\dot{n}_{H_2}$ is the molar flow rate of hydrogen, $\dot{n}_{O_2}$ is the molar flow rate of oxygen, $\dot{n}_{H_2O}$ is the molar flow rate of water, and ε_I is the Faraday's efficiency accounting for the current losses in the cell and will be discussed in section 2.4 [32, 66, 70].

2.4 PEMWE efficiency

This section pertains to a detailed study regarding the different efficiency calculations of a PEM water electrolyser. The efficiencies discussed include cell, voltage, Faradaic, and non-Faradaic efficiency. The efficiency of PEM water electrolyser is crucial and needs to be thoroughly investigated based on the following reasons:

- **Energy consumption:** High efficiency means less electrical energy is required to produce a given amount of hydrogen gas. This translates to lower energy costs and reduces environmental impact, as less electricity needs to be generated from primary energy sources.
- **Cost-effectiveness:** Efficient PEM electrolysis systems can produce hydrogen at a lower cost, making it more economically viable for various applications such as fuel cells, energy

storage, and industrial processes. Lower production costs can help accelerate the adoption of hydrogen as a clean energy carrier.

- **Renewable energy integration:** PEM electrolysis applications in other renewable energy systems deliver high-efficiency electrolysis, allowing for better integration of intermittent renewable energy into the grid, as excess electricity can be stored as hydrogen and used later when renewable generation is low.

Overall, improving the efficiency of PEM water electrolysis is crucial for advancing green production worldwide.

2.4.1 Cell efficiency

The cell efficiency of a PEM water electrolyser refers to the ratio of the electrical energy input to the system to the chemical energy output in the form of hydrogen gas. It is a measure of how effectively the electrolyser converts electricity into hydrogen. However, the term energy efficiency with regard to electrolysis energy conversion systems has gained a variety of interpretations among authors. To ensure that the definition of the cell efficiency is understood, the definition of cell efficiency of a PEM water electrolyser is derived based on the following assumptions [72]:

- The PEM water electrolyser generates pure hydrogen and pure oxygen; however, only the hydrogen generated is regarded as useful output.
- PEM water electrolyser has a low operating temperature (under 100 °C) with only electricity supply as input energy to the system (electricity supply at least equal to that of ΔH as shown in equation (2.6))
- The water supplied to the PEM water electrolysis system is in a liquid state (this means that heat required for water vaporisation needs to be supplied externally).

Therefore, the efficiency of the PEM water electrolyser can be defined as the unit of hydrogen energy output per unit electrical energy input. Based on this definition, the cell efficiency of the PEM water electrolyser can be calculated using three methods, as shown in the literature.

2.4.1.1 Method 1: Cell efficiency calculation using HHV and molar flow rate

The cell efficiency ε_{cell}^{HHV} of a PEMWE cell is defined as the product of the higher heating value of liquid water (HHV) and the ratio of the molar flow rate of hydrogen $\dot{n}_{H_2}$ divided by the average electrical power supplied to the stack P_{avg} . This can be seen within equation (2.34) where (ΔH_R^0) is the change in reaction enthalpy under standard conditions, U_{cell} is the cell voltage, and I_{cell} is the cell current [50, 72].

$$\varepsilon_{cell}^{HHV} = \frac{(\Delta H_R^0)(\dot{n}_{H_2})}{(U_{cell})(I_{cell})} \quad (2.34)$$

The use of HHV, instead of LHV, is due to the level of effectiveness that HHV provides based on the electrochemical materials used as well as the balance of the plant. The LHV is typically used

when hydrogen energy is converted back to electricity (in the case of fuel cells) or heat (in the case of thermal processes) [72].

2.4.1.2 Method 2: Cell efficiency calculation using chemical energy and number of moles

As mentioned in the previous method, equation (2.34) calculates the cell efficiency of the PEM water electrolyser using average hydrogen flow and electrical power. Although equation (2.34) uses the flow of hydrogen as output, the cell efficiency of the PEM water electrolyser can also be calculated if the total amount of generated hydrogen is known by determining the ratio between the total energy output (hydrogen) and the total energy input (electrical supply). However, to calculate the cell efficiency, the chemical energy of the system needs to be calculated, as seen in equation (2.35) [73].

$$\text{Chemical Energy (J)} = \text{Number of moles of hydrogen} \times HHV_{H_2} \quad (2.35)$$

Where the HHV_{H_2} refers to the HHV of hydrogen. The number of moles of hydrogen can be calculated using equation (2.36), where the molecular weight of hydrogen is obtained from Table 2.2 [73].

$$\text{Number of moles of hydrogen} = \frac{\text{Total weight}}{\text{Molecular weight}} \quad (2.36)$$

By converting the electrical energy to Joules, the efficiency of the PEM water electrolyser cell can be calculated using equation (2.37) [73].

$$\varepsilon_{cell}^{HHV} = \frac{\text{Chemical energy (J)}}{\text{Electrical energy (J)}} = \frac{\text{Chemical energy (J)}}{\text{Electrical energy (kWh)} \times (3.6 \times 10^6)} \quad (2.37)$$

2.4.1.3 Method 3: Cell efficiency calculation using Faraday's efficiency

The cell efficiency of the PEM water electrolyser can also be calculated using Faraday's efficiency ε_I . Thus, the cell efficiency can be represented in terms of the product of the voltage efficiency ε_V^{HHV} and the Faradaic efficiency ε_I as illustrated by equation (2.38) [72].

$$\varepsilon_{cell}^{HHV} = \varepsilon_V^{HHV} \times \varepsilon_I \quad (2.38)$$

All the above-mentioned methods successfully calculate the PEM water electrolyser's cell efficiency using different approaches. However, each method produces the same answer. Furthermore, the voltage efficiency ε_V^{HHV} as well as the Faradaic efficiency ε_I will be discussed in more detail within sections 2.4.2 and 2.4.3 [72].

2.4.2 Voltage efficiency

To simplify the efficiency calculation process, illustrated by equation (2.34) [72], the efficiency of the PEM water electrolyser cell can be calculated using only measured voltage values obtained from the cell. This technique is known as the voltage efficiency of the PEMWE cell, and is defined as the ratio between the minimum theoretical voltage $E_{th}(T)$ and real cell voltage $U_{cell}(T)$ at a

specific temperature [50, 72, 74]. However, the voltage efficiency ε_V^{HHV} is mostly calculated using the thermo-neutral voltage at standard conditions E_{th}^0 as illustrated by equation (2.39) [50, 72, 74].

$$\varepsilon_V^{HHV} = \frac{E_{th}^0}{U_{cell}} \quad (2.39)$$

The voltage efficiency at HHV includes all the overpotentials situated at the electrodes of the PEM water electrolyser cell as well as all the ohmic losses occurring within the cell [72]. Furthermore, equation (2.39) is only valid if the current supplied to the cell is completely converted into electrochemical energy that is solitarily used for the rate of the water splitting process [50]. However, in the practical case of PEM water electrolysis, there are too many influencing factors such as unintentional reactions, stray currents, and gas leakages, which are in contrast to the assumptions made within equation (2.39). These losses can therefore be compensated for by calculating the faradaic or current efficiency.

2.4.3 Faradaic efficiency (Current efficiency)

The Faradaic efficiency ε_I , or current efficiency, is defined as the ratio of actual hydrogen produced under practical conditions and theoretical hydrogen produced based on Faraday's law, defined by equation (2.40) [50]. The theoretical hydrogen produced can also be calculated using the ideal gas law illustrated by equation (2.41) [50]. This phenomenon accounts for the parasitic electrical stray currents with the PEM water electrolyser cell, diffusion of gases through the PEM, gas leakages, etc.

Faraday's Law

$$n = \frac{q}{z \times F} = \frac{I \times t}{z \times F} \quad (2.40)$$

Ideal gas law

$$PV = nRT \quad (2.41)$$

Where P is the pressure (1 atm or 101.325 kPa), V is the volume (litres), n is the number of moles per reaction, R is 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.kP.mol⁻¹.K⁻¹), and T is the temperature in Kelvin. By substituting equation (2.40) into (2.41), the theoretical volumetric flow rate $Q_{H_2,theory}$ of hydrogen measured in cubic meters per second can be derived as illustrated by equation (2.42) [50].

$$Q_{H_2,theory} = \frac{V}{t} = \frac{I \times R \times T}{2 \times F \times P} \quad (2.42)$$

Thus, using the theoretical flow rate calculated by equation (2.42), the Faradaic efficiency can be calculated by measuring the actual flow rate of hydrogen $Q_{H_2,actual}$ versus the calculated theoretical flow rate of hydrogen shown by equation (2.43) [50].

$$\varepsilon_I = \frac{Q_{H_2,actual}}{Q_{H_2,theory}} \quad (2.43)$$

Furthermore, the Faradaic efficiency phenomenon indicates the electrons that flow in the external circuit to the electrodes of the PEM water electrolyser to be used in the electrochemical reaction [75]. A summary of all the efficiency definitions can be seen in Table 2.3 below.

Table 2.3: Efficiency definitions comparison based on theory discussed (Combined from [50, 58, 72, 74, 75]).

	Cell efficiency (ϵ_{cell}^{HHV})	Voltage efficiency (ϵ_V^{HHV})	Faradaic efficiency (ϵ_I)
Equation	$\epsilon_{cell}^{HHV} = \frac{(\Delta H_R^0)(\dot{n}_{H_2})}{(U_{cell})(I_{cell})}$	$\epsilon_V^{HHV} = \frac{E_{th}^0}{U_{cell}}$	$\epsilon_I = \frac{Q_{H_2,actual}}{Q_{H_2,theory}}$
Measurand (cell)	Input energy losses	Voltage losses	Current losses
Losses accounted for	Overpotentials, stray current, crossover gases and gas leakages.	Activation, ohmic and concentration overpotentials.	Stray current, crossover gases and gas leakages.
Assumptions	No external heat sources, only generated hydrogen is considered useful output, only form of electrical supply is an external energy source.	No voltage losses.	All the applied current is converted to a chemical reaction.

2.4.4 Influencing factors

The efficiency of PEM electrolysis is determined by various factors that must be thoroughly studied and understood to maximise its potential. This section aims to explore the key influencing factors that affect the efficiency of PEM electrolysis, highlighting their significance and potential avenues for improvement.

Overpotential is a critical factor influencing the efficiency of PEM electrolysis. It represents the excess energy required to achieve the desired electrochemical reaction compared to the thermodynamic potential. Lowering the voltage overpotential can significantly enhance the efficiency of the electrolysis process. This can be achieved by improving catalyst activity, optimising the electrode structure, and reducing the resistive losses within the electrolyser. The catalyst used within a PEM electrolyser strongly influences its efficiency. Many catalyst materials, such as platinum and other transition metals, have demonstrated excellent activity for hydrogen and oxygen evolution reactions. However, the high cost and limited availability of some catalysts can hinder their widespread use. Exploring alternative catalyst materials with comparable efficiency and lower costs is vital for improving PEM electrolysis efficiency.

A study conducted by Mo *et al.* (2020) [76] focussing on experimental studies conducted on “the effects of sheet resistance and wettability of catalyst layer on electro-catalytic activities for oxygen evolution reaction in proton exchange membrane electrolysis cells”, showed that both sheet resistance and wettability of catalyst layers have significant impacts on the oxygen evolution reaction (OER) which can lead to improved operating parameters and operating performance. Furthermore, the design and configuration of the electrodes in a PEM electrolyser significantly impact its efficiency. Factors such as surface area, porosity, and morphology of the electrode materials influence the reaction kinetics and distribution of reactants within the electrolyte. Optimising electrode design and selecting suitable materials can enhance reactant transport, minimise mass transfer limitations, and improve overall efficiency.

Temperature and pressure conditions strongly affect the efficiency of PEM electrolysis. A recent study conducted on the “initial approaches in benchmarking and round robin testing for proton exchange membrane water electrolyzers” conducted by Bender *et al.* (2019) [77] showed that the cell voltage significantly reduces the performance of the PEM water electrolyser cell by 3-4 mV for every single °C reduction. Most of these losses were due to slight temperature offsets and differential temperature changes, accounting for up to a third of the observed losses within the cell. However, the study also showed that the performance deviation of the PEM water electrolyser cell increased with an increase in current density, which was much higher at lower temperatures in comparison to that at higher temperatures. Furthermore, operating at elevated temperatures can enhance the reaction kinetics, reduce ohmic losses, improve mass transfer, decrease stability and increase degradation.

Another study, focussing on “the thermal and electrochemical performance assessment of a high temperature PEM electrolyser” conducted by Toghyani *et al.* (2018) [51], analysed the performance of a PEM water electrolyser cell between 373-403 Kelvin (including other parameter changes such as pressure, GDL thickness, resistance against reactant gas diffusion, etc.). The model showed that at higher temperatures, the reaction rates of the products formed (hydrogen and oxygen) increased due to faster kinetics within the electrochemical reaction leading to an increase in PEM water electrolyser cell performance. Furthermore, as the temperature increased, so did the current density of the cell, causing the maximum concentration of hydrogen at the membrane-catalyst interface to also increase from $1.9 \times 10^{-4} \text{ mol/m}^3$ up to $2.2 \times 10^{-4} \text{ mol/m}^3$.

Furthermore, Azam *et al.* (2023) [78] focussed on “the parametric study and electrocatalyst of PEM electrolysis performance”, which showed that the optimal operating conditions of the PEM water electrolyser cell can be achieved at a cell temperature of 70 °C and water flow rate of 2 mL/min. This is due to factors such as operating temperature control that led to improved cell

kinetics of the charge transfer reaction as well as an increase in membrane conductivity. Additionally, according to Toghyani *et al.* (2018) [51], the increase in operating pressure (which was varied from 5-20 bar) resulted in an increase in open circuit voltage as well as an increase in partial pressure of various species within the cell. The increase in operating pressure also reduced the charge transfer rate of the PEM water electrolyser cell, causing an aggravated cell performance. However, higher pressures led to an increase in the solubility of reactant gases, leading to improved performance. Furthermore, precise control of temperature and pressure is necessary to avoid detrimental effects on membrane stability and system durability.

Another study, focussing on “balanced high pressure PEM electrolysis in batch process up to 110 bar: Test bench development and electrochemical analysis” conducted by Müller-Dollinger *et al.* (2023) [79], showed that for overvoltage below 0.05V a pressure dependent trend could be detected. The observation showed that for current densities higher than 3 A.cm⁻² the overvoltage decreases as a function of pressure. This observation was strengthened by Suermann *et al.* (2017) [80] who focussed on “the high-pressure polymer electrolyte water electrolysis test bench development and electrochemical analysis”. Suermann *et al.* (2017) studied the difference between differential and balanced pressure and observed that with differential pressure operation an increase in cell voltage is noted. As for balanced pressure operation, only a minor cell voltage increase at specific current densities was noted.

Suermann *et al.* (2017) concluded that these pressure operations compensate for the thermodynamic increase in cell voltage. The properties of the electrolyte, such as ionic conductivity, water management capabilities, and chemical compatibility, significantly impact the efficiency of PEM electrolysis. High ionic conductivity promotes faster proton transport, reducing ohmic losses. Effective water management is crucial to maintaining optimal membrane hydration levels and preventing drying or flooding, which can hinder performance. Developing advanced electrolytes with improved properties is essential for enhancing efficiency. The choice of a suitable proton exchange membrane is pivotal in optimising PEM electrolysis efficiency. The membrane should possess adequate proton conductivity, excellent chemical and thermal stability, and low electronic conductivity.

Furthermore, the membrane should enable efficient water management and high gas diffusion rates. Ongoing research in membrane materials and design is focused on addressing these requirements to improve the overall efficiency of PEM electrolysis. An example of a study conducted by Han *et al.* (2015) [81] focussing on “electrochemical performance modelling of a proton exchange membrane electrolyser cell for hydrogen energy” showed that a decrease in electrode thickness as well as membrane thickness leads to an increase in PEM water

electrolyser cell performance. This is due to a reduction in diffusion overpotential as well as ohmic losses.

2.5 Electrochemical characterisation techniques

From chapter 1, it is clear that electrochemical characterisation techniques play an essential role in developing and testing the PEM water electrolyser cell. The PEM water electrolyser cell components can be individually characterised based on manufacturer specifications. However, when each component is integrated to form the complete cell, it is not that simple anymore. Specific characterisation techniques are therefore required to characterise the cell. For this project, a technique is thus required to characterise a PEM water electrolyser cell based on certain specified parameters, delivering electrochemical results that are in close correlation to those of an existing characterisation technique, such as EIS (as discussed in section 1.1 and section 1.2.1). Thus, it is imperative to understand the operation of these characterisation techniques to successfully design a model that can deliver accurate characterisation results without big laboratory setups. Characterisation techniques of concern for this project are the PC, EIS and CI methods which will be discussed within sections 2.5.1, 2.5.2, and 2.5.3.

2.5.1 Polarisation curve characterisation technique (PC)

The polarisation curve technique is a known electrochemical method designed to test the performance of an electrochemical cell by visually illustrating the relationship between the cell voltage and cell current density of the PEM water electrolyser cell [82]. The method gives information regarding the performance losses of the specific electrochemical cell or stack during operation [83] [25] [84]. However, there are two types of polarisation curves: steady-state and non-steady-state. Steady-state polarisation curves refer to monitoring cell potential as the current density changes during constant pressure, temperature, membrane thickness, etc. Non-steady state polarisation curves refer to monitoring the cell voltage by performing a rapid current sweep (suitable current sweep of 0-2 A/cm² [85]).

The PC method makes it possible to analyse the effect of the flow rate on the polarization behaviour, effects of component composition, temperature, and relative humidity of the reactant gases systematically. The polarisation curve under ideal circumstances for a single electrolyser cell has three different regions, as shown in Figure 2.7. These regions include the activation, ohmic, and concentration polarisation. Under ideal circumstances the activation polarisation occurs at the lower current densities due to slow reaction kinetics occurring at the oxygen reduction reaction. The Butler-Volmer equation governs this region, describing the relationship between current density and overpotential due to charge transfer resistance at the electrodes. The charge transfer resistance, representing the resistance against the flow of electrons at the

electrodes of the electrolyser cell, is relatively large in this region compared to the small ohmic resistance which causes the voltage-current relationship to have a logarithmic form [82].

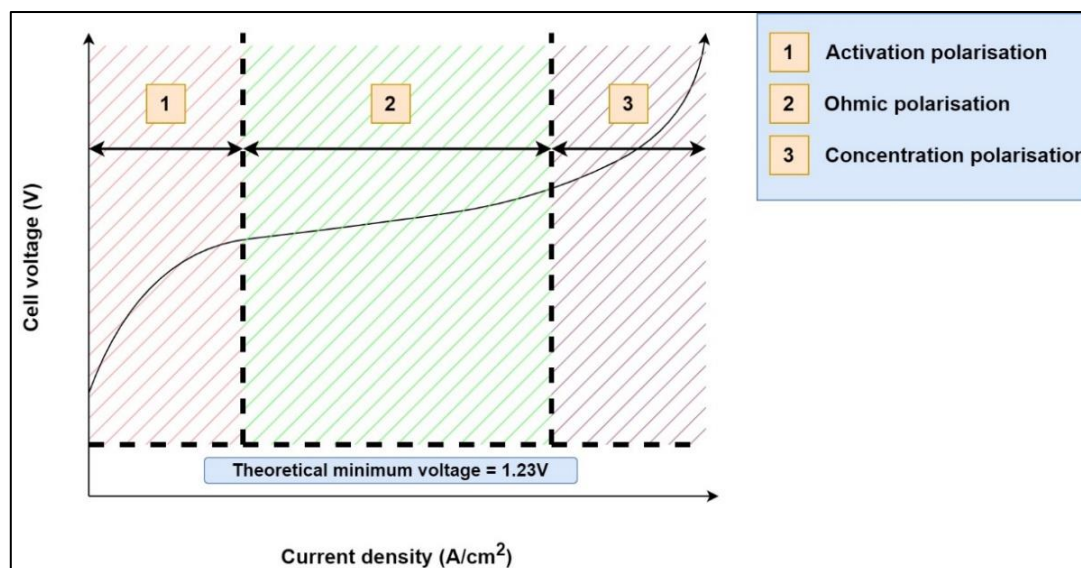


Figure 2.7: Electrolyser cell polarisation curve under ideal conditions (adapted from [58, 83]).

Furthermore, the ohmic polarisation, which forms due to the resistance against the flow of ions within a cell, occurs at the intermediate current densities under ideal circumstances. The ohmic resistance is thus the largest in this region. The charge transfer resistance is non-existent due to sufficient energy supplied to the anode and cathode surfaces to start electron flow. The voltage and current relationship are linear within this area [82] [58]. Lastly, the concentration polarisation region is in the high current density area. The losses occurring within this region are due to mass transport effects within the electrolyser cell [58, 82].

The polarisation curve can be drawn up under different circumstances by obtaining the relationship between the voltage and current based on variations in either temperature, pressure, GDL thickness or membrane thickness [51]. A clear understanding of the overall cell performance can be obtained by investigating the polarisation curve relationship under various operating conditions.

2.5.2 Electrochemical Impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy is a well-known method that offers kinetic and mechanistic data on various electrochemical systems [86]. Research has shown that EIS has been particularly used in system applications that contain fuel cells, batteries, and electrolyzers [25]. This characterisation technique is preferred by many authors due to its ability to distinguish between electrical, electrochemical, and physical processes occurring within the electrochemical cell, as well as providing sufficient information on each of these processes [86].

Furthermore, EIS is used to characterise an electrochemical cell by calculating the total impedance of the cell as a function of frequency (EIS can also determine the losses associated with specific components within the electrochemical cell). The EIS technique is based on the application of an AC signal, usually superimposed on the standard operating DC signal, to an electrochemical cell (when the system is in equilibrium or steady state [86]) over a wide range of frequencies from which the sinusoidal response is monitored. If the input AC perturbational signal is a voltage signal, the corresponding current signal is measured as the output and vice versa.

By converting the electrochemical cell in terms of its electrical circuit parameters, the basic EEC model, representing the electrochemical cell, can be generated from the impedance response of the system driven at different frequencies. Thus, if the EIS technique is applied using the potentiostatic mode, the AC stimulus to the electrochemical cell is a potential signal [87]. This means the response signal measured will be an AC signal oscillating at the same frequency as the input signal, with a change in amplitude and phase, assuming that the electrochemical system operates under dynamic linearity around a fixed operating point [86, 88]. Thus, the time domain applied AC voltage signal can be represented by equation (2.44) and the AC response current signal can be represented by equation (2.45), where V_{Max} is the amplitude of the AC voltage signal, I_{Max} is the amplitude of the current signal, ω is the angular frequency illustrated by equation (2.46), and ϕ is the phase shift of the AC current response with respect to the AC voltage input signal [89, 90].

$$\text{Voltage time domain signal} \quad v(t) = V_{Max} \sin(\omega t) \quad (2.44)$$

$$\text{Current time domain signal} \quad i(t) = I_{Max} \sin(\omega t + \phi) \quad (2.45)$$

$$\text{Angular frequency} \quad \omega = 2\pi f \quad (2.46)$$

Now, using the voltage and current time domain functions, the impedance of the electrochemical cell can be calculated. However, the impedance of the cell is a function of frequency $Z(j\omega)$ and can be determined using Ohm's law as illustrated by equation (2.47) [89, 90]. To successfully calculate the impedance in the frequency domain, the Fourier transform can transform the time domain voltage and current AC signals to the frequency domain. The impedance can then be further expressed in terms of its real and imaginary components as can be seen by equations (2.48), (2.49) and (2.50) [89, 90].

$$Z(\omega) = \frac{\mathcal{F}\{v(t)\}}{\mathcal{F}\{i(t)\}} \quad (2.47)$$

$$\text{Complex Impedance} \quad Z(\omega) = |Z|(\cos \phi + j \sin \phi) \quad (2.48)$$

Real part

$$\operatorname{Re}(Z) = |Z| \cos \phi \quad (2.49)$$

Imaginary part

$$\operatorname{Im}(Z) = |Z| \sin \phi \quad (2.50)$$

To successfully obtain the impedance of the electrochemical cell, the impedance calculated from the responding frequency domain voltage and current stimulus functions must be iterated over a range of frequencies. According to Lazanas *et al* [86], the typical frequency range for most electrochemical analysers ranges from as low as 1 mHz (usually 10-100 mHz) up to 1 MHz (usually up to 100 kHz). Thus, by calculating the real and imaginary impedances for each frequency within the specified range, a Nyquist plot can be drawn to represent the stability of the closed loop electrochemical system graphically. A Nyquist plot is a graph used in electrochemical impedance spectroscopy that plots the negative imaginary impedance against the real impedance across a range of frequencies to analyse resistive, capacitive, and diffusive behaviours in systems like PEM electrolyzers [86, 90]. Assuming that the system is linear time invariant (shown within Figure 2.8), the whole system can be modelled in terms of a transfer function, which will be further discussed later in Chapter 4.

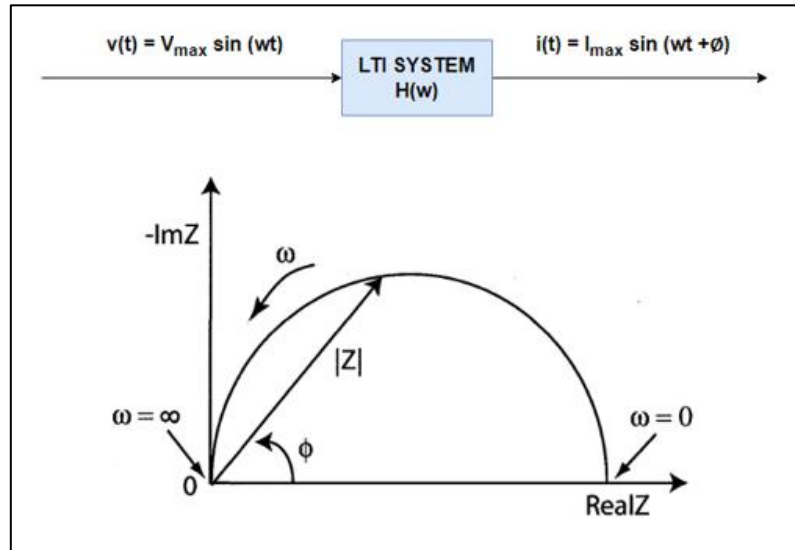


Figure 2.8: Typical Nyquist plot of an LTI electrochemical system (adapted from [86, 90]).

Furthermore, according to Van der Merwe *et al.* [83], the Nyquist plot can be used to identify three different loss regions within a PEM water electrolyser cell. It was proved that each loss region represents different processes within the electrolyser cell.

2.5.3 Current Interrupt (CI)

Although EIS is most commonly used to characterise a PEM water electrolyser cell, its equipment is still quite expensive and bulky. However, another method was developed that utilises much smaller and less costly equipment that can be easily used outside a laboratory environment. This method is known as the CI method, which is mainly used to estimate the ohmic losses within the PEM water electrolyser cell. However, implementing this method in practical systems is not quite

intuitive as little literature is found on this topic. According to Martinson *et al.* (2012) [19], the current interrupt method could be used to analyse the equivalent electrical circuit model of a PEM water electrolyser cell using two methods.

The first method, using the Randles EEC model (which will be discussed in section 0), is called the natural voltage response (NVR) method. It gives information on the circuit behaviour during internal energy dissipation (the initial voltage on the capacitor that is allowed to dissipate) [91].

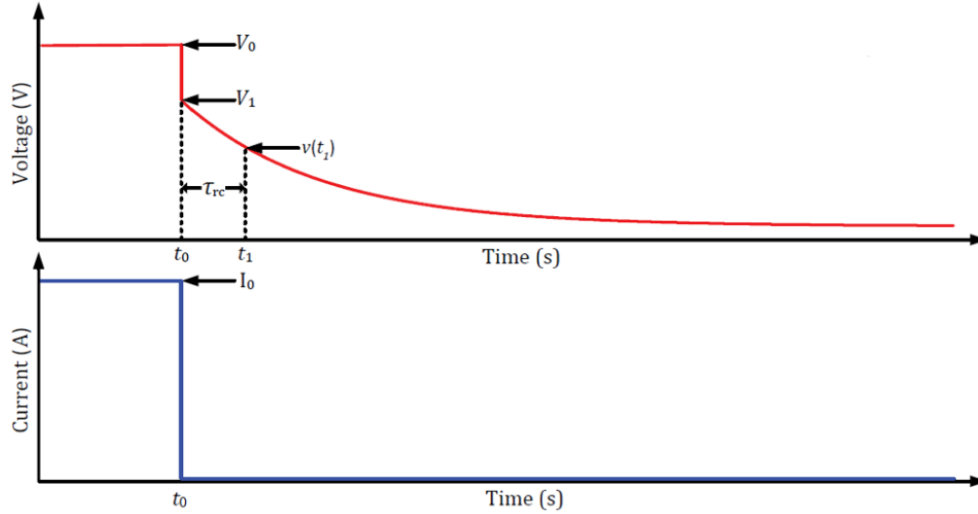


Figure 2.9: Natural voltage response for a PEM water electrolyser cell (adapted from [19]).

During this method, the PEM electrolyser was operated at a specific voltage until steady-state current was reached. Thereafter, the current was interrupted at time t_0 , where the natural voltage response was observed as shown within Figure 2.9. At time t_0 , the current is interrupted, and it is evident from Figure 2.9 that there is an instantaneous voltage drop from V_0 to V_1 due to the internal ohmic resistance of the PEM water electrolyser cell. Furthermore, the discharge of the double-layer capacitor is evident from V_1 up to the end of the voltage versus time plot. Using the results from the plot above, the different equivalent circuit parameters were calculated using the equations below [19, 92].

Membrane resistance

$$R_m = \frac{V_0 - V_1}{I_0} \quad (2.51)$$

Charge transfer resistance

$$R_{ct} = \frac{V_2 - V_1}{I_0} \quad (2.52)$$

Voltage as a function of time

$$v(t) = V_1 \left(e^{\frac{-t_1}{\tau}} \right) \quad (2.53)$$

Double layer capacitance

$$C_{dl} = \frac{\tau}{R_{ct}} \quad (2.54)$$

Using the Randles EEC model, an indication of the ohmic losses R_Ω , as well as reaction kinetics R_{ct} of the PEM water electrolyser is shown. However, when using the Randles cell, it is impossible

to obtain accurate measurements for the double layer capacitance C_{dl} due to V_2 that can adapt any value during R_{ct} . Thus, Martinson *et al.* [19] used a second method known as the current switching (CS) technique to calculate R_{ct} as well as C_{dl} using the Randles Warburg EEC model shown within Figure 1.2. This method utilises system identification by applying a pseudo-random binary sequence (PRBS) to the cell to administer CI. In this model, the Warburg impedance Z_{wbg} , representing the concentration losses of the cell, was calculated using a transfer function derived from the LTI closed-loop system. Firstly, within the transfer function, the membrane resistance R_m was calculated using NVR. Thereafter, three PRBS signals were applied to the cell, where system identification was used to calculate the rest of the parameters. With this, the Warburg impedance was calculated as all the unknowns within the transfer function have been determined [19, 92].

2.5.4 EEC models

For the equivalent model, it is crucial to understand how each component functions and contributes to the final output of the simulation model. Furthermore, it is important to gain a good understanding of the designed EEC models responsible for calculating the electrochemical data of the cell. Thus, different EEC models will be investigated in this section before implementation in the Simulink® environment.

2.5.4.1 Circuit elements

The equivalent electrical circuit elements discussed in this section include resistors, capacitors, inductors, and specialised electrochemical elements such as constant-phase elements (CPE) and Warburg impedance. Understanding the function and contribution (towards the overall current interrupt model performance) of each element is imperative to ensure that the best result is obtained. The elements in conjunction with their Nyquist plot and respective impedance equations can be seen in Table 2.4 [93, 94, 95, 96]. Further discussion based on the function and relevance of each electrical component on the research project outcome is shown in Table 2.4.

Resistor

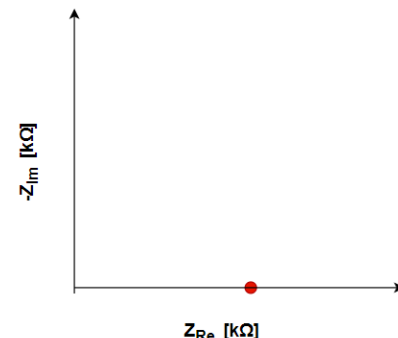
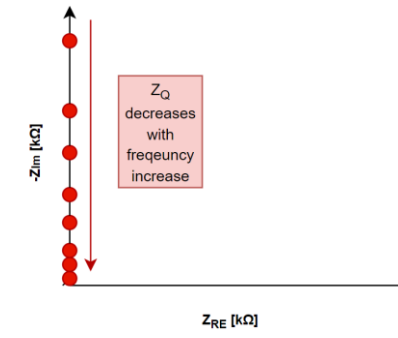
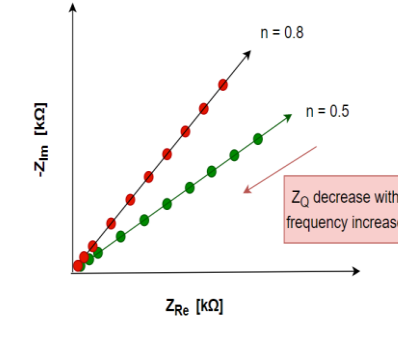
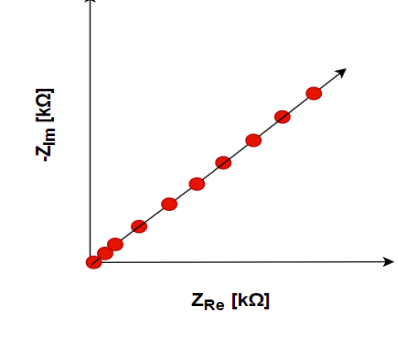
The electrical resistance of an equivalent electrical circuit is described in the time domain by Ohm's law. Since resistance only has a real-part (indicated by the Nyquist plot shown in Table 2.4), it does not depend on the frequency component of the supplied voltage and current as stated by equation (2.55) [58].

$$Z_R(\omega) = R = \frac{V(t)}{I(t)} \quad (2.55)$$

Thus, due to the absence of an imaginary part, the current passing through the resistor is directly in phase with the voltage across the resistor. Furthermore, two types of resistances can be used to represent the impedance response of the PEM water electrolyser cell using an equivalent electrical circuit: the membrane resistance and the charge transfer resistance. Membrane

resistance, R_m , refers to the resistance of the PEM water electrolyser cell due to the membrane [81].

Table 2.4: Equivalent electrical circuit parameters description ([58, 95, 97]).

Element Name	Element symbol	Impedance equation	Nyquist plot
Resistor	R	$Z_R = \frac{V(t)}{I(t)} = R$	 A Nyquist plot for a resistor. The vertical axis is labeled $-Z_{Im} \text{ [k}\Omega\text{]}$ and the horizontal axis is labeled $Z_{Re} \text{ [k}\Omega\text{]}$. A single red dot is plotted on the positive real axis, representing the resistance R.
Capacitor	C	$Z_C = \frac{V(t)}{I(t)} = \frac{1}{j\omega C}$	 A Nyquist plot for a capacitor. The vertical axis is labeled $-Z_{Im} \text{ [k}\Omega\text{]}$ and the horizontal axis is labeled $Z_{Re} \text{ [k}\Omega\text{]}$. A vertical line of red dots is plotted on the negative imaginary axis, starting from the origin and extending downwards. A red arrow points downwards along this line. A text box contains the text: Z_Q decreases with frequency increase.
CPE	Q	$Z_Q = q^{-1}(j\omega)^{-n}$	 A Nyquist plot for a CPE. The vertical axis is labeled $-Z_{Im} \text{ [k}\Omega\text{]}$ and the horizontal axis is labeled $Z_{Re} \text{ [k}\Omega\text{]}$. Two linear segments of red dots are plotted, both starting from the origin. The steeper segment is labeled $n = 0.8$ and the shallower segment is labeled $n = 0.5$. A red arrow points from the shallower segment towards the steeper one. A text box contains the text: Z_Q decrease with frequency increase.
Warburg impedance	W	$Z_{wbg} = \left(\sigma\omega^{-\frac{1}{2}}\right) - j\left(\sigma\omega^{-\frac{1}{2}}\right)$	 A Nyquist plot for Warburg impedance. The vertical axis is labeled $-Z_{Im} \text{ [k}\Omega\text{]}$ and the horizontal axis is labeled $Z_{Re} \text{ [k}\Omega\text{]}$. A series of red dots are plotted along a straight line that starts from the origin and extends at a 45-degree angle into the fourth quadrant.

The ohmic resistance consists of the internal resistance between the PEM water electrolyser cell components, the membrane and the catalyst layer resistance [97]. The membrane resistance is directly proportional to the electrolyte resistance ρ and the electrolyte thickness d [97]. The charge transfer resistance, R_{ct} , is the resistance measured against the flow of electrons to and from the electrode surfaces [95]. The magnitude of the resistance is mainly dependent on the electrode surface, electrode potential and the electrochemical reaction [95]. The charge transfer resistance, representing the activation losses and the cell's charge transfer kinetics, is inversely proportional to the PEM water electrolyser cell's overpotential [95].

Capacitor

A capacitor consists of a non-conductive medium placed between two electrodes where electrical energy is stored. The capacitor in an equivalent electrical circuit contains only an imaginary part and is a negative impedance and is clearly illustrated by the Nyquist plot shown in Table 2.4, stating that as the frequency of the voltage input energy source increases, the capacitive impedance decreases. This causes the current response of the capacitor to be 90° out of phase with the applied voltage waveform. The capacitive impedance can be calculated using equation (2.56) [95].

$$Z_C = \frac{V(t)}{I(t)} = \frac{1}{j\omega C} \quad (2.56)$$

The main capacitive characteristic present within the PEM water electrolyser equivalent electrical circuit is known as the double layer capacitance [95]. The double-layer capacitance obtains its name from the double electrical layer that forms at the interface between the electrodes and the electrolyte [97]. This double layer, separating the charged ions from the charged electrodes, can be represented as a capacitance C_{dl} in an EEC [58].

Constant Phase element

Constant phase elements (CPEs) are electrical circuit components used to model a wide range of behaviours that do not fit perfectly into traditional linear components such as resistors, capacitors, or inductors. CPEs are often employed in electrochemical impedance spectroscopy (EIS) to describe non-ideal behaviour in various systems. CPEs are characterised by their impedance, which is expressed using equation (2.57) [58]:

$$Z_Q = q^{-1}(j\omega)^{-n} \quad (2.57)$$

where Z is the impedance, q is the proportional factor of the magnitude, j is the imaginary unit, ω is the angular frequency, and n is the exponent that determines the phase shift behaviour. The CPE impedance equation is similar to that of a capacitor, where the impedance is inversely proportional to the angular frequency $(j\omega)^{-n}$. However, the key difference is the presence of the CPE proportional factor, q , which allows for a more flexible description of non-ideal behaviour. By adjusting the CPE proportional factor, q , and the exponent, n , the impedance response of a

system can be accurately represented and analysed, as seen in Table 2.5, which allows for a better understanding of the underlying mechanisms and processes in complex systems.

Table 2.5: Constant phase elements impedance representation (combined from [58] [95]).

CPE impedance	N	q
Resistor	0	R^{-1}
Inductor	-1	L^{-1}
Capacitor	1	C
Warburg Impedance	0.5	σ^{-1}

Warburg Impedance

Warburg impedance, also known as the Warburg element or Warburg diffusion impedance, is a type of impedance that arises from diffusion processes occurring in electrochemical systems. It is commonly observed in electrochemical impedance spectroscopy (EIS) measurements. The Warburg impedance describes the diffusion-limited behaviour of species, such as ions or molecules, in a system. It is particularly relevant in systems where mass transport is a limiting factor, such as electrochemical cells or systems involving porous electrodes. The Warburg impedance is represented using equation (2.58) [58]:

$$Z_{wbg} = \left(\sigma \omega^{-\frac{1}{2}} \right) - j \left(\sigma \omega^{-\frac{1}{2}} \right) \quad (2.58)$$

where Z is the impedance, $\sigma \omega^{-\frac{1}{2}}$ is a resistor connected in series with a capacitor $\sigma \omega^{-\frac{1}{2}}$, and $(-1/2)$ represents the square root of the frequency term. The Warburg impedance equation shows that the impedance decreases with increasing frequency, and its magnitude is inversely proportional to the square root of the angular frequency. The Warburg impedance arises from the diffusion of species through a porous electrode or an electrolyte. When an electrochemical reaction occurs at an electrode, the reactants or products involved often need to diffuse through the electrode or the electrolyte to reach the reaction site [58, 95, 97]. This diffusion process can be rate-limiting and can significantly affect the overall impedance of the system. In EIS measurements, the Warburg impedance appears as a -45° diagonal line drawn on the generated Nyquist plot. This slope corresponds to the $(-1/2)$ exponent in the impedance equation. The Warburg impedance is typically observed at low frequencies, where diffusion processes dominate.

2.5.4.2 Circuit equivalents

An electrical equivalent circuit is a simplified representation of a complex electrical system or device using a combination of ideal circuit elements. It is a tool used to model and analyse the

behaviour of electrical systems, allowing engineers and researchers to understand and predict how the system will respond to different inputs or conditions. In an equivalent electrical circuit, the actual components and their interactions in the real system are replaced by ideal circuit elements such as resistors, capacitors, inductors, and voltage or current sources. These ideal elements represent the electrical properties and behaviours of the actual components in a simplified manner.

The selection and arrangement of the ideal circuit elements in an equivalent circuit are based on the characteristics, understanding of the system, and the desired level of accuracy. The goal is to capture key electrical behaviours and interactions while ignoring or simplifying other aspects that are not relevant to the analysis. The choice of circuit elements in an equivalent circuit depends on the specific system or device being modelled. For example, in a simple electronic circuit, resistors, capacitors, and inductors may represent the behaviour of resistive, energy storage, and magnetic elements, respectively. Active components, such as transistors or operational amplifiers, may also be included to model amplification or signal processing functions. The equivalent circuit can be used to analyse various aspects of the system, such as voltage and current distribution, power consumption, frequency response, and transient behaviour. It allows engineers to evaluate the system's performance, efficiency, stability, and other characteristics under different operating conditions or circuit configurations. Equivalent circuits are widely used in various fields of electrical engineering, including electronics, power systems, telecommunications, and control systems. They provide a simplified but effective means to understand and design complex electrical systems, enabling engineers to make informed decisions and optimise system performance.

Thus, two electrical equivalent circuit models, representing a PEM water electrolyser system, was investigated. These models serve as another verification and validation method, which can be used to validate the electrical characteristics of the PEM water electrolyser Simulink® model. However, it is important to note that the electrical equivalent circuit approximates the actual PEMWE system, and its accuracy depends on the level of simplification and the assumptions made. Therefore, it is also essential to validate the equivalent circuit through experimental measurements or simulation to ensure its reliability in representing the behaviour of the PEMWE system.

Randles Cell

The equivalent circuit of the Randles cell, also known as the Randles circuit or Randles model, is a commonly used equivalent circuit to describe the impedance behaviour of an electrochemical cell or system. This model represents a polarisable electrode of an electrochemical cell operating

under the conditions that a single-step electrochemical reaction can occur on the electrode surface and that no diffusion limitation exists [95]. The Randles cell consists of three main elements: a series resistance (known as the electrode resistance, or in the case of the PEMWE, the membrane resistance R_m), the faradaic impedance, which can be simplified to the charge transfer resistance R_{ct} , in parallel with a capacitor known as the double-layer capacitance C_{dl} . The EEC is similar to that of the Randles Warburg EEC shown in Figure 1.2, just without the Warburg impedance. The membrane resistance is illustrated by the x-axis intercept when the frequency tends to infinity, whilst the sum between the charge transfer resistance and the membrane resistance is represented by the second x-axis intercept when the frequency tends to zero. This plot is generated by calculating the electrochemical cell impedance at different frequencies represented by equations (2.59) [95] and (2.60) [95]. The values used within the equation can be calculated by using the current interrupt method as discussed in section 2.5.3.

$$Z(\omega) = R_m + \frac{1}{R_{ct}^{-1} + j\omega C_{dl}} \quad (2.59)$$

$$Z(\omega) = R_m + \frac{R_{ct}}{1 + \omega^2 \tau^2} + j \frac{\omega R_{ct} \tau}{1 + \omega^2 \tau^2} \quad (2.60)$$

Where τ is the time constant calculated through equation (2.54). In this circuit, R_m represents the resistance associated with the membrane, electrolyte, or solution. It is the resistance the current encounters as it passes through the electrolyte, also known as the ohmic losses. The charge transfer resistance, R_{ct} , represents the resistance to charge transfer at the electrode-electrolyte interface. It arises from various processes, such as the kinetics of the electrochemical reactions occurring at the electrode, also known as the activation losses. The double layer capacitance, C_{dl} , represents the capacitance associated with the double-layer formation at the electrode-electrolyte interface [95, 98, 99].

Randles Warburg cell

The Randles cell equivalent circuit with a Warburg impedance, represented by Figure 1.2, is an extension of the basic Randles cell model, which includes an additional element to account for diffusion-limited behaviour in electrochemical systems. It arises due to the diffusion of species, such as ions or molecules, through the electrode or the electrolyte. The Warburg impedance is typically represented by a linear impedance element with a slope of -45 degrees on a Nyquist plot at low frequencies. It accounts for the impedance behaviour resulting from diffusion processes. This model is commonly used in electrochemical impedance spectroscopy (EIS) to describe the impedance response of various electrochemical cells or systems. It is also used to model ohmic, activation, and concentration losses. The Randles Warburg cell consists of four main elements: a series resistance (known as the electrode resistance, or in the case of the PEMWE, the membrane resistance R_m), the faradaic impedance which can be simplified to the charge transfer resistance R_{ct} , and the Warburg impedance Z_{wbg} , in parallel with a capacitor known as the

double-layer capacitance C_{dl} . The Randles Warburg impedance can be represented by equation (2.61) [22].

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

The Warburg impedance can be calculated for a finite length diffusion layer using Butler-Volmer and Fick's second law of diffusion which is represented by equation (2.62) [22].

$$Z_{wbg} = R_d \frac{\tanh \sqrt{\tau_d j\omega}}{\sqrt{\tau_d j\omega}} \quad (2.62)$$

Where R_d represents the diffusion-related resistance homogenous to electrical resistance in ohms, and τ_d represents the diffusion-related time constant homogenous to time in seconds. By including the Warburg impedance in the Randles cell equivalent circuit, the model can capture mass transport limitations that play significant roles, especially in systems such as batteries, fuel cells, or systems involving porous electrodes. One way to model the Warburg impedance is based on system identification techniques introduced by Martinson *et al.* [19]. The input voltage and current signals were used to generate a transfer function from which the equivalent circuit parameters were calculated.

Randles Warburg cell with CPE

Although the Randles Warburg cell can effectively represent the PEMWE cell in simulation, a constant phase element is often used instead of a simple capacitor to account for non-ideal behaviour, such as electrode surface roughness, inhomogeneity or distribution of activation or relaxation processes. The CPE is characterised by a constant phase angle α instead of a fixed capacitance value, as seen from equation (2.57) and Table 2.5. The impedance of the Randles Warburg equivalent electrical circuit containing a CPE is illustrated by equation (2.63) [100].

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

Where Z_Q represents the CPE impedance, as discussed in section 0 [100]. However, a drawback of using a CPE instead of a double-layer capacitor, is that the term q shown within equation (2.57) no longer has the dimension of a capacitance. Thus, in determining the absolute impedance values of the Randles Warburg equivalent electrical circuit, it is important to look at the proportional factor of the CPE impedance magnitude.

2.6 System identification

The input signal supplied to the PEMWE cell is crucial since it is one of the factors that determines the quality of results used for validation. Thus, this section will discuss different perturbation signals, some signal transformation characteristics, and fundamentals required to generate and analyse the signals effectively.

2.6.1 Perturbation signals

Perturbation signals are essential in many experimental techniques and measurements in various fields. These signals intentionally introduce disturbances or variations in a system to study its response and extract valuable information. Perturbation signals help identify the characteristics and parameters of a system. By observing the system's response to a perturbation, researchers can analyse and model the underlying behaviour, such as its dynamics, transfer function, or impedance. Furthermore, perturbation signals are also used to perform frequency response analysis. By applying perturbations at different frequencies and measuring the corresponding response of the system, researchers can construct a frequency response plot or transfer function. This analysis provides valuable insights into the system's behaviour across a range of frequencies, including resonance frequencies, damping characteristics, and frequency-dependent properties. The type of perturbation signal of interest to this study, namely the PRBS signal, was investigated.

2.6.1.1 PRBS

Pseudo-random binary sequence (PRBS) signals are deterministic digital signals that appear random but are generated using specific algorithms [101]. These signals are commonly used in various applications, such as communication systems, testing and measurement, and cryptography. A binary sequence consists of 1s and 0s, representing the two possible states in a digital system. In a PRBS signal, the sequence of 1s and 0s is generated in a way that appears random, exhibiting statistical properties similar to those of a truly random sequence. PRBS signals are typically generated using linear feedback shift registers (LFSRs) or other algorithms that produce a sequence with a long period and good statistical properties. LFSRs are shift registers with feedback connections that allow the sequence to repeat after a certain number of steps, known as the period [102]. By carefully selecting the feedback taps and initial conditions, different PRBS sequences with varying periods can be generated. Thus, by identifying the type of pseudo-random binary sequences (PRBS) that must be generated depending on the specific algorithms and configurations used, specific functions can be performed, such as assessing the performance of data transmission channels in communication systems. By transmitting a PRBS signal through a channel and comparing the received signal with the original, it is possible to analyse the channel's quality, measure parameters like bit error rate (BER), and identify any distortions or impairments in the transmission. Different examples of PRBS signal classes include maximum length sequence (MLS), Gold codes, Barker codes, Kasami codes, and complementary sequences. Since it is advantageous and intuitive to use linear feedback shift registers (illustrated in Figure 2.10) due to their quick response times that generate long pseudo-random sequences with low power consumption, the MLS sequence was of concern for this project.

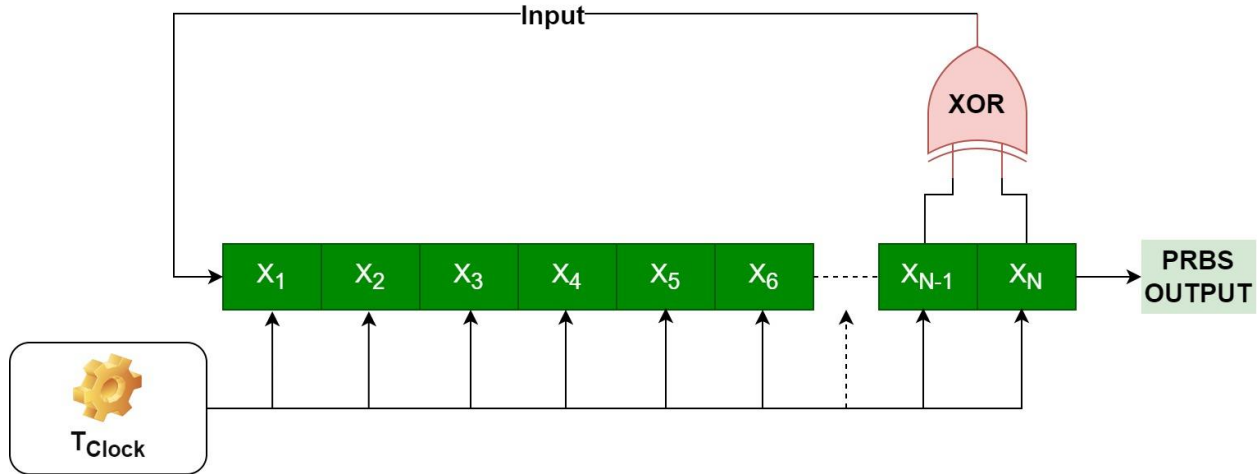


Figure 2.10: n-Stage linear feedback shift register (adapted from [19] [103] [104]).

Maximum Length PRBS, known as m-sequences, are generated using linear feedback shift registers (LFSRs) with specific feedback tap configurations. These sequences have a maximum length (L_m) shown in equation (2.64) [101, 105]

$$L_m = 2^n - 1 \quad (2.64)$$

where “ n ” is the number of stages or flip-flops in the LFSR. The generation of a PRBS signal using the MLS class starts with the initialisation of the LFSR with a seed value, which is a non-zero binary value. The seed should not be all zeros, as it will result in a constant output of zeros. The initial state of the LFSR is critical since it determines the specific m-sequence generated. Furthermore, the LFSR operates by shifting the bits in the register to the right. The rightmost bit is discarded, and a new bit is inserted at the leftmost position. The value of the new bit is determined by performing an exclusive-OR (XOR) operation on specific bits in the register, known as feedback taps. The feedback tap configuration is essential in generating an m-sequence. The taps determine which bits in the shift register are used to calculate the new bit. The specific tap configuration depends on the desired length and properties of the m-sequence. The taps are chosen to cover a wide range of bits in the register, ensuring a long period and good statistical properties. From this, shifting and calculating the next bit continues until the sequence repeats. Once the period is reached (calculated using equation (2.64)), the sequence repeats from the initial state, creating a cyclic pattern [102]. Lastly, it is important to note that PRBS signals are deterministic and not truly random. While they exhibit statistical randomness and can be useful for many applications, they do not provide true entropy like a random number generator based on physical processes. Therefore, they should not be used in applications requiring true randomness, such as cryptographic key generation or gambling.

2.6.2 Signal transformation characteristics and fundamentals

This section will discuss some fundamental signal transformation and analysis phenomena to gain a deeper understanding of different signal representations and influences. These include

topics such as autocorrelation, signal convolution, fast Fourier transform, signal aliasing, and signal-to-noise ratio.

2.6.2.1 Autocorrelation

Autocorrelation is a mathematical technique to measure the similarity or correlation between a signal or function and a delayed version of itself. It quantifies how a signal's values at different time points are related. The autocorrelation of a function, often denoted as $R(\tau)$, is a mathematical function that describes the correlation between the function's values at different time lags (τ). It is calculated by multiplying the function by a delayed version of itself and integrating the product over the desired time range. Mathematically, the autocorrelation of a function $x(t)$ at a time lag τ is given by equations (2.65) and (2.66) [106].

$$\text{Discrete time} \quad R_{ADT}(\tau) = \frac{1}{N} \sum_{n=1}^N x[n]x[n + \tau] \quad (2.65)$$

$$\text{Continuous time} \quad R_{ACT}(\tau) = \int_0^T x(t)x(t + \tau)dt \quad (2.66)$$

Here, $x(t)$ represents the function or signal, and τ represents the time lag or delay between the function and its delayed version. The autocorrelation function provides important information about a signal's temporal structure and repetitive patterns [106]. By analysing the autocorrelation function, one can determine the dominant frequency components, identify periodicity, estimate time delays, detect patterns, and assess the statistical properties of a signal.

2.6.2.2 Aliasing

Signal aliasing occurs when the sampling rate used to digitise an analogue signal is too low, resulting in a distorted representation of the original signal. It leads to the appearance of false frequencies or the loss of high-frequency components in the sampled signal. Signal aliasing can be explained by looking at the Nyquist-Shannon sampling theorem, which states that to capture a continuous-time signal accurately, the sampling rate must be double or higher than the maximum frequency generated within the supply signal [107]. Thus, the Nyquist frequency is half the sampling rate, representing the maximum frequency the sampling process can accurately capture. Any frequency component above the Nyquist frequency will be distorted or misrepresented in the sampled signal. When the frequency of a signal exceeds the Nyquist frequency, it folds back or aliases into the frequency range below the Nyquist frequency. This folding is due to the periodic nature of the discrete Fourier transform (DFT), which converts the analogue signal into a digital representation. Aliased frequencies are the false frequencies that appear in the sampled signal due to folding. They are indistinguishable from genuine frequencies within the Nyquist frequency range [107]. For example, a frequency of 100 Hz and its aliases at 300 Hz, 500 Hz, and so on, would all appear the same in a sampled signal with a sampling rate of 200 Hz. In addition to false frequencies, aliasing can also result in the loss of high-frequency

components. If the original signal contains frequencies above the Nyquist frequency, they will fold back and overlap with lower frequencies, causing distortion and loss of information.

To prevent or mitigate signal aliasing, the sampling rate must be selected appropriately based on the highest frequency present in the signal. The sampling rate should be at least twice the Nyquist frequency to avoid aliasing [107]. This is known as the Nyquist rate. If aliasing occurs, it can be addressed through anti-aliasing filters. These filters attenuate frequencies above the Nyquist frequency before the signal is sampled, preventing them from folding back and causing aliasing.

2.6.2.3 Power spectral density

Power Spectral Density (PSD) measures the amount of power distributed across a signal over a range of frequencies. It provides information about the strength or intensity of a signal's frequency components and is widely used in signal processing, communication systems, and spectral analysis. PSD is derived from the Fourier Transform of the autocorrelation function. The squared magnitude of the Fourier Transform is used to calculate the power at each frequency. The PSD represents the power per unit frequency. Mathematically, the PSD of the autocorrelation function in the continuous time domain $R_{ACT}(\tau)$ is denoted as $S(f)$, where f represents frequency as shown in equation (2.67) [101].

$$\text{Continuous time} \quad S(f) = \mathcal{F}\{R_{ACT}(\tau)\} \quad (2.67)$$

The PSD can be calculated using different methods, including the Periodogram, Welch's Method, or the Bartlett Method. These methods involve applying the Fourier transform to smaller segments of the signal and averaging the power spectra to obtain a more accurate estimate of the PSD.

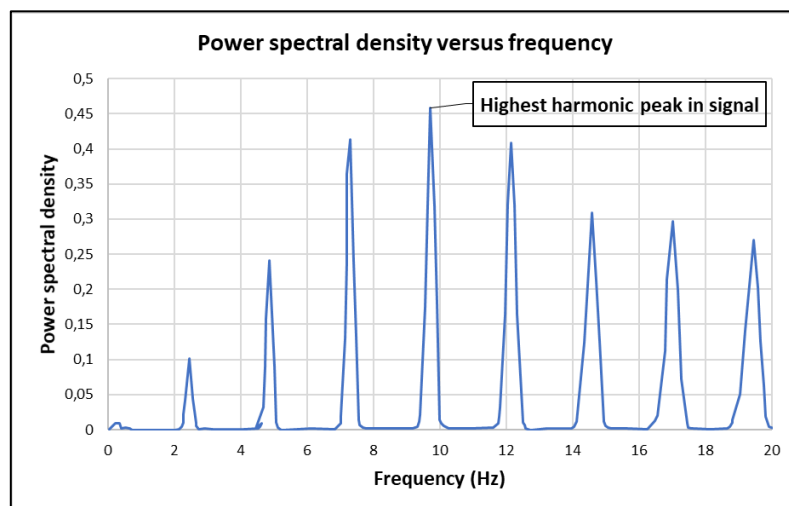


Figure 2.11: Power spectral density versus frequency plot (adapted from [108]).

The PSD provides several important insights into the spectral characteristics of a signal, such as power distribution, frequency content, spectral density, bandwidth, and noise analysis. The PSD is commonly visualised using a power spectral density plot, where the power spectral density is

plotted on the y-axis and frequency on the x-axis. This plot provides a clear representation of a signal's frequency content and power distribution, as seen in Figure 2.11.

2.7 Microcontrollers

A suitable microcontroller is required for perturbation signal generation, current switching control, and PEMWE output analysis and calculation. Thus, it is imperative to choose a microcontroller that can generate quick high frequency perturbation signals with fast response times. This section will examine microcontrollers such as STMs and Arduinos.

2.7.1 STM

The STM32 microcontroller is a series of 32-bit ARM-based microcontrollers developed by STMicroelectronics. The STM32 microcontroller operates based on the ARM Cortex-M processor architecture. It combines a powerful processor core with various on-chip peripherals, such as timers, UARTs, ADCs, and GPIOs, to provide a comprehensive and flexible solution for embedded systems. The microcontroller functions by executing instructions stored in its flash memory. It interfaces with external devices through its input/output (I/O) pins, communicates with other devices through various communication protocols (e.g., SPI, I2C, UART), and interacts with the surrounding world through its peripherals.

For this project, two specific STM32 development boards was compared, namely the STM32F334 Nucleo board and the STM32F411CEU6 Black Pill board, as seen in Table 2.6. In terms of performance, the STM32F411CEU6 Black Pill board has a higher clock speed and larger memory than the STM32F334 Nucleo board. It offers a more comprehensive set of peripherals, including USB connectivity, which can be advantageous for certain applications. However, the STM32F334 Nucleo board has the advantage of an integrated ST-LINK/V2-1 debugger/programmer, making it easier to develop and test applications without the need for an external debugger/programmer. It also provides compatibility with the Arduino ecosystem, allowing users to leverage the extensive Arduino libraries and community support.

The choice between the two boards depends on the specific project requirements. If high performance and a comprehensive set of peripherals are important, the STM32F411CEU6 Black Pill board may be more suitable. On the other hand, if ease of development, integrated debugging capabilities, and Arduino compatibility are desired, the STM32F334 Nucleo board would be a good choice.

Table 2.6: STM32 development board comparisons (obtained from [109]).

Specifications	STM32F334C8T6 Nucleo -64	STM32F411CEU6 Black Pill
Core	Cortex-M4	Cortex-M4
Memory	64 KB	512 KB
RAM	16 KB	128 KB
Peripherals	Timers, UARTs, ADCs, and DACs	Timers, UARTs, ADCs, DACs, and USB
Cost	Low cost	Low cost
Debugger	Integrated ST-LINK/V2-1	Requires an external debugger
Clock speed	72 MHz	100 MHz
Size	Bulky	Small and compact

2.8 Additional information

Additional research related to national standards on the design and utilisation of electrical circuitry, relevant simulation packages, and suitable error margins for model verification and validation was required. These topics were discussed to ensure that safe and productive methods were followed in the study.

2.8.1 Standards

Since this project uses power electronics and electrical power supplies, it is essential to consider different national standards to ensure operational safety. Thus, this section briefly discusses the standards that were adhered to.

2.8.1.1 IEEE

IEEE technical standards are developed by the Institute of Electrical and Electronics Engineers (IEEE). These standards cover a wide range of electrical and electronic engineering topics, including communication protocols, networking, power systems, computer hardware and software, and more. IEEE standards are developed through a rigorous process involving collaboration among experts from academia, industry, and government. The standards ensure interoperability, reliability, and safety in various technological domains. They provide guidelines, specifications, and recommended practices that help engineers and developers design and implement systems and products that meet certain quality and performance criteria. For this project, specific attention was given to IEEE standard 1662-2016 pertaining to recommended practices for the design and application of power electronics systems [110].

2.8.1.2 SANS

SANS standards refer to the set of technical standards developed by the SANS Institute, a leading organisation in the field of cybersecurity education and training. SANS standards cover various aspects of cybersecurity, including best practices, guidelines, and frameworks for securing computer systems, networks, and data. These standards are developed by cybersecurity experts and practitioners with extensive field experience. The purpose of SANS standards is to provide organisations and individuals with practical guidance on effectively protecting their digital assets from cyber threats. They address network security, incident response, vulnerability management, secure coding, and more. For this project, specific attention will be given to SANS 10142-1 and SANS 10142-2 discussing regulations regarding electrical wires, cables, and power electronics [111].

2.8.1.3 IEC

IEC standards refer to the technical standards developed by the International Electrotechnical Commission (IEC). The IEC is an international organisation that focuses on standardisation in electrical engineering, electronics, and related technologies. IEC standards cover various topics, including electrical safety, electromagnetic compatibility, energy efficiency, renewable energy, communication protocols, and more. The purpose of IEC standards is to promote global interoperability, safety, and efficiency in electrical and electronic systems. They provide guidelines, specifications, and testing methods that help manufacturers, engineers, and regulators ensure product and system quality, reliability, and performance. For this project, specific attention was given to IEC 62477-1:2022 and IEC 62477-2:2018 pertaining to the safety requirements for power electronic converter systems and equipment [112].

2.8.2 Simulation packages

This project entails the design of a current switching board that was used to imitate the current interrupt method. The current switching board was required to supply the designed PEM electrolyser cell with a PRBS signal from which the output of the electrolyser was analysed and converted to graphical data comparable to that of EIS. The experimental and simulation software required for this project included Greenlight Innovation controlled by Greenlight Innovation's Emerald®, LTSpice®, STM32CUBE IDE®, JLCPCB®, Matlab® Simulink® and KICAD®. LTSpice® was used to test the preliminary current switching board and alter the components if needed. This software was only used to some extent since LTSpice® offers an ideal simulation environment [113], making it difficult to compensate for practical influences. Thus, Simulink® was used to produce the final simulation product prior to implementation. Simulink® can integrate with both Arduino and STM32 microcontrollers [114], making it possible to refine the simulation environment as closely as possible to the practical setup. It was used to simulate the perturbation signal generator and the current switching board. Matlab® was then integrated with Simulink® to analyse

the PEM electrolyser output and calculate the electrochemical data of the cell. An input signal was required for the current switching board to operate as intended,. This was done by designing a PRBS signal generating algorithm that was implemented on an STM32 microcontroller via STM32CUBE IDE®. Python® was also used as a verification model to observe the similarity between the mathematically generated PRBS signal and the simulated PRBS signal.

The Greenlight Innovation's Emerald® Software was used during experimental tests. The Emerald® software can be used to observe the voltage and current response of the PEM electrolyser cell at any given instance. The recorded data can also be manipulated to draw up a Bode and Nyquist plot, which can be used to compare to the results obtained via EIS under the same conditions. The software can also control system inputs such as heating/cooling temperatures, input/output pressures, DC supply input, etc. Furthermore, Kicad® was used to design the current switching board, which was implemented on the practical test bench setup. Manufacturers such as JLC PCB® was used to build the development board due to their high-quality manufacturing and swift service [115]. More on the experimental software is elaborated on in Chapter 3.

2.9 Critical summary and evaluation

The master thesis topic focuses on the development of a current switching device to characterise and monitor a PEMWE. The main objective is to generate a PRBS input signal using a microcontroller to control the current flowing to the electrolyser cell. Additionally, a current switching board was developed to imitate the current interrupt method. The output of the cell was analysed using Simulink® by calculating the EEC parameters, which was compared to EIS to evaluate the accuracy of the CI method. Several key findings emerged from the review of relevant research articles and studies.

The thesis topic addresses a significant area of research in energy conversion, specifically in the context of PEM water electrolysis. The development of a current switching device and its implementation using a microcontroller and a PRBS input signal can provide valuable insights into the behaviour and performance of the electrolyser cell. By controlling the current flow through the cell, the device enables precise monitoring of key parameters and performance indicators, such as cell voltage stability, current density, and electrolysis efficiency. The integration of a microcontroller into the current switching device offers effective control and monitoring capabilities. The microcontroller can be programmed to implement optimal switching techniques and algorithms (PRBS signal), ensuring accurate and efficient control of the current flow in the electrolyser cell. Using a PRBS input signal allows for the generation of diverse current profiles, which can help characterise the response of the electrolyser cell under different operating

conditions. This approach can provide valuable information about the system's dynamics and ability to handle current input fluctuations. The generated PRBS signal was verified and validated using a self-programmed test Python code to see if the generated PRBS signal corresponds to that of the calculated PRBS signal.

Additionally, the microcontroller enables data collection, processing, analysis, and visualisation for a comprehensive understanding of the cell's behaviour. The choice of switches in the current switching device is crucial for its performance. The literature suggests that selecting efficient, reliable, and compatible switches with the proton exchange membrane water electrolyser cell is essential. Different types of switches, such as MOSFETs, BJTs, etc., can be used. The emulation of the CI method through the development of a current switching board is a practical approach to studying the behaviour of the electrolyser. By interrupting the current flow, it becomes possible to analyse the cell's response and assess its stability and efficiency.

Energy efficiency is another important aspect of the current switching device. Studies have emphasised the need to design and implement the device to minimise power losses and improve overall energy efficiency in the electrolyser cell system. This consideration is crucial for achieving sustainable and cost-effective operation. While the development of a current switching device holds significant promise, some challenges and limitations were closely investigated. These include factors such as voltage stability, current accuracy, response time, and the overall impact of the device on the performance and durability of the electrolyser cell. As for the current switching board, LTSpice® was used as a verification and validation model to see if the switching board delivers the desired output as tested in simulation. During electrolyser output analysis, EIS was further used to assess the validity of the CI model, including the current switching board and the analysis algorithm.

Overall, the project demonstrates an innovative approach to studying the behaviour of the electrolyser cell. By utilising a microcontroller-based PRBS input signal and comparing the Nyquist plot to electrochemical impedance spectroscopy, the research can contribute to the understanding and improvement of PEM water electrolysis systems. The next Chapter focusses on the conceptual and detailed design of the experimental setup components and simulation models.

CHAPTER 3: DESIGN

This Chapter consists of the conceptual and detailed design. The conceptual design contains an overview diagram of the experimental setup that was required for this project. The experimental setup requirements and specifications are also discussed, and the functional flow of the system is clearly discussed. The detailed design consists of the PRBS generator design and the current switching board design. The PRBS generator was designed using Python® and finally implemented on STM32CUBE IDE®. The current switching board was designed using LTSpice® and KICAD® and then simulated and tested using Matlab®/Simulink®. All the topics discussed during this Chapter can be seen in Figure 3.1.

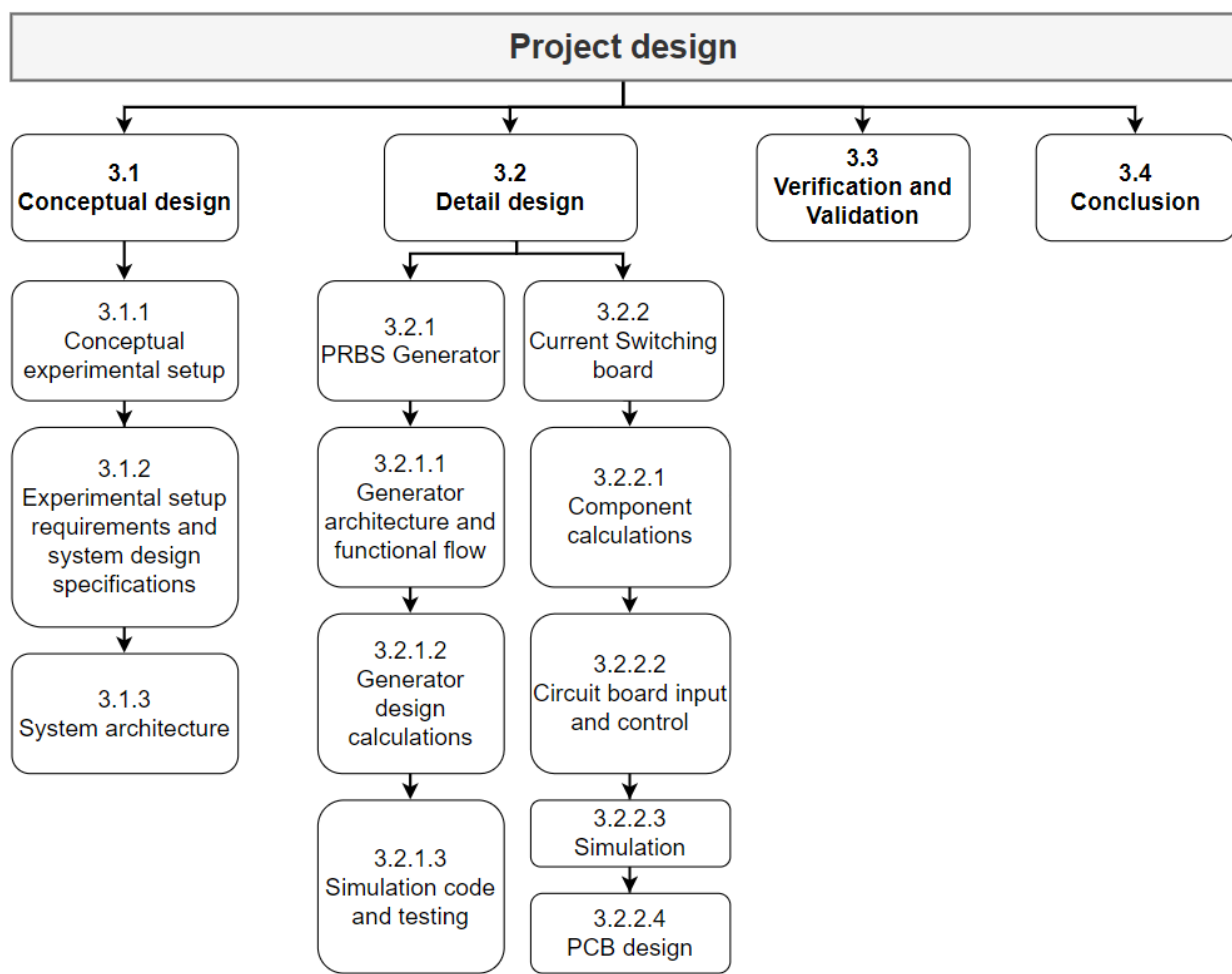


Figure 3.1: Chapter 3 overview plan

3.1 Conceptual design

Conceptual design is a critical step in the current interrupt method. This section consists of an experimental setup giving a broad overview of how all the subcomponents of this project integrate with one another. The experimental requirements and design specifications follow, indicating the requirements for each subcomponent to function as expected. The system architecture diagram

gives an overview of the operation of the system as a whole and communication between each subcomponent. The functional and the operational flow diagrams are elaborated further on in section 3.2.1.1.

3.1.1 Conceptual experimental setup

The experimental setup, shown in Figure 3.2, indicates the important subcomponents required for this thesis. The components include the power supply, the voltage and current sensors, the PRBS generator, the current switching board and the calculation software algorithm. The red solid lines indicate the power flow of the system, which includes the general power supply powering the PEM electrolyser cell and the PRBS generator controlling the current switching board. The PRBS generator is explicitly designed according to the maximum length sequence (MLS) method to deliver a signal with a frequency range from 1 Hz up to 20 kHz. The generated PRBS signal controls the current switching board, which controls the current flow to the electrolyser cell, making it possible to monitor the output current and voltage profile of the cell.

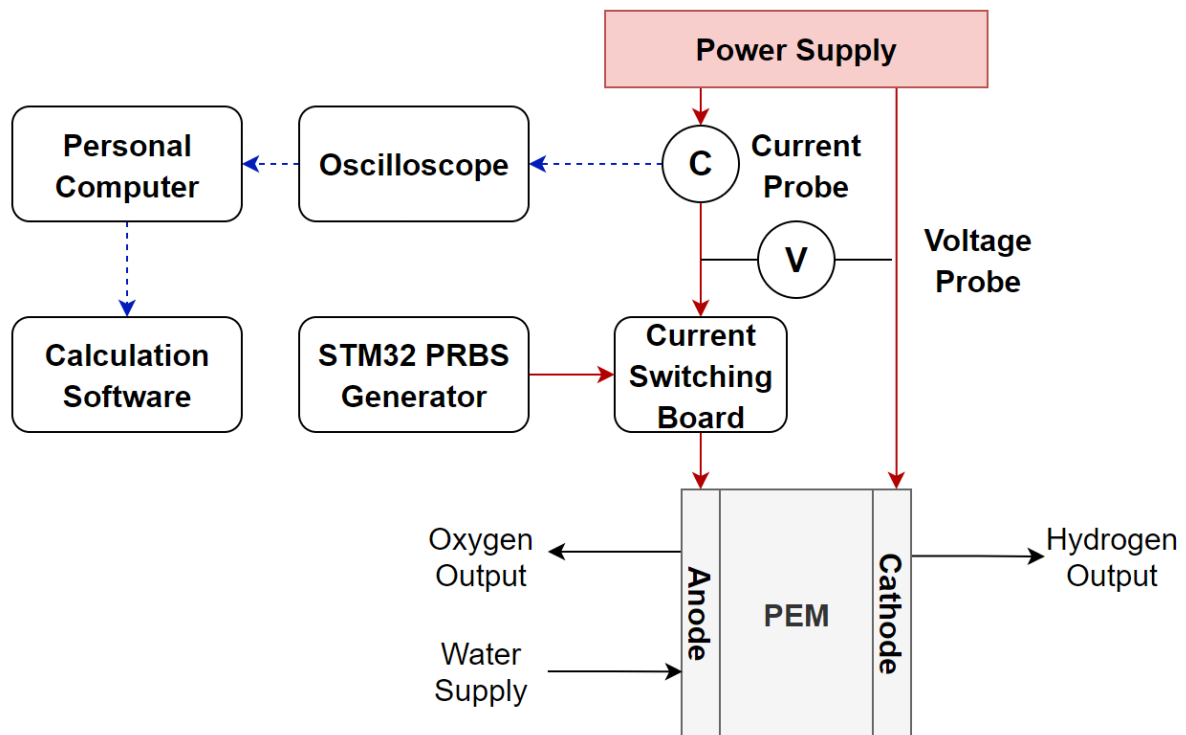


Figure 3.2: Conceptual design of experimental setup

The blue dashed lines indicate the flow of data from the current meter probe to the personal computer. The data is then analysed and converted to usable data that can be easily verified and validated against EIS. The experimental setup shown in Figure 3.2 was used as a reference point for the detailed design, as will be discussed in section 3.2.

3.1.2 Experimental setup requirements and system design specifications

For this project to operate as expected, certain requirements have to be met to deliver results according to the problem statement in section 1.2. In conjunction with section 1.3.4, these specifications were also used to verify and validate the final product.

- A PRBS generator needs to be built that will automatically generate a square wave signal with a frequency ranging from 1 Hz up to 20 kHz (to be determined via cell testing). The signal generator must be implemented on the STM32 using the MLS method.
- A current switching board, responsible for controlling the current supplied to the PEM electrolyser cell, must be designed, built, and implemented. The current switching board is required to deliver a maximum current of 56 A ($\approx 2.2 \text{ A/cm}^2$) with a supply voltage of between 1.7 V and 1.9 V [56, 58]. The switching losses at low frequencies tend to be very low. However, the switching losses at high frequencies will be monitored by comparing the actual signal generated via the STM32 to the generated signal supplied to the PEM electrolyser cell via the current switching board. Further investigation will be done to ensure minimal switching losses during rapid switching [116].
- A suitable current and voltage sensor needs to be implemented. These meters are required to measure all specified data output from the PEM electrolyser cell without losing data. This can be problematic, especially at high frequency since the clock time at which the data is generated is very fast. Thus, the input data points will be compared to the output to estimate whether all datapoints have been captured.
- Simulink® and Matlab® need to be programmed to receive the data from the current and voltage probes and will be done via serial communication as seen in Figure 3.3.

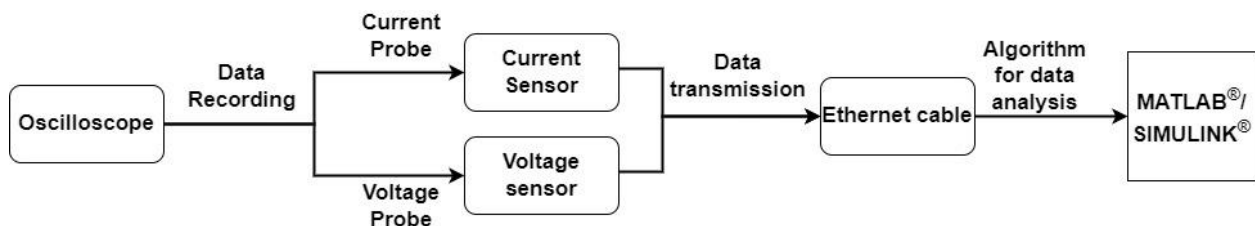


Figure 3.3: Conceptual data flow diagram

Data will be transmitted via an ethernet cable connected from the oscilloscope to the laptop. The data will then be analysed in Simulink® /Matlab®. It is very important to compare the obtained results from Simulink® /Matlab® with those of EIS under similar circumstances for each experiment.

3.1.3 System Architecture

Figure 3.4 outlines the basic system architecture for this project. The STM32 was programmed to generate a PRBS signal using cascaded linear feedback shift registers to generate different frequency bands. The signal was then applied to the current switching board, which controls the

current flow to the PEM electrolyser cell. The output of the cell was then measured using a current and voltage sensor. The data was then processed by the personal computer (Simulink®/Matlab®).

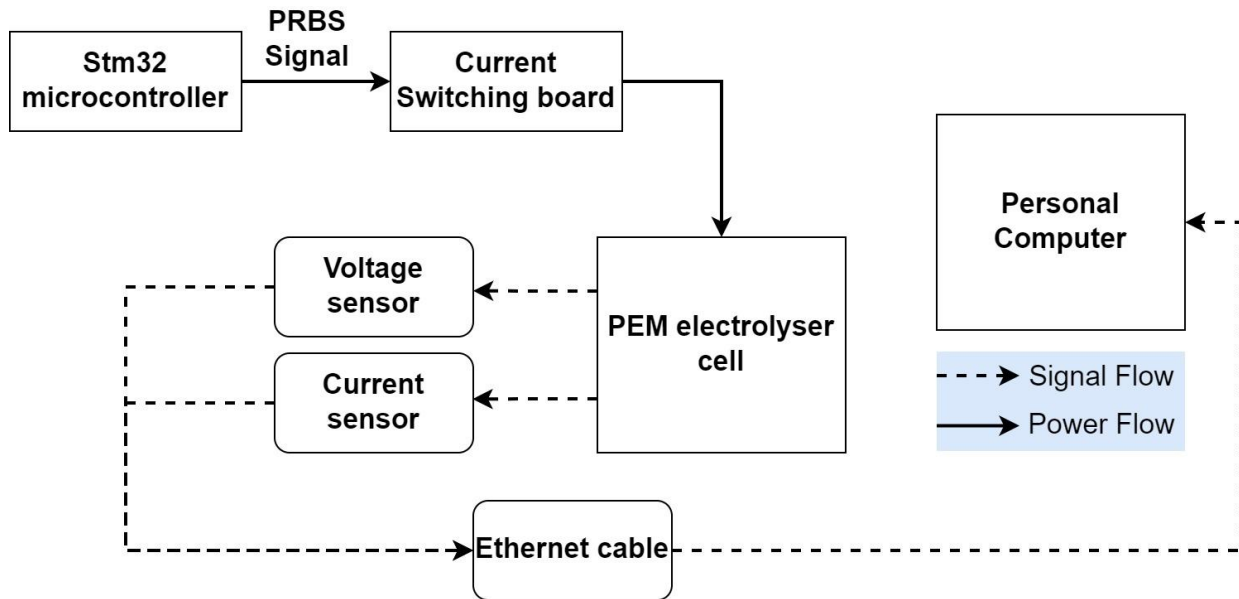


Figure 3.4: Concept overview of system architecture

3.2 Detailed design

The project aimed to design a suitable current interrupt characterisation model that successfully characterises the designed PEM electrolyser cell. For this to be achieved, extra electronic circuitry and algorithms were required. The design of a current switching board and PRBS signal generator will be discussed in this section in relation to Figure 3.2.

3.2.1 PRBS generator

The proposed generator, as discussed in section 2.6.1.1, plays a fundamental role in the analysis of the CI method. This is because the final results generated via the CI method solely depend on the input given to the PEM electrolyser cell and the operating condition of the physical cell. If the input given to the cell is not correct, the output of the cell is irrelevant. In this section, the complete design and verification will be given with base code evident within the drive link from the Appendix. The STM32 used to generate the PRBS signal was the STM32F334R8 nucleo 64 development board and was programmed using STM32CUBE IDE®.

3.2.1.1 Generator operational- and functional flow

Figure 3.5 shows the operational flow diagram of the PRBS generator. The figure clearly indicates the algorithm flow implemented on the stm32 to generate the desired PRBS signal. The next few sections will explain more about the mathematical approach and frequency bands of each LFSR.

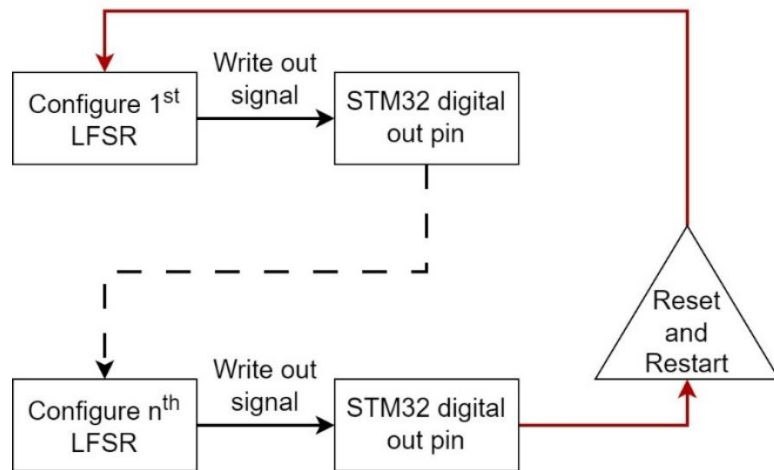


Figure 3.5: Operational flow of the PRBS generator

The functional flow diagram of the PRBS generator is shown in Figure 3.6. The diagram starts by initialising the stm32 nucleo development board input pins, output pins, and timers. Thereafter, the LFSRs were initialised according to the mathematical calculations in section 0.

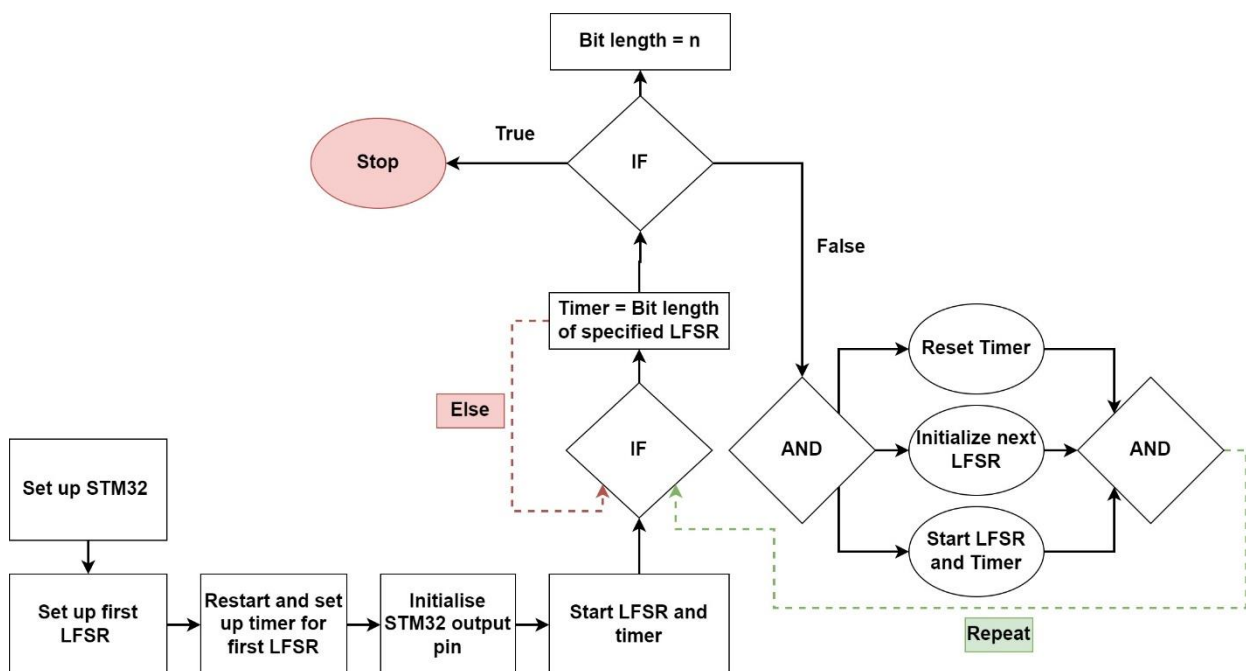


Figure 3.6: Functional flow diagram of the PRBS generator

Each LFSR has a bit length according to the calculated frequency band. When one of the LFSR bit lengths was reached, the timer was restarted and the following LFSR parameters were initialised if the total PRBS bit length was not reached. Otherwise, the program was stopped. This process was repeated until all three LFSRs generated their designed PRBS signals as indicated by the green dashed line in Figure 3.6. Thus, each LFSR shifted the last bit to the specified digital pin on the STM32 development board until the desired bit length was reached. The initialisation of the parameters in between was done within a few nano seconds, making it possible to write

out the signal to the digital pin of the development board in conjunction with parameter and timer initialisation with minimal delays between each of the generated frequency bands.

3.2.1.2 PRBS generator design calculations

The PRBS generator design process requires careful consideration of various calculations and design assumptions to ensure that the generator has the desired properties of the generated sequence. These calculations involve the determination of the designed signal frequency range, the number of LFSRs required for the desired frequency range, the determination of the feedback polynomial of each LFSR, the sequence length of each LFSR, the linearity of the generated signal and parameters that influence the randomness and reliability of the PRBS signal. In the design of the PRBS generator, choosing the right feedback polynomial is an important computation. The bits utilised for feedback in creating the following bits are determined by the tap positions in the Linear Feedback Shift Register (LFSR), which are defined by the feedback polynomial. Sequence lengths and randomisation properties of PRBS sequences vary depending on the feedback polynomials used. The feedback polynomial possibilities must be carefully analysed and evaluated in order to acquire the required qualities for the particular application. Determining the sequence length is another crucial factor to consider. The number of distinct patterns in the created PRBS sequence before it repeats is called the sequence length.

In many applications, longer sequence lengths are preferred because they increase unpredictability and reduce the likelihood of repetition within a certain time interval [19, 86]. Identifying the number of stages in the LFSR and the feedback polynomial to be utilised are the first steps in calculating the sequence length. Choosing a sequence length that considers the hardware resources available and satisfies the application requirements is essential. Furthermore, linearity is an important consideration in the design calculations. The correlation between successive bits in the PRBS sequence is referred to as linearity. For the generated sequence to be reliable and prevent predictability, it should ideally show very little connection. Calculations involving tap locations, feedback polynomials, and shift register configurations are necessary to provide the appropriate linearity features. In addition, the design calculations take timing and clock frequency into account. The pace at which the LFSR creates the PRBS sequence depends on the clock frequency. Many applications depend on proper synchronisation with other systems or data transmission rates, such as precise clock frequency computation that is required to guarantee accurate timing and dependable functioning. Thus, to ensure that the generation signal contains bands within a specific frequency range, different clock frequencies were used to generate the desired output bits. The clock frequency for each LFSR depends on the maximum excitation frequency, which varies depending on the maximum frequency of each LFSR.

PRBS signal generator requirements

Certain criteria had to be discussed and analysed before the design process commenced to ensure that the desired PRBS signal was generated according to design specifications. The criterion for the signal includes a self-generated PRBS signal consisting of a frequency band range to be determined via cell testing, the signal must be generated using a LFSR that is programmed to generate bits according to the MLS method (thus, specific taps have to be initialised to perform the XOR operation), and the seed value of the LFSR is important and needs to be chosen according to the desired functionality of the shift register.

The frequency range of the proposed PRBS signal generator was determined according to the designed specifications. The minimum and maximum frequency of the full PRBS signal was verified based on dedicated literature [86]. Lazanas *et al.* [86] described that the minimum frequency in practical applications is 1 mHz. However, a typical safe range would be between 10 mHz and 1 Hz, since it takes a very long time to conduct a single measurement at these frequencies. The PRBS generator was designed to be stable at these low frequencies, resulting in a stable PEM electrolyser cell output when subjected to an input signal with varying frequency. Furthermore, the maximum frequency of the PRBS signal was determined at the frequency where no new data was generated by the PEM electrolyser cell. Thus, the signal stays constant, making it irrelevant to analyse the PEM electrolyser cell any further (determined by the scope of this project). The maximum PRBS input signal frequency supplied to this cell was designed at 20 kHz [19, 58, 86]. The maximum frequency will be verified within section 0.

Minimum and maximum PRBS band frequency calculation

The minimum and maximum band frequencies for the designed cell, discussed in section 4.1.1.1, were determined by performing quick EIS tests on the cell. The cell was configured and connected using the Greenlight test station, as seen in Figure 3.7.

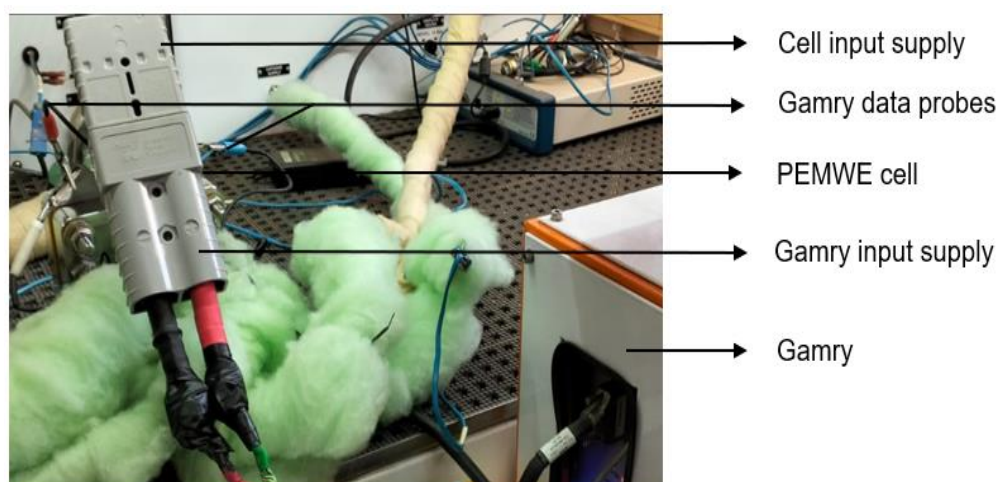


Figure 3.7: PEMWE cell EIS setup

Nine different EIS tests were conducted to determine the minimum and maximum frequency range of the cell. Each test was conducted at a current density of 0.1 A/cm², 0.2 A/cm², 0.3 A/cm² at 40°C, 60°C and 80°C. This specific current density range represents the current density range during CI testing. The Gamry setup used for each experiment can be seen in Table 3.1.

Table 3.1: Gamry parameter setup for EIS testing

Current density [A/cm ²]	Temperature [°C]	Minimum Frequency [Hz]	Maximum Frequency [kHz]	AC Current [A - rms]	DC Current [A]
0.1	40	0.1	20	0.9	2.5
0.1	60	0.1	20	0.9	2.5
0.1	80	0.1	20	0.9	2.5
0.2	40	0.1	20	0.9	5.0
0.2	60	0.1	20	0.9	5.0
0.2	80	0.1	20	0.9	5.0
0.3	40	0.1	20	0.9	7.5
0.3	60	0.1	20	0.9	7.5
0.3	80	0.1	20	0.9	7.5

Each experiment was conducted under the experimental conditions set out in Table 3.1. The DC current was calculated by multiplying the active area of the cell (25 cm²) by the current density. Furthermore, an AC current signal (10% of the DC signal), due to Gamry's electrical current supply limitation, was applied to the cell. However, it can be seen that the AC current in Table 3.1 was set to 0.9 A, this was due to the Gamry limitation of a minimum AC current of 0.9 A. The Bode plot as well as the Nyquist plot were analysed for each experiment. From the magnitude, it was clear that at lower frequencies below 1 Hz, the cell's DC response was evident, which was crucial for determining the steady-state performance of the cell. In terms of the Randles Warburg cell, this part of the magnitude plot was vital in calculating the membrane resistance using the gain in decibels at low frequencies just before the 45° dipping point. It can be seen that at each current density under different temperatures, the significant change in magnitude as frequency increases occurs beyond 1 Hz. Thus, it is safe to assume a PRBS signal's minimum frequency range up to 1 Hz for experimental purposes. However, the time it takes to generate a signal at frequencies below 1 Hz becomes significantly longer.

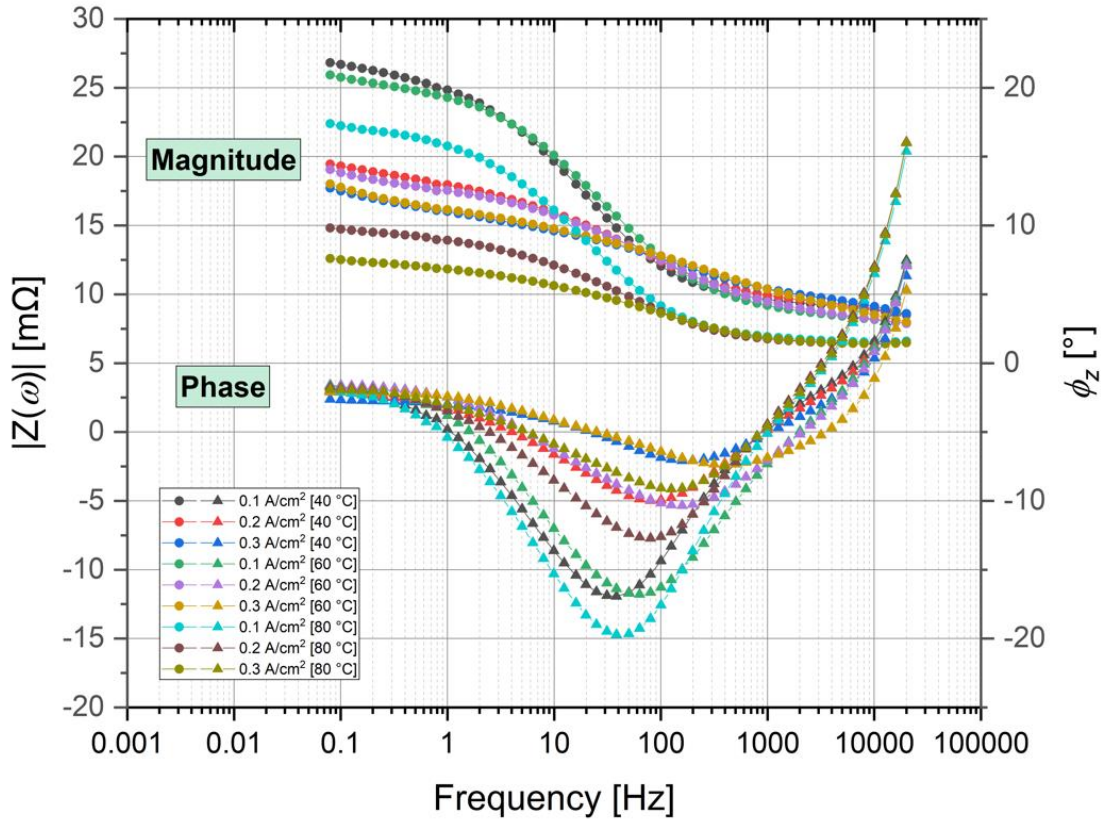


Figure 3.8: Magnitude and phase plot of EIS under different experimental conditions

Thus, an increase in the period of a signal leads to an increase in simulation time during CI testing increasing the overall parameter calculation analysis. Thus, to minimise the total period of the PRBS signal a frequency of 0.8 Hz is chosen as the minimum band frequency. The maximum band frequency is kept as 20 kHz.

PRBS basic calculations

To design a PRBS signal generator the necessary LFSRs are required to generate the desired waveform. As previously stated, more than one LFSR were required to generate a signal with a frequency ranging between 0.8 Hz and 20 kHz. The decision to generate such a signal was made based on previous literature [19, 22, 25, 51, 86], resulting in two LFSRs generating a specific frequency band. Each LFSR generated its respective signal based on specified parameters and was therefore initialised to generate each signal according to a specified timeframe. The clock frequency F_{cl} for each LFSR was carefully calculated based on equation (3.1) [19], which determined the frequency at which each bit of the desired signal was generated on the output of the STM32 microcontroller.

$$F_{cl} = F_{me} \times 2.5 \quad (3.1)$$

The maximum excitation frequency F_{me} based on the maximum band frequency of each LFSR was assumed for each LFSR, as seen in Table 3.2. The maximum excitation frequency was chosen based on the desired clock frequency, which was directly related to the maximum band

frequency describing the maximum frequency of the actual output signal as seen in equation (3.2) [19].

$$F_{max} = \frac{1}{3 \times \Delta t} \quad (3.2)$$

The clock period Δt at which the bits were generated was then calculated according to equation (3.3) [19], which is directly related to the inverse of the clock frequency.

$$\Delta t = \frac{1}{F_{cl}} \quad (3.3)$$

After this, the minimum frequency F_{min} of each LFSR was calculated. For the first LFSR, a minimum frequency of 0.8 Hz was taken, as determined in section 0. From there, a safety overlapping factor was inserted for the next two LFSRs as seen in Table 3.2. For the second LFSR, an overlapping factor of 10% was initialised, ensuring that no data was lost when switching over between the first and second frequency bands. According to Martinson *et al.* [19] a 10% overlapping factor at lower frequencies is sufficient. Thus, the minimum frequency can be used to calculate the sequence length of the next LFSR, as seen in equation (3.4) [19].

$$N = \frac{1}{F_{min} \times \Delta t} \quad (3.4)$$

From this, the number of stages of each LFSR could be easily determined using mathematical manipulation, resulting in equation (3.5) [19].

$$n = \frac{\log(N)}{\log(2)} \quad (3.5)$$

Lastly, to see how long it will take to generate each signal at the designed frequencies, equation (3.6) [19] can be used. This equation is just the product of the clock period at which the bits are written to the output terminal of the STM32 microcontroller and the sequence length of each LFSR.

$$T = N \times \Delta t \quad (3.6)$$

A summary of the calculated parameters for each LFSR can be seen in Table 3.2, describing the mathematical behaviour of each LFSR. However, to ensure that each LFSR generated the desired bits according to the MLS method, specific taps were required to do the XOR operation [19]. Each LFSR was initialised with the same seed value, as seen from Table 3.3 with different bit lengths. With the chosen seed values, one ensures that the calculated sequence length of each LFSR was reached before the sequence starts to repeat itself. Thus, the first LFSR has 512 different sequences before it starts to repeat. Furthermore, the dedicated seed values also ensured that the generated signal had a balanced number of 0s and 1s, resulting in good signal statistical properties and a uniform distribution of consecutive identical bits.

Table 3.2: LFSR design parameters for PRBS signal generator

Description	Symbol	LFSR 1	LFSR 2	Unit
Maximum excitation frequency	F_{me}	163	30000	Hz
Minimum band frequency	F_{min}	0.80	146.70	Hz
Overlapping factor	O_v	0	10	%
Clock frequency	F_{cl}	407.50	75000	Hz
Clock period	Δt	2.45 ms	13.33 μ s	
Sequence length	N	511	511	bits
Number of stages	n	9	9	stages
Maximum band frequency	F_{max}	135.83	20000	Hz
Period of signal	T	1.250 s	6.82 ms	

3.2.1.3 Simulation code and testing

Utilising the data calculated from Table 3.2, Python® was used to set up each LFSR to ensure that the signal was generated according to mathematical calculations. Thus, the Python® code served as a verification method ensuring that the mathematical calculations and physical simulation models corresponded. Specifying the seed value and the taps for each LFSR according to the MLS method, as evident in Table 3.3, each LFSR was individually generated. Both signals contained a total number of bits, as calculated from Table 3.2 of 511 bits (calculated according to equation (2.64)).

Table 3.3: LFSR seed value and tap positions

Linear feedback shift register	Seed Value	Tap positions
First LFSR	000000001	[5;9]
Second LFSR	000000001	[5;9]

The total number of bits when combining both LFSR signals was 1024 bits. The total time it took to generate the entire signal was 3.26 seconds, ensuring that the characterisation process of the designed PEM electrolyser cell occurred quite swiftly.

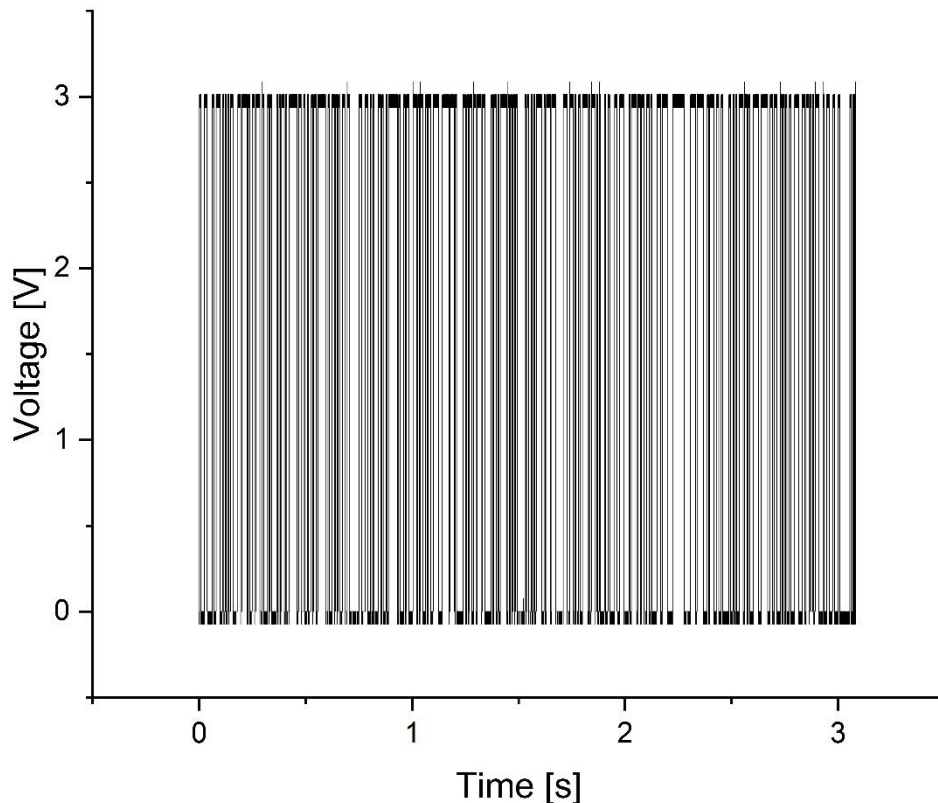


Figure 3.9: Designed PRBS signal with frequency range of 0.8 Hz – 20 kHz

The two different bands in the PRBS signal containing the frequency range of interest can be easily verified from Figure 3.9.

3.2.2 Current switching board

In this section the CS board was designed, simulated, and tested to ensure that the board delivered the expected results. The CS board was verified and validated against existing literature to ensure the validity of the model [19]. Furthermore, the CS board was neatly designed onto a PCB (discussed in section 3.3.2), enabling the user to easily connect the CS board to the system as a whole. The building blocks of the CS board that are discussed and can be seen in Figure 3.10. The PRBS generator, as discussed within section 3.2.1, was implemented on the STM32F334R8 nucleo 64 development board. The designed source code, analysed and tested within Python®, was adapted to program the module within STM32CUBE IDE® successfully. The code included clear initialisations of input and output pins, high-speed and low-speed clock configurations, timer configurations and data communication connectivity. The configuration of the development board is discussed in Chapter 4. Furthermore, Figure 3.10 shows an overview of what is expected when designing the current switching board. From Chapter 1, it is evident that a current switching board is required to control the current flow to the PEM electrolyser cell. Thus, ensuring that the CS board has high-speed switching with low switching and parasitic losses is imperative. It is also important to account for component and user safety during the design of the board.

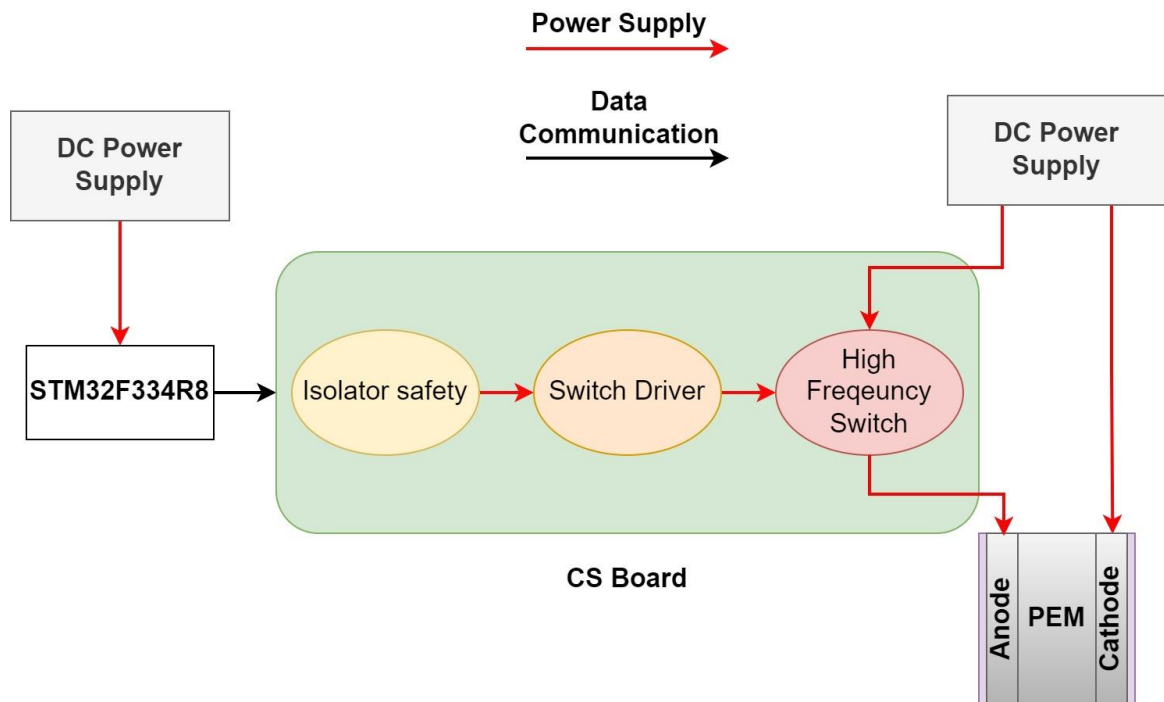


Figure 3.10: Current switching board flow diagram

One safety precaution includes, for example an opto-isolator responsible for isolating the input circuitry from the output. Thus, if a fault occurs on the input side of the isolator, the output side stays protected, and vice versa. This are all discussed during the design section (3.2.2) of the CS development board.

3.2.2.1 Protection circuitry

The protection circuitry of the current switching board plays an essential role in the safety of surrounding PCB components and experimental setup equipment. The protection is typically done by primary and secondary circuit isolation techniques, proper component grounding and ground isolation, overvoltage compensation through Zener diodes, overcurrent protection using current limiting resistors, thermal protection, etc. However, since this is a low voltage low current application, only circuitry input and output isolation, and proper grounding were considered. This was done by implementing an opto-isolator that isolated the PRBS signal input from the switching circuitry.

The implementation of the opto-isolator in simulation (LTSpice®) can be seen in Figure 3.11. Implementing an opto-isolator plays an essential role in the design of modern electronic circuitry due to its safety characteristics. These characteristics include electrical isolation, noise immunity, voltage level shifting, and transient protection. Taking these characteristics into account, it is important to consider the operation of the current switching board. Electrical isolation was implemented between the current switching board's primary input (PRBS signal generator) and

the secondary input (MOSFET and MOSFET driver circuitry). This means that the generated PRBS signal was passed through the opto-isolator by means of a light medium.

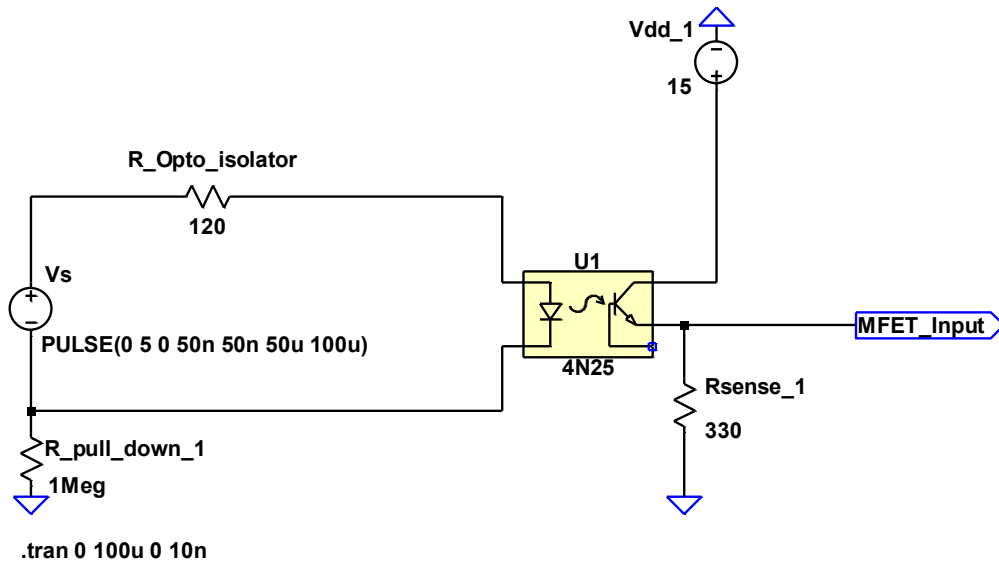


Figure 3.11: Opto-isolator simulation implementation

This ensured that there was complete safety against any voltage leakages, short circuits, ground loops, and noise interference. Thus, a clean signal was generated at the output of the opto-isolator, as seen in Figure 3.12.

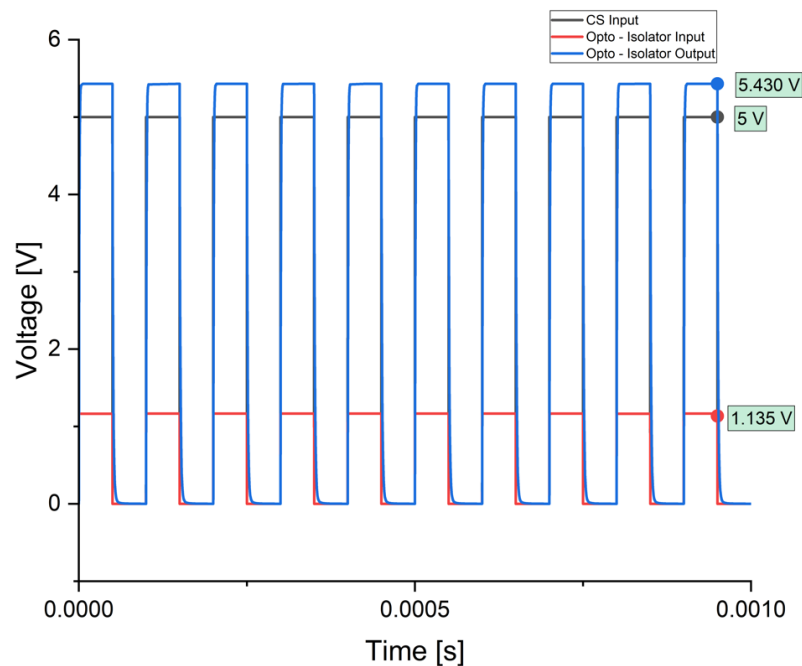


Figure 3.12: Opto-Isolator simulation input versus output

The output in Figure 3.12 is based on the circuit setup shown in Figure 3.11 and shows the input and output of the opto-isolator. The “PRBS Input” voltage source, in Figure 3.11, was initialised with a 5 V peak 10 kHz square wave signal, as seen in Figure 3.12, simulating with a simple transient response of a maximum of 1 ms.

3.2.2.2 Switch driving circuitry

The driving circuitry of the MOSFET is a crucial component in the secondary circuit design. This component is mainly responsible for the voltage level amplification of the voltage signal received from the opto-isolator as it ensures that the gate of the MOSFET is switched on properly. Furthermore, the gate driver ensures that the necessary current is supplied to the MOSFET for rapid charge and discharge of the MOSFET capacitance, enabling fast switching responses and a reduction in power losses. Considering the key research questions stated in section 1.3.4, the switching device used for the current switching board needed to be carefully considered to give meaningful solutions to questions 3 and 4. Thus, for this section, three different MOSFET devices were juxtaposed based on specified criteria, as seen in Table 3.4.

The total gate charge of a MOSFET refers to the total charge required to switch the MOSFET between the on and off state successfully. It also refers to the summation of the gate-to-source charge, the gate to drain charge, and the gate-to-body charge and is very important to consider when using in high-frequency applications that require fast switching speeds. It also directly impacts the rise and fall time of a MOSFET but is not directly proportional. Thus, a lower total gate charge relates to lower switching losses and higher switching efficiencies due to a reduction in power dissipation during switching.

Table 3.4: MOSFET trade-off analysis

Description	Symbol	Weight	IPP055N03LG (MOSFET 1)		IPP70N04S406A (MOSFET 2)		IPP048N04NG (MOSFET 3)	
			Rating (10)	Score	Rating (10)	Score	Rating (10)	Score
Total gate charge	$Q_{g(total)}$	0.15	8	1.2	7	1.05	4	0.6
Rise time	t_R	0.2	7	1.4	3	0.6	8	1.6
Fall time	t_F	0.2	8	1.6	3	0.6	8	1.6
Output capacitance	C_{oss}	0.2	6	1.2	8	1.6	7	1.4
Drain to source resistance	R_{sd}	0.125	8	1	7	0.875	9	1.125
Gate threshold voltage (Max)	$V_{th(gate)}$	0.125	9	1.125	6	0.75	6	0.75
Total				7.525		5.475		7.075

Furthermore, it is also crucial to look at the rise time and fall time of the MOSFET as it directly correlates to the time it takes for the output voltage of the MOSFET to reach 90% (low voltage transition to high voltage transition) and 10% (high voltage transition to low voltage transition) of its final output voltage, respectively. Thus, shorter rise and fall times benefit this application. The

output capacitance refers to the capacitance between the drain and source terminals of the MOSFET. This component can significantly reduce the switching losses of the MOSFET if it is pertaining to a small capacitance allowing for fast capacitor charge and discharging. As for the drain current and drain to source resistance, a trade-off has to be made. During switching, the increase in drain current is directly proportional to the increase in drain resistance. Thus, the higher the drain current, the higher the drain-to-source resistance during operation. Therefore, choosing a MOSFET with a relatively low resistance when fully on is ideal since it also lowers the conduction losses of the MOSFET and increases the switching efficiency during operation. Furthermore, the lower the gate threshold voltage of the MOSFET, the quicker the MOSFET can switch on or off hence, increasing the response speed of the MOSFET. Taking all these into account MOSFET 1, according to Table 3.4, were chosen.

The current switching board can be further developed by utilising the desired MOSFET into the circuitry. The MOSFET can be seen in Figure 3.13, where the opto-isolator circuitry, designed in section 3.2.2.1, was integrated. The switch also contains a MOSFET driver (TC4422) responsible for amplifying the voltage signal received from the opto-isolator. The amplified signal was thus supplied to the MOSFET, ensuring that the MOSFET was properly switched on and off.

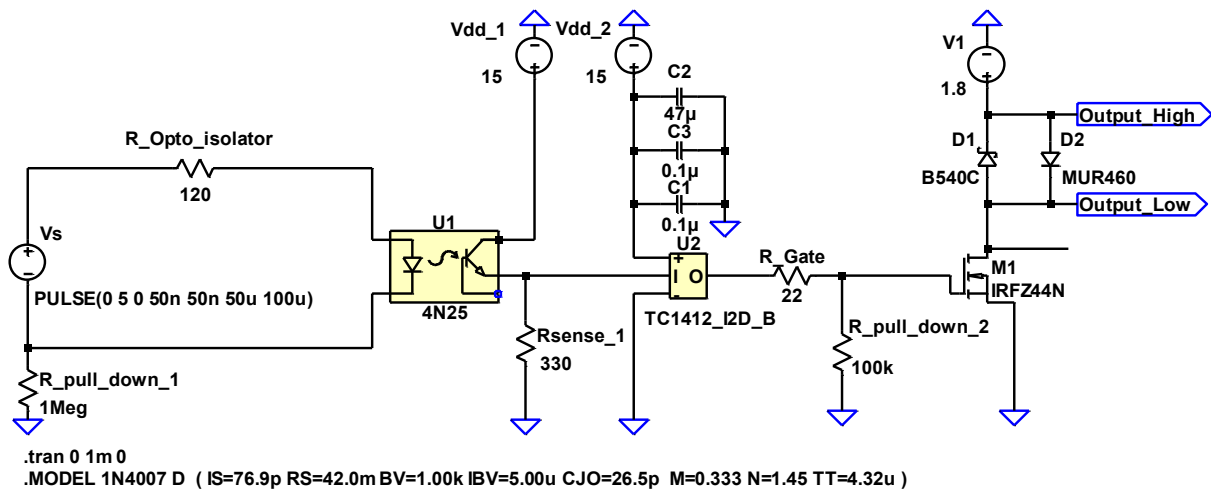


Figure 3.13: Switching circuitry simulation

The output of the MOSFET driver and switch can be seen in Figure 3.14 (simulating using the same settings as discussed in section 3.2.2.1). From the simulation circuit of the current switching board, Figure 3.13, the different PEM water electrolyser mathematical representations could be added to the circuit as discussed in Chapter 2. This includes the Randles cell representation and the Randles Warburg impedance cell representation.

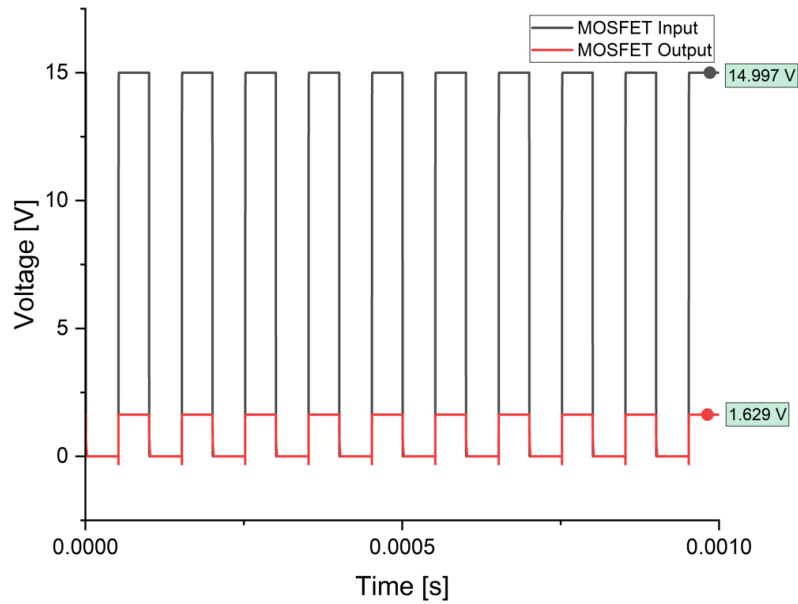
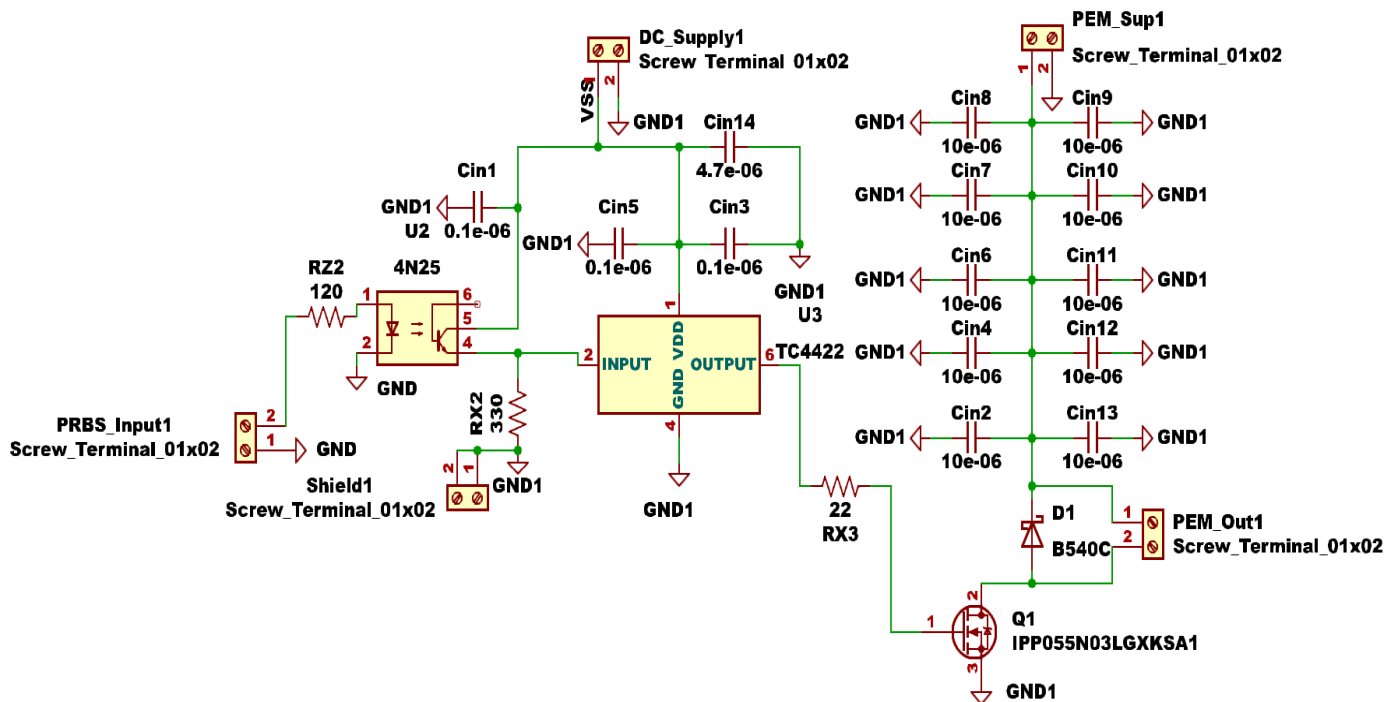


Figure 3.14: MOSFET driver output versus switch output

3.2.2.3 Parasitic losses and noise compensation

The current switching board design as discussed in detail in sections 3.2.2.1 and 3.2.2.2, operated as expected. However, to ensure the safety of sensitive components within the current switching board a few safety components had been added. The complete electrical circuit of the current switching board, as was used for the design of the PCB using Kicad®, can be seen in Figure 3.15.

Figure 3.15: Complete current switching board with safety implementation



Circuit protection for the current switching board was imperative and coincided with the key research question stated in section 1.3.4. The question investigates the minimisation of power losses and an increase in overall energy efficiency in the characterisation process of the proton

exchange membrane water electrolyser cell system. This was accomplished by using white noise elimination and signal losses through the implementation of various capacitors. The first capacitor, namely “*Cin1*”, was implemented to filter out noise generated via the DC power supply. Thus, the bypass capacitor acted as a simple low-pass filter, preventing it from influencing the output signal of the opto-isolator.

Furthermore, a screw terminal was connected to the secondary ground of the current switching board. This terminal was used to house a shield wire that enclosed the output wires connecting the PEM water electrolyser to the current switching board. The shield wire was responsible for lowering the electrical field generated via the output of the current switching board, thus causing a reduction in eddy current losses and skin effect. Lastly, a few decoupling capacitors were added to the DC voltage supply of the MOSFET to ensure that unwanted noise generated via the supply was filtered out and led to an increase in stability of the signal. This was accomplished by providing a low-impedance path for high-frequency transients to dissipate directly through the ground. With this in mind, the capacitors connected so close to the MOSFET provided a quick safety response to sudden fluctuations in supply voltage hindering the MOSFET interferences. During the PCB design, discussed in section 3.3.2, the placement of the capacitors and path to ground were done strategically. The layout was done by placing the components as close to each other as possible since this assisted in the elimination of unwanted parasitic losses and white noise generated by the components. More details on these placements, ground paths, wire thickness, etc., are provided in the PCB design section.

3.2.2.4 Simulation and parameter calculation

The simulation section entails the calculation of the electrical parameters discussed in section 2.5.4. As discussed, two methods were proposed to calculate the electrical parameters of the PEM water electrolyser: the NVR method to calculate the membrane resistance and the CS method to calculate the charge transfer resistance, double layer capacitance and Warburg impedance.

Natural voltage response method (Randles cell)

As discussed in section 2.5.3, the natural voltage response method was used to calculate the electrical parameters of the Randles cell, as shown in Figure 3.16. This method was briefly discussed in Chapter 2 and is closely followed by the experimental setup designed by Martinson *et al.* [19]. R_m represents the membrane resistance, C_{dl} represents the double-layer capacitance, R_{ct} represents the charge transfer resistance, and E_0 represents the standard potential discussed in section 2.3.2.

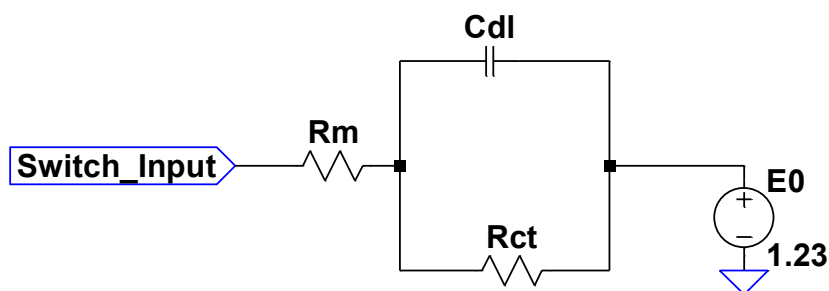


Figure 3.16: Randles cell simulation circuit [19]

Applying this circuit setup to an idealised version of Figure 3.13, the complete current switching board integration with a typical PEM electrolyser mathematical model can be seen in Figure 3.17.

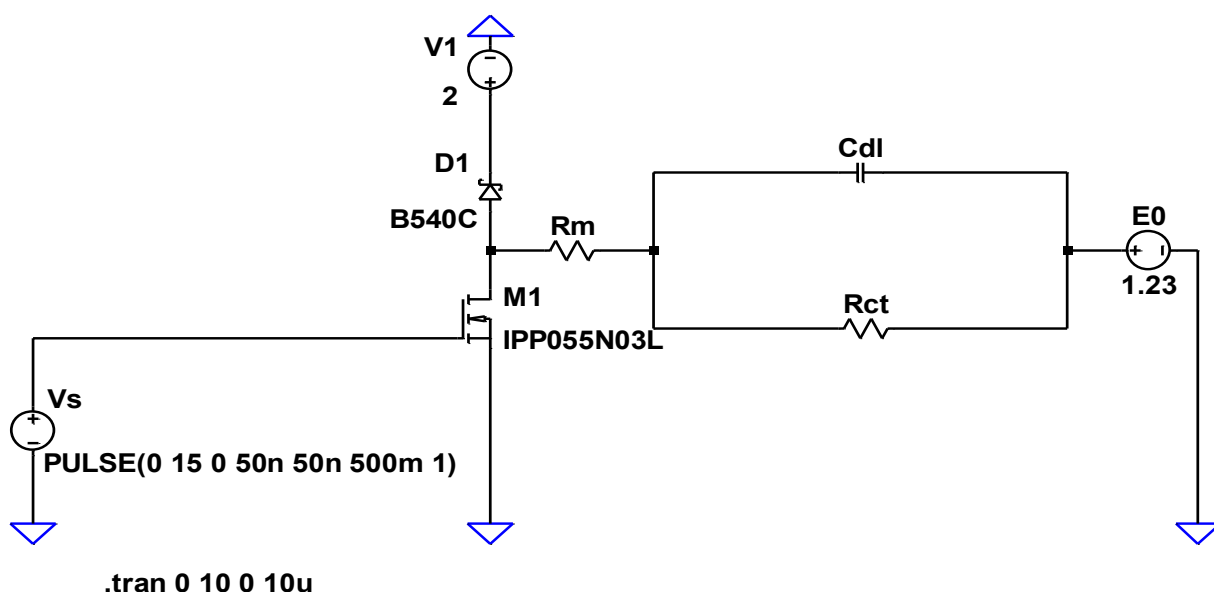


Figure 3.17: Randles cell integration with current switching board

Now, replacing the electrical parameter values with test values obtained from Table 3.5, the model accuracy was determined by calculating the model parameters from the simulated results using the equations explained in section 2.5.3. The NVR method was not further validated as Martinson *et al.* [19] already validated this method by conducting eight different simulation tests. The circuit as a whole was validated and discussed in section 3.2.2.4 with the assistance of Simulink® to ensure that the model was correct.

Table 3.5: Test values for Randles cell circuit integration

Electrical parameter	Test value	Unit
R_m	50	mΩ
R_{ct}	50	mΩ
C_{dl}	300	mF

However, before substituting the parameter values, it is important to consider the simulation settings of LTSpice®. According to Martinson *et al.* [19], the membrane resistance is accurately calculated using the voltage drop measured 0.5 to 10 ns after the current interruption (This will be for fast acquisition). As for the calculation of the charge transfer resistance and double-layer capacitance, a slow acquisition is required, as seen in Table 3.6.

Table 3.6: Simulation settings for Randles cell

LTSpice® simulation setting	Fast acquisition	Slow acquisition	Unit
Stop time	50 μ	1	s
Maximum timestep	10n	10 μ	s

Now, substituting the electrical parameter values with the test values, as seen in Table 3.5, the following cell voltage signal and cell current signal were obtained utilising the fast acquisition settings (Figure 3.18). This current and voltage signal were used to calculate the membrane resistance of the Randles cell.

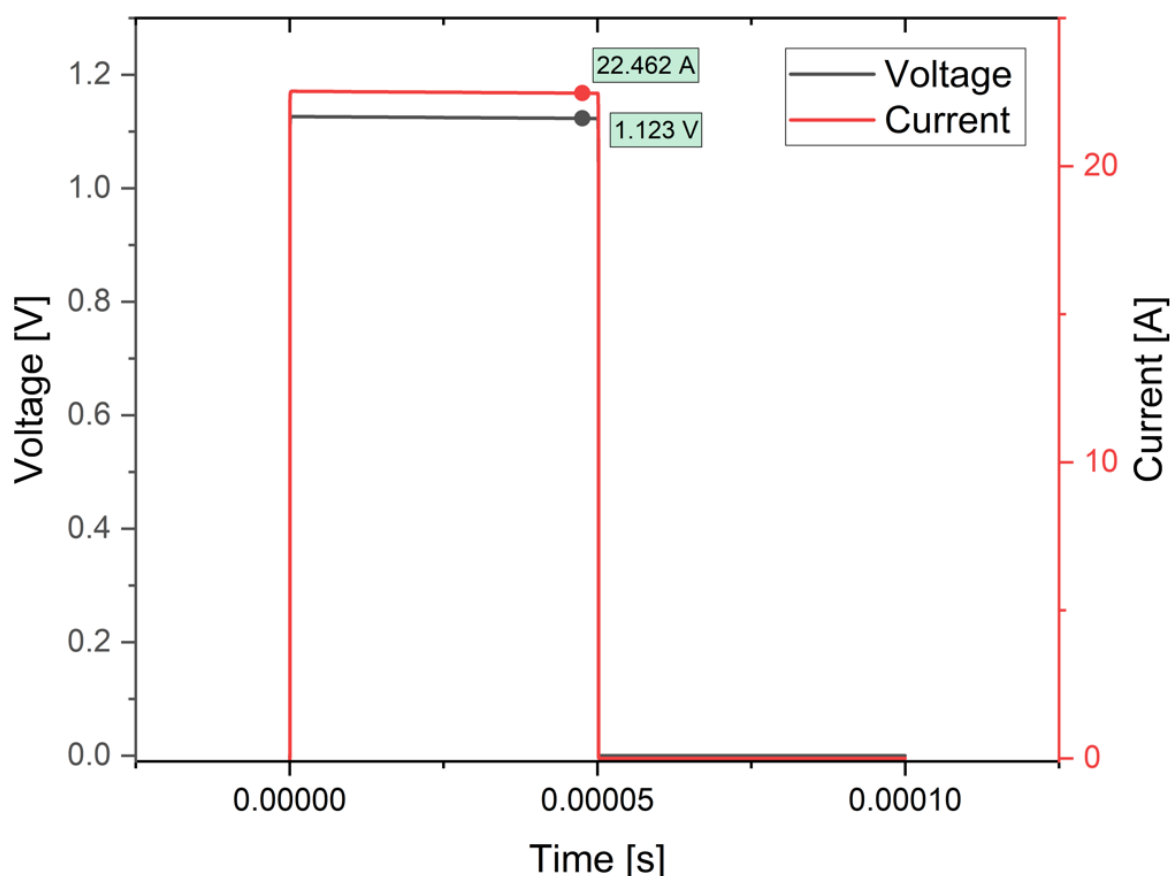


Figure 3.18: Cell voltage and current of Randles equivalent circuit (Fast acquisition)

Figure 3.19 shows the cell voltage and current signals utilising the slow acquisition settings used to calculate the charge transfer resistance and the double-layer capacitance.

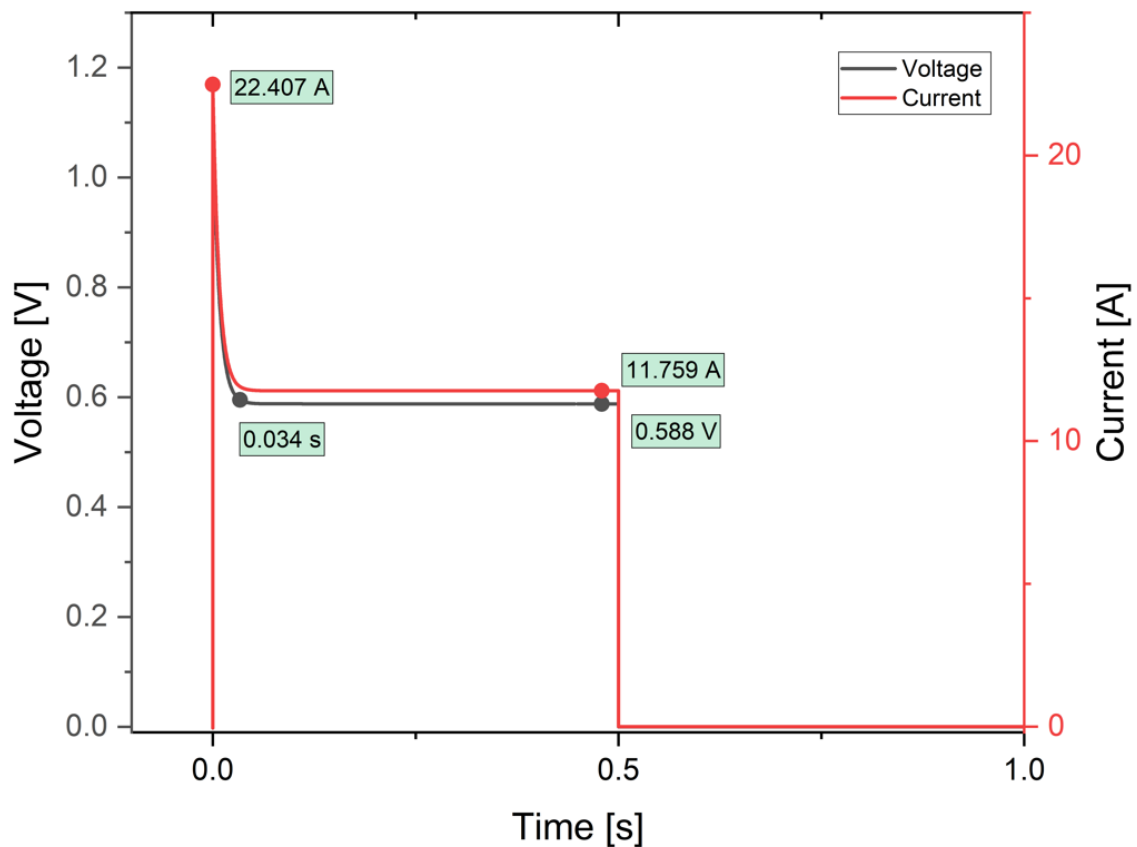


Figure 3.19: Cell voltage and current of Randles equivalent circuit (Slow acquisition)

Utilising the parameter results shown on both simulation graphs (recorded in Table 3.7), the electrical parameters of the Randles cell could be calculated, as seen in Table 3.8.

Table 3.7: Randles cell calculation parameter results

EEC parameter	Calculation parameter	Value - Simulation	Unit
R_m	V	1.12	V
	I	22.48	A
R_{ct}	V_0	0.59	V
	V_1	0.59	V
	I_0	11.76	A
C_{dl}	t_1	0.02	s
	t_0	0.50	s
	$V_{(t1)}$	212.16	V
	τ_{rc}	0.01	s

From Table 3.8, the error results are marginally small, which means that the NVR method was validated according to similar results obtained by Martinson *et al.* [19] for the same electrical parameter initialisation. For this analysis Simulink® and Matlab® were used, tested, and verified,

to analyse the voltage and current graphs and calculate the electrical circuit parameters of the Randles cell (section 0).

Table 3.8: Randles cell electrical circuit parameters

Equivalent Electrical circuit parameter	Simulated value	Calculated value - Simulated	Calculated value - [19]	Error between calculated and simulated values [%]	Martinson et al. [19] errors with respect to simulated values
R_m	50 mΩ	50.00 mΩ	50.04 mΩ	0.01	0.07
R_{ct}	50 mΩ	49.58 mΩ	49.96 mΩ	0.84	0.07
C_{dl}	300 mF	300.54 mF	300.21 mF	0.18	0.07

Current switching method

For this method, a series of steps must be followed to calculate the EEC parameters. These included Matlab® and Simulink®, which were used since it is much more convenient to import the actual PRBS from Python® into the simulation model. The calculation process of the electrical parameters for the equivalent electrical circuit can be seen in Figure 3.20.

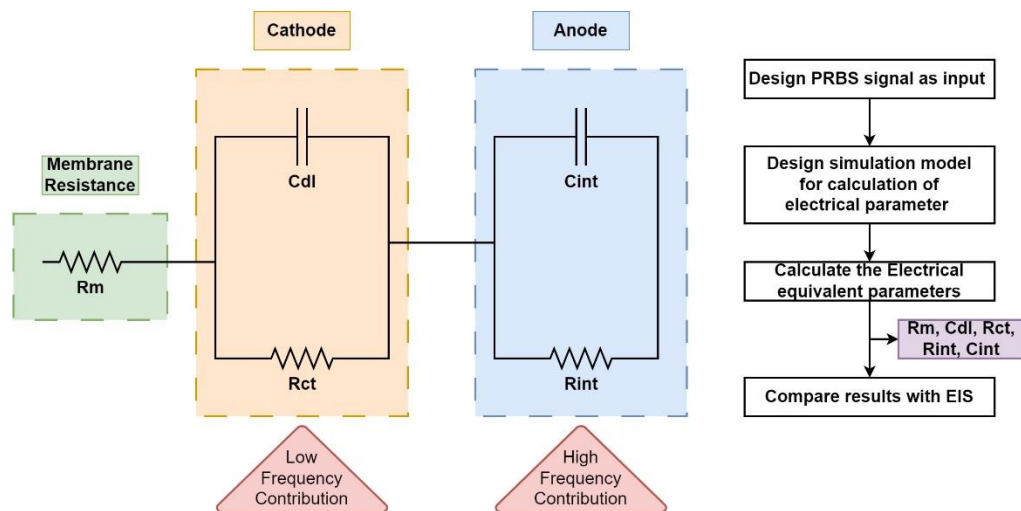


Figure 3.20: Current switching method

Figure 3.20 also shows the detailed electrical equivalent circuit highlighting the electrical components representing the PEMWE cell. The membrane resistance, as indicated in Figure 3.28, is a single series resistance within the electrical circuit quantified as the resistance against the flow of protons through the PTL layer of the cell. The membrane resistance is critical within the analysis of the cell. It can be easily influenced by factors such as temperature, ionomer content in the catalyst layer, membrane degradation and water content. High membrane resistance can also lead to reduced cell efficiency and current density, as well as increased cell voltage which can lead to cell damage. The cathode of the cell is represented by the first parallel branch of the circuit containing the double-layer capacitance and the charge transfer resistance.

This part of the circuit is responsible for the low-frequency contribution to the leftmost side of the Nyquist plot, as analysed from Figure 3.21. The next parallel branch shows the interfacial resistance and capacitance and is responsible for the high-frequency contribution within the Nyquist plot (the frequency distribution off the Nyquist plot starts at high Frequencies on the leftmost side of the plot and decreases further to the right).

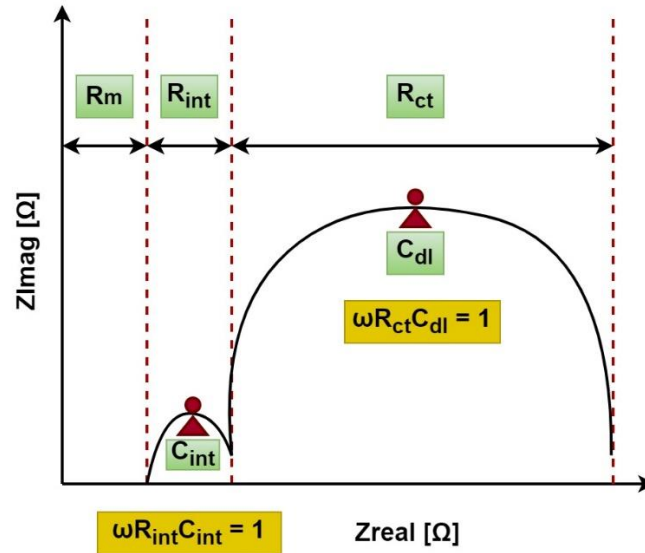


Figure 3.21: Nyquist plot for equivalent electrical circuit

Taking this into account, a model used to calculate the electrical circuit parameters could be designed using Simulink®. For this design, two Simulink® models were developed, namely a generating model and a calculating model. The generating model, as seen in Figure 3.22, was used purely for simulation testing purposes to generate the measured voltage and current signals, which were measured by the oscilloscope under real experimental conditions.

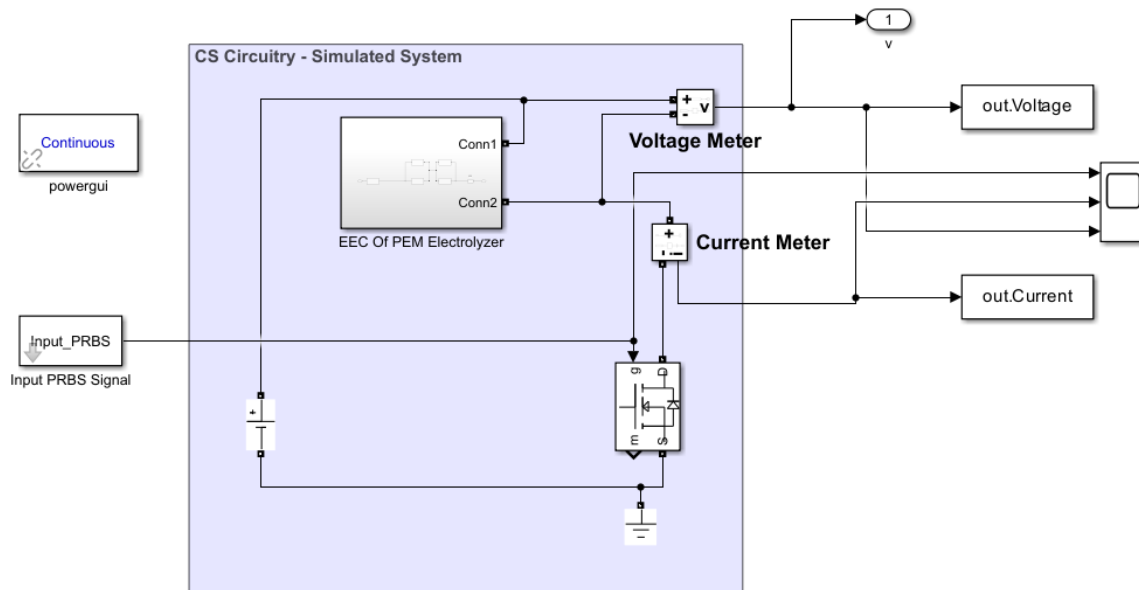


Figure 3.22: Base generating model for electrical parameter calculation

Figure 3.22, shows that the circuit diagram, represented in Figure 3.20, was added in conjunction with the perturbation signal generating circuitry. The PRBS signal was generated based on the workspace algorithm, as seen in the drive link in the appendix. Furthermore, the output voltage was measured across the cell, as seen in Figure 3.27, and was written to the workspace to be used as input to the calculation model, as seen in Figure 3.23. The same method was applied for the input current supplied to the cell.

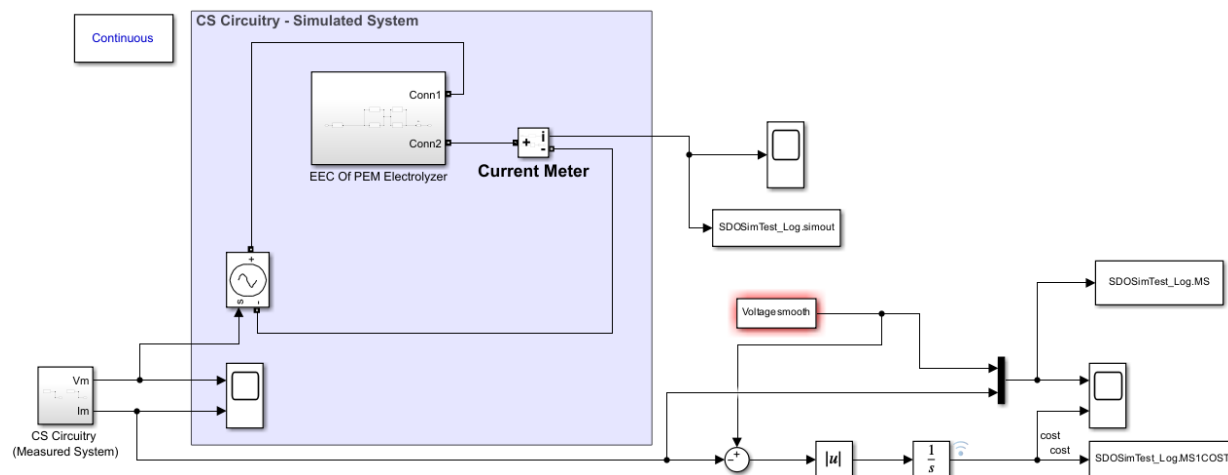


Figure 3.23: Base calculating model for electrical parameter calculation

The measured subsystem block represents the measured voltage and current signals that were imported from the oscilloscope to Matlab®. The internal blocks of this system can be seen in Figure 3.24.

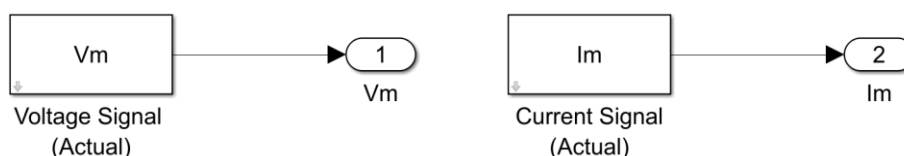


Figure 3.24: Internal layout of measured signal subsystem

The voltage and current signals measured from the actual cell were imported into Simulink® from the Matlab® workspace and connected to the system, as shown in Figure 3.24. Since the cell voltage and cell current were required to calculate the equivalent electrical circuit parameters, the measured current (measured via the oscilloscope) can be compared with that of the actual equivalent circuit simulation model's theoretical current by estimating the equivalent electrical circuit parameters namely R_m , R_{ct} , R_{int} , C_{dl} , and C_{int} . The actual simulation model is evident in the subsystem block of Figure 3.24 and Figure 3.25. The equivalent electrical parameters were then estimated by first using the mean square error method to determine the error between the actual measured cell voltage and the theoretical cell voltage, which takes the absolute value of the difference between the two signals and thereafter integrates the values over the sample size of the signals. From this, a built-in app within Simulink®, namely Response Optimiser, was used to

estimate the electrical parameters by matching the theoretical cell current to that of the actual measured cell current. A simulation example is shown in section 0.

Furthermore, from Figure 3.22, the equivalent electrical circuit parameters are initialised with randomised values. The initialisation is done by creating a starting point for the response optimiser to estimate the actual value of each coefficient. Typically, 150 iterations are used to minimise the error between the two signals. After the new coefficients were estimated, the equivalent electrical circuit parameters were imported into the Matlab® workspace from which the Nyquist and Bode plots are generated. The parameter results could then be compared to EIS by performing a similar experiment under similar conditions to that performed during CI.

Simulation example for calculating electrical parameters

The simulation example was required to ensure the validity of the simulation model and the accuracy of the results before experimental implementation can take place. For this example, Simulink® was used for both the calculated and simulated results. The simulated results were conducted by choosing a set of values for the electrical parameters. The values chosen are shown in Table 3.9.

Table 3.9: Current Switching method simulation parameter specification

Randles Warburg EEC parameters	Value
R_m	5 mΩ
R_{ct}	115 mΩ
R_{int}	2 mΩ
C_{dl}	300 mF
C_{int}	4 mF

The simulation values (Table 3.9), were inserted into the Randles Warburg equivalent electrical circuit designed in Simulink®, as shown in Figure 3.22. The complete simulation circuit, including the perturbation signal designed in section 3.2.1, the ideal NPN MOSFET switch and CS equivalent electrical circuit subsystem, are evident from Figure 3.22. The subsystem, including the circuit design of the equivalent electrical circuit, is shown in Figure 3.25.

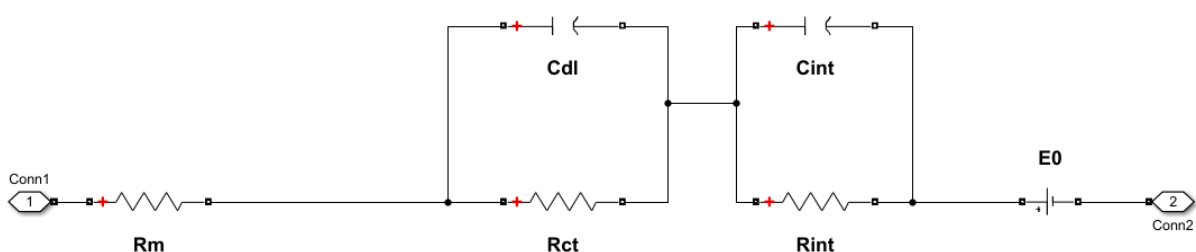


Figure 3.25: Randles equivalent electrical circuit

For this example, the input PRBS was executed for the full 1024 samples with a sampling time of 0.01 seconds, and the current and voltage measurements were taken according to the meter connections, as can be seen in Figure 3.22.

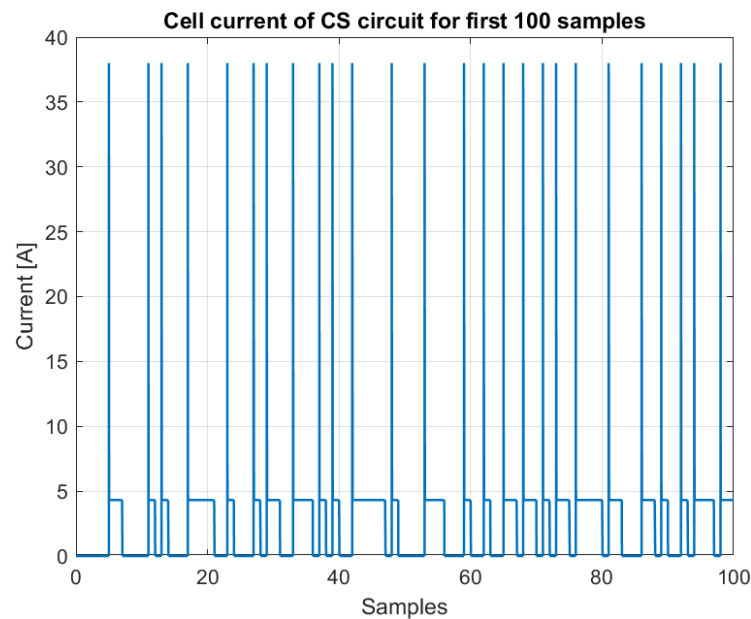


Figure 3.26: Cell Current measurement for first 100 samples of CS circuit

It is essential to note that the cell voltage measured for the electrical parameter calculations, is across the parallel branch of the circuit, including the membrane resistance and standard voltage. The cell current refers to the input current as seen by the membrane resistance. The effects of the standard voltage E_0 , as discussed in section 2.3.2, were also added to the circuit as 1.23 V [19, 117, 118]. After simulation of the circuit, the overpotential and current were recorded as seen in Figure 3.26 and Figure 3.27.

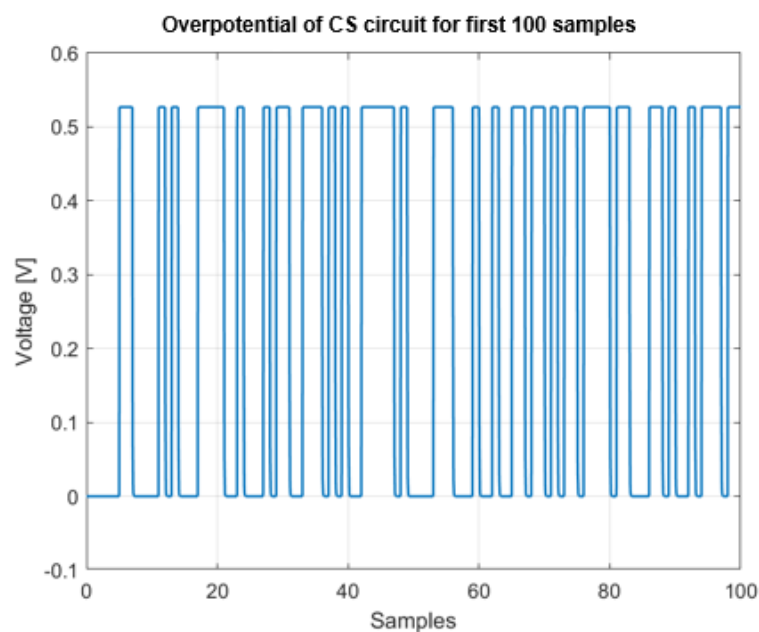


Figure 3.27: Overpotential measurement for first 100 samples of CS circuit

Now, using the overpotential and cell current measured in Figure 3.26 and Figure 3.27 and adding them to the simulation diagram shown in Figure 3.22, the new transfer function coefficients could be calculated from the estimated electrical circuit parameters, as estimated by using the Response optimiser from Simulink®. The calculated equivalent electrical circuit parameters can be seen in Table 3.10.

Table 3.10: Equivalent electrical circuit parameters calculations for CS circuit - Simulation

Randles Warburg EEC parameters	Theoretical value	Simulated value	Error [%]	Error [%] Martinson <i>et al.</i> [19]
R_m	5 mΩ	4.96 mΩ	0.88	6.00
R_{ct}	115 mΩ	115.06 mΩ	0.05	2.58
C_{dl}	100 mF	100.25 mF	0.25	4.26

The error between the equivalent electrical parameters, as seen in Table 3.10, was significantly smaller than that of Martinson *et al.* [19] simulated for the same theoretical values. Furthermore, it was not necessary to use the NVR method, proposed by Martinson *et al.* [19], to calculate the membrane resistance R_m since the error between the theoretical and simulated values was very close. Using NVR, Martinson *et al.* [19] obtained an error of 6%, which is much higher than the 0.88% obtained during current switching. This will be validated within section 3.4.

3.3 Cell testing using EIS for EEC parameter calculation

This section discusses the details of the testing of the PEMWE cell using EIS. The results obtained using this method are important since it must be used to validate the CI method, as discussed in Chapter 3. Therefore, different EEC models were developed to test the validity and fit of the simulation data to the actual cell response data. The fit is important since the Nyquist plot is mainly used for electrical parameter calculation, and without a good data fit, the electrical parameter results calculated will be inaccurate.

3.3.1 EIS simulation electrical parameter calculation

The Gamry used in section 0 can also be used to calculate the electrical parameters of the equivalent electrical circuit by fitting the data obtained in section 0 to the electrical circuit using Gamry Echem Analyst®. This software enables the user to design an electrical circuit and calculate its electrical parameters by fitting a curve to the simulated bode plot and Nyquist plot using the Levenberg-Marquardt algorithm. Eight different electrical circuit models were designed and tested to see which circuit could fit the Bode and Nyquist plots the best. Each circuit was fitted individually to the data seen in Table 3.1 and Figure 3.8. However, for this simulation experiment, only 0.1 A/cm² at 40 °C were shown. The magnitude and phase plot can be seen

within Figure 3.28. The dotted curve in Figure 3.28 shows the actual magnitude, phase and Nyquist plots of the cell discussed in section 4.1.1.1.

It is evident from Figure 3.28 that the actual Nyquist plot has some inductive features and a second curvature at high frequency, shifting the x-intercept to the left. However, this had to be further investigated since it would influence the calculation of the membrane resistance of the PEM electrolyser cell. Certain contributions might result from external parasitic stray contributions coming from the potentiostatic hardware and stray impedance of cables [119]. To explore it, shortened cell tests [120] were conducted using 0.25 mm gold-coated PTLs at room temperature, 40 °C, 60 °C and 80 °C. Thereafter, the Nyquist and Bode plots for each test were recorded.

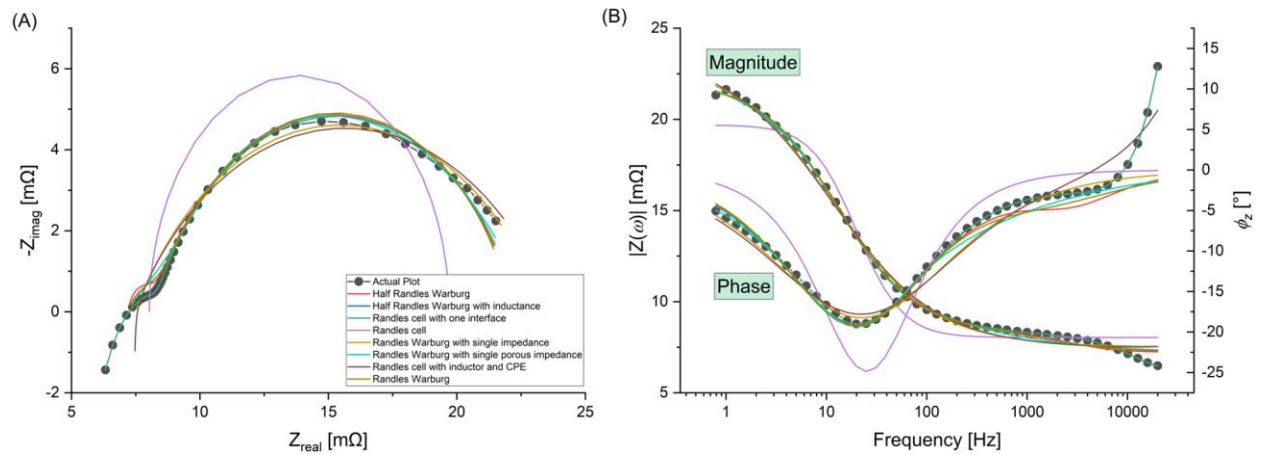


Figure 3.28: EIS EEC model data fitting: (A) Nyquist plot for 0.1 A/cm² at 40 °C and (B) Magnitude- and phase plot for 0.1 A/cm² at 40 °C

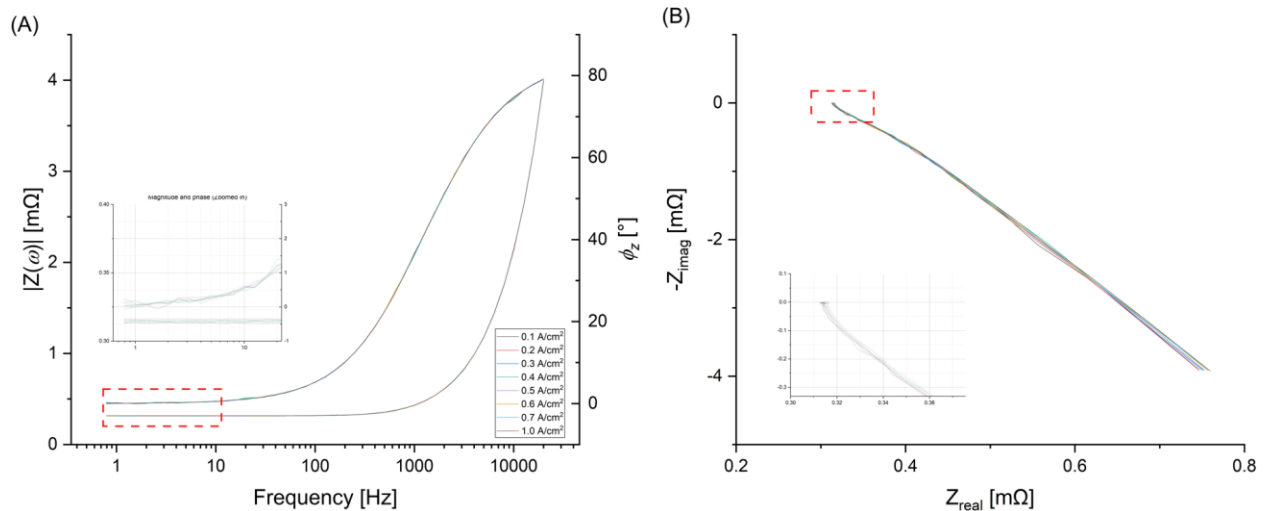


Figure 3.29: Shortened cell tests of 0.25 mm PTL at 40 °C: (A) Magnitude- and phase plot for 0.1 A/cm² and (B) Nyquist plot for 0.1 A/cm²

From Figure 3.29, the positive phase angle and the increase in impedance with an increase in frequency model the behaviour of an inductor. This phenomenon investigated can also be

identified as a displacement of the x-intercept, shown in Figure 3.28. However, further investigation was required to ensure that the inductive contribution was purely external and did not affect hydrogen evolution within the cell. For this, the influence of varying current density and temperature were observed. Figure 3.29 also shows that an increase in current density slightly increased the real part of the impedance of the PEMWE cell due to the local heat gradients (the cell/CCM heats locally when current density increases). However, no significant increases in the imaginary part of impedance was recorded. As for the increase in temperature, a slight increase in impedance were recorded. This phenomenon may be attributed to mechanical stresses within the cell, potentially caused by the deformation of the MEA plates during the bolt-torquing process used to tighten the cell [120].

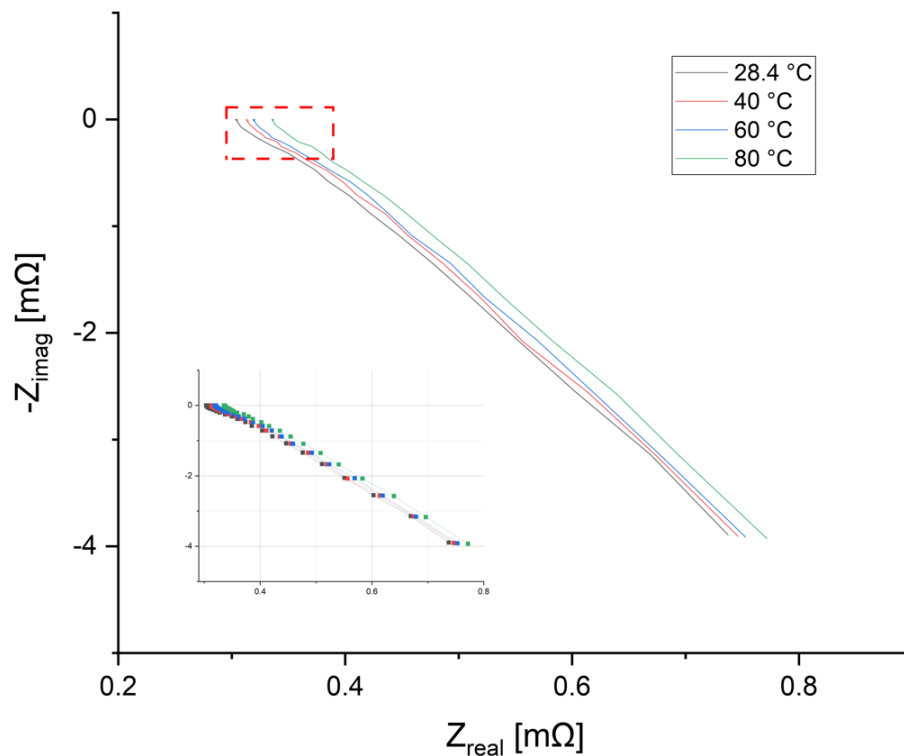


Figure 3.30: Shortened cell tests of 0.25 mm PTL at 0.1 A/cm² at different temperatures

However, based on these results, it can be hypothesised that the inductive contribution originates from external sources rather than from the hydrogen evolution. However, the hypothesis was mainly based on the observation of shortened cell tests. Furthermore, if hydrogen evolution had caused a more significant change in the real part of the impedance, it would have been observed during variations of the current density. Attempts were made to minimise the effects, such as cable twisting, cable shielding, minimal cable distance, etc. More on this are discussed in Chapter 4. Furthermore, each of the models, shown in the drive link in the appendix, has been fitted to the actual data curve, and the percentage error, mean absolute error (MAE), mean square error (MSE) and the root mean square error (RMSE) have been calculated for each curve. The bode plot error values for each model can be seen in Table 3.11.

Table 3.11: Bode plot EIS EEC model fit error results for 0.1A/cm² at 40°C

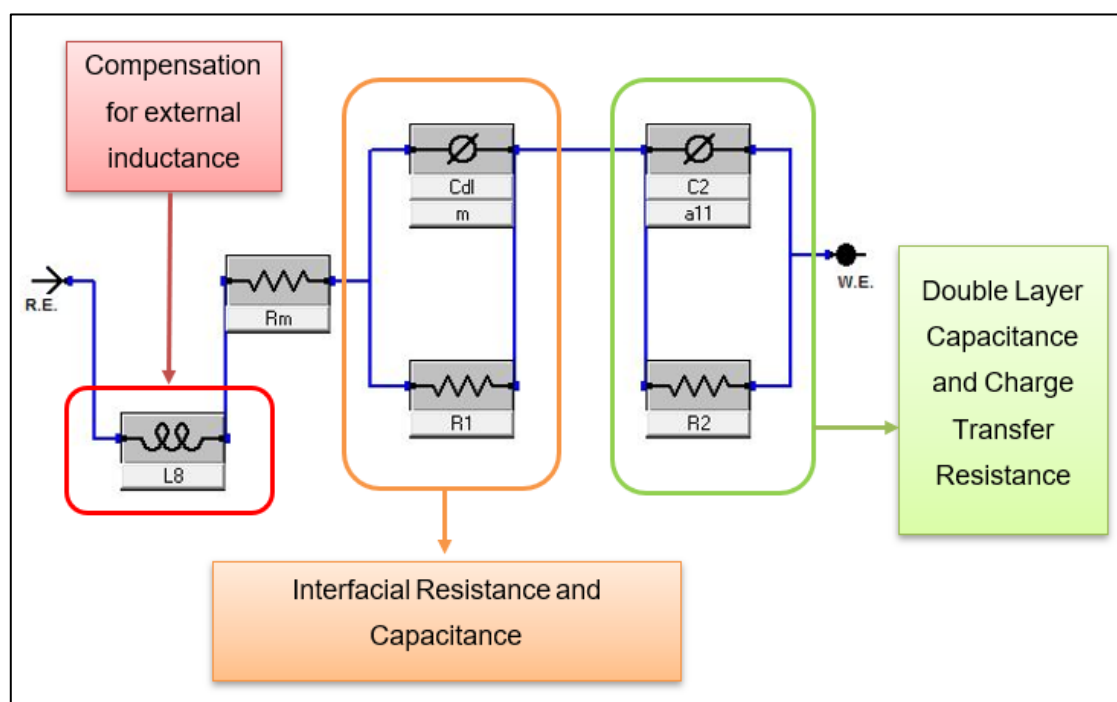
EEC	Plot	% Error [%]	MAE	MSE	RMSE
Half Randles Warburg	Magnitude	1.60	0.14	0.04	0.14
	Phase	38.31	1.39	7.56	1.39
Half Randles Warburg with series inductance	Magnitude	0.30	0.05	0.01	0.05
	Phase	2.45	0.21	0.10	0.21
Randles cell with a modified inductor and an additional interface	Magnitude	0.30	0.05	0.01	0.05
	Phase	2.48	0.21	0.10	0.21
Randles cell	Magnitude	6.56	0.72	0.75	0.72
	Phase	48.72	3.07	13.99	3.07
Randles Warburg circuit with Warburg impedance	Magnitude	3.05	0.28	0.12	0.28
	Phase	25.73	1.40	6.82	1.40
Randles Warburg circuit with porous Warburg impedance	Magnitude	2.07	0.18	0.07	0.18
	Phase	31.01	1.26	7.45	1.26
Randles cell with CPE	Magnitude	3.20	0.30	0.13	0.30
	Phase	37.26	1.38	2.80	1.38
Randles Warburg equivalent	Magnitude	1.73	0.15	0.05	0.15
	Phase	36.34	1.39	7.76	1.40

From the Bode plot data, it was evident that the EEC resulting in the best possible fit was the Randles cell with an additional interface. Furthermore, it is evident from Table 3.11 that the phase plot has very high percentage errors. This was due to the inductive contribution causing a sudden increase in phase degrees at high frequencies. Only the circuits compensating for this contribution with a series modified inductance will fit more closely to the actual plot. For electrical parameter calculations it is important to note the Nyquist plot errors, which are evident in Table 3.12.

Table 3.12: Bode plot EIS EEC model fit error results for 0.1A/cm² at 40°C

EEC	% Error [%]	MAE	MSE	RMSE
Half Randles Warburg	37.48	0.21	0.11	0.21
Half Randles Warburg with series inductance	2.49	0.06	0.01	0.06
Randles cell with a modified inductor and an additional interface	2.51	0.06	0.01	0.06
Randles cell	49.10	0.65	0.68	0.65
Randles Warburg circuit with Warburg impedance	25.42	0.22	0.11	0.22
Randles Warburg circuit with porous Warburg impedance	30.26	0.18	0.11	0.18
Randles cell with CPE	37.09	0.24	0.07	0.24
Randles Warburg equivalent	35.89	0.22	0.12	0.22

Based on the Nyquist plot error results, the Randles cell with an additional interface provided a closer fit to the actual plot than to the other circuits. The EEC circuit can be seen in Figure 3.31.

**Figure 3.31: Randles cell with an additional interface [121]**

The observed inductance with the circuit shown in Figure 3.31 had to be modified based on the shortened cell results discussed in Figure 3.29 and Figure 3.30. The modified inductance ensured accurate cathode and anode values within the circuit, preventing parameter overestimation. With closer inspection, Table 3.11 shows that Figure 3.31 delivers a close fit to the actual EIS data results from the PEMWE cell. This can also be seen from the magnitude and phase plot as shown in Figure 3.28. Therefore, EIS electrical parameter estimation was conducted using Figure 3.31.

3.3.2 PCB design

Utilizing the current switching development board, shown in Figure 3.15, the actual PCB could be designed according to the following specifications: Isolated ground between the primary circuit (opto-isolator input) and the secondary circuit (opto-isolator output and switch circuitry), component placement for minimisation of unwanted parasitic losses and harmonics, track layout design that will ensure the current path to be as short as possible for efficient power distribution as well as wire thickness to protect components against overcurrent.

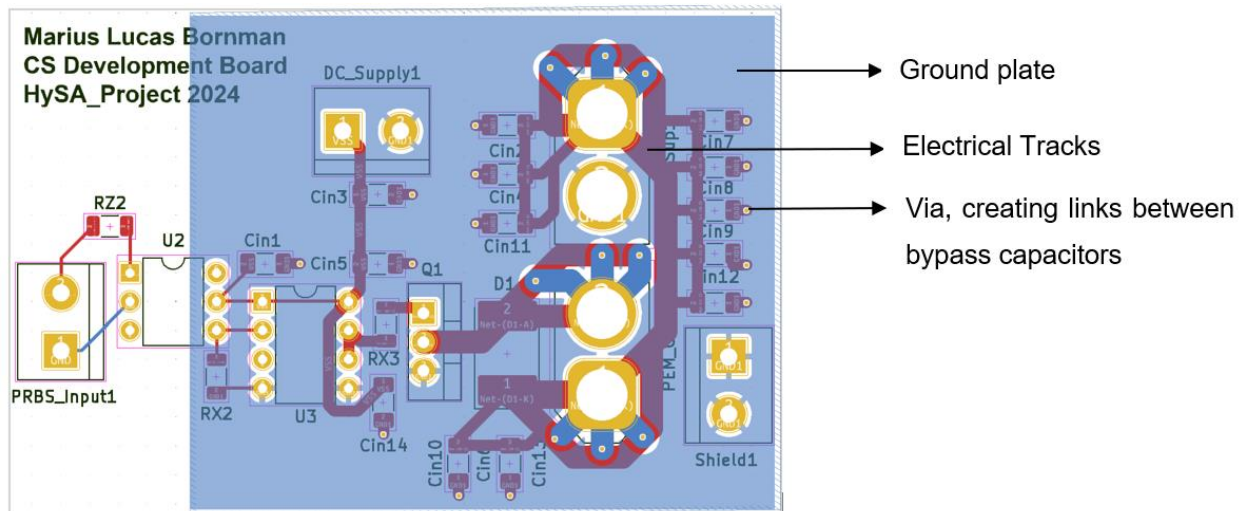


Figure 3.32: Current switching board PCB layout design

The actual design of the PCB, incorporating the specifications, as mentioned in the list above, can be seen in Figure 3.32. Considering the ground isolation, it can be seen that the righthand side of the PCB contains a blue-shaded area inserted on the bottom layer of the PCB from which all components after the opto-isolator were directly connected by virtue of a via. The leftmost side of the PCB utilises the ground of the PRBS supply. Furthermore, it can also be seen that the components were placed as close to one another as possible, enabling the track length to be short. The wire thickness was also designed to incorporate the currents that the components can handle. With this in mind, a preview of the PCB can be seen in Figure 3.33

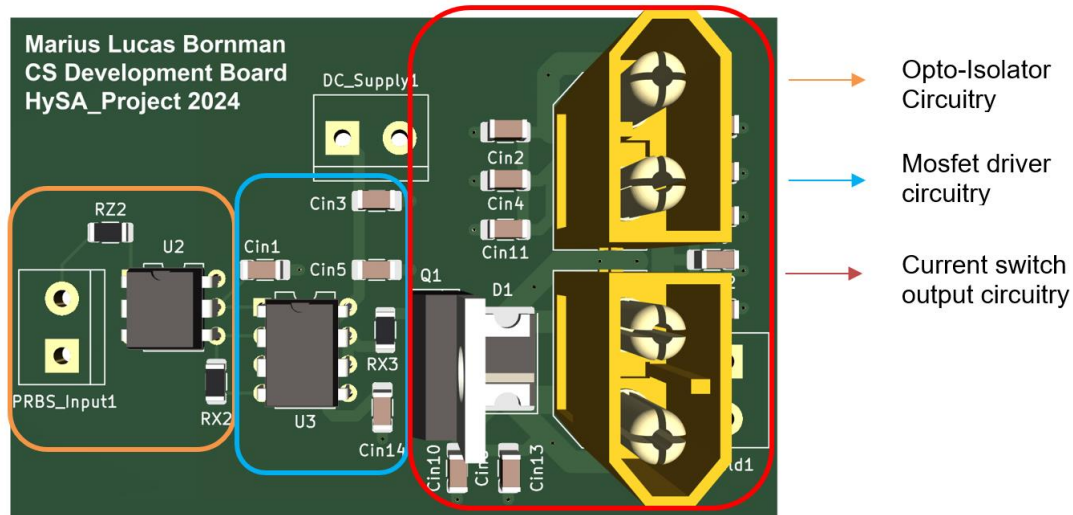


Figure 3.33: Current switching board PCB preview design

Figure 3.33 shows the different circuitries integrated to develop the current switching board. This included the opto-isolator circuitry for supply safety, the MOSFET driver circuitry responsible for attenuating the signal supplied to the switch, and lastly, the current switching output circuitry responsible for generating and delivering the PRBS output to the PEM water electrolyser terminal block.

3.4 Verification and Validation

For this project to work successfully, a model was required to calculate the equivalent electrical parameters of the desired PEM electrolyser cell, as explained in Chapter 1. Thus, during this chapter, a detailed simulation design was discussed to identify the process for parameter calculation. The designed methods were also verified against a similar existing model designed by Martinson *et al.* [19]. However, it was important to validate if the model operates for a range of electrical parameter values. Thus, by increasing and decreasing the electrical parameter values by -10% and 10%, as well as substituting values used by Martinson *et al.* [19], the sensitivity of the model could be validated. However, it was also essential to ensure that the new parameter values obtained via the model was correct. The error values were obtained by comparing the theoretical and simulated values. Furthermore, the error values obtained were compared to those obtained via section 0 since the model of Martinson *et al.* [19] already proved to deliver the desired model parameters accurately.

3.4.1 CI model verification using similar parameter values as Martinson *et al.* [19]

Five different experiments were conducted using similar values as those of Martinson *et al.* [19] to verify if the model delivered results that closely correlate to the literature. Thereafter, the simulation errors were compared to see how the model sensitivity compared to that of the model designed by Martinson *et al.* [19]. The electrical parameter values that were used for the different simulation testing can be seen in Table 3.13.

Table 3.13: Verification of model parameter calculations

Randles Warburg EEC parameters	First experiment	Second experiment	Third experiment	Fourth experiment	Fifth experiment
R_m	10 mΩ	15 mΩ	20 mΩ	25 mΩ	30 mΩ
R_{ct}	100 mΩ	90 mΩ	80 mΩ	75 mΩ	72 mΩ
C_{dl}	125 mF	150 mF	175 mF	200 mF	225 mF

Each experimental model was initialised with the parameters as shown in Table 3.13, utilising the same models and initialisation process as discussed in section 0. The response optimiser, utilising the least square method, had to run twice again to minimise the error between the measured cell current and simulated cell current. The results obtained for the electrical parameters during each experiment can be seen in Table 3.14.

Table 3.14: Simulated parameter verification results

Randles Warburg EEC parameters	First experiment	Second experiment	Third experiment	Fourth experiment	Fifth experiment
R_m	9.92 mΩ	14.90 mΩ	19.91 mΩ	24.85 mΩ	29.77 mΩ
R_{ct}	100.26 mΩ	89.97 mΩ	79.68 mΩ	74.86 mΩ	71.82 mΩ
C_{dl}	125.29 mF	150.08 mF	175.06 mF	199.76 mF	224.03 mF

During each experiment, the response optimiser was executed until the values converged. Table 3.15 shows the error values obtained for each of the experiments. It can be seen that by adjusting the electrical parameter values, the errors stayed below 5%. The largest error for the electrical parameters occurred at experiment five which was 4.60% which was still significantly lower than the maximum errors obtained by Martinson *et al.* [19], as seen in Table 3.10. The errors in comparison to that obtained by Martinson *et al.* [19] were significantly lower. However, the diffusion time constant's error became quite significant as the theoretical value increases. Thus, according to the results obtained for the simulation mode, it was safe to assume that the model was accurate when calculating the electrical parameter values for the Randles Warburg equivalent circuit model.

Furthermore, it can also be seen by adjusting the electrical parameter values that the other electrical parameters stayed relatively constant, which means that the model was not sensitive to changes in a wide range of electrical parameter values.

Table 3.15: Electrical parameter value theoretical versus simulated error verification

Randles Warburg EEC parameters	First experiment: Error [%]		Second experiment: Error [%]		Third experiment: Error [%]		Fourth experiment: Error [%]		Fifth experiment: Error [%]	
	Sim	[19]	Sim	[19]	Sim	[19]	Sim	[19]	Sim	[19]
R_m	0.85	2.10	0.66	4.64	0.44	2.97	0.59	1.90	0.77	1.47
R_{ct}	0.26	2.50	0.34	2.53	0.40	2.50	0.18	2.30	0.25	2.24
C_{dl}	0.23	4.15	0.05	4.26	0.03	5.18	0.12	6.55	0.43	8.01

3.4.2 CI model validation under maximum and minimum range adjustment

To ensure that the model will operate accurately within a specific range of parameter values, testing the model for a possible absolute maximum and absolute minimum range of electrical parameter values for a specific cell was essential.

Table 3.16: Design parameters for validation experiment

Randles Warburg EEC parameters	Theoretical base values	Absolute maximum [10%]	Absolute minimum [-10%]
R_m	5 mΩ	5.5 mΩ	4.5 mΩ
R_{ct}	115 mΩ	126.5 mΩ	103.5 mΩ
C_{dl}	100 mF	110 mF	90 mF

According to the cell specifications discussed in Chapter 4, a maximum and minimum range of approximately 10% on the base values discussed in section 0 would suffice. The theoretical electrical parameters used to initialise the model can be seen in Table 3.16. By initialising the simulation model with the parameters given in Table 3.16, the simulation parameters could be determined, as seen in Table 3.17. As can be seen from Table 3.17, the errors between the theoretical and simulated values were marginally small.

Table 3.17: Validation simulation results

Randles EEC parameters	Absolute maximum simulation – [10%]	Error between absolute maximum theoretical and simulation [%]	Absolute minimum simulation [-10%]	Error between absolute minimum theoretical and simulation [%]
R_m	5.46 mΩ	0.73	4.46 mΩ	0.90
R_{ct}	126.96 mΩ	0.36	103.61 mΩ	0.11
C_{dl}	110.52 mF	0.47	90.17 mF	0.19

Based on the limit test, it can be said that the model still delivers close proximation results with a maximum and minimum range of approximately 10% on the base values discussed in section 0.

3.5 Conclusion

The Chapter started with the conceptual design of the current switching board and analysis algorithm. The experimental process and system requirements for the practical setup were also discussed, as will be needed for the detailed experimental design shown with the flow- and architecture diagram. The following section discusses the detailed design of the project and is divided according to the perturbation signal design, the current switching board design, and analysis algorithm design. The perturbation signal was designed using Python® and STM32Cube IDE®. Three perturbation signals were designed and integrated to generate a frequency band of 0.8 Hz up to 20 kHz. Thereafter, the current switching board was designed using LTSpice® for simulation and Kicad® for PCB design.

Furthermore, the algorithm for calculating the equivalent electrical circuit parameter was designed using Simulink® and Matlab®. The algorithm was tested and designed for both the NVR and CS method. However, it has been noted that the NVR was not required to calculate the membrane resistance as the error between the membrane resistance calculated through the CS method, shown in Table 3.10, was significantly smaller than that of the error calculated by Martinson *et al.* [19] using the NVR method. This simplified the calculation process drastically, as only a single method could calculate all the required parameters. A suitable EIS EEC model was also designed, tested and validated and was similar to that used for the CI electrical parameter calculations. Lastly, the CI model has been validated by performing a sensitivity analysis on the simulation model to see if the electrical parameter errors stayed below a 5% error range. However, it was evident from both simulation experiments that each of the equivalent electrical parameters was calculated with an error below 5%. This shows that the simulation model can calculate the equivalent electrical parameters of a PEM water electrolyser using the current interrupt method.

Chapter 4 includes the physical implementation and testing of the experimental setup and CI method. The model was then tested and compared to EIS performed under the same experimental conditions.

CHAPTER 4: PRACTICAL IMPLEMENTATION AND TEST RESULTS

This chapter entails the practical implementation of the current switching method, as discussed and tested in Chapter 3.

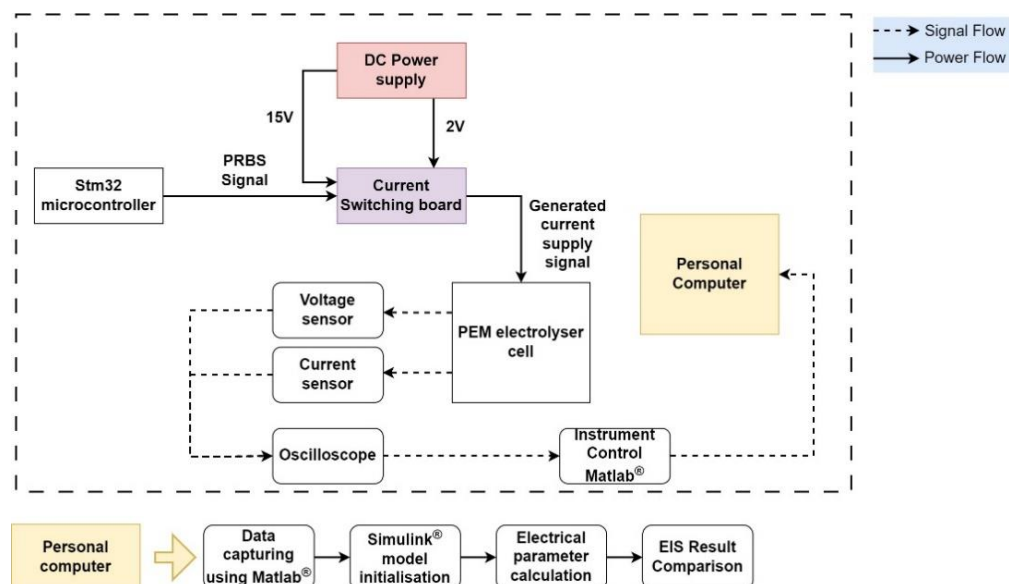


Figure 4.1: System overview

The current switching method was tested by validating the results using EIS under similar experimental conditions. Figure 4.1 provides a system overview for each element of the current switching method.

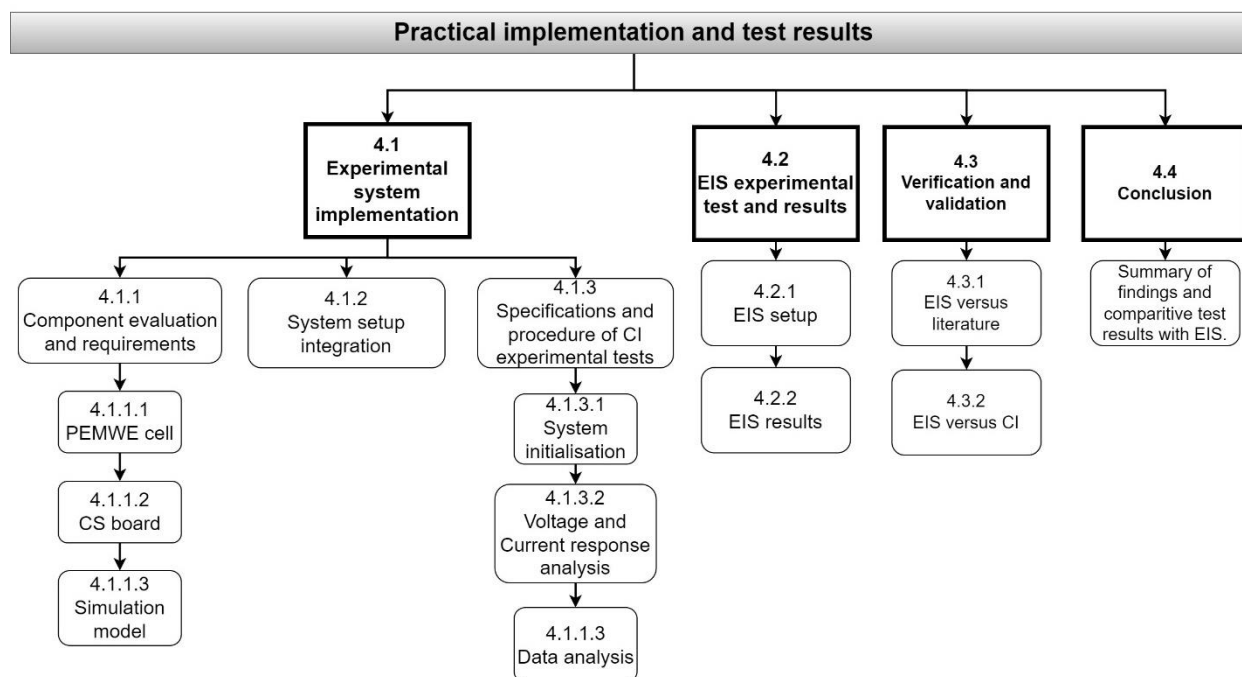


Figure 4.2: Chapter 4 sections layout

The system overview, highlighted in Figure 4.1, shows a detailed flow of the typical current switching method procedure that was followed to deliver results that could be compared to EIS. The personal computer and current switching board, highlighted in Figure 4.1, are the main focus of this chapter as they were responsible for delivering the results used to validate the actual method. The section layout for this chapter is outlined in Figure 4.2.

4.1 Experimental system implementation

In this section, the important components of the current switching method are discussed and evaluated before system integration. After evaluation and component integration, the specifications and requirements for the experimental setup are discussed.

4.1.1 Component evaluation and requirements

Before integration, a thorough discussion is required to ensure that each component functions correctly.

Table 4.1: PEMWE cell characteristics and specifications

PEMWE cell characteristics and specifications	Value	Unit
Membrane electrode assembly specifications		
Membrane type	Nafion 115	
Membrane area	25	cm ²
Membrane thickness: Dry	125	μm
Catalyst type: Anode	IrOx (Tanaka)	
Catalyst type: Cathode	Pt/HSC (High Surface Carbon)	
Catalyst loading: Anode	~ 2.0	mg IrOx/cm ²
Catalyst loading: Cathode	~ 0.15	mg Pt/cm ²
Porous transport layer specifications		
PTL anode uncoated thickness	600	μm
PTL cathode uncoated thickness	500	μm
PTL type: Anode and Cathode	Sintered titanium coated with ~ 70 nm Pt via magnetron deposition	
Water input specifications		
Water flow rate	10	ml/min
Water inlet temperature	40 - 80	°C
Electrical input specifications		
Voltage supply	1.8	V
Current supply: Maximum	2	A/cm ²

The components that were evaluated included the physical PEM electrolyser cell, CS development board, DC power supply requirements, and the sensory circuit and cables. These components are clearly highlighted in Figure 4.1 and are discussed under the respective headings below.

4.1.1.1 PEM water electrolyser cell

The PEM water electrolyser cell used for these experiments was specifically designed for the test bench station used for the final experiments. Table 4.1 summarises the cell characteristic. Furthermore, water temperature was controlled automatically by the test bench station, making it easier to keep the temperature constant during each experimental procedure.

PEMWE cell pressure distribution testing

This section focusses particularly on the critical role of proper active area pressure in for optimising performance and ensuring safe operation. The assembly process involved carefully layering components, including the membrane electrode assembly (MEA), current collector plates, gaskets, PTLs, and endplates. Each component plays a crucial role in facilitating the electrochemical reaction, managing water transport, and ensuring proper electrical contact.

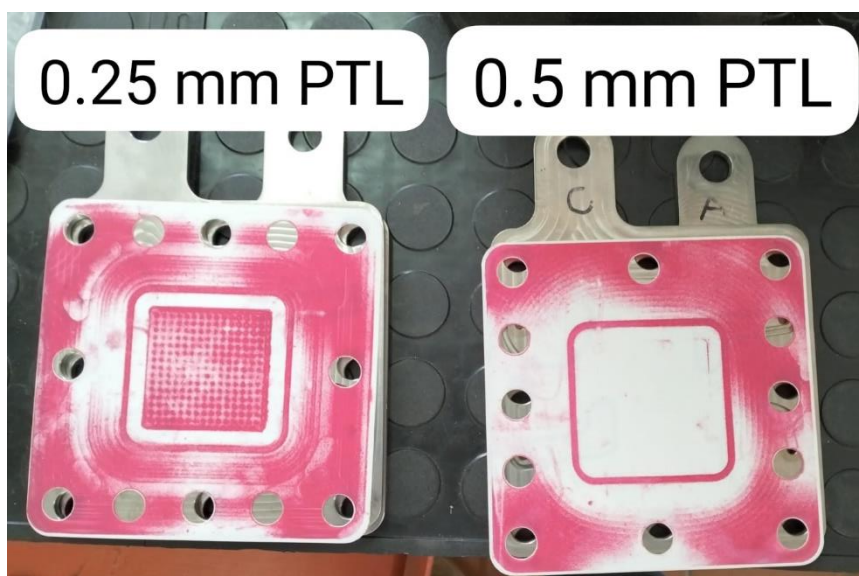


Figure 4.3: Pressure distribution of PEMWE cell with two different PTL sizes

Thus, for the cell assembly, two different thickness PTLs were tested to identify which PTL will ensure proper pressure distribution across the active area of the cell. For each of the two distribution tests, each layering component was properly cleaned and then placed according to the cell assembly specifications. However, instead of inserting a membrane in between the two collector plates of the cell, pressured paper was used. For each of the two PTLs, the cell was torqued at 30 Nm. The pressure distribution (Figure 4.3) showed that the 0.25 mm PTL had a very good pressure distribution across the active area of the cell. As for the 0.5 mm PTL, there

was no pressure distribution across the active area of the cell. Thus, the 0.25 mm PTL was inserted during the final cell assembly.

Cell conditioning procedure for PEMWE cell

The conditioning, also called activation procedures, of the PEM water electrolyser cell plays a pivotal role in the dependability of the performance feedback of the cell and is defined as the time from the first activation of a membrane electrode to its beginning of life [122]. This procedure is essential since it can be used to reverse any losses that occurred after a period of operation [122]. Different preparation strategies are preferred depending on the type of catalyst layers of the PEM water electrolyser. [122] argued that the typical activation duration ranges between 30 minutes up to an hour. Further research was conducted by [122] to determine the efficient duration for various activation methods and membrane electrocatalysts. Further approaches to activate the membrane electrode of the PEM electrolyser cell are discussed by [58, 123, 124, 125].

Table 4.2: PEMWE cell conditioning procedure

Activation method	Description	Activation specification
Water flow and heating	Connect the PEM electrolyser cell to experimental setup and apply water flow and temperatures until operating conditions stabilised.	1) Apply water flow to anode and let cell hydrate for 1 hour. 2) Water and cell temperatures specified either at 60 °C or 80 °C.
Cell conditioning procedure	Condition cell based on specifications acquired via manufacturer.	3) 12 minutes at 0.06 A/cm ² galvanostatic mode at 60°C and 80°C cell temperature.
Cell performance evaluation	Generate VI curves under current controlled conditions from low to high current densities up until 0.91 V.	1) Generate VI curve at water and cell temperature of 40 °C. Step size of 0.1 A/cm ² from 0.1 A/cm ² to 0.6 A/cm ² . 2) Generate VI curve at water and cell temperature of 60 °C. Step size of 0.1 A/cm ² from 0.1 A/cm ² to 0.9 A/cm ² . 3) Generate VI curve at water and cell temperature of 40 °C. Step size of 0.1 A/cm ² from 0.1 A/cm ² to 0.9 A/cm ² . 4) Perform EIS measurement applying AC voltage at 10% of active area (2.5 V), a DC voltage of 25 V and a frequency sweep from 10 mHz up to 20 kHz.

For the cell discussed in Table 4.1, a few tests were conducted in order to evaluate its performance. The tests conducted can be studied in Table 4.2. Figure 4.4 shows that under

constant voltage control, the PEM water electrolyser cell stays constant over time at the applied current density of 0.06 A/cm^2 .

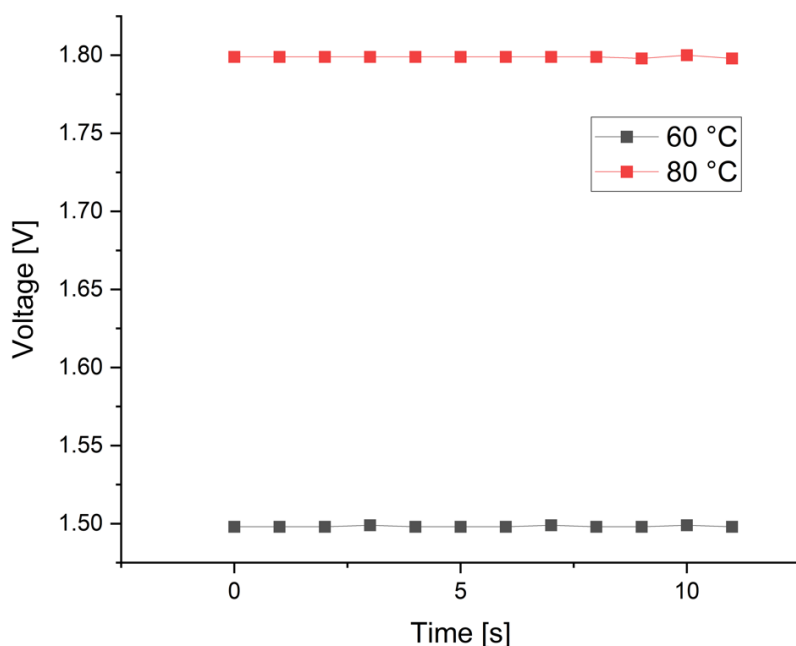


Figure 4.4: Activation procedure for cell conditioning

The stability of the cell operation ensured that the membrane was operating as intended and that there was no short circuiting between the catalyst layers of the cell. According to [122], the cell is successfully conditioned, however, must still be evaluated to ensure that it operates correctly when subjected to current density variations, as seen in Figure 4.5.

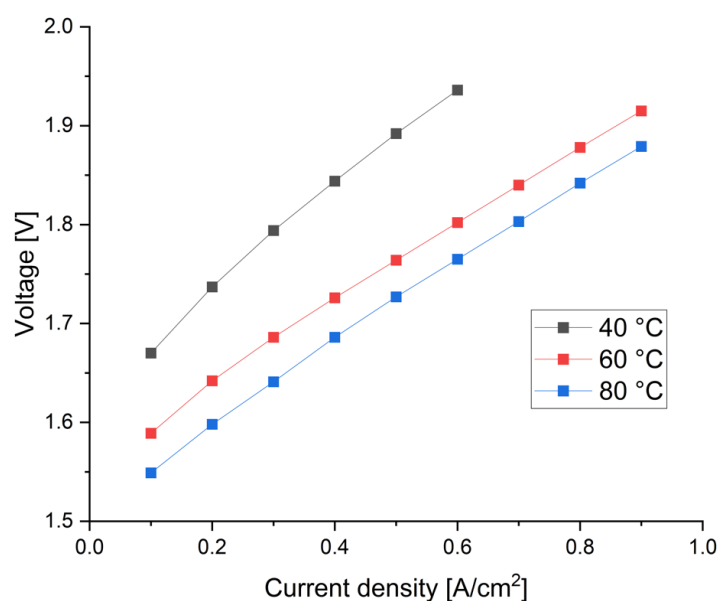


Figure 4.5: Activation procedure for cell performance evaluation

Figure 4.5 highlights the reference polarisation curves for the cell under three different temperatures and was obtained by increasing the current density in 0.1 A/cm^2 increments until the voltage reached approximately 1.91 V for 40 and 60°C . It can be seen at 40°C the optimum voltage was reached already at 0.6 A/cm^2 . In contrast, the polarisation curves for 60°C and 80°C only reached approximately 1.91 V at 0.9 A/cm^2 . Thus, at 40°C , the overpotential was the highest and decreased as the temperature increased.

4.1.1.2 Current switching development board and sensory cables

The current switching board, designed and discussed in detail in section 3.3.2, was responsible for generating the PRBS signal that controlled the current flowing to the PEM water electrolyser cell. The algorithm used to generate the desired PRBS signal, as discussed in section 3.2.1, can be seen in the drive link in the appendix. The final current switching development board can be seen in Figure 4.6.

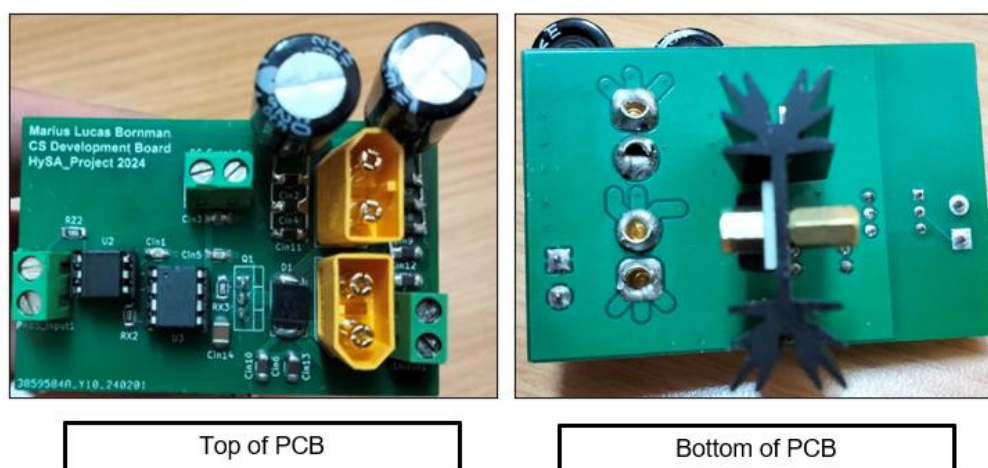


Figure 4.6: Actual current switching development board

The current switching board received a 5 V PRBS signal supply (opto-isolator circuitry input), a 15 V DC supply (MOSFET driver circuitry), and a 1.8 V DC input supply (current switching input circuitry).

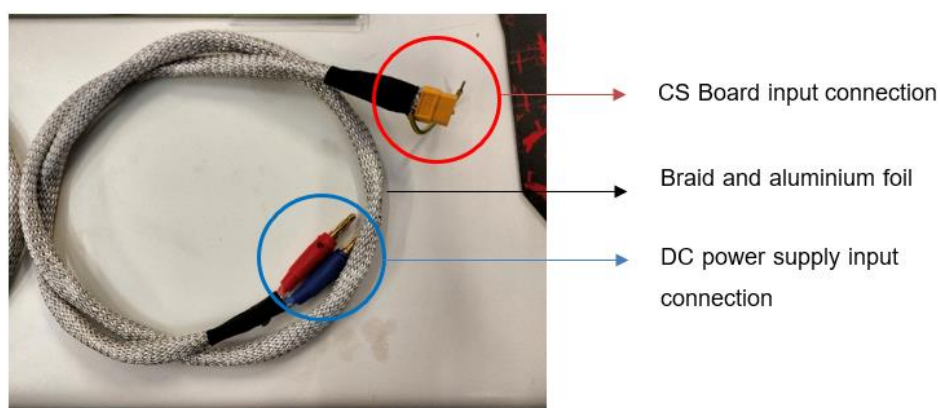


Figure 4.7: DC power supply cable prepping

The DC voltage, supplied to the current switching board, was supplied through specially designed cables responsible for minimising eddy current losses, noise generation and signal interferences. This was achieved by first twisting the cables until a firm twist is formed at each cable end. The cables, including a shield wire mounted on the current switching board responsible for keeping the inductance as low as possible across the wires, were then covered with aluminium foil and fiberglass nickel-plated copper braid. The designed wires can be seen in Figure 4.7. The current switching development board connector and shield wire can be seen in Figure 4.8.

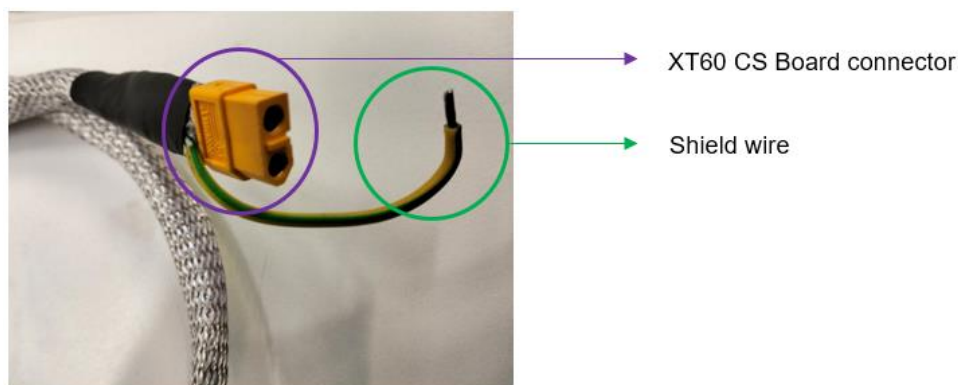


Figure 4.8: CS board connector

The cable connecting the PEM water electrolyser cell, discussed in section 4.1.1.1, to the CS development board, was prepped similarly to that of Figure 4.7. Furthermore, to ensure that the DC output voltage supplied to the PEM water electrolyser cell contained minimal noise, two high capacitance low voltage capacitors were added to the DC input supply side on the CS development board to filter out noise generated via the DC power supply. The two capacitors (Noise filters on output) and a heat sink responsible for heat dissipation of the MOSFET are seen in Figure 4.6 and were the only difference between the simulation (Figure 3.33) and the actual CS development board.

Furthermore, to ensure that the actual measurements via the designed cables were accurate, the impedance of the cables had to be considered since it can influence the electrical parameter calculations. Thus, it is very important where the cell voltage and current measurements are described. When measuring the cell voltage and current on the supply side of the cell before the cable, it is critical to calibrate and calculate the impedance of the cable. The impedance must then be considered when calculating the final electrical parameter values. However, by measuring the cell voltage and current after the supply cable, as shown in Figure 4.9, the impedance of the cable can be discarded since the effect of the cable does not influence the actual measurements. Thus, cable calibration was not considered. The inductive contribution to the EIS measurements, as outlined in Chapter 3, was incorporated into the electrical circuit design.

4.1.1.3 Data measuring and feedback setup for CI

The data measuring and analysis procedure was a critical component of this project, as it delivered the results required to analyse the current interrupt method.

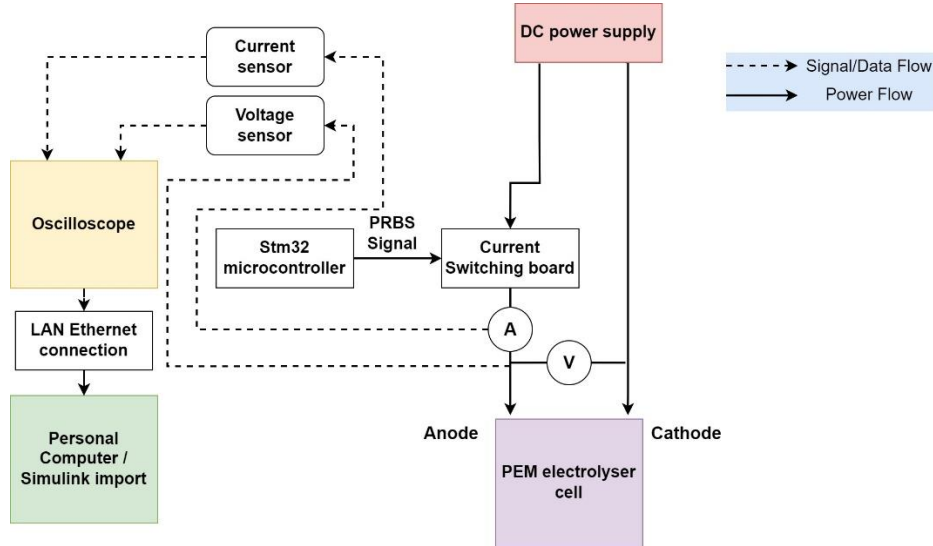


Figure 4.9: Data recording diagram from CI experimental setup

The data recording loop included an oscilloscope that received its data via a current and voltage probe, as can be seen in Figure 4.9. The oscilloscope was set to record a total of 125 MS per channel. The sampling rate was set to 250 kS/s to minimise the effects of aliasing, as discussed by the Shannon Nyquist sampling theorem. The current and voltage were recorded and stored on the oscilloscope. Matlab® was then used to extract these current and voltage signals from their respective channels through the Instrument control toolbox®. For the toolbox to be successfully connected to the oscilloscope, a LAN cable was connected between the personal computer and the scope. Two functions, namely “readwaveform” and “storewaveform”, were utilised to extract and store the waveforms from each channel as a Matlab® file. The data was then imported into Matlab®/Simulink® as discussed in section 3.2.2.4, where the electrical parameters of the electrical circuit could be calculated. The parameters were calculated for nine different experiments each done using a similar approach with varying experimental parameters.

4.1.2 CI experimental setup and integration

Different setups were integrated and connected for the experimental procedure to test the CI method. The first setup pertains to the test bench station utilised for water supply to the PEMWE cell, hydrogen storage and cell temperature regulation. The experimental setup and wiring diagram for the CI method used can be seen in Figure 4.10. The test bench consists of a proper water supply system with variable supply pressure that ensured adequate water circulation. The anode and cathode on the cell were then properly connected to the test bench station, as seen in Figure 4.10. Water temperature control on the test bench station was done internally by controlling

the specific temperature of the cell for each experiment. However, the accuracy of this depends solely on the surrounding environment and temperature control efficiency of the Greenlight Test station®.

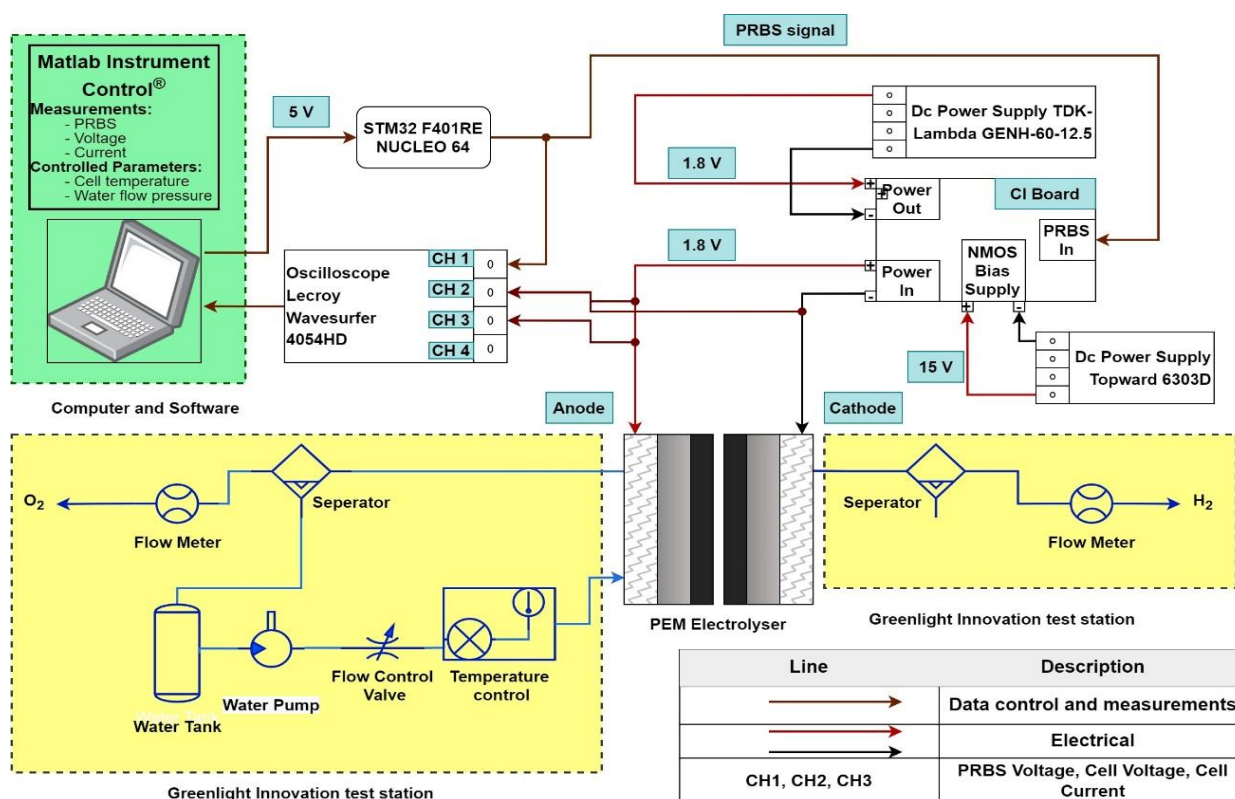


Figure 4.10: CI experimental setup and wiring diagram

The experimental setup further required two external DC power supplies, which were used to supply 15 V to the current switching development board (a limited current supply of 3A) and 1.8 V to the PEM water electrolyser cell (as discussed in section 4.1.1.2).

Table 4.3: Experimental condition specifications

Experiment	Current density [A/cm ²]	DC current [A]	Temperature [°C]
1	0.1	2.5	40
2	0.2	5.0	40
3	0.3	7.5	40
4	0.1	2.5	60
5	0.2	5.0	60
6	0.3	7.5	60
7	0.1	2.5	80
8	0.2	5.0	80
9	0.3	7.5	80

The cables prepared in section 4.1.1.2 were used to connect the electrolyser cell to the DC power supply as well as to the current switching development board. The development board was powered and controlled using the personal computer, as seen in Figure 4.10. The scope was also connected so that the PRBS supply from the CI development board was measured on channel one, the current flowing to the cell was measured on channel two, and the voltage across the cell was measured on channel three. The measurement channels were evident from the circuit diagram shown in Figure 3.2. Each experiment was conducted by firstly ensuring that all water and electrical connections to and from the electrolyser cell was proper and safe. Thereafter, the electrical connections to and from the current switching board were inspected to ensure that all wiring was properly isolated and connected. After all connections were validated, the water was supplied to the PEM electrolyser cell.

After the hydration period of approximately 10 minutes, the current was adjusted on the DC power supply to the specified current density shown in Table 4.3 and the system was switched on. After each experiment the PRBS, voltage and current waveform were recorded and further analysed in Simulink® in order to calculate the equivalent electrical parameters discussed in section 0. In this section, the first experiment is discussed in detail, and thereafter, a summary of the results for the other two experiments are given. Detailed results of each experiment can be found in the drive link in the appendix.

4.1.3 CI experimental tests and results

This section pertains to the experimental test procedure for calculating the equivalent electrical parameters for the PEMWE electrolyser cell discussed in section 4.1.1.1.

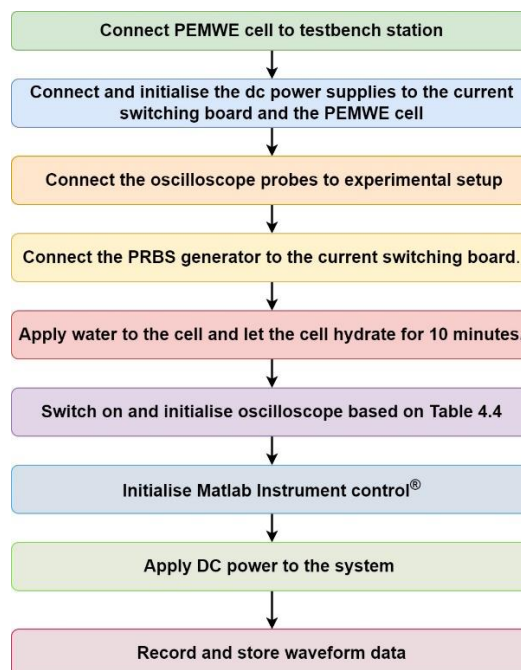


Figure 4.11: CI experimental approach

A detailed discussion is conducted on generating the voltage and current waveforms used to determine the cell parameters. The analysis of these waveforms using Simulink®, verified from section 3.2.2.4, are also discussed. However, each subsystem within the experimental setup needed to be tested to ensure the desired results were delivered. This included the PRBS generator, CI development board, cell voltage and current measurement, Simulink® data analysis, and parameter calculation.

4.1.3.1 System initialisation and setup

The setup integration, as discussed in section 4.1, contains important initialisation parameters before the experimental procedure can start. One of these setups includes the oscilloscope initialisation given in Table 4.4.

Table 4.4: Oscilloscope experimental setup

Oscilloscope setup	Initialisation value
Channel 1	PRBS signal
Channel 2	Voltage signal
Channel 3	Current signal
Sampling rate	250 kS/s
Maximum points	1.25 MS

The oscilloscope was connected to the personal computer via a LAN cable for data transfer and analysis. Thereafter, the two power supplies, discussed in section 4.1, were initialised so that one power supply delivered 15 V to the current switching board and the other power supply delivered 1.8 V to the electrolyser cell via the Current switching board. The second power supply was also set up to deliver specific currents under specific experimental conditions evident from Table 4.5.

Table 4.5: Power supply setup for CI experiments

Parameter setup	Initialisation Value
CI supply voltage – MOSFET bias voltage	15 V
CI supply voltage – PEMWE input supply	1.8 V
DC current supply for 0.1 A/cm ²	2.5 A
DC current supply for 0.2 A/cm ²	5.0 A
DC current supply for 0.3 A/cm ²	7.5 A

Using the wiring diagram shown in Figure 4.10, the experimental setup was analysed to ensure that it was safe before the power was applied to the system. This is important to ensure experimental repeatability and result accuracy.

4.1.3.2 Voltage and current response of experimental setup

By applying the DC power supply voltage and PRBS signal to the PEMWE cell, the oscilloscope measured the respective PRBS, voltage and current signals. The waveforms were then extracted using Matlab® Instrument Control toolbox® and a plotted before the electrical parameter calculations could take place in Simulink®.

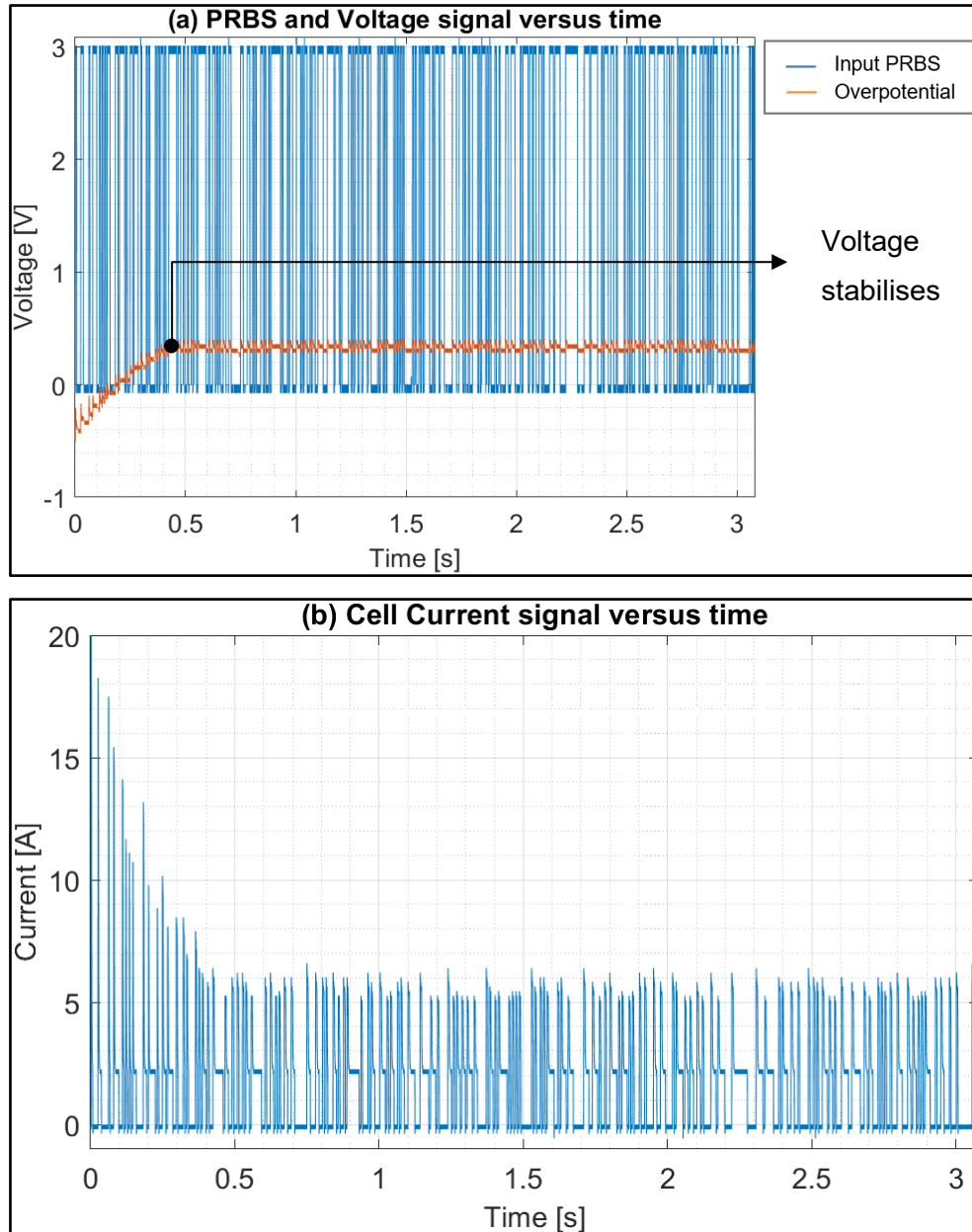


Figure 4.12: Response PEMWE cell under CI at 0.1 A/cm²: (a) Voltage response of cell at 40 °C, and (b) current response of cell at 40 °C

The standard voltage of 1.23 V, as discussed in section 2.3.2, was subtracted from each voltage data point measured from the cell. Thereafter, the overpotential and the cell current were compared to that of the generated PRBS signal to observe how the cell supply voltage and current reacted during current switching.

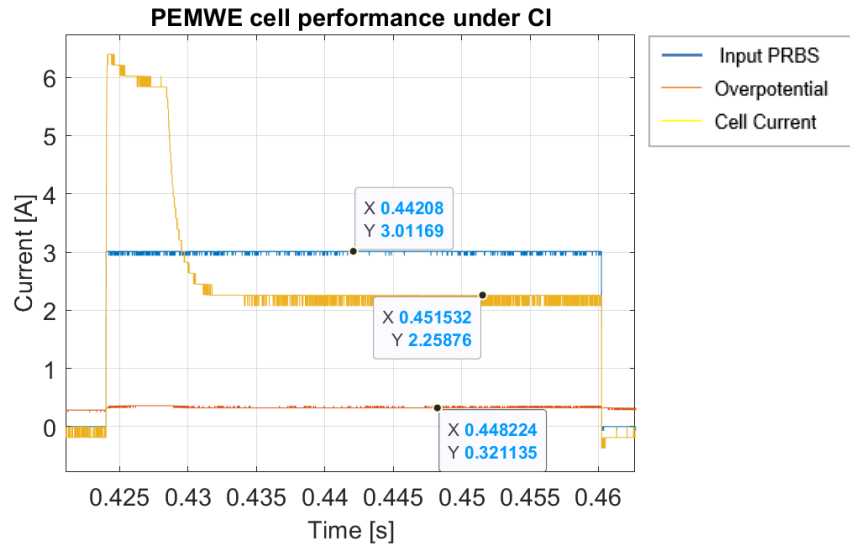


Figure 4.13: Cell performance under current interruption

From Figure 4.13, a single pulse is observed. During switching, the PRBS signal peaked at a constant 3 V for approximately 3 seconds, as seen in Figure 4.12. The observed voltage and current signal during each peak are highlighted in Figure 4.13. The overpotential switched from 0.5 V to 0.68 V during each current pulse. However, for the cell current, an initial current spike on the leading edge of the PRBS signal was observed of approximately 20 A. The current spike was observed throughout the current interrupt experiment and declined exponentially, as seen in Figure 4.12. The initial spike could be due to electrolyte capacitance, internal cell component capacitance and wiring inductance. During each pulse, the spike settled to a value of 2.26 A before the next current interrupt pulse occurred.

4.1.3.3 System analysis and electrical parameter calculation

Applying the measured voltage and current to the Simulink® model discussed in section 3.2.2.4, the simulated current was determined.

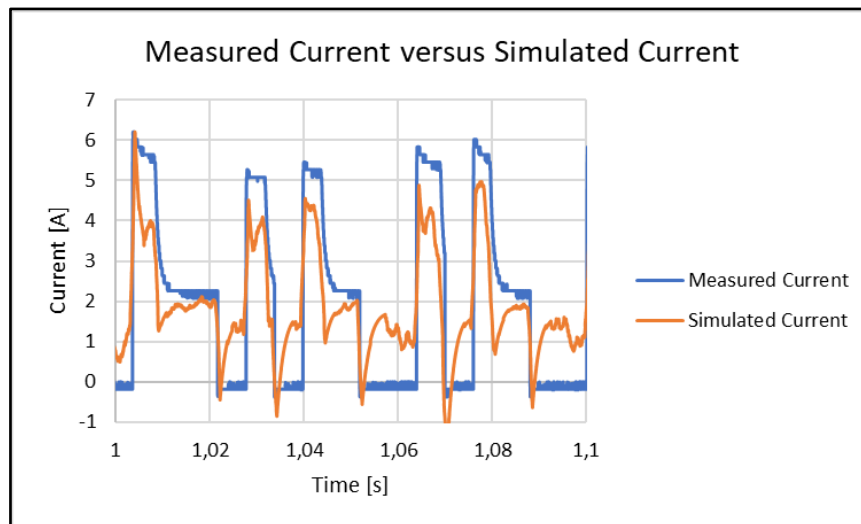


Figure 4.14: Measured versus simulated current Simulink® - Zoomed in

The measured versus simulated current was then compared, as seen in Figure 4.14. The difference between these two functions could be easily observed. Thus, Response Optimiser® could now be employed to try and minimise the error between the two measured plots from which the EEC parameters were calculated. From Figure 4.14, it was evident that the simulated and measured current with predefined electrical parameters values, as discussed in section 3.2.2.4, were not similar. Thus, Simulink® Response Optimizer® toolbox was used to determine the electrical parameter values by minimising the error between the simulated and measured current.

Table 4.6: First experiment electrical parameter values

Electrical Parameter	Value	Unit
R_m	3.49	mΩ
R_{ct}	14.26	mΩ
R_{int}	4.77	mΩ
C_{dl}	1.00	F
C_{int}	1.70	mF

The EEC parameters calculated using Response optimizer® can be observed from Table 4.6. The comparison between the simulated and measured results after optimisation can be seen in Figure 4.15. It was observed that the simulated current was a better fit to the actual measured current than that of Figure 4.14. The error between the two plots after optimisation resulted in 2.919%.

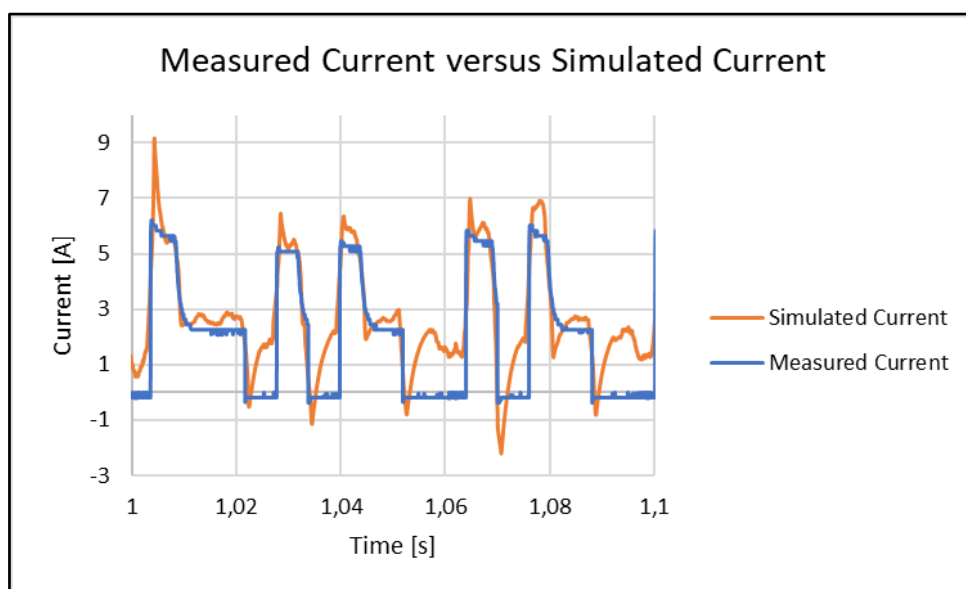


Figure 4.15: Measured current versus simulated current after Response Optimizer®

A comparison between the CI EEC parameter results and EIS are discussed in section 4.3.2. Table 4.7 shows the EEC parameter results using the CI method for each experiment discussed in Table 4.3

Table 4.7: Summary of CI results for all nine experiments

0.1 A/cm²				
EEC Parameters	Unit	40°C	60°C	80°C
		Values	Values	Values
R_m	mΩ.cm ²	87.25	76.5	66.25
R_{ct}	mΩ.cm ²	356.50	349.50	348.75
R_{int}	mΩ.cm ²	119.25	100.25	83.75
C_{dl}	F/cm ²	0.04	0.04	0.04
C_{int}	mF/cm ²	0.07	0.07	0.08
0.2 A/cm²				
R_m	mΩ.cm ²	100.00	94.00	90.50
R_{ct}	mΩ.cm ²	187.75	176.25	177.50
R_{int}	mΩ.cm ²	100.50	77.25	58.25
C_{dl}	F/cm ²	0.04	0.04	0.04
C_{int}	mF/cm ²	0.09	0.11	0.14
0.3 A/cm²				
R_m	mΩ.cm ²	111.00	99.00	87.25
R_{ct}	mΩ.cm ²	139.50	132.75	129.00
R_{int}	mΩ.cm ²	93.00	68.50	48.50
C_{dl}	F/cm ²	0.03	0.03	0.03
C_{int}	mF/cm ²	0.09	0.14	0.18

4.2 EIS setup and integration

This section pertains to the calculation of the electrical parameters using the Gamry station for response recording and Relaxls® for EEC parameter calculation.

4.2.1 EIS setup and conditions

The experimental setup for the EIS experiments was similar to that of the CI method; however, instead of using external DC power supplies, a CI development board and Matlab®, EIS only utilised the Gamry interface 1000®. The connection for the setup can be seen in Figure 4.16.

The Gamry interface® has four different electrodes that connect to the PEMWE cell. The blue electrode (Working sense electrode) connects to the cathode of the cell, and it senses the voltage flowing through the cable. The red and yellow cable connects to the anode of the cell. The potential difference between the white and blue electrodes is the cell voltage. The red electrode is the output of the Gamry interface 1000® amplifier. Lastly, the black electrode refers to the floating ground and increases the sensitivity and accuracy of cell measurements.

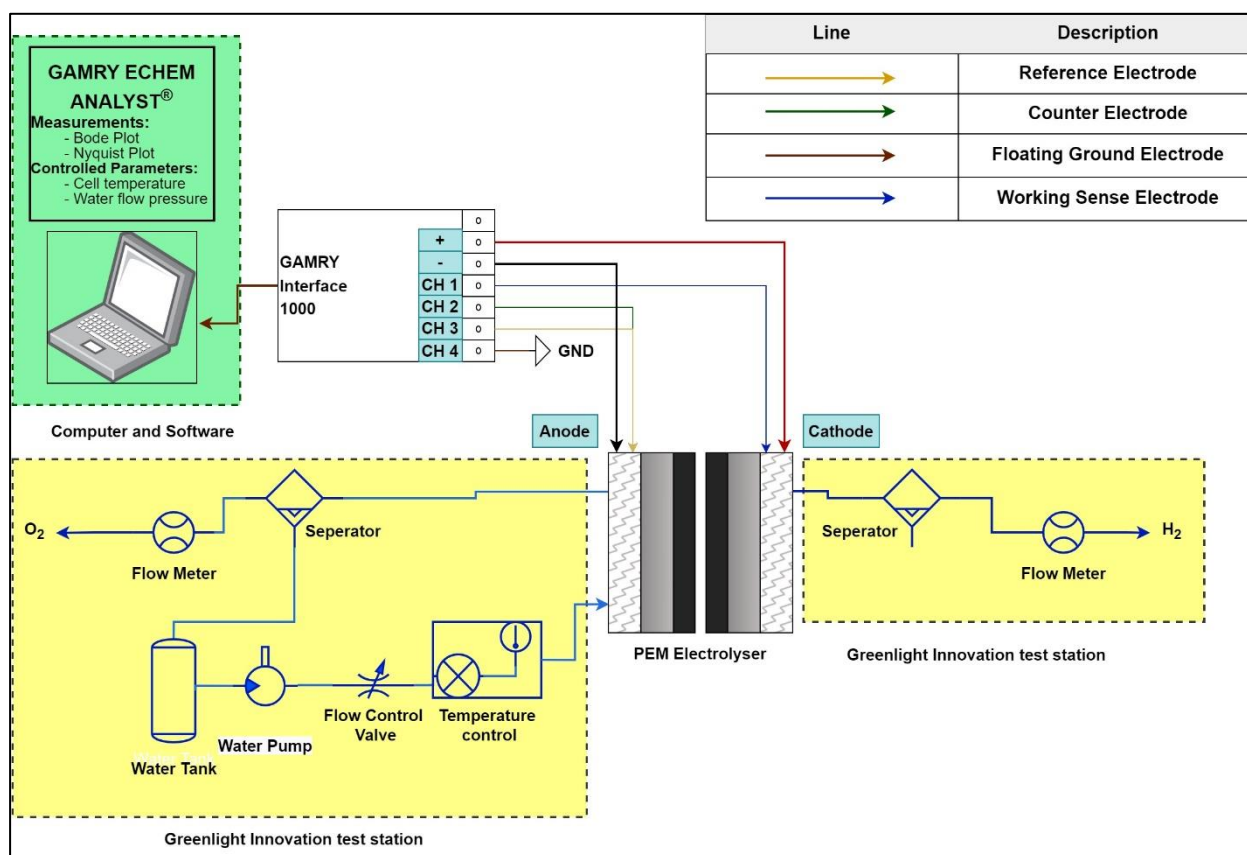


Figure 4.16: Experimental setup for EIS

4.2.2 EIS results

For each of the nine experiments, a similar approach was followed. Each EIS test was conducted directly after the respective CI experiment. After each experiment, RelaxIs® was used, as discussed in section 3.3, to calculate the electrical parameters of the equivalent electrical circuit shown in Figure 3.31.

The parameter calculation was done by fitting the electrical circuit to the respective Bode plot of each experiment. Similar to the CI method, the EIS results for the PEMWE cell supplied with 0.1 A/cm^2 operated at 40°C as seen in Figure 4.17. Using the EEC circuit, selected and shown in Figure 3.31, the generated Nyquist and Bode plots could be fitted to the circuit for parameter calculation. To ensure accurate parameter calculation, the Levenberg-Marquart theorem was used to fit the simulated circuit data to the recorded PEMWE cell data shown in Figure 4.17. The simulation fitting continued until an optimal fit was reached, at which point no further parameter change was observed. Thus, the optimal fit results represent the simulated EEC parameter values calculated based on the true fit to the actual Bode and Nyquist plots. Figure 4.18 visually represents the comparison between the measured Nyquist and Bode plots, indicated through the solid line curves with cross indicators, and the generated plots utilising the EEC evident from Figure 3.20.

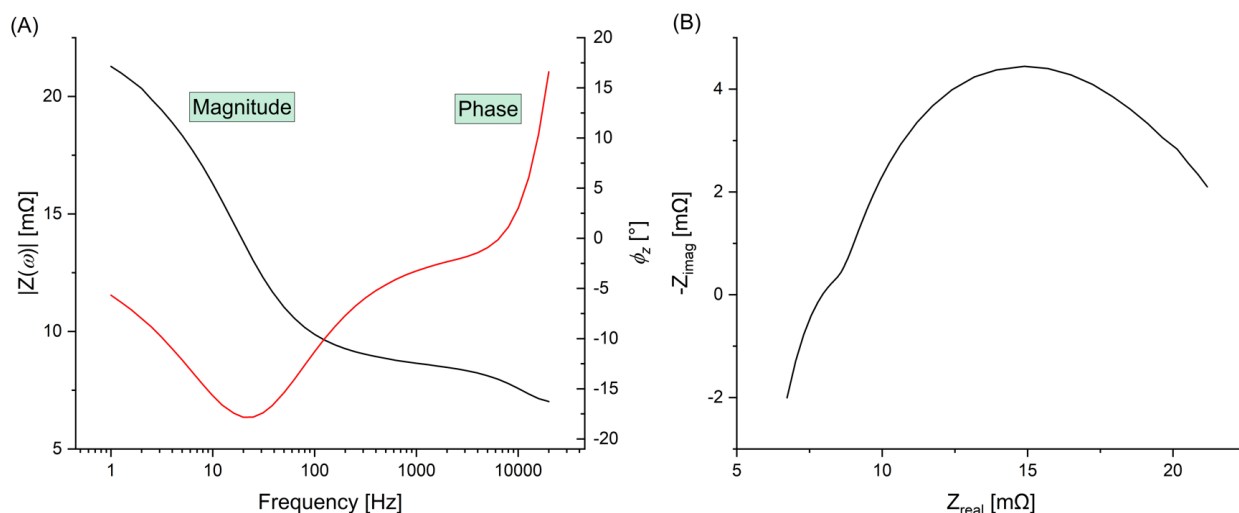


Figure 4.17: EIS tests of at 40 °C: (A) Magnitude and phase plot for 0.1 A/cm², and (B) Nyquist plot for 0.1 A/cm²

These plots show that the fit correlation was quite close, with relatively small deviations between the two plots. Details on the fit errors can be seen in Table 4.8.

Table 4.8: EIS fit error for PEMWE cell for 0.1 A/cm² at 40 °C

Plot	% Error [%]	MAE	MSE	RMSE
Magnitude	0.30	0.04	0.01	0.04
Phase	2.48	0.21	0.10	0.21
Nyquist	2.51	0.06	0.01	0.06

The error values between the three plot fittings were as expected and correlated with the discussion from section 3.3 during the analyses of the different EECs.

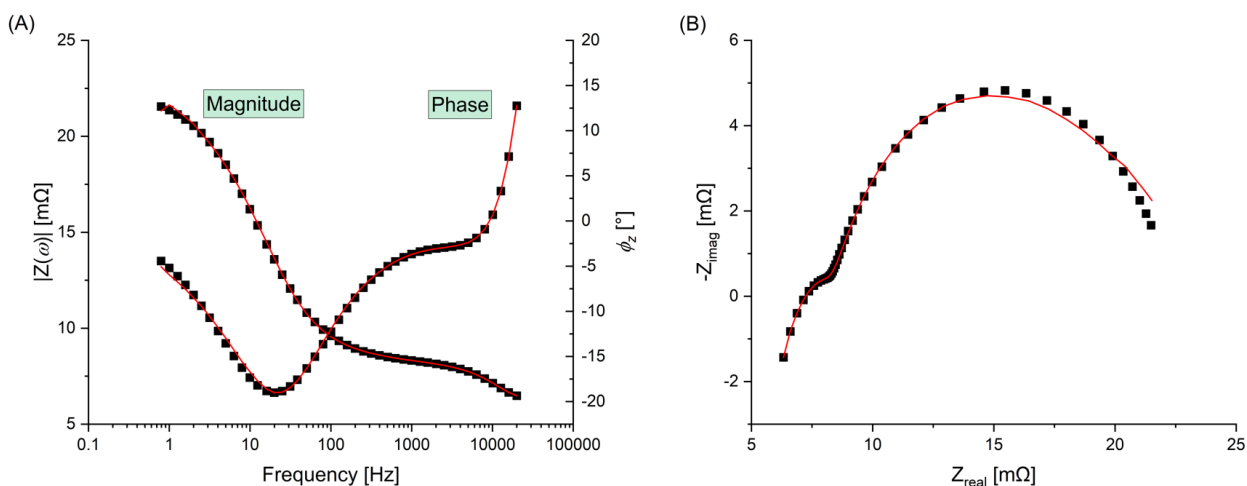


Figure 4.18: EEC EIS fit of at 40 °C: (a) Magnitude and phase plot for 0.1 A/cm², and (b) Nyquist plot for 0.1 A/cm²

The error ranged from a maximum of 2.51% deviation on the Nyquist plot to a minimum error deviation of 0.30% deviation on the Magnitude plot.

Table 4.9: Summary of EIS results for all nine experiments

0.1 A/cm ²							
EEC Parameters	Unit	40°C		60°C		80°C	
		Values	Relative error [%]	Values	Relative error [%]	Values	Relative error [%]
R_m	mΩ.cm ²	87.25	12.42	74.25	18.21	66.00	22.40
R_{ct}	mΩ.cm ²	355.25	0.55	342.50	0.54	339.00	0.60
R_{int}	mΩ.cm ²	118.00	9.53	99.50	12.67	81.25	18.60
Q_{dl}	Ss ^a /cm ²	0.12	1.67	0.12	1.59	0.12	1.70
α_{dl}		0.76	0.51	0.76	0.47	0.76	0.50
Q_{int}	mSs ^a /cm ²	0.40	10.61	0.40	13.07	0.40	19.31
α_{int}		0.85	2.26	0.85	2.46	0.85	3.17
C_{dl}	F/cm ²	0.07		0.07		0.07	
C_{int}	mF/cm ²	0.04		0.05		0.04	
0.2 A/cm ²							
R_m	mΩ.cm ²	104.00	7.66	92.75	8.68	85.75	10.78
R_{ct}	mΩ.cm ²	184.00	0.86	175.25	0.79	175.00	0.83
R_{int}	mΩ.cm ²	98.00	8.70	77.25	11.03	57.75	16.83
Q_{dl}	Ss ^a /cm ²	0.18	2.81	0.17	2.67	0.17	2.86
α_{dl}		0.69	0.94	0.70	0.85	0.70	0.90
Q_{int}	mSs ^a /cm ²	0.40	12.80	0.40	14.35	0.40	19.90
α_{int}		0.91	2.42	0.91	2.76	0.94	3.72
C_{dl}	F/cm ²	0.06		0.06		0.06	
C_{int}	mF/cm ²	0.03		0.04		0.04	
0.3 A/cm ²							
R_m	mΩ.cm ²	110.00	6.49	95.25	8.39	91.00	8.71
R_{ct}	mΩ.cm ²	134.25	1.36	129.50	1.30	125.75	1.16
R_{int}	mΩ.cm ²	88.75	8.95	67.75	12.87	50.00	17.01
Q_{dl}	Ss ^a /cm ²	0.25	3.86	0.24	3.97	0.25	3.69
α_{dl}		0.62	1.48	0.63	1.45	0.63	1.31
Q_{int}	mSs ^a /cm ²	0.40	15.47	0.40	19.18	0.40	22.80
α_{int}		0.95	2.63	0.98	3.28	0.99	3.95
C_{dl}	F/cm ²	0.06		0.07		0.07	
C_{int}	mF/cm ²	0.03		0.03		0.03	

The error values were within the expected range, thus making it possible to estimate the electrical parameter values using Relaxls® simulation software. Each of the experiments specified within Table 4.3 was inserted and fitted on the designed EEC shown in Figure 3.20. However, based on the circuit design, it can be seen that the capacitors were replaced with CPEs making the conversion from Siemens-seconds raised to the power of alpha ($S \cdot s^\alpha$) to Farad (F).

Capacitance

$$C = R \left(\frac{1-\alpha}{\alpha} \right) Q \left(\frac{1}{\alpha} \right) \quad (4.1)$$

Equation (4.1) [126] shows the conversion calculation where “ R ” refers to the respective resistance value in parallel with the CPE, and “ Q ” and “ α ” refer to frequency independent CPE constants [126] [127]. The double-layer capacitance and the interfacial capacitance are then calculated using this equation for each experiment. The results in Table 4.9 for 0.1 A/cm² at 40 °C were obtained by fixing the CPE representing the modified inductance, as shown in Figure 3.20, to a calculated “ Q ” value of 0.132 kH.

The alpha value was initialised as -0,9 and stayed around that range during simulation. The relative error between the actual results and the fitted results shows that the membrane resistance and the interfacial “ Q ” value were quite high. This is due to the inductive contribution which affects the membrane and interfacial resistance, and interfacial capacitance value and was discussed thoroughly in section 3.3 and Figure 3.21. A summary of EIS values for each of the nine experiments can be seen in Table 4.9.

4.3 Verification and validation

This section discusses the verification and validation for the EIS and CI model EEC electrical parameters. The EIS method verifies the parameters against existing literature, which was then used to verify and validate the EEC parameters calculated using the CI method.

4.3.1 EIS result verification against literature

The EEC parameter results, obtained for each experiment as outlined in Table 4.3 is discussed and compared between two known methods. The first method, the CI method, used current switching to calculate the electrical parameter values from the cell’s current and voltage response. In contrast, EIS used an EEC from which the Levenberg-Marquart theorem was used to estimate the best possible electrical parameter values. This was done by fitting the circuit Bode and Nyquist responses to the actual cell response. Furthermore, the comparison between the two methods was very important since a close correlation between the calculated electrical parameters proves the validity of the CI method subjected to low current densities up to 0.3 A/cm². Thus, a careful analysis of each electrical parameter was conducted by comparing the two methods under similar experimental conditions as shown in Table 4.3.

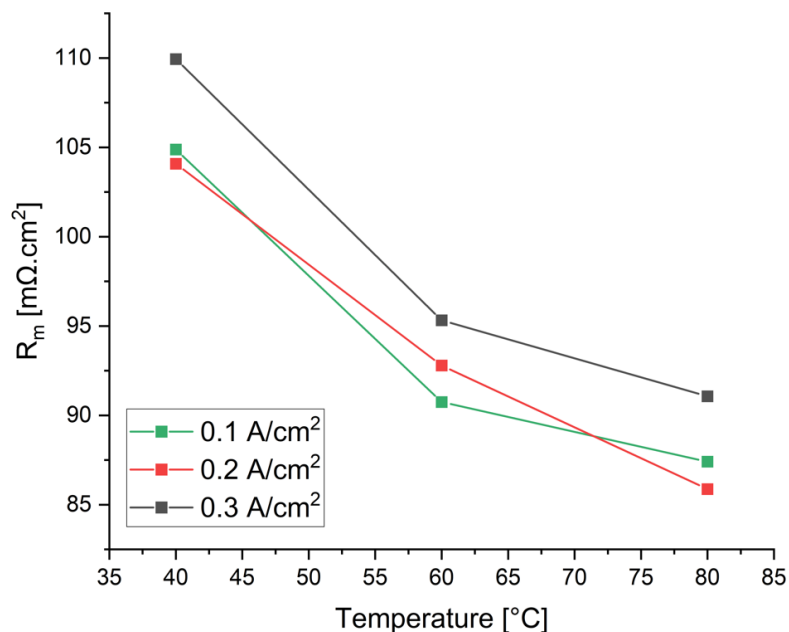


Figure 4.19: Membrane resistance comparison

The results for the membrane resistance were as expected, with a decrease in membrane area resistance as cell operating temperature increased. This decrease was due to the increase in ion conductivity of the PEMWE cell at higher operating temperatures, improved hydration and enhanced ion transport as water viscosity decreased, and a reduction in activation energy of the cell decreasing the transport of ions (according to the Arrhenius-type behaviour) [128, 129, 130]. Based on the plot in Figure 4.19, the membrane area resistance ranged between 65 – 110 mΩ.cm². The membrane area resistance range correlates with the results Slade *et al.* [131] obtained during the testing of the ionic conductivity of different series Nafion membranes.

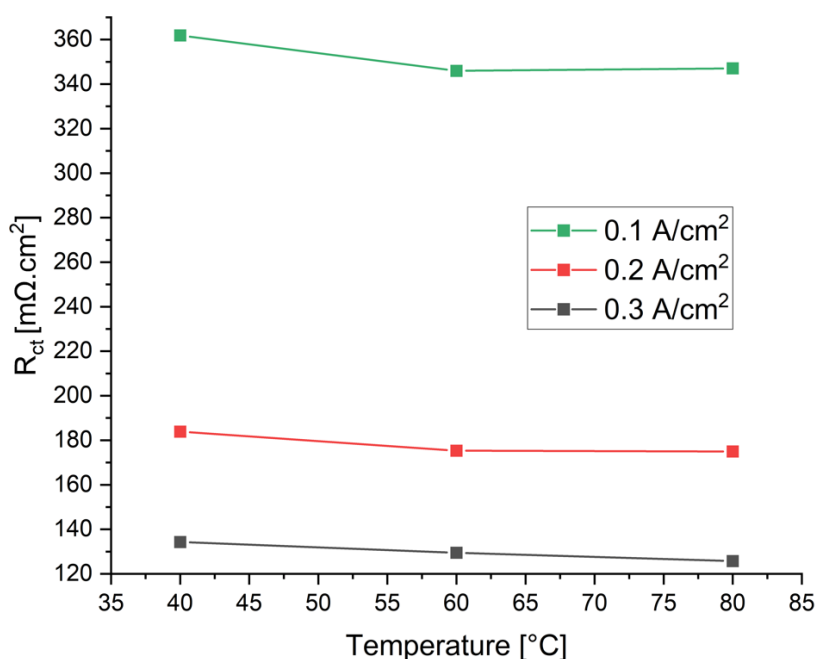


Figure 4.20: Charge transfer resistance comparison

The obtained area resistance of the Nafion 115, with a thickness of 125 μm , resulted in an approximate range of 100 - 130 $\text{m}\Omega\cdot\text{cm}^2$. Thus, the membrane resistance calculated during this project was within range; however, the deviation from the provided range was due to the inductive contribution causing the membrane resistance to shift left, as shown in Figure 3.21 [132, 133], resulting in a slightly lower membrane resistance [134]. From Figure 4.20, a slight decrease in charge transfer resistance was observed as temperature increased due to several factors, such as the electrochemical reaction which follows the Arrhenius behaviour at both electrodes, the direct relation between charge transfer resistance and exchange current density " i_0 " of the cell, improved ionic conductivity affecting predominantly the " R_m ", and minimisation of mass transport limitations [135]. The Tafel equation for activation overpotential is given by $\eta_{act} = b_a \times \ln\left(\frac{i}{i_0}\right)$, where " b_a " is the Tafel slope, " i " is the current density, and " i_0 " is the exchange current density. The charge transfer resistance can then be derived as $R_{ct} = \frac{d\eta_{act}}{di} = \frac{b_a}{i \times i_0}$ [134]. Hence, the Tafel slope can be formulated as seen in equation (4.2) [134].

Tafel Slope

$$b_a = 2.303 \times R_{ct} \times i \quad (4.2)$$

Where " b_a " refers to the Tafel slope of the data plot, " R_{ct} " refers to the charge transfer resistance, and " i " refers to the DC current supplied to the cell during testing. By calculating the Tafel slope at 0.1 A/cm^2 for each temperature shown in Table 4.3, the charge resistance could be verified. It is important to calculate the Tafel slope at very low current densities since the ohmic and mass transport effects can hide intrinsic kinetic parameters. Thus, at lower current densities, the Tafel slope can provide accurate insights into the reaction mechanisms of the PEMWE cell. According to Rao *et al.* [134], a standard value of the Tafel slope is around 70 mV/dec for PEMFC; however, the PEMWE technology is not that different, and values similar to that range can be acceptable.

Table 4.10: Tafel Slope calculation values

Temperature [$^{\circ}\text{C}$]	Charge transfer Resistance [Ω]	DC current [A]	Tafel slope [mV/dec]
40	0.01	2.48	82.82
60	0.01	2.48	79.19
80	0.01	2.48	79.44

The Tafel slope at all three temperatures stayed relatively constant at around 80 mV/dec , which was still in the acceptable range for a practical system [134]. Thus, the charge transfer resistance values obtained could be used to verify the CI method. The effect of current density on the double-layer capacitance was evident from Figure 4.21. An increase in current density led to an increase

in the double-layer capacitance due to the increase in reaction rate, causing the time availability for charge accumulation to reduce [127, 136, 137]. The high Tafel slope values of approximately 80 mV/dec may be attributed to the complex interplay of reaction kinetics and mass transport limitations within the PEMWE system. Additionally, the presence of impurities or catalyst degradation could contribute to an elevated Tafel slope, reflecting deviations from ideal reaction conditions. Furthermore, at low current densities the electrical capacitance followed the behaviour of the Helmholtz capacitor (ideal) and started to increase as the current density increased [127, 136, 137]. This might be due to surface saturation effects that increased due to the increase in charge transferred per unit time. Furthermore, the calculation of the double-layer capacitance values from the CPE fitting values must be verified.

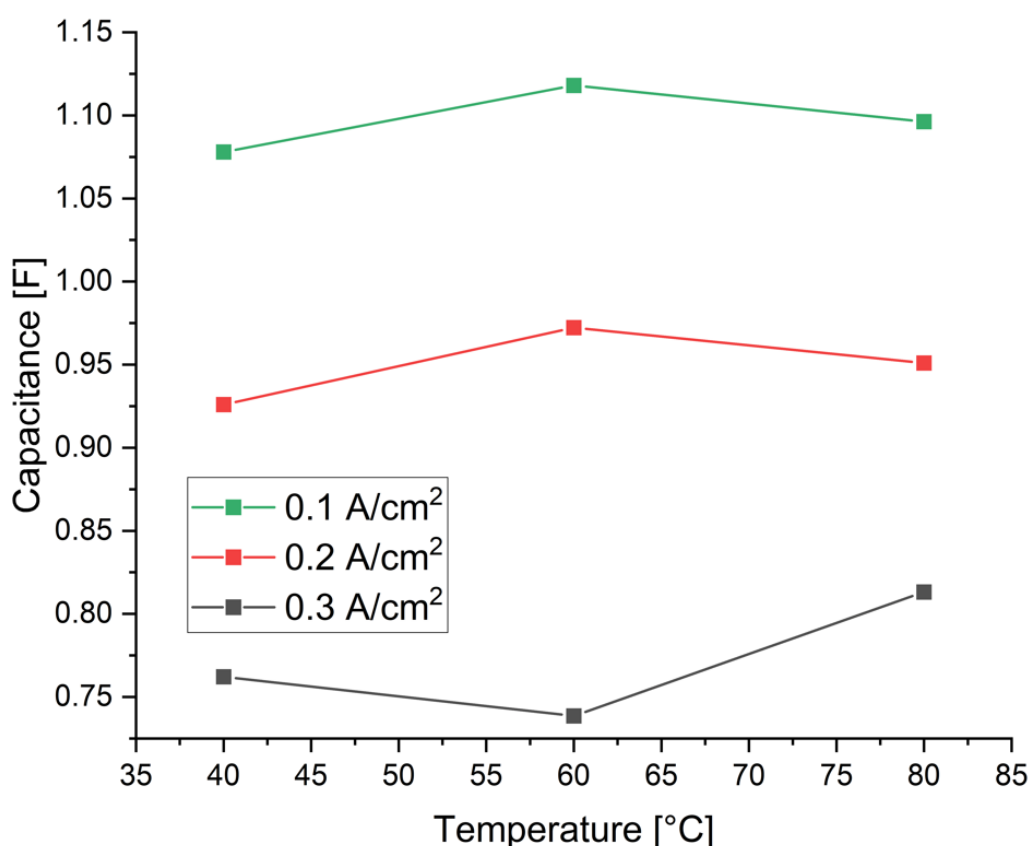


Figure 4.21: Double-layer capacitance comparison

Based on the double-layer capacitance values calculated by Giesbrecht *et al.* [136] on a Nafion 117 membrane, the capacitance was in a similar range. However, since a Nafion 115 was used for this project, a higher capacitance value was observed. This difference arises because the membrane influences double-layer capacitance through its thickness and ion-exchange capacity; a thinner Nafion 115 (125 μm) compared to Nafion 117 (175 μm) increases the effective surface area and ionic conductivity at the electrode-membrane interface, enhancing charge accumulation and thus capacitance [138]. The double-layer capacitance was very challenging to calculate, and not much research was found where specific capacitance values are recorded due to influencing

factors, such as electrode material, surface roughness, electrolyte properties, and cell operating conditions [138]. However, the capacitance can be determined using the Nyquist plot generated via EIS. Thus, if the membrane and charge transfer resistance are within range, the double-layer capacitance must be in range if the semi-circular arc is similar to the literature (observed in [136, 139]).

4.3.2 EIS versus CI

Based on the parameter results shown in Table 4.7 and Table 4.9 for the CI and EIS methods, respectively, a correlation between their EEC parameters can be made. Table 4.11 compares the results for each experiment with their relative errors.

Table 4.11: EIS and CI method comparison

0.1 A/cm²										
EEC Parameters	Unit	40°C			60°C			80°C		
		EIS	CI	Error [%]	EIS	CI	Error [%]	EIS	CI	Error [%]
R_m	mΩ	3.49	3.49	0.13	2.97	3.06	3.21	2.64	2.65	0.31
R_{ct}	mΩ	14.21	14.26	0.33	13.70	13.98	2.05	13.56	13.95	2.78
R_{int}	mΩ	4.72	4.77	0.95	3.97	4.01	1.01	3.25	3.35	2.99
C_{dl}	F	1.09	1.12	2.58	1.13	1.10	2.68	1.10	1.08	1.63
C_{int}	mF	1.70	1.69	0.45	1.77	1.80	1.46	1.89	1.96	3.37
0.2 A/cm²										
R_m	mΩ	4.16	4.00	4.21	3.71	3.76	1.26	3.43	3.62	5.12
R_{ct}	mΩ	7.36	7.51	2.10	7.01	7.05	0.57	7.00	7.01	1.38
R_{int}	mΩ	3.92	4.02	2.36	3.09	3.09	0.11	2.31	2.33	1.05
C_{dl}	F	0.93	0.93	0.03	0.97	0.98	0.31	0.95	0.94	1.12
C_{int}	mF	2.24	2.21	1.63	2.84	2.82	0.51	3.57	3.52	1.37
0.3 A/cm²										
R_m	mΩ	4.40	4.44	1.01	3.81	3.96	3.62	3.64	3.49	4.28
R_{ct}	mΩ	5.37	5.58	3.70	5.18	5.16	0.42	5.03	5.16	2.49
R_{int}	mΩ	3.55	3.72	4.51	2.71	2.43	4.79	2.00	1.94	2.90
C_{dl}	F	0.76	0.75	1.63	0.81	0.83	2.75	0.82	0.83	1.24
C_{int}	mF	2.28	2.26	0.95	3.37	3.38	0.48	4.37	4.54	3.75

4.4 Conclusion

In this chapter, the experimental setup for the CI and EIS methods was discussed. The chapter started with the specification of the PEMWE cell used during each experiment. This included the membrane type, PTL's loadings, electrical supply, etc. Thereafter, detailed tests were conducted

on the cell to establish the pressure distribution across the active area. Furthermore, details were given regarding the design of the cables supplying current to the cell during switching, the CS development board, and how it accommodated the newly designed supply cables. This was very important since stray losses can influence the EEC parameters calculated throughout each experiment.

The CI method was further discussed by identifying a proper experimental setup for EEC parameter calculation. Details regarding this setup were conveyed in Figure 4.10. This was followed by a methodological approach explaining the process from the measured cell response to the EEC parameter calculation. The first experiment, according to Table 4.3, was discussed as an example, and thereafter, a summary of EEC parameters calculated from each experiment was given. The CI method was followed by the EIS method performed under similar experimental conditions. Again, the first experiment performed using the EIS method was discussed, and sensible results were obtained using the EEC designed in section 3.3.

Lastly, the EIS and CI methods were verified and validated based on the research conducted during this dissertation. The EIS method was validated using literature to verify if the calculated EEC parameter corresponds to that of existing articles. A good correlation between the researched articles and the obtained parameters was obtained. This ensured that the EIS method delivered accurate results that can be used to verify and validate the CI method. The EIS model used showed that:

1. The modified Randles cell delivered good results that closely correlated to the literature.
2. The modified inductance within the EEC ensured that the calculated membrane resistance and interfacial components still correlated to the literature. Thus, the modified inductance successfully represented the inductive contribution from the supply to the cell.
3. The use of RelaxIs[®] for parameter estimation through plot fitting was essential for this project to characterise the PEMWE cell through EEC parameter identification.

The validation of the CI method from EIS delivered good results. The CI method delivered EEC parameters that closely correlated to those calculated using the EIS method. Based on this, important conclusions on the CI model were developed and includes:

1. The voltage and current response have to be sized to contain only the switching data generated based on the PRBS signal before applying it to the model. This is essential to minimise simulation time since the oscilloscope records unnecessary data that is not useful during simulation.

2. The model initialisation parameters are quite sensitive. Thus, for these experiments the initial EEC parameters of the model are taken as the values calculated using EIS. This is very important since the model only works well if the initialisation parameters are within the range of the actual desired values.
3. Response Optimiser® is configured to run a simplex search for 100 iterations to test for the best possible fit. The optimisation for each experiment is simulated until the sequence converges. This is typically around 25-40 iterations since the initialisation EEC parameters are within the desired values range. Further deviation will cause longer run times.

The CI method was successfully verified and validated within this chapter. The next chapter discusses the key research question developed to validate the success of this research project, future recommendations, and the project conclusion.

CHAPTER 5: CONCLUSION AND FUTURE WORK

The final chapter of the dissertation serves as a conclusion on the research conducted. The chapter starts off with a discussion of the key research questions pertaining to important information on the successful completion of the project. Thereafter, a summarised discussion of the verification and validation processes within each chapter is given. This is followed by a discussion of future recommendations and improvements, creating opportunities for new research topics. Finally, a conclusion for the project is provided.

5.1 Key research questions

The key research questions, formulated within section 1.3.4, form the foundation of this research project, since each question proves the validity of the project's aims and objectives. These questions are discussed below with reference to the relevant research section to determine the completion of the project.

5.1.1 What are the key parameters and performance indicators that need to be monitored in a PEMWE cell?

The purpose of the question was to specify the key equivalent electrical parameters that need to be determined to characterise the given PEM water electrolyser cell effectively. Through monitoring the PEM water electrolyser cell, important key parameters to assess performance, identify potential issues and ensure safe operation were tracked. Section 2.3 highlighted these components and discusses the importance of each performance indicator. These components include reversible cell voltage required for water splitting, current density required for hydrogen and oxygen production, Faradaic efficiency, and operating conditions such as cell temperature, pressure, water flow rate, etc. System-level performance indicators including power consumption, hydrogen production rate and cell operation efficiency, also contributed greatly towards the characterisation of the cell. Furthermore, safety components such as temperature sensors, pressure release valves, and gas leak detection sensors were installed within the new test bench, shown in Chapter 5, to ensure safe operation. Lastly, all these performance indicators enabled the calculation of the key electrical parameters defined by the CI method. This included the membrane resistance, double-layer capacitance, charge transfer resistance and Warburg impedance validated using EIS, as seen in Chapter 4.

5.1.2 What are the critical design considerations for developing a high-speed, high-precision current switching device for PEMWE characterisation?

During the design of the current switching development board, the development, signal attenuation and switching of the PRBS signal played an important role, as discussed in sections 3.2.1 and 3.2.2. Thus, an effective microcontroller was required to sample at the desired

frequency (0.8 – 25000 Hz) and deliver a signal from the microcontroller to the development board without aliasing. For this research, the STM32F334R8 Nucleo-64 development board was chosen based on its high-performance ARM Cortex-M cores supporting clock speeds of up to 180 MHz and integrated timers and direct access memory capabilities for fast and efficient signal generation. Furthermore, the development board's compatibility with STM32Cube IDE® simplified the programming environment. This is especially helpful during the design of the LFSRs to generate the randomised bits used for PRBS signal development (detailed design discussed within section 3.2.1). As for the development board, an input supply circuitry for this generated signal via the microcontroller was designed to successfully link the microcontroller to the CI setup. The circuitry further incorporated signal attenuation circuitry to efficiently bias the gate of the MOSFET, as analysed in section 3.2.2. The MOSFET was chosen based on its capability to switch at high frequency with minimal switching losses. Thus, a CS signal was delivered that efficiently controlled the current flowing to the cell. The generated voltage and current response from section 4.1.3 is evident of this control.

5.1.3 What are the key electrochemical parameters that can be extracted from the electrolyser's voltage and current response during CS?

Based on the design and operation of the PEMWE cell, an EEC was developed and tested using the Levenberg-Marquart theorem for best possible fits, as discussed in section 3.3.1. According to Table 3.11 and Table 3.12, the EEC delivering the best possible fit with the smallest deviation errors was the Randles cell with an extra interface and series inductance as shown in Figure 3.20. Using this circuit, the electrochemical parameters describing the cell's performance were calculated from EIS based on the best possible fits, as discussed in section 3.3. The same EEC was applied to the CS simulation environment, shown in Figure 3.23, from which the EEC parameter values were calculated based on the current and voltage responses of the cell obtained during each experiment shown in Table 4.3. Thus, for this EEC design, the key parameters included the membrane resistance (R_m), double-layer capacitance (C_{dl}), charge transfer resistance (R_{ct}) and interfacial resistance and capacitance (R_{int} and C_{int}). Each of these parameters played an important role in characterising the cell during operation as discussed in section 0. Each electrochemical parameter was carefully calculated and compared between EIS and CI to ensure the accuracy and validity of the parameter results.

5.1.4 What are the optimal frequency ranges of the PRBS signal for effective system identification without introducing unwanted disturbances in electrolyser performance?

As discussed in section 2.5.2, three important operating regions of the PEMWE cell was shown. For this project, as discussed in Chapter 3, the mass transport region was neglected due to the limited frequency range. Hence, the use of the Randles cell instead of the Randles Warburg EEC

is shown in Figure 3.20. Mass transport will only be observed at very low frequencies. However, the ohmic and activation region were still used for the EEC parameter calculation. The ohmic region is used to determine the membrane resistance and indicates where the Nyquist plot cuts the x-axis at high frequencies. Due to the modified inductance the membrane resistance was shifted and could not be determined from the x-intercept, as discussed in section 3.3. Thus, plot fitting was used to determine the EEC parameters. Figure 4.18(b), shows that the ohmic region, from which the membrane resistance, interfacial resistance and capacitance could be determined, lies within a frequency range of 20.061 – 9.981 kHz. As for the activation region, where the charge transfer resistance and double layer capacitance was determined, a frequency range from 9.981 kHz to 0.990 Hz was observed. Furthermore, the frequency at which the capacitance for each capacitor was calculated was 10.078 kHz for the interfacial capacitance and 12.401 Hz for the double-layer capacitance.

5.1.5 How does the PRBS-based current switching method compare to conventional Electrochemical Impedance Spectroscopy (EIS) in characterising PEMWE dynamics?

The validation between the two methods were thoroughly discussed in section 4.3.2, where all the EEC parameters calculated through each experiment were compared. The EEC values calculated using EIS were closely verified using existing literature, ensuring that the membrane resistance, charge transfer resistance and the double-layer capacitance closely adhere to similar article scenarios. Thereafter, the EIS values were deemed valid for verification and validation of the CI method in section 3.3. The CI model was initialised using the calculated EEC parameters from Table 4.9, and RelaxIs® was utilised to determine the parameter values after the sequence converged for each experiment. A close correlation between the values was found with a typical relative error of between 0.3% and 5%, as seen in Table 4.11. This shows a good correlation between the two methods, thus proving that the CI method can deliver accurate PEMWE cell parameters.

5.2 Verification and validation

The verification and validation procedure followed throughout this project plays an essential role in its successful completion thereof and is discussed in detail in this section.

The literature study compiled in Chapter 2 discusses research topics relevant to this project. This includes analysed case studies providing insight into the modelling and simulation of EECs used for PEMWE cells. The case studies further provide information on typical EEC parameters important to study cell operation and efficiency, which was useful during the design and modelling of the cell evident from sections 3.2 and 3.3 where the CI and EIS models were designed and

validated. The literature study also gave further insight into the calculation of electrical parameter values using EIS, as discussed in section 2.5.2. The discussion of the case studies and EIS in section 2.5.2 gave insight into the method validation and verification of EIS with CI discussed in section 4.3.

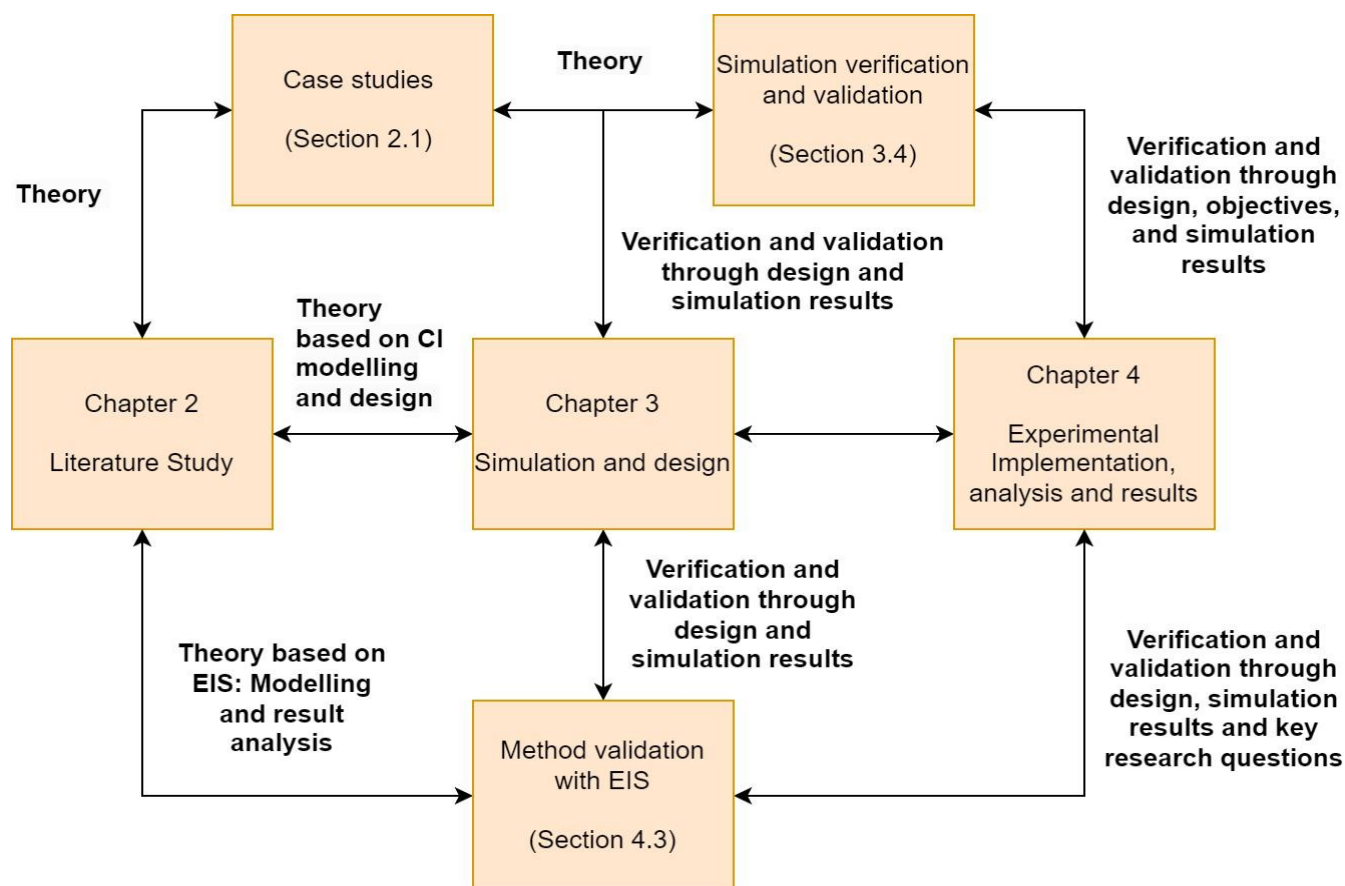


Figure 5.1: Verification and validation procedure

The references used in section 2.6.1 to study the theory behind the design of a PRBS signal and how it correlates to the CI method were discussed in section 2.5.3. The references were further used to design and simulate the generated PRBS signal using LFSRs as discussed in section 3.2.1. The design properties of the PRBS provided further insight into the design of the CS development board. Python® was used to test the generated PRBS signal measured from the microcontroller. The designed frequency range, voltage requirement of the cell, and systems inputs were analysed, discussed, and designed, as shown in Figure 3.33. The actual PCB design was further discussed in Chapter 4, as can be seen from Figure 4.6.

The references used to discuss and verify the CI method in section 2.5.3 were further utilised in section 3.2.2.4. However, without section 2.5.4.2, the EEC modelling the behaviour of the specified PEMWE cell (specified in Table 4.1) could not have been designed. Thus, according to

the discussion from section 0, a modified Randles cell EEC was designed (Figure 3.20) and implemented in the CI model, as designed and simulated in section 3.3. The CI method was verified and validated in section 3.4 by testing the stability of the model during EEC parameter variations. Further verification and validation were conducted within section 4.3 by comparing the CI method to EIS by analysing the correlation between the EEC parameter values under the same condition during each experiment discussed in Table 4.3.

5.3 Summary

Chapter 1 briefly introduced the proposed research project with a background on the use of the PEMWE technology. The background further elaborated on the use and previous designs of the CI method to characterise the PEMWE cell successfully. The aim of this project, to gain competence in the analysis and design of a suitable current interrupt characterization model that will successfully characterize the designed PEM electrolyser cell, was then formulated from which distinct research objectives were derived. The primary objective of this project was to further investigate the CI method as a possible alternative to EIS by implementing a CS development board used to generate controlled voltage and current responses. The responses were then further analysed using a designed CI model for EEC parameter calculation. The secondary results gave an indication of the process followed to reach the primary objective of the project. Furthermore, key research questions, research methodology, and citations of publications achieved were also discussed.

Chapter 2 provided a literature study of the proposed project aim and objectives, as discussed in Chapter 1. The study discussed the importance of using PEMWE technology and the physical operation of the cell. This was portrayed through the case studies, focussing on the modelling and characterisation of the cell under different conditions. However, to model the cell using the CI method, a detailed analysis was required on the controlled operation of the cell, the modelling of the cell using an EEC, and verification and validation of results using an existing cell characterisation method. Thus, different EECs were considered, and the significance of each (in terms of their EEC parameters and circuit limitations) was discussed, creating a starting point for modelling the CI method. The validity of the method was further discussed, and EIS was proposed as a possible method to ensure the accuracy of the CI process.

The next chapter included the design and simulation of the CI method. The chapter started with the conceptual design of the proposed experimental system and discussed the system requirements based on the systems main components. The components, including the PRBS signal generator, CS development board, CI simulation model and EIS EEC, were discussed thoroughly within the design section, providing more delineative system models for the

experimental setup. This is evident from section 3.2, which started with the design of a PRBS generator that were used to control the current flowing to the PEMWE cell. All calculations and design requirements were discussed in detail in this section, which produced an algorithm-based PRBS signal (LFSRs) with a frequency range of 0.8 Hz – 20 kHz and a maximum signal duration of 3.2568 seconds. However, the microcontroller could not directly supply this signal to the cell. A medium was required to attenuate the generated signal to the desired system requirements.

Therefore, a CS development board were designed as a central signal-carrying system block utilising the input of the PRBS signal and the input and output supply of the PEMWE cell. After careful consideration regarding electronic components, each subsection was designed according to the design requirements. This included the protection circuitry, important for isolating the input and output signal, the gain stage, used to attenuate the signal to design specifications, and the switching circuitry generating the controlled response for current control on the PEMWE cell. After the analysis of each subsystem, the development board was analysed and tested to ensure that the design requirements for the system were met. The complete EEC of the development board and a prototype is evident from sections 3.2.2 and 3.3.2.

Based on the discussion within Chapter 2, a modified Randles cell was developed for the CI model and implemented within Matlab®/Simulink®. The model pertaining to the modified EEC was developed to receive the measured voltage and current response under certain experimental conditions discussed in Chapter 4. A generated current signal, due to the modified EEC, was then compared to the measured signal using Response Optimiser®. The error between the two fittings was minimised by adjusting the modified EEC parameters until the sequence converged. Thus, the EEC parameter results of the experimental setup were delivered. However, to ensure that the obtained results were accurate, a similar model was implemented in Relaxls®, from which the EEC parameters were calculated using EIS. The results obtained between the two methods were further investigated in the next chapter. The CI model was verified and validated using the literature.

Chapter 4 pertains to the implementation and evaluation of the experimental setups, discussing the correlation between the CI and the EIS methods under similar experimental conditions. The PEMWE cell used for the experiment were first tested to ensure that the active surface of the cell was fully utilised. This is very important since poor pressure distribution across the active area of the cell could lead to inaccurate or insensible results. Furthermore, based on the suggestions of the case studies discussed in Chapter 2, the conditioning process of the cell had to be implemented initially to ensure healthy cell operation during testing.

Supply cables had to be prepped to account for the parasitic losses due to the electrical supply cables connecting the system components. The prepped cables were specifically used to connect the power supply of the PEMWE cell to the actual cell through the CS development board. Section 4.1.1.2 discussed this process in detail, ensuring that the cables minimised the losses as much as possible. This was especially important during the experimental setup design of the CI method since cable placing and minimal cable distance played a large role in the losses of the system. The CI method was implemented for each experimental specification in Table 4.3 and the calculated EEC parameters were recorded. However, a detailed process discussing the first experiment was given, from which a clear methodology could be followed. A similar process discussed in Chapter 3 was followed.

The calculation of the electrical parameters using EIS gave some challenges since the inductive contributions from the Gamry® supply affected the calculations of the EEC parameter results, as discussed in Chapter 3. Thus, according to the literature, a modified inductance had to be implemented within the EEC to account for this inductive contribution. Thereafter, RelaxIs® was used to calculate the EEC parameters based on the recorded bode and Nyquist plot from each experiment. The fitting of the recorded plots on the EEC delivered the desired electrical parameters of the PEMWE cell subjected to specific experimental conditions.

Verification and validation of the calculated results of EIS were done based on the theory of the type of membrane used within the cell, cell operation results, etc. After validation of the results, the EEC parameters obtained during EIS were compared to CI. The correlation between the EEC results obtained via the two methods was quite close. Thus, it was concluded that the charge transfer resistance, double-layer capacitance and membrane resistance were verified against an existing method which is a continuation of the project conducted via Martinson *et al.* [19] who only verified and validated the membrane resistance against existing literature.

The final chapter of the dissertation meticulously discussed the key research question formulated within Chapter 1. Furthermore, the verification and validation procedure throughout this project was also discussed. Lastly, a detailed summary and future recommendations for this project were given, and possible project alterations that could increase the efficacy of the CI method are discussed. A conclusion for the chapter follows.

5.4 Future recommendations

During the completion of the research project, specific improvements and future implementations to the system were identified, which are as follows:

- The implemented PRBS signal was designed with a certain frequency range to minimise the characterisation time compared to that of EIS. It was observed that by decreasing the frequency from 0.8 – 0.1 Hz, the simulation of the PRBS signal increased drastically. However, by eliminating the low frequencies, the mass transport region of the cell, responsible for calculating the Warburg impedance, was neglected. Thus, to successfully characterise the cell, the mass transport must also be evaluated. The discharge behaviour of the PEMWE cell can also be investigated and modelled using an updated EEC. Furthermore, the effects of degradation can also be investigated since the present approach might put substantial stress on a PEMWE cell.
- The CI model used for EEC parameter calculation is very sensitive. Thus, the initialisation parameters of the EEC have to be selected in close proximity to the actual values for accurate parameter estimations. Thus, during this project, the electrical parameters were first determined using EIS and thereafter implemented in CI to see if the model converged and if the CI and EIS parameter results correlated. Thus, an updated model is required to eliminate the sensitivity during parameter calculations, ensuring accurate results during simulation.
- Further investigation of the inductive contribution of the Gamry® during EIS experiments must be done to ensure accurate electrical parameter calculations. The source of the contribution is not entirely pin-pointed within this project, and identifying the stray contributor can be advantageous during system modelling.
- Due to the initial design requirements of the CS development board, the current rating of the board is only applicable for 25 cm² PEMWE cells. An updated board with a higher current supply rating is required if PEMWE cells with larger surface areas want to be tested, for example, the 55 cm² PEMWE cell.

5.5 Conclusion

The research conducted throughout this project played an essential role in the development of a CS device to characterise a PEMWE cell. The problem statement and aim of the research project were thoroughly discussed and have been achieved through the concluded results obtained within this project. The key research questions formulated within Chapter 1 were also thoroughly analysed and discussed, and all primary and secondary objectives set out for this project have been met. A CI model utilising the development board have been proposed, the system model and setup has been designed and implemented, and the obtained results are verified and

validated. The discussion of the results obtained shows the CI model sensitivity. Furthermore, testing of the Warburg impedance during mass transport of the cell is also recommended.

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