Investigations of novel AC:DC dynamic operations on PEM electrolyser

- Master Thesis -

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Daniel Sales Roger

Aalborg University
AAU Energy

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Participant(s):
Daniel Sales Roger

Supervisor(s):
Xiaoti Cui
Søren Højgaard Jensen

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Summary:

This project work is part of AAU's MSc program of Energy Engineering with specialisation in Fuel Cells and Hydrogen Technology.
The aim of this master thesis is to test the AC:DC operation on a PEM electrolyzer single cell. AC:DC operation is a new technology for dynamic operation that has been already tested on SOEC and showed long time degradation and thermal benefits.
Through the analysis of the experiments, the report shows the possible positive impacts that can also have the AC:DC application on PEM water electrolysis. Several tests are carried under the AC:DC operation and compared with the impact that would have running the PEM electrolyzer cell on a DC current. To be able to do it, a test setup composed by a container with distilled water, a hot plate, a water pump, and a power supply are used to run the different experiments on the PEM electrolyzer cell mouonted on a sandwiched structure. EIS and Galvanodynamic tests are carried during the different experiments to study how the PEM electolyzer cell changes its properties under the two different operations.

Preface

This report is the result of the master thesis from a student of the Hydrogen and Fuel Cell Technology (HYTEC) specialisation of the Energy Engineering master of the Faculty of Engineering and Science at Aalborg University. Is recommended to have the nomenclature printed as a handy companion to ease the reading. Throughout the report, comma has been used as triad separator, while period is used for decimals. SI units and IEEE style has been used for references. Figures, tables and equations are numbered as: chapter number, figure/table/equation number of the chapter. Each chapter starts with a brief introduction.

Aalborg University, June 1, 2023

Daniel Sales

Daniel Sales Roger
<dsales21@student.aau.dk>

Nomenclature

Letters	Description	Unit
AC:DC	AC:DC operation	-
Area	Area	m^2
AEC	Alkaline electrolysis	-
AC	Alternate current	-
AEM	Anion exchange membrane	-
z	Amount of electrons	-
BPP	Bipolar plate	-
C	Carbon	-
CO	Carbon monoxide	-
CO_2	Carbon dioxide	-
CL	Catalyst layer	-
ΔH_R	Change of the enthalpy of reaction	J/kg
CPE	Constant phase element	-
DC	Direct current	-
EIS	Electrochemical impedance spectroscopy	-
e	Electron	-
F	Faraday constant	C/mol
freq	Frequency	Hz
GDL	Gas difussion layer	-
HF	High frequency	-
H_2	Hydrogen	-
HER	Hydrogen evolution reaction	-
Z	Impedance	Ω
L	Inductor	H
IrO_2	Irridium dioxide	-
KPIs	Key performance indicators	-
l	length	m
LF	Low frequency	-
MF	Medium frequency	-
MEA	Membrane electrode assembly	-
Ohm	Ohmic	-
O_2	Oxygen	-
OER	Oxygen evolution reaction	-
Pt	Platinum	-
PEM	Polymer electrolyte membrane	-
PTL	Porous transport layer	-
KOH	Potassium hydroxide	-
R	Resistance	Ω

Letters	**Description**	**Unit**
RuO_2	Rutenium dioxide	-
SOEC	Solid oxide electrolysis	-
ρ	Solution resistivity	-
V_{th}	Thermoneutral voltage	V
Ti-fel	Titanium fiber	-
TOT	Total	-
H_2O	Water	-

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Chapter 1

Introduction

1.1 Background

Hydrogen is a clean and renewable energy source that can be used for a variety of applications, including fuel cell vehicles, energy storage, and industrial processes. Nevertheless, the current production of hydrogen is primarily based on fossil fuels, which contributes to greenhouse gas emissions and climate change [1].

Polymer electrolyte membrane (PEM) water electrolysis is a promising technology considered one of the main competitors for the production of green hydrogen in the future (Figure1.1). PEM water electrolysis offers an alternative approach of producing hydrogen by using electricity generated from renewable sources, such as wind or solar, to split water molecules into hydrogen and oxygen.

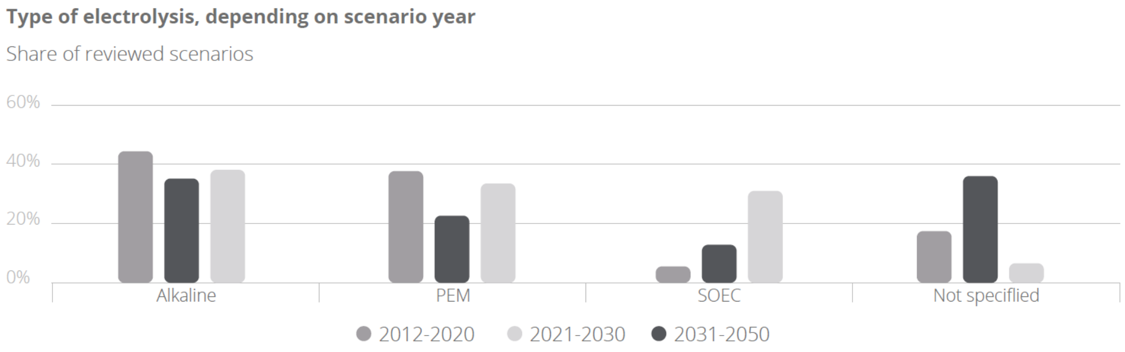

Figure 1.1: Type of electrolysis technology assumed in analyzed scenarios [2]

PEM water electrolysis operates at relatively high current densities compared to other traditional water electrolysis technologies. Furthermore, PEM water electrolysis thanks to its compact system design can be easily scaled up or down to meet different production needs, making it a versatile and flexible technology for hydrogen production. In particular its great dynamic performance such as fast start up and quick response make it a good candidate for integrating with intermittent renewable energies for energy storage or hydrogen production. Another advantage that offers PEM water electrolysis is the high purity of the produced hydrogen [3].

However, there is still lack of knowledge or experiences regarding the influences of frequent dynamic operations on its key performance indicators (KPIs, e.g., degradation rate). In spite of its advantages, PEM water electrolysis still faces several technical and economic challenges, such as the need for efficient catalysts, durable membranes, and cost-effective systems.

1.2 Water Electrolysis

Water electrolysis is the process whereby water is split into hydrogen and oxygen. The process can be represented by the following chemical equation:

$$H_2O(g/l) + \Delta H_R \rightarrow H_2(g) + \frac{1}{2}O_2(g) \tag{1.1}$$

In 1.1, ΔH_R is the change in the reaction of enthalpy for this endothermic reaction, the amount of energy required for breaking up the chemical bond. This quantity is calculated from the sum of the enthalpies of formation of the reactants minus the sum of the enthalpies of formation of the products. The water is fed as reactant, and the reaction takes place at the electrodes. Due to the limited self-ionization of pure water, acid is used as electrolyte and electrolcatalysts are applied to lower the activation energy. The decomposition of water begins once a potential higher than the thermodynamic reversible potential is applied to the electrodes since various activation barriers have to be overcome. Using ΔH_R, the Farady constant F, and the amount of electrons z transfered during the reaction, the thermoneutral voltage can be calculated by

$$V^0_{th} = \frac{\Delta H^0_R}{zF} = 1.481V \tag{1.2}$$

At the anode water is oxidized, and the released electrons are transported trough the external electrical circuit and oxygen is formed (OER). Protons travel trough the acidic electrolyte to the cathode where they are reduced by the electrons from the electrical circuit to hydrogen (HER). The amount of hydrogen generated is ideally twice the amount of oxygen generated. The two half reactions are showed in the following equations:

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \tag{1.3}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{1.4}$$

1.2.1 Overpotentials

As mentioned previously in the section several barriers need to overcome to decompose the water. These barriers are the so called kinetic losses: activation, ohmic, and mass transfer losses. The activation losses result from the direct transfer of electrons (charge-transfer kinetics) between the electrode and the electrolyte of the OER and HER. This phenomena leads to irreversibilities on the anode and the cathode, called anodic activation overpotential and cathodic activation overpotential, that added together form the activation overpotential. Ohmic losses arise from the resistance to the flow of protons through the electrolyte. According to Ohm's law it is directly proportional to the current applied to the electrolysis cell. Mass transport losses can be either diffusion losses or bubbles overpotentials. The first occur when gas bubbles partially block the pores network of current collectors and limits the supply of reactant water to the active sites. On the other hand, bubbles overpotentials arises when very large gas bubbles shield the electrochemical acitve area, reducing the catalyst utilization. The actual voltage for splitting the water molecules is the sum of the thermoneutral voltage plus all the irreversibilities within the cell. Figure 1.2 shows an I-V curve with the contributions of the different overpotentials:

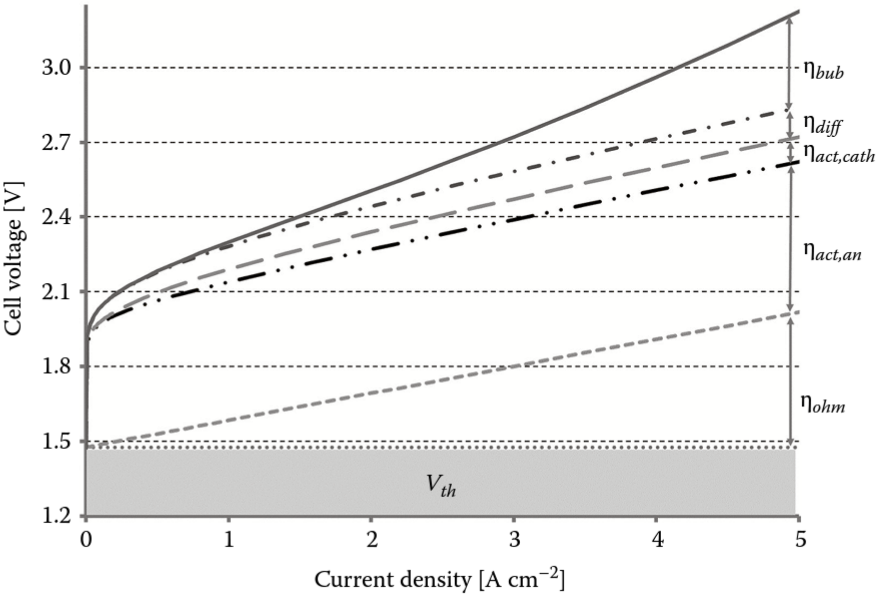

Figure 1.2: Overpotentials in a conventional PEM electrolysis cell [4]

1.2.2 Alkaline Electrolysis

Between the main electrolysis technologies alkaline electrolysis (AEC) is the most mature one, reaching the megawatt range at commercial level for large-scale industrial applications. An aqueous solution of KOH is used as electrolyte in alkaline electrolyzers. The alkaline cell is composed of two electrodes separated by a diaphragm used to avoid the recombination of hydrogen and oxygen that are being produced. AEC technology exhibits relatively low capital cost due to the avoidance of noble metals. However, low current density and operating pressure negatively impact system oversize and production costs.

1.2.3 Solid Oxide Electrolysis

Solid oxide electrolysis (SOEC) is a technology still under development whose technical advantages are a potential higher efficiency than the other technologies. This technologies can also be used to produce CO from CO_2 and syngas H_2/CO from H_2O/CO_2. The most common electrolyte material is yttria-stabilized zirconia which show high conductivity and thermal stability at high working temperatures (800-1000ºC). High working temperature permits to reduce electrical power demand. As an endothermmic process, SOE could considerably reduce the cost of hydrogen if heat is supplied by waste heat.

1.2.4 PEM electrolysis

Proton exchange membrane (PEM) water electrolysis involves the use of a specialized electrolysis cell that contains a proton exchange membrane. This membrane separates the anode and cathode compartments of the cell while allowing for the transport of protons from the anode to the cathode. When an electric current is applied to the cell, water molecules in the anode compartment are oxidized to form oxygen gas and positively charged hydrogen ions (protons). The protons migrate through the proton exchange membrane to the cathode compartment. At the cathode, the protons combine with electrons from the electrical circuit to form hydrogen gas. Meanwhile, oxygen gas is released at the anode. Among its main advantages are high power density, pure hydrogen production and flexible operation. On the other hand, a high capital cost and water purity requirements are the disadvantages of this technology.

1.2.5 Anion Exchange Membrane Electrloysis

Another technology that is under early stage development is anion exchange membrane (AEM) electrolysis. This technology combines an alkaline environment with a membrane similar to the one from PEM. This combination takes some of the advantages of both technologies. The liquid electrolyte not only reduces the ohmic resistance but also improves the reaction kinetics. The hydrogen permeability on AEM is usually around one order of magnitude less than PEM, and can be substantially thinner [5]. However, degradation caused by the alkaline electrolyte is still challenging.

Figure 1.3 depicts the technology set-up for the mentioned electrolysis technologies:

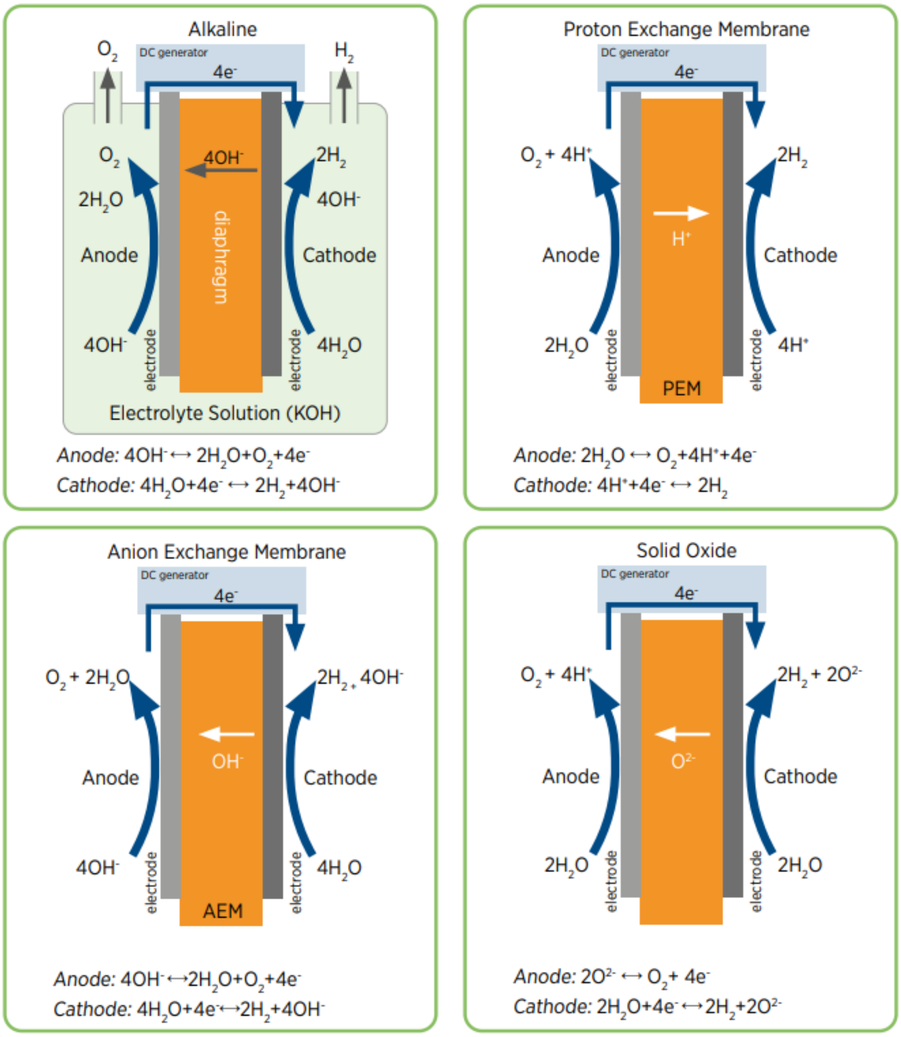

Figure 1.3: Conceptual set-up of electrolysis cell technologies [6]

1.3 AC:DC operation

The AC:DC operation is a new technology for dynamic operation of large-scale solid oxide electrolyzer (SOEC). It was patented in 2019 by DynElectro ApS. The main idea is to add a pulsed operation where an AC current (or voltage) is applied on top of a DC current (or voltage), so the electrolyzer also work shortly at fuel cell mode. An example for AC:DC operation is shown in Figure 1.4:

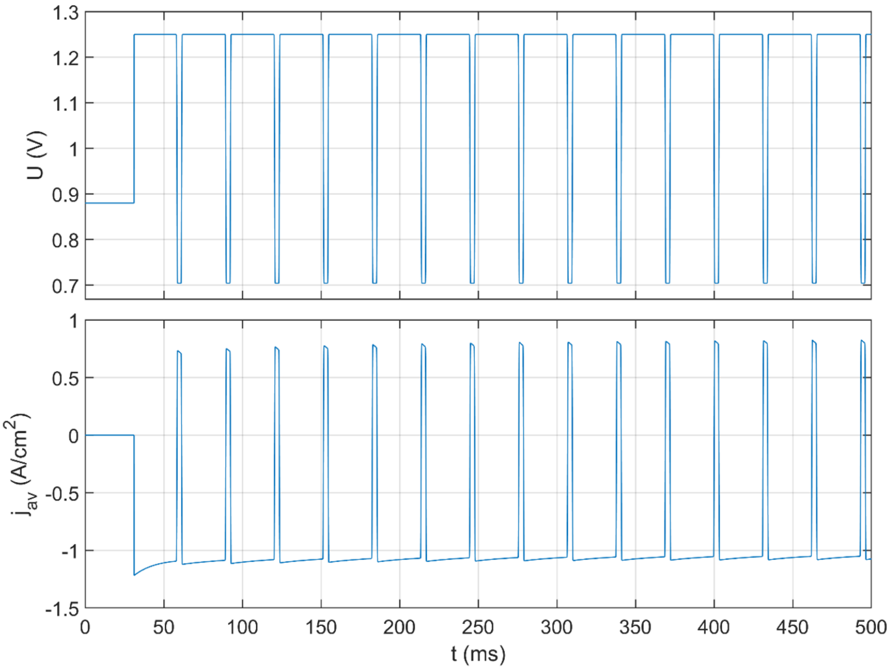

Figure 1.4: AC:DC operation experimental data [7]

For this experiment a 3ms voltage pulse is used to run the electrolyzer in fuel cell mode. This pulse is introduced after 30ms where the SOEC is working on electrolyzer mode. This voltages induced a current of about -1.1 A/cm2 for the 30 ms on electrolyzer mode and a current of 0.75 A/cm2 during the 3ms of fuel cell mode. That left an average current density of 0.932 A/cm2.

The tests for SOEC confirmed the operation method reduce degradation up to 7 times and remove temperature variations in dynamically operated SOEC stacks. It is also reported to prolong lifetime via improved resilience against impurities by desorption via electrochemical oxidation/reduction [7]

1.4 PEM cell electrolyzer components

The main components of a PEM cell electrolyzer are the membrane, catalyst layers (CL), porous transport layers (PTL), bipolar plates (BPP) and end plates (EP).

The catalysts layers and porous transport layers on either side of the membrane constitute the membrane electrode assembly (MEA) showed in figure 1.5. Expensive noble materials are typically used as electrocatalysts in PEM electrolysis. Platinum and Iridium dioxide are the most commonly used materials at the cathode for the hydrogen evolution reaction (HER) and at the anode for the oxygen evolution reaction (OER), respectively. IrO_2 shows high corrosion resistance but relatively high activity compared to Rutenium dioxide which exhibits the highest activity. However, RuO_2 has some problems with stability that precluded practical application. On the other hand, nonnoble metal formulation solution, would be interesting for OER, but conductivity, electrocatalytic activity, and stability are challenging aspects. Platinum electrocatalysts have best catalytic activity and high corrosion resistance as HER. In particular, platinum nanoparticles supported on carbon black are the standard catalysts for HER.

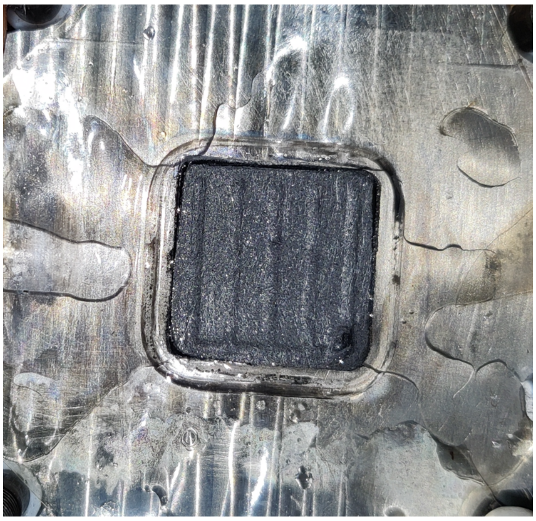

Figure 1.5: Membrane electrode assembly used in the laboratory

The porous transport layer is the component of the cell responsible of the mass transfer, electrical and heat conduction between the catalyst layer and the bipolar plates. The materials that are commonly used for the porous transport layers are Ti-felt for the anode and carbon cloth for the cathode side.

The membrane is used for the elctrolyte and it separates the anode and the cathode. The most common material used for the membrane in PEM electrolysis is Perfluorosulfonic acid polymer Nafion is its common commercial denomination. Excellent chemical stability, high proton conductivity and area specific resistance of about 0.15 cm^2 are among its best features, besides having low crossover and mechanical strength. The drawback of Nafion is the cost, and many researchers are focusing on finding cheaper alternative membranes. Furthermore, the Nafion conductivity decreases at temperature above 100°C because of membrane dehydration. Hydrocarbon membranes are a good alternative to Nafion, having an appropiate conductivity and a better resistance to crossover, besides their lower cost.

The bipolar plates (Figure 1.6) are the components that ensure the transportation of the reactants which are in this case the deionized water that is feed to the PEM electrlyzer and the generated hydrogen and oxygen. Currently, several types of materials are used in bipolar plates, including titanium, graphite, and coated stainless steel. Titanium shows excellent properties but passivation (formation of a passive oxide layer) decreases its electric contact resistance and thermal conductivity, and consequently decreasing the stack performance over time. The low coating imperfections make stainless steel a solution exposed to destruction of coating due to corrosion increasing the ohmic resistance. Bipolar plates and current collectors are the most expensive components in PEM electrolysis.

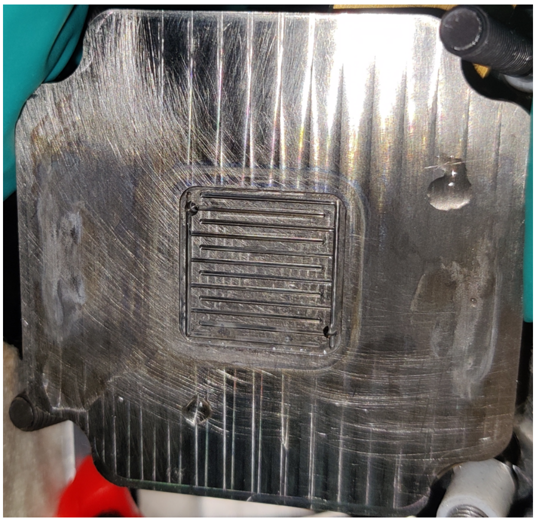

Figure 1.6: Bipolar Plate used in the laboratory

The current collectors (Figure 1.7) work in the same conditions of bipolar plates. They have the function to conduct the electrons from the catalytic layer to the bipolar plates and remove the gases from the catalytic layer. Therefore, porosity and conductivity are important properties for current collectors. The most common materials for this component are titanium and stainless steel.

Figure 1.7: Current collector used in the laboratory

1.5 Problem Statement

The present project aims at extending the application of AC:DC operations to PEM cell electolyzer, and investigate if they can also has positive impacts on KPIs for PEM water electrolysis. The DynPEM project will include:

- Investigating the KPIs of single cell testing under steady-state and AC:DC operations.
- Assessments of the impacts and feasibility of AC:DC dynamic operations for an PEM cell electrolyzer system.
- Carrying tests with a PEM cell electrolyzer to investigate the possible impacts on KPIs by performing several characterization techniques.
- Enhance and perfect technical and analytical skills to perform experiments with PEM electrolysis

Chapter 2

Experimental setup

In this chapter the setup used in the laboratory to run the experiments is explained. Then an explanation of the different testing procedures and electrochemical methods implemented to carry the different tests is given.

2.1 System Layout

The MEA utilized in the experiments has an active are of 2.89 cm^2, and its solid electrolyte is composed of Nafion® 117. The anode catalyst layer is made of 0.3 mg cm^{-2} IrO_2 and the cathode catalyst layer 0.5 mg cm^{-2} Pt/C, respectively. The gas diffusion layer (GDL) on the anode side is constituted by 350µm of Ti-felt with a 81% porosity, and Sigracet® 35DC carbon was used for the GDL on the cathode side. All the components are mounted on a sandwiched structure as in figure 2.1

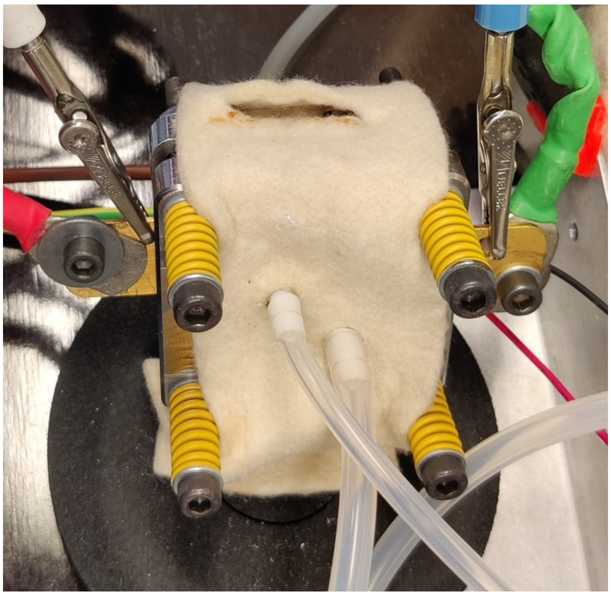

Figure 2.1: Sandwiched PEMWE used in the laboratory

The test setup is shown in figure 2.2. The distilled water is stored in a container that is heated with a hot plate that is controlled manually. The temperature is monitored with a thermometer. A pump is used to pump the water from the container to feed the electrolyzer cell. The pump is connected to a power supply. The circulation system is connected twice to the anode side, to provide the water once, and to collect the released oxygen that comes back to the bottle on the other side. On the cathode side another plastic tube is connected to the outlet were the produced hydrogen exits the cell. The current collectors are connected to the Gamry Reference 3000 and the current booster, that supply the power to perform the different tests carried during the project.

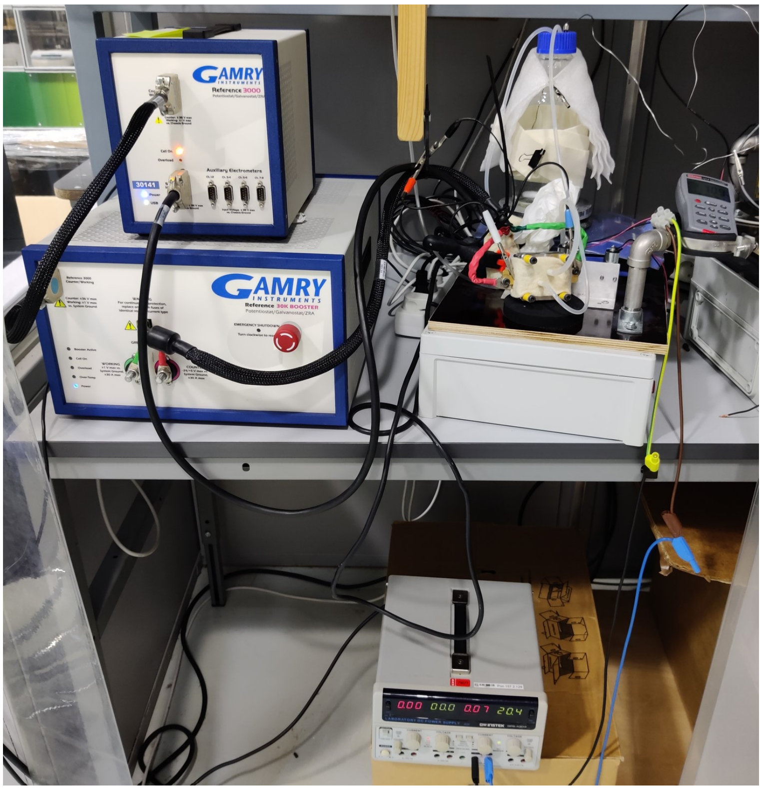

Figure 2.2: Test Setup from the laboratory

2.2 Testing procedures

Before statring the experiment the water needs to be heat first up to the desired temperature which is in this case between 60ºC and 80ºC. This process takes some time to stabilize the temperature. Once the water reaches the desired temperature, which is measured with a thermometer, the pump is turned on with the power supply at 24V 0.07A for 5 minutes to preheat the PEM cell electrolyzer. The water flow rate was measured to 3.85ml/s. After this procedure the setup is ready to start the experiment with the Gamry Reference 3000. All the experiments are carried at atmospheric pressure.

2.3 Electrochemical methods

To facilitate the experiments, a Gamry Reference 3000, combined with a 30k Booster, was employed. The methods utilized to characterize the PEM cell electrolyzer are analogous to those utilized for characterizing fuel cells and, as such, are well established although the practical applications of the two techniques differ significantly. The characterization techniques utilized for this project are Galvanostatic Electrochemical Impedance Spectroscopy, Galvanodynamic scan, Galvanostatic and Chronopotentiometry.

2.3.1 Galvanostatic Electrochemical Impedance Spectroscopy

The Galvanostatic EIS technique is used to characterize the electrochemical interface by extracting the impedance spectra of the PEM electrolyzer. Galvanostatic mode gives precise control over the current that is induced to the examined cell, thus avoiding overloading. In EIS, a small AC amplitude perturbation is added on top of a constant DC current with a changing frequency. The amplitude of the AC current is set to 5 per cent of the DC current. The impedance spectra is typically measured by sweeping frequencies over the range from 10mHz to 10kHz.

This technique provides information about the electrochemical reactions occurring inside the electrolyzer. The reactions can involve electrolyte resistance, adsorption of electroactive species, charge transfer at the electrode surface, and mass transfer to the electrode surface. Each of this processes can be considered as an electric component. They can be represented as a resistance, capacitor, or constant phase elements that can be arranged in series or in parallel as an electrochemical circuit 2.3.

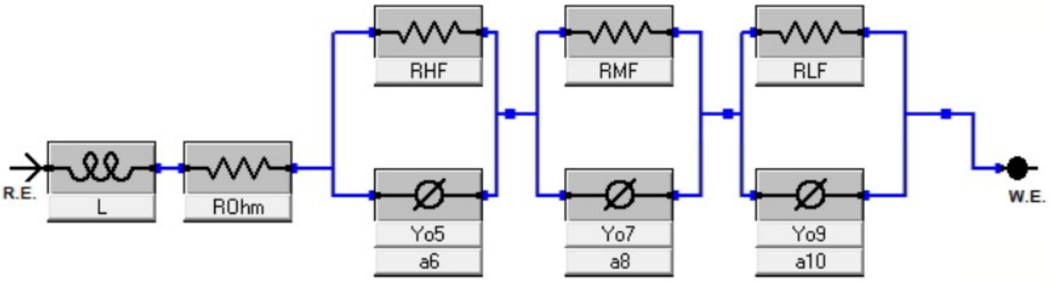

Figure 2.3: Electrical circuit representation of a PEMEL

The output of the experiment is a complex impedance spectrum, that makes possible to show the results in a typical Nyquist plot with the real impedance as the X axis and the imaginary impedance as the Y axis 2.4. The impedance of a resistor is its resistance that depends on the length l, the surface area A, and the solution resistivity ρ:

$$Z_R = \frac{\rho l}{A} \tag{2.1}$$

The elements in parallel with the resistances are called constant phase elements (CPE), and they represent the nature and roughness of the interface between the electrocatalyst and the ionomer electrolyte [8]. The impedance of a CPE is calculated by the following expression:

$$Z_{\mathrm{CPE}} = \frac{1/Y_0}{(j\omega)^a} \tag{2.2}$$

Where Y_0 is a constant that represents the capacitance and the parameter a is another empirical constant that has its value normally between 0.5 and 1 when is representing a CPE. When the parameter a is equal to 0.5 it represents a pure capacitor. The impedance of an inductor is represented by

$$Z_L = j\omega L \tag{2.3}$$

The impedance of the elements in parallel such as the resistors with the CPE for this case can be calculated as:

$$\frac{1}{Z_{//}} = \frac{1}{Z_R} + \frac{1}{Z_{\mathrm{CPE}}} \tag{2.4}$$

Therefore for the electrical circuit presented in figure 2.3, the total impedance will be:

$$Z_{\mathrm{TOT}} = Z_L + Z_{\mathrm{ROhm}} + Z_{//\mathrm{HF}} + Z_{//\mathrm{MF}} + Z_{//\mathrm{LF}} \tag{2.5}$$

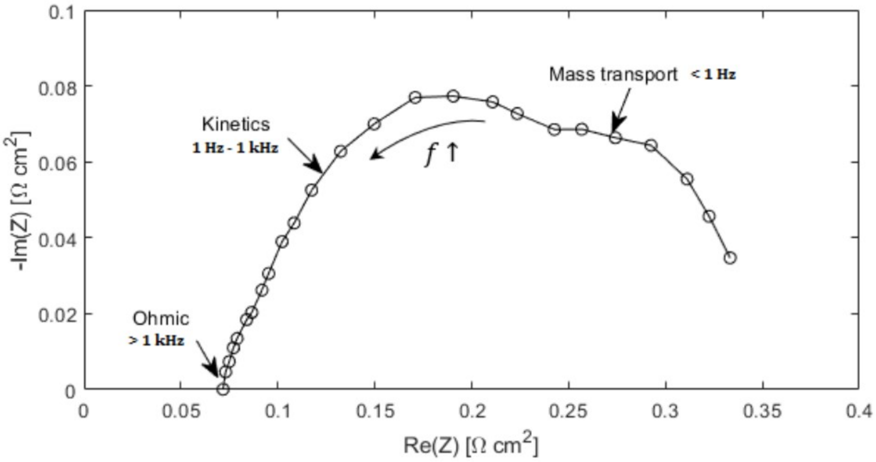

Figure 2.4: Nyquist plot of a PEM fuel cell [9]

The intercept of the high-frequency arc with the real axis in the Nyquist plot spectrum represents the internal ohmic resistance, whereas the high, medium and low frequency regions are associated with the charge-transfer resistance (kinetic loop), and the mass transfer resistance. The total ohmic resistance is the sum of the contributions from contact resistances between components and ohmic resistances of the cell components such as membrane, CL, GDL and BPP. The high frequency resistance is normally associated with the charge transfer losses of the oxygen evolution reaction (OER). The contribution of the hydrogen evolution reaction (HER) on the high frequency resistance is small compared with OER the [10]. In figure 2.5 can be seen that the polarisation resistance of the cathode can be much lower than the polarisation resistance on the anode. It can be concluded from this observation that the contribution of the cathodic process to the charge transfer resistance can be neglected and is mainly associated with the anode. The process of the HER in acidic aqueous and its fast response is the explanation of having a low polarisation resistance. On the other hand, the OER is rather slow consisting of a two electron process and therefore its bigger polarisation resistance. The low and medium frequency resistances represent the electrochemical process of mass transportation losses, which can be associated with the gas diffusion at the porous transport layers.

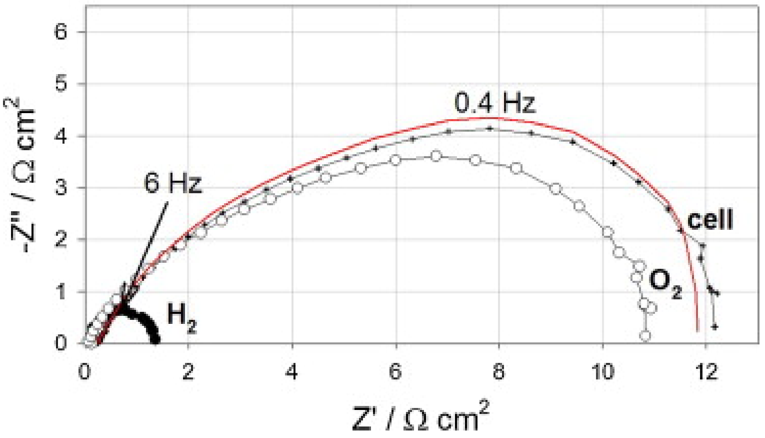

Figure 2.5: Impedance spectrum of (•) the cathode (HER), (o) the anode (OER) and (+) total PEM cell measured at 80 °C and 1.4 V [10]. Characteristic frequencies are indicated at the summit of the arcs

The plots presented in the last two figures are called Nyquist plots. Since the Nyquist plot does not reflect the frequency where the point was reflected, the Nyquist plots in this project are always accompanied with a Bode plot where frequencies are displayed in front of the imaginary impedance. Imaginary impedance was used instead of absolute impedance to better identify the points and relate them between the Nyquist and the Bode plots.

2.3.2 Galvanodynamic scan

The PEM cell electrolyzer polarization curve was obtained using Galvanodynamic scan. The main purpose of getting the polarization curve is to determine the change in the cell voltage generated by the variation of the applied current under steady state conditions.

A linear current sweep of 1mA/cm^{-2}s is used to get the polarisation curve, always under galvanostatic control. The mesurement is aborted if the cell voltage is higher than 2.5V.

In the Galvanodynamic mode, a current induced is varied from 0.001 A/cm^{-2} to 1.8A/cm^{-2} at an increasing rate of 1 mA/cm^{-2}s. The voltage is measured to determine the various points along the I-V curve. The information obtained during the experiment is highly valuable for characterizing and distinguishing between the different voltage losses. Additionally, it is of great interest in degradation investigations because it can indicate the extent to which the I-V curve has altered from one initial state to another degraded state.

2.3.3 Galvanostatic

Galvanostatic is a polarisation technique used to maintain the PEM cell electrolyzer on steady state with a constant current. This technique is used to measure corrosion rate and electrochemical reactions. It allows the controlled polarisation of the metal surfaces at the electrolyte, in order to observe the anodic and cathodic behaviours.

2.3.4 Chronopotentiometry

A Chronopotentiometry is another polarisation technique used to create the AC:DC operation for the PEM cell electrolyzer. In this technique the cell is operated under Galvanostatic mode to control the current while the resulted potential is measured. This technique allows to create short steps of time in milliseconds range such as the ones required to run the PEM electrolyzer cell on the AC:DC operation.

Chapter 3

Descritption of the experiments

This chapter shows the procedures carried for the different tests. The sections from Chapter 3 that give the explanation about how the tests were carried out, are related with their corresponding section in Chapter 4, where results from the tests explained in this Chapter 3 are presented.

3.1 Old membrane tests

The chronology for the tests carried with the old membrane on the PEM cell electrolyzer followed the following description: first a 24h on direct current, second 20h on AC:DC operation, third 32h DC current test, fourth 24h AC:DC operation test, and fifth an alternated 12h on AC:DC operation and 12h on DC current test. The timeline for the procedures carried on the electrolyzer with the old membrane is shown in the following figure 3.1.

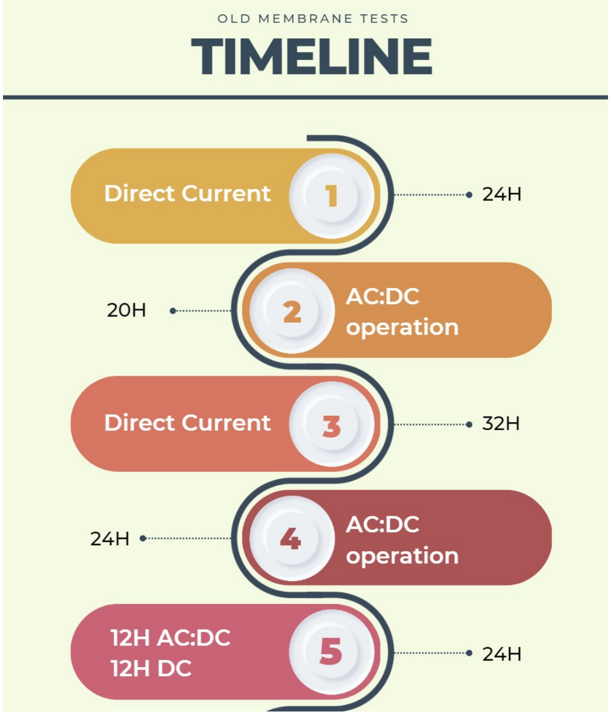

Figure 3.1: Timeline for old membrane test

3.1.1 1st 24h Direct current test

The first tests of the project were carried with the PEM membrane that was used three months before for last time for a previous project. The electrolyzer was already assembled in the sandwiched structure with all the cell components. A Galvanostatic mode was used to see if the membrane needed some activation time. Therefore a DC current of 932mA/cm^2 was induced on Galvanostatic mode for a total time of 24h. The current value was calculated so the DC current tests would have the same average current as the AC:DC operation tests. EIS was curried always under a DC current of 2.89A and an AC current of 0.145A rms. IThe initial frequency was 10^5 Hz and the final freq. 0.2Hz. The Galvanodynamic scan to obtain the polarisation curve started with an initial current of 0.001A/cm^2 and with an increase rate of 1mA/cm^2*s reached up to 1.6/cm^2. The settings for this experiment were a temperature of 68.6°C and the pump was set with a voltage of 20.4V and a current of 0.06A.

3.1.2 2nd 20h AC:DC operation test

The first 20h experiment where the AC:DC operation was tested, was carried with a temperature of 71°C. The test was splitted in two parts since after more than 17h usb connection was lost. After losing the connection the test was restarted for more than two hours until the end of the test. The AC:DC operation was created with the Chronopotentiometry electrochemical technique. The current supplied to the PEM cell electrolyzer is shown in figure 3.2.

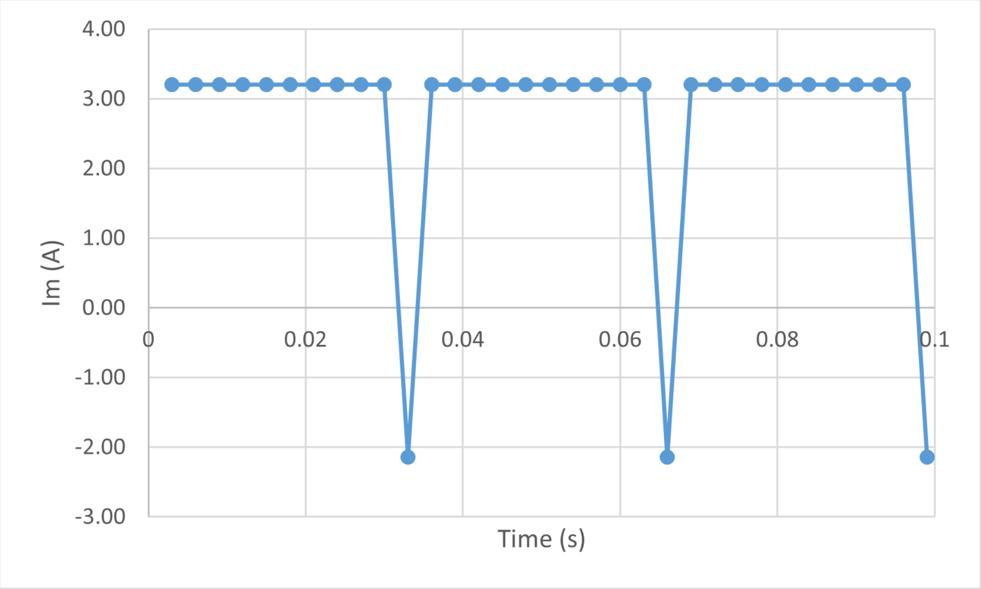

Figure 3.2: AC:DC operation current signal for 3 periods of 33ms each

The sample time was of 3ms. The period was set to 30ms with a current of 1.1 A/cm^2 and 3ms with a negative current of 0.75 A/cm^2.

3.1.3 3rd 32h Direct current test

A 32h experiment was carried on a DC current. The experiment was structured in periods of 4h running on 932mA/cm^2 which is the equivalent average current of the AC:DC operation used to run the previous test. During the experiment some data loss was experienced meaning that the characterization techniques (EIS and IV curves) were only recorded during the first 12h of the test.

3.1.4 4th 24h AC:DC operation test

An AC:DC operation test was run again, this time for 24h. The followed structure was the same as in the previous test with periods of 4h running on the AC:DC operation with the same operation parameters as during 3.1.2. Polarisation and EIS were taken with the same procedures as in the previous tests.

3.1.5 5th 12h AC:DC and 12h Direct Current test

Another test was carried with the PEM cell with an alternating first 12h with the AC:DC operation and later with a direct current under Galvanostatic mode for 12h. At the beginning of the test an EIS analysis at different current densities was carried. The purpose of this test was to see how the EIS impedance is affected by using different current densities. EIS test at current densisties of 1.5A/cm^2 and 2A/cm^2 were carried, apart from the test at 1A/cm^2.

After the test the PEM cell was disassembled and the membrane was removed. After a visual inspection (Figure 1.5), not any visual symptoms of degradation were observed.

3.2 New membrane

A new membrane was used for running new tests. The membrane was first activated for 72h with a DC current of 500mA/cm^2. Water consumption was 120ml/day. Temperature was set to 70ºC. Water was added once a day. When adding the water temperature fell to 60ºC and it increased until reaching the 70ºC where it was before adding the water. After the activation procedure the first polarisation curve was taken.

Two different test were carried with this membrane. The first one was a 5 days test using the AC:DC operation, and the second one was a 2 days test on DC current, which was initially planned for 5 days as well but due to technical problems was finalized after the first 2 days of the test.

3.2.1 AC:DC operation test 5 days

The procedure of the test follows cycles of 8h running on AC:DC operation that for runs 14 times. The AC:DC operation runs on 48 subcycles each one of 10min due to software constrains. This 10min cycle runs 18181 periods of 33ms were the current for the first 30ms is at 1.1A/cm^2, and it is followed by a 3ms were the current is set to -0.75A/cm^2. The first 30ms the electrolyzer is on electrolyzer mode while the other 3ms on fuel cell mode.

The test started at 11:24PM on the 2nd of April. The first day, 3rd of April at 10AM the temperature was measured to be 72.4ºC. 72.6ºC was the temperature before adding water at 1:15PM and it dropped to 61.1ºC. Second day, 4th April there was a connection lost at 8.34AM. Temperature at 10AM was 72.4ºC as well. At 10.13AM connection was reestablished. That means that for 1 hour and 39 min the test didn't run. At 2.55PM 220ml (220ml/day) were added. Third day, 5th April there was a connection lost at 4.50AM. Connection was reestablished at 9.18AM and 140ml (240ml/day) of water were added. The following cycles ran the test until 10PM on 7th of April with a total of 120h running on AC:DC operation mode.

The rest of the days parameters were not possible to be checked but stability was checked during the first days to be sure that such things as water consumption and temperature were constant.

3.2.2 DC current test 2 days

The procedure of this test followed a cycle of 8h running on DC current for 14 times, to run the test for a total time of 5 days. The test was started on 12th April at 1.21PM. Temperature was 72.2ºC at 2.42PM. 13th of April at 11.05AM temperature was 71.9ºC. At 2.05PM temperature was 72.5ºC before adding 230ml of water (water consumption per day). After adding new water temperature dropped to 62ºC. 14th of April at 9.15AM temperature was 72.5ºC and 240ml were added. Temperature dropped to 59.7ºC. At 11.30AM 240ml were added. Temperature dropped from 70.9ºC to 60.9ºC. The pump broke at 6PM so the test had to be aborted. This means that the test in the end only ran for 48h.

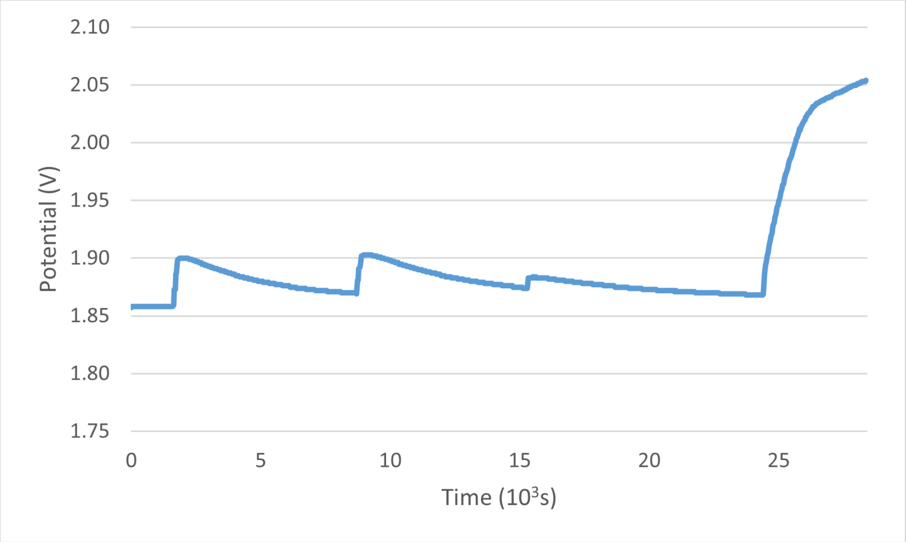

Figure 3.3: Voltage vs time showing the moment of pump failure

After 48h pump broke and stopped working. It was not until 1h later that the test was aborted. Figure 3.3 shows the voltage versus time during the the last 8 hours of the test. The first 3 peak in the voltage represent the times where water was added and temperature dropped to around 60ºC. The last peak in the potential reflects the time where the pump stopped working.

3.2.3 New pump and performance recovery

On April 17th water pump was changed. After changing the pump a Galvanostatic mode ran at 932mA/cm^2 but after the first 10min it needed to be aborted since voltage was around 2.7V. This doesn't correspond with the voltage before the pump broke which reached only 2V. The problem was that the new pump had been used in previous contamination test. Therefore a cleaning was carried. First new deionized water was circulated through the pump and electrolyzer, and removed for 3 times. Afterwards, plastic pipes were changed and deionized, water was circulated again and removed from the cycle. Once everything was clean, new water was added and heated until reaching 72.5ºC.

A DC Galvanostatic mode at 0.5 A/cm^2 ran for 16h to see how much the voltage could recover during that period of time. After this test, another 16h test was run with the AC:DC operation mode. For this test on AC:DC in particular, and since the high voltages experienced, the AC:DC ran on 30ms with 0.55A/cm2 and 3ms with -0.375A/cm^2 while the DC 466mA/cm^2. This could tell us if the AC:DC operation could be used for recovery. Both 16h test showed an initial recover. Hence, a different test was carried to observe the possible recovery advantages of using AC:DC operation in front of the steady state operation. For this purpose, a cycle of 2h on AC:DC operation was run followed by 30min on standby and 2h on steady state. Both of them were covered at low current densities as previously since voltages were really high.

After this test and due to the cut in performance of the membrane after being contaminated by the new pump, the PEM cell was disasembled and the membrane was changed again to try to run again the 5 days test with the DC current.

3.3 2nd New membrane

Since the 5 days test on the DC current was not successful the purpose of using a new one was mainly to run the 5 days test with a DC current. A 3 days activation was required to activate the new membrane. For this purpose the PEM ran on steady state at 500mA/cm^2 for 3 days. Power supply stopped running after the 3 days of activation of the new membrane.

Two weeks after the power supply was broken a manual polarisation curve was taken. Before taking the curve the PEM electrolyzer was preheated and left at 0.5A/cm^2 for 20min. Then, the current was decreased to 0.1A/cm^2 for 5min just right before start taking the values to get the new polarisation curve.

Chapter 4

Results and discussion

In this chapter the results from the different test made at the laboratory with the PEM electrolyzer cell are displayed through the different sections. There are 4 main sections, the first 3 show the results of the test carried under the 3 different membranes used, and the last one is a discussion from the results presented in the 3 previous sections. On the first 3 sections all the test results from each test are shown with the same structure, the EIS impedance and the IV polarisation curves first, and then followed by a small discussion about what can be observed from the results presented in each test. There is also recapitulation on the first two sections from the different tests carried with each membrane. The last section which is called discussion is a recapitulation of all the tests seen from 2 different point of view: the EIS impedance, the IV polarisation curves.

4.1 Old membrane tests

4.1.1 1st 24h Direct Current test

The first tests for this project carried in the PEM cell electrolyzer showed a membrane in an advanced degradation state. The results reflected high voltages, close to 2.5V at 1.6A/cm^2. The initial voltage was 2.112V at 1A/cm^2, and it was reduced after 24h to 2.051V, giving a decreasing rate of -2.54mV/h. The polarisation curves are shown in figure 4.1.

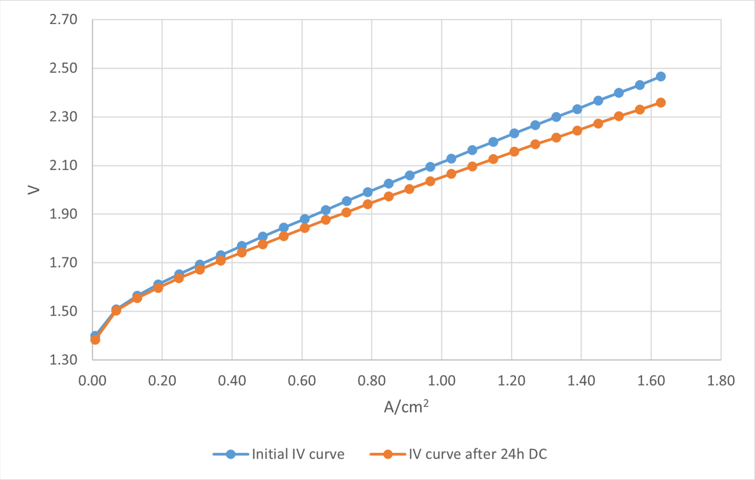

Figure 4.1: Polarisation curves for 24h DC current test

The Ohmic resistance was reduced as well, starting from 108.5mΩ and ending with

96.86mΩ. The High frequency resistance was initially 49.41mΩ, and 39.61mΩ in the end. The two EIS curves that were analyzed are shown in figure 4.2.

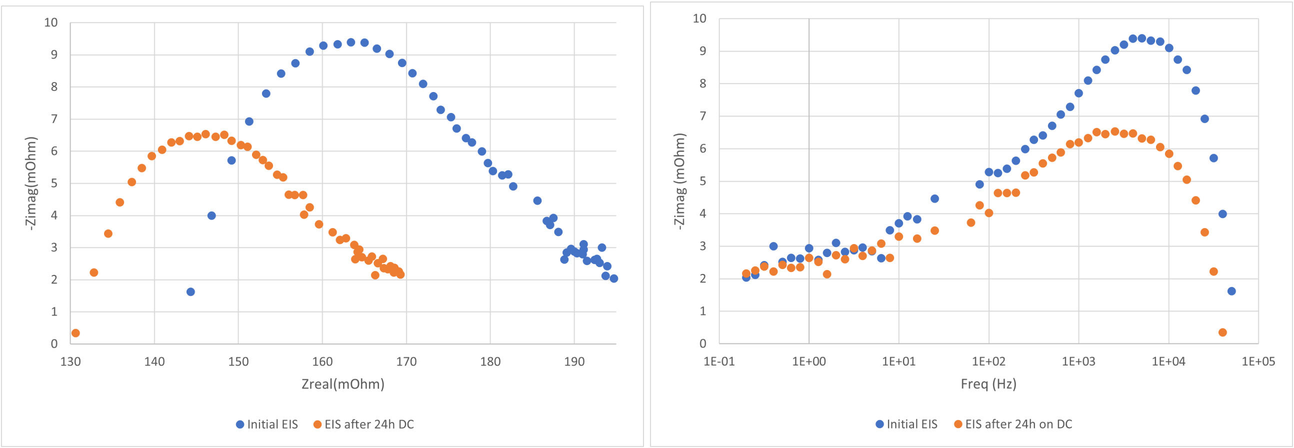

Figure 4.2: EIS impedances for 24h DC current test, Nyquist plot on the left side, Bode diagram on the right side

The effects of this first test were a DC current was held during 24h are reflected in the previous figures where the cell voltage, and the ohmic and transfer losses (high frequency resistance) are reduced. The test shows an activation process of the membrane after being for months not used. This activation process could be occurring reflecting a cleaning and reactivation of the membrane, PTLs, and catalyst layers, that were left in an atmospheric environment were they could have been accumulating some dust. Once the water was circulated again and after the first hours, the majority of the particles accumulated in the components could be removed from the PEM electrolyzer cell.

4.1.2 2nd 20h AC:DC operation test

The following test was where the AC:DC operation was tested for first time for 20h. Water consumption was 200ml (240ml/day, 10ml/h).The voltage response from the current applied, shown in the previous chapter in figure 3.2, to create the AC:DC operation is shown in the following figure 4.3.

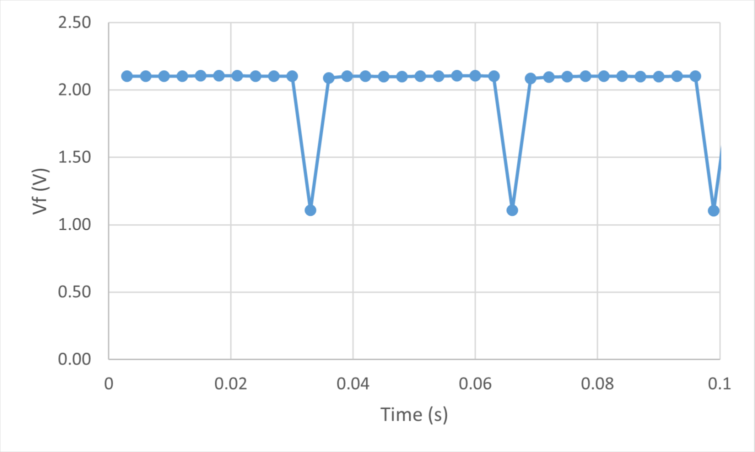

Figure 4.3: Cell voltage for 3 AC:DC operation periods of 33ms, with 3ms sample period

The sample time was 3ms. Figure 4.3 shows a voltage held at 2.1V for 30ms and at 1.1V for only 3ms. The first part of the period the PEM cell electrolyzer runs on its normal operation, on the electrolyzer mode. On the other hand, the last 3ms of each period is where a negative current is applied (Figure 3.2) in order to operate the cell in fuel cell mode. Each period has a time of 33ms.

In the following figures 4.4 and 4.5 the results from the characterization techniques applied during the test are shown:

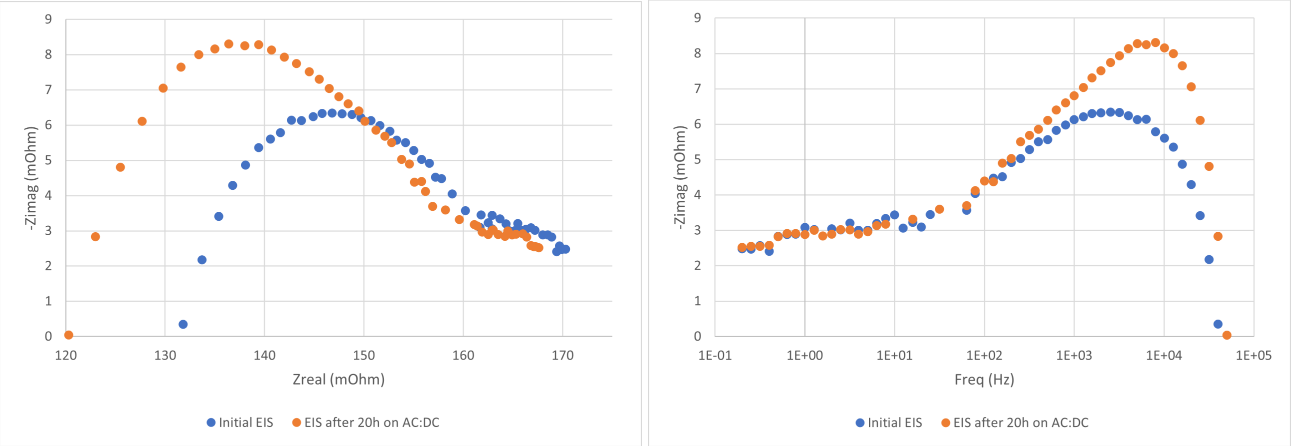

Figure 4.4: EIS impedances for 20h AC:DC operation test, Nyquist plot on the left side, Bode diagram on the right side

The initial resistances were 98.24mΩ for the Ohmic and 38.92mΩ for the high transfer resistance. In the end these values were 86.27mΩ and 46.84mΩ, respectively. Both values decreased in this case.

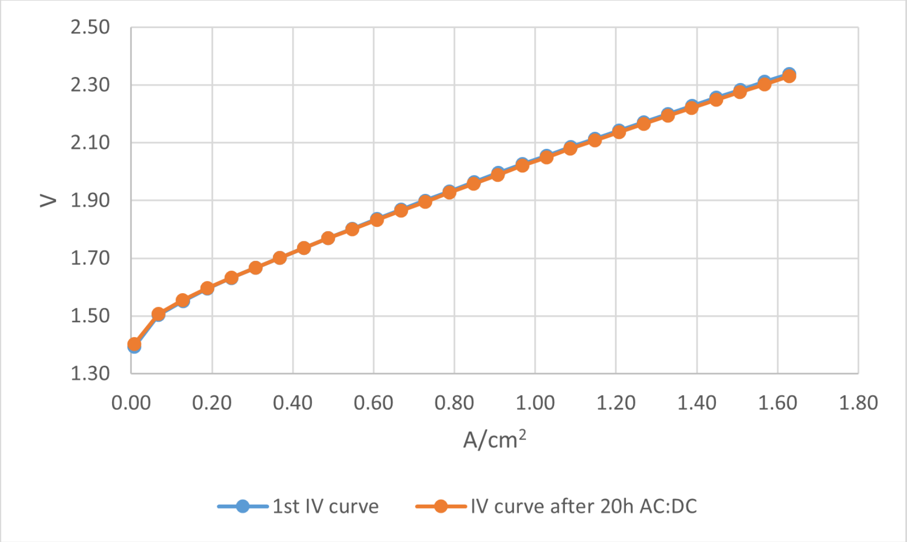

Figure 4.5: Polarisation curves for 20h AC:DC operation test

In figure 4.5, the voltage polarisation curves during the test were analyzed. From a visual point a change in the cell voltage cannot be seen. However, if the curve is seen in more detail as in figure 4.6, the voltage showed a decrease of -0.25mV/h at 1A/cm^2 .

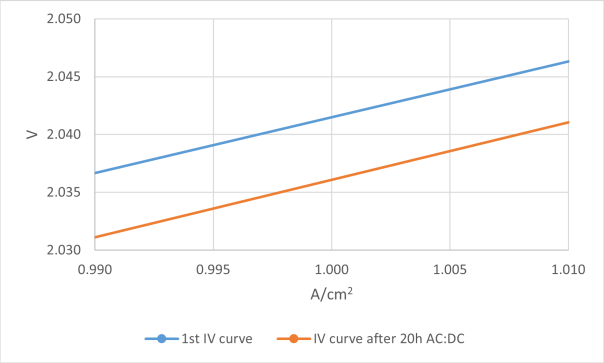

Figure 4.6: Polarisation curves for AC:DC test at 1A/cm^2

The results of this first test where the AC:DC operation is applied for first time showed that such parameters as cell voltage and ohmic resistance are reduced as in the previous test, but not the high frequency resistance. The change of tendency in the high frequency resistance can be a sign of growth of the charge transfer resistance.

4.1.3 3rd 32h Direct Current test

The following test run for 32h under a DC current. The results are shown only for the first 12h of the test 4.7, since the computer for the laboratory did not store the rest of the data from the following hours until the end. The measured initial temperature was 64ºC.

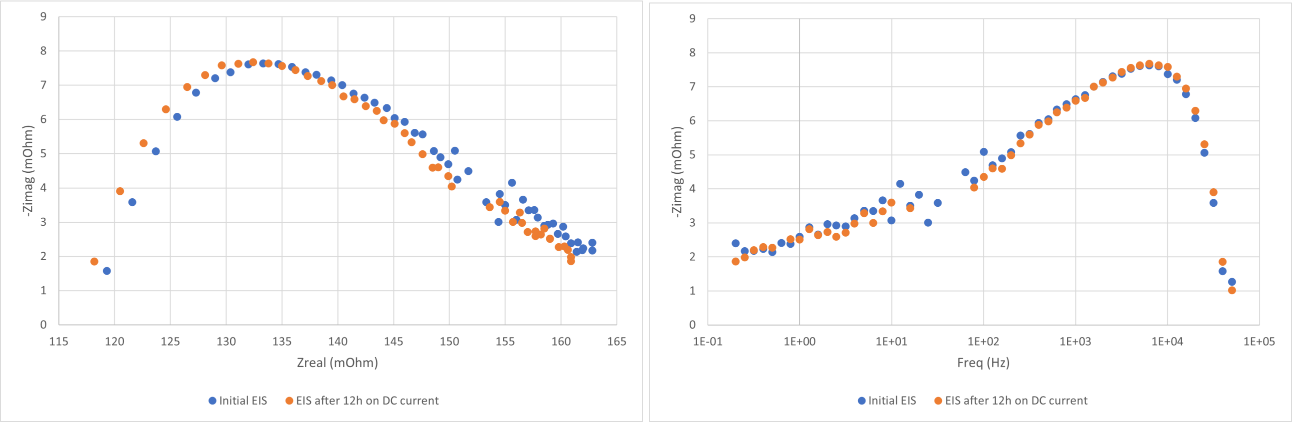

Figure 4.7: EIS for 12h direct current test, Nyquist plot on the left side, Bode diagram on the right side

The variations were really small, the Ohmic and high transfer resistances had initially values of 82.79mΩ and 45.62mΩ, while in the end the resistance values were 81.22mΩ and 46.56mΩ, respectively.

The voltage in the ohmic zone at 1A/cm^2 had a small decreasing rate of -0.05mV/h (Figure 4.8).

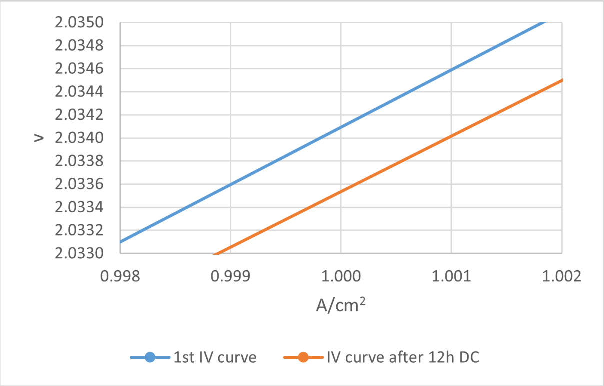

Figure 4.8: IV curve detail at 1A/cm^2 for 12h range of DC current test

The results of this test were unfortunately for a really short period of time (only 12h period). Small variations in the cell voltage and the impedance spectrum were observed, but all of them followed the same tendencies as in the previous AC:DC operation test for 20h explained in section 4.1.2. The cell voltage kept decreasing as it also did the Ohmic resistance, while on the other hand a small increased was perceived on the high frequency resistance.

4.1.4 4th 24h AC:DC operation test

During the following test the PEM cell electrolyzer was carried for 24h under the AC:DC operation. The EIS results are showed in the following figure 4.9.

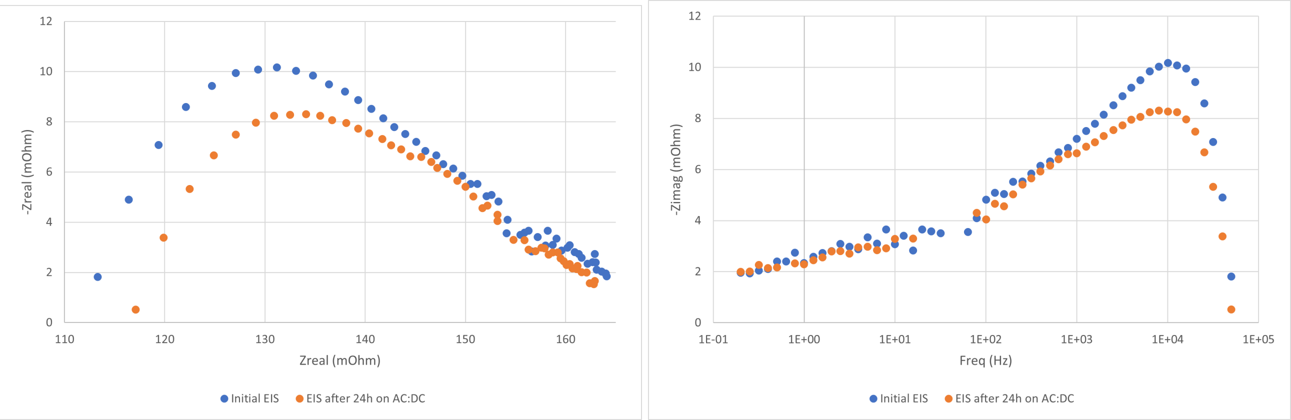

Figure 4.9: EIS impedances for 24h AC:DC operation test, Nyquist plot on the left side, Bode diagram on the right side

The EIS fittings showed an Ohmic resistance that increased from 75.84mΩ to 81.42mΩ. The high frequency resistance decreased its value instead from 55.82mΩ to 49.91mΩ. The polarisation curve was analyzed. It can be seen that there was an increment on the voltage in the ohmic zone (1A/cm^2) of about 0.37mV/h as shown in figure 4.10.

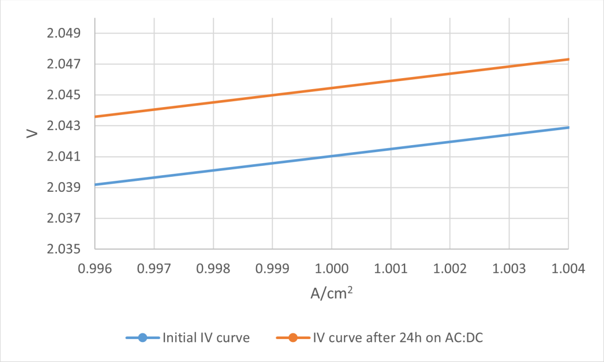

Figure 4.10: IV curves at 1A/cm^2 for 24h AC:DC operation test

The results from this last test were the AC:DC operation was applied during 24h, showed a change in tendency for all the parameters. For first time the cell voltage and the Ohmic resistance increased their values, while the high transfer resistance decreased. An explanation to this change can be that the components are finally done with the reactivation process explained in section 4.1.1, and they start a new phase where actual degradation process can be perceived. In other words, this is the point where all reversible losses are recovered and irreversible losses become dominant.

4.1.5 5th 12h AC:DC and 12h DC test

In this section the results from an alternated 12h running on AC:DC operation and later another 12h held on a DC current are shown. But first of all, at the beginning of this test EIS tests were carried for different current densities of 1.5A/cm^2 and a 2A/cm^2, apart from the typical test at 1A/cm^2. The results from these 3 tests are shown in figure 4.11.

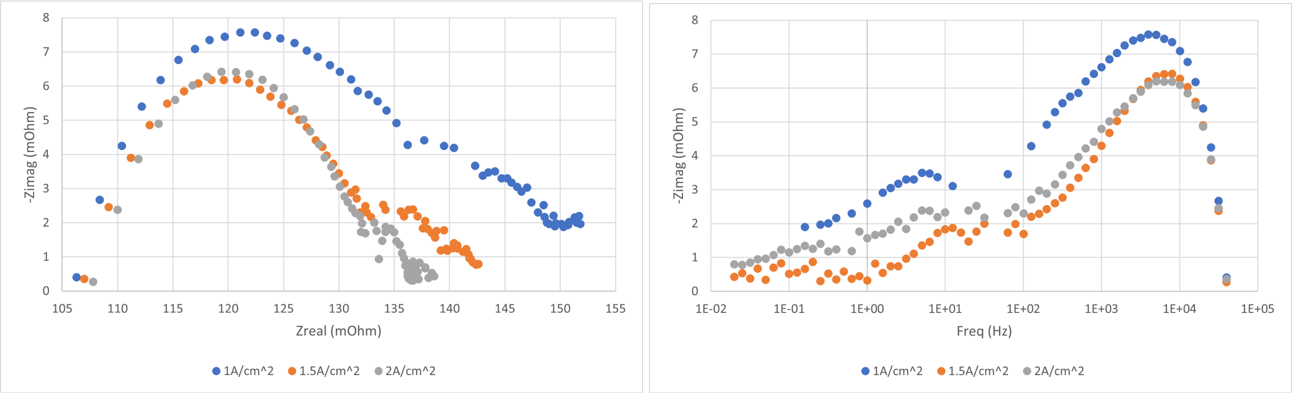

Figure 4.11: EIS impedances at 1, 1.5 and 2A//cm^2 current densities, Nyquist plot on the left side, Bode diagram on the right side

EIS fittings were made to identify the different resistances 4.1.

Current (A/cm^2)	Ohmic(mΩ)	High freq(mΩ)	Medium freq(mΩ)	Low freq(mΩ)
1	69.24	45.84	26.44	10.78
1.5	71.19	44.38	18.05	8.92
2	71.85	45.13	16.33	4.30

Table 4.1: Resistance values at 1, 1.5 and 2A/cm^2 current densities

From the Nyquist plots at different current densities it can be seen that while the Ohmic ressitance tends to sligthly increase with the current, the high frequency remained on relatively stable values, and the medium and low resistances decreased when the current increased. This observation shows that mass transfer losses are lowered since the decrease of the medium and low frequency resistances. On the other hand, with higher currents more hydrogen is produced, which causes gas crossover phenomenon, leading to an increase in the Ohmic resistance.

The results from the characterization made during the AC:DC operation and DC current operation tests are showed in the following figure 4.12.

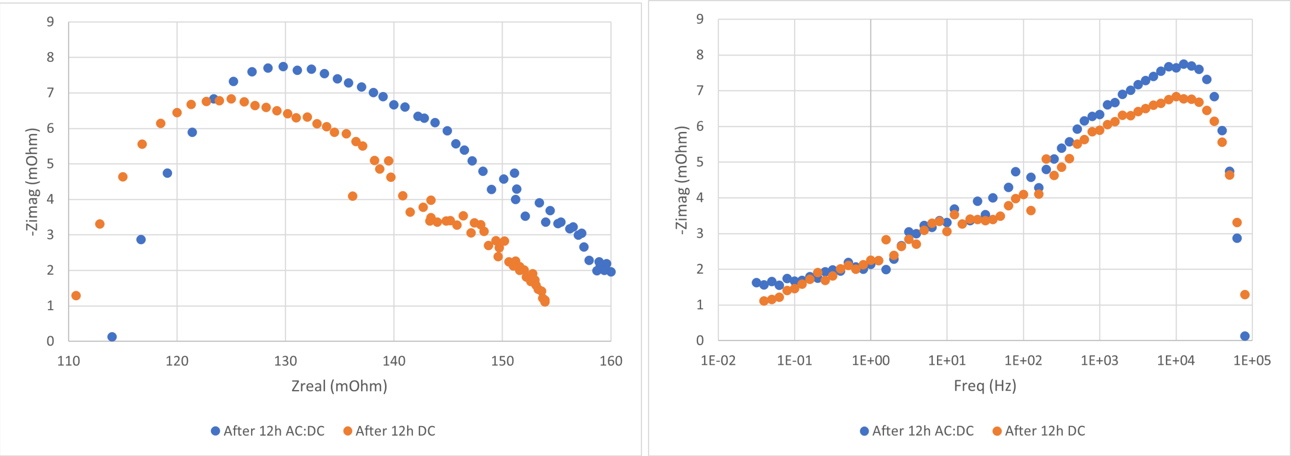

Figure 4.12: EIS after 12h of AC:DC operation and after 12h of DC current tests, Nyquist plot on the left side, Bode diagram on the right side

The resistances were 79.13mΩ and 47.29mΩ for the Ohmic and the high transfer respectively, after running the PEM cell electrolyzer for 12h on AC:DC operation. This values changed after running the PEM cell for another 12h with a DC current to 74.94mΩ and 43.65mΩ. This results showed an Ohmic resistance that is once again decreasing in every test, and a high frequency resistance that since the previous test and during these two test starts to decrease.

4.1.6 Old membrane tests summary

In the following tables the parameters from the EIS fittings from the different tests are shown.

$Y_0 5(S * s^a)$	a6 (-)	$Y_0 7(S * s^a)$	a8 (-)	$Y_0 9(S * s^a)$	a10 (-)
1.58e-3	0.710	0.423	0.5	29.6	0.5

Table 4.2: CPE parameters used for fittings in EIS impedance in old membrane tests

The CPE parameters were calculated as an average of the parameters calculated for by the first fittings made for each of the tests. Since a8 and a10 averaged less than 0.5 meaning that its behaviour cannot be represented as a CPE, the values were fixed to 0.5 to represent its effect as if they were just pure capacitors.

Test	Time (h)	Ohmic(mΩ)	High freq(mΩ)	Med freq(mΩ)	Low freq(mΩ)	Total (mΩ)
Initial	0	108.5	49.41	29.09	9.70	201.9
DC	24	96.86	39.61	25.16	10.23	173.92
AC:DC	44	86.27	46.84	26.46	11.06	173.48
DC	56	81.22	46.56	25.70	10.19	176.22
AC:DC	80	75.84	55.82	25.48	9.66	178.41
AC:DC	100	81.42	49.91	24.90	8.55	165.74
AC:DC	112	79.13	47.29	26.33	10.22	163.67
DC	124	74.94	43.65	25.42	10.98	155.3

Table 4.3: Resistance values for fittings in old membrane tests

The results from the table 4.3 reflect an Ohmic resistance that decreases in every test, which could be a sign of the membrane reactivation, since the membrane wasn't activated for 3 months. Besides that, it could also be a sign of membrane thinning, that begins once all the reversible losses from the activation are recovered. The high frequency resistance also shows some particular behaviour. Whereas during the first 24h of test under DC current, its value decreased considerably, for the next 56h showed an increse independently of the operation mode it was running on, and for the next test until the end its value decreased again. A graph of the evolution for the different evaluated resistances during the old membrane tests was made. The following graph shows a visual image of the evolution of the different resistances 4.14.

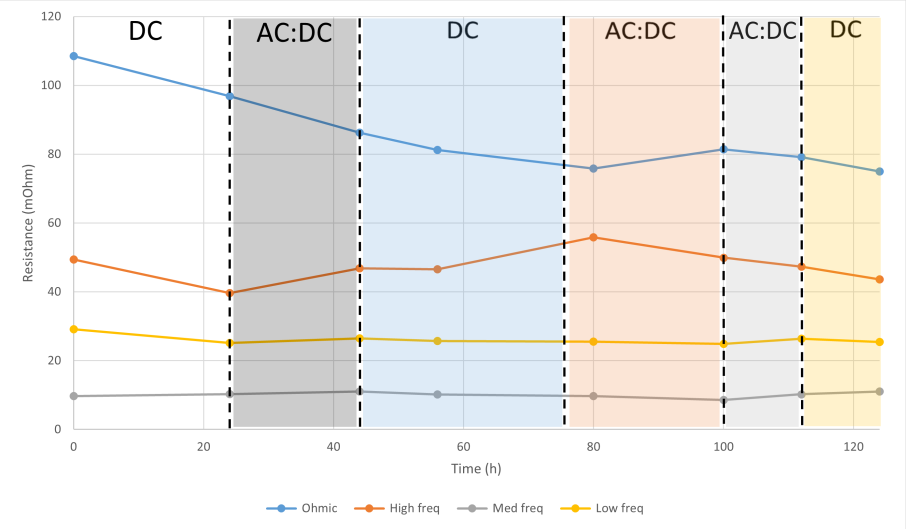

Figure 4.13: Old membrane frequency resistance values from tests over time. Dashed lines represent the end and beginning of following test, while the points represent when the EIS measurement was made

From the previous figure no tendency is found depending on the operation mode used for each of the tests. Another way to see the previous results is shown in figure 4.13, where the resistances are coupled in two Ohmic + High frequency resistance and Medium + Low frequency resistance to see if any characteristic pattern when running the different operation modes.

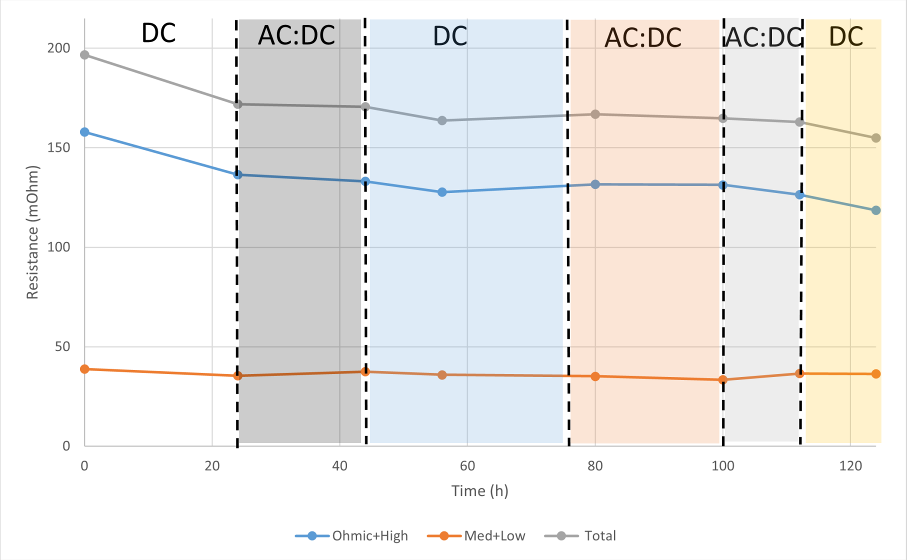

Figure 4.14: Total and coupled resistance values for tests over time. Dashed lines represent the end and beginning of next test, while the points represent when the EIS measurement was made

No tendency was found in the last figure as well. All the resistance values seemed to follow a decreasing tendency but no differences can be seen when the test runs on DC current operation or AC:DC operation mode. However, an initial recovery during the first DC current test is seen with a clear reduction of all the Ohmic resistance values. A further and more exhaustive analysis can be seen in section 4.4.

4.2 New membrane

A new membrane was used for running new tests. The membrane was first activated for 72h with a DC current of 500mA/cm^2. Water consumption was 120ml/day. Temperature was set around 70ºC. Water was added once a day. When adding the water temperature fell to 60ºC and it increased until reaching the 70ºC where it was before adding the water.

The CPE values were calculated as an average from the initial fittings, and fixed as constant values. The CPE values used for the EIS fittings are shown in the following table 4.4

$Y_05(S*s^a)$	a6 (-)	$Y_07(S*s^a)$	a8 (-)	$Y_09(S*s^a)$	a10 (-)
3.75e-3	0.710	0.691	0.672	32.2	0.596

Table 4.4: CPE parameters used for new membrane EIS impedance fittings

4.2.1 AC:DC operation test 5 day

The AC:DC operation used for this test was the same as in previous tests. Water consumption per day was between 220ml and 240ml. In the following figure 4.15 the cell voltage for 3 complete AC:DC operation periods is shown:

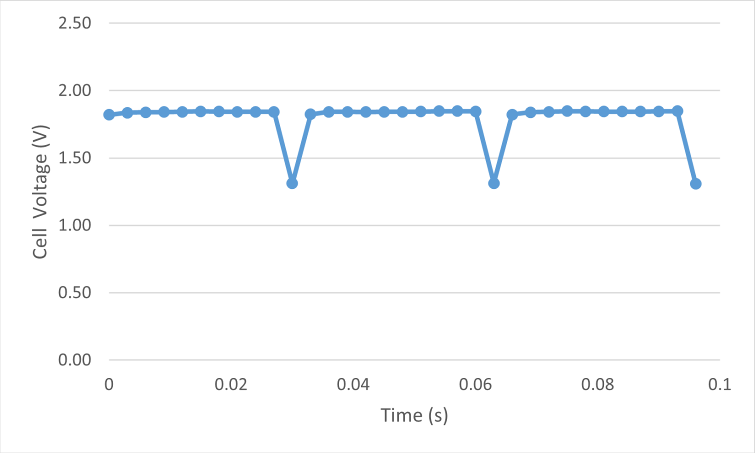

Figure 4.15: Cell voltage for 3 AC:DC operation periods of 33ms, with 3ms sample period

With the new membrane the AC:DC operation held the voltage at 1.84V for 30ms and at 1.31V for only 3ms. Compared with the values shown in section 4.1.2 this time the voltage on normal operation its lower, it was 2.1V with the previous membrane, whereas the voltage on fuel cell mode is higher than before, where it was 1.1V. The polarisation curve was taken every 24h with a Galvanodynamic scan (4.16).

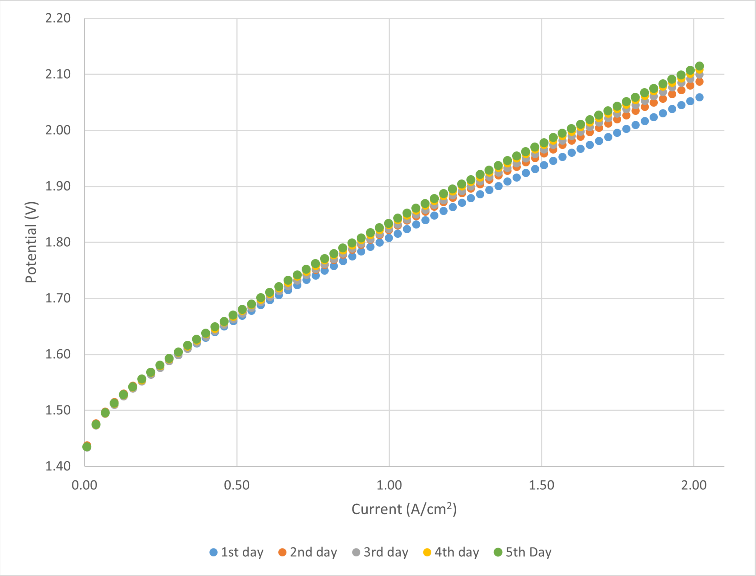

Figure 4.16: IV curves for 5 days AC:DC operation test

The Voltage averaged an increment of 7.6mV per day at current densities of 1A/cm^2 which is equivalent to 0.316mV/h.

EIS was taken every 24h as well (4.17).

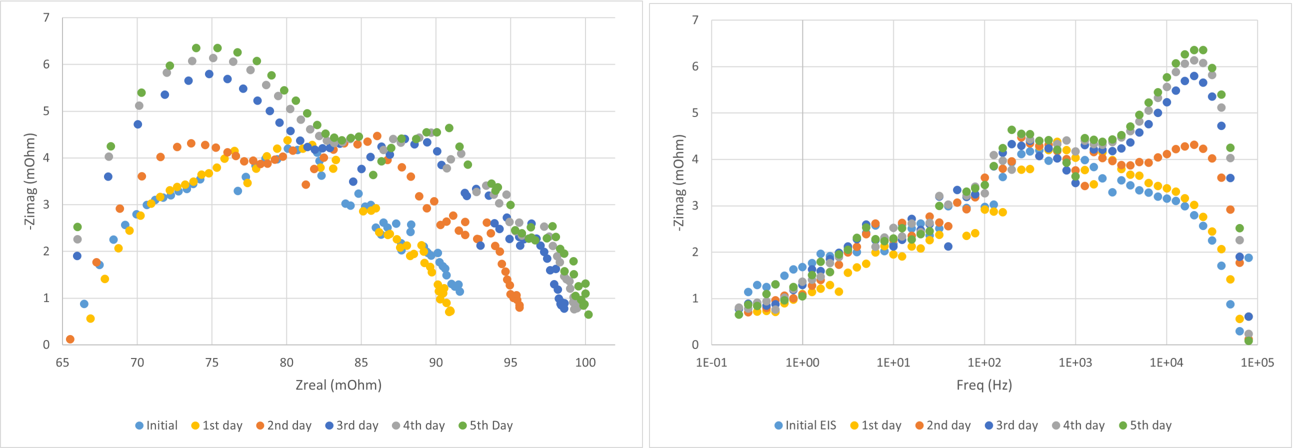

Figure 4.17: EIS impedances for 5 days AC:DC operation test, Nyquist plot on the left side, Bode diagram on the right side

A graph and a table with the resistance values from the EIS fittings taken every 24h is shown in 4.5.

Test time (h)	Ohmic(mΩ)	High freq(mΩ)	Medium freq(mΩ)	Low freq(mΩ)
0	45.24	27.72	12.61	6.66
24	45.92	27.54	13.04	4.88
48	45.07	32.78	12.64	5.92
72	44.72	36.56	12.29	5.87
96	44.07	38.18	12.31	5.67
120	43.96	38.85	12.2	5.86

Table 4.5: Resistance values for 5 days AC:DC operation test

The results from the 5 days test running on the AC:DC operation showed several things. The cell voltage increased at a relatively high rate if we compare it with the previous tests. This change can be associated with this test being the first test that runs with the new membrane. In this case the membrane has been just running before for 3 days to activate, but there are not any reversible losses. Therefore the voltage increases as it does when the cell performance degrades. Similar behaviour can be reflected in the EIS resistance values. The Ohmic resistance is being reduced at a slower rate than in previous tests. This experiment shows only the irreversible losses that cannot be recovered. The high frequency reflects a big increase between the first and third days of the test going from 27.72mΩ to 36.56mΩ. The medium a low frequency resistances only showed a small decrease.

4.2.2 DC current test 2 day

The results from the 48h DC current test are presented in the following graphs 4.18 and 4.19. The results show the last curve after 48h of test where the pump broke.

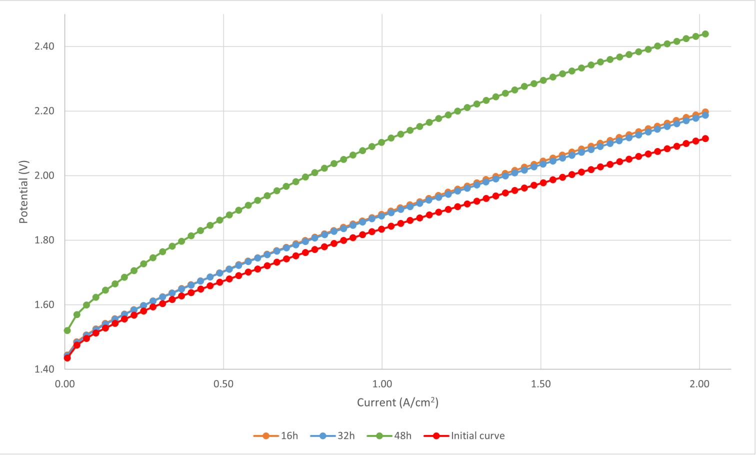

Figure 4.18: Polarisation curves for 48h DC current test

The average increment for the Voltage was of 17mV per day at 1A/cm^2 without considering the curve taken when the pump broke. This value is equivalent to 0.708mV/h. Only during the first 16h the cell potential increased from 1.83V to 1.88V at 1A/cm^2. For the next 16h the potential experienced a really small decrease. In the end the cell potential increased from 1.88V to 2.1V at 1A/cm^2, when the pump stopped working.

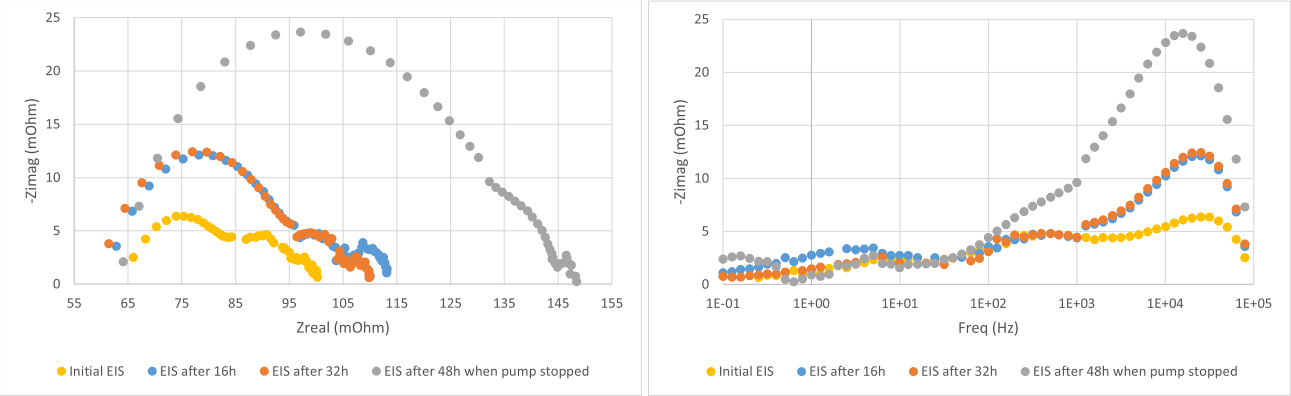

Figure 4.19: EIS impedances for 48h DC test, Nyquist plot on the left side, Bode diagram on the right side

A table with the resistance values and parameters from the EIS fittings was made:

Test time (h)	Ohmic(mΩ)	High freq(mΩ)	Medium freq(mΩ)	Low freq(mΩ)
0	44.31	38.36	13.44	4.49
16	44.86	50.14	11.04	8.07
32	44.28	50.57	11.28	8.00
48	47.48	86.53	8.10	4.19

Table 4.6: Resistance values for 2 days DC test

The results from this test, excluding the values once the pump stopped working, reflected similar behaviours as in the previous test running on the AC:DC operation. The cell potential kept increasing, although at a higher rate this time, mainly after the first 16h of the test. The Ohmic resistance was kept with similar values, while the high frequency resistance increased a lot during the first 12h of the test. On the other hand, the medium decreased during the first 16h, whereas the low frequency resistance did the opposite. The first 16h of the test reflect that during that time something happened that made increase a lot some of the resistance values and the potential. Once the pump broke the high frequency resistance and the cell potential experienced a big increase on its values.

4.2.3 New pump and performance recovery

Due to the high registered cell potential a DC Galvanostatic mode at 0.5 A/cm^2 was run for 16h to see how much the voltage could recover during that period of time (4.20).

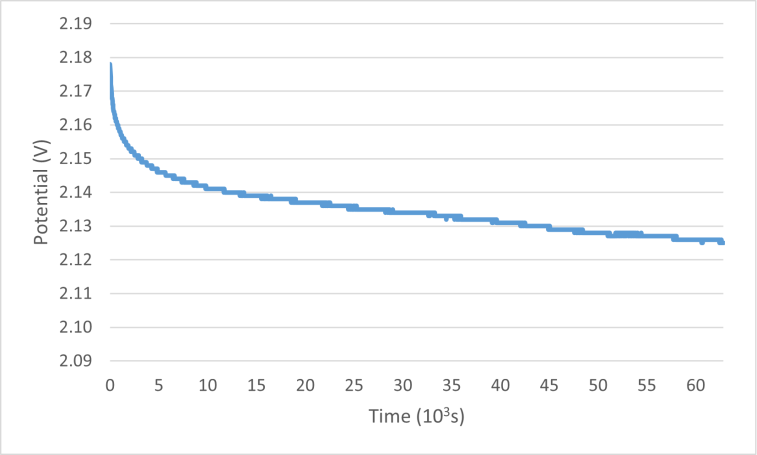

Figure 4.20: Cell potential vs time where cell potential recovery is observed after changing the pump

The voltage recovered faster at the beginning from an initial 2.178V to 2.144V after a 100min. From here till the end it recovered to 2.126V after 16h. After the first 16h on 0.5 A/cm^2, the AC:DC operation was run for another 16h. The same kind of behaviour was reflected. There was a fast recovery initially continued by a slower recovery. The first 10 min of the test averaged 2.092V, and the last 10 min 2.044V. In between, it can be seen that by the minute 100 already dropped to 2.058V (Table 4.7).

Test time (min)	Average cell potential (V)
0-10	2.092
10-20	2.077
90-100	2.058
260-270	2.055
540-550	2.052
950-960	2.044

Table 4.7: Cell potential during 16h on AC:DC operation to investigate cell potential recovery

ACDC operation and DC current tests were alternated for 2h each with a 30min rest in between for total of 20h. From the ACDC operation recovery wasn't seen while from the DC current test the data was lost. EIS tests were made when the pump broke, after the 16h running on AC:DC and after alternating AC:DC and DC for 20h 4.21. The biggest change appeared on the Ohmic and high transfer resistances. The Ohmic resistance was of 47mΩ at the time of failure and after the 16h on AC:DC increased to 96mΩ and it was 98mΩ after the 20h test of alternating AC:DC and DC operations. In the case of the high frequency resistance which was of 86mΩ by the time the pump failed this value increased to 211mΩ after the AC:DC test, and recovered to 137mΩ after the test were AC:DC and DC operation were alternated.

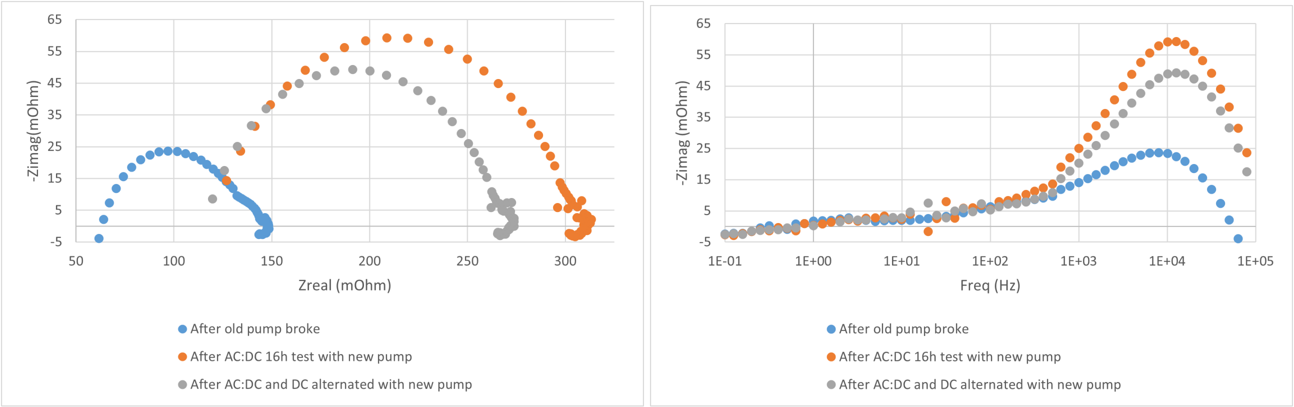

Figure 4.21: EIS impedances after the pump broke and after changing it

The results reflected that the change of the new pump added new losses that were not present before in the PEM cell electrolyzer. From figure 4.21 it can be seen that the Ohmic and the High frequency resistance increased both about two times what the previous value was before changing the pump (from blue to orange curves). At the same time it can be observed that in their respective curves in the Bode plot the peak of the orange curve was moved a little bit to the right respect to the blue curve, which means that the frequency of the high frequency resistance increased. By going back to section 2.3.1, equation 2.2, an increase in the value of ω decreases the CPE impedance. Therefore, the CPE impedance decreased while the resistance increased about two times. Since the resistance is inversely proportional to the surface area, this behaviour can be attributed to a loss of the contact surface between the components of the PEM cell electrolyzer.

The PEM cell electrolyzer was disassembled and the membrane was removed. The state of the membrane and one the bipolar plates are shown in the following pictures in figures 4.22 and 4.23.

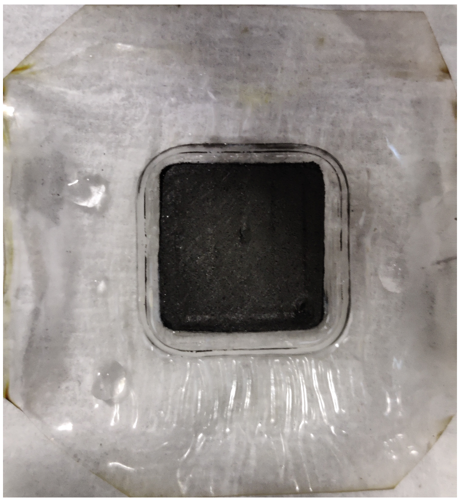

Figure 4.22: PEM membrane

Figure 4.23: Bipolar plate from the anode side

While the PEM membrane visually did not have any symptoms of corrosion or contamination, the bipolar plate from the anode side showed both of them. In picture 4.23, a white color is perceived where the flow channels are, which could be reflecting some symptoms of contamination of the water that circulated through a pump that was used before for contamination tests. Around the flow channels another colors can be seen that could appeared as a symptom of oxidation. More exhaustive analysis could be carried to determine with more exactitude what kind of processes reflect these observations.

4.2.4 New membrane test summary

The results from the EIS from the first two tests carried with this membrane are plotted in the following figure 4.24.

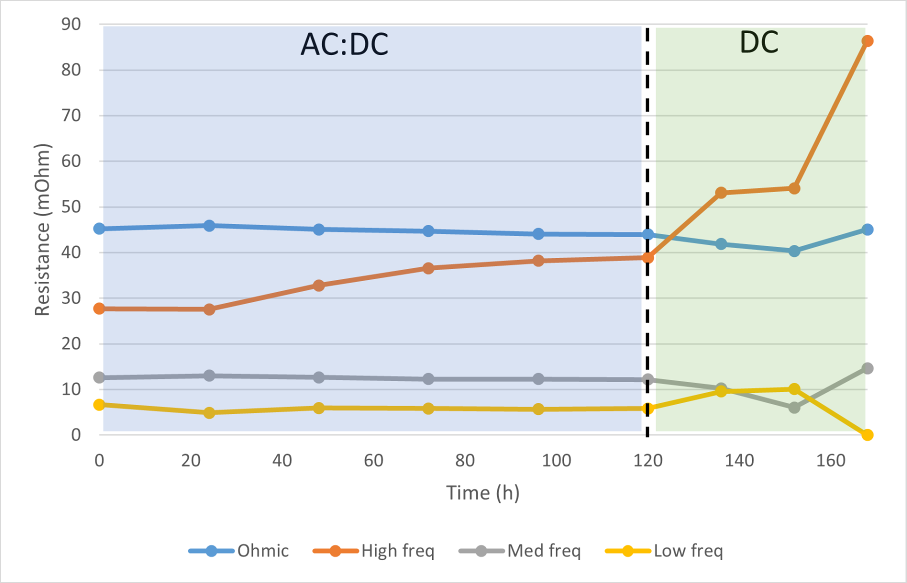

Figure 4.24: Resistance values from EIS fittings for AC:DC test. Dashed line represents the end and beginning of new test, points represent when the EIS measurement was made

The last point in the previous graph represents the last test carried when the pump stopped working. As commented previously in sections 4.2.1 and 4.2.2, the Ohmic resistance experienced only small changes during the tests, only showing a little decreasing rate. The high frequency resistance reflected an increase during the AC:DC test, that suddenly during the first 16h of the DC current test increased faster its value. The medium and low frequency resistances are kept with similar values during the AC:DC operation test, while during the DC current test they experienced bigger changes, but that cannot be associated with any tendency.

4.3 2nd New membrane

During the activation days were the current was held at $0.5A/cm^2$ the voltage stayed at 1.66V. In the following figure the polarisation curve taken manually two weeks later is shown.

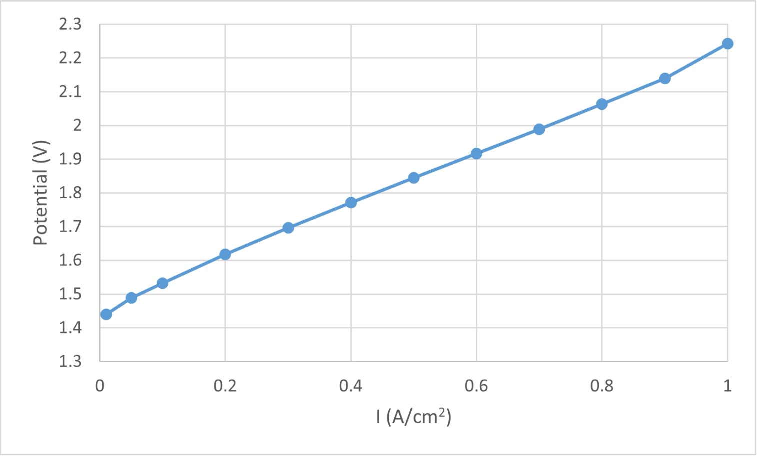

Figure 4.25: Polarisation curve taken manually two weeks after power supply stopped working

This polarisation curve presents a cell potential that is 1.85V at 0.5A/cm^2. This means that during this two weeks where the PEM cell did not run voltage increment was of 190mV.

4.4 Discussion

Figure 4.26 presents the timeline of the different tests delimited by the dashed lines. The points establish when the EIS impedance was examined. A histogram of the resistance values was made with the increment per hour of the fitting values for the AC:DC operation and for the DC operation tests 4.27. The increment was determined by calculating the difference between the fitting values of one EIS test and the previous one, and then dividing by the number of hours running the PEM electrolyzer between the tests. The increment is a positive or negative value that reflects if there was an increase or decrease of the resistance value and how fast was it. The units used for this increments are mΩ/h. An arrow indicates when the membrane was replaced with a new one.

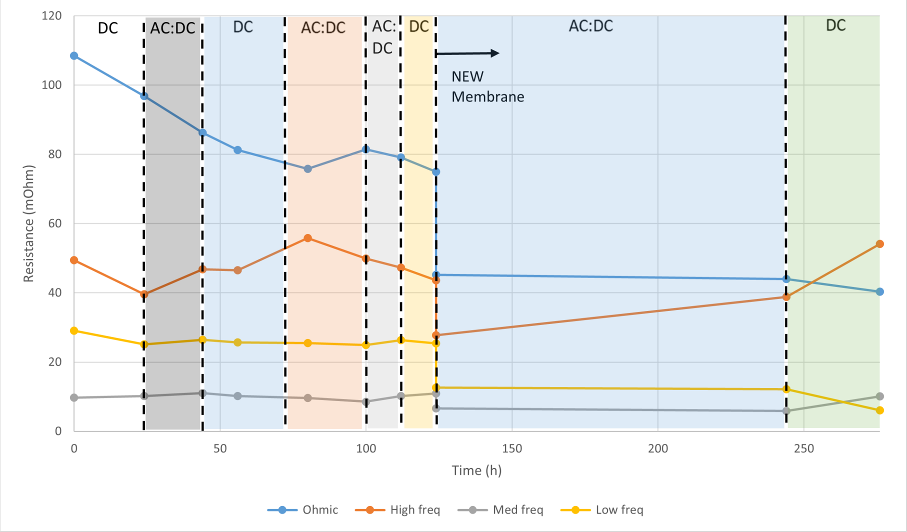

Figure 4.26: Resistance values from EIS impedance measurements over time. Dashed lines represent the end and beginning of new test. Points indicate when the EIS measurement was made, and arrow when the membrane was replaced

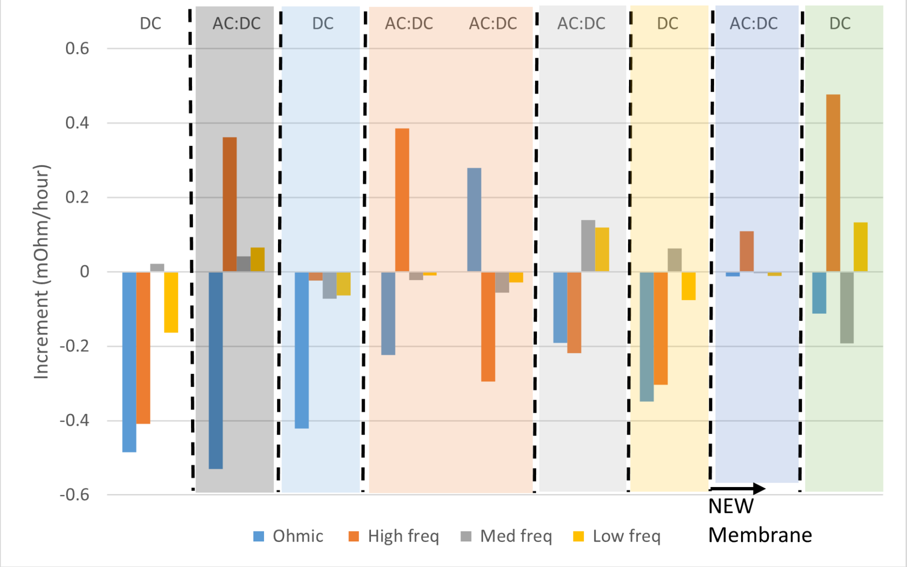

Figure 4.27: Resistance increment values for EIS tests. The increment is calculated from the points presented in figure 4.26 where EIS tests where made. Dashed lines represent the end and beginning of next test and are associated with the dashed lines presented in the previous figure 4.26

The increment values displayed in figure 4.27, don't reflect any clear pattern depending on the operation mode use to run the PEM electrolyzer. The Ohmic resistance is mainly decreasing during the tests before replacing the membrane. There is only one

AC:DC test where the Ohmic resistance increases, the rest reflects the process of reactivation mentioned in the previous section 4.1.6. With the new membrane the Ohmic resistance also decreased it's value. The high frequency resistance showed a random response in every test that cannot be associated with any tendency, whereas the medium and low frequency resistances almost reflected only smaller changes.

Another similar couple of graphs were made with the total resistance values and the coupled values, Ohmic + High frequency resistances, and Medium + Low frequency resistances. The values were gathered together in different ways to see if any kind of tendency could be found. The timeline exposed in the following figure 4.28 presents the resistance values, while the next figure 4.29 shows the increment values calculated in mΩ/h.

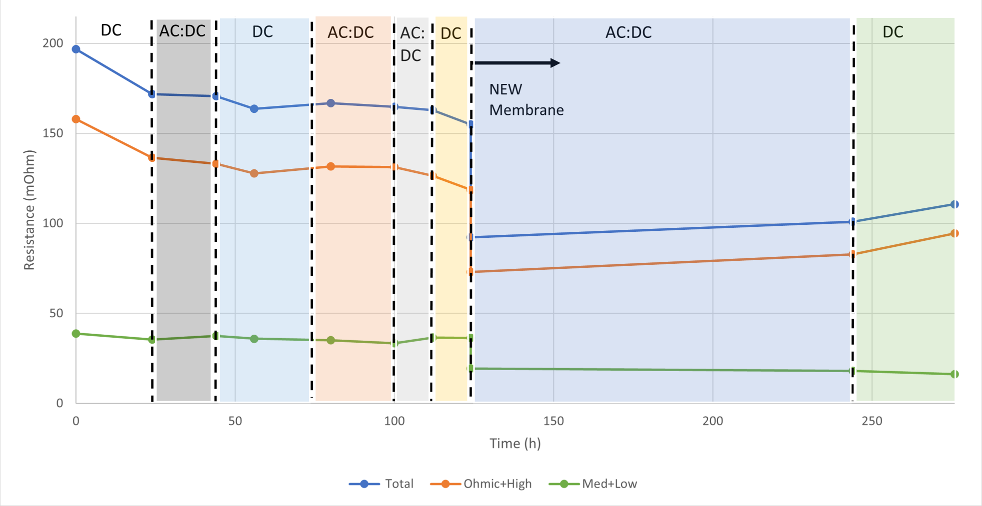

Figure 4.28: Total and coupled resistance values from EIS impedance measurements over time. Dashed lines represent the end and beginning of new test. Points indicate when the EIS measurement was made, and arrow when the membrane was replaced

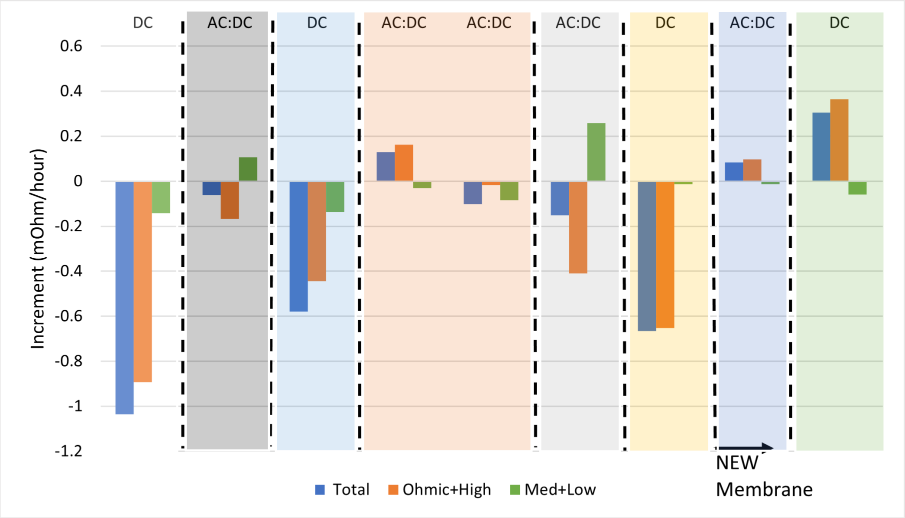

Figure 4.29: Total and coupled resistance increment values for EIS tests. The increment is calculated from the points presented in figure 4.28 where EIS tests where made. Dashed lines represent the end and beginning of next test and are associated with the dashed lines presented in the previous figure 4.28

The results shown in figure 4.29 showed how during the first tests before replacing the membrane the Total and Ohmic+High frequency resistance values reflected larger increase when the PEM electrolyzer run on DC current than when it run on the AC:DC operation. This tendency changed completely when the membrane was replaced. While the AC:DC operation kept low increment values, the DC current test manifested an opposite behaviour from what was seen in the previous DC current tests. The increment values switched from negative during the first DC current tests, to positive during the new membrane test on DC current. The sum of the Medium and Low frequency resistance values didn't reflect any tendency.

On the other hand, another similar couple of graphs were made in figures 4.30 and 4.31 to show the cell voltage variation at $1\mathrm{A/cm^2}$ for the different tests over time carried with the PEM cell electrolyzer.

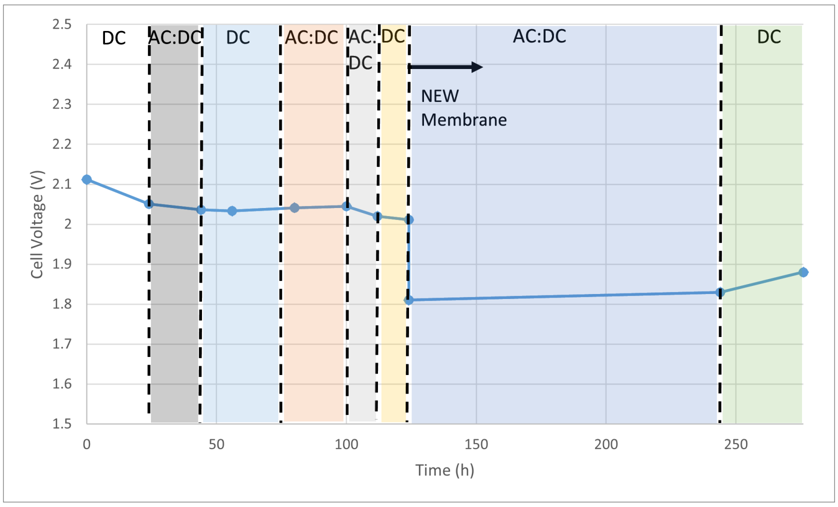

Figure 4.30: PEM cell voltage at 1A/cm^2 for the different carried tests. Dashed lines represent the end and beginning of new test. Points indicate when the EIS measurement was made, and arrow when the membrane was replaced

Figure 4.31: PEM cell voltage variation at 1A/cm^2 for the different carried tests. Dashed lines represent the end and beginning of next test and are associated with the dashed lines presented in the previous figure 4.30

During the first 3 tests the PEM cell voltage decreased each time less and less, this fact could reflect the reactivation period of the PEM membrane and the other components of the PEM cell electrolyzer. On the fourth test under AC:DC operation the cell reflected for first time a positive variation, which turned negative again during the last two test carried with the old membrane. The results from the old membrane tests carried under the AC:DC operation did not show any appreciable difference compared with DC current test due to the variability of the results. The first test on DC current and the fifth test on AC:DC operation reflected the biggest changes with voltage variations exceeding -2mV/h. The rest of the test carried always had a cell voltage variation under the ±1mV/h. In both new membrane tests the variation was positive independently of which kind of operation mode was used to run the PEM cell electrolyzer. The variation was bigger during the last 2 days of DC current test than during the 5 days on AC:DC operation.

Chapter 5

Conclusion

The conclusion of this master thesis will always come considering that the timing for testing was short and not long enough to come up with consistent and accurate data. While the longest experiment ran for 5 consecutive days, most of the tests ran for only 24h long. Besides that, it needs to be taken into account that some of the parameters during the tests were controlled manually, such as the temperature, which compromises the accuracy of the results. Despite using manual control, water temperature was held always oscillating around the 1°C range, although that was not possible when water was added. The timing for adding new water each time was considered so it could not affect the results of the characterization techniques (EIS and IV curves) since temperature dropped around 10°C when water was added. Nevertheless, the conclusion of this master thesis can be considered as a starting point reflecting what kind of behaviours can be expected when running the novel AC:DC operation on a PEM electrolyzer.

The electrochemical impedance spectroscopies carried along the different tests did not show many differences between the two operation modes, the AC:DC operation and the DC current mode. But, reviewing the results there are two of them that could be distinguishing elements, which are the variability of the total resistance and the Ohmic+High frequency resistances from figure 4.14. While the average changes in absolute increment were $0.646\text{m}\Omega/\text{h}$ and $0.588\text{m}\Omega/\text{h}$ for total resistance and the Ohmic+High frequency resistance value in the DC current tests, the average absolute increment in the AC:DC operation test was $0.105\text{m}\Omega/\text{h}$ for the total resistance and $0.17\text{m}\Omega/\text{h}$ for the Ohmic+High frequency resistance value. This means that the AC:DC operation keeps under better state the total resistance more than 6 times, and the Ohmic+High frequency resistance value more than 3 times than the DC current operation. Further investigations with longer tests should be carried to determinate with more exactitude how big is the difference between the two operation modes, and what could be the consequences in long time effects for the PEM electrolyzer.

The cell voltage was also analyzed during the different tests carried. The results did not reflect any kind of different behaviour between the two operation modes used to run the PEM cell electrolyzer. Considering the longevity of the carried tests and after analyzing the results it can be concluded that no positive benefits were observed when AC:DC operation was used when compared with DC current tests. Longer tests are needed to be able to identify larger and valuable changes on the PEM cell voltage. The 5 days test was the longest and most valuable test which reflected a voltage variation of 0.316mV/h. This value was supposed to be compared with another 5 days DC current test. This 5 days DC current test was started, but the pump was broke after the first two days. A second attempt was started with the 2nd new membrane but when activating the 2nd membrane, the power supply stopped functioning.

For future work updating the laboratory setup would be the first thing to consider. The update is required to be able to monitor the temperature automatically and therefore be sure that the water going into the PEM cell electrolyzer is always at the same temperature. The other important point would be to run longer test were long degradation effects can be identified. Another point that was not possible because of the timing and issues in the laboratory was to test PEM electrolyzer using the AC:DC operation under dynamic load. It would be really interesting to see the potential for the AC:DC operation by analyzing the possible degradation effects compared with the effects that it has to run the PEM electolyzer just by following the load.

Bibliography

[1] Francesco Pavan Jose M Bermudez Stavroula Evangelopoulou. *Hydrogen Energy System Overview*. 2022.

[2] IEA. *Task 38*. 2020.

[3] V. Himabindu S. Shiva Kumar. *Hydrogen production by PEM water electrolysis – A review*. 2019.

[4] Hui Li Dmitri Bessarabov Haijiang Wang. *PEM electrolysis for hydrogen production*. Taylor and Francis Group, 2015.

[5] Marian Chatenet et al. *Water electrolysis: from textbook knowledge to the latest scientific strategies and industrial developments.* 2022.

[6] International Renewable Energy Agency. *Green Hydrogen Cost Reduction*. 2020.

[7] Anne Lyck Theis Løye Omid Babaie. *Electrothermally balanced operation of solid oxide electrolysis cells*. 2022.

[8] Stefania Siracusano et al. *Electrochemical Impedance Spectroscopy as a Diagnostic Tool in PEM electrolysis*. 2018.

[9] Paolo Bonomi et al Behzad Najafi. *Rapid Fault Diagnosis of PEM Fuel Cells through Optimal Electrochemical Impedance Spectroscopy Tests*. 2020.

[10] P. Millet C. Rozain. *Electrochemical characterization of Polymer Electrolyte Membrane Water Electrolysis Cells*. 2014.