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Modeling and Analyzing Load Profiles for Fuel Cell Powered Cargo Bicycles

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Resumo

Células de combustível de membrana de troca de prótons (PEMFCs) estão na vanguarda no que diz respeito ao setor dos transportes devido à sua alta eficiência e baixa emissão de gases poluentes. O grupo de investigação de células de combustível do "German Aerospace Center" (DLR) lançou um projeto de testes para o uso de bicicletas elétricas de carga movidas a células de combustível em serviços de entregas dentro de cidades. Tanto o desempenho como a degradação destas células ainda são desconhecidos quando utilizadas em condições reais de operação.

Nesta dissertação são analisados diferentes ciclos de carga que simulam condições reais de utilização e é estudado o desempenho e degradação da célula de combustível quando submetida a estes ciclos. Técnicas ex situ e in situ são utilizadas para fazer uma caracterização minuciosa da célula. Dentro das in situ, voltametria cíclica (CV) e análise da impedância electroquímica (EIS) são as duas técnicas usadas. Para verificar as mudanças físicas à superfície dos diferentes elementos da célula, "scanning electron microscopy" (SEM) e "X-ray photoelectron spectroscopy" (XPS) são as duas técnicas de ex situ utilizadas. Por fim, foi desenvolvida uma unidade de aquisição de dados para obter informação em tempo real via internet da bancada de testes onde a célula está conectada.

Abstract

Proton exchange membrane fuel cells (PEMFCs) are at the forefront for transportation applications due to their high efficiency and low pollutant emissions. The Polymer Fuel Cell Group of the German Aerospace Center (DLR) is rolling out a demonstration project for the usage of electrical cargo bicycles powered by fuel cells in urban delivery services. The expected performance and degradation of these fuel cells are yet to be known when they are subject to real operating conditions.

The goal of this master's thesis is to analyze different load cycles that simulate real driving profiles and study the performance and degradation of the cell over time. To study this, ex situ and in situ characterization of the cell is performed. In situ techniques are based on Cyclic Voltammetry (CV) and Electrochemical Impedance spectroscopy (EIS). To evaluate the changes on the surface of different parts of the cell and assess its degradation, Ex situ analysis is performed using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Additionally, a data acquisition unit is developed to gather real-time information from the testing station.

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Daniel José Damas da Silva Leal

*“When something is important enough,
you do it even if the odds are not in your favor.”*

Elon Musk

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Abbreviations and symbols

PEMFC	Proton Exchange Membrane Fuel Cell
PEM	Proton Exchange Membrane
OCV	Open Circuit Voltage
FCREX	Fuel cell Range Extender
GPS	Global Positioning System
ORR	Oxygen Reduction Reaction
HOR	Hydrogen Oxidation Reaction
GLD	Gas Diffusion Layer
MEA	Membrane Electrode Assembly
CCM	Catalyst Coated Membrane
CV	Cyclic Voltammetry
ECSA	Electrochemical Surface Area
EIS	Electrochemical Impedance Spectroscopy
PTFE	Polytetrafluoroethylene
SEM	Scanning Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
EDX	Energy-dispersive X-ray Spectroscopy
AST	Accelerated Stress Test
CL	Catalyst Layer
MPL	Micro Porous Layer
PFSA	Perfluorosulfonic Acid
BOT	Begin of Test
EOT	End of Test
SQL	Structured Query Language
PDO	PHP Data Objects
FC-DLC	Fuel Cell Dynamic Load Cycle
WLTP	Worldwide Harmonized Light Vehicle Test Procedure

Chapter 1

Introduction

1.1 Motivation and Context

Worldwide energy consumption has been steadily increasing for the past decades with a large portion of energy production being generated from non-renewable energy sources (around 75% in 2017) [1]. This pattern of electricity production causes environmental concerns and creates a need for focus on renewable/alternative energy sources [2]. Small scale power generating systems such as wind turbines, photovoltaic panels and fuel cells play an important role in fulfilling the energy needs of consumers by using the concept of distributed production. These systems can be installed near the consumers eliminating the need for high voltage lines for the purpose of energy transport.

Today more than 75% of the European citizens live in cities and are affected daily by the increase in pollution and excessive traffic. Most of the pollutant gas emissions originates from the transportation industry. The increase in goods being delivered at home due to the growth of e-commerce calls a need to find new solutions for deliveries, specially last mile deliveries [3]. Electric bicycles (Pedelects) are a viable alternative to last mile deliveries since they are a means of transport which does not generate pollutant emissions (on-site) and can be driven on roads, bike paths, public transport routes and pedestrian areas. However, these bicycles, when used with a battery, cannot supply sufficient energy to cover multiple shifts and fail when operated under sub-zero conditions [4]. Since the limiting factor in these bicycles is the battery, the German Aerospace Center (DLR) is developing an alternative, the FCREX (Fuel Cell Range Extender), therefore addressing one of the biggest problems with batteries in Cargo Pedelects.

Proton exchange membrane, or polymer electrolyte membrane, fuel cells (PEMFCs) are at the forefront for transportation applications because of their high efficiency and low pollutant emissions [5]. These cells operate at low temperature operation, have dynamic operations capabilities and quick start-up time, therefore posing a good alternative to electrical vehicles. However, this technology is held back by three key aspects: longevity, durability and cost. Its durability relies mainly on the membrane electrode assembly (MEA) while its cost is mainly determined by the platinum used in the catalyst due to its high price and limited supply. The catalyst accounts for 45% of the total stack cost while the bipolar plates account for 27%, as can be seen in figure 1.1.

The main motivation for this dissertation was to assess the performance of the single fuel cell incorporated in the cargo pedelec fuel cell stack. Real driving conditions were simulated in the cell to recognize its durability in the long term. A data acquisition unit was built to record test data and oversee the cell outside of the lab.

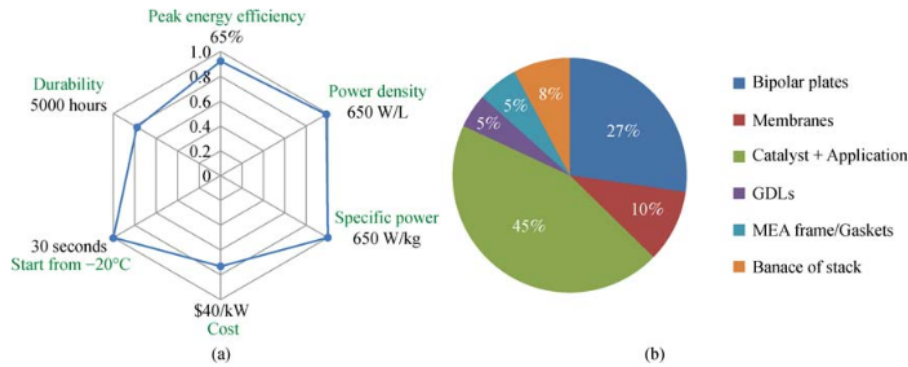


Figure 1.1: PEMFC systems: (a) 2020 targets versus 2015 status (blue) for light-duty vehicle applications; (b) cost breakdown of a fuel cell stack assuming the production of 500k systems per year [6]

1.2 Structure of the thesis

Besides this intro, the dissertation is divided into five chapters. The second chapter portrays a review of the fuel cell principles as well as a degradation study to get some knowledge in how the cell should perform under certain conditions.

The third chapter focus on the characterization of the cell by showing the assembling process of the cell, explaining which materials are used and how they are assembled, as well as a description of the improvements made to this process. A brief description of the load cycles and characterization techniques is also done. Plus, the adaptations made to the test bench are reported along with a explanation of the monitoring system developed.

In the forth chapter the results obtained both from the base tests and the load cycling tests are analyzed and discussed in order to understand what happened to the fuel cell and to distinguish the performance of the different cycles.

Finally, chapter five shows the final conclusions of this dissertation along with some suggestions for future work.

Chapter 2

Proton Exchange Membrane Fuel Cells

In this chapter a review of the fuel cell principles is made as well as a study of its components. Next a fuel cell degradation review is conducted to better understand how the load cycles and other conditions, like start/stop, can affect the fuel cell performance.

2.1 Basic Principles

A fuel cell is an electrochemical system that converts the chemical energy of fuel into electrical energy without fuel combustion [7]. Therefore, the products of this electrochemical reaction are water, electricity and heat, which is an improvement compared to the internal combustion engines which produce greenhouse gases. A PEMFC (Proton Exchange Membrane Fuel Cell) uses hydrogen (H_2) and oxygen (O_2) as fuel and it has a low temperature operation point ($<100^\circ\text{C}$). Since the oxygen is readily available in the atmosphere it is solely necessary to provide hydrogen to the fuel cell.

The main parts of a PEMFC are: the membrane electrode assembly (MEA) which is composed of the Proton Conducting Membrane and two catalyst layers (CL), porous gas diffusion layers (GDL), bipolar plates (often called current collectors) and sealing gaskets [5].

H_2 is fed to the anode side and goes through the GDL, which helps improve the efficiency of the system [8], to the catalyst layer where the hydrogen oxidation reaction (HOR) occurs as can be seen in equation 2.1. The protons resulted from this reaction go through the proton exchange membrane (PEM) to the cathode side while the electrons go through an external electrical circuit to reach the same side. This happens because the PEM only allows proton transfer. At the same time oxygen gas (O_2) is fed to the cathode side and goes through the GDL to reach the cathodic catalytic layer where it bonds with the electrons and the protons forming water, according to the Oxygen Reduction Reaction (ORR) in equation 2.2. This water is then pushed out of the cell. The overall reaction of the cell is shown in equation 2.3.



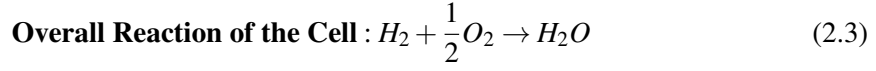
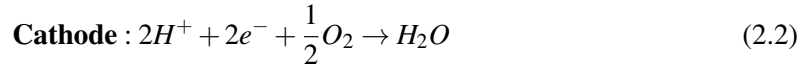


Figure 2.1 represents the schematic of a PEM fuel cell.

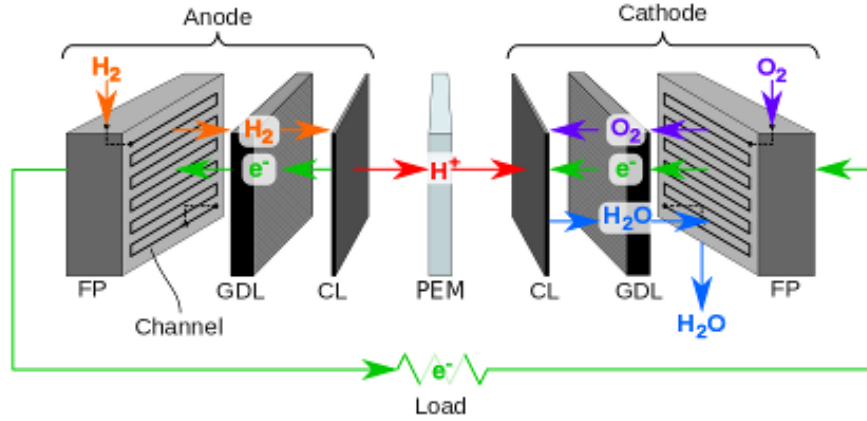


Figure 2.1: Schematic of a Polymer Electrolyte Membrane Fuel Cell [9]

Advantages of this technology over a conventional energy conversion device [7, 2, 10]:

- Greater efficiency (around 60%);
- No moving parts which makes the system more robust;
- Does not emit gases that pollute the environment such as: SO_x , NO_x , CO_2 , CO ;
- Modular and scalable;
- Easy installation.

2.1.1 Current-Voltage characteristics

Electrochemical cells are devices capable of generating electrical energy from chemical reactions and vice-versa. The maximum electrical work available from a fuel cell source can be calculated from the Gibbs free energy as shown in equation 2.4 [11],

$$\Delta G = -\eta F E^0 \quad (2.4)$$

where η is the number of electrons exchanged in the reaction, F is Faraday's constant (96 486 C/mol) and E^0 is the ideal cell potential, which is 1.23V.

The standard reference potential (E^0) is a quantitative measurement of the open circuit voltage at normalized conditions: cell temperature at 298.5K and the partial pressures of oxygen and

hydrogen at 1atm [12]. The cell potential (E) varies with the temperature and pressure of the reactants and is given by the Nernst equation 2.5:

$$E_{cell} = E^0 + \frac{RT}{2F} \ln \left[\frac{p_{H_2} \cdot (p_{O_2})^{0.5}}{p_{H_2O}} \right] \quad (2.5)$$

Due to the low voltage output of the fuel cells it is necessary to stack cells in cascaded series and parallel in order to increase the power capacity [2].

The cell potential is lower than the theoretical potential because there are polarization losses and interconnection losses when the cell is connected to the load. There are three main voltage losses: activation losses, ohmic losses and mass transport losses. [13]

The activation losses (V_{act}) are caused by the slowness of the reaction kinetics on the surface of the electrodes [14]. There's a certain amount of energy needed to start the chemical reaction that produces a non-linear voltage drop at low current densities. The oxygen reduction is slower than the hydrogen oxidation, so most of the activation polarization losses are due to the oxygen reduction reaction (ORR). The voltage drop due to activation polarization can be described by the Tafel equation 2.6 [13]:

$$V_{act} = \frac{RT}{\alpha n F} \ln \left(\frac{i}{i_0} \right) \quad (2.6)$$

where α is the electron transfer coefficient, the value of which varies between 0 and 1 depending on the catalyst material [14], n is the number of electrons involved, i is the fuel cell current density ($A\,cm^{-2}$) and i_0 is the exchange current density ($A\,cm^{-2}$).

The ohmic losses (V_{ohm}) come from the resistance to the flow of electrons through the electrically conductive elements and the flow of ions through the membrane as well as the cell interconnections. Ohmic losses can however be reduced by decreasing the electrode separation which increases the ionic conductivity. The voltage drop due to the ohmic polarization is linear and can be expressed by Ohm's law 2.7 [11]:

$$V_{ohm} = i \cdot R_{ohm} \quad (2.7)$$

where R_{ohm} is the internal cell resistance ($\Omega\,cm^2$).

The mass transport losses or concentration losses (V_{conc}) are caused by the consumption of reactant gases in the catalyst layer which leads to an increase in the concentration gradient. This voltage drop becomes prominent at high current densities and in extreme cases it is possible that there's insufficient reactant gas flow because of blockage of the pores due to the high amounts of produced water (product of the reaction). Equation 2.8 expresses the voltage drop due to concentration polarization [14].

$$V_{conc} = -\frac{RT}{nF} * \ln \left(\frac{i_1}{i_1 - i} \right) \quad (2.8)$$

where i_l is the limiting current density, which is the current density point that the reactant concentration reaches zero.

Therefore, the voltage of a fuel cell can be calculated with equation 2.9:

$$V_{cell} = E_{cell} - V_{act,cell} - V_{ohm,cell} - V_{conc,cell} \quad (2.9)$$

Accordingly, the voltage of a fuel cell stack can be expressed by equation 2.10, where N_{cell} is the number of cells in series in the stack.

$$V_{out} = V_{cell} \cdot N_{cell} = E - V_{act} - V_{ohm} - V_{conc} \quad (2.10)$$

A typical polarization curve from a PEMFC showing the potential as a function of the current density can be seen in figure 2.2.

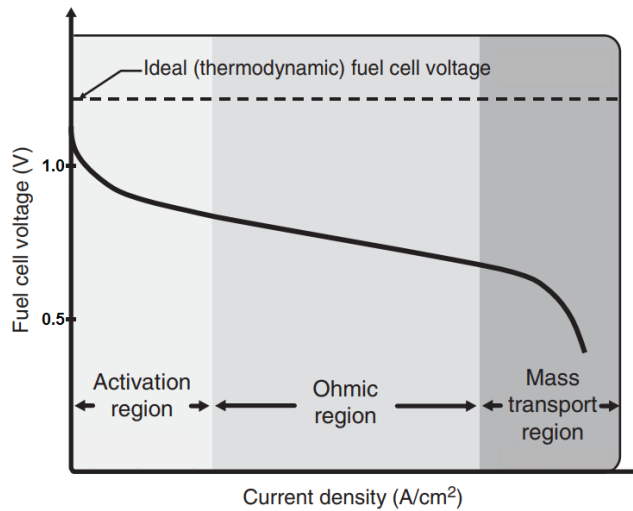


Figure 2.2: Ideal Polarization curve of a fuel cell (Adapted from [15])

The efficiency of the fuel cell is defined by the amount of Gibbs free energy that is available as useful electric energy in the output [11]. Equation 2.11 describes the ideal efficiency of a fuel cell device.

$$\eta_e = \frac{\Delta G}{\Delta H} \quad (2.11)$$

where, at standard conditions, ΔH represents the chemical energy from the reaction of hydrogen/oxygen, which is 285.8 kJ/mol and ΔG represents the free energy available for useful work, which is 237.1 kJ/mol. According to these values, at standard conditions, the fuel cell efficiency would be 83%, but the actual efficiency is lower due to the losses that we addressed previously [16].

The efficiency of an actual fuel cell can be expressed in terms of the ratio of the operating fuel cell potential and the ideal potential, as can be seen in equation 2.12.

$$\eta_e = \frac{\text{useful output energy}}{\Delta H} = \frac{\text{useful output power}}{\frac{\Delta G}{0.83}} = \frac{V_{cell} \cdot I}{\left(\frac{V_{ideal} \cdot I}{0.83}\right)} = 0.675 V_{cell} \quad (2.12)$$

2.1.2 Double layer charging effect

Since only the protons go through the membrane and the electrons have to flow from the anode to the cathode through an external load, a double layer of opposite polarity is formed between the cathode and the membrane [12]. This double layer can store electrical energy and behave like a super capacitor. The equivalent circuit of a PEM fuel cell considering this effect can be seen in figure 2.3, where R_{act} and R_{conc} are the equivalent resistances of activation and concentration voltage drops, R_{ohmic} is the internal resistance of the fuel cell and C is the equivalent capacitor. The voltage across C is:

$$V_C = \left(I - C \frac{dV_C}{dt} \right) (R_{activation} + R_{concentration}) \quad (2.13)$$

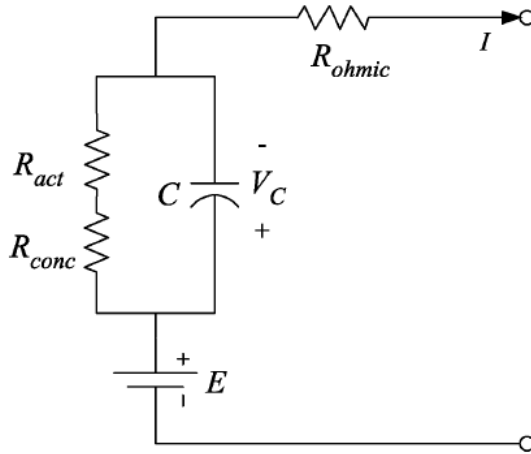


Figure 2.3: Equivalent circuit to the double layer charging effect [12]

2.2 Components

A PEMFC is assembled with a bipolar plate, GDL, Catalyst layer, sealing gaskets and a membrane, as you can see in figure 2.1.

2.2.1 Membrane Electrode Assembly

The key component of a fuel cell is the MEA as that is where the chemical reactions happen. A typical MEA is composed of a Polymer Electrolyte Membrane (PEM), two catalyst layers and two gas diffusion layers (GDL). An MEA with this configuration is known as a 5-Layer MEA also commonly known as a gas diffusion electrode (GDE) since the catalyst layer is impregnated in the GDL [17]. An alternative version is the 3-Layer MEA which is composed of a PEM and two catalyst layers, each of them applied to one side, anode and cathode. This type of MEA is commonly called Catalyst Coated Membrane (CCM) and will be the terminology used from now on. Figure 2.4 helps understand this MEA terminology. The MEA components are briefly described in the next sections,

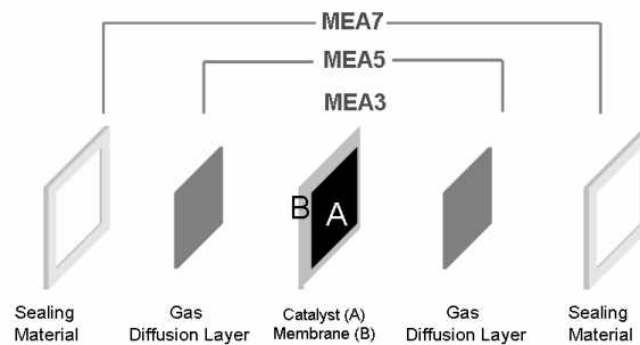


Figure 2.4: Different MEA layers [18]

2.2.1.1 Polymer Electrolyte Membrane

The Polymer Electrolyte Membrane is a thin layer of a solid polymer electrolyte (width between 10-15 μm) and should have good mechanical, chemical and thermal stability, elevated proton conductivity, high durability and impermeability to reactant species to prevent electron transport and crossover from the hydrogen from the anode to the cathode [5].

The state of the art technology for PEMs are Perfluorosulfonic acid membranes (PFSA) being the most prominent Nafion[®], which was created by the DuPont Company in the 1960s. These membranes are highly conductive to protons and they have good electrochemical stability compared to the other types of membranes [19]. PFSA membranes have three functional regions:

- Polytetrafluoroethylene (PTFE, also known as Teflon)-like backbone (hydrophobic region);
- Side chains of fluorinated carbon that connect the PTFE backbone to the acidic region;
- Ions clusters consisting of sulfonic acid sites (hydrophilic region).

The conductivity of the Nafion membranes is strongly dependent on the amount of water they contain. If the membrane is well humidified, the proton transport is based on structural diffusion, also called Grotthuss mechanism, in which the protons transfer along the hydrogen bond network of

water molecules. On the other hand, when the water content of the membrane is lower, the protons are carried through the membrane on top of water molecules (vehicle mechanism) [20].

Membrane degradation happens as a result of mechanical, chemical or thermal degradation. Mechanical degradation is mostly due to swelling and shrinking or excessive or non-uniform contact pressure. High RH conditions cause swelling of the membrane and as a consequence of the membrane being subjected to compression due to being constrained by the other layers. On the other hand, the membrane is subjected to tension when it shrinks as a consequence of low RH. This can cause cracks and pinholes on the membrane, allowing the crossover of reactant gases. [21]

Thermal degradation is almost negligible at normal temperature operation conditions (45-80 °C). However, at sub-zero temperatures it can cause structural damage to the membrane.

Reactant gas crossover and metal ion contamination are the two main factors contributing to chemical degradation. The former leads to hydrogen peroxide radicals formation that results in breakage of the membrane's backbone structure, causing losses in proton conductivity.

2.2.1.2 Electrodes

The electrodes are formed by coating a "catalyst ink" onto the polymer electrolyte membrane, forming the catalyst layer where the electrochemical reactions take place. Generally, the catalyst present in the ink is supported by carbon that provides electrical conductivity and helps reducing catalyst loading [22]. The most used catalyst material is platinum, however it is an expensive material hence researchers are continuously trying to lower the Pt loading. The electrodes must have really good electrical conductivity to assist the electrons movement towards the external circuit, as well as proficient proton conductivity to allow the migration of hydrogen protons through the membrane. Pt loading is usually higher in the cathode than in the anode due to oxygen reduction reaction being more complex and kinetics being slower.

The most dominant causes of catalyst layer degradation are: Pt particle growth, Pt migration and carbon corrosion. Pt particles may dissolve and deposit on the surface of other Pt particles and lead to Pt particle growth [23]. This reduces the electrochemical surface area (ECSA) leading to a decrease in the stability of the catalyst. Pt migration happens when dissolved Pt particles diffuse into the membrane, especially during long term tests, dramatically reducing the conductivity of the membrane. Pt particle migration and growth have increment with certain operation conditions like high potential or humidity cycles.

Carbon corrosion is usually negligible in normal fuel cell operation, however, the platinum present in the electrode can catalyze the reaction of carbon oxidation. The two main factors for the phenomena are the start-up/shutdown cycles and fuel starvation.

2.2.2 Gas Diffusion Layer

The gas diffusion Layer (GDL) plays an important role in gas diffusion and water management in the fuel cell. The GDL is placed on either side of the membrane between the catalyst layer and the gas flow fields and allows the diffusion of reactant gases into the catalyst layer. It acts as

an electrical conductor creating a path for electron transfer between the catalyst and the current collector bipolar plates while it provides mechanical support to the electrolyte membrane [24] [25]. Besides that, it aids water vapour to diffuse across the MEA, hydrating it and thus increasing its ionic conductivity while providing a path to the liquid water produced in the reaction to move from the catalyst layer to the flow fields, where it will be pushed out of the cell. Usually, GDLs are made of porous carbon paper or carbon cloth and their normal thickness is around 100-300 μm [5]. Normally, the GDL is wet-proofed with a PTFE (Teflon) to prevent the pores of the GDL from being clogged with liquid water, otherwise the gas transport can be limited leading to "mass transport" limitations, which limits the max current density [26]. A further improvement to the GDL is adding a Microporous layer (MPL) forming a dual-layer GDL. This layer is made of carbon black powder and PTFE and reduces the contact resistance between the Macroporous Layer of the GDL and the Catalyst Layer, which enhances the surface area for the reactions to occur. The Dual Layer GDL can be seen in figure 2.5.

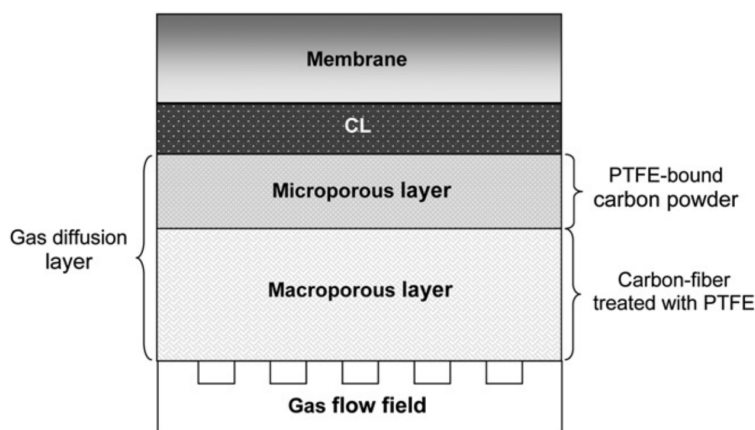


Figure 2.5: Dual-layer GDL for PEM Fuel Cell[27]

The compression of the GDL during operation and the erosion by gas circulating through the layer are the main reasons for GDL mechanical degradation. PTFE decomposition and carbon corrosion, provoked by high potential induced oxidation, cause hydrophobicity loss and changes in the pore structure of the GDL, reducing the capability of removing water from the MEA and thus inducing unstable operation of the cell [23].

2.2.3 Bipolar Plates

The bipolar plates have a multifunctional character in PEM fuel cells and they account for 60% to 80% of the fuel cell weight and around 30% of their cost. They are a key component of the fuel cell, as they aid with the uniform distribution of the reactant gases, water management (removing the products from the cell), heat management and carrying the current away from the cell [28]. Every single cell has two bipolar plates that sandwich the MEA and both GDLs (anode and cathode). In a stack they connect each single cell electrically in series.

The materials used for manufacturing bipolar plates can be divided into two groups: metals or carbon-based. In the past, carbon-based bipolar plates, especially high-dense graphite, were the most used due to the stability of the graphite at the PEMFC harsh conditions. Graphite has a very low surface resistance, originating higher current output and lack of poisoning agents but the material's inherent brittleness prevents its use on mobile or transportation applications [29]. Additionally, the fabrication of the flow fields requires machining, which is a costly process. As a result, metallic bipolar plates are the most used by the scientific community at the moment.

Metals (excluding noble metals) have good mechanical stability, high electrical conductivity and low gas permeability. However, due to the corrosive operating environment of PEMFCs (low PH) they are chemically unstable and prone to corrosion of dissolution which can poison the PEM membrane and hence lower the proton conductivity. Moreover, the thin oxide layer formed on top of the plate will increase the electrical resistance and therefore reduce the power output. In light of these issues, metallic plates coated with a thin protective layer are a good alternative to improve on the corrosion and contact resistance issues of the metallic bipolar plates. The coating can be of two different types: carbon based or metal based. The most used metal for bipolar plates manufacturing is Stainless Steel (SS) considering its low cost and better chemical stability.

2.3 Degradation Mechanisms

The viable commercialization of this technology to use on electrical vehicles still has some bottlenecks, due to the short lifetime of PEMFC [30]. The life time of a PEMFC system operated under real world conditions in a vehicle is expected to be at least 5000h with low degradation, but it sits currently around 2500h [31]. The degradation is still high, and the voltage losses can go up to 22mV (around 2% of the open circuit voltage) per cold start up.

The start-stop cycles are the ones that have more impact on the performance of the fuel cell, as can be seen in figure 2.6.

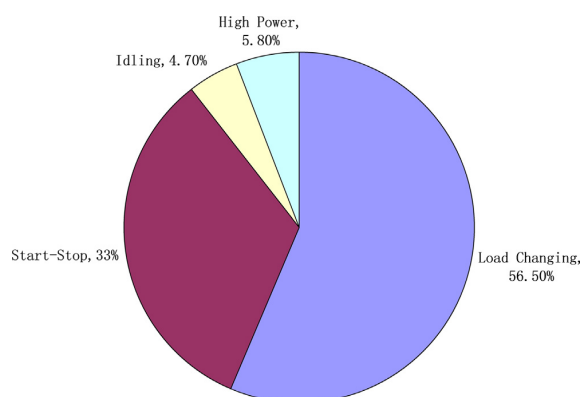


Figure 2.6: PEMFC performance degradation rate caused by different operation conditions[32]

2.3.1 Load cycling

A dynamic driving cycle is a specific type of a load cycling where the real world operation conditions of a vehicle are simulated. In these load cycles the start-up, idling, constant load running, overload running, full power running and variable load acceleration are tested. Compared to the steady-state operating condition these tests are less time consuming and the operating conditions change more dramatically. These tests can cause serious performance degradation as a result of oxidant starvation, local hotspots and physical degradation [31]. There are several studies [33] performing dynamic driving cycles to evaluate the performance degradation of a PEM fuel cell in real-world.

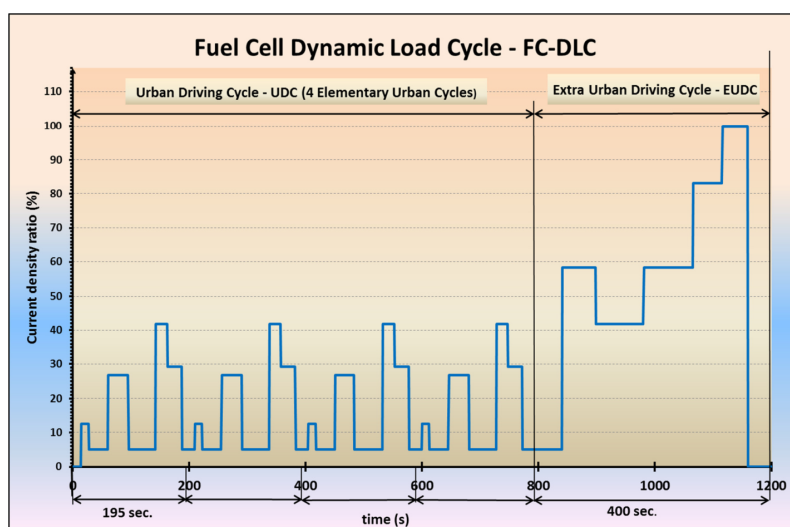


Figure 2.7: European harmonized fuel cell dynamic load cycle (FC-DLC) [33]

P. Gazdzick [34] tested a 25cm^2 single cell based on the European harmonized fuel cell dynamic load cycle (FC-DLC - figure 2.7) for five one-week periods, consisting of 6 days of running continuous load cycles (each lasting 20min) and one day of characterization and refresh of the fuel cell. After the five sequences he could observe that between the first and second sequence the irreversible degradation rate was linear for all the different current densities. Between the first and the fourth sequence the voltage decay was around $0.3\text{--}0.6\text{ mV h}^{-1}$ for the different loads. However, in the fifth sequence for a load of 25A there was a strong increase in degradation, hinting at an MEA failure.

R. Lin [31] tested a 50 cm^2 single cell based on the FC-DLC for 200 cycles and after 100, 150 and 200 cycles the performance of the cell was recorded to evaluate the degradation. It was observed that the voltage decay was higher in higher current densities. At 1 A cm^{-2} the average voltage decay rate is $225\text{ }\mu\text{V}$ per cycle while at 200 mA cm^{-2} it was around $31\text{ }\mu\text{V}$ per cycle.

P. Pei [32] tested a 50 cm^2 single cell based on the FC-DCL for 370h and after 100, 200, 280 and 370h the polarization curves were recorded to analyze the fuel cell performance. Once again it

was observed that the degradation is always higher in high current densities. The degradation rate was higher between during 280-350 h operation than 0-280 h.

Table 2.1: Load cycling tests on state of the art MEAs

	P. Gazdzick [34]	R.Lin [31]	P. Pei [32]
$\lambda H_2/\lambda O_2$	1.5 / 2.0	1.2 / 2.5	1.2 / 2.5
RH (%)	50	100	100
Outlet Pressure (bar)	1.5	0.2	1.0
Cell Temperature (°C)	80	80	70
Active Area (cm²)	25	50	50
Pt coating A & C (mg cm⁻²)	0.25 (total)	0.4 & 0.4	0.4 & 0.4
Test Time (h)	720	67	370
Degradation rate (mV h⁻¹)	1.05 (1 A cm ⁻²)	0.675 (1 A cm ⁻²)	2.3 (0.7 A cm ⁻²)

2.3.2 Start-up/shutdown cycling and Reverse current mechanism

Both start-up and shutdown are dynamic processes that fuel cells inevitably have to confront in automobile applications. The temperature and the gas humidity, for example, have a different profile compared to steady-state conditions. To perform the start-up it is necessary to increase the temperature and humidity, while during shutdown it is necessary to decrease both of them [35]. The local gas mixture at the anode, which is normally called hydrogen/air interface, is the major feature of both of these processes, a feature that is responsible for performance degradation.

During start-up the first step is to feed the anode side with hydrogen and the cathode side with oxygen or air. Air diffuses into the anode either through the gas connections or not perfectly secure seals, or even through the membrane, so there's an hydrogen/air boundary during the fueling of hydrogen. After some time the air gets pushed out to the anode outlet by the hydrogen making the air/hydrogen interface disappear, leading to the open circuit voltage (OCV) state.

During shutdown of the fuel cell the same boundary can be formed. When the load is shut off, the air and hydrogen are stopped but residual gases will remain on the anode and cathode. Because of the concentration difference the oxygen will cross the membrane to the anode, creating the air/hydrogen boundary. This interface will last longer than the other one because of the slow air permeation.

Figure 2.8 illustrates this air/hydrogen interface formed both during start-up and shutdown. At the top of figure 2.8 it is possible to see the two regions: the one filled with hydrogen and the one filled with air, and that the hydrogen region is close to the anode inlet, while the air is being pushed to the outlet. Region B is filled with air and because of that oxygen reduction happens on both the anode and cathode, resulting in a high potential ($\sim 1.443V$) at the cathode, which causes oxygen evolution and carbon corrosion in the catalyst layer [36]. In the cathode side in region B protons are being released from the reaction of the water and carbon and they are going through the membrane

because the vertical pathway is shorter than the horizontal. Hence, on the anode side of the region B the Oxygen will be reduced (ORR) temporarily causing a reverse current mechanism.

The reverse current mechanism can also happen with fuel starvation. This is a problem that occurs in fuel cell stacks due to the uneven gas distribution to all the cells in the stack.

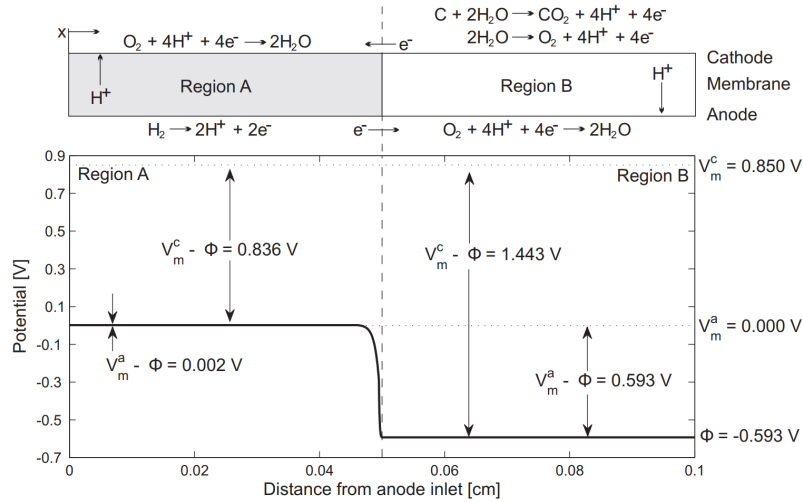


Figure 2.8: Potential distribution along the anode flow path during reverse-current conditions[36]

Table 2.2 summarizes the voltage decay rate based on start-up and shutdown conditions. These durability tests are Accelerated Stress Tests (AST) to evaluate the long term durability of the cell when exposed to these conditions for a long period of time.

Table 2.2: Summary of accelerated durability tests for a single cell (Open circuit voltage around 1V) in the literature [37] [35]

Experimental factors	Number of cycles	Voltage Decay Rate
Cold Start-up	10	22 mv drop per cycle at 150 mA cm^{-2}
Air/Fuel boundary	80	5 mV drop per cycle at 400 mA cm^{-2}
Shutdown process	200	0.31 mV drop per cycle at 400 mA cm^{-2}
Start/Stop cycling	500	0.66 mV drop per cycle at 1000 mA cm^{-2}

Chapter 3

Fuel cell test and characterization

A description of the fuel cell assembly is presented in this chapter, detailing which materials were used and how they were assembled. Also, the conditions for the three cycles performed on the fuel cell are explained and the protocol used for the driving cycle operation. A brief description of the *in situ* and *ex situ* techniques used to characterize the performance of the cell is also made. Lastly, the adaptations implemented in the test bench are described as well as the monitoring system developed.

This master's thesis is part of an European Project in cooperation with the German Aerospace Center with the objective of developing a fuel cell cargo pedelec. All the tests performed were based on a single cell made in-house that will be incorporated into a fuel cell stack with 20 single cells in series. Each single cell will be working with a maximum output of 60 A. The stack will be incorporated into a modular system called FC-REX (Fuel Cell Range Extender) and has a nominal electrical power output of around 600 W with a peak power of 750 W.

The two complete driving cycles will be tested at 1.0 bar to assess the possibility of having the cargo pedelec working without a pressurizer for the air. That would be one less thing to be incorporated onto the bicycle that would draw power and add more weight to it.

3.1 Fuel Cell Assembly

The cell used for testing the driving cycles for this master's thesis was assembled manually in the laboratory. The components used are indicated in the table 3.1.

The dimensions of the components were chosen in order to have an active area of 60 cm² on the cell. The assembling process of the cell can be seen in figure 3.1.

The first step of the assembly process is cleaning both bipolar plates using an alcohol solution and drawing the lines for the respective elements, in order to help with placing them in the correct positions. Afterwards, the sealing gasket is cut into a frame shape and placed between the first and third rectangle sealing the MEA on both sides. Next, the first piece of GDL is placed in the smaller rectangle, covering the entirety of the flow field area, with the Macro Porous Layer facing the flow field. The Catalyst Coated Membrane is the next component put into place covering the second rectangle with the cathode side (higher Pt amount) facing down. Subsequently, the other

Table 3.1: Components used in cell assembly

Component	Features	Supplier
Catalyst Coated Membrane	Thickness: 18 μm Pt Loading: 0.1 mg cm^{-2} (anode) 0.4 mg cm^{-2} (cathode)	GORE® PRIMEA® MEAs
Gas diffusion layer	GDL 25BC (modified from the project DECODE)	SGL Carbon®
Sealing Gasket	Ice Cube Thickness: 350 μm	Freudenberg®
Bipolar Plate	Gold coated stainless steel plate Straight flow field: cathode side Curved flow field: anode side (30 channels - width: 1mm)	DLR homemade

piece of GDL is fixed on top of the MEA and lastly, the second bipolar plate will sandwich all the components.

The torque was applied diagonally starting at 1 Nm^{-1} with increments of 0.5 Nm^{-1} in each bolt until it reached 10 Nm^{-1} . Each hole for the bolts has a fitting to prevent short circuits. In order to find out the best torque that should be applied in the bolts a test was conducted by keeping the same current and gas flows and only changing the torque applied, coming to the conclusion that the best range of torque was between 8 and 12 Nm^{-1} . The middle value was chosen to run the tests.

The assembling seen in figure 3.1 was the one used for the load cycling tests, but there were different ones that were tested before. This is a new cell designed at the DLR for the fuel cell stack that will be powering the cargo pedelec.

Initially the cell did not have a Sealing Gasket (Ice Cubes) because the thickness of the material caused insufficient contact between the GDL and the MEA, which led to problems with the performance of the cell. After that, ice cubes were placed around the screw holes due to short circuits in the cell caused by contact between the two bipolar plates. Finally, the Ice Cubes were attached only on one side (usually on the cathode side) around the GDL. Normally the ice cubes are used on both sides of the cell, but in this cell that was not possible due to the contact issues not allowing the gases to have a good diffusion and affecting the performance.

3.2 Testing Protocol

After assembling, the fuel cell was submitted to two different dynamic driving cycle tests by following a specific protocol with different phases, as described in figure 3.2. A third cycle was conducted (repeating one of the driving cycles using different conditions) but only lasting five days of operation, meaning that it stopped in the 4th phase of the testing protocol.

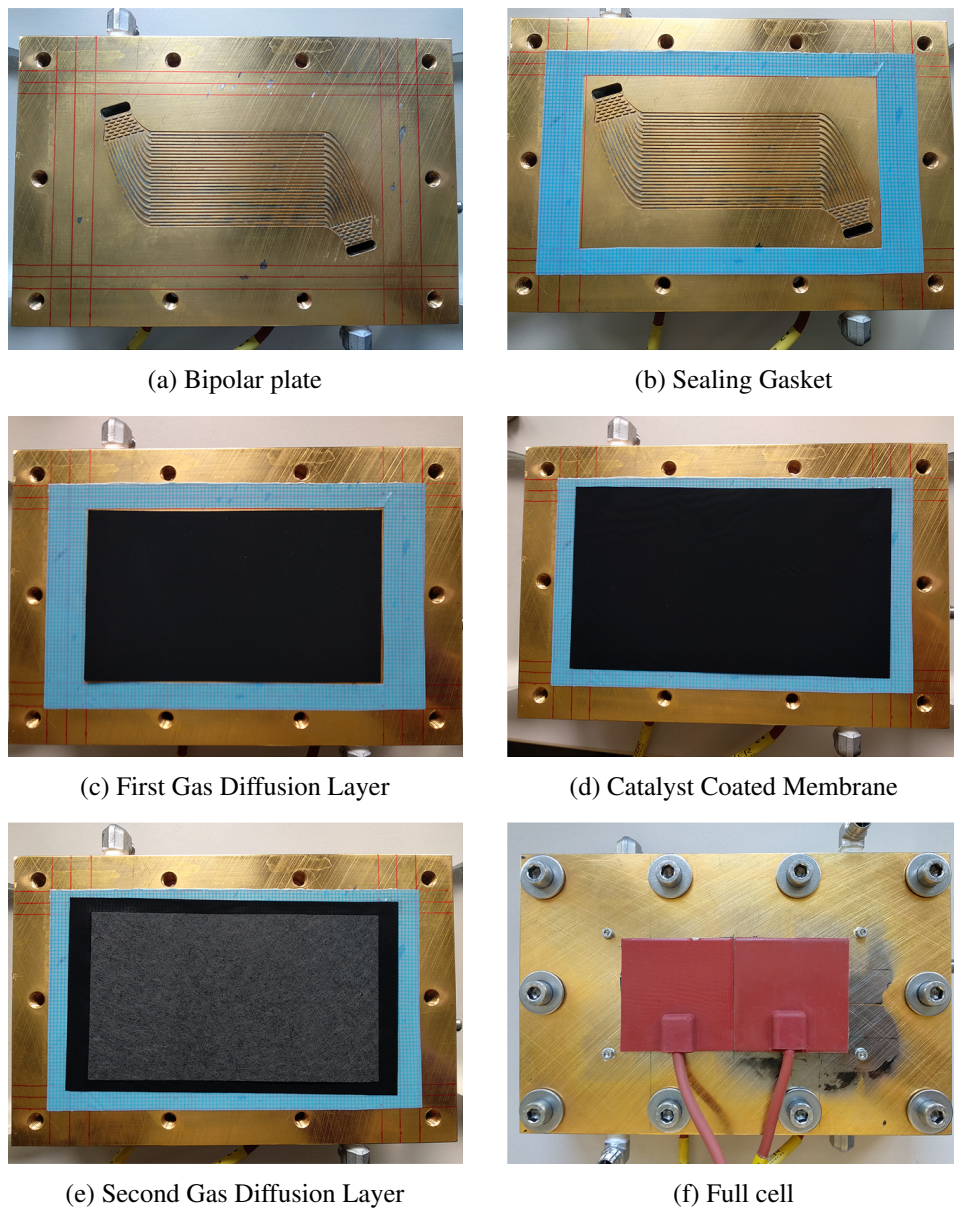


Figure 3.1: Fuel cell assembling process

The first step is called "MEA Break-in", which consists in activating the MEA. The MEA needs to be properly humidified before starting the operation, otherwise it won't perform adequately. This procedure was done with the cell temperature at 80°C and a Relative Humidity (RH) of 100%. After conditioning, if the cell has a stabilized potential of at least 600 mV at 1 A cm⁻² it is considered as valid for running the test. The conditioning protocol used was the following:

1. Start up the test bench;
2. Heat the bubblers up to 80 °C;
3. Start the gas flow for 1 A cm⁻² using the stoichiometry of 1.5/2 for H₂/Air;

4. 10 minutes without turning on the load;
5. Heat the cell's bipolar plates up to 80 °C;
6. Turn on the load and put it into potentiostatic mode;
7. Define the voltage as 800 mV and decrease 50 mV every 5 minutes until reaching 400 mV;
8. Change to galvanostatic mode and define the current as 60 A and let it run for 1/2h until the voltage is stable (not changing more than 5 mV during 2 minutes).

Afterwards, an electrochemical characterization was performed consisting of polarization curve, EIS and CV measurements, called the Beginning of Test (BoT) characterization.

Each test has three durability periods, each of one them being 117h, then followed by a shutdown overnight (approx. 10h). During shutdown, also called refresh period, the heaters of the cell are stopped, bringing the cell to room temperature, and the outlets are open to let air go inside and refresh the membrane. Before shutdown and after restarting the fuel cell, nitrogen was purged for five minutes in both the cathode and anode sides to push remaining water and reactants out of the cell, thus avoiding formation of air/hydrogen boundary when opening the gas outlets. At the time of restarting operation, the cell is again heated up to 80°C and then electrochemical characterization is performed to evaluate the fuel cell degradation. Then the next period begins and the same protocol is performed.

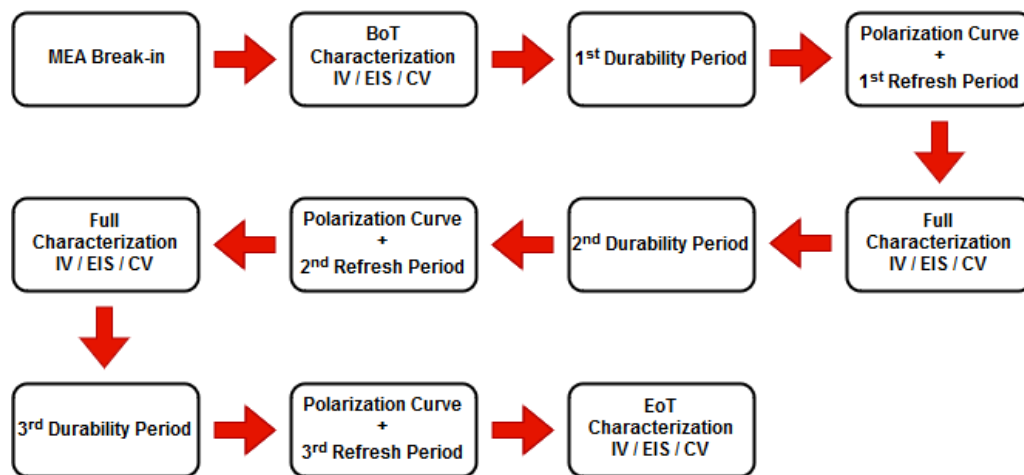


Figure 3.2: Testing protocol

Figure 3.3 shows the interface used to operate the test bench. The interface is running on SIMATIC WinCC and allows the automatic control of the cell pressure and temperature; regulate the gas flows and humidity and which mode the cell operates: galvanostatic or potentiostatic mode. For the data acquisition part, done by a PLC on the back of the test bench, the system records the values of the cell temperature, current and voltage; inlet and outlet pressure; temperature of the inlet tubes and all the temperatures of the bubblers. There's two different modes to run the test

bench: a pre-programmed setup where it is only allowed to change some of the values and a manual mode where each valve can be opened/closed individually giving total control over the hardware.

A view of the fuel cell connected to the test bench is shown in figure 3.4. The anode is the side seen in the picture. It is possible to observe both gas pipes connected to the inlet of the cell (superior part). Both are insulated to prevent the gases from cooling down. The tubes on the lower part are the outlets of the cell. The red piece attached to the center of the bipolar plate is the heat pad of the cell. The current cables are connected as shown in figure B.2.

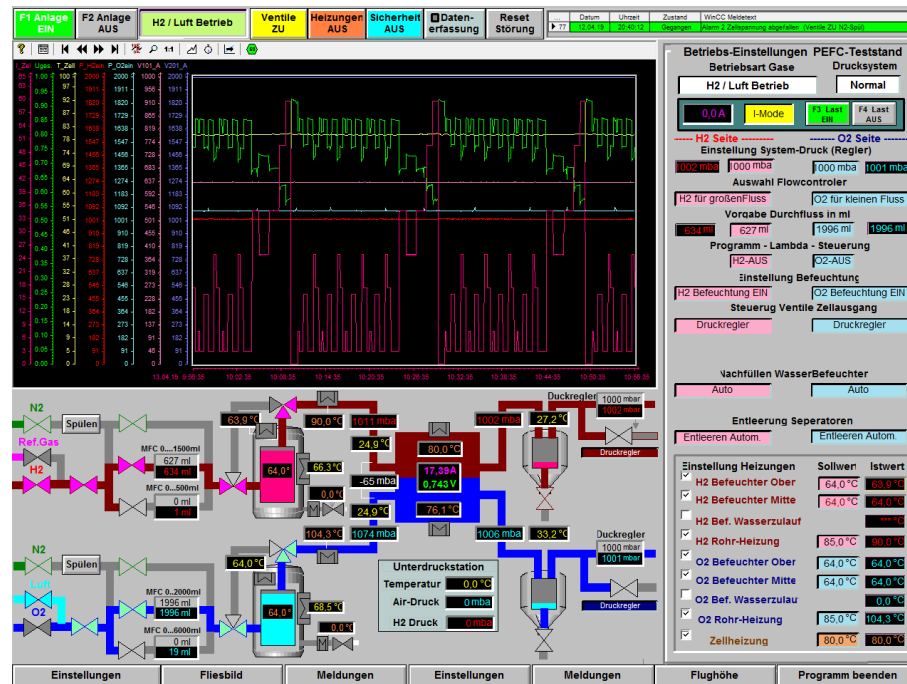


Figure 3.3: Test Bench software interface

3.3 Base Tests

Ahead of starting the dynamic load cycles, three different tests were conducted on the 60 cm² single cell to assess the performance of the cell: the impact of distinct inlet gases' relative humidity and back pressures and performance comparison to a 25 cm² cell.

The 25 cm² single cell made in-house was assembled as a means of comparison for the performance of the new 60 cm² cell. These cells were extensively tested for the past years in the labs and thus constitute a way to perceive how the new cell stacks up against the common design. The components used were the same (GLD, MEA and Gaskets) in order for the results to be considered valid. Both cells were set to 80°C, 50% RH, stoichiometry of 1.5 / 2 for hydrogen and air and a back pressure of 1.0 bar.

To perceive the influence of the inlet gases relative humidity in the performance of the fuel cell, a test was conducted with the cell's temperature set to 80°C and running in galvanostatic mode with

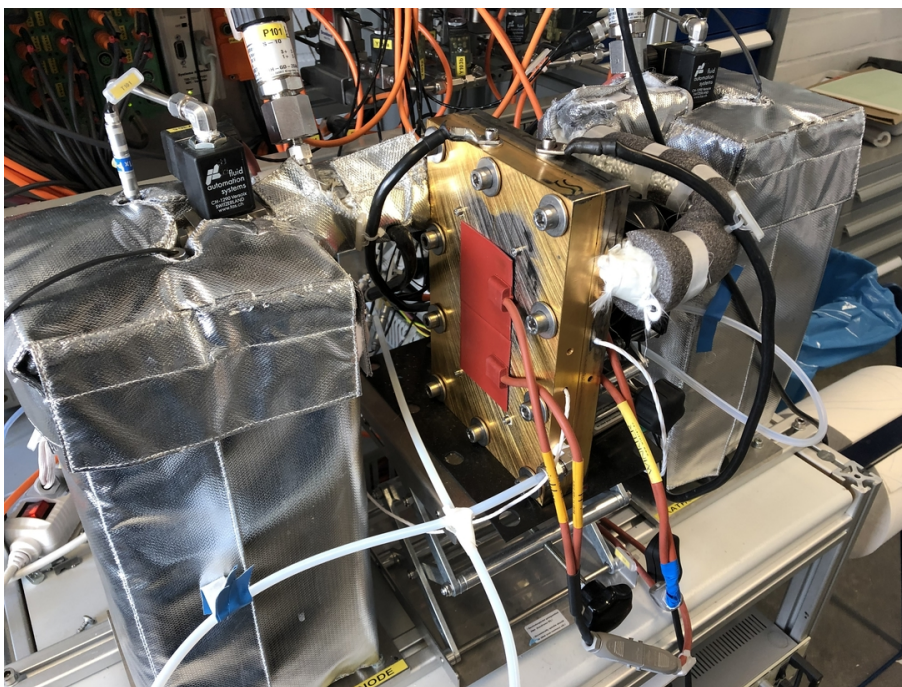


Figure 3.4: Fuel cell connected to the test bench

a current density of 0.6 A cm^{-2} , corresponding to 36 A. The reactants' flow was set accordingly to the stoichiometry of 1.5/2 for H_2 and Air for the respective current density chosen. The different RH were set as the same value for both cathode and anode side.

The third test was conducted to observe the back pressure effect on the cell's performance. Polarization curves were recorded for three different outlet pressures: 1.0 bar, 1.5 bar and 2.5 bar. The temperature of the cell was set to 80°C while running in galvanostatic mode. The curves were measured at constant 1.5 / 2 stoichiometry for H_2 and air, respectively, with minimum flows of 105 ml min^{-1} and 333 ml min^{-1} .

3.4 Dynamic Load Cycles

The purpose of testing these load cycles is to simulate real-world driving conditions in a laboratory environment and assess the durability of the fuel cell when being exposed for a long period of time to the same load cycle repetitively [33]. These cycles reproduce different operations regimes including prolonged Open Circuit Voltage (OCV) exposure, fast load variations, steady state periods and full power running.

Two different dynamic load cycles were tested on the single 60 cm^2 fuel cell: the Fuel Cell Driving Load Cycle and the Worldwide Harmonized Light Vehicles Test Procedure. The conditions used for the load cycling tests can be observed in table 3.2. All the experiments were conducted with a constant flow for a current density of 1 A cm^{-2} , the stoichiometry ratio being 1.5 for H_2 and 2.0 for air. Both gases were first humidified by passing through their respective bubblers

(humidifiers). The temperature of the gas inlet tubes was held at a temperature of 5°C degrees above the cell temperature to avoid water condensation in the humid gases [34]. The data of the fuel cell was record every 10s during the all operation.

Table 3.2: Experimental Conditions for the dynamic load cycles

Parameter	Value
Cell Temperature	80 °C
Anode Inlet Tube Temp.	85 °C
Cathode Inlet Tube Temp.	85 °C
Anode Flow	627 ml min ⁻¹
Cathode Flow	1996 ml min ⁻¹
H ₂ /Air stoichiometry	1.5 / 2
Gas inlet humidification (anode/cathode)	50 / 50 %
Outlet Pressure	Varying

3.4.1 Fuel Cell Driving Load Cycle

The first test performed was based on the Fuel Cell Driving Load Cycle (FC-DLC) protocol. The FC-DLC is based on the New European Driving Cycle (NEDC). The NEDC is divided into two sections: Urban driving cycle and Extra Urban driving cycle. The first section is composed by four cycles of low speed (urban driving), each one with a period of 195 seconds, and the second section is an highway cycle with a duration of 400 seconds. The total time of the cycle is 1180s and the equivalent theoretical distance is about 11 km.

In order not to expose the fuel cell to long periods of OCV conditions, all the periods of the cycle corresponding to a stop (0% load) were replaced by a current density of 5% of the maximum load, except for the first and last stop [33]. The current profile for one cycle can be seen in figure 3.5.

A small change was made to the FC-DLC by adding up 20 more seconds to the last stop to make it easier to build the cycle in the function generator, thus increasing the duration of one cycle to 1200s (20 min).

3.4.2 Worldwide Harmonized Light Vehicles Test Procedure

The second test performed was based on the Worldwide Harmonized Light Vehicles Test Procedure (WLTP). Due to progression in technology and driving conditions, the New European Driving Cycle became outdated, therefore the European Union created a new test to replace the NEDC. Unlike the NEDC, the WLTP was developed taking into account real driving data gathered from around the world [38].

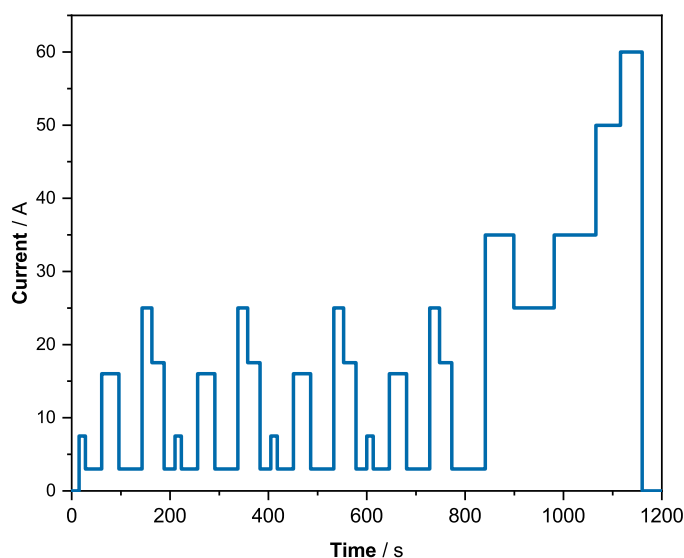


Figure 3.5: European Load Cycling Test

The WLTP has three different vehicle classes based on the power/mass relation and the cargo pedelec fits in the class 1 group. The driving cycle for this group is divided in two parts: low average speed and medium average speed. Each part has stops, accelerations and braking phases.

Since the cycle comes in speed instead of load ratio (%) it was necessary to adapt the cycle to run it on the test bench. The procedure was similar to the one made with the FC-DLC by the European Union, consisting in transforming the cycle into vertical steps ("squaring the cycle") while keeping the area under the cycle the same. The value of the absolute area for the adapted cycle was close to the original cycle but not the same. For this driving cycle, opposed to the FC-DLC described in figure 3.5, the stops were not switched to low current to avoid OCV exposure. The current profile adapted for the test bench can be seen in figure 3.6.

3.5 Electrochemical Characterization

Electrochemical Impedance Spectroscopy and Cyclic Voltammetry characterizations were conducted using a ZAHNER ZENNIUM PP241 potentiostat with THALES software. The station used for both tests can be seen in figure B.1. The polarization curves were performed using only the test bench equipment. The outlet pressure was set accordingly to the test conditions.

3.5.1 Polarization curves

Polarization Curves allow the characterization of the performance of the cell at different current densities, thereby analyzing the different operation regions for different operation conditions like relative humidity, inlet gas flow, and temperature. Before and after each period of testing, polarization curves were recorded to estimate the degradation rate of the fuel cell.

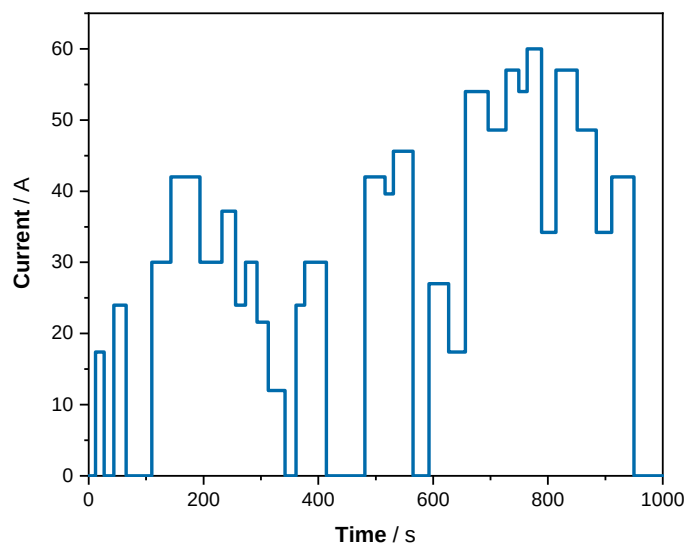


Figure 3.6: Worldwide Harmonized Light Vehicles Test Procedure adapted for the test bench

The voltage difference between the end and the beginning of a period of testing (117h) represents the overall amount of voltage losses. This value can be separated into two different components: reversible and irreversible voltage losses.

The reversible voltage loss is the recoverable part of the overall voltage loss and is calculated as the voltage difference between the beginning of the period t_{i+1} and the end of period t_i .

$$\Delta V_{rev,i} = V(t_{i+1}) - V(t_i + \Delta t_i) \quad (3.1)$$

The irreversible voltage loss is the non-recoverable part of the overall voltage loss and is defined as the voltage difference between the start of period t_i and the start of period t_{i+1} .

$$\Delta V_{irrev,i} = V(t_i) - V(t_{i+1}) \quad (3.2)$$

The polarization curves were performed in galvanostatic mode and the current applied to the fuel cell was controlled using the test bench interface. Each step of current was applied for 1 minute to let the voltage stabilize, being the first step 0 A (OCV) and the last one 60A (1 A cm^{-2}). The current set points used are described in table A.1. The stoichiometry was constant and set as 1.5 / 2 for hydrogen and air, respectively, meaning that for each step of current the gas flows are set accordingly. Up until 10 A the inlet gas flow is always the same to avoid fuel starvation.

3.5.2 Cyclic Voltammetry

Cyclic Voltammetry is a powerful tool to characterize the fuel cell catalyst. A two-electrode configuration is used with a reference electrode and a working electrode. As already stated in section 2.2.1.2, the cathode's electrochemical activity is the most studied part because of the slow kinetics of ORR, thus the cathode being the working electrode and the anode the reference electrode.

The hydrogen is used as a reference electrode because its standard potential is defined as 0 V. The procedure requires sweeping back and forth the potential of the working electrode. The forward scan will oxidize the hydrogen adsorbed in the electrode to H^+ and the reverse scan will reduce the H^+ to $H_{adsorbed}$ [39]

During the oxidation of hydrogen in the surface of the catalyst, the hydrogen atoms are desorbed according to the following reaction:



The current response is plotted as a function of the working electrode voltage scan, in what is called a cyclic voltammogram, as illustrated in figure 3.7:

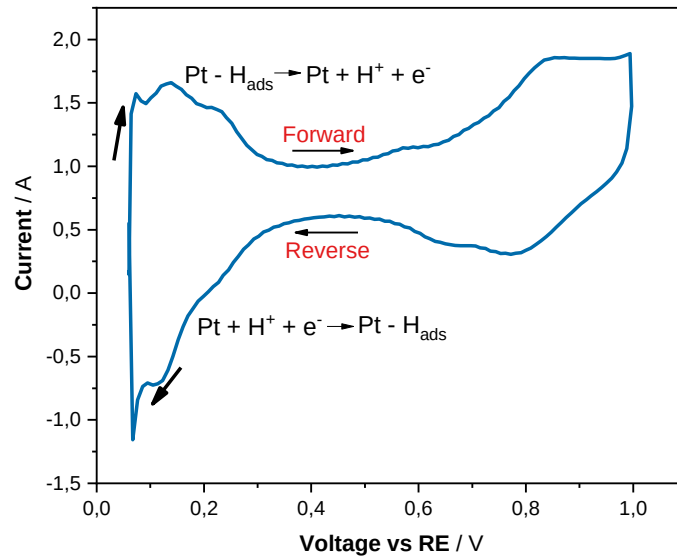


Figure 3.7: Cyclic voltammogram of PEM fuel cell cathode electrode [Adapted from [39]]

The electrochemical active surface area (ECSA) can be determined from the analysis of the cyclic voltammograms based on the absorption/desorption of the hydrogen on the electrode surface by applying the following equation [39]:

$$ECSA(m_{Pt}^2 g_{Pt}) = \frac{q_{Pt}}{\Gamma \cdot L} \quad (3.4)$$

In which q_{Pt} refers to the hydrogen adsorption charge density ($C m^{-2}$ retrieved from each CV; Γ refers to the charge required to reduce a monolayer of protons on Pt and is equal to $210 \mu C m^{-2}$ and L represents the Pt content or loading in the electrode ($g m^{-2}$). The number of hydrogen atoms desorbed during this reaction can be measured by the number of electrons liberated and in that way it is possible to know the number of adsorption sites present in the catalyst layer. This is the definition of active surface of the electrode [40].

To perform this electrochemical characterization nitrogen was purged through the working electrode (Cathode) and hydrogen was fed through the reference electrode (Anode). The flow

for both gases was 125 ml min^{-1} and the relative humidity was raised to 100% by increasing the temperature of the bubblers to 80°C . The absolute outlet pressure was set accordingly to the test conditions. For each test, five cycles were performed to assure the validity of the results, with a voltage range from 60 mV to 1V with a slew rate of 20 mV s^{-1} . The CV was obtained after each refresh of the cell.

3.5.3 Electrochemical impedance spectroscopy (EIS)

The EIS consists of sending a sinusoidal current (galvanostatic mode) or voltage (potentiostat mode) perturbation in a wide frequency range (typically from mHz to kHz) to the fuel cell and measuring the response. The response of the fuel cell can be plotted with the real and imaginary part of the impedance spectrum, creating a Nyquist plot [41]. The high frequency region (1 - 10 kHz) impedance is associated with the ohmic resistance (PEM resistance), while the frequency range between around 10 and 100 Hz is correlated to the charge transport in the catalyst layer. Lastly, the low frequency region is related to the mass transport in the cell.

All the electrochemical impedance spectroscopy measurements were performed in galvanostatic mode for currents of 3A and 36A, corresponding, respectively, to 0.05 A cm^{-2} and 0.6 A cm^{-2} , with a range of frequencies from 100 mHz to 100 kHz, starting at 1 kHz. The AC signal amplitude for the 3 A test was 200 mA and for the 36 A test was 1 A. The stoichiometry was set accordingly to the current density with a ratio of 1.5/2 for hydrogen and air, respectively.

3.6 *Ex Situ* Characterization

Physical/*Ex situ* characterization techniques provide a different insight into what's happening with the cell by giving information about the physical and chemical structure of the different components of the fuel cell. The places where the samples were taken for the different characterization techniques can be seen in figure 3.8. The physical characterization was only performed for the two FC-DLC cycles (1 bar and 2.5 bar). For the WLTP it was not possible to perform these tests due to time constraints.

3.6.1 Scanning electron microscopy and Energy-dispersive X-ray spectroscopy

To examine particle growth, porosity, thickness of the MEA and platinum migration, some samples of different places of the MEA were analyzed using a Zeiss UltraPlus scanning electron microscope. The distance between the lens and the MEA cross section or catalyst layer was kept between 4.2 and 8.1 mm. The electron beam voltage was set between 1 to 50 kV. To complement the Scanning Electron Microscopy (SEM) analysis of the catalyst layer, an Energy dispersive X-ray spectroscopy analysis was performed using a Peltier cooled Si (Li) detector to get an elemental characterization of the electrode surface.

To get a view of the layers of the MEA (cross-section) a specific procedure needs to be done before sending the sample to SEM analysis. The sample needs to be submerged in liquid nitrogen

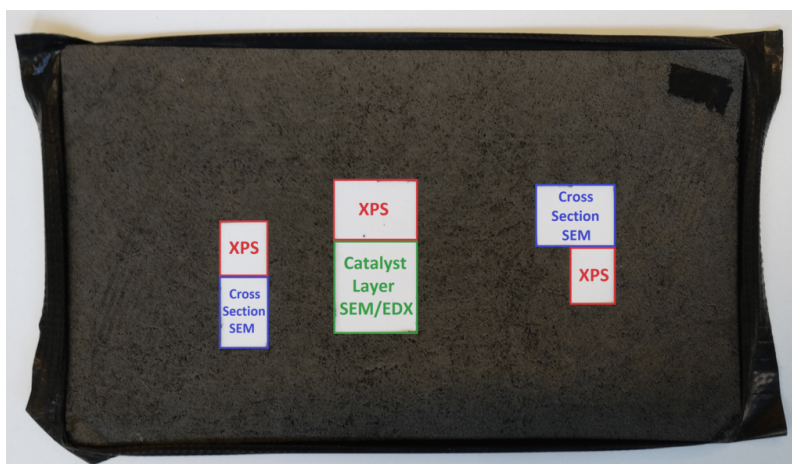


Figure 3.8: Samples used for the different physical characterizations

for a few minutes and then broken in half to obtain a clear image of the layers, otherwise the surface would be rough and it would be impossible to measure the thickness.

3.6.2 X-ray photoelectron spectroscopy

To examine platinum migration to the macro porous layer of the GDL some samples from the inlet, outlet and middle section of the anode and cathode sides were analyzed in an X-ray photoelectron spectrometer. This technique gives an elemental composition in a spectrum with the binding energy of the different elements. The X-ray photoelectron spectroscopy (XPS) spectra is obtained by irradiating the surface of the material with an X-ray beam while measuring the kinetic energy and electrons emitted from the surface of the material [42]. The depth resolution of the XPS is between 1 and 10 nm while the SEM's is around 20 μm .

3.7 Test bench upgrade

In order to perform the load cycling tests described previously in this chapter, some improvements to the test bench were made. To run the cell with these load cycles, the test bench needs to be working in galvanostatic mode, which means that the load attached to the fuel cell will be keeping a certain current and the voltage response of the cell will be recorded. However, the test bench used during this master's thesis did not allow for the possibility of creating a script with different steps for the current over time and that was a fundamental part for testing the cycles. The solution found was connecting a function generator directly to the load, and that way controlling the current of the load with the function generator instead of using the computer. The function generator used with both of the driving cycles displayed is shown in figure 3.9. In CH1 (right side) is the FC-DLC and in CH2 (left side) is the WLTP.



Figure 3.9: Function Generator with both cycles displayed

3.7.1 Function Generator

The load connected to the test bench was an electronic load from *Höcherl & Hackl GmbH* with a maximum output current of 60 A.

The load was connected to the PLC by a serial connection (RS-232) using a D-sub 25-pin connector. As a means to control the load with the function generator, two D-sub 25-pin breakout connectors were used to change the needed connections. One of the connectors was attached to the cable coming from the PLC, and the other one to the cable coming from the load, and then the connections were made between the two breakout connectors.

The pins previously used for the connection of the load to the PLC were kept the same, except for the two pins that control the output of the load: pins 3 and 16, respectively the negative analog control input and positive analog control input (0...10V) which were connected to the function generator as can be seen in figure 3.10 [43].

The load was operated in current mode, since we wanted to fix the current and get the voltage response from the fuel cell. The control of the current is linear with the voltage analog input meaning that, for example, if we want a current of 30A, we need to send a signal of 5V to the load.

The function generator has a built-in function to create arbitrary waves which makes it possible to save them to the internal memory. The peak-to-peak voltage used was 10 V with an offset of 5V for both cycles. The frequency was set accordingly to the duration of one cycle.

3.8 Monitoring System

There was a lack of a basic monitoring system outside of the lab, even if only for the purpose of knowing whether the cell was still running the load cycle. Hence, a basic monitoring system was

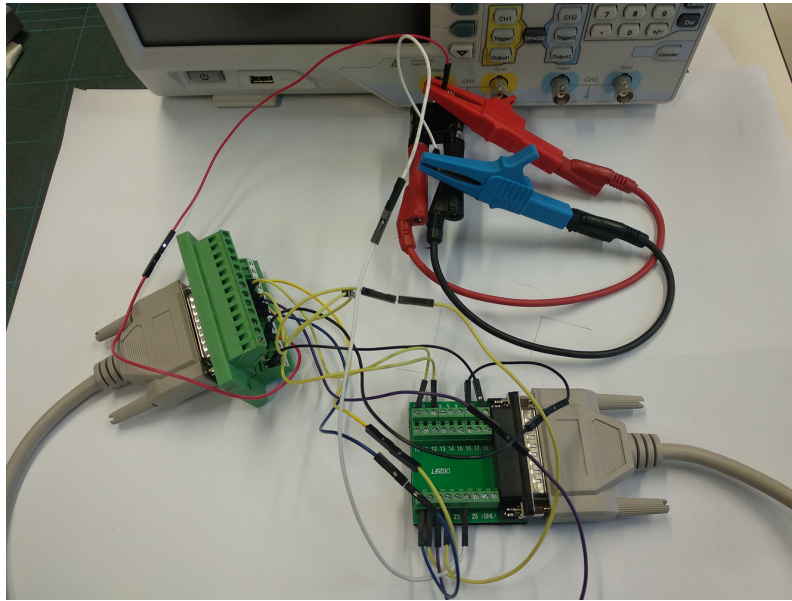


Figure 3.10: Connection between the function generator and both load and PLC

created that can later also be attached to the cargo bicycle. Figure 3.11 shows a diagram of the implementation used. Basically there are four sensors connected to the fuel cell: one voltage sensor, two current sensors and one GPS sensor. The GPS sensor was merely used so it would already be implemented for future integration on the bicycle. The microcontroller reads the values of the sensors and sends them via an HTTP POST request to the server, which has a script running to receive the data and then sends it to the database. In order to display that information to the user, the website pulls the information from the database.

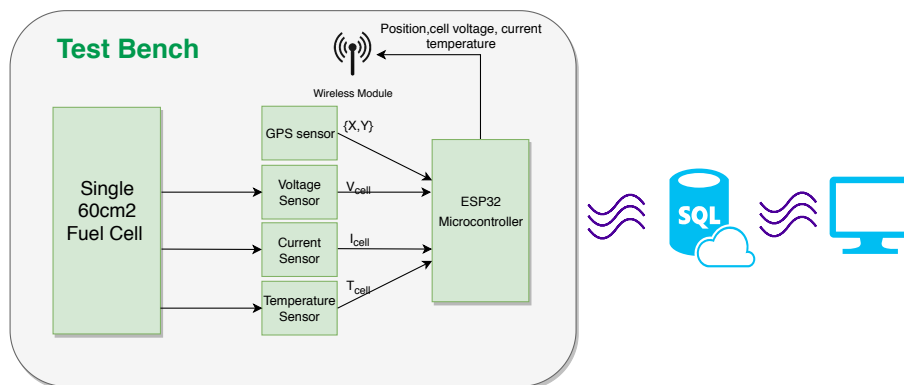


Figure 3.11: Diagram of the monitoring system implemented

3.8.1 Microcontroller

The microcontroller used to capture the voltage, current and temperature of the cell was an ESP32 from Espressif Systems. The ESP32 has a Xtensa dual core 32-bit CPU clocked at 80 MHz (which

can go up to 240 MHz) with an integrated Bluetooth and Wi-Fi module [44]. The ESP32 integrates two 12-bit SAR (Successive Approximation Register) ADCs with 18 analog channels in total. To develop this work, an evaluation board (ESP-32-DevKitC) with an integrated USB interface was used for rapid prototyping. Espressif Systems provides the Arduino framework for the ESP32. The board was programmed in C with Visual Studio Code using the Arduino Framework.

3.8.1.1 Sensors

The current sensor used is manufactured by Allegro MicroSystems. The ACS770LCB-100U is a low-offset linear Hall circuit with an extremely stable output voltage [45]. The voltage output is proportional to the magnetic field strength generated by the current flowing through the copper conduction path. It is an unidirectional sensor with a maximum current input of 100 A. The output has an offset of 0.5 V and the primary current flows from terminal 4 to 5. Figure 3.12 shows the sensor diagram and evaluation board used.

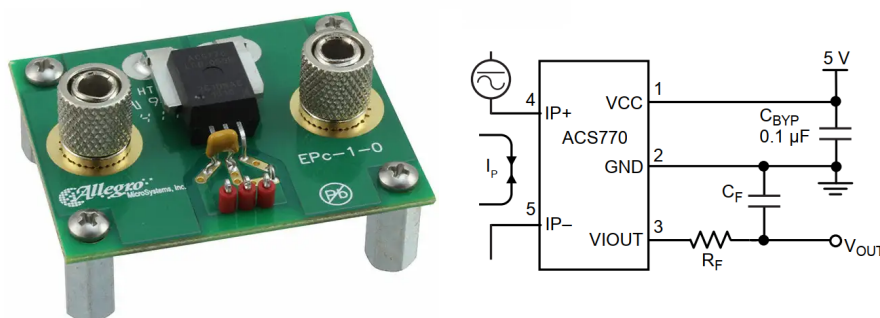


Figure 3.12: ACS770LCB-100U evaluation board and diagram

The temperature sensor used was a PT100 with a 4-wire configuration for better measurement reliability and accuracy. It determines the temperature by measuring the resistance of the platinum, which has a $100\ \Omega$ resistance at $0\ ^\circ\text{C}$ and $138.5\ \Omega$ resistance at 100°C . These sensors are much more reliable for industrial processes than NTC thermistors.

A 1°C change in the temperature will cause a $0.385\ \Omega$ change in the platinum resistance, which is really low for the microcontroller to read accurately, so an external circuit was connected to measure the resistance with better accuracy. The MAX31865 is a resistance-to-digital converter with an integrated 15-bit ADC. It has a resolution of around 0.03°C and sends the data over SPI. An evaluation board from Adafruit, shown in figure 3.13, was used with this integrated circuit. Two boards were used in order to connect the two temperature sensors that were measuring both bipolar places of the cell.

The GPS sensor integrated in the system was an Adafruit Ultimate GPS Breakout board, which is built around the MTK3339 chipset. It has a built-in antenna but for better accuracy and faster fix an external antenna can be connected via the uFL connector. Also, a CR1220 coin cell can be inserted to keep the RTC running, allowing a warm start.

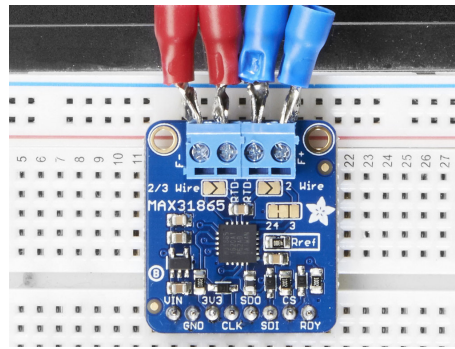


Figure 3.13: PT100 amplifier board

The data acquisition unit built on the breadboard is shown in figure 3.14.

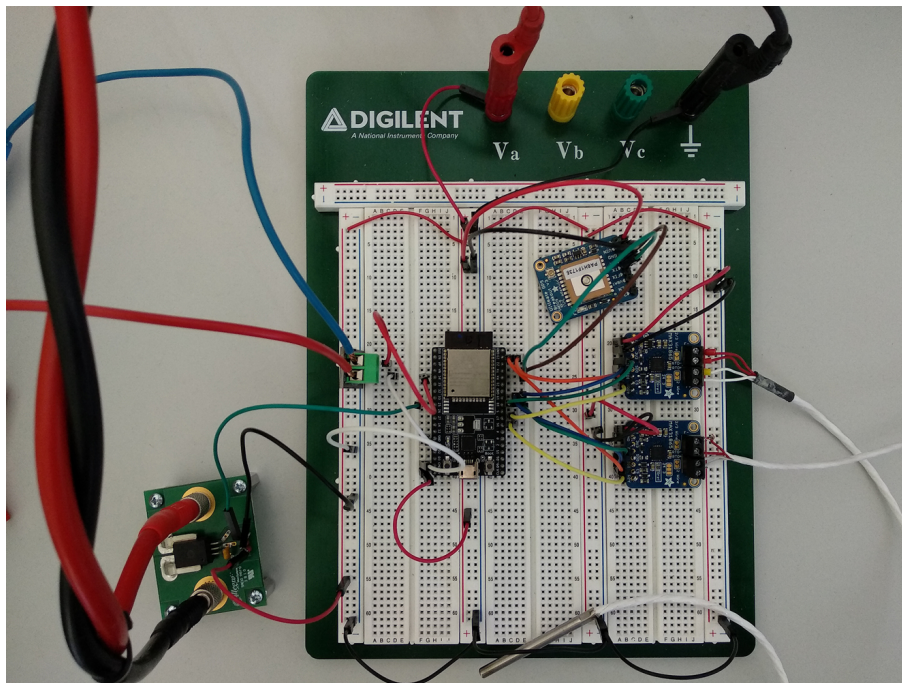


Figure 3.14: Data Acquisition Unit

3.8.2 Software

A description of the program running on the ESP32 is made in this subsection along with an overview of the website.

3.8.2.1 Microcontroller

Two of them were used to measure the voltage and current of the cell. The voltage was measured within a range of 0 to 1 V since the cell never goes higher than 1 V. The current was measured

from 0 to 60 A, which represents a range in voltage that can go from 0 to 3 V, according to the characteristics of the current sensor used.

The temperature values were obtained via a digital pin and two digital output pins were used to control which slave was sending the data by changing the value of the select slave pin of each temperature evaluation board. The GPS position was captured with the GPS module and then the ESP32 got the values via serial communication.

First, the ESP32 starts the Wi-Fi module and tries to connect to the Wi-Fi network selected during the development. Until it connects, every 5s a new attempt is made. Then, the board captures the values of the voltage and current, followed by the readings of the temperature sensors over the SPI data pin. If the GPS signal is available, a reading of the position is obtained too over the RX pin.

After collecting all the values from the sensors, an HTTP POST request is made to a specific page of the website. The HTTP POST request contains a string with the name of the variables and the registered values. The ESP32 then awaits for a return code, and if the code means that an error happened, the board tries to send another HTTP POST request. If successful, the HTTP request is closed and the board repeats the same process, starting at capturing the values, in 10 seconds.

On the server side, a script was created to read the HTTP POST request from the client (ESP32). This script is always waiting for the message. After decoding the string of values, the server sends the data to the database.

3.8.2.2 Website

The website was built with PHP alongside a MySQL database. It is stored in the Microsoft Azure services.

To protect the website from SQL injections and to keep the users' data safe, all the queries made to the database use PDO prepared statements. By using these, the SQL query is sent to the database without the parameters (placeholders). The parameters are bound to the placeholders and sent simultaneously with the query, which prevents the insertion of malicious parameters in the queries. The passwords are encrypted with PHP password encryption, which stores an hash in the database instead of the real password.

The "Real-Time Data" page of the website is shown in figure 3.15. This page shows an overview of the fuel cell by displaying the voltage, current, temperature of both sides and the location of the cell. The values displayed are refreshed every 10 seconds without reloading the page if the DAQ is connected to the test bench. In order to do this a JQuery method was used so that every 10 seconds it checks whether there are new values in the database and if so, they are updated in the boxes without refreshing the page. Otherwise that page would be constantly refreshing and it would be a jarring experience for the user. The same thing happens with the map. The Google Maps used refreshes every 60 seconds (this can be adjusted) by only reloading the position on the map.

The web page seen in figure 3.16 recreates the graphic that is displayed in the test bench software, but of course with only a few of the parameters. The X-Axis displays the time in hours,

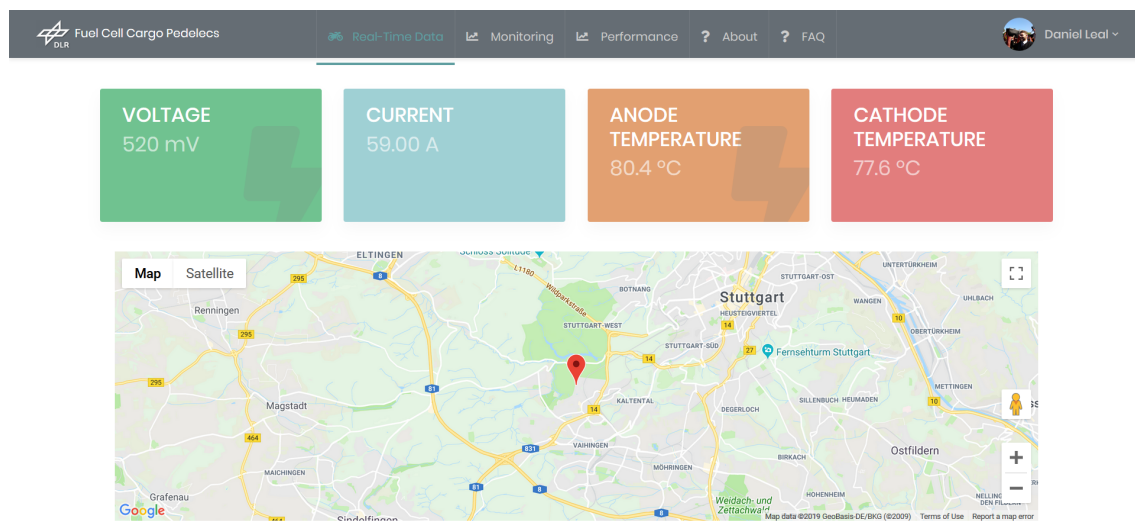


Figure 3.15: Overview of the fuel cell values on the web page

minutes and seconds. The right Y-Axis displays the voltage and the left one the temperature and current. This dynamic graph allows for the selection of three different time periods to display the information: 1 minute, 5 minutes or 10 minutes. It is possible to switch between them and the graph will instantly update the values. Aside from that, every 10 seconds a new set of values at the current time is entered into the graph without refreshing the web page.

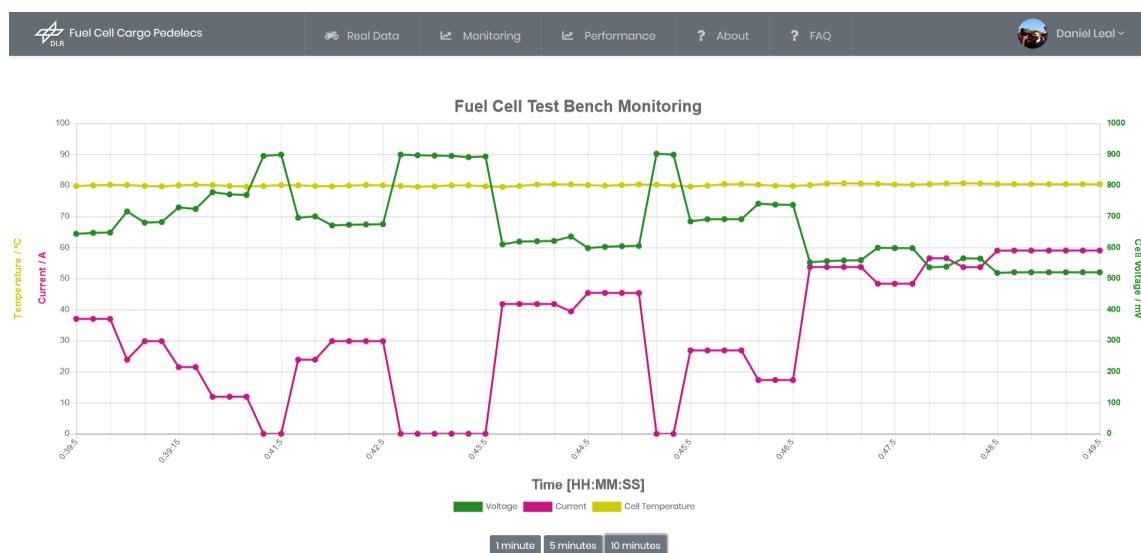


Figure 3.16: Fuel cell test bench monitoring page on the website

The "performance" web page seen in figure 3.17 shows the polarization curves of the FC-DLC and WLTP tests. There's two buttons to switch between the two polarization curves instantly. This page's intent is to showcase that the results can be easily incorporated into the website.

There are two other pages in the website which only have text and documentation. One of them briefly describes the project and the other one is a Frequently Asked Questions page.

The website has a mobile version too albeit with fewer features. Since the screen is smaller, the graphs did not scale properly, and thus the mobile version only shows the Real-Time Data, About and FAQ pages.

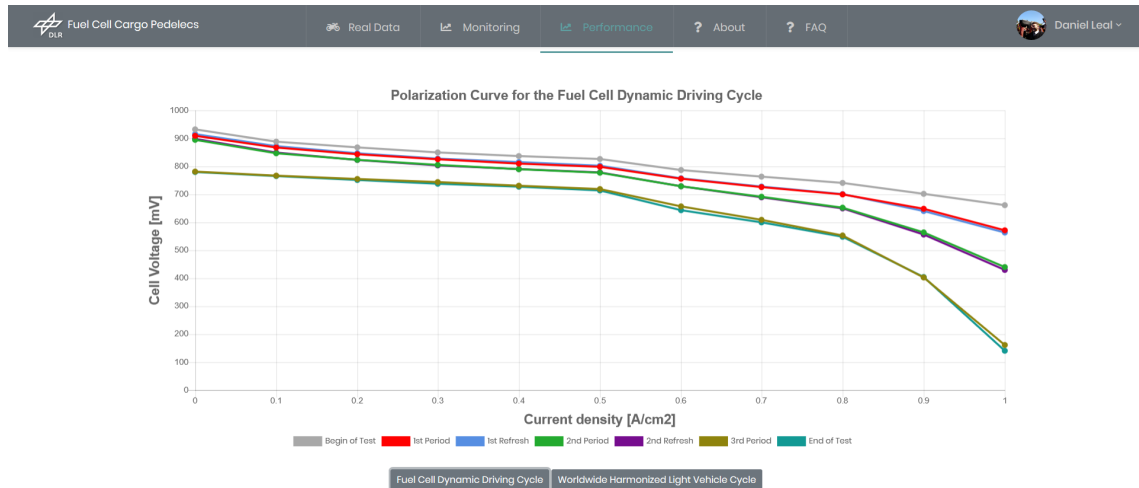


Figure 3.17: Polarization curves of the cycles performed shown in the website

Chapter 4

Analysis of results

This section is divided in 2 subsections. First an interpretation of the base tests is done to better understand how the new cell stacks up against the typical cell design used in the DLR. Then the driving cycles are analyzed by looking at the voltage response of the cell along time and the results obtained with the *ex situ* and *in situ* techniques.

4.1 Base tests

To evaluate some base characteristics of the cell, three different tests were performed before starting the dynamic load cycles in order to have a better grasp of how the new cell behaves and get to know all the different parameters that can be controlled.

4.1.1 Influence of the Relative Humidity

In figure 4.1 one can observe the cell voltage for the different relative humidity of the inlet gases for three different outlet pressures: 1.0 bar , 1.5 bar and 2.5 bar. The temperature of the gases for the different relative humidity, always considering the cell temperature of 80°C, are shown in table 4.1.

The difference in performance from 50% to 100% RH is the same or lower than from 40% to 50%, thus it is not viable to humidify the inlet gases up to 100% because just by decreasing the RH from 100% to 50% the power used for humidification reduces to about 40%. Hence, the reduction of the RH of the reactants plays an important role in increasing the fuel cell efficiency [46].

Decreasing the RH to 25% shows a mostly linear decrease in performance in all of the three pressures. The performance loss is around 30 mV when compared to 50% RH. Below 25% is where the problems start appearing with drastic voltage drops occurring at 1 bar and 1.5 bar, but more specifically at 1 bar. This drop in performance is caused by the low water content in the membrane, increasing the internal resistance and thus reducing the proton conductivity, which causes some areas of the MEA to be deactivated.

Without humidification means that neither the hydrogen nor the oxygen went through the bubblers. Instead, they went through an external pipe connected directly to the inlet of the cell. This process is called bypassing. At this point at 1 bar the cell was not holding up the voltage and was

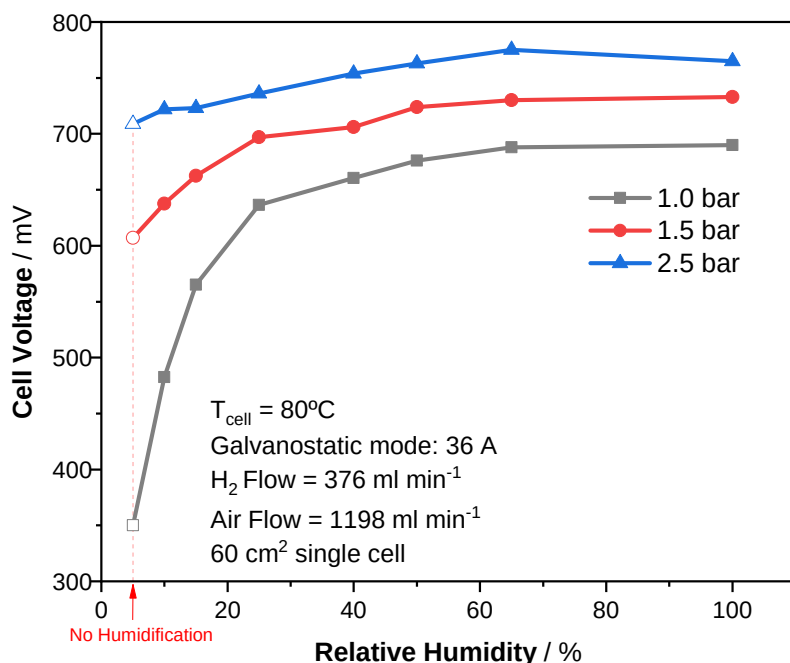


Figure 4.1: Influence of the relative humidity in the fuel cell performance

dropping it very fast. The value was captured prior to this happening but it was observed during the operation. The MEA gets too dehydrated for it to be able to have sufficient reactions to hold the performance.

The relative performance loss for the different inlet gases RH, when compared to the reference value of 100% RH, which means the inlet gases are at 80 °C, can be seen in 4.1.

Table 4.1: Relative performance loss for different input gases relative humidity ($T_{cell} = 80\text{ °C}$; reference RH = 100%)

Relative Humidity (%)	Gas Temperature (°C)	Performance Loss (%)		
		1 bar	1.5 bar	2.5 bar
No humidification	~23	49.3	17.2	7.4
10	32	30.1	13.0	5.6
15	39	18.1	9.6	5.5
25	49	7.8	4.9	3.8
40	59	4.3	3.7	1.4
50	64	2.0	1.2	0.3
65	69	0.3	0.4	-1.3

4.1.2 Effect of back pressure on fuel cell performance

Figure 4.2 shows the polarization curves with the filled dots and the power output curves with the dashed open dots. It is clear that an increase in the pressure raises the performance of the cell.

By increasing the pressure, gas concentration on both sides rises since the volume remains the same. This means there's more collisions between particles on the electrode's surface, therefore accelerating the kinetics of the fuel cell reactions, leading to an improvement in performance [47]. It is easily observed by looking at the power output curves that the performance gap between the different pressures gets bigger as the current increases.

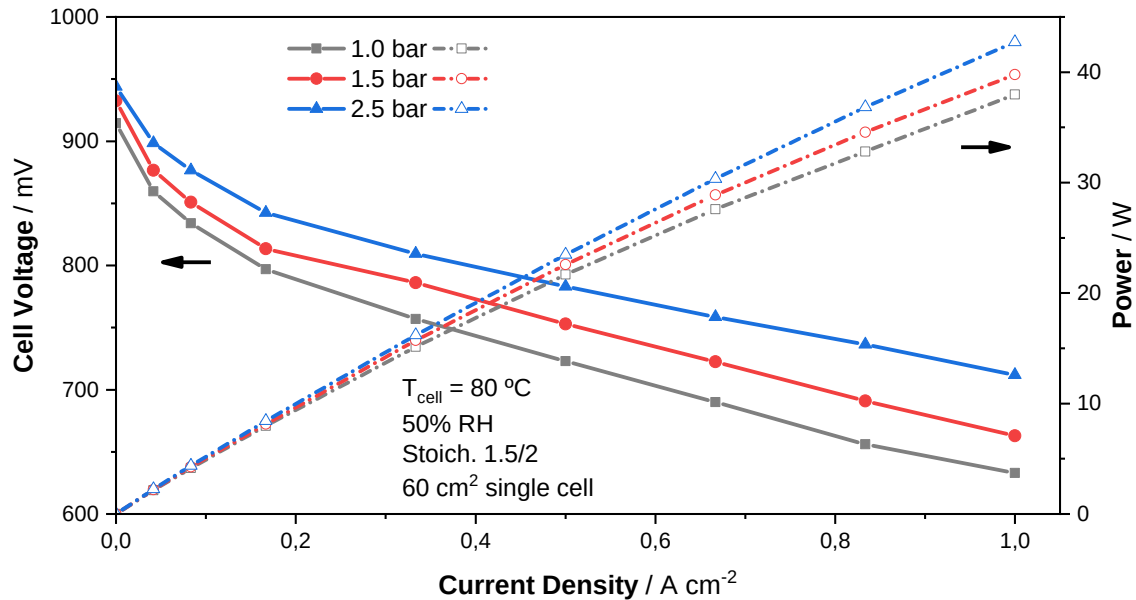


Figure 4.2: Polarization and power output curves for different pressures

As represented in table 4.2, the performance gains are higher for 2.5 bar than 1.5 bar when compared to the reference value of 1.0 bar. At 1.5 bar the maximum performance increase is around 5%, whereas for 2.5 bar it is around 12 %. As it was already noticeable by the power output curves, the performance gains are greater at higher currents due to the improvement of the mass transportation process. A boost in the reaction rate will be more noticeable at the higher currents due to the urgency of more fuel to fulfill the power requirements.

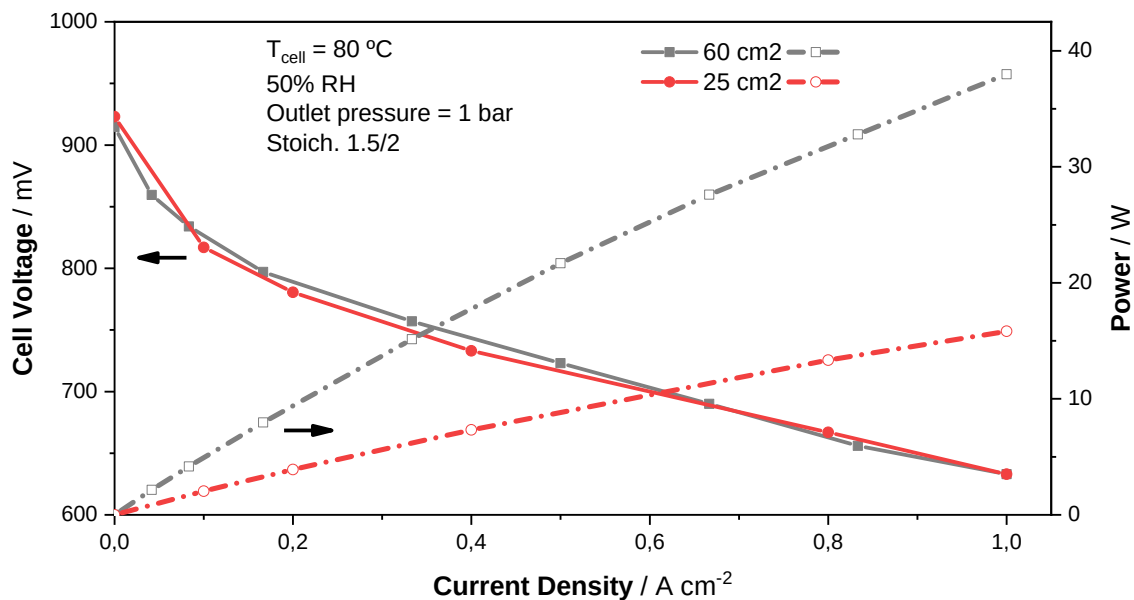
4.1.3 Performance comparison to the 25 cm² cell

In order to identify whether the newly built cell for the cargo pedelec project follows the typical performance of a cell developed at the DLR, a 25 cm² cell was assembled and conditioned using the same protocol described in 3.2. The smaller cell has a ceiling gasket on both sides unlike the new one which has just the one in the cathode side due to contact issues. Figure 4.3 shows the polarization curves and the power output of both cells on the conditions previously described. It is undeniable that the polarization curve of both cells is really similar, even overlapping at certain points. This confirms that the performance obtained from the new cell is on par with the state of the art fuel cell performance.

Table 4.2: Relative performance gain for different outlet pressures ($T_{cell} = 80\text{ }^{\circ}\text{C}$; $P_{ref} = 1\text{ bar}$)

Current Density (A cm^{-2})	Performance gain (%)	
	1.5 bar	2.5 bar
0	1.97	3.23
0.04	1.98	4.54
0.08	2.04	5.10
0.17	2.07	5.71
0.33	3.83	6.94
0.50	4.15	8.30
0.67	4.71	9.93
0.83	5.34	12.27
1.00	4.74	12.48

However, as expected, the power output is not the same for both cells since they have different active areas. At 1 A cm^{-2} the bigger cell has an electrical power of around 38 W as opposed to the smaller one which has an electrical power of 16 W. Therefore, the 60 cm^2 cell generates around 2.4 times more electrical energy than the 25 cm^2 cell, which is exactly the difference in active area between both cells.

Figure 4.3: Performance comparison of the 25 cm^2 cell to the new 60 cm^2 cell

4.2 Durability tests

In order to investigate the effect of dynamic driving cycles on the new cell performance, the FC-DLC cycle described in 3.4.1 and the WLTP cycle described in 3.4.2 were applied to the fuel cell test bench station. Bear in mind that the FC-DLC was performed a second time, the reason being that after collecting the results of the complete test there was a "strange" phenomenon involving the refresh periods, and as a way of isolating the issue the FC-DLC was tested again but this time only for one period, as opposed to the traditional three periods, with an outlet pressure of 2.5 bar instead of the normal 1.0 bar.

For future reference and to avoid any confusion, the Fuel cell dynamic load cycle (FC-DLC) that ran for three periods was tested with an outlet pressure of 1.0 bar, and from now on will be simply referred as FC-DLC, the same for the WLTP cycle (same conditions). The second FC-DLC test, that only ran for one period was tested with an outlet pressure of 2.5 bar, and will be referred as FC-DLC 2.5 bar.

The tests were performed at constant flow rates of 627 ml min^{-1} for hydrogen and 1996 ml min^{-1} for air, corresponding to respective stoichiometry ratios of 1.5 and 2 at the maximum current density used in the tests, which was 1 A cm^{-2} . It is worth noting that these tests are actually considered Accelerated Stress Tests (AST) due to the load cycling as well as humidity cycling which are stressing for the membrane, leading to high levels of degradation. Sometimes excessive drying of the MEA can happen too due to the water removal by the high gas flows.

The load profile of two subsequent cycles of the FC-DLC protocol, each one lasting 20 minutes, along with the cell voltage recorded every 10 seconds in the test bench is provided in figure 4.4. The white dots represent each voltage value recorded by the Siemens PLC installed in the test bench and the red steps the current density profile applied to the cell with the external load.

Whenever there are big leaps in the current the voltage takes some time to stabilize due to the changes happening in a very short time.

For the WLTP driving cycle, the two subsequent cycles, each one lasting around 16 minutes and 40 seconds, are reproduced in figure 4.5. It is easily recognizable that this load cycle is much more dynamic than the FC-DLC and has a higher average current too. Another difference is the stops being simulated as OCV (no current) as opposed to the strategy of having a small current to not expose the fuel cell to prolonged OCV state.

The full durability tests consist of three periods of 117 h (almost five days) each. Each period covers a continuous sequence of the FC-DLC or WLTP followed by a refresh procedure with the intention of recovering some of the performance lost during operation and to allow the distinction between reversible and irreversible losses. At the Beginning of Test and after each refresh, a full electrochemical characterization as described in section 3.5 is performed. Plus, before each refresh a polarization curve is recorded to determine the irreversible voltage losses.

The test bench parameters during the refresh procedure done after each period of operation is detailed in figure 4.6. After stopping the driving load cycle, the cell is operated in a steady-state condition (potentiostatic mode set for 700 mV) with minimum flow rate to avoid any impact from

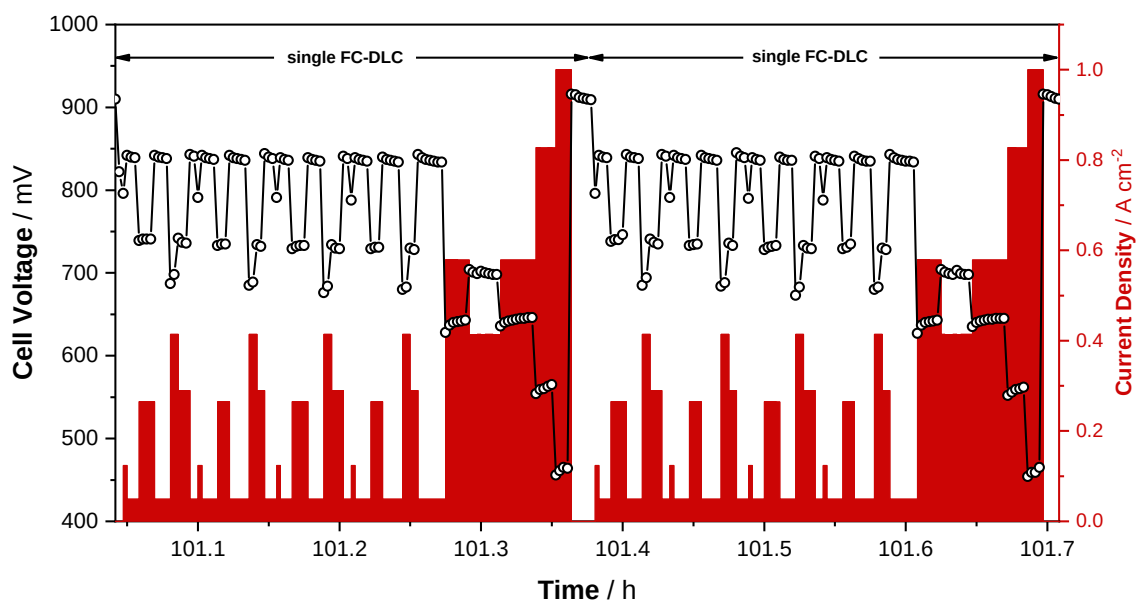


Figure 4.4: Load profile of two subsequent Fuel Cell Dynamic Load Cycles (FC-DLC)

the higher flow rates in the performance characterization considering that the polarization curves are measured with constant stoichiometry, instead of constant flow, for all the current test points. The gas flow peaks around the 246 hour mark by the time the polarization curve is recorded (time mark for the second refresh). Afterwards, both sides of the cell are flushed with nitrogen for approximately five minutes to remove the water which accumulated in the electrodes and to push the remaining fuel out of the cell to avoid the hydrogen/air boundary that can cause damage to the membrane during shutdown. Then the external load is switched off, the gas supply is stopped, the cell outlet valves are open to let air diffuse into the cell and at the same time bringing it to ambient pressure, and the heaters are stopped letting the cell cool down to room temperature. Notice the temperature of the bubblers never reaches room temperature.

After around 10h the heaters for both cell and humidifiers are turned back on and when they reach the target temperature, the cell is once again operated in a steady state condition to stabilize the performance before doing the full electrochemical characterization.

The complete voltage profile over time of the FC-DLC test performed for 351h, plus the shutdowns, is represented in figure 4.7. Each period covers 351 cycles of continuous FC-DLC operation. Keep in mind that every voltage value is recorded every 10 seconds, meaning that there are thousands of points in the picture, and, as a result, the voltage values at different loads form a curve over time. Each curve represents a current density set-point that is indicated in the right side of the figure. In this cycle there were nine current set-points, but only eight of them are represented in the right side due to two of them being too close in value and nearly forming a line together.

During the second refresh, while doing the full electrochemical characterization, a strange phenomenon occurred in the cell. After performing the Cyclic Voltammetry the open circuit voltage decreased around 100 mV, which is not normal behaviour. The fuel crossover could have increased

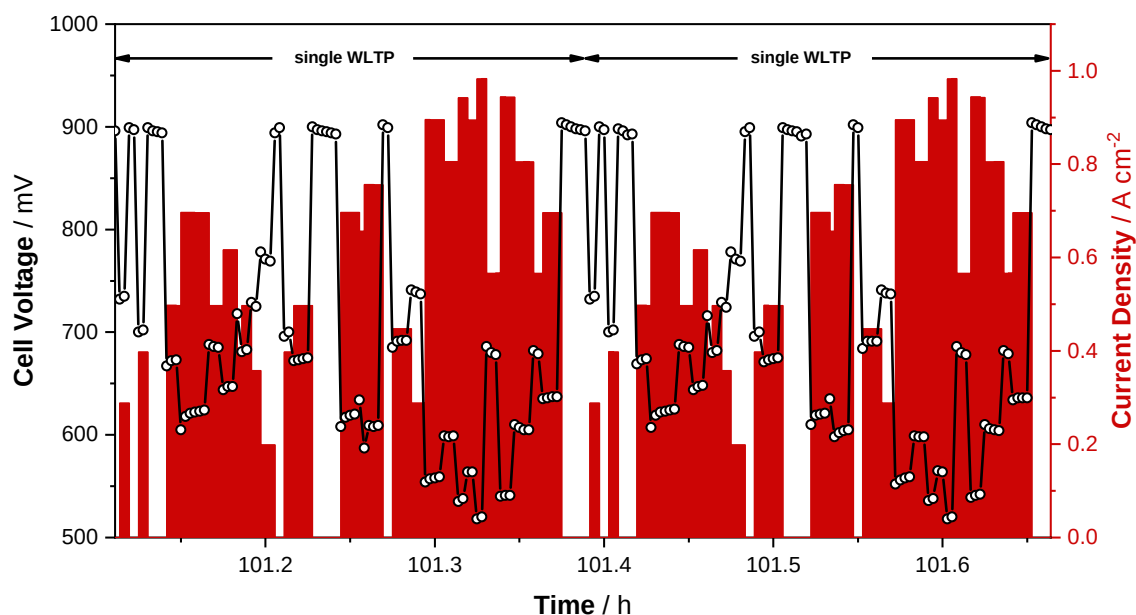


Figure 4.5: Load profile of two subsequent Worldwide Harmonized Light Vehicle Test Procedure (WLTP)

for some reason, but that's the opposite of what typically happens after a CV, therefore there's no exact explanation for what happened.

The voltage decreases rapidly at 1 A cm^{-2} and 0.83 A cm^{-2} when compared to low current densities. As the current density decreases, the performance losses decrease too. This happens because of the mass transfer limitations at high current density. As the cell gets more and more degraded, it becomes harder to generate high amounts of power, hence the performances losses becoming more accentuated at high current densities. It is possible to see that the voltage loss at 1 A cm^{-2} was really hefty, more than 400 mV of decrease in voltage, much higher than expected and probably due to the humidity cycling.

Apparently, the voltage decay becomes faster from one period to the next one. From period 1 to period 2 there's a noticeable increase in the curve slope, meaning that the decay becomes bigger, which will be analyzed later when the polarization curves are discussed.

For the WLTP, the complete voltage profile over time is shown in figure 4.8. Each period covers 421 cycles of continuous WLTP operation. Similar to the FC-DLC, the points create a curve representing a specific current density. Considering that this cycle has more load test points it is harder to distinguish some of the curves because a few of them have a tendency to overlap. Nonetheless, 9 out of the 16 current density points are marked in the right side of the graph.

It is clearly evident that the voltage decay at high current densities was lower when compared to the FC-DLC. The voltage decrease at 1 A cm^{-2} was around 300 mV, which is substantially lower than in the other test. This probably has to do with the humidity cycle not being as severe in the WLTP compared to the FC-DLC, since most of cycle is not done with low load values, thus not having as many excessive ratios of gases that contribute to humidity cycling by drying off the

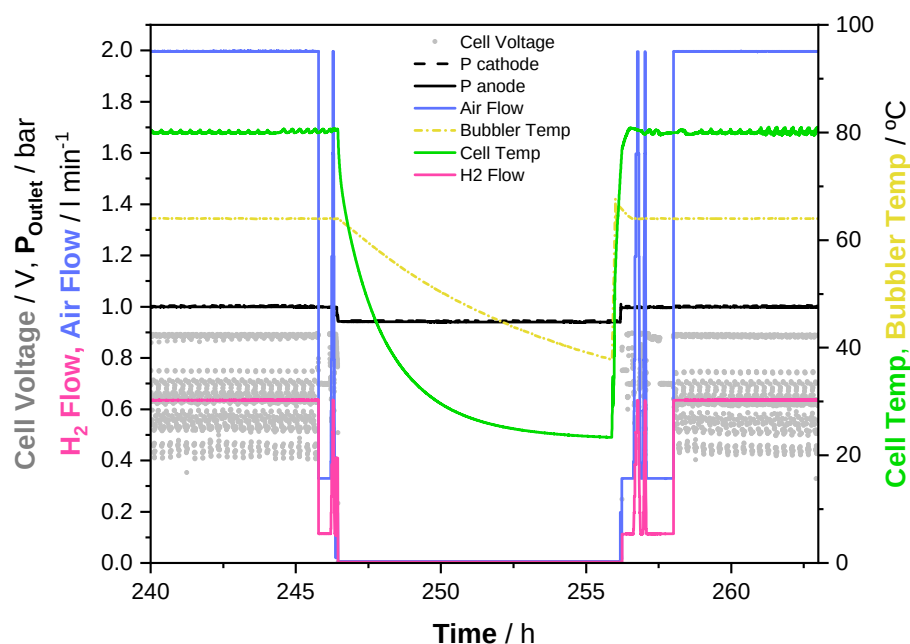


Figure 4.6: Test bench parameters during the refresh procedure

MEA in these low load periods. Looking at the 0.62 A cm^{-2} current density curve it is possible to recognize that the voltage decay becomes faster from period 2 to period 3, which is in agreement with studies conducted at the DLR.

The points seen between the OCV curve and 0.20 A cm^{-2} current density curve are points that were captured in the middle of a change between a load point and open circuit. It is interesting that the values captured in the middle of change seem mostly periodic.

For the third test, the FC-DLC 2.5 bar that was performed only for one week with an outlet pressure of 2.5 bar, instead of the usual 1.0 bar, the voltage profile is displayed in figure 4.9. This durability test was performed to assess the impact of the outlet pressure on the performance in a load cycling test.

Compared to the FC-DLC Period 1, there's a large difference in the voltage decay, especially at high current densities. At 1 A cm^{-2} the voltage decrease is around 50 mV, while in the FC-DLC Period 1 it was more than 100 mV. The same happens for the other current densities, however it is always more noticeable at higher current densities due to the mass transport limitations.

The outlet pressure increases the water content in the membrane (due to the higher concentration of gases), thus not allowing the membrane to dry as much as at 1.0 bar, reducing the effect of the humidity cycling and resulting in less degradation.

4.2.1 Polarization Curves

The polarization curves were measured at the beginning (i.e. after refresh) and end of each period. The label 1st period means that the polarization curves was measured at the end of the first period, and 1st refresh means that it was measured after the first refresh (beginning of second period). The

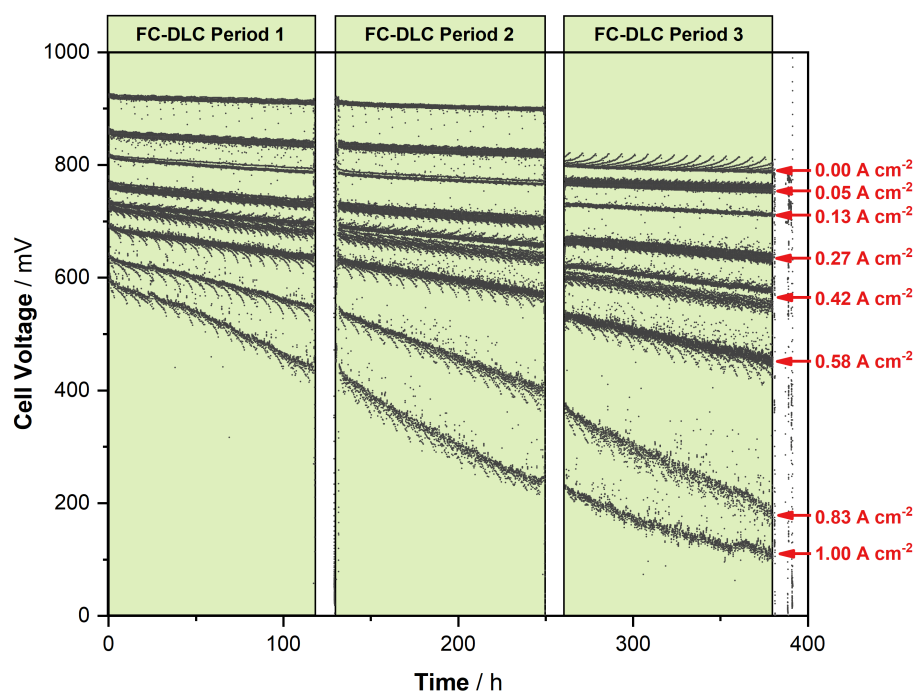


Figure 4.7: A complete fuel cell dynamic load cycle performed for 351h

same applies to the other labels. The polarization curves recorded during the durability tests are shown in figures 4.10, 4.11, and 4.12 .

Looking at the activation region (current densities below 0.2 A cm^{-2}) of the three tests, it is noticeable that for all of them the voltage losses are low, which means that degradation is small at low current densities. Note that the 3rd period and end of test (EoT) curves in FC-DLC test were affected by the previously described issue, leading to an accentuated degradation, but if the curves were to be shifted up according to the losses caused by the electrochemical characterization in the 2nd refresh, they would follow the trend of the remaining curves, which is small degradation in this area.

In the current density range from 0.2 to 0.8 A cm^{-2} , FC-DLC shows an higher decrease in performance after each period of operation compared to the WLTP. For current densities higher than 0.6 A cm^{-2} there's an hefty drop in performance in FC-DLC 3rd period, indicating that the cell is heavily degraded after 351h of operation. WLTP performance is more stable in this current range but still exhibits a higher decrease from 2nd to 3rd period.

Undoubtedly, the FC-DLC 2.5 bar has a lower decline in performance after one period of operation confirming that the outlet pressure plays a significant role in the degradation process. The higher water content by virtue of the increased pressure improves the humidity along the cell thus leading to lower degradation.

When it comes to the higher current density (1 A cm^{-2}), FC-DLC cannot reach that target after performing the complete durability test. The catalyst layer may be degraded affecting the kinetics of the reactions, thus reducing the output power of the cell. Even though the WLTP test can reach

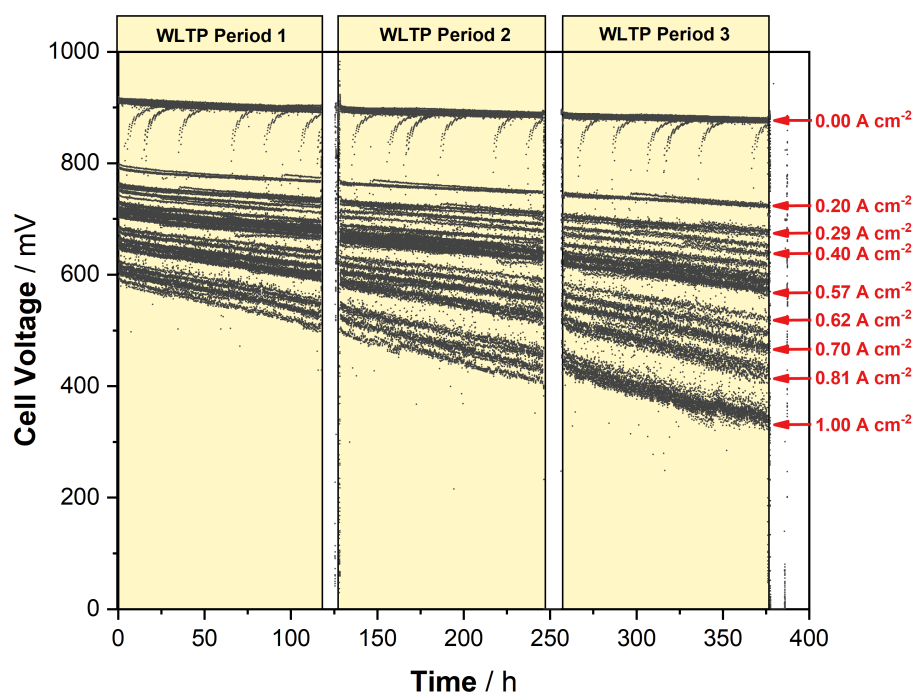


Figure 4.8: A complete worldwide harmonized light vehicle test procedure performed for 351h

this target, it is clear that the voltage losses increase at this point, mainly due to mass transportation issues.

The goal of the refresh is to recover part of the voltage losses occurring upon continuous operation, however, for the FC-DLC that was not the case. Rather than improving after the refresh, the performance either remained the same or got worse, as can be seen in figure 4.10. The curves referring to each period (recorded at the end of the 117h of continuous testing) have better performance than the ones referring to the refresh (recorded after the refresh procedure). That was the main reason why a second FC-DLC at 2.5 bar was performed, to find out if at higher pressures the refresh would have the expected behaviour, something which was verified, as it is possible to observe in curves 1st refresh and 1st period in figure 4.12. On the other hand, in the WLTP test the refresh already had some positive impact. This will be discussed further in the next subsection.

4.2.1.1 Reversible and Irreversible losses

As described in section 3.5.1, the overall voltage losses can be separated into two components by using the polarization curves. Table 4.3 shows the reversible and irreversible voltage losses of the three load cycles tests performed for different current densities. Each load cycle is then divided into its respective periods of testing. Note that in some of the reversible losses the values displayed are negative, which means that cell performance did not improve with the refresh procedure and instead it got worse.

The majority of the performance for the FC-DLC test got worse after the refresh, except in the 1st and 2nd period for low current densities. All the other current points got worse which was not

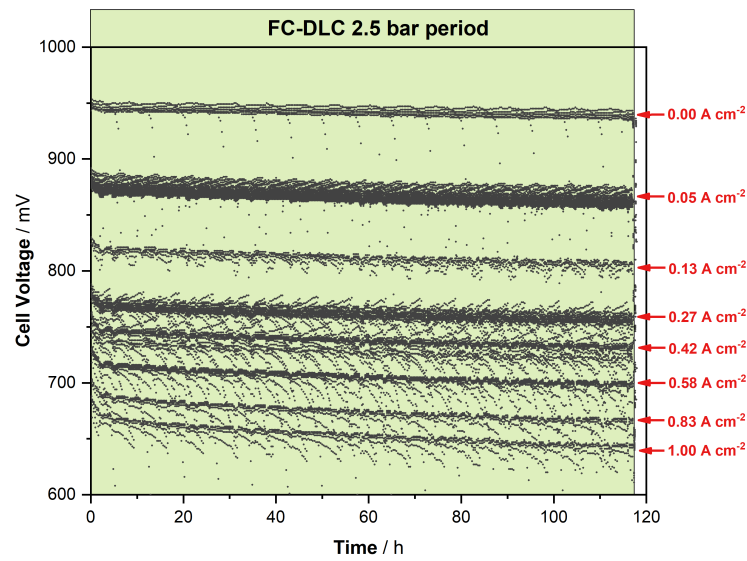


Figure 4.9: Fuel cell dynamic load cycle performed for 117h at 2.5 bar

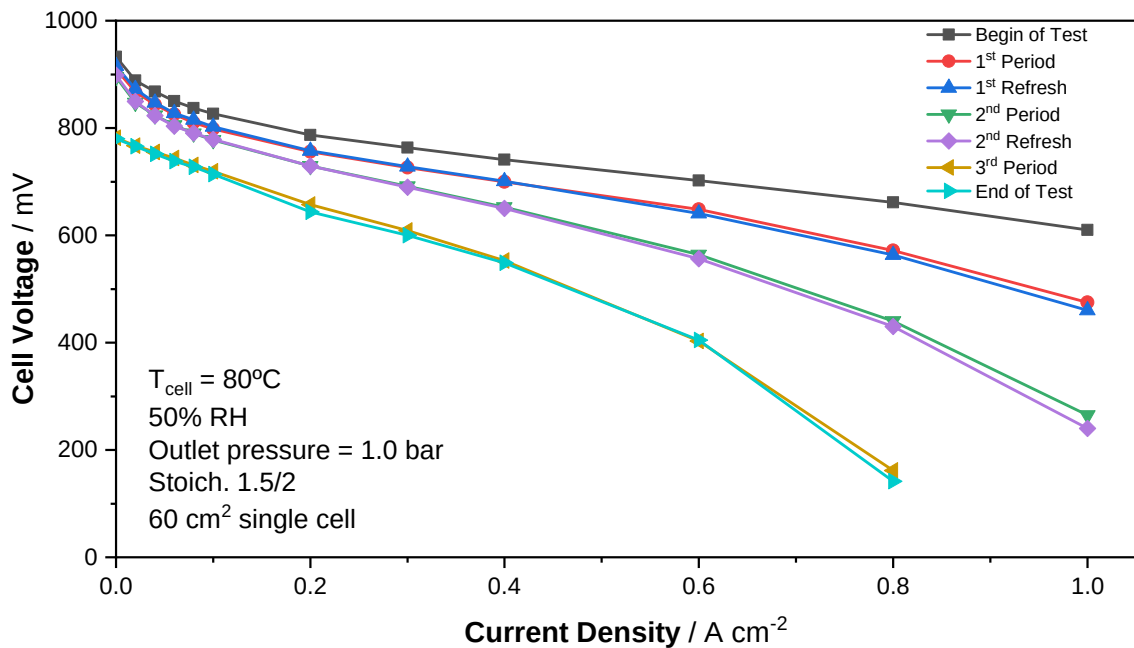


Figure 4.10: Polarization Curves for Fuel Cell Dynamic Load Cycle test (FC-DLC)

expected. During continuous operation, due to the humidity cycling, the membrane is subjected to high mechanical stress as a result of the swelling and shrinking caused by the water content changes in the membrane. The refresh procedure, by stopping the gas flow and reducing the cell temperature to room temperature, has the intention of reducing the mechanical stress applied to the membrane. However, if the cell already had a pinhole or micro cracks as a result of the humidity cycling, the drying process during the shutdown could have enlarged the micro cracks and increased the gas

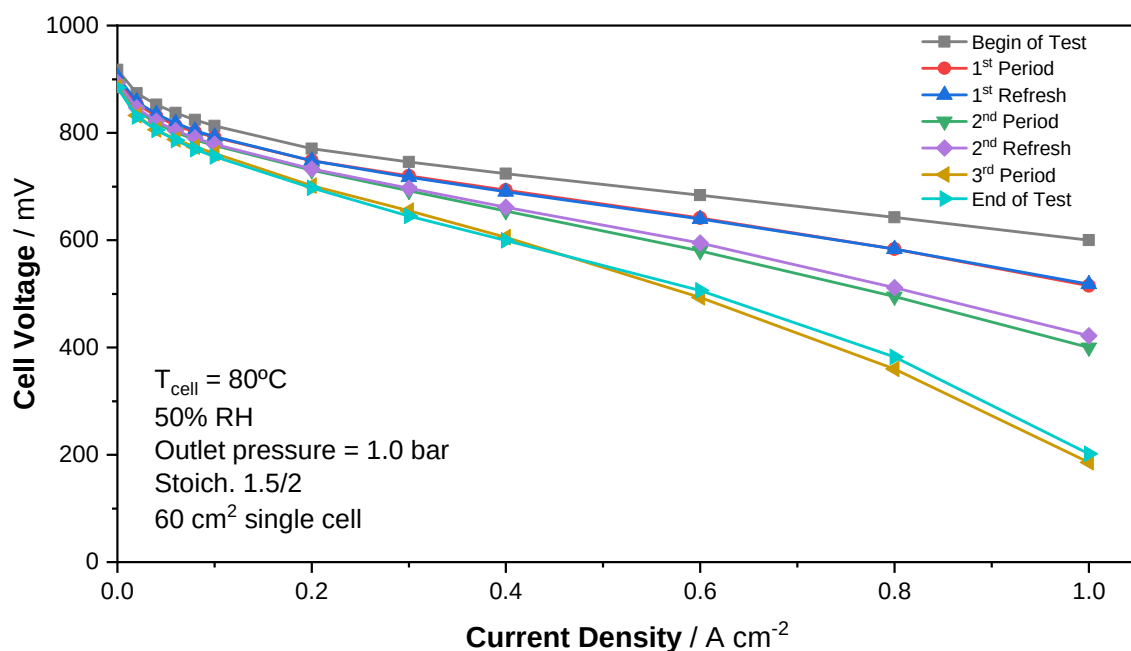


Figure 4.11: Polarization Curves for Worldwide Harmonized Light Vehicle Test Procedure (WLTP)

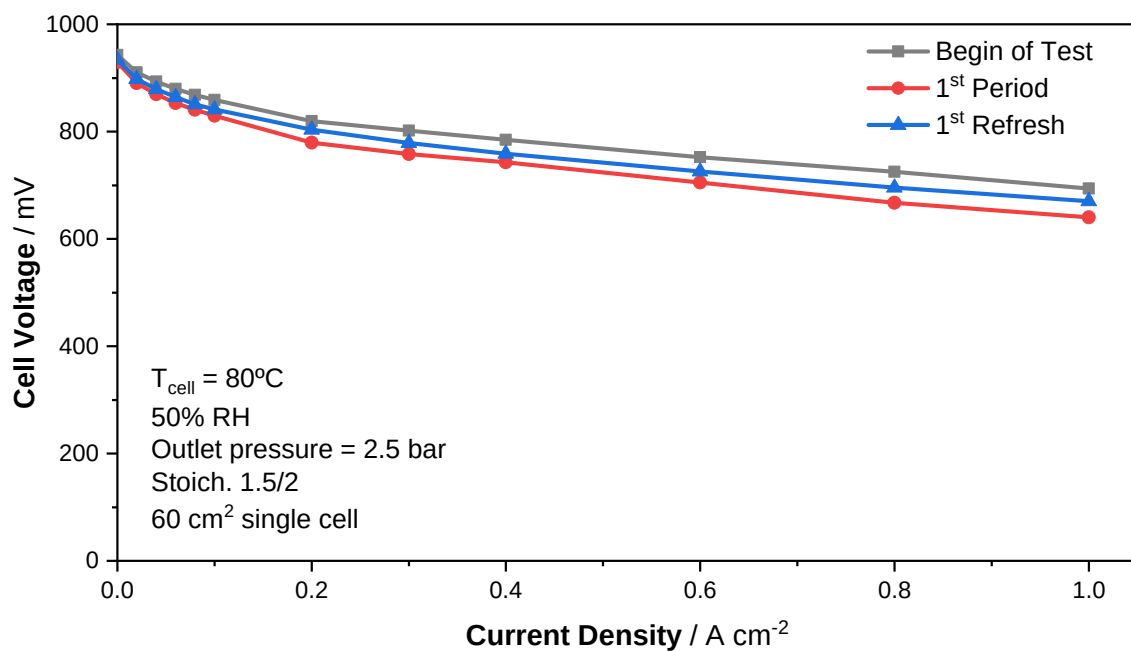


Figure 4.12: Polarization Curves for Fuel Cell Dynamic Load Cycle 2.5 bar (FC-DLC 2.5 bar)

crossover. In fact, the increase in gas crossover was noticeable in the CV measurements that will be presented later.

FC-DLC 2.5 bar presents considerable reversible losses, primarily at current densities of 0.8 A cm⁻² and 1.0 A cm⁻², reaching 40 mV recovered. The higher outlet pressure, which increases

water content in the membrane, combined with the increase in water production at high current densities causes flooding inside the cell. Water accumulates in the electrodes and GDL partially blocking the transport of the reactants causing mass transport losses. These losses are mostly recoverable during the refresh procedure by pushing the water out of the cell when the gas flows are stopped.

The WLTP test exhibits some recoverable losses (maximum of 23 mV), but it falls short when taking into account the irreversible losses, which are much higher especially at high current densities. During OCV operation (this cycle has a significant OCV exposure) there's platinum oxide formation on the electrode's surface that decreases the catalyst activity of the oxygen oxidation reaction. To recover this effect a cathode potential below 0.65 V is needed to reduce the platinum oxide. During the shutdown, when the cell is flushed with nitrogen, the cathode potential goes way below that, thus reducing the platinum oxide and contributing for most of the recoverable losses obtained [34].

Looking at the irreversible losses part of the table, it is clear that the FC-DLC performed worse than the WLTP, as already stated earlier. At 0.8 A cm^{-2} the total irreversible losses for the FC-DLC are around 520 mV, while in the WLTP they are only about 260 mV. There's a hefty gap between the two at high current densities. Just as a reminder, the values shown for the FC-DLC low current densities in the 3rd period are taking into account the issue that happened during the 2nd refresh.

Table 4.3: Reversible and irreversible voltage losses of the different tests

	Current Density (A cm^{-2})	FC - DLC			FC-DLC 2.5 bar		WLTP	
		1 st P.	2 nd P.	3 rd P.	1 st Period	1 st P.	2 nd P.	3 rd P.
Reversible Losses (mV)	0	6	4	-2	5	7	2	-1
	0.1	4	1	-5	12	2	2	-6
	0.6	-8	-8	2	21	-2	15	13
	0.8	-8	-10	-20	28	0	17	23
	1	-15	-25	-	40	3	22	16
Irreversible Losses (mV)	0	17	17	119	9	13	12	9
	0.1	24	24	65	18	20	15	23
	0.6	62	84	152	27	44	45	89
	0.8	98	134	289	30	59	72	129
	1	150	220	-	14	82	96	220

To understand how the irreversible voltage decay rate increases with the current density from one period to another, linear regressions of the voltage values obtained from the polarization curves from the beginning of one period to the beginning of the next one were made. The slope of the linear regressions represents the irreversible voltage decay rate for the different periods of the FC-DLC and WLTP tests and the result is shown in figure 4.13.

For the WLTP test, the voltage decay had a small increase from the first period to the second. For all the different loads, the voltage decay in the first two periods is comprehended between 0.1 and 0.8 mV h^{-1} . On the other hand, the FC-DLC shows a bigger increase from the first period to the second, particularly at 1 A cm^{-2} , that had a voltage decay of 1.88 mV h^{-1} in the 2nd period. The same voltage decay was registered in the 3rd period of the WLTP, which shows that the fuel cell degraded much sooner in the FC-DLC test. In fact, for current densities of 0, 0.1, 0.8 and 1 A cm^{-2} , the 2nd period of the WLTP shows the same or smaller voltage decays than the 3rd period of the FC-DLC.

In the FC-DLC 3rd period, the current density of 0.8 A cm^{-2} exhibits a substantial increase in the voltage decay (2.46 mV h^{-1}) related to the failure of the MEA. This is further proved by the cell's inability to reach the 1 A cm^{-2} target.

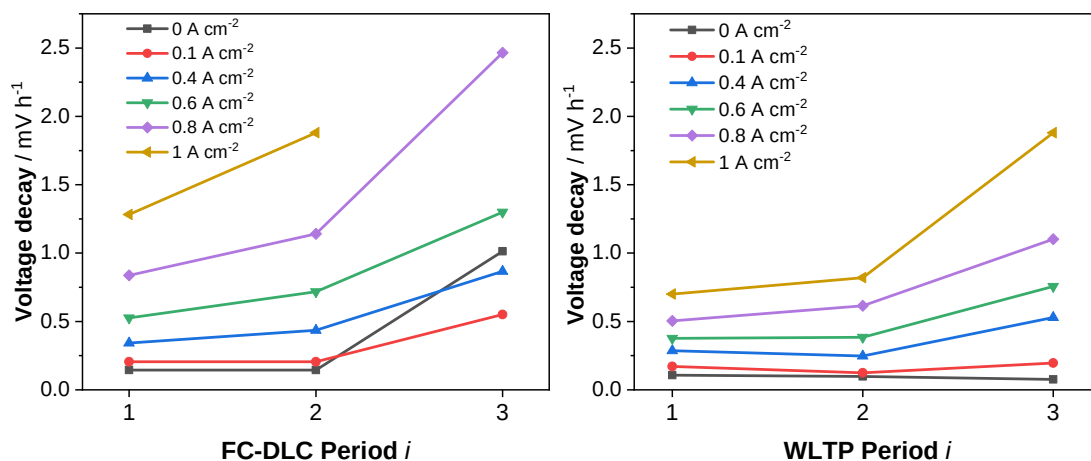


Figure 4.13: Irreversible voltage decay rate of the individual periods analyzed for different current densities of the FC-DLC test (left) and WLTP test (right)

4.2.2 Electrochemical Impedance Spectroscopy

As described in section 3.5.3, electrochemical impedance spectroscopy measurements were performed after each refresh of the cell to evaluate the impedance changes. The tests were performed at 0.05 A cm^{-2} and 0.6 A cm^{-2} . Due to problems with the station used for the EIS and CV measurements, it was not possible to perform electrochemical characterization for the WLTP test after the 1st refresh. The test bench used during the tests damaged the potentiostat of the Zahner station due to an overvoltage. The Nyquist plots of the EIS measurements performed at 0.05 A cm^{-2} are illustrated in figure 4.14.

The impedance increases after every period of testing, but there are no big differences between the tests at BoT and 1st refresh. The important thing to look at in these plots is the impedance change from one period to another, using the Beginning of Test (BoT) as a reference. Plots of different current densities should not be compared directly.

The real part of the high frequency arc represents the ohmic resistance, which includes the membrane resistance plus the GDL, bipolar plates and contact resistances [48]. Looking at that part there's a very small increase after every period of operation for all tests. This could be a result from a non-uniform contact that becomes more pronounced over time. For the FC-DLC, there's an increase of $1.35 \text{ m}\Omega$ from the beginning of test to the end of test regarding the ohmic resistance.

The total resistance of the cell is given by the real part of the low frequency arc. From the 1st to 2nd refresh, FC-DLC shows an increase of around $4 \text{ m}\Omega$. It is not a major increase as expected, since the resistance changes in this zone represent the mass transport losses, and at this current density those problems are not noticeable.

For a better perspective on the resistance changes, figure 4.16 shows a column plot with both ohmic and total resistance of the cell for the different tests.

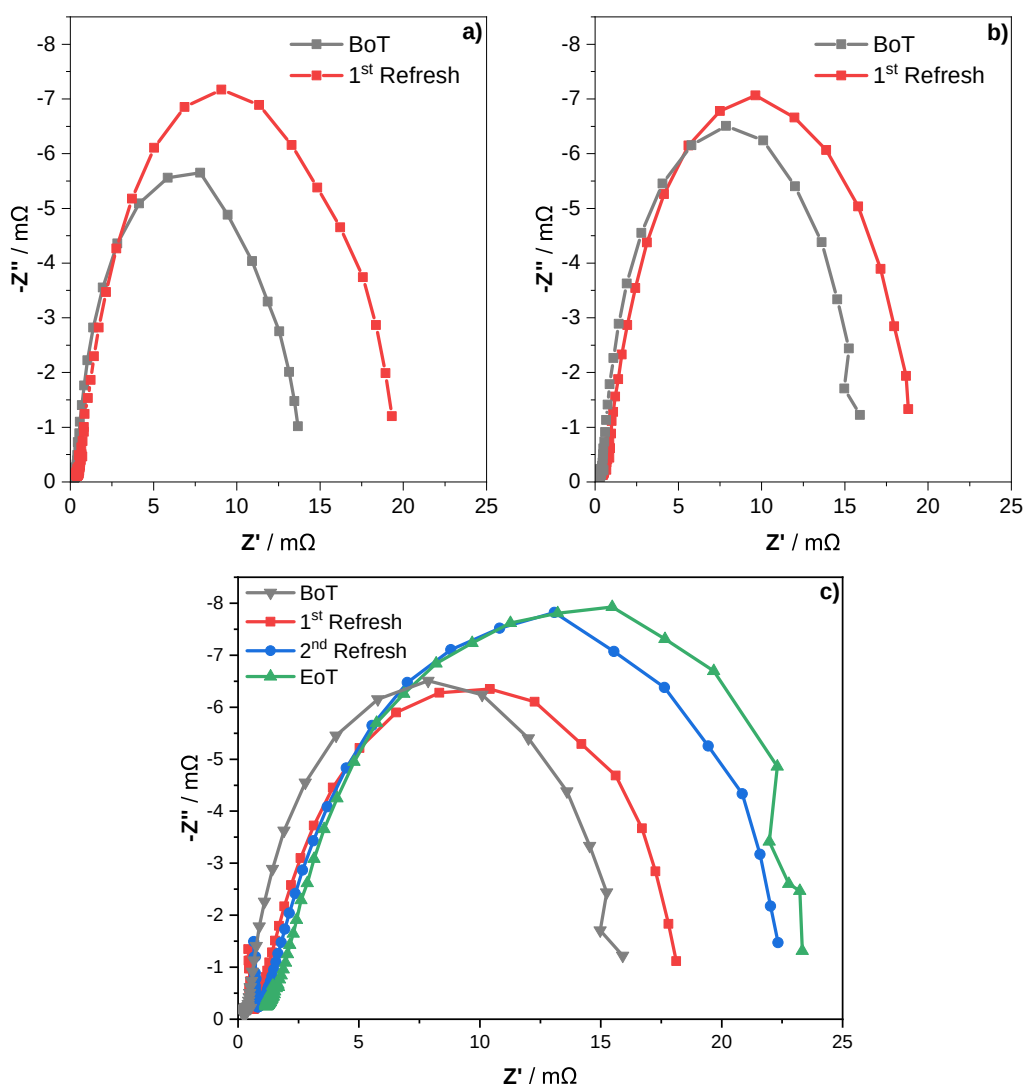


Figure 4.14: Nyquist plot at 0.05 A cm^{-2} for FC-DLC 2.5 bar (a), WLTP (b) and FC-DLC (c)

The Nyquist plots of the EIS measurements performed at 0.6 A cm^{-2} are shown in figure 4.15. There's a considerable increase in the total resistance of the FC-DLC test at EoT (increase of $26 \text{ m}\Omega$

when compared to the BoT total resistance). This shows that there are major transporting losses at the end of the test mainly due to the increase of the charge transfer resistance within the catalyst layer. This was already proved by the massive increase in irreversible losses reported at high current densities in the FC-DLC EoT. The diameter of the Nyquist plot has a significant increase too at the EoT, which can be related to the electrochemical surface area (ECSA) decrease reported in the CV measurements that will be discussed in the next subsection. The highest impedance point of the imaginary part is correlated to the double layer capacitance, and an increase generally has a negative impact in the ECSA.

WLTP shows an increase in the total resistance from BoT to 1st refresh (but smaller than the FC-DLC) while the FC-DLC 2.5 bar remains mostly the same, which goes in line with the small irreversible losses reported in that test.

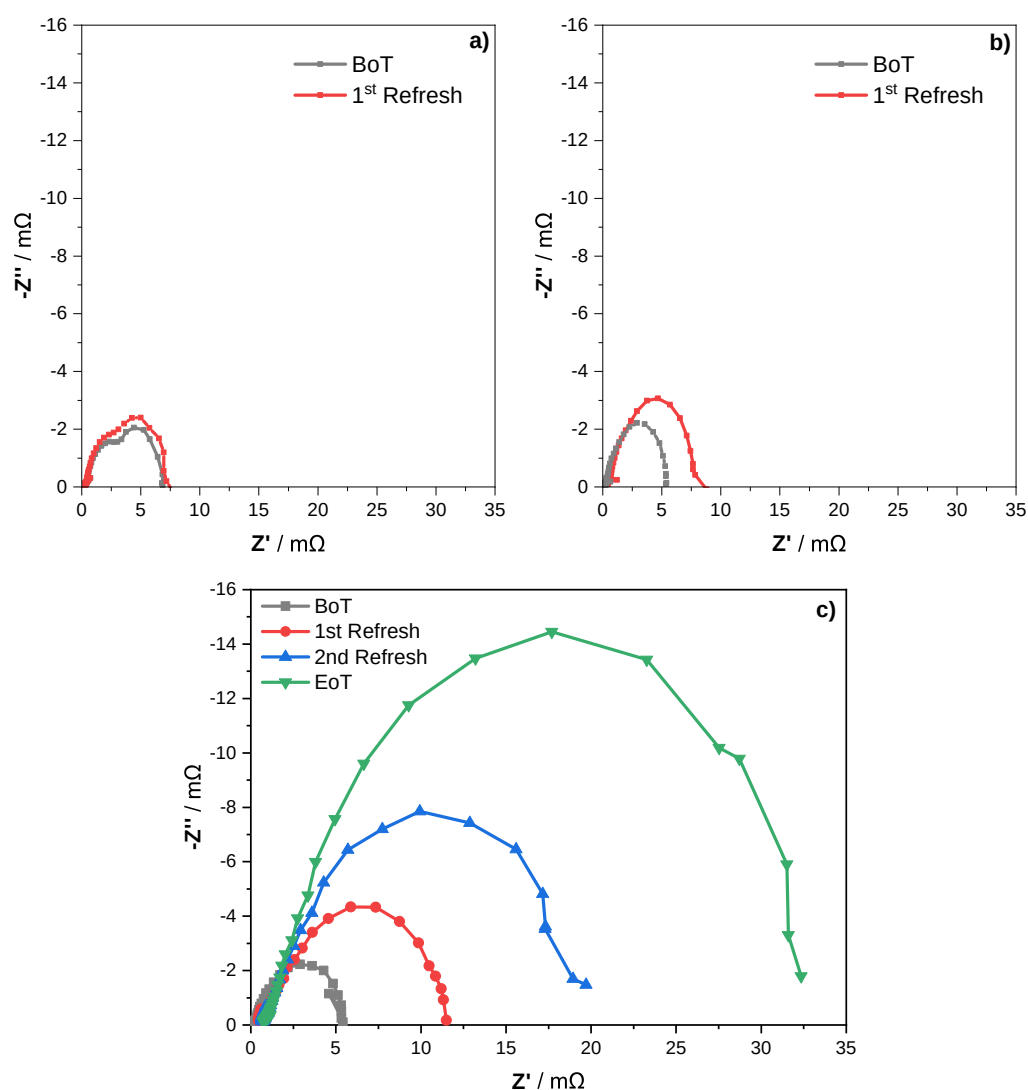


Figure 4.15: Nyquist plot at 1 A cm^{-2} for FC-DLC 2.5 bar (a), WLTP (b) and FC-DLC (c)

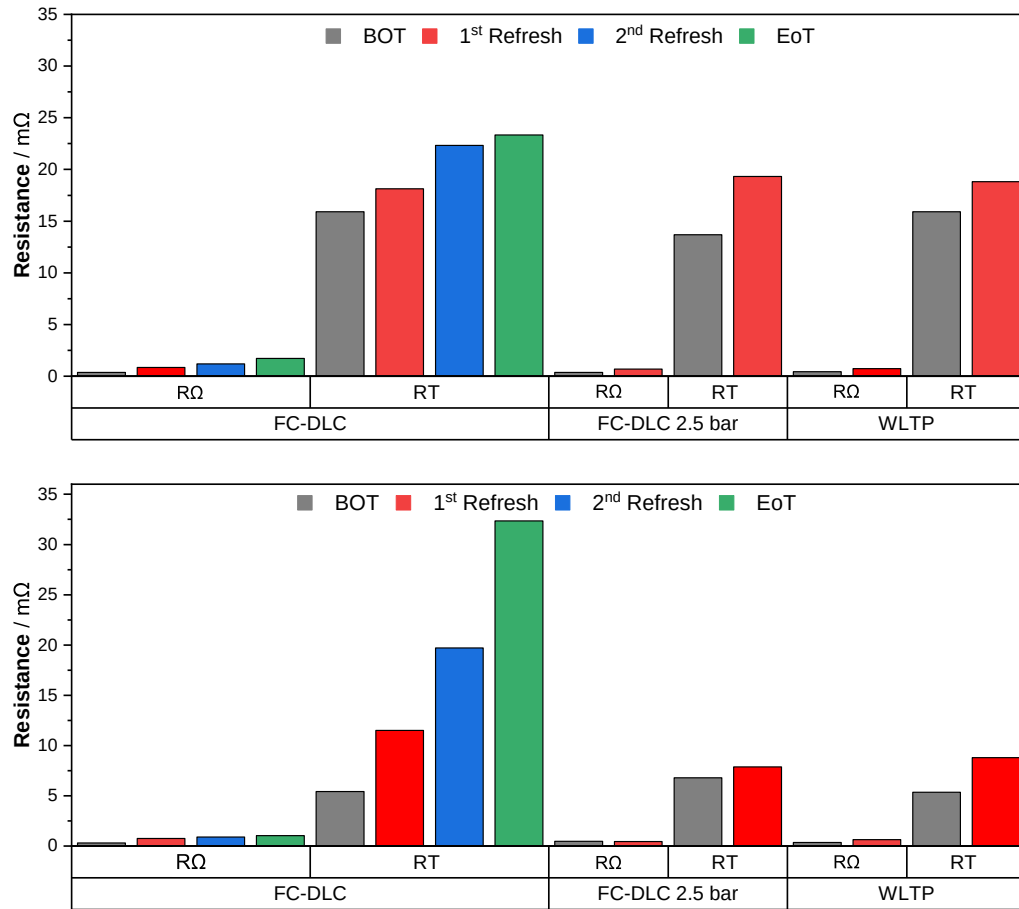


Figure 4.16: Ohmic Resistance ($R\Omega$) and Total resistance (RT) of the cell at 0.05 A cm^{-2} (top) and 1 A cm^{-2} (bottom)

4.2.3 Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were performed in the conditions described in 3.5.2. Figure 4.17 shows the CVs for the three load cycles. Once again, the WLTP characterization was stopped after the 1st refresh due to problems with the equipment.

The center part of the plot (the flattest one) is associated with the double layer capacitance. If this zone shifts up a bit, it means that there's an increase in fuel crossover. In the FC-DLC 2.5 bar test there was a slight shift in the 1st refresh, but nothing major, while in WLTP the opposite happened. The fuel crossover directly impacts the performance of the cell and its efficiency because even though the reactant is consumed, it's not generating electrical output since it is reacting on the wrong side.

The most interesting part is what happened to the FC-DLC after the second period of operation. The CV curve completely shifted up, suggesting that there's a short circuit inside the cell, probably due to a pinhole in the membrane, which leads to an increase in the fuel crossover. The 2nd refresh corresponds to the characterization done ahead of starting the third sequence of operation, and at that point a decrease around 100 mV in open circuit voltage was reported. The decrease in open

circuit voltage is directly correlated to the reaction of hydrogen with oxygen in the cathode side. It is now clear why there was such a massive decrease in performance at low current densities at the beginning of the 3rd period of the FC-DLC test. A pinhole was formed during the electrochemical characterization, but the reason is still unknown.

Looking at the peak around the 0.1 V mark, it is possible to observe that at BoT the higher peak happens in the FC-DLC 2.5 bar. This zone is where the desorption of hydrogen happens, and by calculating the absolute area it is possible to know the ECSA, as stated in section 3.5.2. The calculations for all the peaks were done and the FC-DLC 2.5 bar test had the higher ECSA, meaning that the higher pressure had an impact on the number of reactive sites in the catalyst layer.

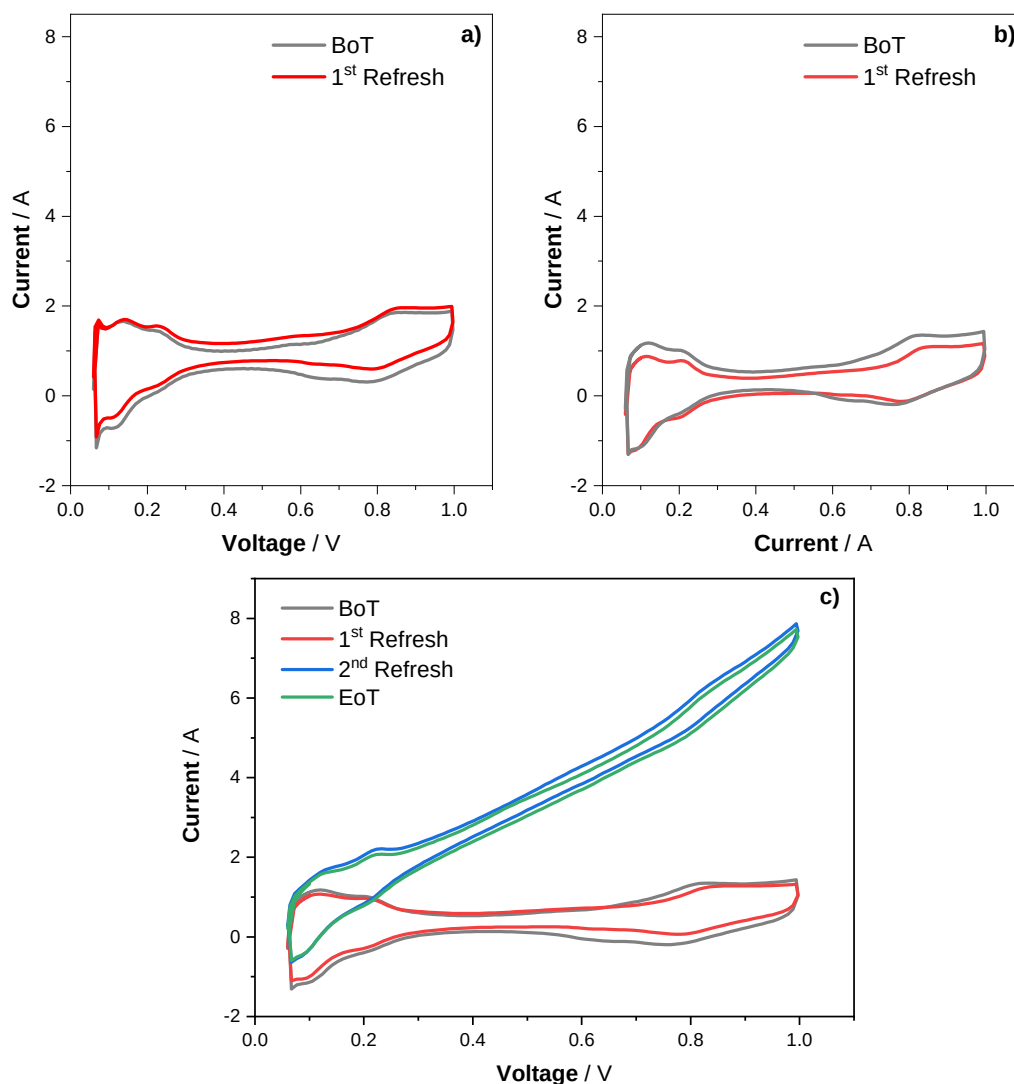


Figure 4.17: Cyclic voltammograms for cathode side during FC-DLC 2.5 bar (a), WLTP (b) and FC-DLC (c)

Resorting to the CV curves and using equation 3.4, the electrochemical surface area of the cathode side was calculated for all the curves shown in the CV measurements. The relative ECSA losses of the cathode catalyst layer are presented in figure 4.18.

A constant decrease in the ECSA for all tests is observed, the FC-DLC 2.5 bar being the one with the smallest percentage of losses. FC-DLC shows a 35% decrease in the EoT when compared to the beginning of test. The increase in ECSA losses is higher from the 2nd refresh to EoT than from the 1st to 2nd refresh, which makes sense due to the increase in performance loss reported in the EoT.

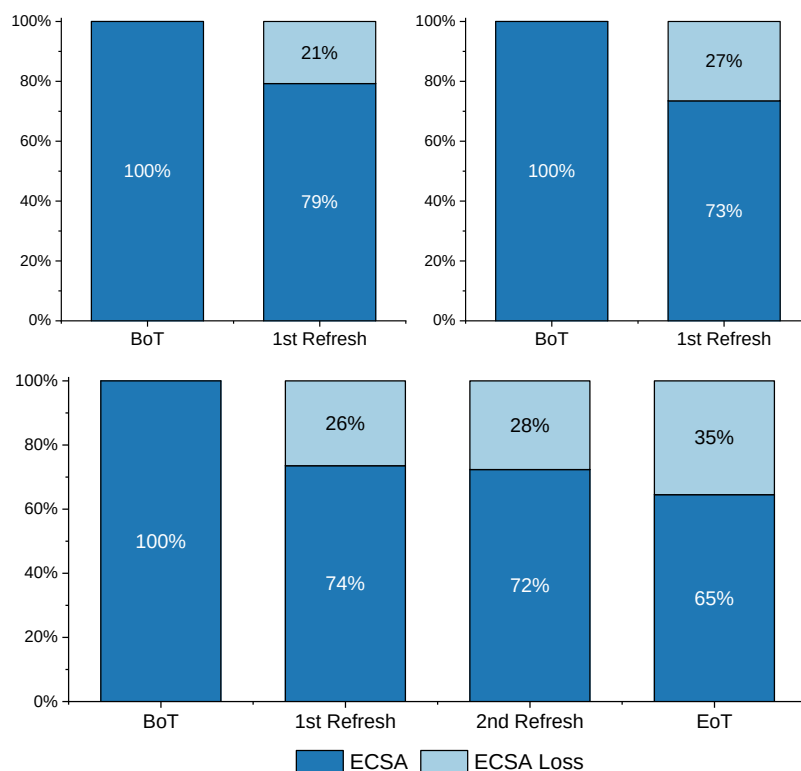


Figure 4.18: Relative cathode ECSA changes for WLTP test (top-right), FC-DLC 2.5 bar test (top-left) and FC-DLC (bottom)

4.2.4 Scanning Electron Microscopy

To investigate the formation of a Platinum band inside the membrane and the thickness changes in the MEA, a cross section of the MEA after conditioning and another one after the end of the FC-DLC test were sent to SEM. Figure 4.19 shows both cross sections. The top white part is the cathode catalyst layer and the bottom white part is the anode catalyst layer. Then there's three layers of the Proton exchange membrane. The middle layer is a PTFE reinforcement to improve the mechanical stability of the MEA and the other two layers are the anode and cathode sides of the PEM.

In the beginning there was already a Pt band formation inside the PEM cathode side, but after the FC-DLC test that band is much more concentrated and it goes deeper inside the PEM cathode layer. Regarding the structure, after performing the test, the layers are deformed and certain parts are getting thinner, which contributes to a decrease in performance. The anode catalyst layer had a lot of roughness after performing the test.

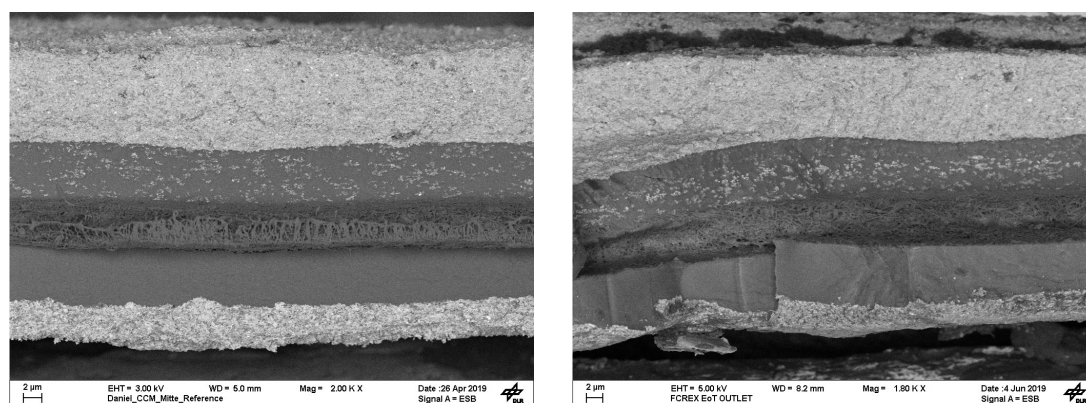


Figure 4.19: Cross section of the MEA after conditioning (left) and after the full FC-DLC performed (right)

The SEM/EDX performed in the catalyst layer is shown in figure 4.20. One of the samples was taken after one week of testing and the other one after the full FC-DLC cycle. It is noticeable that the surface of the catalyst is rougher at the end of the test, which may lead to an increase in the resistance of the surface.

The white dots represent the platinum and at the end of the FC-DLC test not only are they more concentrated but some of them are slightly bigger too, proving that there was platinum agglomeration, which is expected after a long period of testing.

By looking at the tables 4.4 and 4.5 it is evident that the fluorine mass% is higher at the end of the FC-DLC test, suggesting that there's some contamination coming from the PTFE of the MPL.

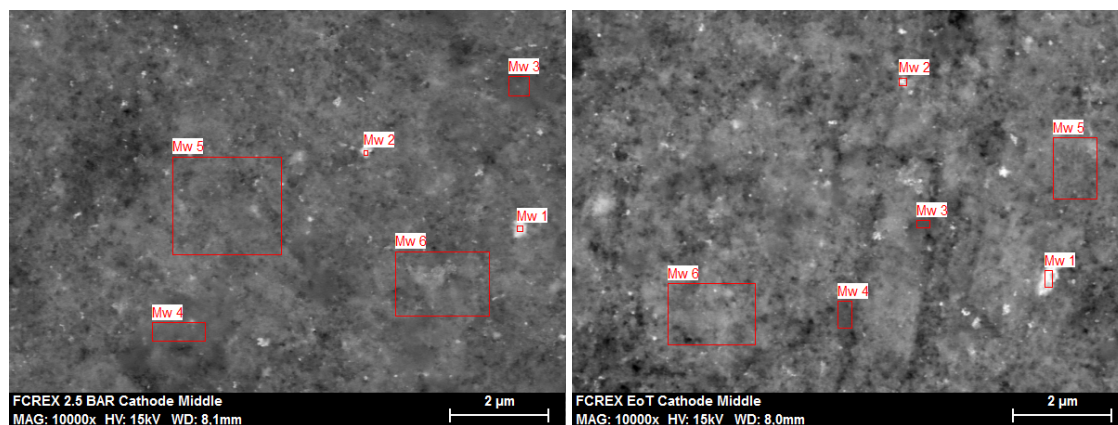


Figure 4.20: EDX performed on the catalyst layer after 1 period (left) and 3 periods (right) of operation

4.2.5 X-Ray Photoelectron Spectroscopy

XPS was performed in the Macro Porous Layer of the GDL to investigate the presence of Platinum on the surface of the MPL. Six samples from the end of the FC-DLC test and another six from the end of the FC-DLC 2.5 bar test were analyzed. The samples were from both the anode and

Table 4.4: Mass % spectrum of catalyst layer after one week of testing

Spectrum wt %	C	O	F	S	Pt
Mw 1	45.35	3.08	10.17	0.61	40.78
Mw 2	46.16	2.60	10.37	0.71	40.16
Mw 3	52.44	2.91	9.81	0.45	34.39
Mw 4	52.03	2.15	10.38	0.42	35.02
Mw 5	46.44	3.04	11.85	0.53	38.14
Mw 6	47.41	2.57	11.26	0.40	38.35

Table 4.5: Mass % spectrum of catalyst layer after three week of testing

Spectrum wt %	C	O	F	S	Pt
Mw 1	43.63	2.24	10.44	0.52	43.17
Mw 2	47.47	2.69	12.26	0.46	37.12
Mw 3	51.95	2.34	10.32	0.55	34.84
Mw 4	48.25	2.16	10.03	0.50	39.06
Mw 5	48.02	2.57	11.77	0.50	37.14
Mw 6	44.40	2.46	11.17	0.47	41.50

cathode sides of the MPL from the center, inlet and outlet positions of the cell for a better general understanding. Three more samples were sent with a GDL only conditioned and they didn't show any presence of Platinum, as expected as it was done to have a reference. Figure 4.21 shows one of the XPS spectra obtained from the measurements. The four elements that are present in the MPL are represented in the figure in their respective binding energy peaks.

To calculate the relative percentage of a certain element in the sample, the absolute area of the peaks was calculated and then divided by the atomic subshell photoionization cross section value of the respective element. Then the value obtained was divided by the sum of all the elements in the sample. The relative percentage of platinum in the samples is shown in table 4.6.

All the samples have small traces of platinum, but one of them clearly has more than the rest: the FC-DLC Cathode Inlet. This shows that there is always Pt migration, even if in a really small scale. However, the average relative percentage of platinum is higher in the FC-DLC than in the FC-DLC 2.5 bar test which is expected since it ran for a longer period of time.

Looking at both the Anode Inlet samples, the Fluorine percentage is substantially smaller in both of them which suggests some kind of contamination happening in that zone of the cell considering it happened in the same spot twice.

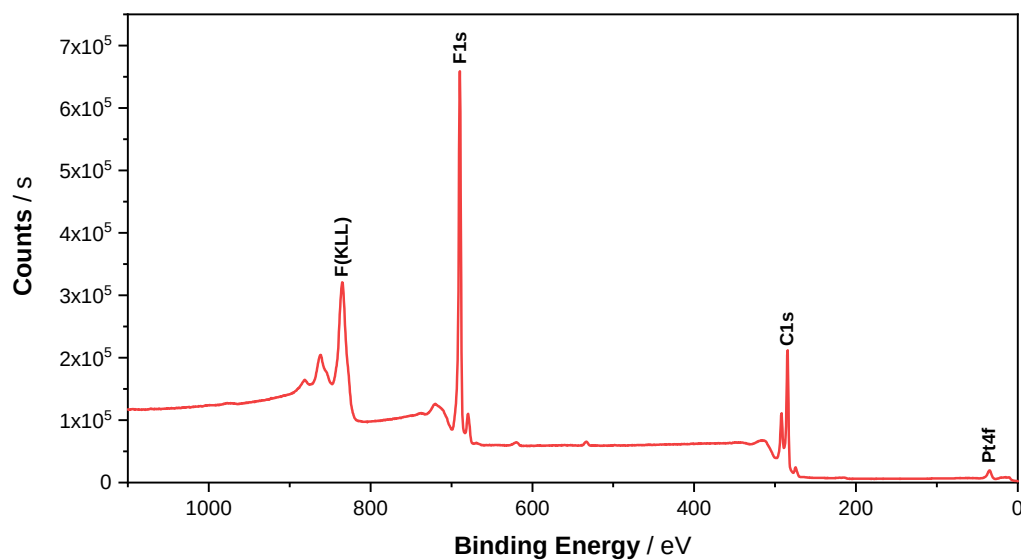


Figure 4.21: XPS spectra of the anode MPL after the FC-DLC test

Table 4.6: Relative percentage of Platinum and Fluorine found in the GLD

		Relative Percentage (%)	
		Pt	F
FC-DLC Cathode	Inlet	0.027	73
	Middle	0.004	72
	Outlet	0.005	71
FC-DLC Anode	Inlet	0.005	48
	Middle	0.007	71
	Outlet	0.005	72
FC-DLC 2.5 bar Cathode	Inlet	0.002	73
	Middle	0.001	72
	Outlet	0.002	72
FC-DLC 2.5 bar Anode	Inlet	0.002	49
	Outlet	0.009	71
	Middle	0.001	72

Chapter 5

Conclusions and future work

The investigation developed initially about the basic principles of the proton exchange fuel cells was crucial to better understand the basic phenomena happening in the laboratory while the degradation study was the baseline for all the tests performed on the fuel cell.

In order to run the load cycling tests some adaptations had to be made to the test bench so that it allowed the load to be controlled externally with a function generator that was programmed to run the chosen load cycles and assess the performance of the cell.

Before starting the load driving cycles, some base tests were made on the cell to better understand how it performed and how good the assembling process was since it was changed in the beginning of the master's thesis. It was possible to conclude that the cell had a similar performance to the cells already extensively tested in the company, which was a good sign. The maximum power output obtained from the cell was around 40 W and there were minor deviations determined by the outlet pressure used.

The impact of the driving load cycles on the fuel cell degradation was studied by submitting the cell to two different load cycles and repeating one of them to assess if the outlet pressure had an impact on the degradation.

Polarization curves of the FC-DLC test showed a higher performance loss in all of the current densities, meaning that the test was more stressing to the cell, probably due to the humidity cycle being more aggressive as a result of the long periods of idling.

FC-DLC mostly showed irreversible losses during all of the periods of operation, which demonstrates that its refresh periods did not have a positive impact on the recovery of reversible voltage losses. On the other hand, WLTP shows some improvements stemming from the refresh procedure and probably associated with the excess of water during the operation that caused flooding and thus lowered performance.

Contrasting to both of these results, FC-DLC performed at 2.5 bar showed a good percentage of recoverable, which lead to the conclusion that the outlet pressure has a significant impact in cell degradation.

Cyclic voltammograms showed a massive increase in the fuel crossover by the end of the FC-DLC test, justifying the huge performance loss at open circuit voltage during the last period of

operation. The total resistance of the cell had a substantial increase from the 2nd period until the end of test mainly due to the increase of the charge transfer resistance of the catalyst layer.

Ex situ measurements showed platinum migration to the GDL after performing a complete durability test and Pt band formation inside the cathode side of the proton exchange membrane. A change in the thickness along the cross section of the MEA was observed too with some thinning spots detected.

This proves that these cells do not yet have the desired durability to be commercially viable when used without additional batteries in light vehicles. The FC-DLC cycle performed for 351h corresponds to a vehicle utilization of around 12000 km in one year and if the cell reaches this state in such a short amount of time, it is not viable to use them in a real car by themselves. One of problems is the open circuit voltage and the constant changes in the current. A way for this technology to be viable is to use a fuel cell coupled with a battery. The cell would be operating only in the ohmic zone so as not to provoke excessive degradation. The WLTP showed less degradation but still a lot more than the desired amount for commercial applications.

The cargo pedelec project had the idea of using the fuel cell at ambient pressure, but with the results obtained during this master's thesis it is possible to conclude that the usage of this cell at ambient pressure is not feasible, but at higher pressures it could be viable since the performance is more stable over time.

Regarding the monitoring system developed, it was a valuable way to oversee the fuel cell outside of the lab and in the future it will be integrated into the fuel cell cargo pedelec in development.

Future work would include the improvement of the data acquisition unit by adding more sensors to the system and further improving the website tools to provide a better overview of the test bench outside of the lab.

Appendix A

Supporting Information

A.1 Polarization Curves

Table A.1: Polarization curve set-points

Current	Current Density	Air Flow	H₂ Flow
A	A cm ⁻²	ml min ⁻¹	ml min ⁻¹
0	0	333	105
1.2	0.02	333	105
2.4	0.04	333	105
3.6	0.06	333	105
4.8	0.08	333	105
6	0.1	333	105
12	0.2	399	125
18	0.3	599	188
24	0.4	798	251
36	0.6	1198	376
48	0.8	1597	502
60	1	1996	627

A.2 Load Driving Cycles

Table A.2: Worldwide Harmonized Light Vehicle Test Procedure test points time/load (100% load = 60 A)

Step	Time (s)	Dwell (s)	Load (%)	Current (A)
1	0	12	0	0
2	12	15	29	17.4
3	27	17	0	0
4	44	21	40	24
5	65	45	0	0
6	110	33	50	30
7	143	51	70	42
8	194	38	50	30
9	232	24	62	37.2
10	256	17	40	24
11	273	20	50	30
12	293	20	36	21.6
13	313	29	20	12
14	342	19	0	0
15	361	15	40	24
16	376	38	50	30
17	414	67	0	0
18	481	35	70	42
19	516	15	66	39.6
20	531	34	76	45.6
21	565	28	0	0
22	593	34	45	27
23	627	29	29	17.4
24	656	40	90	54
25	696	31	81	48.6
26	727	22	95	57
27	749	15	90	54
28	764	25	100	60
29	789	25	57	34.2
30	814	37	95	57
31	851	33	81	48.6
32	884	27	57	34.2
33	911	39	70	42
34	950	51	0	0

Table A.3: Fuel Cell Dynamic Driving Cycle test points time/load (100% load = 60 A) [33]

Step	Time (s)	Dwell (s)	Load (%)	Current (A)
1	0	15	0	0
2	15	13	12.5	7.5
3	28	33	5	3
4	61	35	26.7	16.02
5	96	47	5	3
6	143	20	41.7	25.02
7	163	25	29.2	17.52
8	188	22	5	3
9	210	13	12.5	7.5
10	223	33	5	3
11	256	35	26.7	16.02
12	291	47	5	3
13	338	20	41.7	25.02
14	358	25	29.2	17.52
15	383	22	5	3
16	405	13	12.5	7.5
17	418	33	5	3
18	451	35	26.7	16.02
19	486	47	5	3
20	533	20	41.7	25.02
21	553	25	29.2	17.52
22	578	22	5	3
23	600	13	12.5	7.5
24	613	33	5	3
25	646	35	26.7	16.02
26	681	47	5	3
27	728	20	41.7	25.02
28	748	25	29.2	17.52
29	773	68	5	3
30	841	58	58.3	34.98
31	899	82	41.7	25.02
32	981	85	58.3	34.98
33	1066	50	83.3	49.98
34	1116	44	100	60
35	1160	21	0	0

Appendix B

Lab equipment

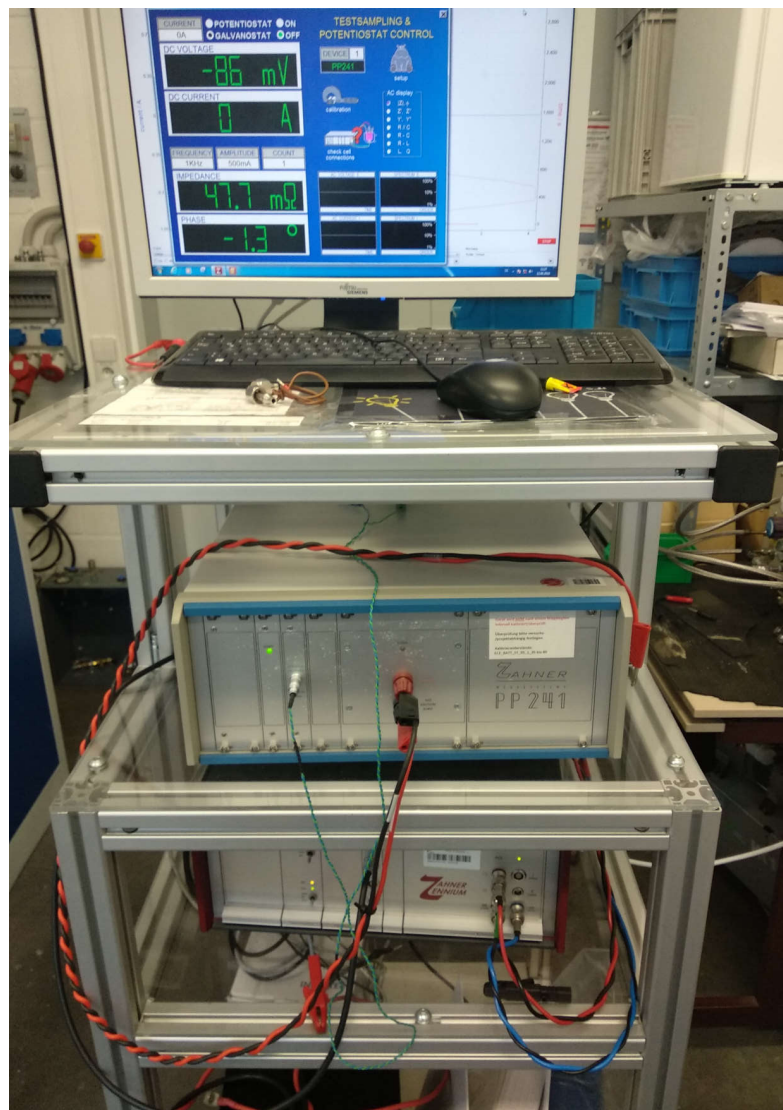


Figure B.1: Zahner workstation used for the EIS and CV measurements

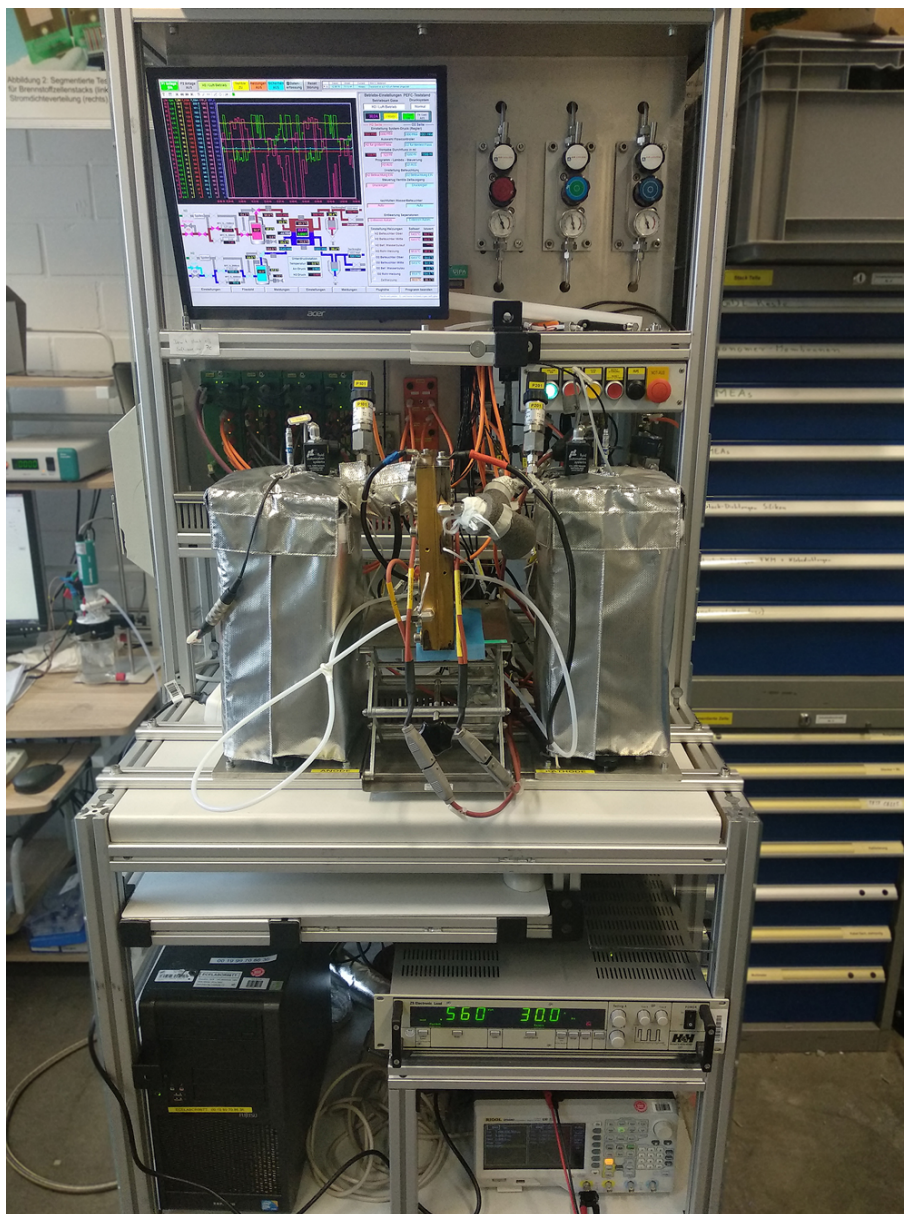


Figure B.2: Test bench used during the experiments

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