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DURABILITY TESTS OF PROTON-EXCHANGE MEMBRANE FUEL CELLS (PEMFC) FOR AUTOMOTIVE APPLICATIONS

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INTRODUCTION

The urge of tackling climate change and so to stop the increase of the global temperature has brought to the requirement for the global energy system to go through a deep transformation which eventually would move the economy towards a decarbonization. As a matter of fact, the era of fossil fuels is coming to an end. It is reckoned that the use of technologies linked to fossil fuels sources are going to reach a peak and rapidly decline afterwards while the demand of power is predicted to double by 2050 and triple by 2100 (Nocera, 2009). Currently fossil fuels energy sources cover the 80% of the energy use so it is clear from the prediction showed above that the decrease of energy production coupled with the increased demand of energy would lead eventually to a demand-supply gap that will have to be fulfilled somehow. The gap must be covered in a way that would allow the energy supplies to be “accessible, reliable and affordable, and delivering energy to business at competitive prices, while at the same time ensuring that energy is generated ad used in a way that protects the environment” (Sir Philip Lowe, Executive Chair, Energy Trilemma, World Energy Council).

These issues inevitably cause the need to further develop all the technologies and infrastructures that are driven by renewable energy. As far as energy technologies are concerned, they are usually evaluated according to several parameters such as performance metrics, input of natural resources, infrastructures requirement, durability and adaptability. The evaluation of the electrochemical energy technologies according to these criteria gives a favorable outcome as they are able to give a good combination of these factors. The positive evaluation gives reasons to move towards this typology of technology. Electrochemical devices work converting the chemical energy from reactants into electricity, they can be either batteries, which use as reactants the exact material they are made of during the discharge phase in order to give power, while they would need power during the charge phase in order to recreate the initial state of the reactants and be able to start the whole discharging process. Fuel cells are another kind of electrochemical devices which are able to produce power using reactants coming from outside the system instead.

One of main aspects that pushes towards this kind of energy generation is the unrivaled thermodynamic efficiency especially compared to more traditional conversion devices such as heat engines. In fact, whereas traditional technologies convert heat coming from a combustion into mechanical work and then eventually into electricity through a generator, electrochemical devices such as fuel cells would produce directly DC electricity as long as a fuel (like hydrogen) and an oxidant (oxygen) are supplied in a way that a major portion, compared to a classic combustion, of the initial enthalpy is converted into useful energy.

The electrochemical energy conversion is given by the separation of oxidized and reduced species and so the occurring of the partial reactions separated by a certain distance. Reactant gases must be provided through porous electrodes where they lose or gain electrons thanks to a catalyst material embedded in the pores. A separation of charge occurs while the electrons lost by the oxidizing specie go through an external circuit producing current and eventually reach the reducing specie in the other electrode. The ions coming from the lost of electrons of the oxidizing specie would flow through the electrolyte that separate the two electrodes and would react with the incoming electrons completing the reaction. The electrolyte is one of the main component of the system, its material must be very selective as it ought to be impermeable to electrons but let the ions go through.

Even though the basic mechanism of the system shown by the brief explanation above has been known for more than a century, the development of this technology did not make any particular progress until the second half of the 19th century, when all the issues and problems correlated with the massive exploitation of fossil fuels sources came finally into light. It was only in the late 1950s when the polymeric proton exchange membrane, which is one of the most promising material nowadays, started to be used as electrolyte by General Electric. Further development were done for the GEMINI space program developed by NASA. Since then, many other terrestrial applications have been investigated for a wide range of different sectors such as automotive, stationary power systems and portable power systems as well.

Nevertheless this technology is still considered “new” and its commercialization has not found its right pathway yet, as it has probably been hindered by significant issues that characterize this technology. The most important problems concern in turn their cost, which is still too high to allow the proper entrance in the market, and their durability. Durability is the capacity of a certain device to not change the performance for as much time as possible, its decay is not given by a catastrophic failure but by a certain decrease in the performance that is not reversible. What mainly challenges the durability of the PEMFC are issues like dynamic load cycling, startup/shutdown and freezing/thawing. The lifetime of fuel cells indeed decreases the most depending on how often the requested power changes. This kind of issue needs to be analyzed more deeply especially for automotive applications, that need to assure the power in many different loads situations. Proton exchange/polymer electrolyte membrane fuel cells (PEMFC), represent the best option for the automotive application precisely for this reason, as their low operating temperature (50°C-100°C) allows a really fast start-up and a more efficient response to the variation of the required power due to the different traffic condition, which would request stopping/running or acceleration/deceleration in a short time range. The goal of this work is actually to indagate about this issue through tests that aim to find out how the durability of the lifetime of the fuel cell would react to a dynamic load that simulates the driving conditions. The fuel cell that was tested was given by *Spektronik*, a company headquartered in Singapore. Specifically, the fuel cell that was selected is called *Protium-150* and it is characterized by a graphite plate stack of 25 cells, integrated with a heat management system (cooling fan with pwm control) and a fuel supply system. All its technical features, together with all the information about the fuel supply are shown by the tables below.

Specifications:

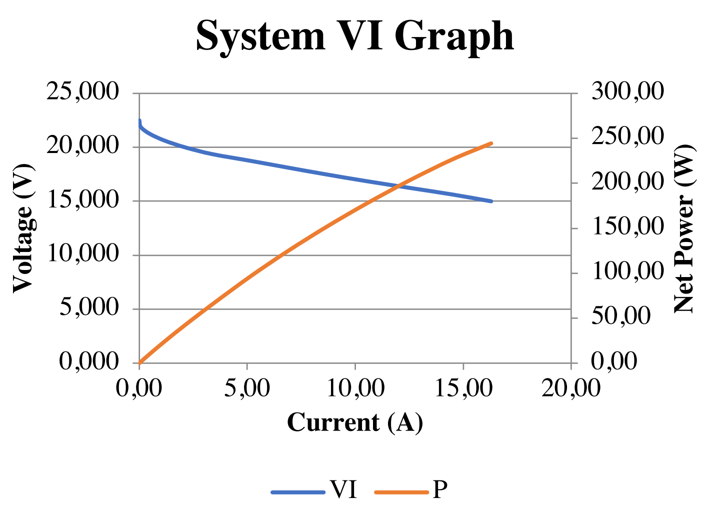
Rated Power	150 W
Rated Current	12.5 A
Voltage Output	12-18VDC
Start-up Time	5s
Op. Amb.Temp.	(0,40]°C
Op. Altitude	1500 mAGL
System weight	470g
Max Dimension	109x101x84mm

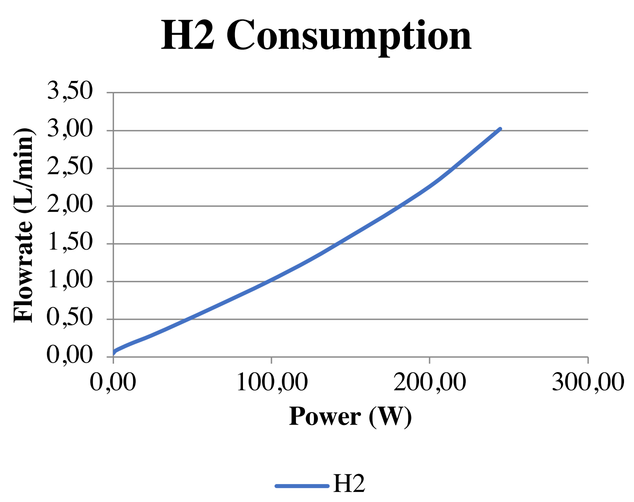
Figure 1. Picture of the Fuel Cell purchased for the tests, all the specifications are on the left.

Fuel Supply:

Hydrogen Gas	Dry, 99.999% purity
Delivery Pressure	0.4-0.7 bar (6-10 psig)
Fuel Consumption	1.9L/min
Gas Tubing	Silicone, 1.6 mm ID
Supply & Purge Control	Solenoid valves with integrated pressure sensor

Together with all these features the manufacturer gave also some data referring to the nominal condition thanks to which it was easy to clarify how the situation looked like before starting with the durability tests and have a better vision on how the tests would affect the capability of the device to work. The data received from the company are plotted below.





The polarization curve has been obtained starting from the OCV (Open Circuit Voltage, i.e. the maximum value of voltage achievable only under condition of no electrical load) and then fixing a voltage decrement rate equal to 0,25V/cell/min. All the balance of plant is powered by the fuel cell, which is supposedly able to give a maximum power equal to 150W. The hydrogen supply was measured with an average ambient temperature equal to 25°C and its pressure was equal to 10 psi. The fuel cell was tested in a laboratory where it was required to meet a dynamic load for multiple times per day while several measurements were made. The fuel cell was placed in a bench where it was connected to a back-up power system, to a potentiostat/galvanostat that worked as its load, to the laboratory computer through a serial port communication that, thanks to a code written with MATLAB, was able to collect all the data concerning the mass flow rate and the operating temperature of the cell, and obviously to the tank of hydrogen through its fuel supply system. During the testing time many typologies of measurements were taken, such as all the data about current, voltage, power together with the fuel flow rate and its pressure, and all about the operating condition of the fuel cell like its temperature. The temperature of the room as well was kept in consideration, as it can affect the hydration of the fuel cell and the mass flow rate of the fuel, being the tests performed during the summer. Once all these data were collected, they were postprocessed to obtain first the polarization curve and then to perform other kinds of analysis and plots. The polarization curve is a standard technique that shows the tests results plotted as the cell voltage as a function of the current density. The data needed to build the polarization curve come from a quasi-steady test where the voltage is kept constant at a certain value until the current stabilizes, then the voltage is plotted as a function of the last stabilized value of current as it will be better clarified by this analysis further on. The main drawback about polarization curves as diagnostic tools is that they provide knowledge about the performance of the device as a whole, so they are a useful indicator of the overall performance and they do not give any information about the status of each components of the cell or each mechanism during the normal operation as they cannot be obtained unless a specific test mode is implemented. In order to compensate these failings, another popular measurement technique was exploited in a way that information about a wider range of phenomena could be obtained. This diagnostic tool is called Electrochemical Impedance Spectroscopy (EIS) and it is implemented applying a low-level alternative current (AC) to the fuel cell in such a way that the impedance of the system can be determined across the frequency range able to give the desired information (i.e. from 1 mHz to 100 kHz). These diagnostic tools will be further presented in the next chapter , while their results, together with all the data obtained through the test, will be shown once that the test procedure will be deeply explained. In fact, every testing day followed a precise routine that aimed to analyze the long-term response to a typical operating condition that in this case it was represented by the succession of cycles whose goal is to simulate a normal car task while driving in a city. As anticipated, the testing pattern that was implemented represents a typical *modus operandi* when durability is concerned as it is all about how much time the device takes before its performance decreases as much as previously established.

1. FUNDAMENTALS OF FUEL CELLS AND DIAGNOSTIC TOOLS

1.1. Fundamentals of fuel cells

A single fuel cell is made of the electrolyte sandwiched between the two electrodes, that face, on the opposite side, the gas diffusion layer. The all set is placed between two bipolar plates.

The electrolyte is the core of the system and it is what characterizes and gives the name to the cell. It gives the physical distance between the two electrodes allowing the separation of the charge and so the production of useful energy through the flow of electrons in the external circuit. A PEMFC electrolyte is made by a polymeric membrane which is obtained modifying polyethylene by substituting fluorine for hydrogen and then adding a sulfonic acid, the HSO_3, that is ionically bonded and thus is able to attract H^+ protons as long as it is adequately hydrated. This material was developed by DuPont Co and it is known as Nafion.

The electrodes consist of a porous medium which hosts the catalyst material in a way aimed to maximize the electrochemically active surface area, i.e. the surface area that is in contact with the reactants, in order to enhance the speed of the reaction. Besides being porous, the hosting material must be also conductive as it must be able to electronically connect all the set. As far as PEMFCs are concerned, the catalyst material is usually platinum and it is embedded in the pores of carbon cloth, which is usually a carbon-based powder named XC72 (Cabot). The catalyst and the carbon cloth are affixed in a gas diffusion layer, whose task consists in making the reactants reach the reaction points in the most efficient way and to remove the water produced by the reaction on the other side in order to avoid any flooding. The gas diffusion layer must be conductive as it ought to be electronically connected to the bipolar plate that encloses the fuel cell in order to assure that the flow of electrons produced in one cell can move towards the next one and make the reaction happen. As already anticipated above, a single fuel cell is never able to provide to the whole load coverage for general applications, so it has to be connected in series with other ones forming a stack. The produced current goes from one cell to another, as it is conducted by the bipolar plates, so that the electrons would react in the closest cathode. The bipolar plates are commonly made of graphite, as they need to be conductive. Flow channels are engraved in the graphite in order to facilitate the reactants distribution on the electrode surface and to make the byproducts of the reaction flow away.

Fuel cells are able to convert the chemical energy into electricity thanks to the creation of a gradient in the electrochemical potential across the proton-selective membrane which separates the electrodes. The selectivity of the membrane allows the occurring of the separation of charge that creates the gradient as the two semi-reactions take place. In fact, the membrane allows only the hydrogen ions to have a high mobility as long as it is kept hydrated.

As anticipated, the hydrogen, which is given in the anode side of the membrane, works as fuel and thanks to the catalyst is able to release its electrons and let its H^+ ions according to this reaction:

$$2H_2 \rightarrow 4H^+ + 4e^-$$

The membrane, being selective, gives a low resistive pathway to the ions while not letting the electrons and the fuel particles go through. In fact, the electrons are supposed to pass by an external circuit where the useful energy is produced and to reach the cathode side afterwards.

In the cathode, they will react with the protons coming from the membrane and the oxygen that is supplied, usually as external air. This reaction gives as by-product water:

$$4e^- + 4H^+ + O_2 \rightarrow 2H_2O$$

What can be noticed right away is that the only by-product of the reaction would be water, which means “zero emissions” even though water needs to be managed in order to avoid the flooding of the system. The overall reaction is obviously given by the union of these two semi-reaction:

$$2H_2 + \ O_2 \ \leftrightarrow 2H_2O + electricity + heat$$

1.2. Fuel Cells Diagnostic Tools

As anticipated, extending the lifetime of the fuel cells would be a great move forward the large scale deployment of these devices. In order to face and solve the durability issue, a set of activities, which can be classified as Prognostic and Health Management (PHM) activities, are required. PHM is first composed of monitoring and data processing which are followed by health assessment, diagnostic and prognostic to finally exploit all the collected information to obtain a prediction of the lifetime of the device. With all this knowledge, the decision making aimed to preserve and extend the durability of the fuel cells can be implemented in a more efficient way. This work focuses on the first part of this process. As anticipated by the introduction, during the durability tests, the fuel cell was monitored as its load port was connected to a potentiostat that could drive the functioning of the fuel cell while collecting all the data about current, voltage, power and time. Moreover, the fuel cell communicated through a serial port connection with the laboratory computer so that a MATLAB code, that was associated to the serial port, was able to obtain the data about the fuel mass flowrate and the operating temperature of the cell. Once all these data were gathered, they were processed in order to be seen in a clear way with plots, but they were also exploited to implement two diagnostic procedures, the creation of the polarization curves and the electrochemical impedance spectroscopy, whose generalities will be further explained by the following sub-chapters.

1.2.1. Polarization Curve

The polarization curve is the standard and most popular technique for evaluating the performance of fuel cells. It is basically a plot that shows the cell voltage change with current, yielding in such a way information on performance losses. In fact, the higher is the current at high voltage the higher is the power in output and so the better is the performance of the cell. Polarization curves cannot be obtained during normal operation, as a specific procedure is required. The testing pattern established for the data collection needed to build the polarization curve was implemented three times per day in order to analyze not only the decrease of the performance with the succession of the testing days, but also to see if and how the power output would decrease as the operating hours would go on. The following picture shows a typical polarization curve for a PEMFC.

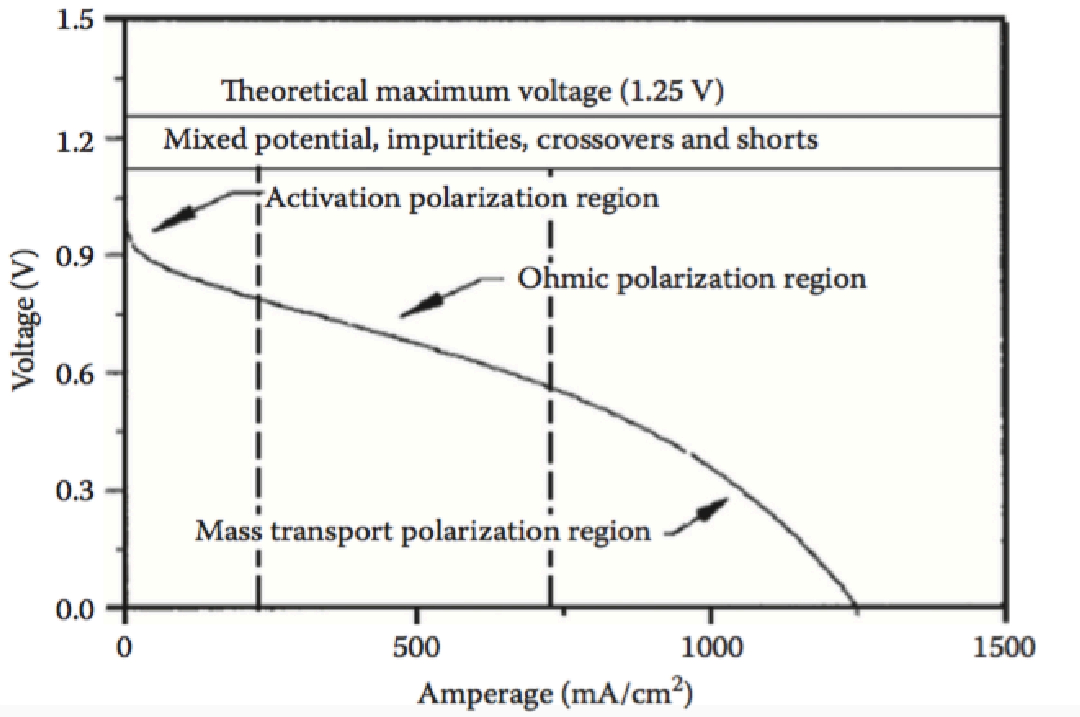


Figure 2. A typical polarization curve for a PEMFC. (Reproduced from Journal of Power Sources*, 70, Lee, J.H., Lalk, T.R., and Appleby, A.J., Modeling electrochemical performance in large scale proton exchange membrane fuel cell stacks.)*

The first point of the curve (i.e. when the current approaches to zero), is called the open-circuit voltage (OCV) and it is the voltage provided by the cell under the condition of no electrical load and it is the maximum value of voltage achievable as the losses are all equal to zero. As the picture shows, the theoretical OCV is always higher than the one that can be measured in the reality due to the fuel cross-over from the anode to the cathode, or due to losses caused by leakages. Being the OCV associated to a null current, this situation does not have any practical interest as it is the condition under which no power output occurs. As the power starts being released, it starts being useful to analyze the working potential as a function of the current changes, which is what the polarization curve shows. Being affected by the losses, the working potential is always lower than the OCV and it keeps decreasing as the current increases. The polarization losses are mainly due to three reasons:

- Kinetic-related activation losses
- Cell resistance losses
- Mass transport losses

Each of these losses affects a specific reason of the curve as it can be easily noticed by the figure. The expression that summarizes the steady-state V-I characteristics of the fuel cell and that shows how the losses affect the OCV is the following:

$$V_{cell} = OCV - V_{activation} - V_{ohmic} - V_{concentration}$$

Where

V_{cell} is the output voltage of the fuel cell

OCV is thermodynamic potential that occurs under the equilibrium condition (no electric load)

$V_{activation}$ is the voltage loss caused by the rate of the semi-reactions on the electrodes

V_{ohmic} is the voltage drop mainly due to the resistance of the material of the electrolyte to the proton flow but also due to the resistance of the circuit to the electrons flow

$V_{concentration}$ is due to the decrease I concentration gases or the transport of mass.

All the expressions that describe these over-voltages depend on the current and their details can be found in references. Building the polarization curves for the fuel cell under investigation did not require any of these equations as the curves were created thanks to the data collected as it will be better explained in the chapter concerning the tests results.

1.2.2. Electrochemical Impedance Spectroscopy (EIS)

The Electrochemical Impedance Spectroscopy (EIS), is an *in situ* investigation method that is very popular as it is a nondestructive technique that is able to achieve information about a wide range of electrochemical phenomena. This technique is based on applying a low-level alternative current waveform to the electrochemical system under exam, recording the AC voltage across the cell and the AC current through the cell and eventually taking the ratio of AC voltage/AC current to obtain the impedance. The stimulus that is given to the system is characterized by a low-level, so that the system is not damaged, and its frequency is in most cases sinewave so that the impedance can be evaluated in the range of interest, which is usually from 1 mHz to 100 kHz. The impedance represents the system response to the given stimulus and it is able to yield information about not only the structure of the interface, but also about the reactions and the mass transport phenomena taking place there. In fact, during the oxidation of the fuel at the anode and the reduction of the oxygen at the cathode, different kinds of reactions occur while the concentration gradient influences all the process.

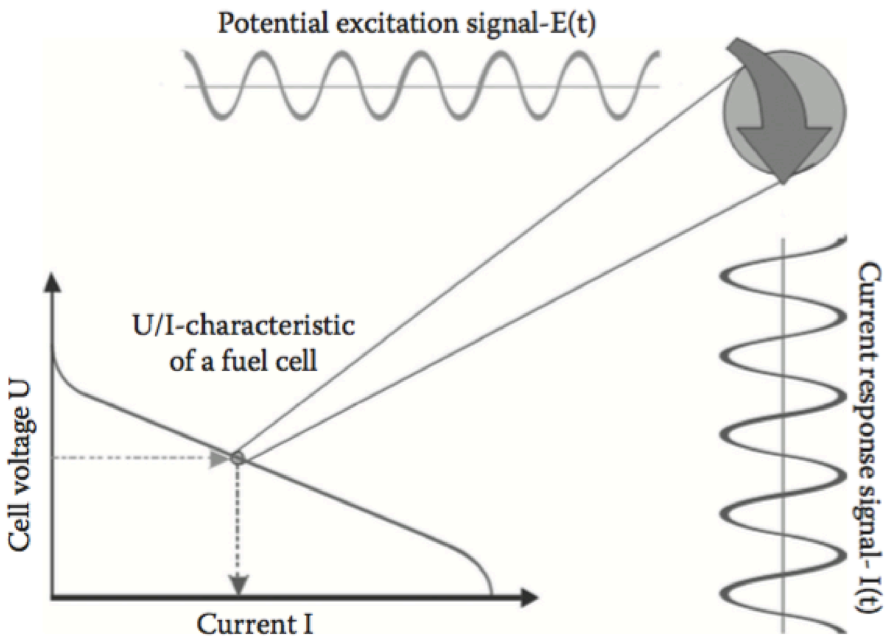


Figure 3 Representation of EIS applied to a fuel cell

All the reactions steps that occur within the fuel cell are characterized by different time constants whose transformation into the frequency domain allows the distinction of each process from one to another. Specifically, the high frequency range mostly regards the electrolyte (R_{Ω}) and contact resistances, the lower frequencies concern the double-layer charging and charge transfer reactions, while in the lowest one slow process such as diffusion processes are observed.

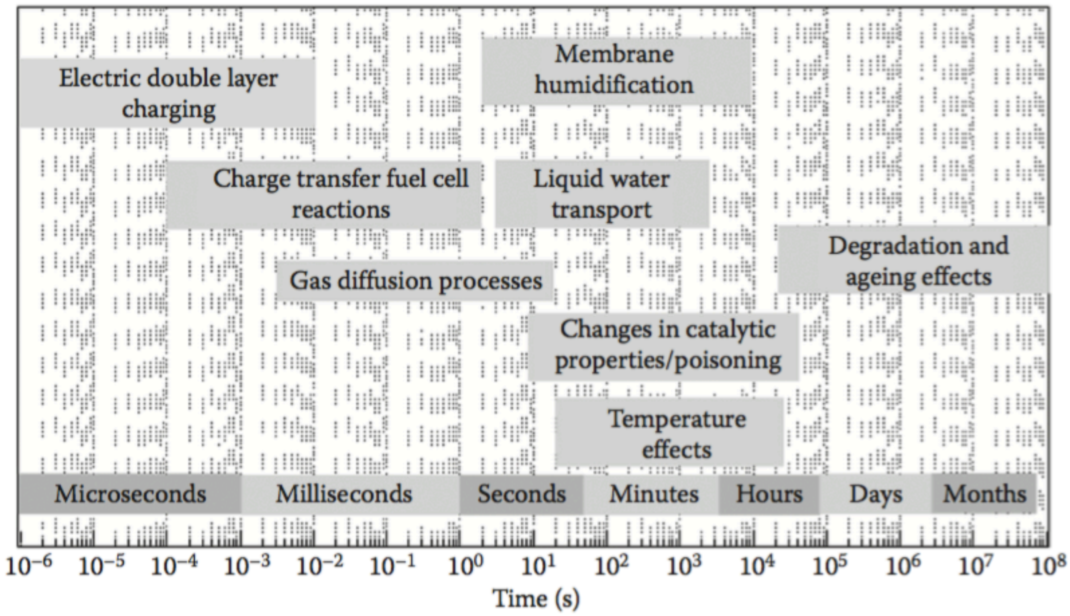


Figure 4 Representation of the many frequencies characterizing each fuel cell reactions

The most common representations of electrochemical impedance spectra are the Bode plots, which shows the logarithm of impedance magnitude $|Z|$ and the phase-shift (α) versus the logarithm of the frequency (f) and Nyquist plots, where it can be seen the imaginary part of the impedance versus its real part. The Nyquist plots are really useful in order to distinguish between the different diffusion processes and evaluate the deviation of the double-layer capacity from ideal behavior. An equivalent circuit can be exploited to show the electrode/electrolyte interface where all the reaction steps involved can be represented by the impedance elements. These elements are represented as ohmic, capacitive and inductive components whose impedance depends on the frequency of the AC signal. The way all these impedances are linked depends on the relationship between the processes that they represent, steps that occur at the same time are represented by a connection in parallel while steps that occur subsequently are represented by a series connection. The diagram that has been chosen to analyze the results of the EIS performed to the fuel cell that was tested for the aim of this work is the Nyquist plot, as it will be shown by the chapter about the test results. Even though EIS is a really efficient technique which allows to obtain a good amount of information, the time required to obtain the measurements could become very large and the tests procedure could become not only too time consuming, but also very costly. The testing time that was available for this work was obviously limited and this is the reason why it was clear from the beginning that there was the need to overcome this issue modifying the traditional EIS procedure. The technique that was proposed exploits the concept of EIS while being faster and giving results comparable to the proper one. According to this procedure, the cell must be perturbed by a small chirp signal containing a large number of frequencies instead of series of small sinusoids at different frequencies. This method is called *Fast* EIS and it allowed to obtain the data about the impedance in a very short time. The signal that was selected for the purpose of the analysis is called Pseudo Random Binary Sequence (PRBS), which is a discrete time periodic signal that switches between two levels. Specifically, the current signal that was sent to fuel cell followed the pattern showed by the plot below.

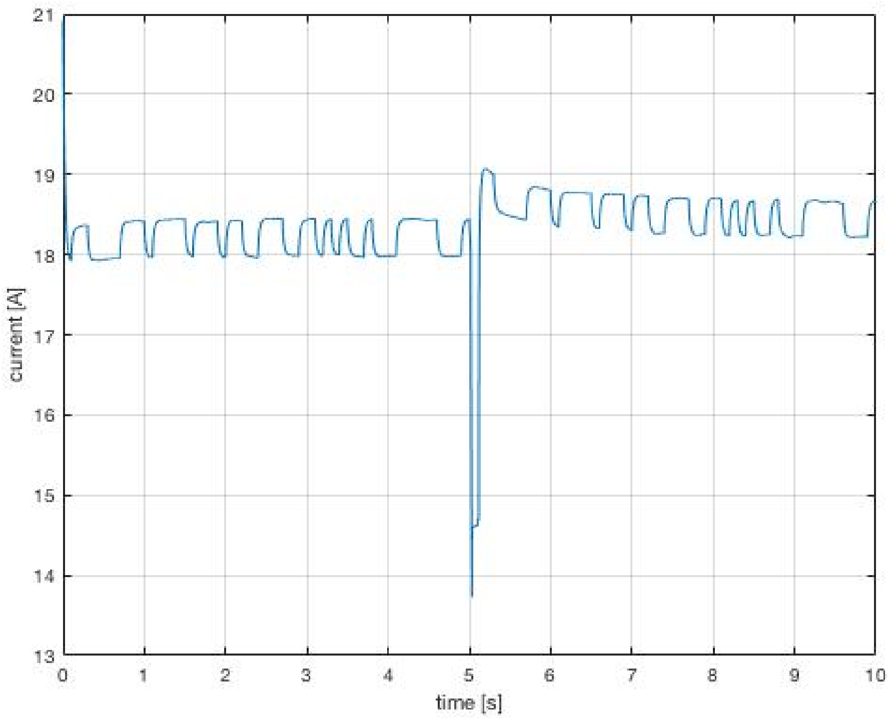


Figure 5 Evolution of the current signal that was sent to the cell

As it can be seen from the plot, the signals that the fuel cell system received were actually two. This was because, while in operation, the fuel cell used to short-circuit, so there were sent two signals to be sure not to lose any information in case of a short circuit during the time of the signal.

The next plots show the Power Spectral Density (PSD) of the signal, which represents basically the amount of information that can be obtained from a specific frequency.

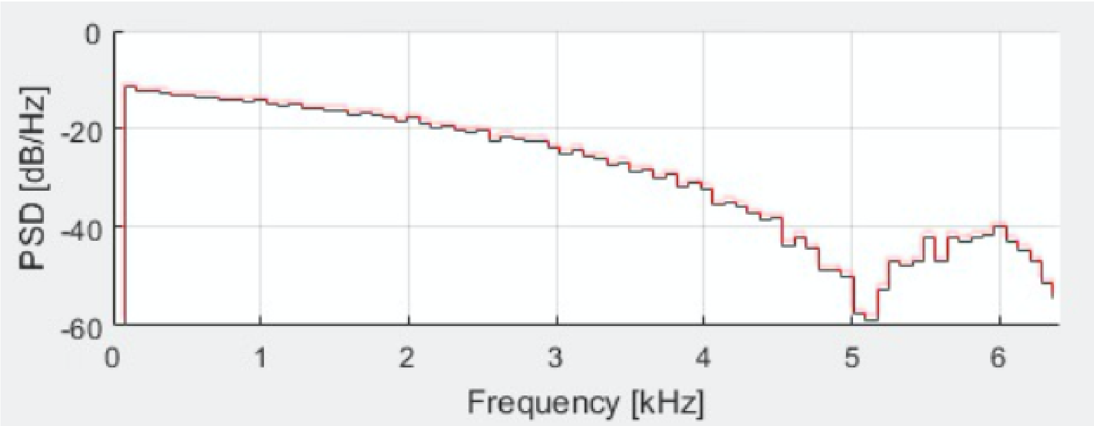


Figure 6 Power Spectral Density of a PRBS signal

As it can be easily noticed, the spectral density for a PRBS signal shows that the signal contains information spanning across many frequencies, especially low frequencies, where the PSD is higher. Again, the idea is to use a signal that covers multiple frequencies instead of individual sine waves of different frequencies to reduce the measuring time. There are other short signals with rich frequency content. However, PRBS is extremely easy to generate, even with cheap equipment. According to the test procedure, the signal had to be sent to the fuel cell system through the potentiostat at the beginning of each day and also during the cell operation every pre-fixed intervals of time. The PRBS signal only lasted around 10 seconds during which the potentiostat gathered all the data about current, voltage and power that were necessary to the code that was implemented to obtain the impedance. In fact, the post-processing of the data leaded to the impedance whose real and imaginary part could be plotted in order to obtain the Nyquist diagram from which it was easy to see how the performance of the cell got worse and worse as the operating hours were going on.

2. AUTOMOTIVE APPLICATIONS AND TEST PROCEDURE

2.1. Applications of Fuel Cells in Vehicles

The development of fuel cell vehicles would definitely be an important step forward the decreasing CO_2 emission, as a really important portion of the total is actually due to motor vehicles. Besides helping the environment and the economy, it is known that fuel cells have a higher efficiency than internal combustion engines.

As already explained, PEMFCs are the most suitable to be applied to vehicles thanks to their ability to allow fast start-ups and shut-downs due to the low operating temperature. Nevertheless, when it comes to automotive applications, one of the main concerns that needs a deeper analysis is the capability of the device to assure any amount of power required by the traffic conditions. As a matter of fact though, the efficiency of this technology during transient is still an issue that needs to be further analyzed. The dynamic loading cycling situation gives indeed a faster degradation of the cells and thus it is one of the main causes capable to decrease the durability of their lifetime. In order to investigate this aspect, it was necessary to put the fuel cell object of the test in a situation that would allow to simulate the condition that a normal vehicle in the traffic would be supposed to take care of. This typology of durability testing applied to cars is usually performed using the so called driving cycles, which are pre-defined schedules of vehicle operation usually expressed in terms of vehicle speed as a function of time. These cycles are produced by different organizations of different countries as they are really useful to verify the performance of the vehicles in a way that can be reproduced anytime under the same condition. To discover the consequences of the application of a dynamic load, the driving cycle that needed to be selected had to belong to the 'transient' category, according to which the vehicle would be supposed to be changing almost continuously its speed.

The driving cycle that has been chosen is called Urban Dynamometer Driving Schedule (UDDS), which can be found in the database of the EPA (US Environmental Protection Agency). This cycle is also known as "The City Test", as it represents the city driving conditions, and its speed pattern is plotted in the graph below.

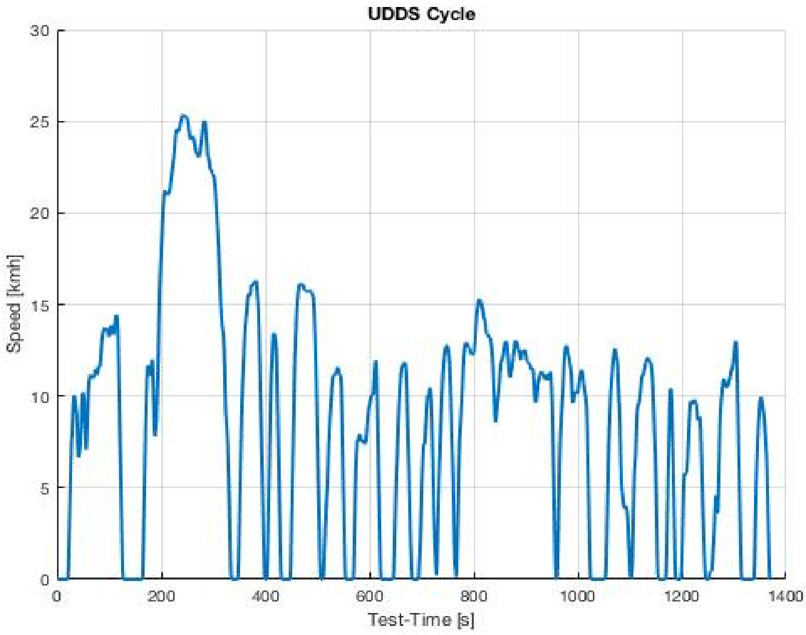


Figure 7 Speed Profile of the UDDS cycle

The UDDS driving cycle is used for light duty vehicle testing and its main features are showed by the following table.

Table 1 UDDS main features

Total distance	11996.85 m	Average speed (trip)	31.6 km/h
Total time	1369 s	Average driving speed	36.6 km/h
Driving time	1180 s	Standard Deviation of Speed	21.46 km/h
Drive time	247 s	Maximum speed	91.15 km/h
Drive time spent accelerating	506 s	Average accelaration	0.000 m/s^2
Drive time spent decelerating	427 s	Average positive acceleration	0.429 m/s^2
Time spent braking	271 s	Average negative accelaration	- 0.464 m/s^2
Standing time	189 s	Standard deviation of accel.	0.637 m/s^2
% of time driving	86.19%	Standard dev. of positive accel.	0.421 m/s^2
% of cruising	18.04%	Number of accelerations	48
% of time accelerating	36.96%	Accelerations per km	4.001 /km
% of time decelerating	31.19%	Number of stops	14
% of time braking	19.80%	Stops per km	1.17/km
% of time standing	13.81%	Average stop duration	13.5 s

The fuel cell was supposed to produce the amount of power that was necessary to assure to a hypothetical car the possibility to meet this cycle. The power output that the fuel cell was supposed to give was needed as input to the EC-Lab® software, which is a multi-device software that is able to control several potentiostats/galvanostats produced by the company Bio-Logic that designs research instruments for many applications, especially electrochemical ones. The Bio-logic device that was in the laboratory was connected to the fuel cell as its load. To obtain the power output profile that is necessary to meet the UDDS cycle, the ADVISOR software package was exploited. It is a vehicle simulation software developed by the US National Renewable Energy Laboratory (NREL) that uses a database that contains several kinds of vehicles, including simplified hydrogen ones, and also many types of driving cycles, including the UDDS. Thus, once the fuel cell car and the driving cycle had been selected, it was really simple to obtain the power output profile when the simulation had run through ADVISOR.

The plot shows the power out of the fuel cell needed to meet the UDDS requirement according to ADVISOR once that a rather simplified model of fuel cell car without energy storage and the desired driving cycle had been selected to run the simulation.

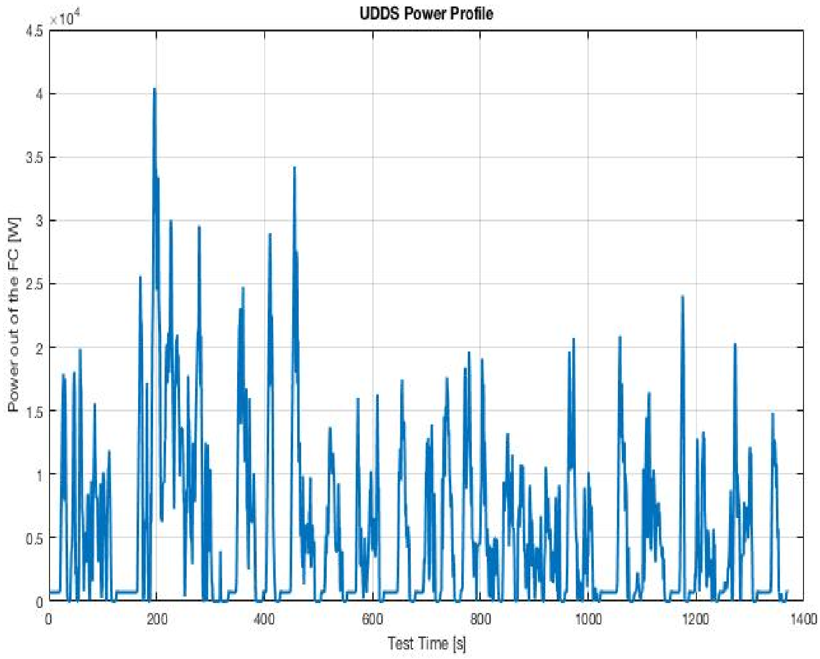


Figure 8 Power out of the Fuel Cell correspondent to the UDDS

As anticipated, the selected driving cycle needed to be characterized by many power fluctuations in order to challenge the fuel cell as much as possible. In order to have a better idea of the variations, the power had been evaluated not only as a function of time but also as a function of the frequency thanks to the Fast Fourier Transform (FFT). The plot below shows the comparison of the FFT of the UDDS cycle with the New European Driving Cycle (NEDC) which is the driving cycle typically used in Europe while the UDDS is more used in the United Sates. It is easily shown as the frequency of the UDDS is higher than the NEDC one, so this is the reason why the American cycle had been preferred. Submitting to the fuel cell to a more dynamic cycle means to challenge its capacity to face up transients in a much more effective way.

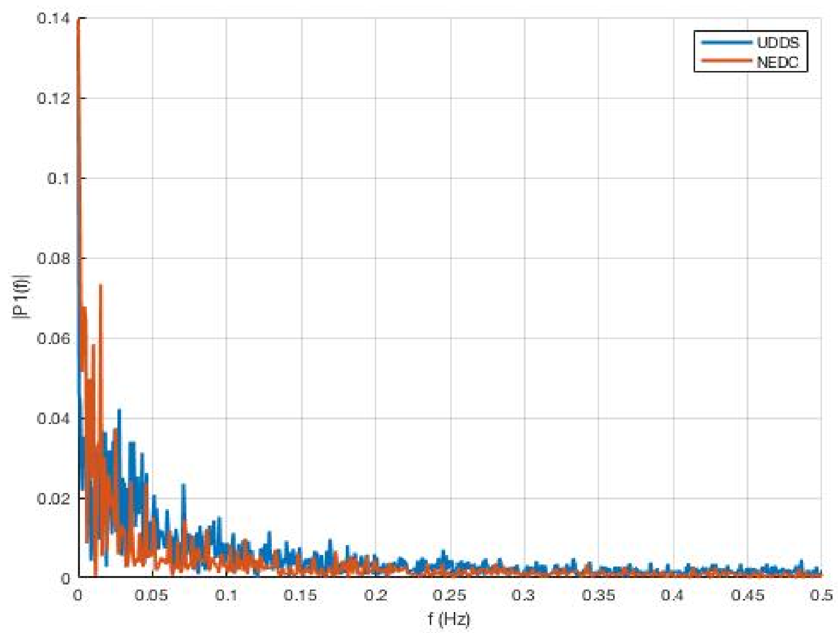


Figure 9 Comparison of the FFT of the power profile of UDDS and NEDC cycle

2.2. Test Procedure

Once the cycle had been selected, the fuel cell was ready to be submitted to the durability tests in order to find out how much time was necessary to it to fail. The failure was considered by the manufacturer to occur when the power was 10% less than the nominal one. The test procedure followed a fixed schedule which was made of 15 cycles in total, but more specifically it followed this pattern:

- At the beginning of each day, several fixed values of voltage were given as input to the software in order to obtain the correspondent values of current given by the fuel cell. The post-processing of these data would give as a result the polarization curve.
- A current following a pseudorandom binary sequence (PRBS) was sent to the fuel cell in order to perform the fast EIS.
- 5 UDDS cycles and again the PRBS to obtain a second fast EIS.
- 5 UDDS cycles, another PRBS and a second Polarization Curve.
- 5 UDDS cycles and the last Polarization Curve of the day.

In this way, it was also possible to see and analyze how the fuel cell performance would behave throughout a whole day of testing. The performance would not start decreasing as soon as the number of cycles would go on, but it would generally increase with the number of cycles in the beginning. The reason why the performance would initially improve is due to the level of hydration of the membrane which would get higher as the fuel cell kept working, while it would decrease during non-activity periods. The performance would start going down only after that the membrane is hydrated enough, which can take some time depending on how long the fuel cell has not been working (only a night or a whole weekend). The content of water in the membrane obviously depends on the temperature as well, so both the operating temperature of the fuel cell and the temperature of the room where measured during the tests.

3. RESULTS: POLARIZATION CURVES

3.1. From the data to the polarization curves

As already anticipated by the introductive chapters, all the data that the machine was able to gather during the testing days were postprocessed using MATLAB in order to obtain the polarization curves and the Nyquist diagrams of the impedances. Specifically, the data needed to build the polarization curves were collected every beginning of the day and every 10 and 15 cycles by the same machine that was connected to the load port of the fuel cell. This machine had as input the voltage profile that was required to be delivered by the cell and as output all the data about current corresponding to that specific value of voltage. In fact this is the typical *modus operandi* when a polarization curve has to be formed: a constant value of voltage was requested to the fuel cell which, in order to accomplish this requirement, delivered a certain amount of current that varied with time. The evolution of current though, used to be stopped by the short-circuit that characterized the working way of this cell and then the evolution of current would start again as shown by the following plot. This pattern (current evolution, short-circuit and then current evolution again) was repeated by the fuel cell around 4 times for each voltage value (blue lines).

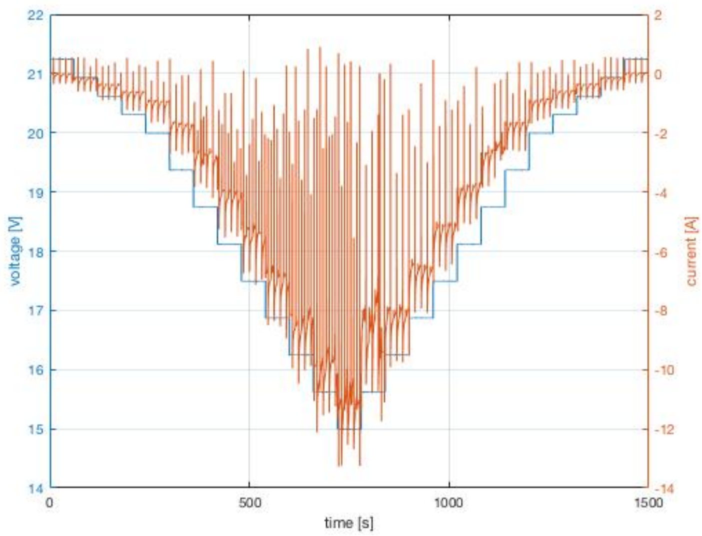


Figure 10 Example of the data necessary to build the polarization curve.

The last current evolution was used for the polarization curve as it was thought to be the more stabilized one. From this last current evolution with time, the average value of the current was computed. This mean current value was the one plotted in correspondence of that specific voltage step while building the polarization curve.

As it can be seen from the plot, the voltage that was required by the machine, starting from the OCV, was kept constant in time for a while and then it decreased of a certain fixed amount. When it reached 15 V, it started to increase of the same amount until its value was equal to the OCV again. The current that the cell had to deliver to satisfy the voltage followed a certain time evolution that was eventually stopped by the occurring of the short-circuit. The short-circuit can be easily noticed by the peaks of the current in the example-plot above. As anticipated, the post-processing of these row data consisted in calculating the value of current corresponding to each voltage value. During each voltage step indeed, the current increased gradually with time until the occurrence of the short-circuit, when it immediately reached the peak only to go back to the starting value of the evolution afterwards.

3.2. Polarization Curves

The following section shows the results of the post-processing of the data showed by the last plot. The polarization curves, showing the voltage or the power as a function of the current, are a powerful tool which can be really useful to evaluate the overall performance of the fuel cell system.

As already explained, when it comes to durability, the failure mode of the device is not given by a catastrophic failure, but it is caused by a decreasing of the performance. This is the reason why the polarization curves were not only used to study how the performance and so the power of the cell changed with the operating hours, but also to establish when the device had failed and the tests could be stopped. In fact, according to the manufacturer, the fuel cell life could be considered over when the power that could be produced had decreased of around the 10%. The following plots show an example of what was obtained from the data gathered during some of the first days of testing.

As it can already be noticed, the performance of the cell would decrease during a testing day.

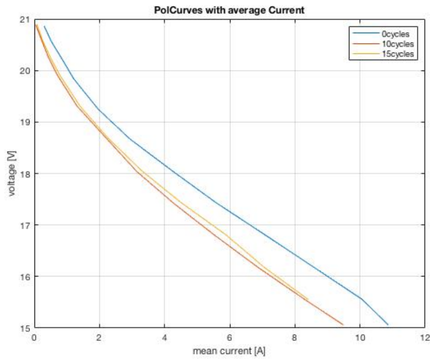


Figure 11 Polarization Curves referring to the first testing day (15th of March)

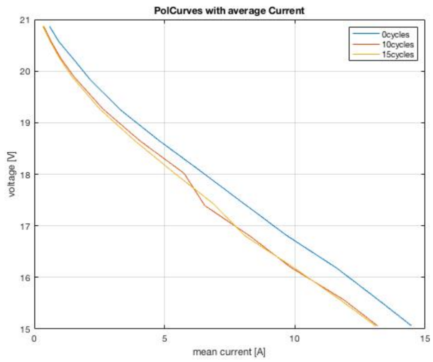


Figure 12 Polarization Curves Referring to the 5th day of testing (21st of March)

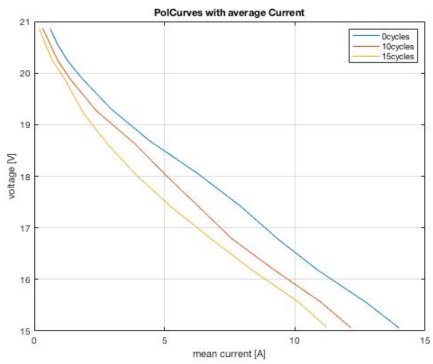


Figure 13 Polarization Curves referring to the 7th day of testing (25 March)

It is clear that the first cycle of the day (blue line) was characterized by a better performance than the last ones, but when the comparison between the polarization curves of different days was made something different came up, as it was anticipated while explaining the tests procedure and as it will be shown by the next plots.

This second group of curves refers to the first week of testing and it shows the comparison between different testing days but after a the same amount of cycles.

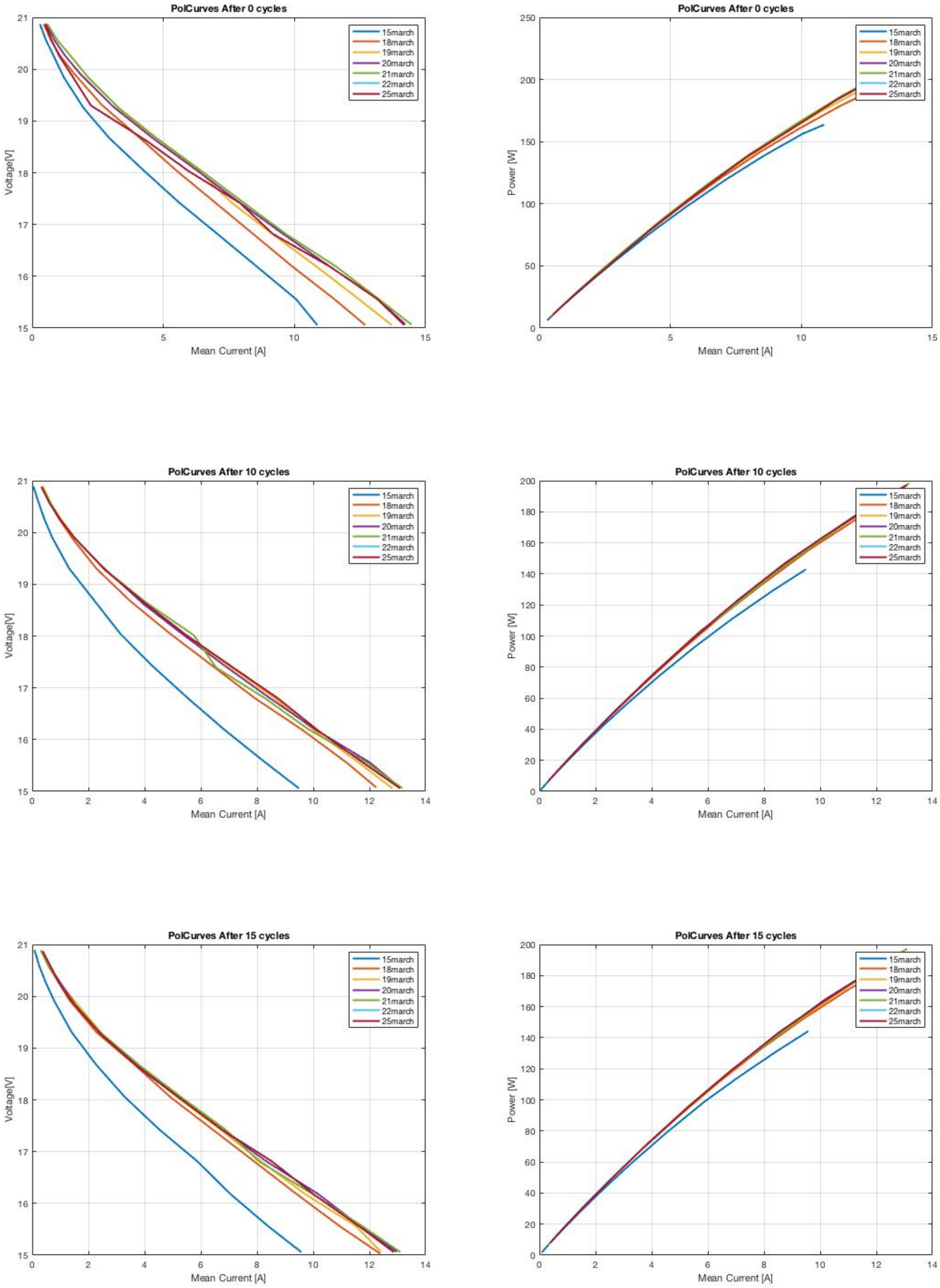
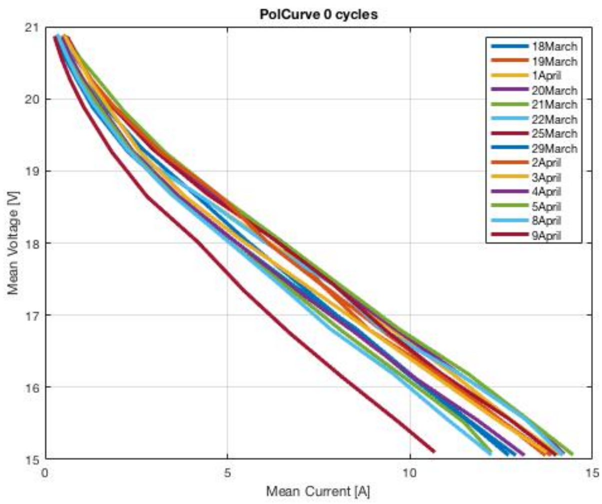


Figure 14 Voltage (on the left) and Power (on the right) versus Current after 0,10,15 cycles during the first week.

From this set of polarization curves, it is easy to see how the performance of the device started to improve once that it had been used for a while. In fact, the first day of testing was characterized by the worst performance of the week (blue line). The reason of the improvement of the polarization curves after some operating hours is given by the level of hydration of the membrane which is extremely able to influence the performance of the fuel cell. As a matter of fact, the more continuously the fuel cell keeps working, the greater amount of water is produced and the more the membrane gets hydrated. The membrane material needs indeed to be always hydrated enough in order to assure the hydrogen ions mobility which is what allow the circuit to be closed and so the electrons to flow. If the fuel cell has not been used for a while, the membrane would need some working time to reach a high enough content of water. Before the first day of testing, the fuel cell had not been used for several days so this is why the first day was characterized by a worse performance than the following ones. In fact, when a fuel cell has not been used for a while, it is not unusual to submit it to a reconditioning phase, which consists on imposing a certain voltage value for several minutes and then on decreasing it and wait again some minutes. This is a way to hydrate the membrane before the real operation starts. The quantity of water within the membrane is an interesting and crucial matter as it has to reach a tradeoff between a scarse amount, which would not allow the ions mobility, and an excessive quantity which would lead to the flooding of the system.

To sum up, it has been shown how in the beginning the fuel cell did not exactly react at the succession of the operating hours as it was expected as the performance and the power delivered kept improving during the first days of testing. The graphs about the whole testing duration will be displayed subsequently and they will finally show the fuel cell decay.

Here are listed all the graphs regarding all the testing days. Also because of the reasons just explained, it has been chosen not to plot the polarization curve referring to the very first day of testing (15th of March), when the fuel cell had not been used for several days, as it was thought the whole system could use the first day to get more stabilized.



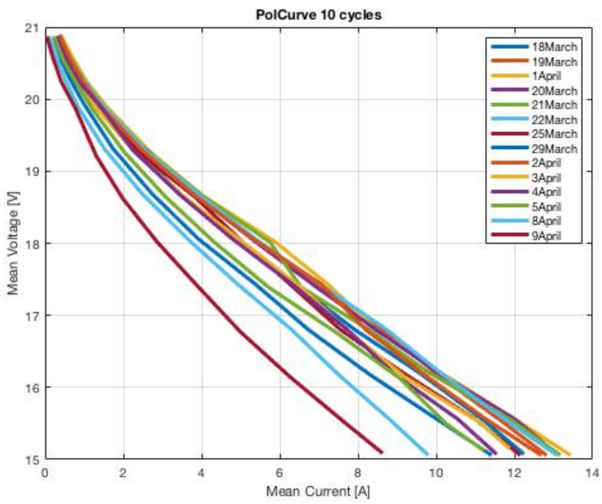


Figure 15 Polarization Curves referring to the whole duration of the tests (18th of March until 9th of April) after 0 cycles (upper graph) and 10 cycles (down)

The plots above show how the polarization curves (after 0 and 10 cycles) regarding the last day of testing stand out of the beam of polarization curves gathered in the previous days.

The reason that could be able to explain this behavior could be that, besides being the lifetime of the cell practically over as the performances level was not assured anymore, the last testing day (9th of April) came after a weekend, so the membrane was probably drier than the previous days. The lower water content together with the failure that had been reached by then, leaded to the worst performances ever recorded during the testing days. Nevertheless, as the polarization curves after 15 cycles can show, once that the membrane obtained a more sustainable level of water, its performance improved substantially, getting even better than the polarization curve obtained on the day before the weekend started.

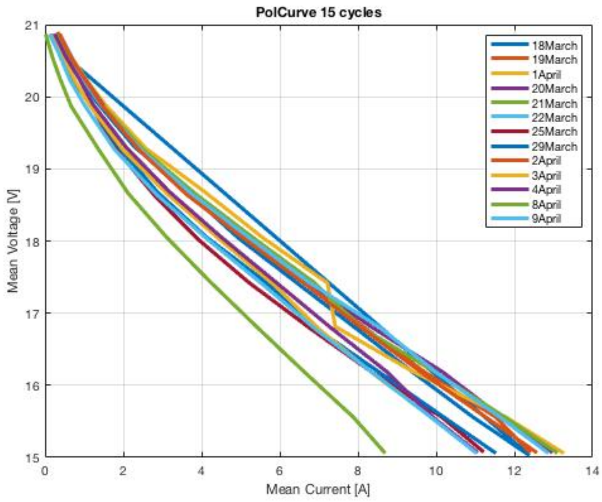


Figure 16 Polarization Curves referring to the whole duration of the tests (18th of March until 9th of April) after 15 cycles

The power delivered by the fuel cell did not decrease continuously, as some days are characterized by a better performance than the previous ones, but anyway the occurring of the decay cannot be denied as it is clearly shown by the graphs. After almost two weeks of testing, during which the fuel cell kept working for about 8 hours per day, when the polarization curves started to stand out of the beam formed by all the previous ones, the power delivered was finally too low and it was established that the fuel cell had reached its failure.

4. RESULTS: EIS

The polarization curves were not the only tool exploited to monitor how the fluctuations of the load imposed to the fuel cell are able to influence the durability of its lifetime. In fact, while the polarization curves can give a picture of only the overall system behavior showing the decreasing of the performance given by less power delivered as the operating hours go on, there is another popular tool that is able to give a better idea of the single components as well. As anticipated before, the diagnostic tool that was exploited for the analysis is called Electrochemical Impedance Spectroscopy (EIS), and its basic principle lays on computing the impedance given by the cell as a result of an alternate current signal that is imposed exactly for this purpose. The current signal that is selected must obviously be characterized by a low enough amplitude in order to avoid any damage to the fuel cell. The alternate current results in an alternate voltage response which allows to calculate the impedance exploiting Ohm's law:

$$Z(\omega) = \frac{E(\omega)}{I(\omega)}$$

Where ω is the frequency of the signal. The resulting impedance is obviously a complex quantity with a magnitude and a phase shift that depend on the frequency of the signal, which is why changing the frequency of the applied signal would bring a different impedance and thus it would allow to obtain the impedance of the system as a function of the frequency. If the frequency of the imposed signal varies between a large enough range, phenomena with different characteristic times can be analyzed through the results. The range that most interests electrochemical applications goes from 0.1 Hz to 100 KHz. The EIS procedure can be performed both in-situ and ex-situ. In the first case, which is the most popular and the one that has been performed for the purpose of this analysis, the AC impedance of the fuel cell is measured as a whole, while the second technique allows to study the single components separately. It has already been explained how applying many sine-wave signals of different frequencies would be extremely time consuming, especially as far as low frequencies are concerned, and that to face up this issue it has been chosen to apply a single signal able to cover multiple frequencies. As anticipated by the EIS introductive chapter, the signal that has been considered to be ideal for the purpose and the available timing of the research is called Pseudo-Random-Binary-Sequence (PRBS) which does not only contain information spanning across many frequencies, but it also is characterized by a power spectral density that happens to be higher in the region corresponding to the low frequencies. Therefore, the PRBS signal is able to give enough information even about all the phenomena and slow reactions in the fuel cell that are characterized by a long characteristic time and thus are related to impedance in the low frequency range. This kind of phenomena are actually really important ones so it is crucial to have the low frequencies region covered enough. The plot below shows the current signal that was imposed to the fuel cell together with the resulting voltage.

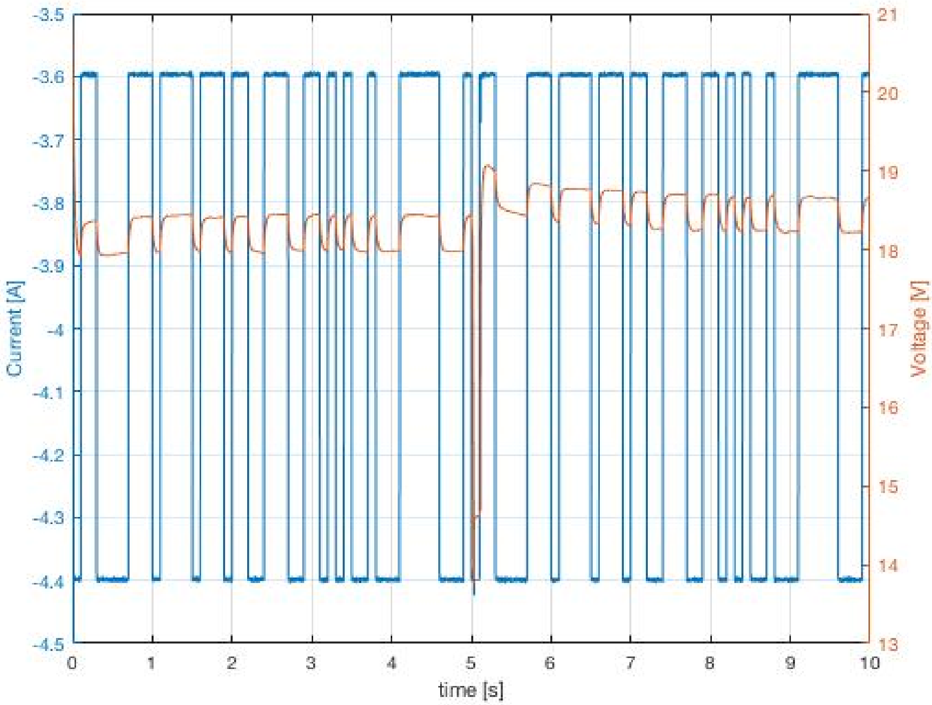


Figure 17 Current following the PRBS signal and the resulting voltage imposed to the fuel cell before starting with the cycles the 18th of March.

The data like the ones plotted above were post-processed through a MATLAB code in order to obtain the impedance of the fuel cell to varying the frequencies. The most common way to show the impedance spectra is given by the Nyquist plot, where the imaginary part of the impedance is plotted against the real part. The plot normally contains two or more semicircles, each one representing a different frequency range. The frequency range, together with the interpretation of general EIS measurements and modeling, is still a debates object. The next subchapter will try to give some basic notions about the Nyquist plots, its meaning and the equivalent circuit that can be extrapolated from experimental data. This basic knowledge is given before presenting the results of the impedance investigation of the fuel cell object of this research as it could help on interpreting the experimental data obtained.

4.1. Nyquist Plot and Equivalent Circuit

The impedance spectra shown by the Nyquist plots, or in general by any kind of plots, can be schematized and represented by equivalent circuits as well. The creation of circuits corresponding to the impedance given by EIS is a popular way of presenting this typology of investigation even though the correlation between the elements of the circuit and the physical properties or the process involved in the fuel cell is still not clear enough, as it will be further explained later on. In order to give a comprehensive vision of the EIS technique, the link between the equivalent circuit and the Nyquist plot is presented exploiting also the review study performed by Nyia et al., where are reviewed all the results obtained by the recent published researches about EIS. Some interpretation keys as well are in this way given.

4.1.1. Equivalent Circuit

The equivalent circuit modeling of fuel cells can be of two different kinds: process models and measurements model. In the first case, the governing equations of the electrochemical system are obtained and the impedance is obtained analytically. The physical properties of the system are then obtained through the comparison between the measured impedance and the one computed analytically. This models are rarely implemented as the governing equations are really complex and they need many simplifications. It is therefore hugely complicated to reach a predicted impedance close enough to the measured one. The measurements models instead are based on obtaining the impedance through measurements and then on producing an equivalent circuit able to give the same impedance for interpreting the physical properties of the electrochemical system.

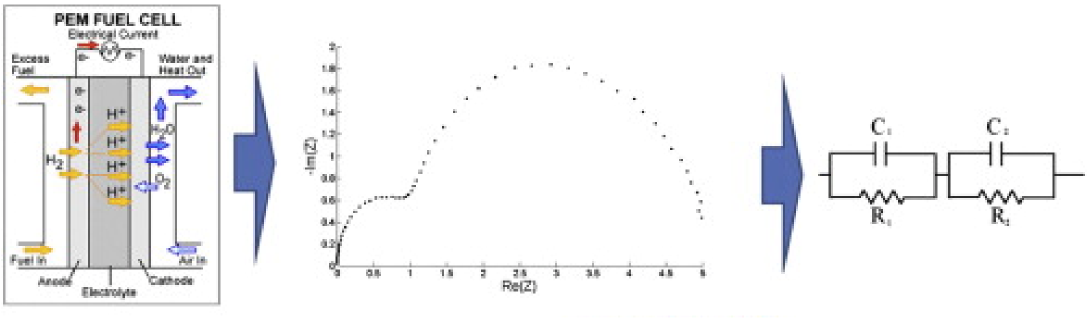


Figure 18 Schematic Representation of the measurements modeling

The parameters in these models though are not directly linked to the properties of the fuel cell so the governing parameters of the processes that take place in the fuel cell cannot actually be correlated to the values of the equivalent circuit elements in the measurement models. Nevertheless each of the involved processes has a different characteristic time which can be translated into the frequency domain, giving some indications about the processes in high, intermediate and low frequencies in the impedance plot. Even though the frequency range and the related interpretations in the EIS modeling is still matter of debates, some guidelines are now presented in order to clarify the link between a certain impedance spectrum and an equivalent circuit that could be useful in the attempt of interpreting the results of the EIS performed during this research. The equivalent circuit can contain various impedance elements able to represent the involved reaction steps. Typically, these elements are schematized as ohmic, capacitive or inductive components whose complex impedance depends on the frequency of the AC signal. The linking of the elements depends on temporal succession of the processes represented by these elements. Subsequently occurring phenomena are schematized through a series connection, while the phenomena that occur simultaneously are linked through a parallel connection. In case of fuel cells, all these processes are represented by the so-called Faradaic impedance Z_F which is linked in parallel to the capacitive element C, as the following picture will show. The Z_F-C block is in series with R_{ohm}, which represents the ohmic resistance of the circuit to the flowing of the current.

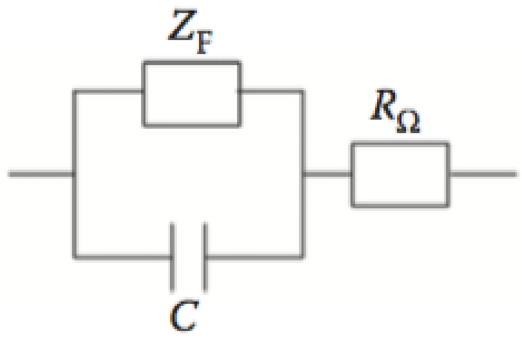


Figure 19 Common equivalent circuit describing the frequency response of a fuel cell

More often, the Faraidaic impedance is simply considered as a resistance, which is called charge-transfer resistance R_{CT}. The resulting equivalent circuit is shown below.

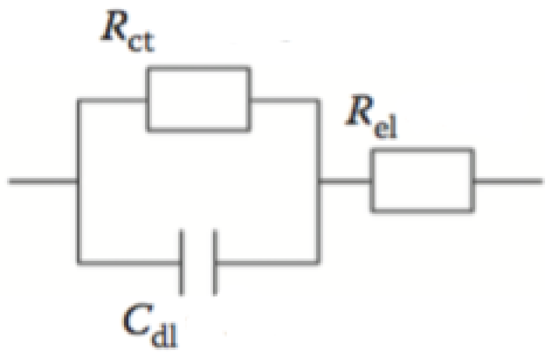


Figure 20 Simplest case of equivalent circuit

As it is known, a parallel connection between a capacitor and a resistor produces a semicircle in the Nyquist plot, while the ohmic resistance in series with the R-C block is represented by the first intersection of the plot with the real axes, being that part of the impedance characterized by a null imaginary part. The second intersection of the semicircle is given by the sum of the ohmic resistance and the charge-transfer resistance, which specifically is equal to the diameter of the semicircle. The following Nyquist plot shows the impedance spectra in the frequency range from 10 mHz to 10 kHz corresponding to the above equivalent circuit. All the other parameters just presented, such as the electric/ohmic resistance and the charge-transfer resistance are highlighted as well.

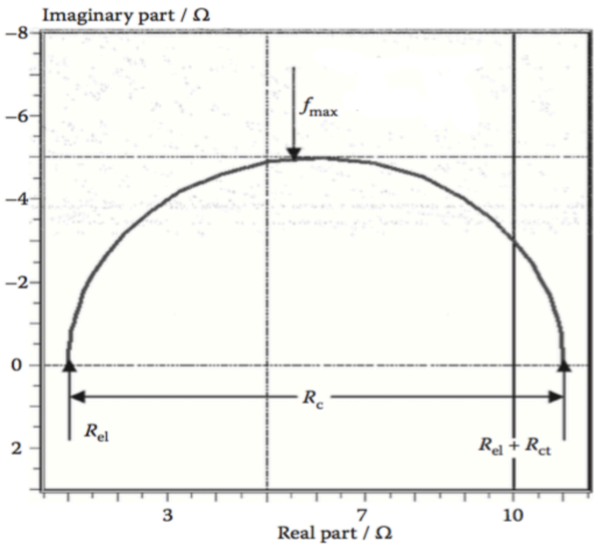


Figure 21 Nyquist Plot for the equivalent circuit of Figure20, frequency range: 10mHz-10kHz

Therefore, it is possible to obtain directly from the graph the ohmic resistance, while the charge-transfer one can be evaluated determining the diameter of the semicircle. It is even possible to obtain C_{dl} through the maximum frequency f_{max} with a simple equation:

$$2\pi f_{max} = \omega_{max} = \frac{1}{C_{dl}R_{ct}}$$

4.1.2. Frequency Range

The link between the capacitance and the frequency has been shown also by the study done by Nyia et al. in their review of the EIS technique. In their study, they exploit another example of equivalent circuit, which is displayed in the picture below.

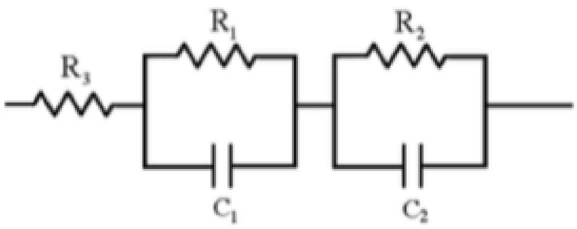


Figure 22 Equivalent circuit proposed by Niya et al. in their EIS review for the Journal of Power Sources 240(2013)281-293

The following figure shows the Nyquist plot for $R_1 = R_2 = R_3 = 1\ \Omega$, and $C_1 = 0.01$ F, $C_2 = 0.1$ F for a frequency range of 10 mHz-100kHz (the most common range as far as EIS measurements of fuel cells are concerned) with 100 points. The plot below is given by the convolution of two semicircles. The graph starts from 1 Ω as the intersection of the plot with the real axes is given by the only part of the circuit characterized by an impedance with the imaginary part equal to 0 and thus the part where $R_3 = 1\ \Omega$ lays. In fact, as already explained, this part of the circuit usually represents the ohmic resistance of the fuel cell. The other resistors values in the R-C blocks, define the semicircles diameter, in the below example given by Niya et al., $R_1 = R_2 = 1\ \Omega$ and thus the total range covered by the two semicircles is equal to $2\ \Omega$.

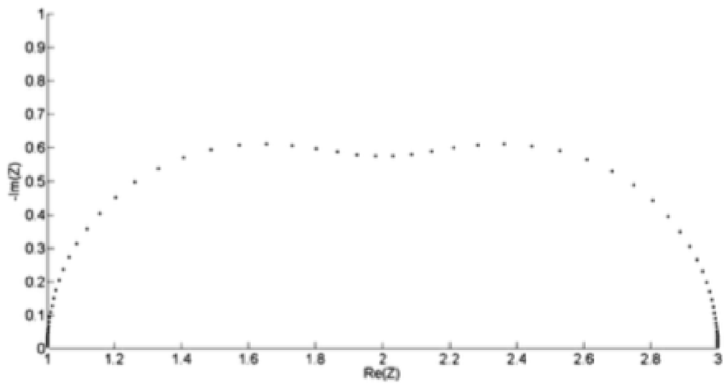


Figure 23 Nyquist Plot for $R_1 = R_2 = R_3 = 1\ \Omega$ and $C_1 = 0.01$ F, $C_2 = 0.1$ F for a frequency range of 10 mHz-100kHz

As a general rule, the right hand side of the plot is given by low frequencies while the left side is characterized by high frequencies region, as shown by the scheme below.

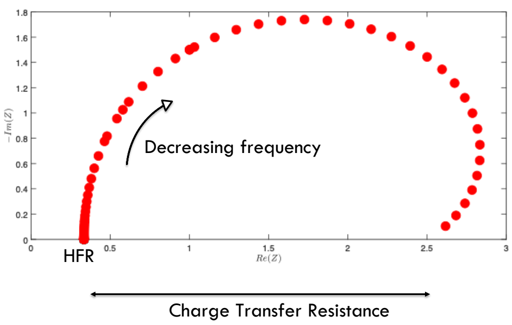


Figure 24 Frequency variation characterizing the Nyquist Plot.

The capacitors of the R-C blocks move the semicircles in the frequency range. In order to see how the position of the semicircle would be influenced by the capacitance value, another Nyquist plot has been built by the team operating for this study. In this example, $R_1 = R_3 = 1\ \Omega$ while $R_2 = 10\ \Omega$ and $C_1 = 0.01$ F, $C_2 = 0.1$ F, in such a way that the two semicircles are perfectly distinguishable from each other.

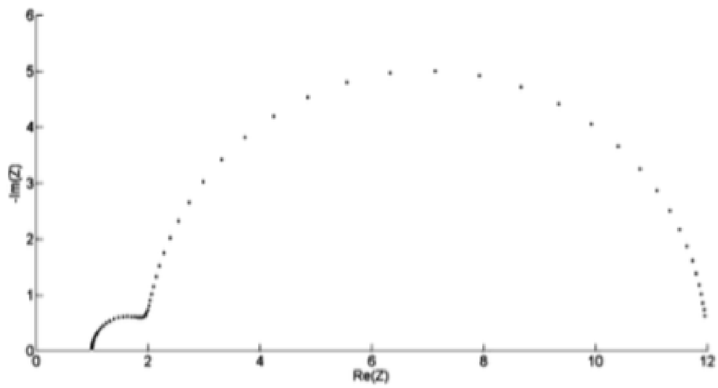


Figure 25 Nyquist Plot for $R_1 = R_2 = 1\Omega$, $R_3 = 10\ \Omega$, and $C_1 = 0.01$ F, $C_2 = 0.1$ F for a frequency range of 10 mHz-100kHz.

This example aims to show that the low frequency semicircle is related to the higher capacity (C_2 = 0.1F). Therefore, the higher capacitances influence the low frequency region of the Nyquist plot. This consideration can also be explained by the definition of the time constant of a parallel resistor-capacitor. In fact, the time constant is defined as t = RC, so the higher capacitances lead to larger time constants which means to slower reactions. The slowest reactions are the most important ones as they are obviously the most controlling, and hence the low frequency is the most important region of the Nyquist plot.

4.1.3. Nyquist Plots

All the Nyquist plot built with the data gathered during the tests will follow below. As anticipated, the PRBS signal was imposed to the cell at the beginning of each day and then after 5,10 and 15 cycles. All the data were then processed in order to obtain the Nyquist plots that will be shown below. The plots display how the impedance spectra of the cell varies as the days were going on. Specifically, it is easy to see how the semicircle generally increases its size and how it moves towards the right hand side of the graph, being the first intersection point of the graph always in movement towards the increasing real axes. The ohmic resistance increases indeed as the cell is submitted in more and more cycles, meaning that all the losses associated with this parameters become more important as the cell keeps being submitted to a transient load. The plots that will be shown now represent the behavior of the cell during each day of testing after 0,5,10 and 15 cycles respectively.

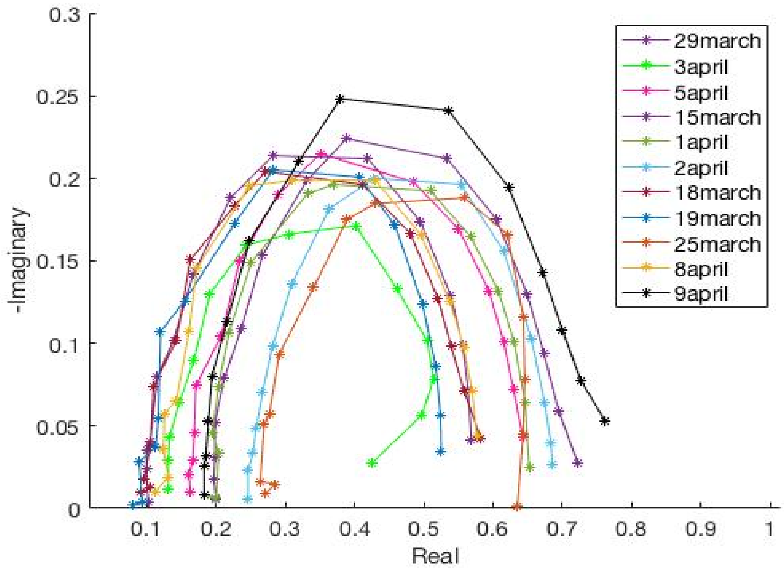


Figure 26 Nyquist Plots after 0 cycles

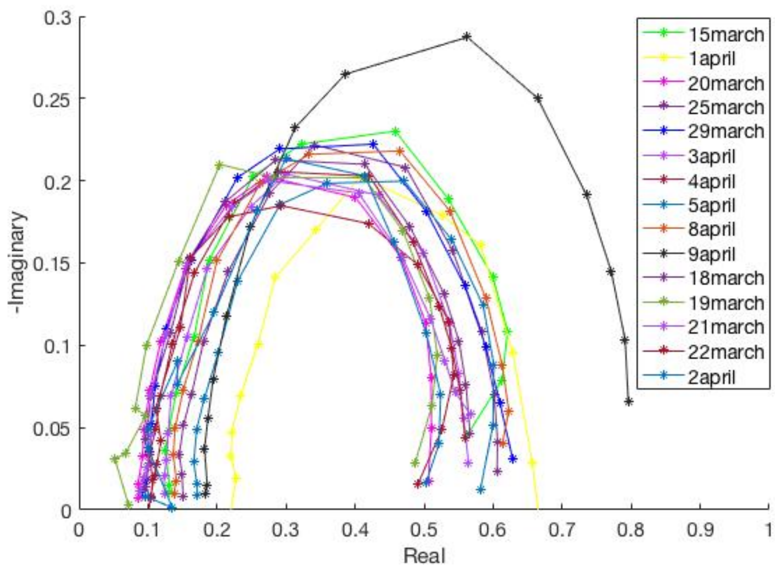


Figure 27 Nyquist Plots after 5 cycles

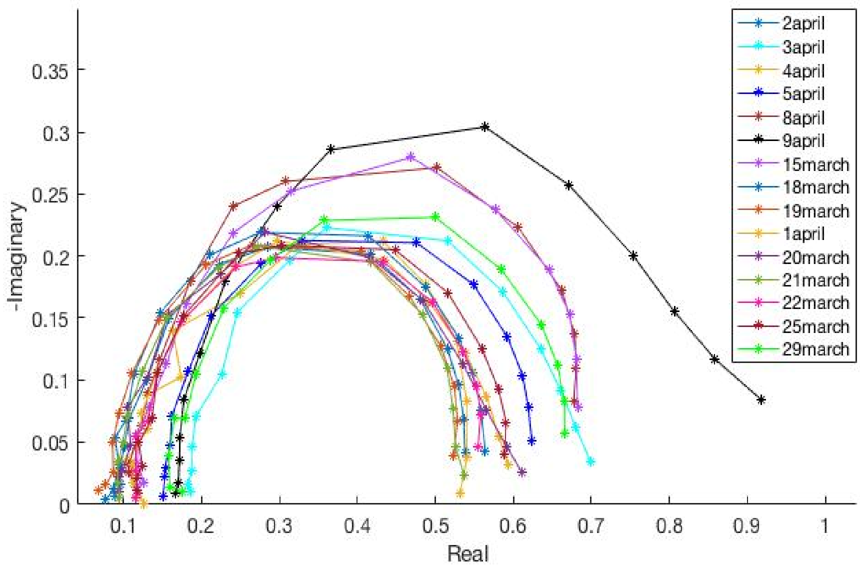


Figure 28 Nyquist Plots after 10 cycles

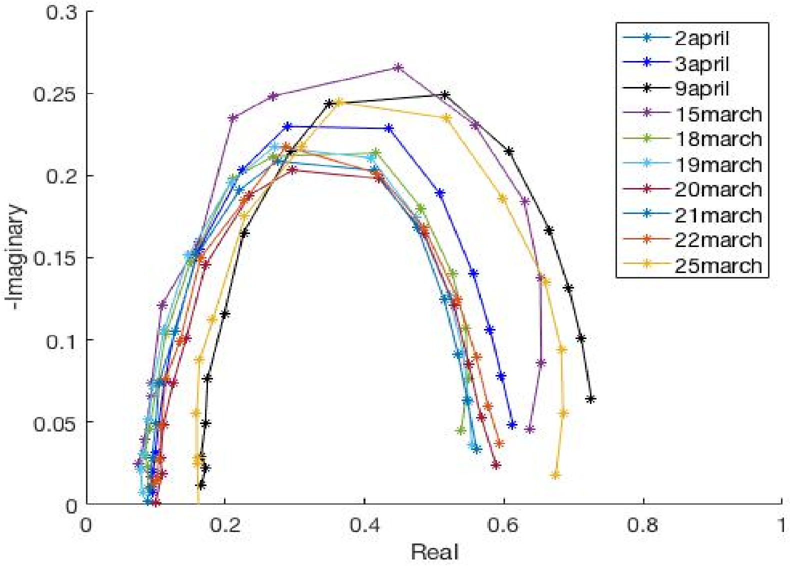


Figure 29 Nyquist Plots after 15 cycles

Once that it is possible to see clearly how the impedance spectra vary with the days, some considerations can be made:

- Generally, the semicircle representing the impedance of the cell in the Nyquist plot increases its size as the time goes on.

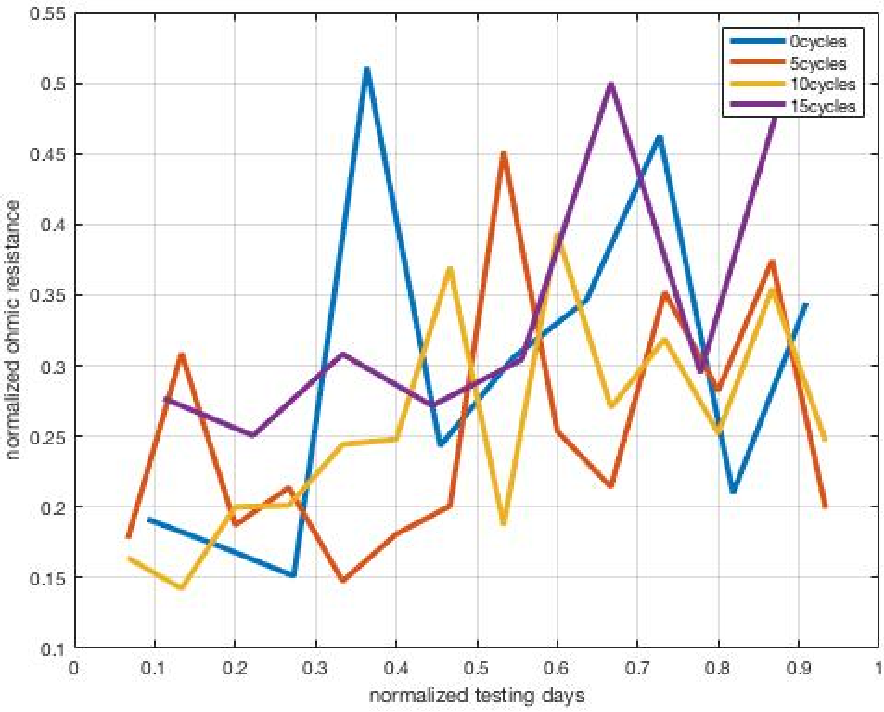
- Beside increasing, the semicircle moves towards the higher part of the real axes, which means that the ohmic resistance increases due to the submission of the transient load.

- The worst impedance is usually given during the last day of testing (9th of April, black line), when the curve stands out of the beam built by the other ones, as it used to happen in the polarization curves plots. It is clear that the lifetime of the fuel cell was over by then.

- The impedance spectrum obtained during the first day of testing (15th of March) usually shows a bad performance, which very often goes really close to the performance given by the last day. It is probably due to the fact that the fuel cell had not been used for a very long time before the tests started. As the aim of this work is to investigate the durability of the fuel cell, the behavior showed on the first day is not considered to be very interesting for this purpose.

- The parameters that could be extrapolated from these spectra, such as the ohmic resistances, the charge transfer ones and so on and so forth, could be used to build a degradation model of the fuel cell.

One of the main parameters of the fuel cell, which can even be deduced visually from the Nyquist plots, is the ohmic resistance that in turn can be obtained through the intersection of the plots with the real axes. The ohmic resistance gives information about the capacity of the system of conducting the ions. As the time during which the fuel cell is submitted to the load increases, this capacity decreases as shown by the behavior of the power delivered, and thus the resistance should supposedly increase. From the Nyquist plots it is easy to notice how the resistance gathered during the last day (black line) is usually among the higher ones, but it can be seen as well that the resistance does not decrease continuously, as it rather shows a fluctuating behavior. The next plot wants indeed to show the varying nature of the resistance.



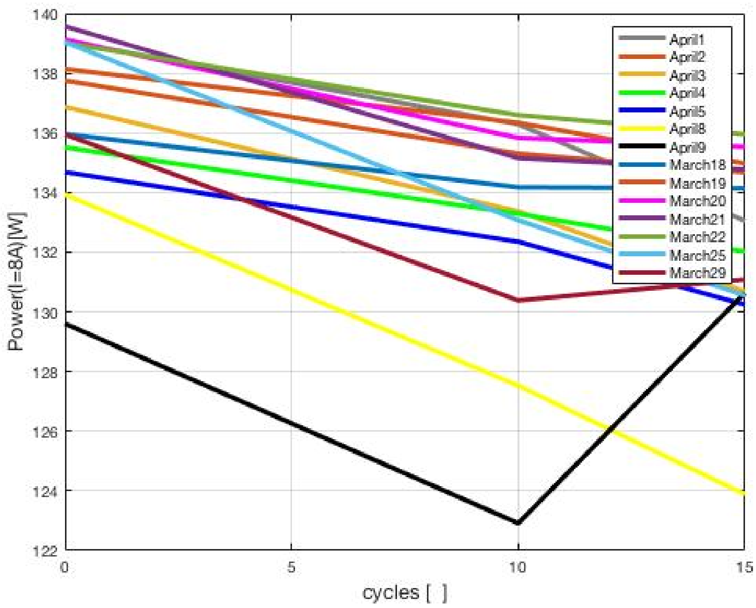
The plot shows the drastic fluctuations that characterized the behavior of the resistance, which is probably due to the fact that the efficiency of the ionic conduction does not only depend on the age of the fuel cell, or in how much time the cell has been working even though it is a fact that the resistance got higher at the end of the life of the fuel cell, especially as far as the resistance after 15 cycles is concerned.

5. DEGRADATION MODEL

As already anticipated by the previous chapter, many of the parameters that had been extrapolated from the data gathered during the tests could be used in order to build a degradation model. This model would be useful as it would be able to describe the aging process of the cell when submitted to a transient load. The response of the cell to this kind of stress is necessary to study the feasibility of the automotive applications. For the purpose of this analysis, two parameters had been chosen to build the model, each one of them has been extrapolated from the data obtained through each of the two diagnostic tools that have been used to check the behavior of the cell, which in turn are the polarization curve and the impedance spectroscopy.

5.1. Degradation model: power production

From the polarization curve data, the model that has been built aims to show how the degradation of the cell brings a decrease of the amount of power that the cell is able to produce. In order to first have a comprehensive vision of the behavior of the power through the testing days, it has been chosen to show the power corresponding to a fixed value of current, equal to 8 amps, as a function of the number of cycles.



Once again, the plot shows how the curves referring to the last days of testing stand out of the beam given by the data gathered during the first days, displaying in a clear way the failure of the cell. The worst value of power can be easily noticed, it is reached the 9th of April (black line) after 10 cycles, while it improves after 15 cycles. Starting from the scenario shown by the plot, a degradation model aimed to describe the decrease of the power given by the fuel cell was built. In fact the model starts from the distribution of power at a fixed value of current (I=8 amps), but instead of showing the relationship with the number of cycles, it has been chosen to study the power corresponding to the same amount of current as a function of the testing days. During each test day though, it is known that the polarization curves were performed three times, and thus at the end of each day three values of power were gathered, each one of them corresponding to the polarization curve after 0,10,15 cycles. Being the pursuit the obtaining of the power as a function of the testing days, an average between the values corresponding to 0,10,15 cycles was computed and the relationship between this average value and the days was reached. The plot that follows shows this evolution.

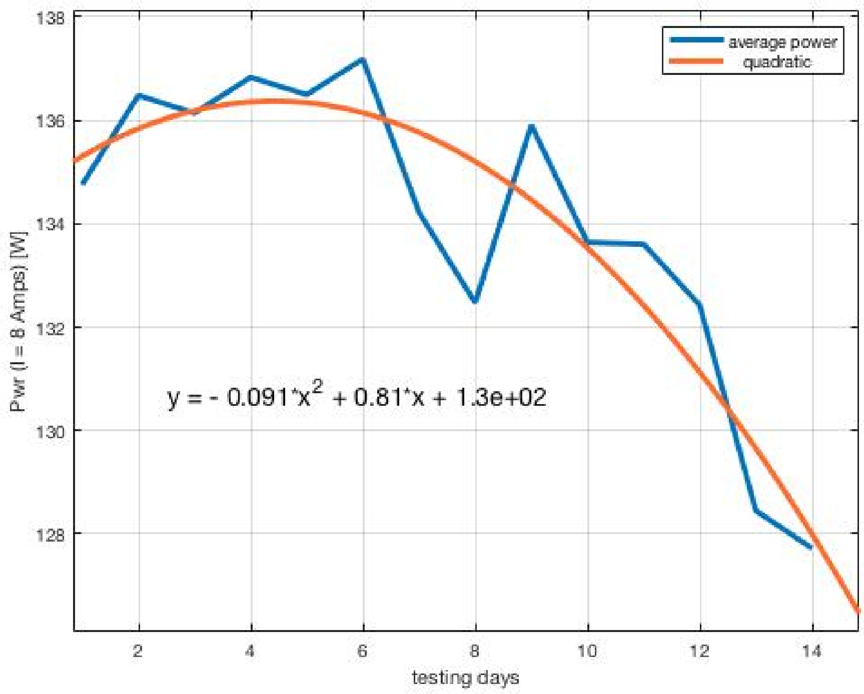


Figure 30 Average power distribution corresponding to a fixed value of current as function of the number of the testing days.

The plot shows how the daily average of the power values reached when the current was equal to 8 amps generally decreases through the days. In order to obtain a general law able to describe and maybe rule this decrease, the empirical data evolution had been approximated by a quadratic equation. The quadratic expression allows to obtain the decrease of the power as a function of the days, when this specific kind of load is applied. The equation is shown below:

$$P_{8amps} = 0.091 \cdot d^2 - 0.081 \cdot d + 1.3 \cdot 10^2 \ [W]$$

Where P_{8amps} is the average between the amount of power measured after 0,10,15 UDDS cycles at a current equal to 8 amps and d is the number of testing days that the cell has been submitted to. The value of current has been chosen as it is always halfway from the minimum amount of current and the maximum value (the maximum is always around 15 amps). Choosing this parameter at a different current value does not really affect the distribution, as the next plot will show.

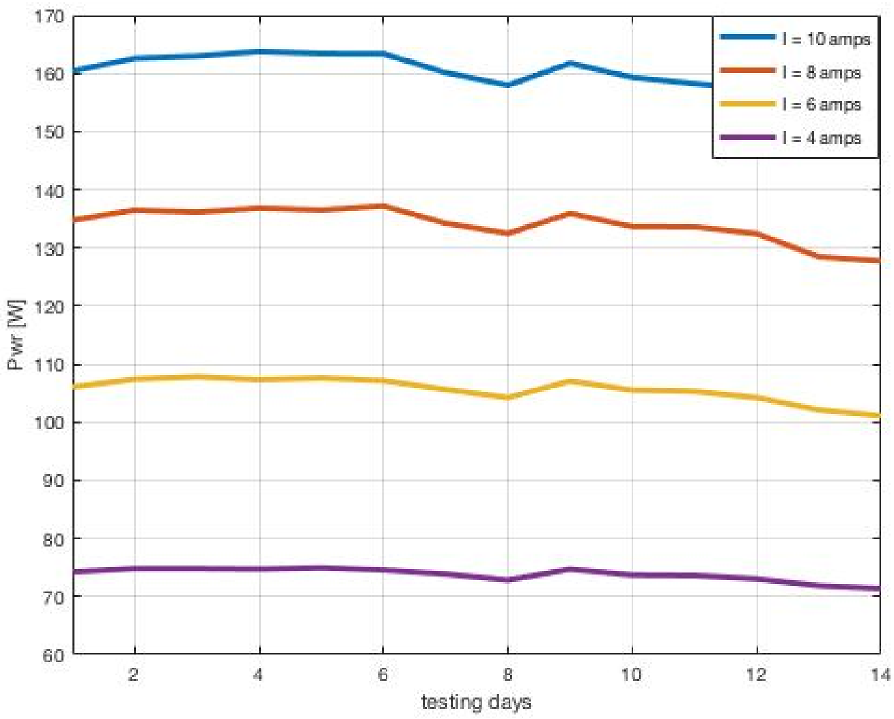


Figure 31 Comparison between power distributions at different values of current

5.2. Degradation model: ohmic resistance

Another parameter that could be exploited to describe the degradation of the fuel cell is the ohmic resistance. As anticipated, the ohmic resistance is a parameter that quantify the opposition that the circuit submits to the current flow. As the cell ages and it continues to deteriorate due the continuous application of the transient load, the performance of the device keeps getting worse, the power delivered is less and thus the circuit is less able to assure a current flow that is efficient as it used to be in the beginning of the lifetime of the cell. An increase of the ohmic resistance means that the current flow is more hindered and thus that the cell is decreasing its performance. The behavior of this important parameter has already been showed in the previous chapter, through a plot that contained the evolution of the ohmic resistance as a function of the testing days after 0,10,15 cycles. This plot shows that the resistance gets higher as the cell is getting closer to the failure, but not in a continuous way as it keeps having many fluctuations during the whole testing time. With this kind of varying data, it is not so trivial to build a comprehensive model

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