



Universidade do Minho  
Escola de Engenharia

Anthony Machado Dos Santos

Manufacture and characterization of a micro  
fuel-cell





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Professor Doutor Luís Miguel Valente Gonçalves  
Carlos Alberto Jorge Leite Faria

## DECLARAÇÃO

Nome: Anthony Machado dos Santos

Endereço eletrónico: anthonymdossantos@gmail.com      Telefone: 931433696

Bilhete de Identidade/Cartão do Cidadão: 13370747

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Orientador/a/es:

Professor Doutor Luís Miguel Valente Gonçalves

Carlos Alberto Jorge Leite Faria

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Assinatura:

*“Your focus determines your reality.”*

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## RESUMO

Hoje em dia, os equipamentos eletrônicos alimentados a bateria estão prestes a alcançar um ponto decisivo. Com o consumo energético dos componentes eletrônicos a seguir uma tendência decrescente e as baterias a aumentarem as suas capacidades, torna-se necessário procurar tecnologias alternativas para continuar a evoluir. As células de combustível são consideradas o próximo grande passo em termos de energia devido às suas várias vantagens, como a sua eficiência e a sua reduzida pegada ambiental. Com células de combustível é possível alcançar altas densidades energéticas mantendo uma elevada eficiência e um peso reduzido, algo essencial para pequenos equipamentos eletrônicos. No entanto, os elevados custos ainda impedem as células de combustível de se imporem nos vários mercados, desde dispositivos eletrônicos a sistemas de transporte.

Esta dissertação pretende estudar a possibilidade de adaptar uma célula de combustível com membrana de troca iónica para a mais económica célula de combustível de metanol direto, assim como os vários circuitos auxiliares necessários para obter melhor desempenho na célula. A célula utilizada foi uma Horizon Mini PEM fuel cell. Estes circuitos são o sistema de abastecimento de combustível, que possibilita o correto fornecimento de combustível à célula, um sistema de gestão de energia, de forma a permitir a célula fornecer uma tensão de saída adequada para uso, e um sistema de controlo, para efetuar a gestão de todos os sistemas referidos anteriormente.

Foram realizados vários testes, incluindo testes na célula, para tentar melhorar as suas capacidades. O sistema de abastecimento de combustível foi criado recorrendo a uma microbomba para fornecer o combustível e um conversor *step-up* para alimentá-la. Várias simulações foram realizadas numa primeira fase, com a implementação a ser efetuada em *breadboard*. O sistema de gestão de energia foi criado usando um conversor *step-up* da Linear Technology e componentes auxiliares, de forma a fornecer uma tensão de saída viável na célula, tendo sido implementado em circuito impresso. O sistema de controlo que deveria ter sido produzido tinha por base a plataforma Arduino e o microcontrolador Atmel ATmega 328.

Palavras-Chave: Célula de combustível, DMFC, PEMFC





## ABSTRACT

Nowadays, battery powered electronic devices are reaching a decisive point. With components energy consumption following a decrease tendency and batteries steadily improving their capacities, it is now necessary to look for other technologies to keep evolving. Fuel cells are considered the next big evolution for energy due to their great advantages, like efficiency and low environment impact. With fuel cells, it is possible to achieve high power density while keeping high efficiency and maintaining a low weight, which are key features to small electronic equipment. However, high prices are still keeping fuel cells from a breakthrough in all kinds of uses, from electronics to transport systems.

This dissertation intends to study the possibility of adapting an existing proton exchange membrane fuel cell to the cheaper to use direct methanol fuel cell, as creating several auxiliary circuits that are essential to a better performance of the fuel cell. The used fuel cell was a Horizon Mini PEM fuel cell. These circuits are a fuel supply system, for a correct fuel supply to the cell, a power management system, to enable the cell to have an adequate voltage for external usage, and a microcontroller system, to control all the previously referred systems.

Several tests were done, including performance tests for the fuel cell, to try to improve its capabilities. The fuel supply system was created using a micropump to provide fuel and a step-up converter to power it. Various simulations were made initially, and the first implementation was made on a breadboard. The power management system was created using an existing Linear Technology step-up and auxiliary components, to provide an eligible output voltage for the cell, being implemented on a printed circuit board. The control system was not produced, but was intended to using as basis the Arduino platform and the Atmel ATmega 328 microcontroller.

KEYWORDS: FUEL-CELL, DMFC, PEMFC



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## LIST OF ABBREVIATIONS AND ACRONYMS

PEMFC	Proton exchange membrane fuel cell
DMFC	Direct methanol fuel cell
R&D	Research and development
PhD	Doctor of philosophy degree
DC-DC	Direct current to direct current
PEM	Proton exchange membrane
MEA	Membrane electrode assembly
GDL	Gas diffusion layer
SOFC	Solid oxide fuel cell
MCFC	Molten carbonate fuel cell
PAFC	Phosphoric acid fuel cell
AFC	Alkaline fuel cell
GE	General Electric
NASA	National Aeronautics and Space Administration
NEDO	Department of the New Energy and Industrial Technology Development Organization
CHP	Combined heat and power
IC	Integrated circuit
MOSFET	Metal oxide semiconductor field effect transistor
PWM	Pulse width modulation
IDE	Integrated development environment
VDR	Voltage dependent resistor

# 1. INTRODUCTION

## 1.1 Background

The dissertation is the final curricular unit from the master's degree in industrial electronics engineering and computers, from Universidade do Minho, whose purpose is to promote initiative, decision making and creative and critical thinking. The dissertation consists of an individual research and development work lasting one year.

This dissertation and its R&D work are integrated in a PhD thesis and some of the work is the result of a joint effort between both master's degree student and doctoral researcher. The remaining tasks will be developed by the student, always under the guidance of both mentors.

## 1.2 Motivation

Nowadays everyone uses devices that are battery powered, be it a laptop, a smartphone or a MP3 player. The portable electronic breakthrough has given everybody the capability to have in their pocket more processing power than the one than was necessary to send Apollo 13 to the moon. Almost every one of these devices are battery powered and while batteries have advantages, technology is now reaching a point where the increase of capacity necessary to keep a device powered on is so massive that the portability of said device is compromised.

This first happened with laptops and it is now seen on tablets, smartphones and smartwatches, all smaller devices whose portability is increasingly crucial. After years in which components manufacturers have been able to decrease energy consumption, physical limitations are now being reached that makes impossible to keep this reduction without sacrificing performance. It is therefore necessary to look for alternative power source to this kind of devices and fuel cell can be easily considered as one of the best options to keep evolving.

Fuel cells can bring great benefits to users and manufacturers, like their high efficiency and low environmental impact and make it possible to achieve higher power density while maintaining a high efficiency and keeping the whole weight down, all key features to small electronic

equipment. However, high prices are still keeping fuel cells from a breakthrough in the most different kind of uses.

### 1.3 Objectives

This dissertation intends to study the possibility of adapting an existing proton exchange membrane fuel cell to be used with methanol as fuel, turning it into a direct methanol fuel cell.

Alongside with the fuel cell several auxiliary circuits will be studied, designed and implemented, including a fuel supply circuit, a DC-DC converter and a microcontroller, all necessary to create a complete fuel cell powered system. A majority of the components used in these circuits will be commercially available versions with established reputation in order to enhance the system reliability.

This dissertation expectation is to confirm the potential of fuel cell as an energy source to small electronic devices and verify its viability as a superior energy source. Difficulties on the manufacturing process are expected, even resorting to massively employed techniques. With successful integration on an electronic device, it is expected to be proven the possibility to produce fuel cell that can be used on everyday equipment's and encourage the study of this technology as a solution to increase gadgets autonomy.

#### 1.3.1 Proposal

The first goal is adapting the fuel cell. The fuel cell will be a Direct-Methanol Fuel Cell (DMFC), a specific kind of Proton- Exchange Membrane Fuel Cell (PEMFC), which uses methanol as fuel and water as oxidizing agent. The designed fuel cell will use a proton-exchange membrane commercially available and will use a system of micro channels to direct both fuel and oxidizing agents. The fuel cell should be able to provide a 0,2 ampere current with a voltage of about 1 volts and have a size of about 32 cm<sup>2</sup>. Secondly, a fuel cell prototype should be implemented, following the design previously obtained. Various prototypes made of multiple manufacturing processes will be implemented in different phases to examine the reliability, accuracy and performance of the different manufacturing methods. Both these goals will be completed by the doctoral thesis student and are not part of this particular dissertation. However, the final prototype will be used for a later analysis and integration.

Simultaneously, a series of circuits necessary for the correct functioning of the cell will be designed, implemented and tested. These circuits are vital to the fuel cell system and its implementation on an electronic equipment.

- Power management circuit: this circuit will be responsible for the conversion of current and voltage values obtained from the fuel cell to values that suit the specific use of the system.
- Fuel supply circuit: this circuit will be responsible for the correct supply of the fuel cell and consists of various components.
- The whole fuel cell system will be controlled by a programmable microcontroller. This microcontroller shall be responsible for startup management in the fuel cell and for the enabling and disabling of the system circuits in due course.

After all these circuits and systems are designed and implemented, they will be coupled together and the system will be tested as a whole. The cell will be then analyzed and characterized in order to verify if the expected performance is achieved. Operation temperature will be between 20 to 90° C, current output from 250 mA to 1 A and voltage output between 3.3 to 5 V. The size of the cell will also be considered.

If all these goals are completed, the cell shall be tested on an electronic device and its performance analyzed and compared to a normal lithium ion battery.

## **1.4 Dissertation's organization**

This dissertation is organized into seven chapters.

In the present chapter is presented the background of this dissertation, the motives and objectives that were proposed.

The second chapter presents the whole coverage of the state of art, including an introduction to fuel cells and their evolution, operation process and classification. While all fuel cells are addressed, the greater focus is on both proton exchange membrane fuel cell and direct methanol fuel cell.

Chapter three addresses the theoretical study needed for the completion of the dissertation, including the fuel cell study and the auxiliary system study.

Chapter four presents the implementation of all the circuits addressed in chapter three. The testing methodology is also presented as some of the problem and solutions found during the project's accomplishment.

Chapter five shows the testing and results achieved during and after implementation. These results are from both the individual circuits as well as the complete and final design.

Chapter six presents the conclusions of the obtained results and proposes improvements that could be made on future work.



## 2. STATE OF ART

### 2.1 Fuel cells

A fuel cell is an electrochemical device that converts chemical energy into electrical energy. For this, the device must have a series of necessary elements and a fuel and oxidizing agent supply. Fuel cells have been developing since their discovery in mid-nineteenth century and have diverged for several different operating principles and components with their evolution.

The fuel cell operating principle was discovered by William Grove in 1839. The continuous fuel cell development and study was prolonged on the nineteenth century, but the scientific community unanimously regarded them as too expensive to use on a real life situation. The emergence by then of technologies like internal combustion engine and electromagnetic induction, both with manufacturing costs substantially lower and a considerably higher simplicity level only strengthened that idea. The start of the space war resurrected fuel cell, as this kind of mission needed a higher level of efficiency. Research and development funded by the American space agency, as by various industrial companies, are still present in today's fuel cell.

As mentioned previously, a fuel cell is a device that transforms chemical energy into electrical energy, provided that there are two elements present, fuel and carburant. The fuel used, also called reducing agent, is the hydrogen, in its pure version or embedded in a compound, while the carburant, also called oxidizing agent, is oxygen. The cell is also composed of two electrodes, one negative, the anode, and one positive, the cathode, and an electrolyte between them.

#### 2.1.1 Evolution of fuel cells

The first device that can be considered a fuel cell in its most primordial form is the gas voltaic battery developed by the physicist William Robert Grove. This battery combined hydrogen and oxygen with a platinum catalyzer, being the first recorded case of creating an electrical current from an electrochemical reaction, and is presented on figure 2.1 [1].

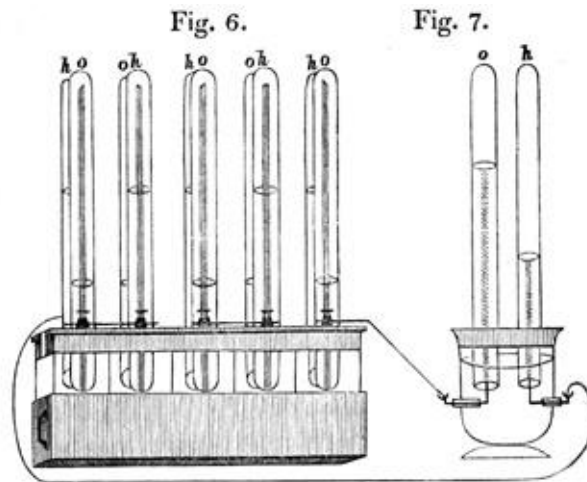


Figure 2.1 – Grove's Gas Voltaic Battery is considered the first fuel cell in history [1].

The term fuel cell was used firstly by the German chemist Ludwig Mond, in 1889, in collaboration with his assistant Carl Langer. Using as base a gas named Mond-gas, derived from coal, Mond's fuel cell was able to provide 6 A per 0.1 m<sup>2</sup> at 0.73 V. This cell introduced the fundamental basis that are still used in nowadays cell and can be seen on figure 2.2. At this point, other chemists were investigating fuel cells, but the general conclusion was that, despite the good performance in a laboratory environment, the cost associated with fuel cells were too high for real world usage. Only in the mid-twentieth century designs were produced using Mond's cell as basis. Engineering professor Francis Bacon presented a system capable of producing 5 kW [2].

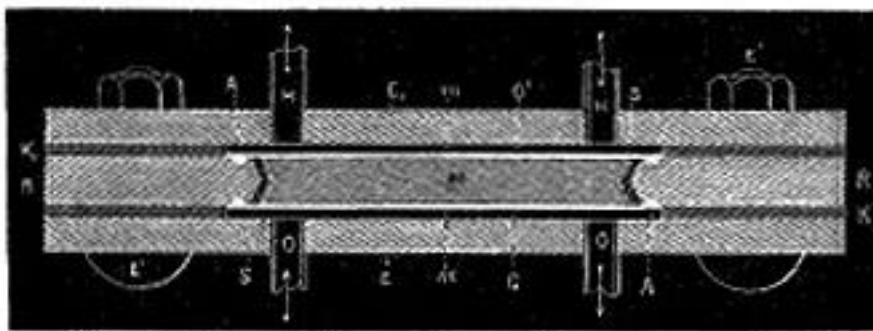


Figure 2.2 – Ludwig Mond was the first to use the fuel cell denomination. Mond's cell has been the basis of fuel cell development, being only implemented almost one century after it's creation [2].

While initially fuel cell development was focused on coal as fuel, other types of cells were created with the continuous evolution and research. Emil Baur and his colleague Preis

developed the first solid oxide fuel cell in 1937 and Bacon was responsible for the great evolution of the alkaline fuel cell, also called the Bacon cell in his honor [3]. Bacon and his cell can be seen on figure 2.3.



*Figure 2.3 – Francis Bacon was responsible for the creation of the alkaline fuel cell, one of the most important developments in the fuel cell department [3].*

The alkaline fuel cell became one of the most important development in fuel cell history. Pratt & Whitney Aircraft, after licensing the Bacon Fuel Cell, was chosen by the National Aeronautics and Space Administration (figure 2.4) to develop an alkaline fuel cell to be used as power supply for the auxiliary unit of the Apollo spatial module. This cell was able to supply power to the communication, water production and life support systems for two weeks [4].



*Figure 2.4 – A bacon fuel cell was chosen by NASA to provide energy for the Apollo spatial module [4].*

The American space program opened a new opportunity window for the fuel cell development. General Electric was one of the companies involved and had one of the most ambitious research program. This effort became productive when two researchers, Willard T. Grubb and Leonard Niedrach started their investigation on the “ion exchange membrane cell” that became the Proton Exchange Membrane Fuel Cell in 1955. First able to generate only 0.02 W, the “Grubb-Niedrach fuel cell” was simpler in design and operation than Grove’s cell, and was further improved when Niedrach was able to devise a way of depositing platinum onto the fuel cell. This final design was used by NASA in its Gemini Program, and consisted of 96 cell in three parallel group of 32 cells, able to provide 1 kW.

The following decades brought great advancements on fuel cell technology, with the Cold War embargos and oil crisis forcing manufacturers to invest on fuel cell research as a viable alternative energy. Concerns about air pollution also instructed the reduction of harmful vehicle exhaust gases and was eventually adopted in many countries around the world. Low ecological footprint and high efficiency were to become two of the main reasons for fuel cell adoption. In this context, Direct Methanol Fuel Cell (DMFC) were created in the mid-fifties. Initially, the performance was quite low, but more recent investigations brought together DMFC and PEMFC, by using Proton-Exchange Membranes (PEMs) on DMFC, increasing performance and endurance from DMFC.

### 2.1.2 Fuel Cells Components

Although there are several types of fuel cells, all have the same basis constitution: two plates, which can be bipolar, an electrolyte, two catalyzers, an anode and a cathode, and two sealants. The electrolyte and catalyzer ensemble can also be called, on certain fuel cells, as membrane electrode assembly (MEA), constituted by a membrane that works as electrolyte, the two catalyzer and also two gas diffusion layers (GDL). The fuel is provided through the anode, while the carburant is delivered by the cathode.

Each of these components have distinctive functions. The GDL grant a direct and uniform access of the fuel and carburant to the catalyst layers. This increase the rate of each semi reaction, for a superior performance. The electrodes allow a reaction between oxidizer and fuel without causing corrosion or consumption thereof. One of the fundamental conditions of the electrodes is being electronics conductor, necessary due to the need for contact between fuel,

electrolyte and electrode. The electrolyte has as its purpose enabling diverse ions ( $H^+$ ,  $OH^-$ ,  $O_2^-$ ,  $CO_2^{-3}$ , others) flowing from one electrode to the other, across the electrolyte [5].

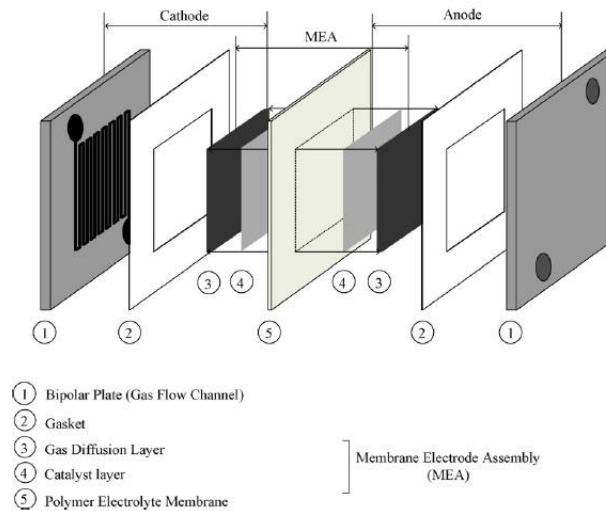


Figure 2.5 – A typical PEM schematic, with its several components [6].

### Fuel Cell Components Analysis

Each of the components of the fuel cell has a specific purpose, with all parts working together. All fuel cells share the same key components, but in some cases, like on proton exchange membrane fuel cells and direct methanol fuel cells, a different terminology is used. These components can be seen on figure 2.5.

### Electrolyte

The electrolyte (proton exchange membrane on DMFC and PEMFC) function is to simultaneously allow protons (hydrogen ions) originating from the anode to pass through it and prevent electrons from doing the same, forcing them to go through the collector from the anode to the cathode, providing therefore electric energy. Another function of the electrolyte is to be a barrier between both gas layers.

### Catalyzer

The catalyzers, anode and cathode, are electrodes that contain catalysts that causes the fuel to undergo an oxidation reaction, which generates both protons and electrons. The catalyst most used is platinum since it is the best material to achieve a lower activation energy on both

oxidation and reduction reactions. Nickel can also be used as catalyst on the cathode. Both catalyzer must be simultaneously on contact with fuel, oxidizer, electrolyte and gas distribution layer.

### Gas Diffusion Layer

The GDL is located between catalyzers and diffuser plates. The GDL is usually a porous material composed of a dense array of carbon fibers, functioning as an electronic connection between plates and catalyzers. This allows the passage of reactant components and also the byproducts of the reactions, like water and heat. It also protects the catalyzers from erosion or corrosion and is generally hydrophobic to improve water transport. This hydrophobia is commonly obtained by treating the GDL with Teflon®.

### Diffuser plates

The diffuser plates are responsible to provide both fuel and oxidizer and dispose the water and heat resulting from the reactions. They are also responsible to carry the current away from the cell and it is through these plates that it is possible to connect several cells in series.

### Retainers

The retainers are the external part of the fuel cell and have as function avoid gas leaks that could harm the cell's performance. The materials used must be stable in acid and humid environments and also tolerate hydrogen and air contact at the fuel cells operation temperature. The retainers are also called gaskets.

#### 2.1.3 Fuel Cells Classification

As previously mentioned, several kinds of fuel cells exist nowadays. While they share the same basic constitution, these cells differ on type of electrolyte used in its manufacture, sort of fuel employed and operating temperature. As such, different fuel cells see different real world application, although some are competing with each-other. The following cells are currently the most used, but several other are also on production and many more are still on a R&D status [7].

### *Solid Oxide Fuel Cell*

Solid oxide fuel cells (SOFC) are one of the most recent designs of fuel cell created. While older designs require delicate and expensive materials, like precious metals or acids, the SOFC was the design resulting from trying to reduce material costs and take advantage from the produced heat.

SOFC uses, as the name indicates, a solid oxide electrolyte, using cheaper ceramic materials comparing with other fuel cells. Their operating temperature is around 500 to 1000 °C, a high value that improves reaction kinetics. SOFC are one of the most efficient design of fuel cell commercially available, with efficiency that can reach over 60% when converting fuel to electricity and even 80% if the produced heat can be harnessed. They can provide from 2 kilowatts to some megawatts.

Advantages of SOFC are their low cost, high efficiency and stability and a great fuel flexibility. However, the high operating temperatures needed causes long start-up times and compatibility issues [8].

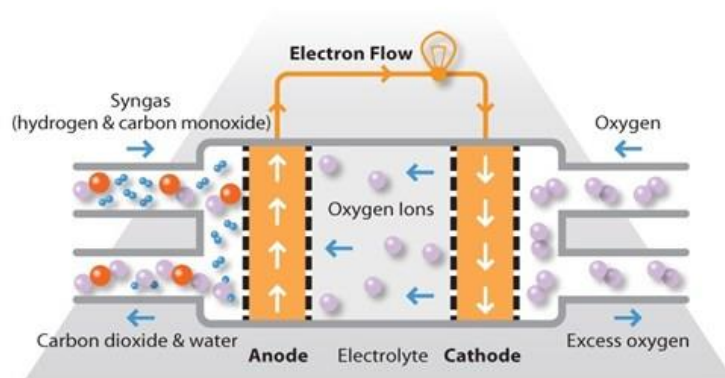


Figure 2.6 – Reactions and products of a solid oxide fuel cell [8].

### *Molten Carbonate Fuel Cell*

Molten carbonate fuel cells (MCFC) use a molten carbonate salt suspended in a porous ceramic matrix as the electrolyte. Their operating temperature is very high, about 650 °C, which allows the reaction to occur well without the boost provided by noble metal catalysts. As with SOFC, efficiency can attain values as high as 80% if heat harnessing is considered. They are able to supply power values in the megawatts range.

The great advantage of MCFC is the capability of using various fuels, like coal-derived fuel gas, methane or natural gas. However, MCFC need  $\text{CO}_2$  to be injected to the cathode. The liquid nature of the electrolyte also causes problems, as does the high operating temperature [9].

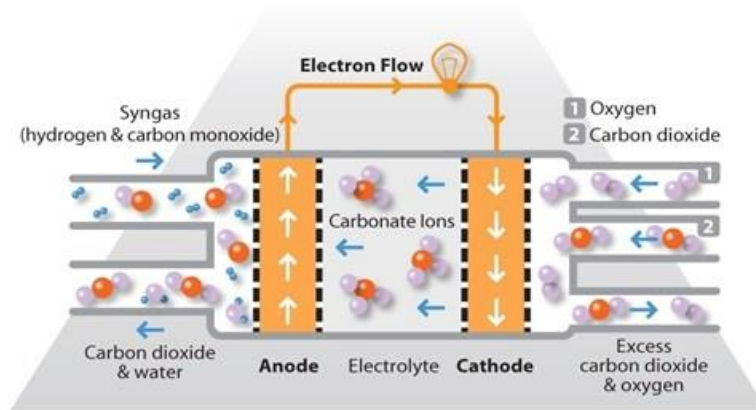


Figure 2.7 - Reactions and products of a molten carbonate fuel cell. [9]

### Phosphoric Acid Fuel Cell

Phosphoric Acid Fuel Cells (PAFC) uses both anode and cathode made of carbon and silicon structure with a fine platinum catalyst layer and a phosphoric acid electrolyte between them. Their operating temperature is around  $180\text{ }^\circ\text{C}$  and they have an output between 100 and 400 kilowatts, with an efficiency that can reach 70%.

The PAFC is one of the oldest designs available and almost every fuel cell sold before 2001 is a PAFC. Their greatest advantage is their high resistance to the presence of carbon dioxide. However, they have a low power density, especially when compared with methanol based fuel cells. They are used to power fuel cell equipped vehicles like buses and are still being researched for other uses [10].



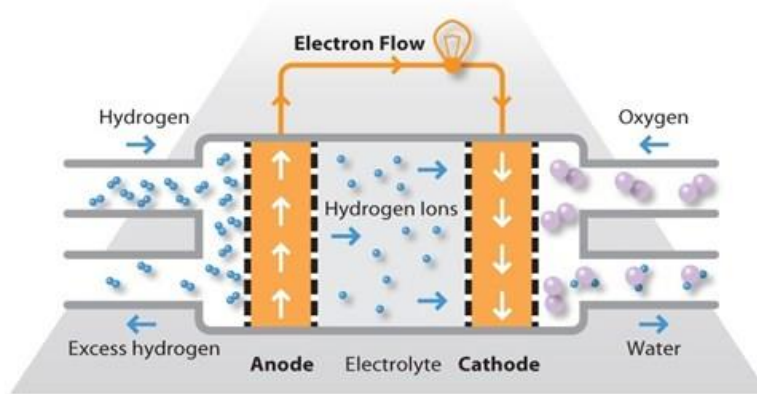


Figure 2.8 - Reactions and products of a phosphoric acid fuel cell [10].

### Alkaline Fuel Cell

Alkaline fuel cells (AFC), also called by some the Bacon fuel cell, are one of the first and probably the most developed designs of fuel cell. The electrolyte used is an alkaline one, like potassium hydroxide, and is normally fueled by pure hydrogen. While originally their operating temperature could go as high as 250 °C, they are now around 70 °C and even reach values as low as 23 °C. With efficiency reaching 60%, they are the cheapest fuel cells to manufacture.

AFC have several advantages, like high output voltage and low manufacturing costs, due to the cheap electrolyte and the usage of not-noble materials on the electrodes. However, they are highly sensible to carbon dioxide presence. The usage of pure hydrogen also is a disadvantage for this fuel cell technology [11].

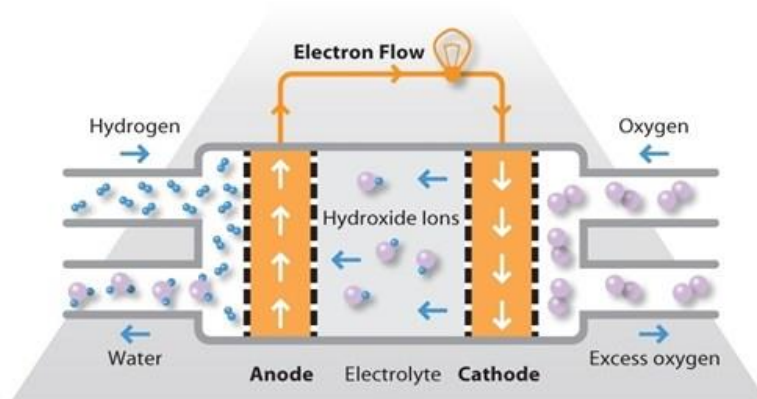


Figure 2.9 - Reactions and products of a alkaline fuel cell [11].

### *Proton Exchange Membrane Fuel Cell*

Proton Exchange Membrane Fuel Cells (PEMFC) are one of the most promising and simpler fuel cell designs. The electrolyte is a water-based acidic polymer membrane and the cell has a low operating temperature, between 30 and 100 °C. This forces the usage of sophisticated catalyzers and electrodes, which use platinum or other noble metal as catalyzer.

PEMFC use pure hydrogen as fuel and have a very low tolerance to CO: more than 10 parts per million can heavily decrease the cell's performance. They also must have a complex water management system, as the membrane must always be humid, but not without too much water to not compromise the performance. Efficiency range between 30 to 40%. However, even with all these disadvantages, PEMFC are one of the fuel cell technology with the bigger probability of a breakthrough, as they also have many advantages: they are one of the few cell whose power requirements are dynamic, they have an high power density and can be miniaturized. Water is the only waste product, and that makes them one of possible “power source of the future”, especially in terms of vehicles. Several manufacturers are currently implementing PEMFC systems on new vehicle prototypes [12].

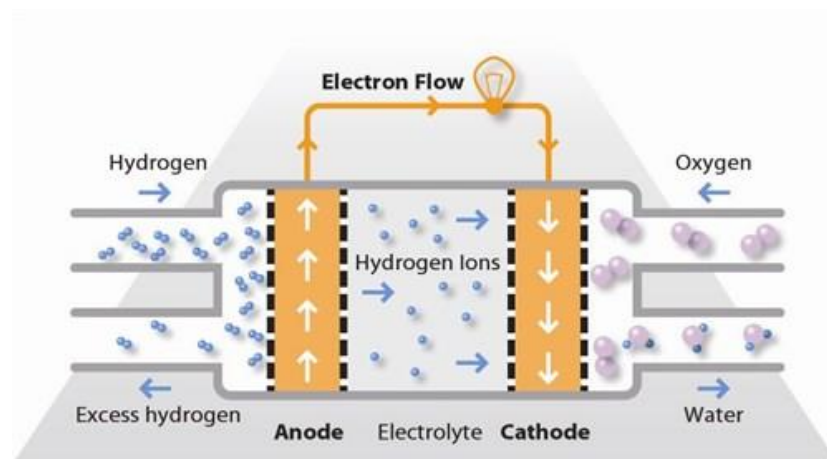


Figure 2.10 - Reactions and products of a proton exchange membrane fuel cell [12].

### *Direct Methanol Fuel Cell*

Direct Methanol Fuel Cells (DMFC) are one of the most recent fuel cell technology, being created during the 1990s by several American institutions. DMFC are very similar to PEMFC,

using a similar configuration with a polymer membrane as electrolyte. However, the anode on the DMFC is able to extract hydrogen directly from liquid methanol, its fuel, hence the name. Operating temperatures are low, from 20 to 90 °C, though the cell efficiency is also lower, ranging the 30%.

Most of the advantages of the DMFC comes from its fuel. Methanol is inexpensive, has a high energy density and can be easily transported and stored. It also has de possibility to be supplied in cartridges. The main disadvantage of the DMFC is its low power requirements. This makes the DMFC ideal for low power mobile electronic devices, either as substitute to the traditional ion battery or as a charger [13].

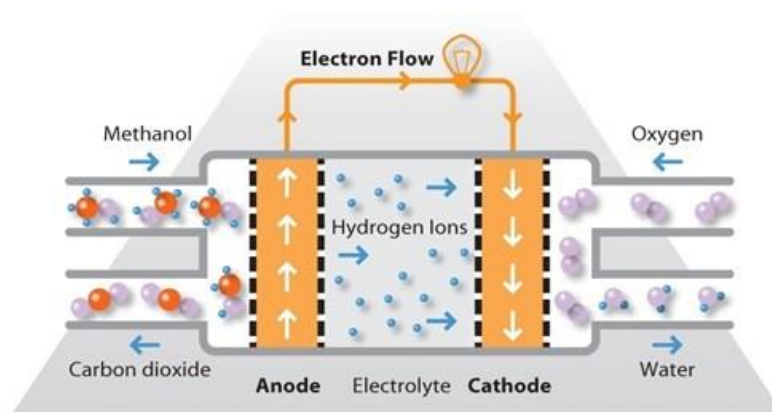


Figure 2.11 - Reactions and products of a direct methanol fuel cell [13].

## 2.2 Proton Exchange Membrane Fuel Cell

PEMFC are one of the most successful fuel cell design being used on many real world cases.

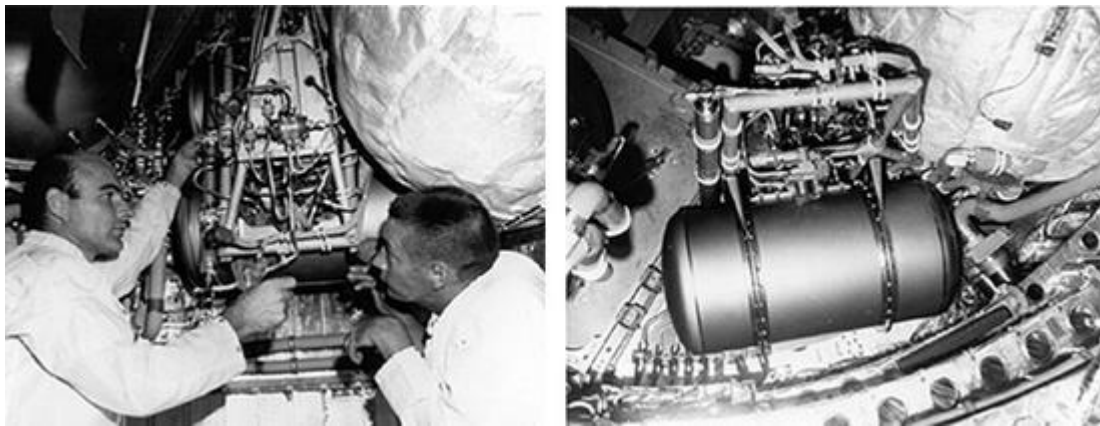
### 2.2.1 Proton Exchange Membrane Fuel Cell Emergence

PEMFC first originated in the early 1960s, when NASA was financing several companies to come up with a clever and efficient fuel cell design to be used on their Project Gemini. Thomas Grubb and Leonard Niedrach are credited as the inventors of the PEMFC, when working with General Electric (GE) on a fuel cell design for the US Navy (figure 2.12). Fueled by hydrogen, the first cell was compact and portable, but expensive, as the catalysts were made of platinum.



*Figure 2.12 – Grubb and Niedrach are considered the creators of PEMFC*

GE was responsible to the greatest improvements on PEMFC in the 60s and 70s. Project Gemini 5 and later Project Gemini flights were all powered by PEMFC made by GE, after initial problems forced NASA to go for batteries on Project Gemini 1 through 4 (figure 2.13). GE was also responsible for the creation of a technique called water electrolysis that allowed the use of PEMFC as undersea life support power supply [14].



*Figure 2.13 – General Electric was responsible for the PEMFC powering the Gemini project [14].*

The 70s also saw many vehicles manufacturers to see PEMFC as a potential future for the motoring world. The oil embargo resulting from the Cold War forced this manufacturer to look for alternatives as fuel and PEMFC were already showing great potential. Several German, Japanese and US manufacturers experimented on PEMFC, increasing power density of PEMFC and developing and improving hydrogen fuel storage.

The 90s brought more attention to the PEMFC. Germany, Japan, UK and California were seriously investing on PEMFC as an alternative power source and expecting hydrogen fueled vehicles to really be the future of motoring. The 90s also brought the creation of DMFC (explained later), a methanol fueled derived design based on PEMFC.

### 2.2.2 Proton Exchange Membrane Fuel Cell applications

PEMFC are now the most used kind of fuel cell worldwide. PEMFC characteristics indicate it to be best as a substitute to common batteries on small devices or in vehicles, as in CHP source on small houses.

#### *Japan CHP funding program*

By 2007, Japan was one of the leading country on PEMFC technology and increasing concerns about environmental issues forced the Japanese government to adopt new policies about these aspects. The New Energy and Industrial Technology Development Organization (NEDO), a Japanese administrative agency, started a program to introduce fuel cell vehicles and stationary fuel cells on Japanese society.

The latter had great success, with sales beginning on 2009 and with more than 13000 PEMFC stationary system implemented on Japanese homes. Japanese car manufacturers are also starting to invest on PEMFC as an alternative power source thanks to this program [15].



*Figure 2.14 – Japan is leading worldwide in home PEMFC systems.[15]*

### *Hyundai and Toyota's commercial Fuel Cell vehicles*

All the investment made by manufacturers on the 70s is started to yield serious results, with several manufacturers vehicle manufacturer has a fuel cell based concept vehicle, though these models are not commercially available, functioning only to show the progress that manufacturers have made with the technology.

However, South Korean manufacturer Hyundai launched in 2012 the Hyundai Tucson ix35 FCEV, the first mass produced fuel cell vehicle. Already available on South Korea and USA, the Tucson is to be made available on fifteen countries worldwide this year.

Japanese manufacturer Toyota also launched a fuel cell powered vehicle, the Toyota Mirai. Like the Hyundai, the Mirai was initially only available on its home country, but has since expanded sales to the USA and is expected to launch in some EU country this year [16].



*Figure 2.15 – The Toyota Mirai is one of the first fuel-cell powered vehicles for common users.*

### 2.2.3 Advantages of Proton Exchange Membrane Fuel Cell

#### *Hydrogen advantage as a fuel*

##### **Environment friendly**

Hydrogen is probably the more environmentally friendly fuel available right now. The only byproduct of using a PEMFC is water and hydrogen isn't even toxic, causing no harm to the planet.

## Fuel Efficient

Hydrogen is one of the most powerful and efficient fuel. Compared to gasoline or methanol, hydrogen produces more energy per kilogram. Theoretically, an amount of hydrogen could take a fuel-cell powered car twice as far as a car running on the same amount.

## Easy production

Hydrogen is the most abundant element in the universe and can easily be produced locally from several sources, like biomass, coal or water. Electrolysis is one of the best way to obtain hydrogen from water.

## *Proton Exchange Membrane Fuel Cell advantages relative to batteries*

PEMFC can be seen as one of the biggest challenger to the lithium batteries, particularly on electric vehicles. PEMFC introduces several advantages relative to lithium batteries that can be exploited by fuel cell powered vehicles.

PEMFC have the highest energy density of all the fuel cells, which means more power available to the user or a bigger mileage for the same consumed fuel. For example, the Toyota Mirai has a performance of about 3.5 l/100 km of fuel, while the similar Prius, with electric and gasoline motor, has a performance of 4.2 l/100 km, while having a smaller engine.

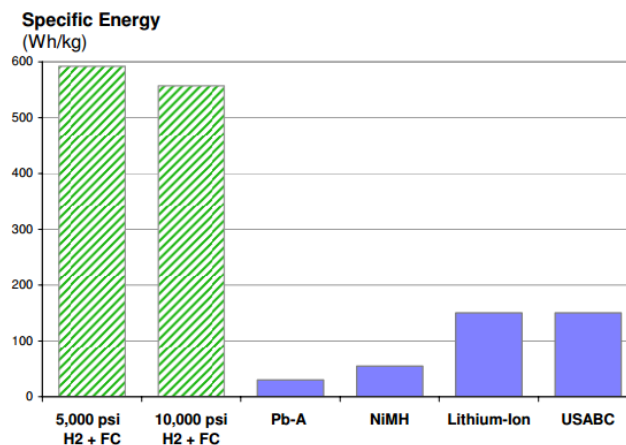


Figure 2.16 – Comparison between energy produced in several common power supply, including fuel cell[17]

PEMFC also introduces other advantages, being more compact than lithium batteries and being generally simpler. PEMFC charging is also a lot simpler and faster than lithium batteries, needing only to add more fuel to have more available power [17][17][18].

#### *Proton Exchange Membrane Fuel Cell advantages relative to combustion motors*

PEMFC may be the strongest competitors that combustion motors have encountered. PEMFC are considered the next big thing as a vehicle power supply, with several manufacturers having prototypes ready and even some with commercial models available.

Like with lithium batteries, the high energy density of PEMFC and Hydrogen is a great advantage, allowing a better fuel consumption ratio when compared with pure combustion moto. As example, the Hyundai Tucson ix35 PEMFC powered vehicle has a performance of 4.8 litters of fuel for each 100 km done, while the diesel version has a 6.8 l/100km performance and the petrol version has a 6.4 l/km performance, with a weaker engine.



*Figure 2.17 – The Hyundai Tucson PEMFC powered shows a better performance when compared with diesel or petrol version*

PEMFC have also a lower maintenance need and a higher reliability has they have few, sometimes none, moving parts, contrary to combustion motors. They are completely silent, even coupled with electric motors, as opposed to combustion motors.

However, the biggest benefit relative to combustion motors is the fact that PEMFC are totally green, only producing water as a byproduct, with no greenhouse gas. Hydrogen is also a renewable fuel, amply available [20].



#### 2.2.4 Problems with Proton Exchange Membrane Fuel Cell

PEMFC, like other fuel cell technologies, have progressed greatly since their invention, but still need more work to have a true breakthrough that establishes them as a true alternative on the energetic world.

##### *Hydrogen disadvantages as a fuel*

###### Expensive

While hydrogen is, in theory, a great fuel and an easy one to obtain, due to the frequency it occurs on the universe, hydrogen production is highly expensive. Right now, liquid hydrogen is used as fuel and the process used to liquefy hydrogen is a costly one.

A way to cheapen the process is using high-pressure gas hydrogen, like the new fuel cell vehicles do, but even then it's still more expensive than other fuels. To compare, a full tank of compressed hydrogen for the Toyota Mirai, corresponding to 485 km of range, costs about 50\$, while for the same range, a Toyota Prius only needs 21\$ of fuel, the average driver needs 44.5\$ and an electric vehicle like the Tesla Model S costs only 9.6\$[21].

Also, hydrogen production, transportation, distribution and storage is still difficult and expensive, even with costs lowering with evolution of hydrogen production techniques.

###### Highly Flammable

Hydrogen is a powerful fuel, but this also brings disadvantages. Hydrogen is one of the most flammable fuels actually available and can be dangerous.

###### Almost no infrastructure

While fuel cell and hydrogen vehicles have always been seen as the future of transportation, efforts to bring infrastructures to support them have been very small or even null. This has slowly been improving, with 100 hydrogen stations being expected in Japan by the end of this year, 50 on Germany by mid-2015, 21 on South Korea by 2020 and 28 stations on California by 2016.

Other countries are starting to open new hydrogen fueling station, with UK, Iceland, Turkey, Netherlands, Canada, Denmark or Norway also having at least one public hydrogen fueling station open right now.

### *Still dependent on fossil fuels*

While hydrogen consumption as a fuel is clean of greenhouse gases, the process to harness hydrogen from water or other compounds still uses many fossil fuels. Coal, oil and natural gas are the most used nowadays, but electrolysis is showing prospect to be a decisive factor to cut the need of fossil fuels.

### *Water and Carbon Monoxide management*

Fuel cells are highly sensitives to contamination that hamper their performance. Every kind of fuel cell is sensitive to some specific topics and PEMFC are sensitive to carbon monoxide contamination.

Contamination comes via hydrogen fuel. Commonly, Hydrogen fuel is produced not by electrolysis, that produces “clean” hydrogen, but by steam reforming coal or natural gas hydrocarbons, that result in a mixture of gases, including monoxide carbon.

Platinum, the main compound of the catalyst on the membrane is easily poisoned by carbon monoxide. One part per million is the maximum acceptable value of CO that can go poison the catalyst. To counter this, platinum-ruthenium catalyst were implemented, that made the maximum acceptable value of CO increase ten times, but still easily attainable.

Water management is another problem on PEMFC. The membrane must be humid for it to work, but with operating temperature exceeding the 60 °C, that is hard to achieve. Also, while the membrane must be humid, it can't be flooded with excessive water, which happens on the GDL. An equilibrium must be achieved to maintain the membrane humid without excessive water.

### *Heat dissipation*

Besides producing output current, all fuel cell technologies also produce heat output that deteriorates the fuel cell electrical performance. PEMFC efficiency is about 40%, with 60% energy lost in heat form. With the increase of heat output, the electric output lowers, so a heat dissipation is needed to increase the cells efficiency.

As alternative, PEMFC are being used as CHP, using the heat produced by the cell as a positive output, not as a loss of efficiency.

#### 2.2.5 Future of Proton Exchange Membrane Fuel Cell

While PEMFC were once seen as the future of the portable power supply, constant evolution on batteries have been constantly delaying PEMFC evolution. Heavy investments by key players in the electric market, like Japan, Germany and USA, have brought back the PEMFC as an alternative to lithium batteries and combustion motors.

2016 and 2017 are supposed to be the breakthrough years for fuel cell vehicles. With the already successful launch of the Toyota Mirai and Hyundai ix35 FCEV this year, more manufacturers are expected to launch fuel cell powered vehicles in the near future, with Honda, one of the pioneers of fuel cell research for vehicles, expecting to launch a new fuel cell vehicle in 2016, after successful testing in California on 2008.

Static PEMFC are also looking as strong as ever, with Japan in the front of the run. The DENO CHP program brought more than 13000 static PEMFC to Japanese homes, but more sales and evolution are expected these next years.

Small sized PEMFC have been, however, practically substituted by DMFC, as these are cheaper to make and can be better for these kind of applications.

### **2.3 Direct Methanol fuel cell**

As previously mentioned, DMFC are one of the most recent and promising fuel cell designs and is one of the strongest candidates to replace common lithium batteries on the long run.

### 2.3.1 Direct Methanol Fuel Cell emergence

While the DMFC itself was only created in the 90s, methanol electro-oxidation was first researched in 1922 by E.Muller. In the early 1950s, investigations to create a methanol based fuel cell were started. The great struggle was finding what electrolyte and catalyzers could be used with methanol. Firstly, alkaline electrolyte were used, the most common at the time, but acidic electrolytes were also tested.

The incorporation of platinum as a catalyst, following the works of Cathro and of Jansen and Molhuysen, in the 1950s, and Watanabe and Motoo, in the 1960s, gave hope to the achievement of creating a methanol based fuel cell. Many studies were made to develop the methanol electro-oxidation, from the 60s to the 90s, with other improvements being made to both catalyzers, anode and cathode. The creation of several analysis techniques, like spectro-electrochemical studies or low-energy ion scattering, improved the capability of these groups to investigate certain properties of primordial DMFC.

The 1990s started a new era for the DMFC. All previous studies converged and culminated into the creation of the first real methanol based fuel cell by Dr. Surya Prakash, a superacid specialist, and Dr. George A.Olah, a Nobel laureate, both from the University of South California. Prakash and Olah cell was the first fuel cell able to convert methanol into electricity directly. Following this development, the University of South California and the Jet Propulsion Laboratory, in a collaborative effort, created the first true DMFC with a Nafion membrane, presenting it in 1992.

### 2.3.2 Direct Methanol Fuel Cell applications

DMFC were the first to bring the possibility of using fuel cells as substitutes to common lithium-ion batteries. Using methanol as a fuel bring great advantages, as it is a liquid fuel, easier to refill, which enables the system to be simplified. However, efficiency is sacrificed on DMFC, when compared to common PEMFC or other fuel-cells. Lower power, but higher energy density are characteristics that make DMFC ideal to portable electronic applications.

The prospect of using DMFC as an alternative energy source for electronic devices to lithium batteries, whose capacities are reaching their physical limits, mean that there were a great investment, from institutes, university and even manufacturers in this area [22].

Different studies to integrate DMFC on both MP3 players and PDA were realized by the Faculty of Industrial Design Engineering of the Delft University of Technology. While the first showed up that DMFC has much to improve to be able to challenge lithium batteries [23], the second was able to show that DMFC can be on par with these same lithium batteries and still be improved [24].

Another possible use of DMFC is using it as a charger instead of a direct power supply. Lithium batteries are used as such, with high capacities, but DMFC can also be used in this fashion, as Toshiba showed up with the Dynario.

Unfortunately, after years where DMFC was promised to be the next big thing, progress has been very slow. While in the mid 2000's, many manufacturers were investing on DMFC research, one company has taken over the whole DMFC monopoly, SFC Energy, which reduced the progress of this technology.

#### *Toshiba Dynario*

The Toshiba Dynario was the first commercial DMFC charger. The Dynario was developed from 2003 to its limited launch, on 2009. The Dynario is a DMFC charger able to charge multiple devices via USB port. With an output of 5 V and 500 mA, the Dynario was incompatible with several devices and was bigger than expected, with its 14ml reservoir only able to charge a cell phone two times. Also, with a cost of approximately 325\$ for the charger and of 150\$ for 5 refill cartridge of 50 ml, and only 3000 units produced and sold exclusively on Japan, the Dynario was extremely expensive and rare, but was also the first commercial device that showed up the whole potential of DMFC technology [25].



*Figure 2.18 – The Toshiba Dynario was one of the first DMFC powered devices available to the mass market. It failed to gain traction.*

### *Apple's DMFC Patents*

IT giant Apple Inc. was always interested on fuel cell technology because of its promise to overthrow lithium ion batteries on the long run, however, only on 2011 Steve Jobs company took steps on this direction, registering on the United States Patent and Trademark Office four patents trademark involving DMFC, some suggesting the possibility of a DMFC powered Macbook laptop [26], [27]. Last July, new rumors came forth with the possibility of Apple introducing fuel cell technology on their laptop, in partnership with Intelligent Energy, a British fuel cell developer [28].

### 2.3.3 Advantages of direct methanol fuel cells

DMFC are regarded as one of the few technologies that can compete with lithium batteries in the near future. DMFC and methanol presents several advantages when comparing them with other power sources.

### *Methanol advantages as a fuel*

Methanol is the key element that makes DMFC the most promising fuel cell design for low power application. Methanol holds several advantages when comparing to other fuels or power supply.

### High octane rating and high flash point

Methanol has a higher octane rating than other fuels, 102. Comparing, gasoline has an octane rating that ranges 86 to 98 and ethanol has an octane rating of about 94. This makes methanol one of the least volatile fuels, avoiding accidents.

### High energy density

Methanol has an enormous energy density of about 6000 Wh/kg. When comparing with the best lithium ion polymer, with an energy density of 600 Wh/kg on a best case scenario, methanol has a theoretical 10-fold superiority.

### Easy to transport, distribute and produce

Methanol is a liquid that is as easy to transport and distribute as gasoline or other fuels. Also, it is cheaper to produce than gasoline, being based on natural gas instead of petrol.

### Environmentally friendly

Methanol is one of the greener fuels available nowadays. As a molecule, methanol is easily biodegraded without environmental harm. While toxic when ingested in large quantities, methanol is water soluble and is easily disposed that way.

### The methanol economy

Methanol has been, for years, suggested as the natural substitute for petrol as a fuel source. George A. Olah, one of the creators of the first methanol based fuel cell and a Nobel Prize winner, was the first advocator of methanol economy as a future economy scenario where methanol substitutes petrol, based on methanol's advantage as a fuel by itself or as a way to produce hydrogen [28] [29] [31].

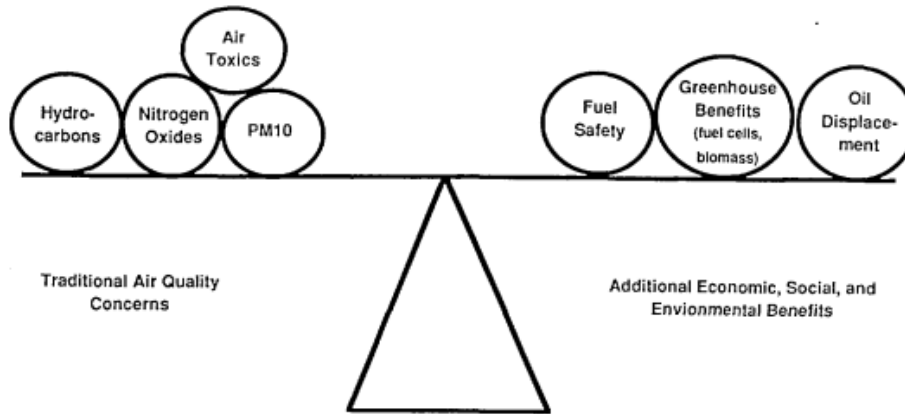


Figure 2.19 – All the methanol advantages brought the possibility of the creation of a methanol based economy, instead of the traditional oil based economy

#### *Direct methanol fuel cells advantages relative to batteries*

DMFC main competitor is the common lithium battery that power almost every portable device actually commercially available.

The main advantage of DMFC is its higher energy density, result of methanol's usage. This translate into greater operating time for portable devices such as laptops or cell phones and also into greater power availability, which can translate into higher performance.

This is not, however, the only advantage of DMFC technology. DMFC have the potential to be smaller and lighter than lithium batteries. They are also simpler in design, which can result, on the long run, into lower production costs.

Another great advantage is the possibility to instantly recharge your device. While lithium batteries take hours to charge, DMFC can be recharged simply by inserting more fuel, as a cartridge or directly into the cell.[32]

#### *Direct methanol fuel cells advantage relative to gasoline combustion motors*

While DMFC are not the principal fuel cell technology used in vehicles, it can be implemented as well as PEMFC, sharing similar configuration and design. DMFC powered vehicles are rare, with PEMFC dominating this realm, but DMFC also introduce certain advantages when comparing with gasoline combustion motors.



DMFC powered electric motors are cleaner than gasoline combustion motors, as the only reaction byproduct of a DMFC is water, being a zero emission fuel technology. DMFC have also a greater kilometer range when comparing with ion battery powered vehicle. When comparing with PEMFC, methanol is cheaper than hydrogen and easier to store.

#### 2.3.4 Problems with direct methanol fuel cells

While DMFC are still viewed as one of the energy technology with the most future potential, they are still many problems that need to be solved for a breakthrough in the market to happen.

##### *Methanol disadvantages as a fuel*

While methanol as many advantages as a fuel, it is not without its disadvantages.

##### *Lower energy density*

While methanol as a higher energy density than lithium, it is still lower than gasoline, which is a disadvantage for DMFC powered vehicle.

##### *Least volatile*

While methanol being less volatile than gasoline is an advantage in preventing accidents, it also difficult the startup process, needing significantly more heat to do so.

##### *More expensive*

Methanol is more expensive than gasoline nowadays, although there is a possibility that the price can lower if production and need increase.

##### *Corrosive*

Methanol is highly corrosive and reactive to certain materials, like plastic and many metals, like aluminum, zinc and manganese.

### *No infrastructures*

There is virtually no infrastructure for methanol usage as a fuel. Without infrastructures, methanol cannot become a valid fuel.

### *Methanol crossover*

Methanol crossover is one of most problematic phenomenon occurring on DMFC. While using higher methanol concentration provides higher energy density, it also allows methanol leaks to the membrane, reducing the cells performance due to this methanol leak mixing with the cathode. Through this, the methanol pass through the membrane and are directly oxidized by the oxygen on the cathode [33].

This causes two simultaneous problems:

- a) Higher methanol consumption and higher heat output without higher current output.
- b) Severe decline of the cathode voltage.

### *Heat dissipation*

Methanol oxidation causes a heat output, besides the current output. The efficiency of DMFC is about 30%, which means that 70% of the energy is loss as heat. The higher the heat output on the DMFC, the lower the output electric energy is. As such, a heat dissipation way is needed to increase the practical efficiency of the cell.

### *Low energy density*

While methanol by itself as good energy density, 10 times above the existing in lithium, the cell by itself has not an energy density as good.

DMFC can be passive systems, without requiring additional equipment. This cell simplicity can play against itself, as the fuel and carburant supply can vary during the cell's usage and affect negatively the cell's performance. Also, carbon dioxide accumulation on the anode and water accumulation on the cathode diminish the contact superficies to allow the oxidizing reaction to occur.

The way to solve this problem is using pumps to maintain a constant flow of fuel and air, but with costs in terms of power consumption.

#### 2.3.5 Direct Methanol Fuel Cell future

The increase of lithium battery capacity, as the usage of new kinds of batteries, like lithium ion or lithium polymer, and the reduction of power consumption from electronic devices, due to the improvement and advancement of manufacturing processes, have been key factors to the stagnation of DMFC development. However, lithium battery capacity increase is now reaching a physical limitation, since it is necessary to significantly increase the size thereof to increase its capacity, clearly a negative point in a time where the evolution of electronic devices tends toward a decrease in dimensions, especially in thickness. Power consumption decrease is also slowing down, as manufacturers are still searching for ways to keep the performance of their product increasing, even when reaching the minimum limit on the size of a transistor on silicon.

Due of this, DMFC can catch up and regain a bright future in the field of portable equipment power supply. While still having technical problems to solve, DMFC can be smaller, better, less-costly, with a lower ecological footprint and higher efficiency when compared to lithium batteries. Refueling of DMFC can be fast and cheap, keeping a DMFC cost competitive on a long run analysis [34].



## 3. THEORETICAL STUDY

### 3.1 Fuel Cell

Although initially the creation of a DMFC was intended for this project, the timeline dictated that it was a better choice to use an existing fuel cell, in this case a PEMFC, adapting it to be powered by methanol, instead of pure hydrogen, essentially turning it into a DMFC. This conversion would not interfere with the following work, as the fuel cell would work as any other DMFC.

#### 3.1.1 The given PEMFC

The used PEMFC is a Horizon model, the Horizon Mini PEM Fuel Cell. The Mini PEM Fuel Cell is a model created for an education purpose with design as shown on figure 3.1 and specifications as shown on table 1. The Mini PEM Fuel Cell can be obtained for 239€ for a five units set, in the Horizon online store [35].



Figure 3.1 - The Horizon Mini PEM Fuel cell [35].

Table 1 – Horizon Mini PEM Fuel Cell properties [35].

**Fuel Cell Properties**

<i>Output Voltage</i>	0.6 V (DC)
<i>Output Current</i>	0.45 A
<i>Power</i>	270 mW
<i>Color</i>	Blue
<i>Dimensions</i>	32 x 32 x 32 mm
<i>Total Weight</i>	27.3 g

About Horizon Fuel Cell Technologies, they are a company founded in 2003 in Singapore that specializes on PEMFC, from multi-kilowatts PEMFC to both sub-watts and micro-size PEMFC. They are responsible for the creation of various science experiment kits, like the one used on this dissertation, as for several other fuel cell kits for usage in the automotive or aerospace industry, for example. They are currently the world largest producer of sub-megawatts fuel cells. More information can be obtained on their website [36].

3.1.2 Operating principle of PEMFC

As previously referred, PEMFC is one of the simpler and most promising design. They were also the first fuel cell design that used a membrane, more accurately a polymer electrolyte membrane (PEM), as electrolyte, and creating the notion of Membrane Electrode Assembly (MEA), also used on DMFC.

*Membrane Electrode Assembly*

The MEA is a central piece of both PEMFC and DMFC, and can be of three kinds: the MEA3 that is composed of the PEM and catalyst layers, the MEA5 that adds two GDL and the MEA7, with two sealing layers.

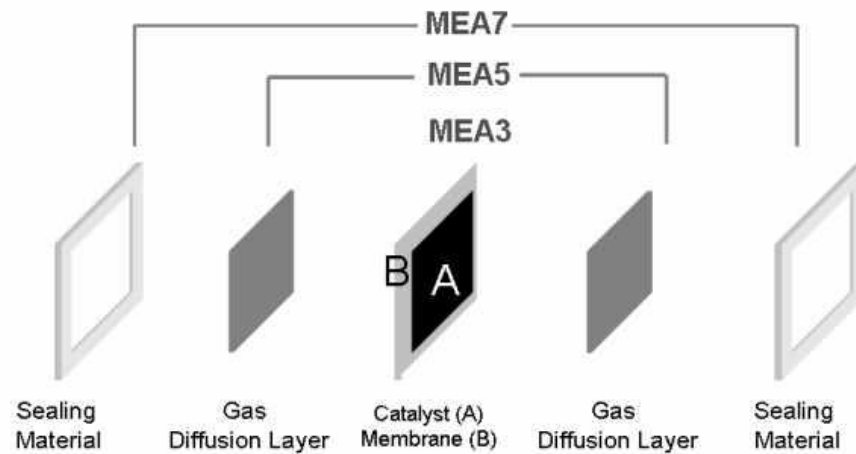


Figure 3.2 – Composition of the MEA [37].

The MEA is by far the most expensive component of a PEMFC, ranking roughly 75% of the total PEMFC cost. The MEA function is essentially the combined function of all its component combined, and must be able to allow hydrogen ions, or protons, through the membrane, without allowing both H<sub>2</sub> and O<sub>2</sub> gases to contact with each other, must be able to be hydrated, so that ion penetration happens and must be able to operate at high temperatures.

The performance of the whole PEMFC is closely related with the MEA's performance. To improve performance, several manufacturers are working with the material used on the PEM (usually Nafion®), others are changing the fabrication method [38].

### *Polymer Electrolyte Membrane*

The PEM is the central part of the MEA, being the electrolyte used by PEMFC. The PEM can be made of different materials, but the most used one is Nafion®, from Dupont. Other used materials are perfluorinated ionomer membranes and Dow membranes, from Dow Chemical Company.



*Figure 3.3 - A Nafion® membrane from Dupont.*

A membrane must have considerable properties to be used as PEM on a PEMFC.

- Chemical and electrochemical stability in fuel cell operating conditions;
- Elevated proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity;
- Good water uptakes at temperatures of approximately 100 ° C, the operating temperature;
- Thermal and hydrolytic stability;
- Chemical properties compatible with the bonding requirements of the MEA;
- Extremely low permeability to reactant species to maximize efficiency;
- Mechanical strength and stability in the operating conditions;
- Resistance of fuel transport through it;
- High durability;
- Facilitation of rapid electrode kinetics;
- Flexibility to operate with a wide range of fuels;
- Production cost compatible with the commercial requirements of the fuel cell;

Other effects also take place that can affect the overall performance of the fuel cell like the cell's water management and the membrane thickness [38].

Membranes are still evolving so that PEMFC can become an even better power solution for the future. Right now, a Dow membrane, one of the highest performers available, cost in between 800 and 2000\$ per m<sup>2</sup>, while Nafion® 117, the highest performer from Dupont, can exceed



1200\$ for the same amount. It is estimated that the cost must go as low as 200\$ per m<sup>2</sup> for PEMFC to take of as a viable day-to-day power supply [39].

### *PEMFC operation process*

As other fuel cells, a chemical reaction must happen to produce electric energy. PEMFC use pure hydrogen as fuel and oxygen as carburant. While the hydrogen must be carefully handled, being normally provided as a cartridge, the oxygen is normally given by the air.

The hydrogen is delivered in gas form through the anode, where the catalyst helps to broke down H<sub>2</sub> molecules into several H<sup>+</sup> ions, or protons, and electrons. The reaction happening, called hydrogen oxidation reaction, is described by the equation 3.1.



The positive charged H<sup>+</sup> ions proceed through the PEM, migrating to the cathode side of the MEA. At the same time, oxygen is provided into the cathode side. This oxygen will react with the protons that originated from the anode, with an oxygen reduction reaction occurring, represented by the equation 3.2. The result of this reaction is the appearance of H<sub>2</sub>O, the only byproduct of PEMFC chemical reactions.



The negative charge electrons can't follow the protons, being blocked by the PEM, to the cathode, needing thus another way to flow. The creation of an external load circuit, another way for the electrons to go from the anode to the cathode, forms the output current from the fuel cell, effectively transforming all these previous chemical reactions into electric energy. The overall reaction occurring on the PEMFC can be described by equation 3.3 and the whole PEMFC operation process is visible on figure 3.4 [40].



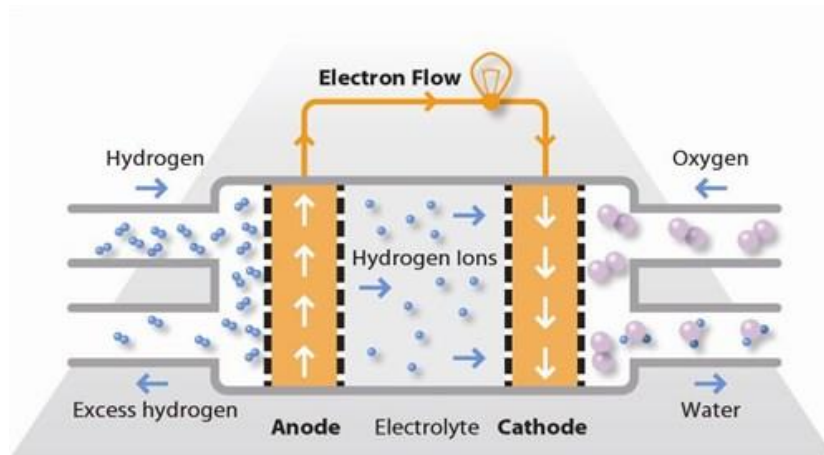


Figure 3.4 - Operation process of PEMFC

### 3.1.3 Operating principle of DMFC

While PEMFC showed great promise as a technology, the high cost and difficulties of using hydrogen as a fuel made manufacturers look into alternative fuels, using the same structure for the electrolyte, including the whole MEA and PEM. Methanol was one of the fuels used, leading to the creation of DMFC, that are considered by many a subcategory of PEMFC.

#### *Membrane Electrode Assembly*

The MEA on a DMFC is quite similar to the one on PEMFC. The MEA from DMFC uses the same typology, using three to seven layers depending on the used MEA. The most used MEA is, however, the 5 layered MEA5.

While the structure of PEMFC and DMFC MEA are akin, the performance of each one is very disparate. Per example, a DMFC has a maximum theoretical thermodynamic voltage of 1,18 V at 25 °C, while a PEMFC has a 1,25 V maximum voltage, at the same temperature. These values are defined by the half-cell reactions occurring on both anode and cathode. In practice, these values are, however, much lower [41].

#### *Polymer Electrolyte Membrane*

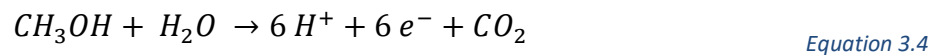
As with the PEMFC, the polymer electrolyte membrane is a key component from the DMFC's MEA. Generally, the same materials are also used, with the same essential features, however,

several materials have proven to be as good or even better than Nafion® and similar materials, as membrane. Zirconia and silica nano-composite membranes were found to reduce crossover [42].

### *DMFC operation process*

DMFC distinguish themselves from other cells by using methanol as a fuel instead of pure hydrogen. Methanol is easier to handle than hydrogen, leading to a more straightforward approach on the delivery system.

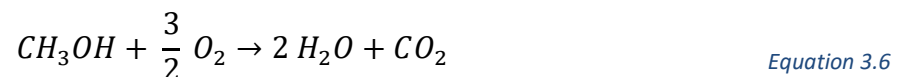
The methanol is delivered in liquid form, mixed with distilled water, from the anode, where the catalyst separates  $H^+$  ions, electrons and dioxide carbon,  $CO_2$ , from both  $CH_3OH$  and  $H_2O$ . The reaction happening is an oxidation and is defined by the equation 3.4.



Like on a PEMFC, the protons pass through the PEM, moving into the cathode side of the MEA. At the same time, oxygen flows *via* the cathode side, reacting with the protons coming from the anode, with an oxygen reduction reaction occurring, represented by the equation 3.5.



Like on the PEMFC, the DMFC's PEM stops electrons from flowing to the cathode through it. The electrons need a different passage to flow from one electrode to another, passage provided by an external circuit that serves as output of the cell, supplying the user with an electrical current. The overall reaction occurring on the DMFC can be described by equation 6 and the whole DMFC operation process is visible on figure 3.5 [43].



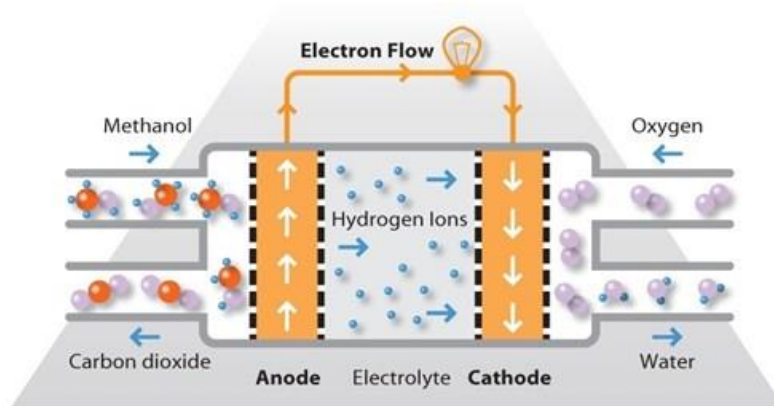


Figure 3.5 – Operation process of DMFC

## 3.2 Auxiliary Systems

### 3.2.1 Fuel Supply subsystem

The fueling system is the subsystem responsible to pump fuel into the fuel cell. As the fuel is the main component for the transformation from chemical reaction to electrical energy, this subsystem is vital to the correct operation of the whole fuel cell.

#### *Expected requirements*

As the fueling system will be powered by the start-up power supply and keep steady by the cell itself, a very low power profile is needed for it to not affect the cell's efficiency.

For an optimal performance of the cell, counting on methanol crossover and other problems usual on DMFC, the flow rate must be between a specific range of about 0,2 to 0,8 ml/min. These values were provided by the manufacturer. To establish a constant flow rate, a micro pump is needed. The pump shall have its own power supply, as it has specific requirement for it to work.

#### *Selected components*

The chosen micro pump was the MP5 Micropump from Bartels. Several papers and studies use it to provide fuel to their fuel cell, and its immediate accessibility, as samples were already available at the time of the project initiation [44] [45]. The MP5 is the smallest and lightest micro pump available from Bartels, with a low power consumption and cheapest price.



Figure 3.6 - The Bartels MP5 Micropump [46].

The MP5, as other Bartels micro pump, is based on a piezoelectric diaphragm in combination with passive check valves. When voltage is applied on the micro pump, a piezo ceramic mounted on a coated brass membrane is deformed, with the fluid being displaced from the chamber to the selected direction, with the check valves controlling which direction is selected. When a voltage reduction happens, the membrane deformation is such that allows the fluid to enter the chamber.

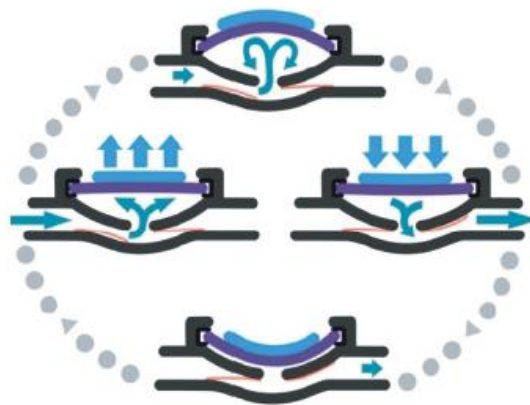


Figure 3.7 - Operation principle of Bartels MP5 Micro pump [46].

The MP5 is able to pump liquids and gases at different speeds when using diverse kinds of waves, voltage and frequency. Several controllers are available to use with the MP5 pump, allowing different configurations [46].

mp5	Order code: mp5		
Pump type	piezoelectric diaphragm pump		
Number of actuators	1		
Dimensions without connectors	14 x 14 x 3.5 mm <sup>3</sup>		
Weight	0.8 g		
Fluidic connectors	tube clip (outer diameter 2 mm, length 3 mm)		
Electric connector	flex connector / phone jack		
Power consumption	< 200 mW		
Self-priming	yes <sup>2</sup>		
Pumping media	liquids or gases		
Operating temperature	0 – 70°C		
Life time	5000 h <sup>3</sup>		
IP code	IP44		
Materials in contact with media	polyphenylene sulphone (PPSU), polyimide (PI), nitrile butadiene rubber (NBR)		
Suitable evaluation controller	mp-x, mp6-EVA and mp6-OEM		
Typical values of flow and back pressure for selected media (values defined with mp-x: 250 V, SRS):			
Gases	Max. flow		15 ml/min (300 Hz)
	Linear range		0 – 5 ml/min @ 0 – 50 Hz
	Max. back pressure		30 mbar (300 Hz)
Liquids	Water	Max. flow	5 ml/min (100 Hz)
		Linear range	0 – 3 ml/min @ 0 – 30 Hz
		Max. back pressure	250 mbar (100 Hz)
Repeatability (30 Hz, 250 V, SRS)			< 12 %
Viscosity			<~ 120 mPas

Figure 3.8 - Technical data of the MP5 Micro pump

### 3.2.2 Power management subsystem

While the fuel cell is the component responsible to convert the energy resulting from chemical reactions to an electric current, it does not mean that the output current and voltage can be immediately used to power an equipment. It needs to be converted to a viable voltage to be applied to existing devices.

#### *Expected requirements*

Depending on the conditions of the fuel cell, the output voltage can go from as low as 50mV to as high as 600mV. These voltages are too low to be of viable use so, to turn the whole system into a usable power supply, a circuit must be implemented so that the voltage can be increased into a standard voltage, used to power devices. That voltage can be either 3,3V, 3,7V, 4,2V or 5V. 3,3V and 5V are used to power several electronic processors and devices, while 3,7 and 4,2V are standard lithium ion battery voltages.

The power management subsystem must also have some kind of start-up circuit that can power both control and fueling subsystem before the fuel cell starts running. This could be done by either a lithium ion battery or a super capacitor that would be charging during the fuel cell operation, ready for another cold start.

### *Selected components*

The heart of the power management subsystem is the step-up converter that can transform the output voltage from the fuel cell to the required operating voltage. This step-up can be one of several ICs available commercially from several manufacturers. For ease of use and availability, the research focused on Linear Technology ICs.

Linear Technology is an American company that focuses on high quality and performance analog ICs. Founded in 1981, Linear has a revenue superior to 1000 million US dollars and currently have over 4000 employees and 7500 products on the market [47].

The Linear 3100 family has several models that fits the desired profiles. Table 2 represents a summary of all the considered ICs characteristics, as well as the intended specifications.

Table 2 - Characteristics of the considered ICs for the energy management system.

Specification	Desired IC	LTC3105	LTC3107	LTC3108	LTC3109
<b>Voltage output</b>	3,3 V, 3,7 V, 4,2 V or 5 V	From 1,5 to 5,25 V	3.6 V	2.35 V, 3.3 V, 4.1 V or 5 V	2.35 V, 3.3 V, 4.1 V or 5 V
<b>Voltage input</b>	As low as possible	From 0,225 V to 5 V	From 0,02 V to 0.5 V	From 0,02 V to 0.5 V	From 0,04 V to 0.5 V
<b>Components required</b>	As low as possible	Capacitors, resistors and a lithium battery	Capacitors, resistors and a transformer	Capacitors, resistors and a transformer	Capacitors, resistors and two transformers
<b>Start-up Voltage</b>	As low as possible	0,25 V	0,02 V	0,02 V	0,03 V
<b>Efficiency</b>	As high as possible	From 30 to 80%, depending on input voltage, output voltage and output current	From 5 to 50% depending on transformer and voltage input	From 5 to 50% depending on transformer and voltage input	From 3 to 45% depending on transformer, capacitor and voltage input

While the LTC3105 has the highest efficiency and flexibility (no fixed output voltage), it also has the most complicated circuits, requiring a lithium battery, that would increase severally the complexity and size of the whole system [48]. The others ICs have several similar specifications: all have a low input and startup voltage, ideal for a fuel cell system with no fixed voltage, all use transformers and while the output voltage is fixed, most contains interesting settings. From these, the LTC3108 [49] was chosen: it is more versatile when comparing with the LTC3107 [50], as it has several more output voltages configurations, and simpler when compared with the LTC3109 [51], only needing a single transformer.



### 3.2.3 Control subsystem

Although the fuel cell itself is simple, only pumping fuel to it and collecting the output current, the whole fuel cell system has several subsystems, the ones talked in this chapters, that must be controlled in some way so that the proper operation order is maintained and also to monitor all the subsystems and variables on the system, so all these keeps running properly.

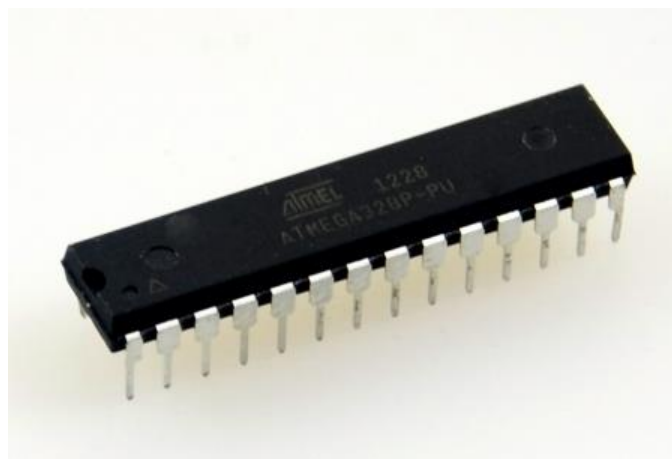
#### *Expected requirements*

The control subsystem center is a microprocessor. This microprocessor should have a low energy consumption, so that it could be powered by both fuel cell, without a several efficiency loss, and start up system. It should have some essential peripherals, like analog to digital converters, digital to analog converters, timers and Pulse-Width Modulation systems.

Besides the microprocessor, that will effectively control the system, the control subsystem should have several analog comparators and amplifiers to convert the various voltages and currents on the system to appropriate values that won't damage the processor.

#### *Selected components*

The chosen microprocessor is the Atmel ATmega 328P. It is one of the most used microprocessors of the world, used in the famous Arduino® boards and many more. It is a perfect microchip to use when a low-powered, low-cost microcontroller is needed.



*Figure 3.9 - The Atmel ATmega 328p*

The ATmega 328P is used on many low power profile boards, like the Arduino Uno and Nano, and is a versatile chip, able to be powered by 3,3V and 5V power sources and using different

oscillators to be used on a multitude of tasks. Some features of the ATmega 328 are presented on the figure 3.10 [52].

### Features

- High Performance, Low Power AVR® 8-Bit Microcontroller
- Advanced RISC Architecture
  - 131 Powerful Instructions – Most Single Clock Cycle Execution
  - 32 x 8 General Purpose Working Registers
  - Fully Static Operation
  - Up to 20 MIPS Throughput at 20 MHz
  - On-chip 2-cycle Multiplier
- High Endurance Non-volatile Memory Segments
  - 4/8/16/32K Bytes of In-System Self-Programmable Flash program memory (ATmega48PA/88PA/168PA/328P)
  - 256/512/512/1K Bytes EEPROM (ATmega48PA/88PA/168PA/328P)
  - 512/1K/1K/2K Bytes Internal SRAM (ATmega48PA/88PA/168PA/328P)
  - Write/Erase Cycles: 10,000 Flash/100,000 EEPROM
  - Data retention: 20 years at 85°C/100 years at 25°C<sup>(1)</sup>
  - Optional Boot Code Section with Independent Lock Bits
  - In-System Programming by On-chip Boot Program
  - True Read-While-Write Operation
  - Programming Lock for Software Security
- Peripheral Features
  - Two 8-bit Timer/Counters with Separate Prescaler and Compare Mode
  - One 16-bit Timer/Counter with Separate Prescaler, Compare Mode, and Capture Mode
  - Real Time Counter with Separate Oscillator
  - Six PWM Channels
  - 8-channel 10-bit ADC in TQFP and QFN/MLF package
    - Temperature Measurement
  - 6-channel 10-bit ADC in PDIP Package
    - Temperature Measurement
  - Programmable Serial USART
  - Master/Slave SPI Serial Interface
  - Byte-oriented 2-wire Serial Interface (Philips I<sup>2</sup>C compatible)
  - Programmable Watchdog Timer with Separate On-chip Oscillator
  - On-chip Analog Comparator
  - Interrupt and Wake-up on Pin Change
- Special Microcontroller Features
  - Power-on Reset and Programmable Brown-out Detection
  - Internal Calibrated Oscillator
  - External and Internal Interrupt Sources
  - Six Sleep Modes: Idle, ADC Noise Reduction, Power-save, Power-down, Standby, and Extended Standby
- I/O and Packages
  - 23 Programmable I/O Lines
  - 28-pin PDIP, 32-lead TQFP, 28-pad QFN/MLF and 32-pad QFN/MLF
- Operating Voltage:
  - 1.8 - 5.5V for ATmega48PA/88PA/168PA/328P
- Temperature Range:
  - -40°C to 85°C
- Speed Grade:
  - 0 - 20 MHz @ 1.8 - 5.5V
- Low Power Consumption at 1 MHz, 1.8V, 25°C for ATmega48PA/88PA/168PA/328P:
  - Active Mode: 0.2 mA
  - Power-down Mode: 0.1 µA
  - Power-save Mode: 0.75 µA (Including 32 kHz RTC)

Figure 3.10 - ATmega 328P features

## 4. IMPLEMENTATION AND PRELIMINARY TESTING

### 4.1 Auxiliary Circuits Implementation

The first step in the fuel cell system implementation is establishing what is necessary for the auxiliary circuits to operate as intended. These auxiliary subsystems are fundamental for the correct operation of the whole system and their performance is critical for the success of the objectives.

#### 4.1.1 Fuel Supply System Implementation

##### *Micropump preliminary testing*

While all the tests were not done in the same day, complicating the control of variables like ambient temperature and pressure, they were done in the same location and with the same installation.

The tests were intended to analyze several aspects of the MP5 micro pump. The final objective was to find voltages and frequencies values that allow the pumping speed to be the one needed for the fuel, of about 0,2 to 0,8 ml/min. The full characterization of the micro pump was also an objective in order to analyze its behavior and performance. All tests were done using distilled water as liquid fluid and using a rectangle wave form, as it is the easiest obtainable on aftermarket controllers, if needed. Testing time was 5 minutes, with the water and container being weighted before and after pumping.



Figure 4.1 – Micropump testing setup.

### Voltage influence on the pumped flow

With this test, it is intended to see the influence of changing the supply voltage in the pumped flow. The reference frequency used was 100 Hz, and the voltage was changed in 50 V intervals.

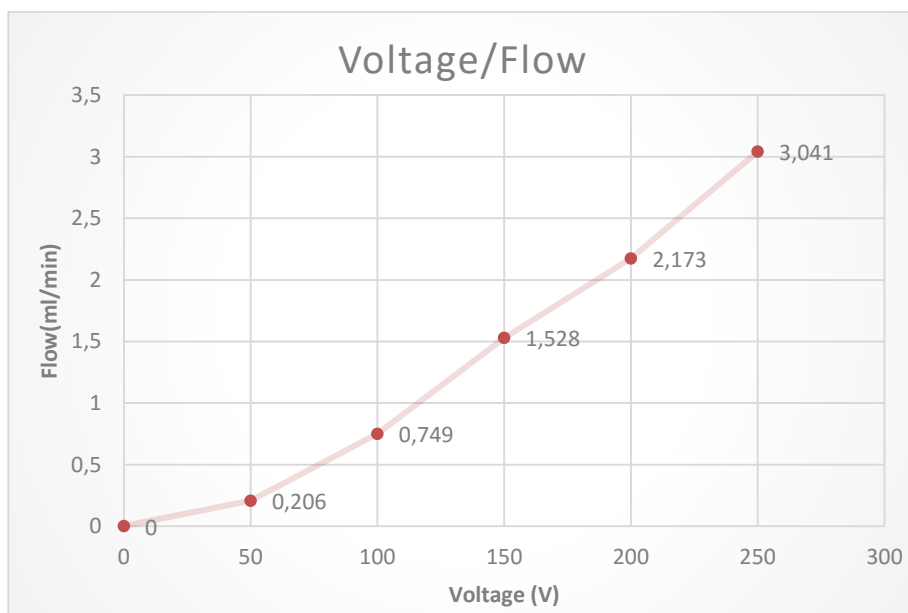


Chart 4.1 – Voltage/Flow Chart

It is possible to see a certain linearity in the effect in pumped flux with the increase in voltage. With the objective being between 0,2 and 0,8 ml/min, the gap between 50 and 100 V seems to be the ideal one to achieve the ideal flow per minute.

### Frequency influence on the pumped flow

This test intends to verify the influence of changing the supply frequency in the pumped flow. Both voltage referred previously, 50 V and 100 V, were used to test from 50 to 300 Hz.

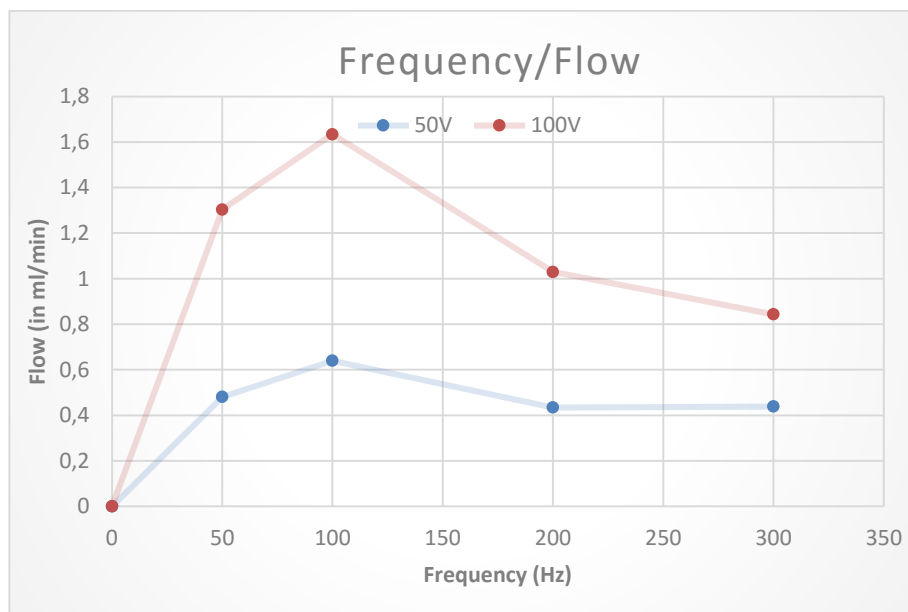


Chart 4.2 - Frequency/Flow chart

It is clear in this chart that the best performance is obtained between 50 Hz and 150 Hz. Contrary to what happens with the relation between voltage and flow, the frequency/flow relation is not a linear one. This chart supports the 50-100 V zone as the ideal one to the proposed flow rate, and encourages the 50-150 Hz zone as one that allows the best flow control.

### Full characterization of intended flow rate zone

Both previous tests allowed to find an ideal area of operation in voltage and frequency. To gain a superior knowledge of this area, further testing, with greater precision, were performed. Voltages tested were 50, 75 and 100 V, with frequencies between 0 and 125 Hz, with a 13 Hz range.

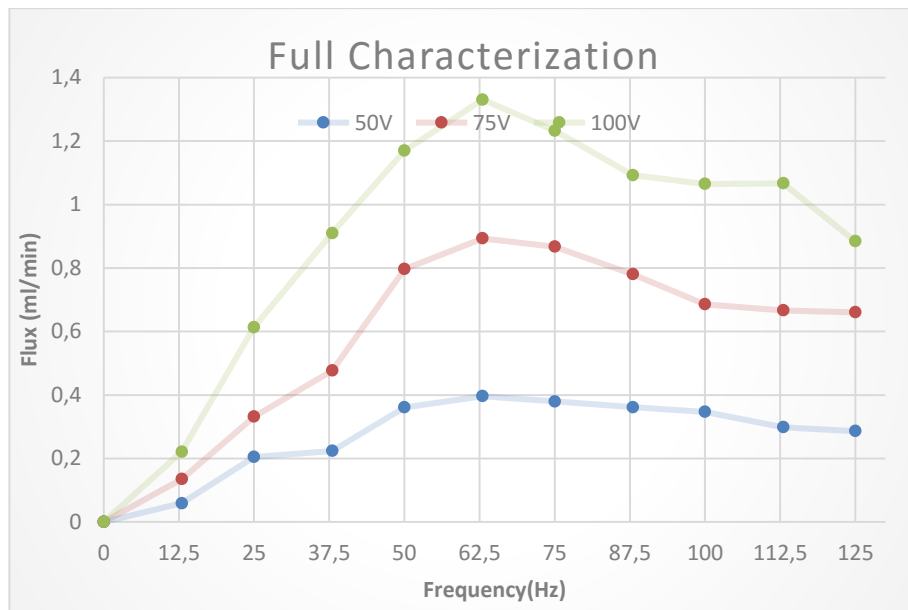


Chart 4.3 - Full characterization of MP5 Micropump

As it can be seen in chart 3, any of the used voltage can provide the required flow rate, although when powered with a 50 V voltage, the MP5 isn't able to attain the 0,8 ml/min peak that may be required. It can also be observed the same lack of linearity, as in the previous tests, after achieving the peak flux rate, in about 62,5 Hz.

Both the 75 V and 100 V tests show that the full range of flow rate required can be achieved at relatively low frequency: on the 75 V range, 0,2 ml/min are achieved between 12,5 and 25 Hz, with the 0.8 ml/min attained at 50 Hz; on the 100 V test, 0,2 ml/min were obtainable on the lowest frequency tested, 12,5 Hz, and 0,8 ml/min were surpassed on the 37,5 Hz test.

It can be observed that with the same kind of input wave, the results were different from test to test. This can be explained by the different ambient variables and by the existence of some air bubbles.

### Input current visualization and calculation

As this is a micro scale project, low power consumption is a crucial aspect of the development of auxiliary circuits. Bartels MP5 micro pump promised low current requirements, with power consumptions bellow 200 mW. This test was done using a digital oscilloscope to display the input current on the MP5 micro pump with a specific setting. To display the current, a 10 kΩ

resistor was put in serial mode with the micro pump, and the oscilloscope was connected to this resistor, presenting the voltage wave form, which is similar to the current wave form.

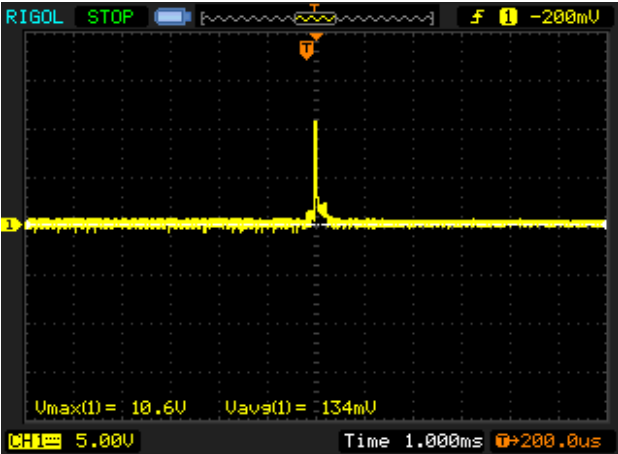


Figure 4.2 - Positive 10k resistor voltage waveform (100V, 75Hz)

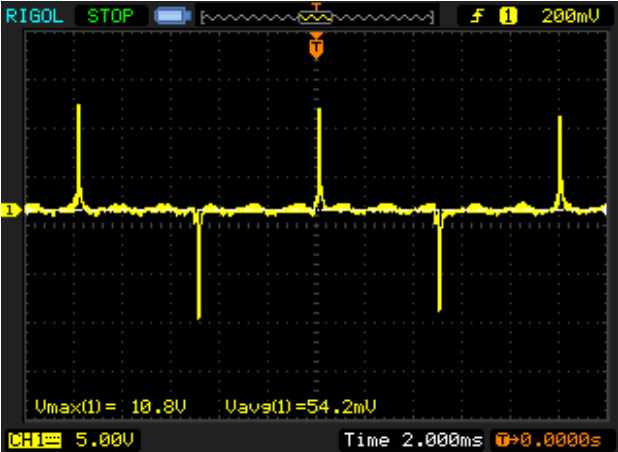


Figure 4.3 - Full 10k resistor voltage waveform (100V, 75Hz)

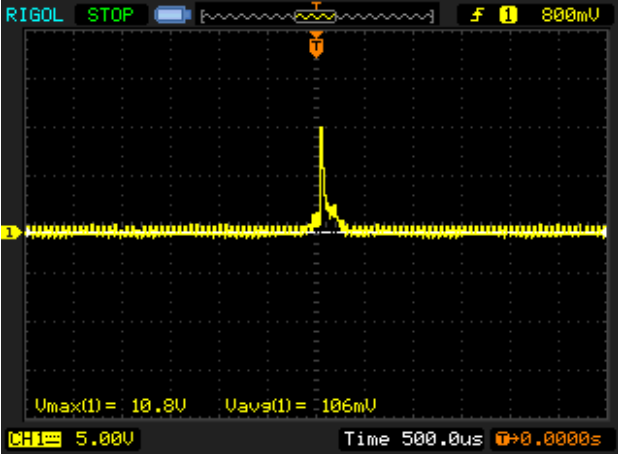


Figure 4.4 - Positive 10k resistor voltage waveform (100V, 100Hz)

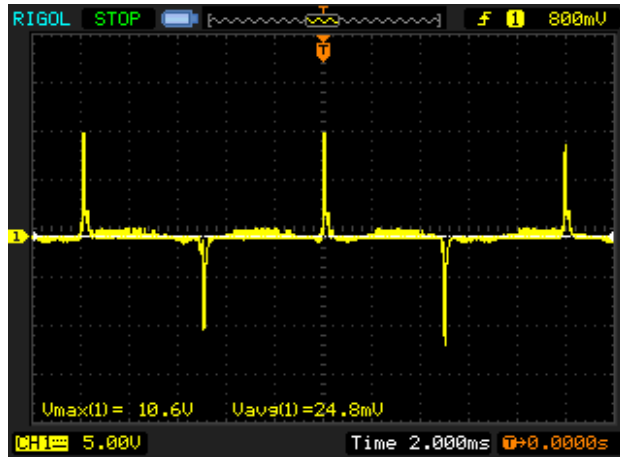


Figure 4.5 - Full 10k resistor voltage waveform (100V, 100Hz)

The peak voltage in the resistor is about 11 V. Using Ohm's law, the current can be calculated and is presented on equation 4.1:

$$I = \frac{U}{R} = \frac{11}{10k} = 1,1m \quad \text{Equation 4.1}$$

The average current can be estimated using an integral and the area of the peak current. As seen in fig. 7 and fig. 8 and calculated in equation 1. , the peak current is 1.1 mA. The peak occurs in t=0, with the current being 0 mA at about t=0.25 ms and the period is 10 ms (5 ms ON and 5 ms OFF). The average current can then be estimated, as shown on the equation 4.2 bellow:

$$I_{avg} = \frac{(1,1 \times \frac{0,25}{2})}{5} = 28\mu A \quad \text{Equation 4.2}$$

The power can then be estimated to be:

$$P = 100 \times 28\mu = 2.8mW \quad \text{Equation 4.3}$$

For these calculations to be entirely correct, the calculated current should be the RMS current. However, the average value in each cycle can be seen as approximation to the RMS current.



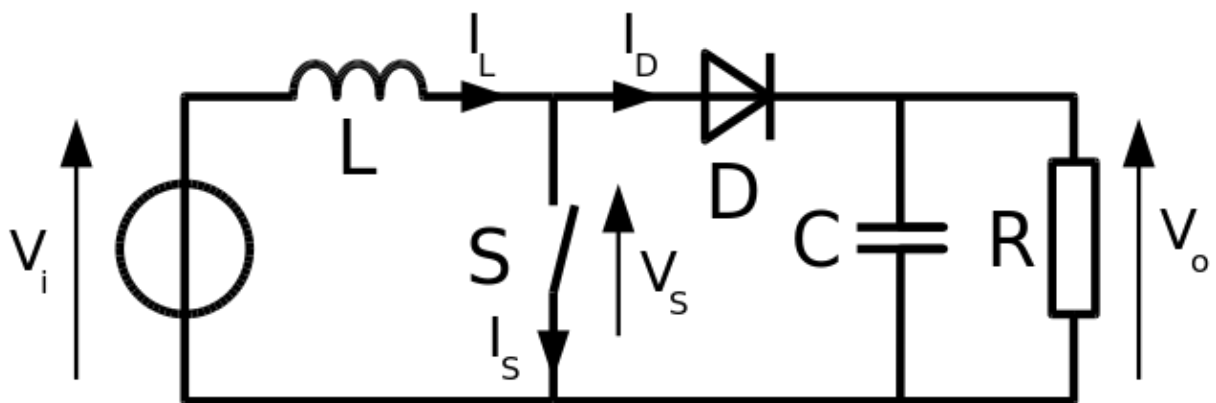
### *Micropump power management*

As previously addressed, Bartels microcontroller portfolio had no viable controller to use on this project, as all of them are too power-hungry for a low-powered system. Therefore, an external power supply was needed to power the pumps with the correct voltage and current. Ideally, the given voltage should be changed by the controller subsystem, if needed.

The selected circuit is a boost converter, also called step up converter, able to increase the received voltage, 5V, to approximately 100V. Initially, the circuit will be simulated on an electronic simulation software, being implemented on a breadboard [53].

### *Boost converter theoretical approach*

A boost converter is a DC-DC power converter that has an output voltage greater than the input voltage. It is a circuit with two semiconductor components, a transistor and a diode, and an energy storage component, that can be a capacitor, an inductor or both.



*Figure 4.6 - Boost converter generic schematic*

A boost converter always has two steps on its operation. These steps occur on each state of the input PWM wave on the MOSFET.

The first step happens on the high value of the input PWM wave. On this instant, the MOSFET operating as a switch is on, enabling the current to flow between the positive and negative terminals of the power supply. This allows the inductor to store electric current, as seen on figure 4.7.

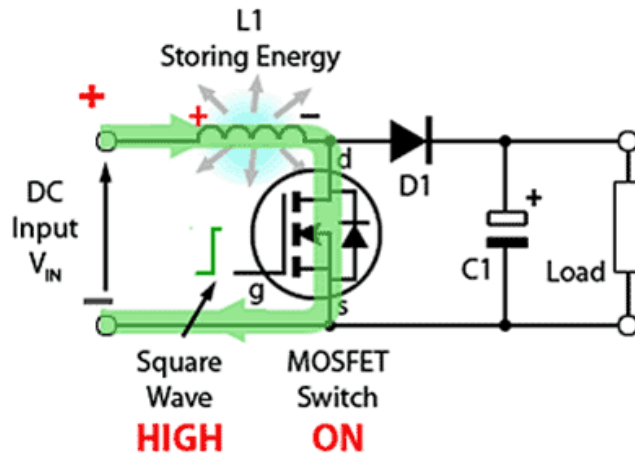


Figure 4.7 - Energy storing phase of boost converter operation

The second step occurs when the input PWM wave has a low value. The MOSFET switch goes off, opening the remainder of the circuit that was offline on the first step. This heavily decrease the circuits current, causing the inductor to act as another voltage supply, effectively providing the circuit with two voltage supply in series, with an higher voltage that the original power input. This can be observed on figure 4.8.

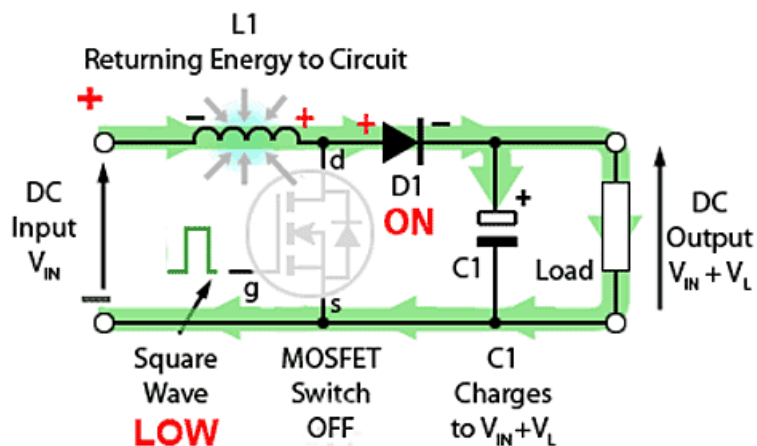


Figure 4.8 - Energy powering phase of boost converter operation

If using a fast enough PWM wave as input, the inductor will never fully discharge between cycles, so the load will always have at disposal a higher voltage than the one provided the power supply. The capacitor is also being charged at that combined voltage, therefore being able to power the load while the switch is on and the right side of the circuit is not being powered by the power supply. The diode prevents the capacitor from being discharged by the switch [54] [55].

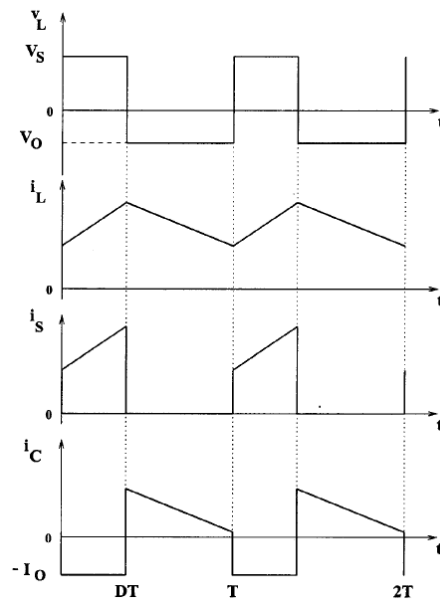


Figure 4.9 - Variables chart on a boost converter

### Boost converter components design

Certain components of the boost converter must be carefully dimensioned to obtain the desired specifications. To correctly choose the components, numerous rules and calculations can be made, following the specifications of the Texas Instrument guide for boost converters.

The chosen components were the following:

- MOSFET – STMicro STD11N50M2 [56]
- Diode – STMicro STTH1R06U [57]
- PWM source – ATmega 328P from Arduino Uno [58]
- Inductor – Panasonic ELC-15E103L [59]

### Boost converter simulation

After determining the value of the various needed components, the circuit must be simulated in order to confirm both values and correct operation of it. The used simulation software was the PSIM from Powersim Inc.

## PSIM Simulation

The PSIM Simulation is an electronic software simulation from Powersim Inc. normally used for power electronics and motor drive simulations, but that can be used for any kind of electronic circuit simulation. The PSIM simulation software is a modular software, with additional modules that can be added to the main program for increased functionality.

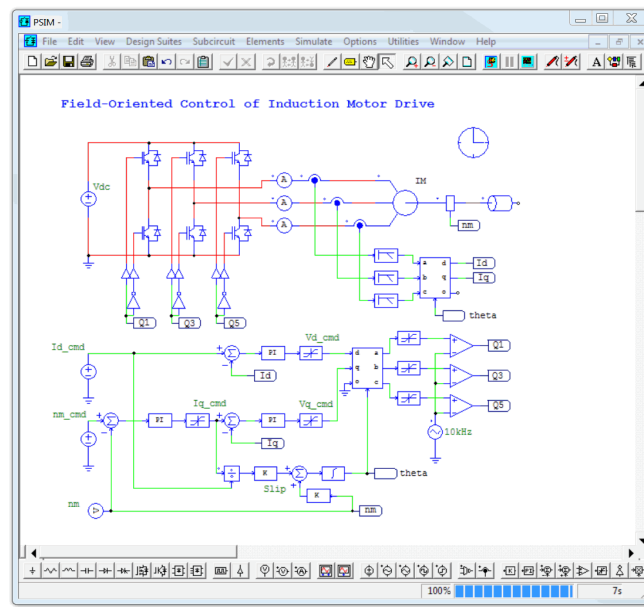


Figure 4.10 - PSIM interface

PSIM is considered one of the fastest and lightest electronic simulator, while still achieving an excellent simulation accuracy. This means that the PSIM is specially designed multiple-cycle simulation. Several form of control circuit can be simulated, from analog circuits to Matlab/Simulink, including s and z-domain transfer function or even custom C code.

To display and analyze simulation results, PSIM has an integrated application called Simview. Simview includes several waveform processing functions, such as multiple screen and line style. Post-processing functions are also available, like addition and subtraction or average and RMS value calculation [60].

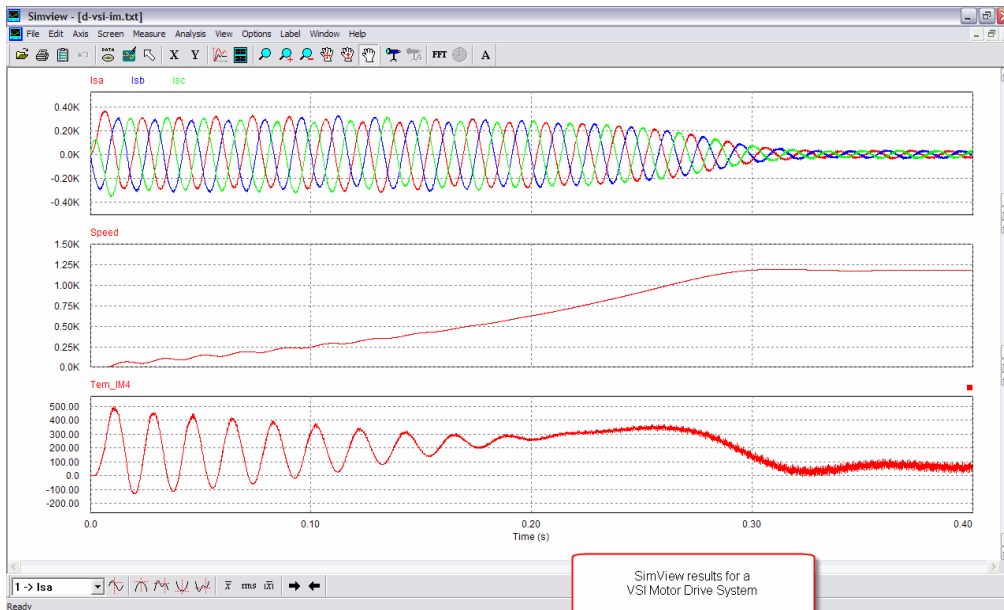


Figure 4.11 - Simview interface

## Simulation and results

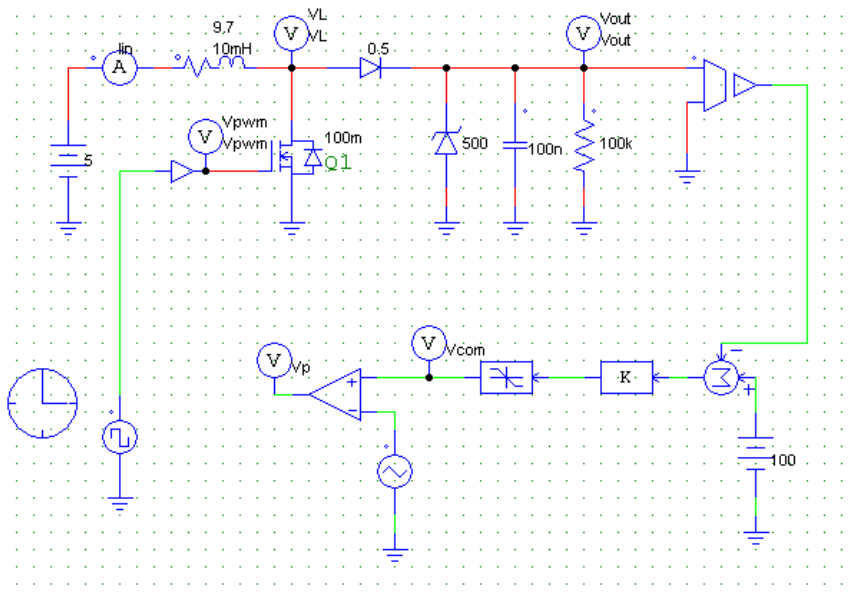


Figure 4.12 - Boost converter simulation circuit

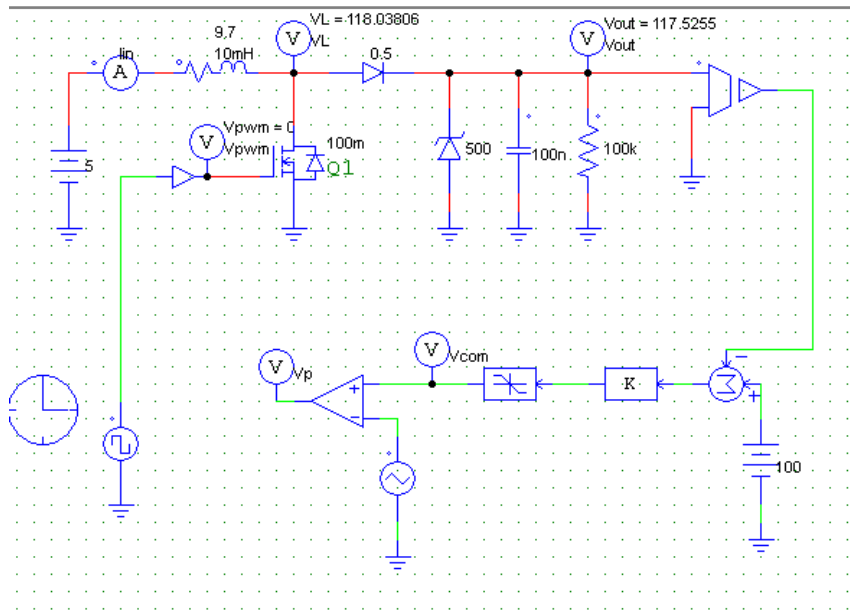


Figure 4.13 - Boost converter simulation results

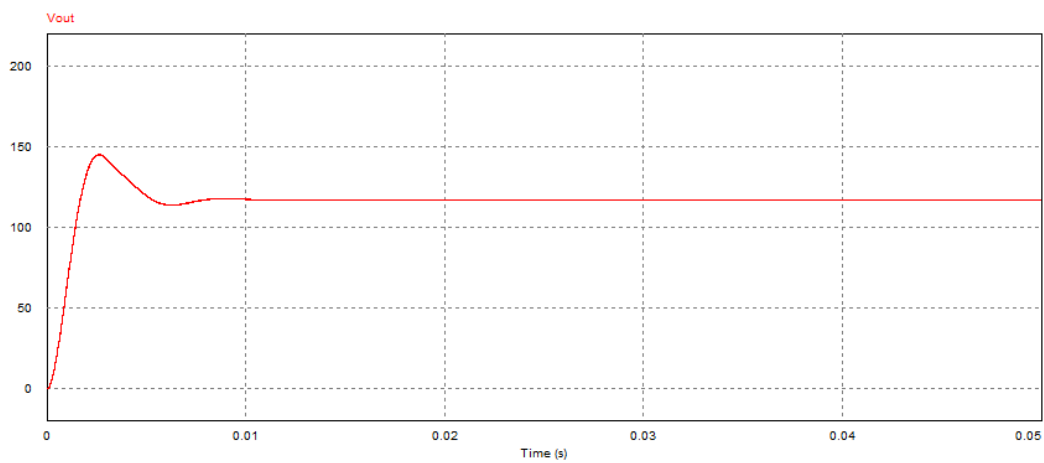


Figure 4.14 - Boost converter simulation output voltage wave

#### 4.1.2 Power Management System Implementation

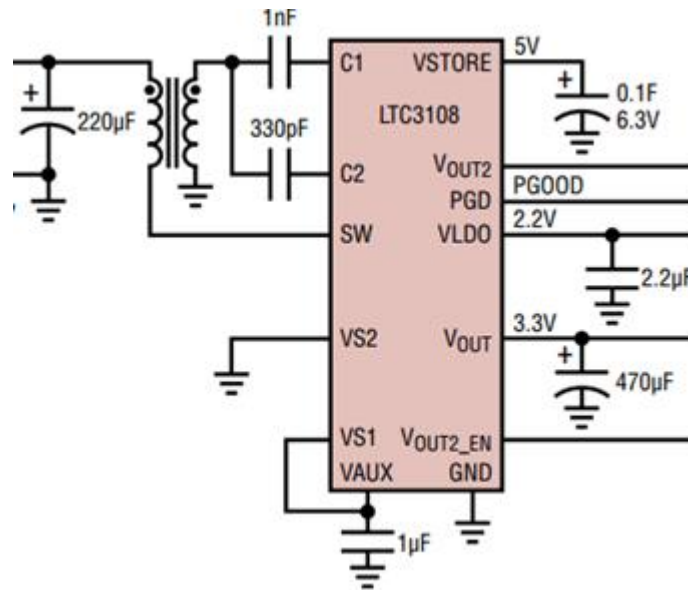


Figure 4.15 - The LTC3108 with its auxiliary components [49].

For the power management system, the LTC3108 was used, as described previously. Linear Technology provides a good datasheet for it, with several given components to use for a proper functioning of the step up IC.

The voltage output used was both 3.3 and 5V, so all components were dimensioned considering this voltage. The transformer used was recommended on the LTC3108 datasheet and is a Coilcraft LPR6235-253PMR, with a 1:20 ratio [61]. The super capacitor (0.1 F) allows the system to operate even when the fuel cell is not producing energy.

#### 4.1.3 Control System Implementation

Unfortunately, the control system was not implemented. However, many considerations about it were already made.

The control system would use the Atmel ATmega 328P microprocessor. As previously mentioned, the ATmega 328P is a low cost, low power microprocessor that is used in many assembled board that would simplify the testing process. The 328P was already used as a PWM source for the boost converter, so it would only need added code to control all the subsystem.

The ATmega 328P should be responsible for starting the system. This start-up must follow a specific order:

1. The microcontroller is powered by a battery or supercapacitor (preferably the later) and is the first component to start, as it is the one responsible to enable the power for the rest of the system.
2. With the microcontroller operational, the cell must be the next component to be started, as it is the most stable and powerful energy source. As such, the fuel supply system must be initiated to enable the cell to deliver energy.
3. After the cell is working, with fuel in its inwards, the main power source must be shifted from the battery/supercapacitor to the cell. To do that, the power management system must be enabled, to transform the output voltage from the cell to a viable voltage to power the microcontroller and the fuel supply system.
4. With the whole assembly operational, the microcontroller must be able to supervise the various voltages on all the systems, to maintain the ensemble operational and with smooth transition states.
5. With the cell now working as the main power supply, the supercapacitor must be charged for the next boot.

Firstly, the software would be built using the Arduino language, as it was done with the PWM source. The following step would be to translate the code into C language, as it is the fastest processing language for this kind of microcontroller. Also, the first tests would be made using the Arduino Uno board, but the objective would be to switch to an in-house made PCB with only the ATmega 328P and the necessary peripherals.

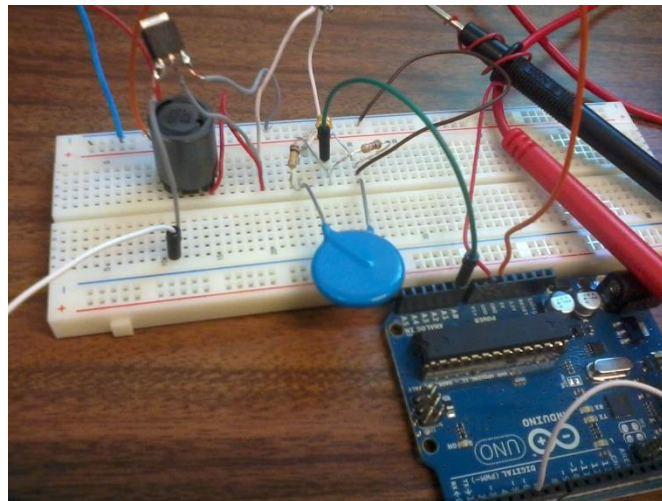


## 5. TESTS AND RESULTS

### 5.1 Auxiliary Circuits testing and results

#### 5.1.1 Fuel Supply System tests

After validation by simulation, the fuel supply system was implemented. The first implementation was done on a breadboard, to further confirm the whole system was functioning as intended.



*Figure 5.1 - Boost converter implementation on breadboard*

The PWM is provided by the Arduino board, and the software was designed using the Arduino IDE available at the Arduino home site [62] and is provided on the annex first. As previously referred, the used MOSFET is the STMicro STD11N50M2, the used inductor is the Panasonic ELC-15E103L and the used diode is the STMicro STTH1R06U. To insure the security of the whole circuit, a VDR was added.

After implementation, an oscilloscope was used to analyze the resulting voltage wave. As seen on figure 5.2, the resulting output wave is a saw tooth wave of almost 150 V. A perfect constant wave can be attained with further improvements. The input wave is a common PWM 5V amplitude with a duty cycle of about 80%. The amplitude can be regulated with the frequency of the PWM. The final intent of this feature is for the PWM to be automatically regulated with the desired output voltage, a feature controlled by the microcontroller.

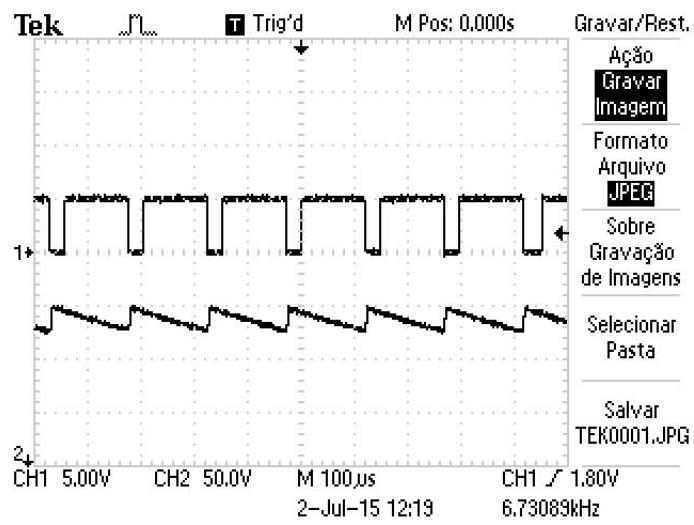


Figure 5.2 - Resulting voltage wave (channel 2) of the boost converter, as seen on a digital oscilloscope

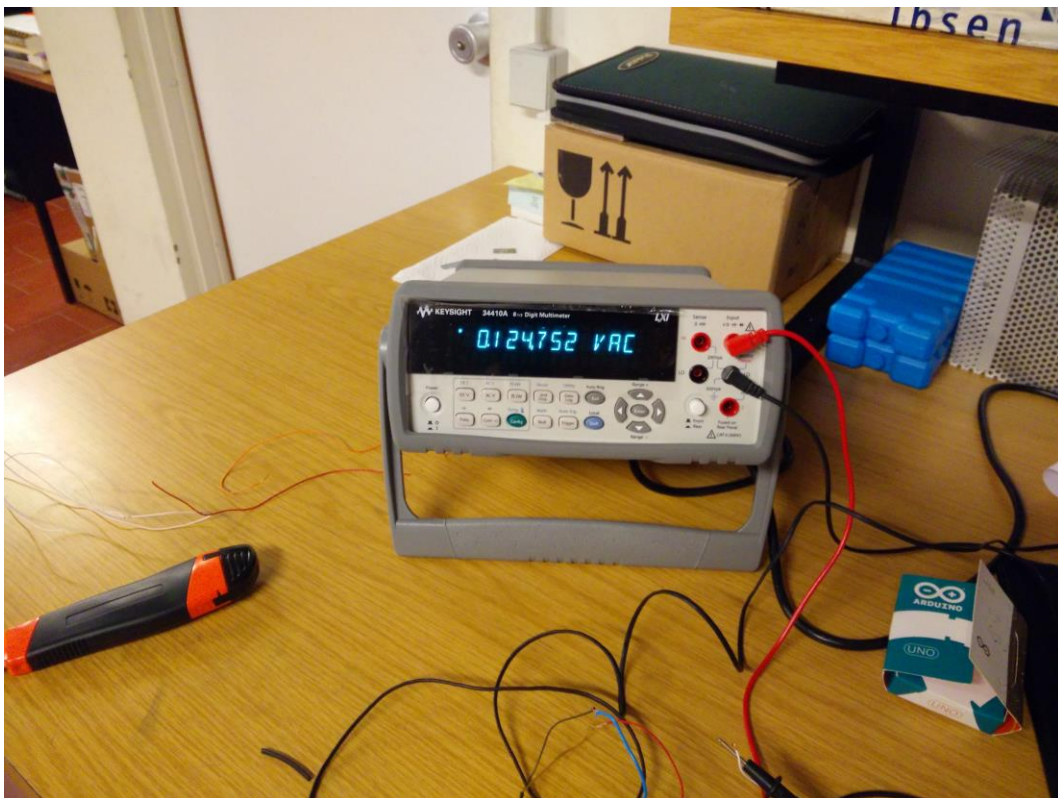


Figure 5.3 - Voltage output of the boost converter, seen on a digital multimeter

5.1.2 Power Management System tests

No simulation was done before implementing the power management system. Following the documentation available for the LTC3108 step-up converter, the circuit was directly assembled on a breadboard, for testing. The circuit can be seen with more details on figure 5.4, with the testing assembly detailed on figure 5.5.

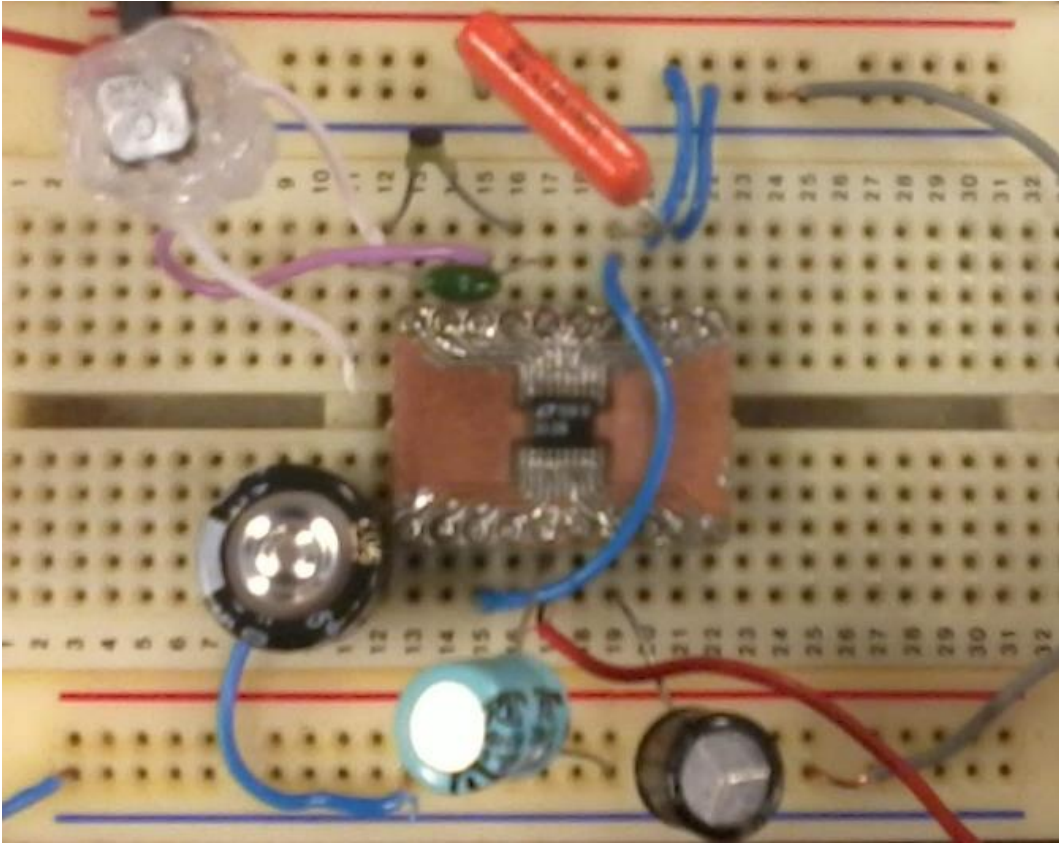


Figure 5.4 - Power management system assembled on breadboard, with a soldered LTC3108 in the center

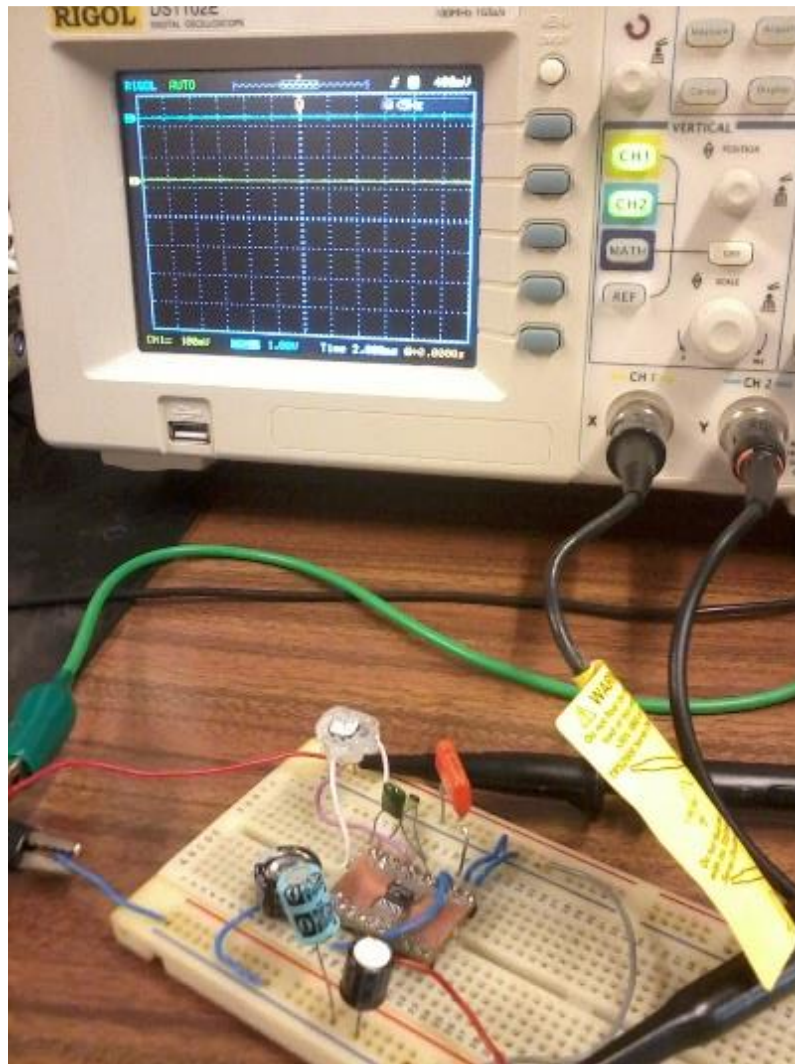


Figure 5.5 - Test setup for the LTC3108 based power management system

The result of this tests is presented on figure 5.6. With an input voltage of 0,1 V (channel 1 on the oscilloscope, yellow), the output voltage is 3.3 V (channel 2, light blue).

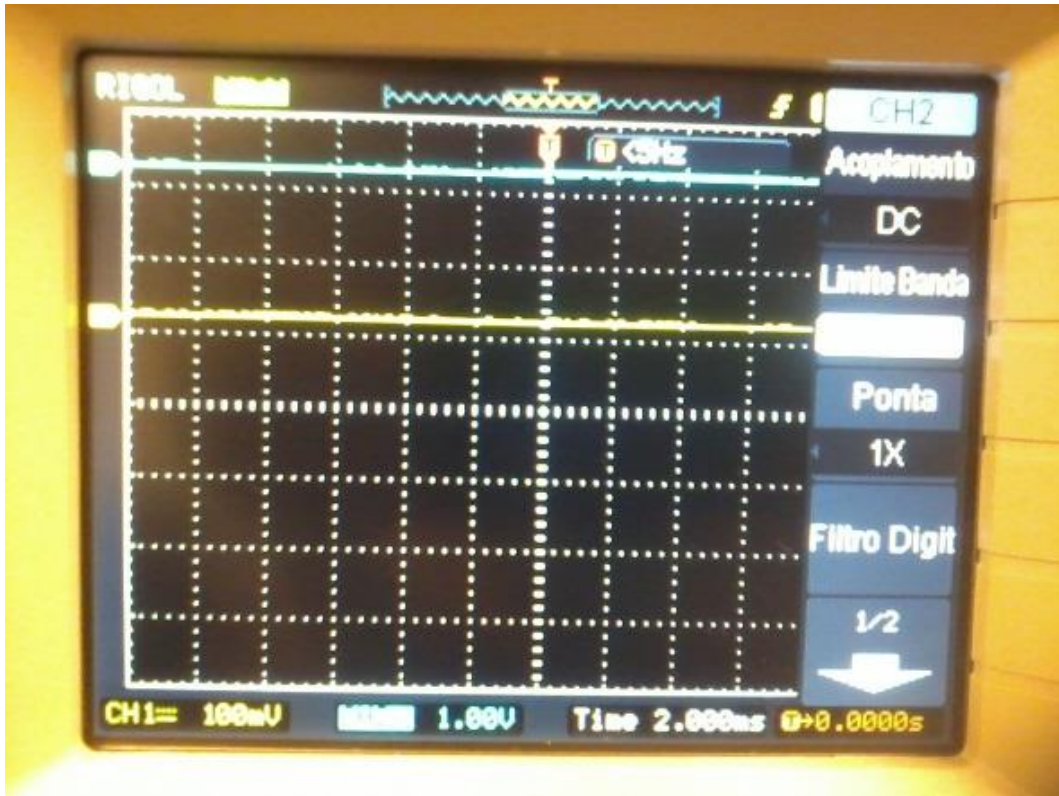


Figure 5.6 - Oscilloscope analysis of the power management system

A PCB was created for this system. The PCB schematics are represented on the figure 5.7, with photos on both figure 5.8 and 5.9.

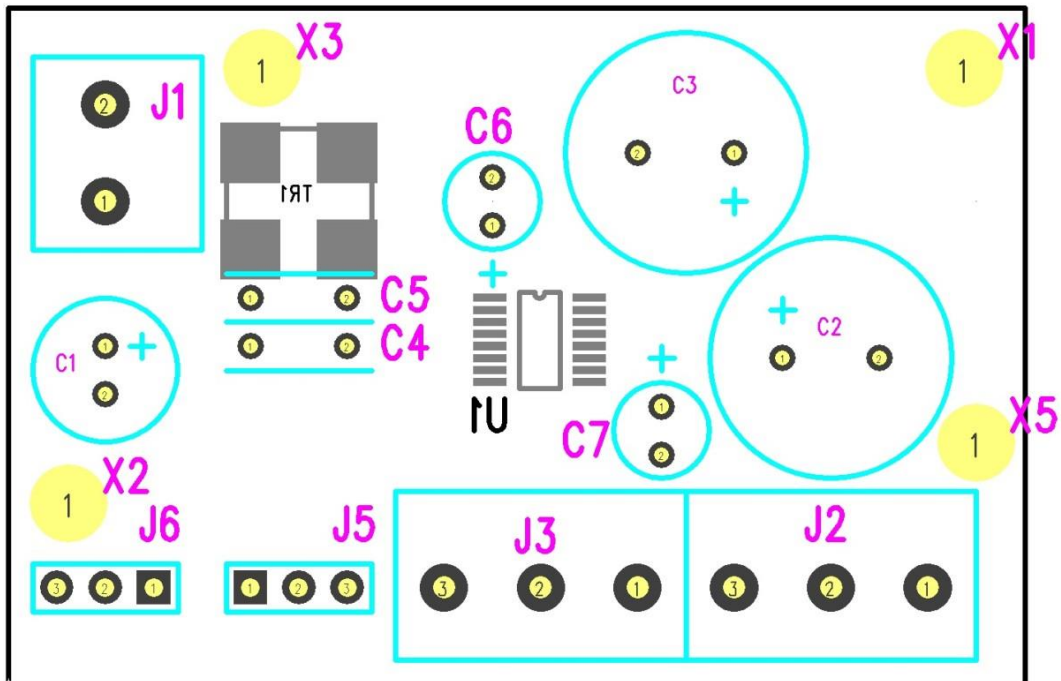
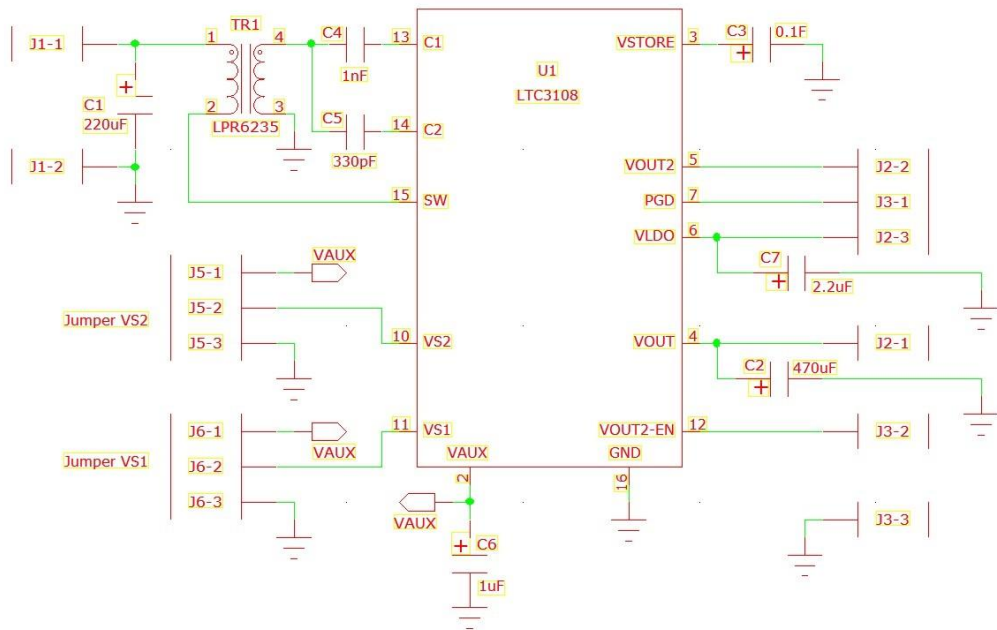


Figure 5.7 - PCB designed for the power management system



Figure 5.8 - Upper side of the designed PCB, with several capacitors and connectors

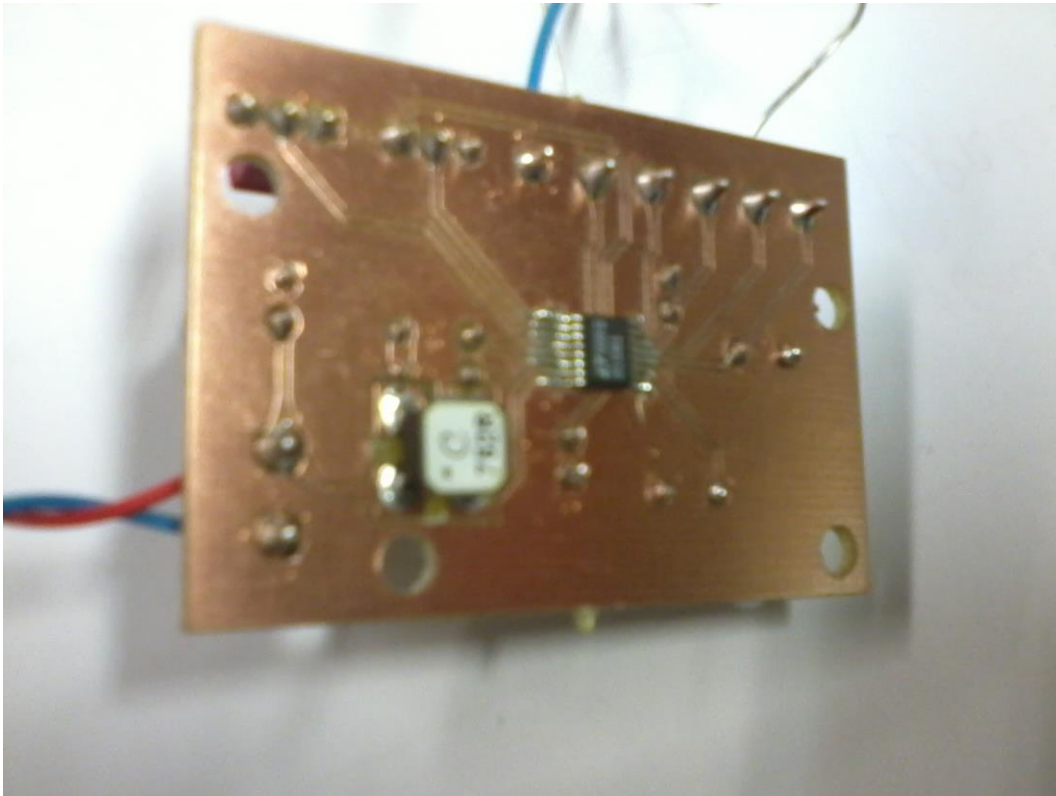


Figure 5.9 - Under side of the designed PCB, with LTC3108 and the inductor

## 5.2 Fuel Cell

Before implementing or dimensioning any auxiliary circuit, several tests were made to confirm the behavior of the fuel cell. While the fuel cell has defined specifications when being used as a PEMFC, with hydrogen as fuel, there is no documentation for it when using methanol as fuel. Several tests were made, but results were highly unpredictable: with the same conditions, output voltage could go as high as 300 mV or as lowly as 20 to 25 mV. Table 3 show some results obtained.

*Table 3 - Results obtained with the fuel cell*

<b>DAY</b>	<b>PEAK OUTPUT VOLTAGE</b>	<b>TIME OF PEAK</b>
<b>18/03</b>	176 mV	3 mins after boot
<b>02/04</b>	300 mV	2 mins after boot
<b>24/04</b>	96 mV	11 mins after boot
<b>30/04</b>	144 mV	5 mins after boot
<b>05/05</b>	121 mV	8 mins after boot
<b>06/05</b>	89 mV	6 mins after boot
<b>26/05</b>	76 mV	5 mins after boot
<b>02/06</b>	112 mV	3 mins after boot
<b>09/06</b>	94 mV	7 mins after boot
<b>17/06</b>	49 mV	11 mins after boot
<b>23/06</b>	35mV	9 mins after boot

Numerous other tests were done, but these were the ones with the best outcome for each day. Photos from these setups can be seen on figure 5.10, 5.11 and 5.12. Different setups were tested, but with no big performance difference between them.



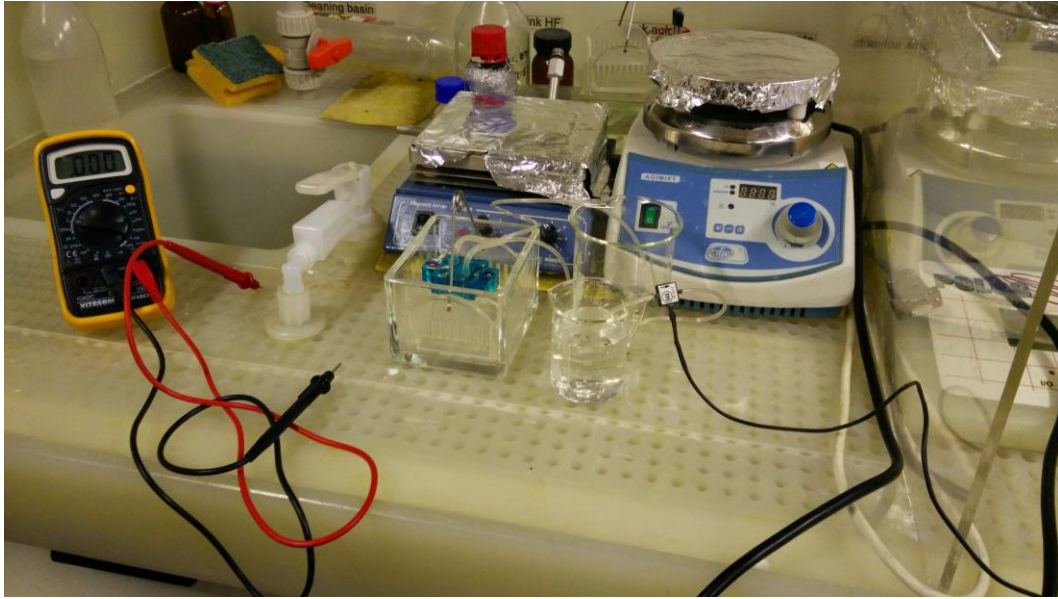


Figure 5.10 - First testing setup.

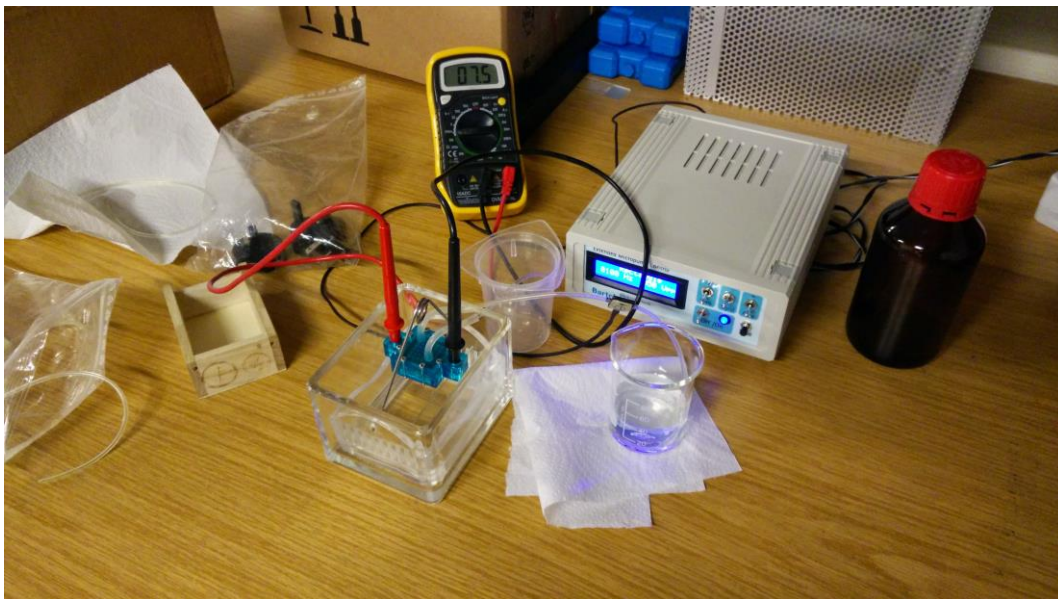
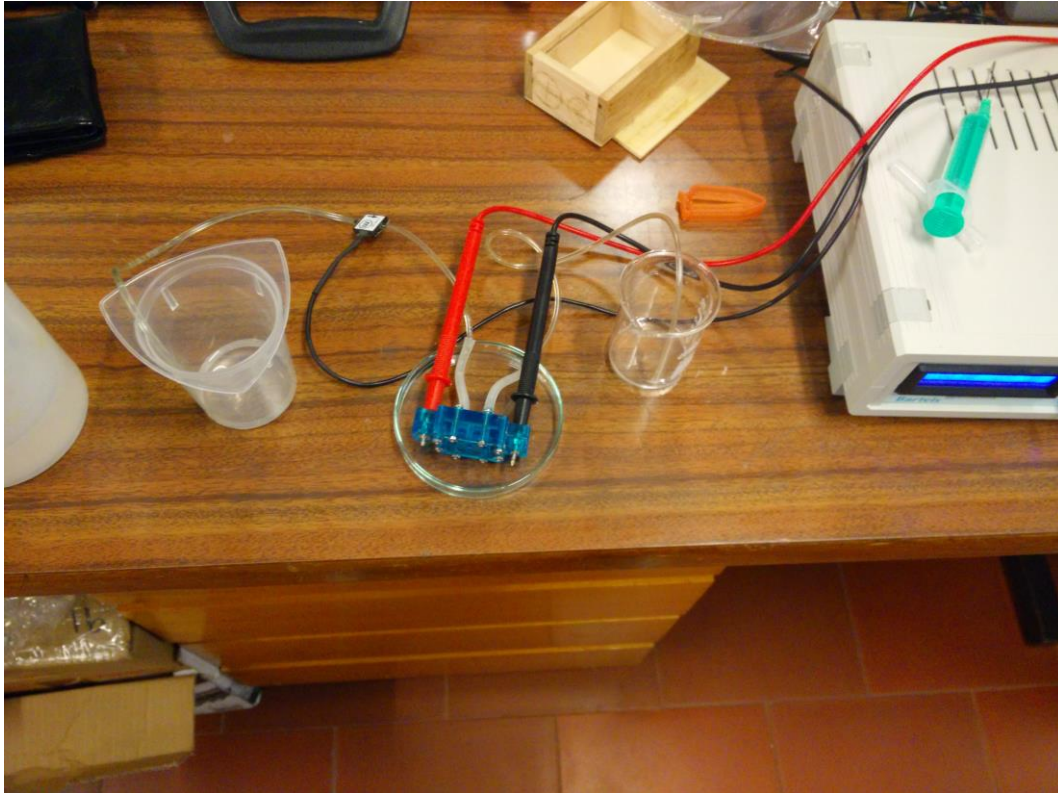


Figure 5.11 - Second testing setup, with similar configuration of the first.



*Figure 5.12 - Final testing setup, with the fuel cell on another position, for better airflow.*

With these extremely erratic outcome, others tests were done to analyze the cell's behavior, to try to find an approach that could give proper and consistent results. After careful investigation, several analysis were made to study the influence that numerous factors have on the cell's performance.

#### 5.2.1 Fuel cell performance with different methanol concentration

The most important component to a membrane based fuel cell performance, besides the membrane assembly, is the used fuel. On a DMFC, methanol is used as fuel, but it is always diluted on distilled water, to avoid problems like methanol crossover.

While the most common concentration of methanol/distilled water is 10/90%, it is theoretically possible to increase the cell's performance increasing the methanol concentration to 15 or even 20%. The improved performance is due to the presence of more hydrogen ions, but the augmented methanol concentrations severally increases the possibility of methanol crossover, compromising the cell and its performance to levels that may be worse than with lower methanol concentration.

These tests were made after the cell suffered severe damage and use, so in either case, the peak output voltage is lower than the initial tests. The tests were done during thirty minutes, with no air supply, using only differing methanol solution, and using a H<sub>2</sub>SO<sub>4</sub> solution to clean the cell in between cells.

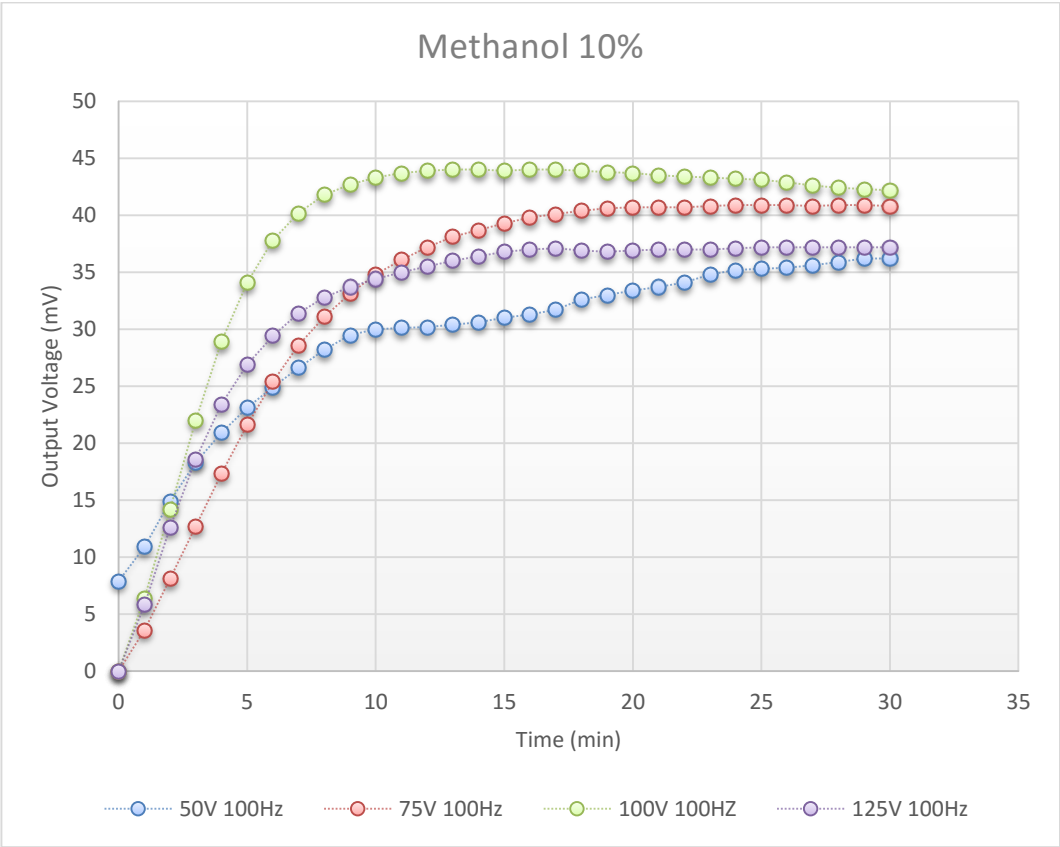


Chart 5.1 - Fuel cell voltage output with methanol 10% on different flows

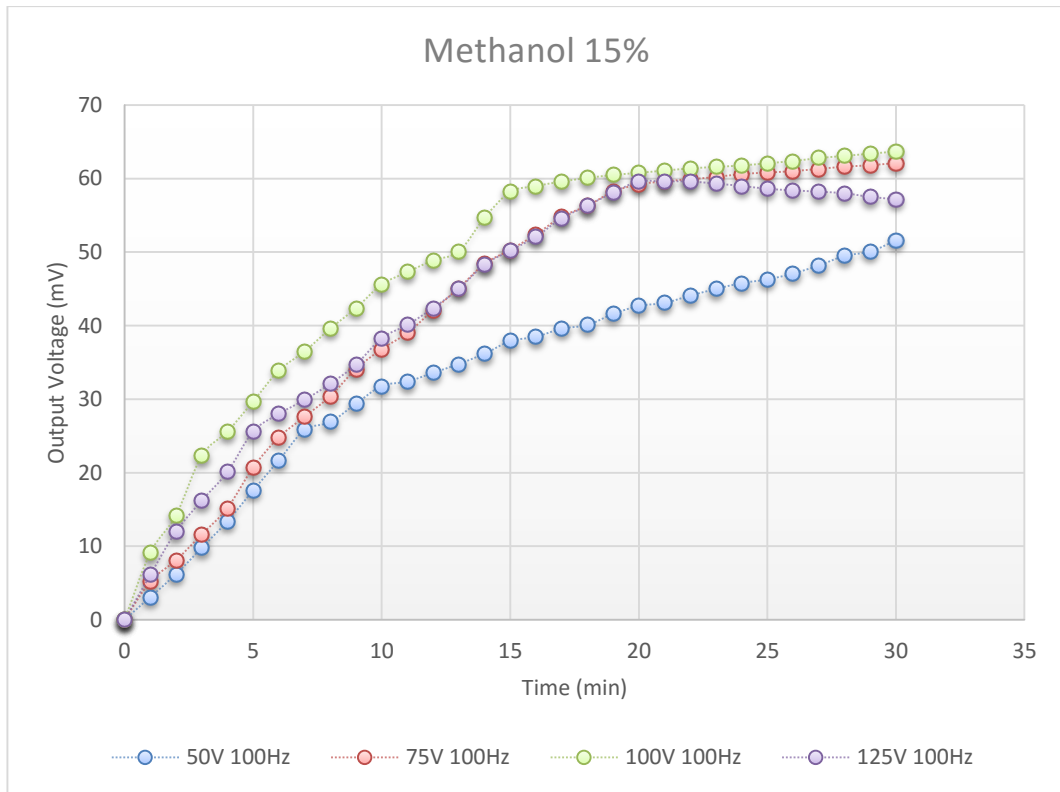


Chart 5.2 - Fuel cell voltage output with methanol 15% on different flows

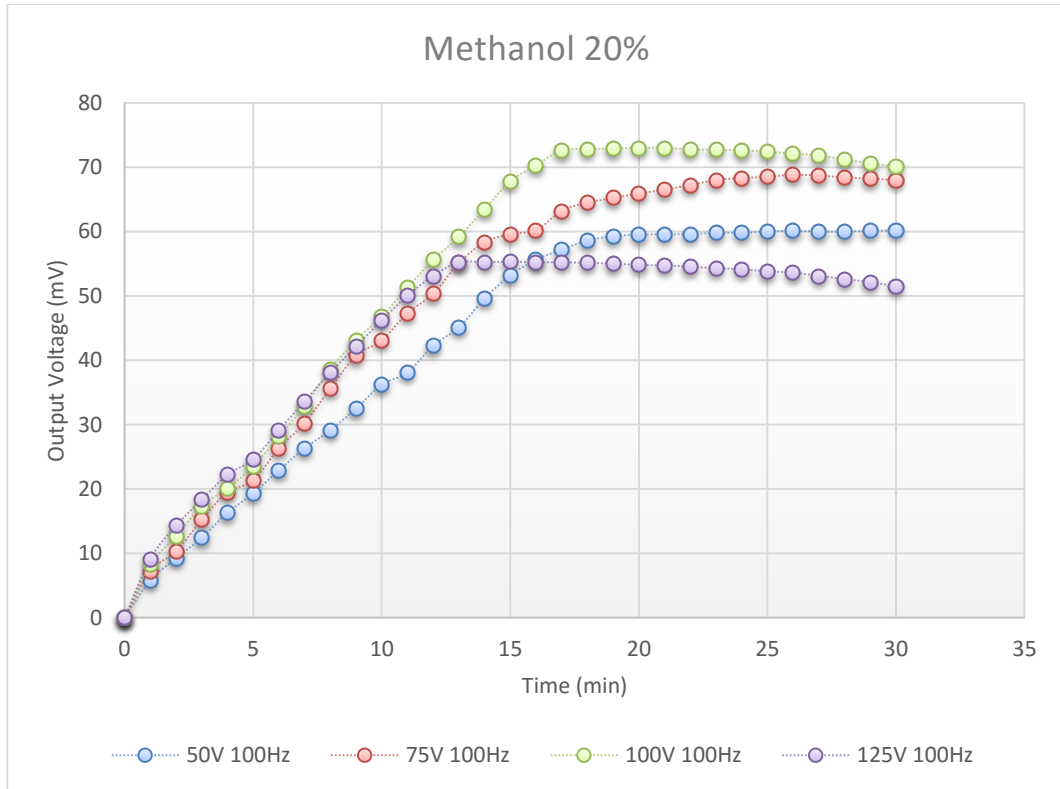


Chart 5.3 - Fuel cell voltage output with methanol 20% on different flows

Curiously, while having some similarities, the cell's voltage output are severally different plot. Using a 10% methanol solution, the cell is unable to reach its full potential, not going, with any kind of flow, even to 45 mV. The cell's voltage grow rapidly until circa ten minutes, with a diminished, but steadily growth until the end of the test.

Using a 15 or 20% shows a different evolution pattern, with a more constant growth, but not so fast in the beginning. This can be produced by the increase of the hydrogen ions caused by the increased methanol concentration. However, and especially on the 20% concentration chart, we can see that methanol crossover occurs closer to the beginning than in either others concentration, and as more serious consequences, as the voltage can drop rapidly.

The results obtained are condensed on the table 4.

*Table 4 - Fuel cell output voltage comparison*

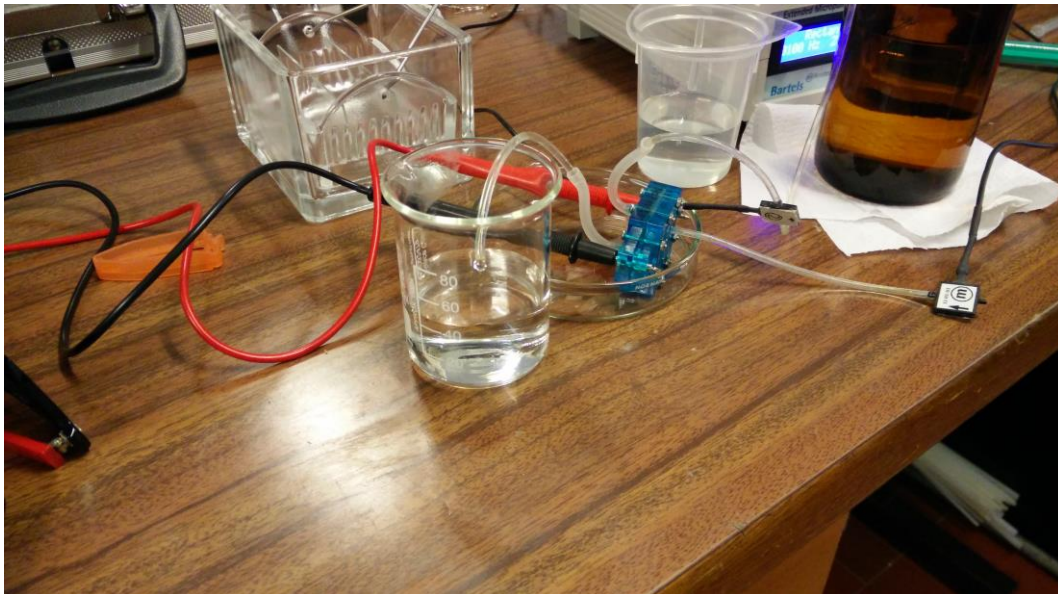
<i>Methanol concentration (in percentage)</i>	<b>Flow voltage (in volts)</b>	<b>Fuel cell output voltage (in millivolts)</b>			
		10 min	20min	30 min	Peak
10	50	30	34,1	35,9	35,9
	75	34,9	40,4	41,6	41,6
	100	43,1	43,2	42,1	43,6
	125	34,6	36,2	36,3	36,5
15	50	31,8	42,7	51,6	51,6
	75	36,8	59,2	62,1	62,1
	100	45,6	60,8	63,7	63,7
	125	38,3	59,6	57,2	59,6
20	50	36,2	59,5	60,2	60,2
	75	43,1	65,9	68	68,8
	100	46,8	73	70,1	73
	125	46,2	54,8	51,5	55,3

### 5.2.2 Fuel cell performance with different air supply

On DMFC, oxygen supply is critical to good performance, as it is one of the vital components of the DMFC reaction. Increasing oxygen supply can also help bypass some of the methanol crossover problems.

To analyze if a dedicated air supply system could increase performance, the same setup was used with different ways to supply air to the cell: one using a common PC fan, one using another MP5 micropump dedicated to provide air to the cell and the usual setup, without a dedicated air supply, using only the normal air contact.

The tests were made using methanol 10% during 30 min. The flow provided was 100 V/100 Hz for the fuel. The fan was a common PC fan with a diameter of 120 mm, connected to 12 V. The air flow provided by the micropump was powered by an input wave of 250 V/100 Hz.



*Figure 5.13 - Air flow testing setup with micropump. The setup was similar with fan and without dedicated air supply.*

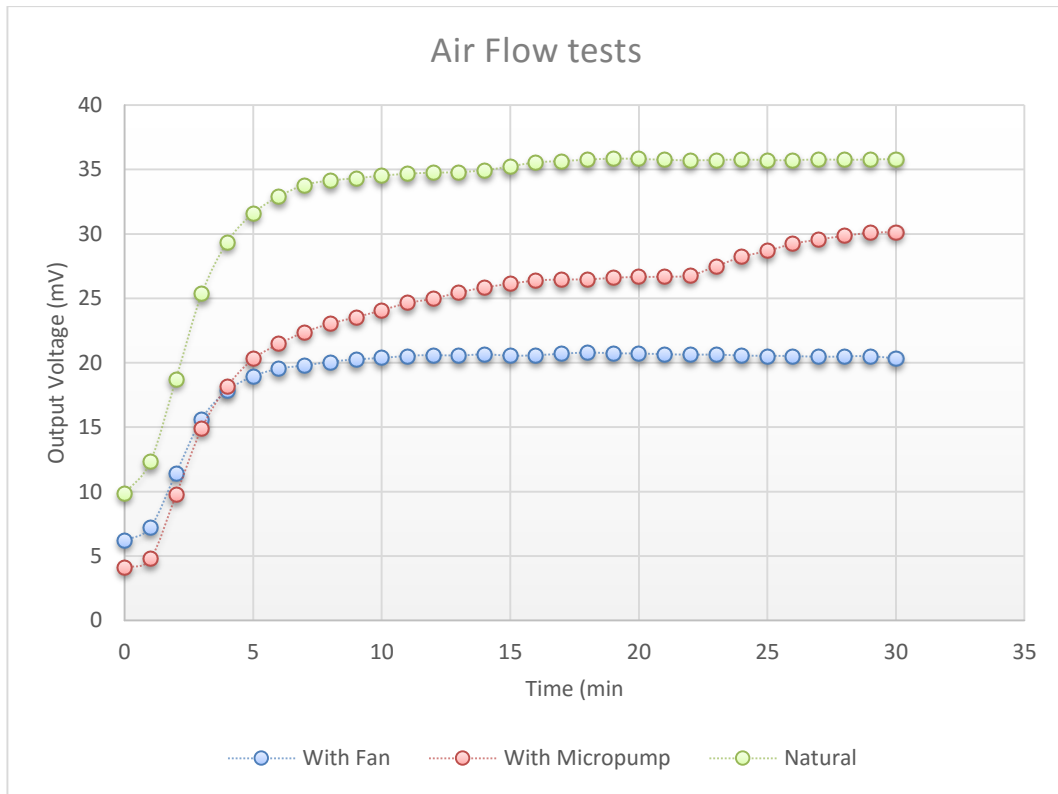


Chart 5.4 - Air flow tests with 10% methanol

While it was expected to see a better performance with a dedicated air flow supply, the results obtained were disappointed. However, it should be noted that the damaged membrane, as referred in chapter 5.2.4, could be the cause of these results.

### 5.2.3 Fuel cell performance with different intermediate cleaning

While not as critical as the other performance alteration causing factors, the intermediate cleaning can affect cells performance in laboratory results. Some literature says that instead of using the common sulfuric acid ( $H_2SO_4$ ), using a solution of sulfuric acid with oxygenated water ( $H_2O_2$ ) can provide increased performance after cleaning the cell.

As such, this exact test was performed. The cell was cleaned using a  $H_2SO_4$  solution, with 10% concentration, and with  $H_2O_2$  and  $H_2SO_4$ , with a concentration of 5%  $H_2SO_4$  and 15%  $H_2O_2$ , during 20min, before testing with a 10% methanol solution. This tests were made during 60 minutes.

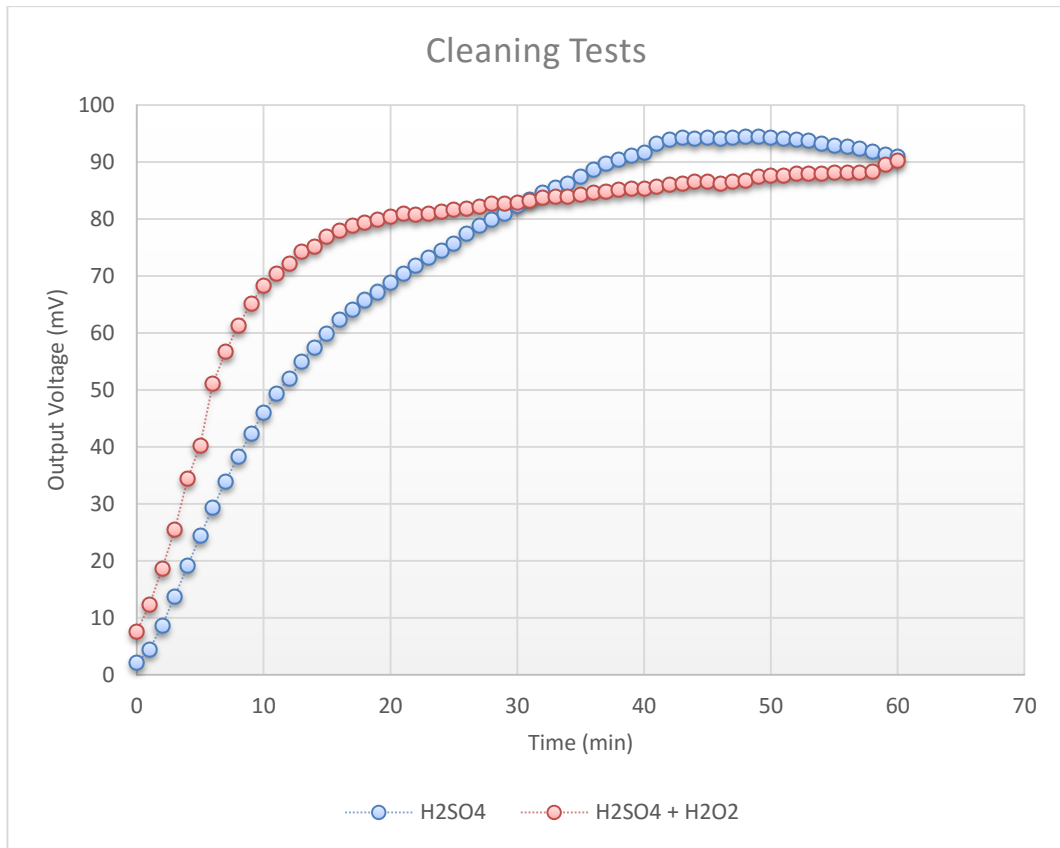


Chart 5.5 - Cleaning tests with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>

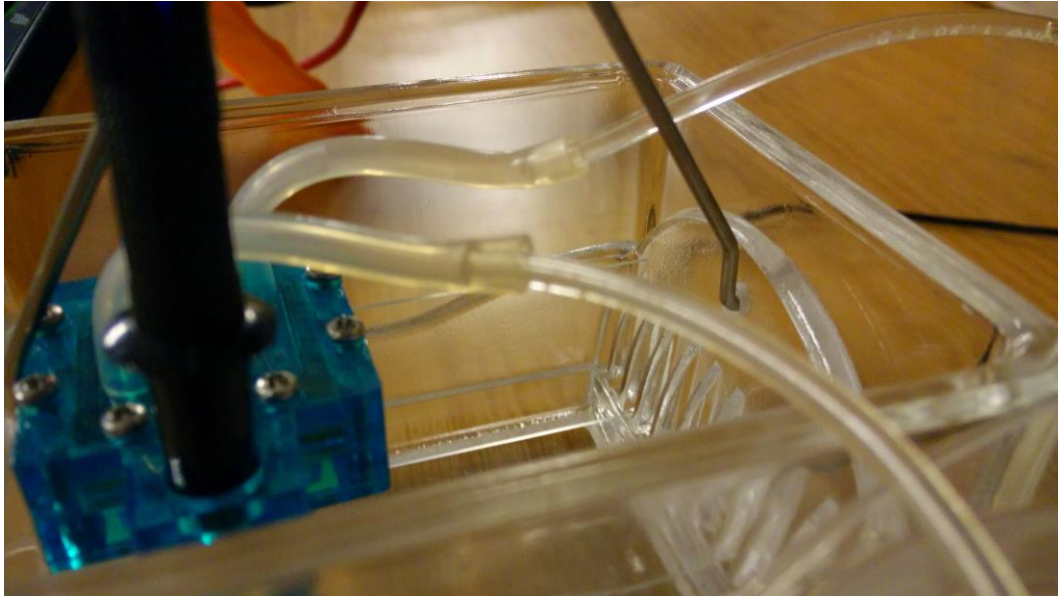
While some claim that the H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> solution provide better results in the long term, the observed difference is small. What can be perceived, however, is that after cleaning with only H<sub>2</sub>SO<sub>4</sub>, methanol crossover occurs earlier than with the H<sub>2</sub>SO<sub>4</sub> plus H<sub>2</sub>O<sub>2</sub> solution.

#### 5.2.4 Identified problems with the fuel cell testing

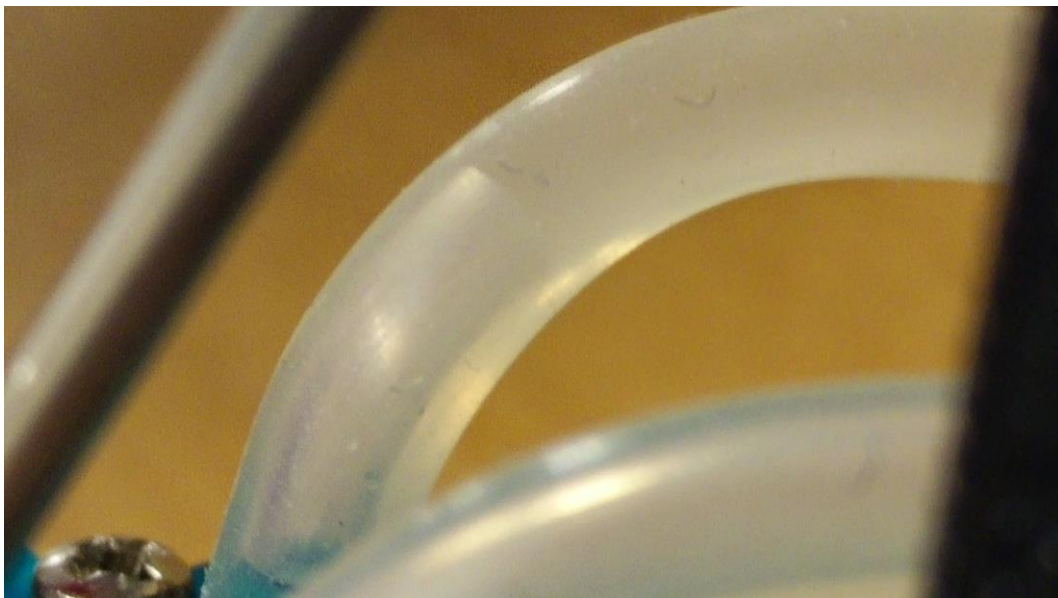
Several problems were identified while doing tests.

The most recurring problem were air bubbles that would form from the cracks between the pipes coming from the cells and the ones coming from the micropump. This kind of bubbles can be seen on the figure 5.14 and 5.15.





*Figure 5.14 - Connection between tubing of the fuel cell and micropump. This transition was responsible for many of the bubble formed.*



*Figure 5.15 - Air bubble formed on the tubing of the cell*

Another problem was found in the membrane used on the fuel cell. Several contamination was discovered after analysis via EDS, outside the scope of this work.



## 6. CONCLUSIONS AND FUTURE WORK

This dissertation had as generic objective the creation of a fuel cell system which would use methanol as opposed to the usual hydrogen. Methanol is a cheaper fuel, which requires little to no changes in the fuel cell itself. To accompany the fuel cell, three systems were to be developed: a system that would be used to fuel de cell (fuel supply system), a system to convert the cell's output to a viable voltage (power management system) and a system that would use a microcontroller to do the enabling of these systems and control the whole assembly (control system).

### 6.1 Conclusions

Unfortunately, not all the system were developed, and the assembly process was not finished. The fuel cell presented several problems that took time to solve and made impossible to start the final subsystem, the control system. The other systems were, however, completed successfully. Several tests on the fuel cell were also made, to further improve the knowledge of what can and cannot affect the cell's performance and operation.

#### 6.1.1 Fuel cell

About the fuel cell, an intensive study was made to analyze de viability of the PEMFC to DMFC conversion. Unfortunately, the used fuel cell, due to its old age and extensive usage, was far from ideal to this project. The MEA was severely damaged, with high corruption of the MEA elements, which caused erratic results, that could go as high as 0,3V and as low as 0,02V. To improve its performance, several experiments were made, with the following conclusion:

- Increasing the methanol concentration brings a better performance, but increases the effects of the methanol crossover;
- Using a dedicated air supply does not increase the cell's performance as it should;
- Changing the cleaning solution, adding  $H_2O_2$ , does not carry a benefit in terms of output voltage;
- Air bubbles formed easily in the cracks between the connection between tubes from the cell and the micropump, as from the fuel being in contact with the air. These bubble severely undermine the fuel flow and may have caused some of the bizarre

phenomenon in certain tests, as drastic increases or decreases of performance in short periods.

- After analysis on the EDS, the membrane was shown as heavily damaged and contaminated.

The used fuel cell severely conditioned the rest of the dissertation. Many hours were spent studying it and trying to improve its performance, which made it impossible to fully finish all the proposed objectives. However, in the end, it was possible to use the cell with the circuits developed.

### 6.1.2 Fuel Supply System

To supply the fuel to the cell, a fuel supply system was developed. The heart of the system was the MP5 micropump for Bartels, a model used on many other fuel cell system. While Bartels has several controllers that can be used with the MP5, all of them were too power hungry to be used, so a DC-DC converter was created to supply with both the required voltage and frequency for the correct micropump operation.

Firstly, studies were made to analyze the required voltage and frequency to meet the target 0,2 to 0,8ml/min fuel flux necessary to the correct operation of the cell. Using a Bartel MP-X controller, several experiments were prepared using distilled water as fuel, to further increase the understanding of the setup and workings of the MP5 micropump. After establishing an objective voltage and frequency, the design of the DC-DC converter started.

The implemented DC-DC converter was a boost converter that was able to operate at a minimum of 100V with alternating frequency. As a PWM generator, an Arduino Uno board was used. While a perfect constant wave was not attained, the saw tooth was able to power the micropump with some flickering of the flux that do not affect its performance.

### 6.1.3 Power Management System

Even if the fuel cell was fully operational, its output voltage would need to be transformed to a viable voltage to be used on a specific device, either 3.3 or 5V, as these are the most used voltages nowadays.

To transform the output, which, as tests showed, could fluctuate from 0,03V to 0,3V, another DC-DC converter was needed. However, as 3.3 and 5V are “standard” voltages, several IC were available to do this conversion. The best option was the one more flexible about the input voltage, which is the output voltage of the fuel cell, to better respond when the cell would fail to provide its best performance and the voltage would drop. As such, the Linear Technologies LTC3108 was chosen from the several models studied, as it was the most appropriate.

The LTC3108 was firstly implemented on a breadboard, following the recommended setup given by Linear Technologies. After confirmation of the proper functioning of the LTC3108, a PCB was designed and created, with confirmation of its operation.

#### 6.1.4 Control System

Unfortunately, due to the several problems that surged on the cell’s study, time proved to be too short to implement the control system. While no implementation was made, this system was studied and its basic functions were defined.

The control system would use an Atmel ATmega 328P, the same one used to provide the PWM to the power management system. The control system would be responsible to correctly execute the start-up of the system, using a supercapacitor to start the fuel cell and only after the cell providing enough energy to power all the system, the microcontroller would turn off and charge the supercapacitor, with the cell providing energy to the whole system, including micropump, DC-DC converters and the microprocessor.

The software required would be built in C, and the Arduino Uno would be the board to start programming and testing the microcontroller. After the testing period completed, only the ATmega 328P, and the necessary peripherals, would be used, on a proper PCB designed in the end.

## 6.2 Future Work

While all the systems developed during this dissertation were tested with the given Horizon Mini PEM fuel cell, with all the issues that it gave. To fully establish if these circuits are able

to be used with a properly functioning cell, they should be tested with another, fully working, cell, as in theory they should be operational with no problems.

An essential step on a future work is executing the implementation and programming of the controller system. Without this system, the fuel cell cannot be properly implemented on an existing device, to power it.

After the implementation of the control system, all the circuits and the fuel cell should then be put together to establish the correct functioning of the whole assembly. Some changes may be needed, but the circuits would probably work as expected.

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